off area, a pressure-sensitive tape is used to form a sharp line and prevent the leakage of plating solution under the plastic tape.

Plastic tape is expensive to use. When many similar parts are to be selectively plated, rubber sheet, held in place by pressure-sensitive tape, may be used for stopping off areas not to be plated. Rubber stoppers, plastic plugs, or corks, sealed with wax, are used for stopping off internal areas of cylindrical parts. Rubber or plastic tubing can be used to stop off areas of small cylindrical parts.

Rinsing and Drying

Although one of the simplest operations in plating, rinsing is often the most difficult to accomplish. The primary requirements are that the rinsing be effective in removing the solutions used in the preceding tank and that no contaminants be introduced into the subsequent tank. Rinse baths, whether hot or cold, usually are provided with some means for constant changing of the water, good agitation, and skimming of the surface. Agitation of both the water and part is usually necessary. The surface skimmer may consist of jets of water shooting across the surface to rinse surface films into an overflow trough at the far side of the rinse tank. Water should enter at the bottom of one side of a rinse tank and escape over a weir outlet along the top at the opposite side of the tank. Constant monitoring of the water quality versus product quality is essential with the increased demand to lower water usage. The amount of contamination in rinse tanks can be regulated by controlling the flow of fresh water into the rinse through a valve actuated by a conductivity cell.

The temperature of the postplating rinse bath depends to some extent on the mass of the work being rinsed, because the workpiece must supply all the heat of evaporation for drying. Thin-gage materials require rinse temperatures of 93 to 100 °C (200 to 212 °F); otherwise, the workpiece cools before evaporation is complete. Parts made from thicker materials may be rinsed in water at 82 to 88 °C (180 to 190 °F).

Rapid and thorough drying of the plated work is important, to prevent water marks and stains and to eliminate the moisture from residual salt that may not have been entirely removed from crevices or recesses by rinsing. Residual salt and moisture can be a source of corrosion.

Drying practice is also influenced by the shape and orientation of the workpiece as it leaves the final rinse. In many applications, hot-water rinsing is followed with oven drying, wherein hot air is blown directly against the work. In automatic installations, oven temperatures are maintained at 105 °C (220 °F) or higher and the work passes through in 3 to 5 min. Centrifuges with a hot air blast are used for barrel-plated work.

Hydrogen Embrittlement

If an electrodeposited coating is to be applied to a highly stressed part or a high-strength (over 1100 MPa, or 160 ksi) heat-treated steel part, it is important that the processing not decrease the static or fatigue strength of the part. Hydrogen embrittlement does not affect fatigue life. Coatings having high residual stresses, such as chromium, affect fatigue life; however, this is not the case with cadmium.

Cadmium deposited from a cyanide solution is more likely to produce hydrogen embrittlement than any other commonly plated metal. Heat-treated steels, particularly those plated and used at 35 HRC and above, are susceptible to hydrogen embrittlement. Most susceptible is spring steel that has not been adequately stress relieved after forming. The requirements of Federal Specification QQ-P-416F may be used as a guide for stress relief before plating and hydrogen embrittlement post-treatment (Table 13). Other guidelines vary from these, but the latest revision (F) seems to be the most stringent.

Table 13 Heat treat specifications required to stress relieve cadmium-plated components

Hardness, HRC	Stress relief before plating			Hydrogen embrittlement relief (within 4 h of plating)		
	Temperature		Minimum time, h	Temperature		Minimum time, h
	°C	°F		°C	°F	

34-54	175-205	350-400	4	. . .	. . .	. . .
36-45	. . .	. . .	. . .	175-205	350-400	8 23(a)
46-54	. . .	. . .	. . .	175-205	350-400	23
>55	120-150	250-300	23	120-150	250-300	23

(a) Fasteners and bearings

Although the thickness of the plated deposit appears to have no direct bearing on hydrogen embrittlement, it is always more difficult to release the hydrogen (by baking) from heavy deposits.

By adhering to the following procedures, hydrogen embrittlement can be minimized or made inconsequential:

- Use mechanical cleaning methods, such as brushing, blasting, and tumbling.
- Wherever possible, avoid the use of strong acid-pickling solutions and extended exposure to acid pickling.
- If pickling is essential to the preparation of medium-strength and high-strength steel parts, bake the parts at 175 to 205 °C (350 to 400 °F) for 3 h after pickling and before plating.
- In plating, use the higher current densities to produce a more porous deposit; 755 A/m^2 (70 A/ft$^{2)}$ in a cyanide bath without brighteners has been satisfactory for steel at 46 HRC.
- After plating, bake parts at 175 to 205 °C (350 to 400 °F) for 3 to 24 h. The shorter baking periods are generally adequate for parts with a tensile strength below about 1520 MPa (220 ksi); longer baking periods are recommended for steel of tensile strength above about 1520 MPa (220 ksi) or for lower-strength parts if sharp notches or threads exist. Parts greater than 25 mm (1 in.) thick should also be baked for 24 h. The elapsed time between plating and baking must never exceed 8 h and should be carried out as soon as possible, preferably within 4 h.
- Plate parts to a thickness of about 5 μm (200 μin.), bake for 3 h at 195 °C (385 °F), activate in cyanide, and then complete the plating to the required final thickness.

The applications of shot peening and baking, as related to the hardness of the steel to be plated, are described in Federal Specification QQ-C-320 (Amendment 1) and are summarized in the article "Industrial (Hard) Chromium Plating" in this Volume.

Tests for Adhesion of Plated Coatings

The tests used for evaluating adhesion of plated coatings are largely qualitative. A bend test, described in Federal Specification QQ-P-416, involves observation of the degree of flaking that occurs as a specimen is bent. Additional tests are scrape/scratch, short blasts from a glass bead machine (reduced pressures), and bake/cold water quench, all of which tend to show blistering or peeling. In another test, a pressure-sensitive tape, such as surgical adhesive or masking tape, is attached to the plated surface. The tape is quickly stripped from the specimen by pulling it at right angles to the surface. If adhesion is poor, loose plate or blisters will appear as flecks on the surface of the adhesive.

Another good test for adhesion, on parts that have been baked after being plated, is a visual inspection for blisters in the plate. If a good bond has not been established, the plate will most often pull away from the basis metal and form blisters.

Chromate Conversion Coatings

The corrosion of cadmium plate can be retarded by applying a supplemental chemical conversion coating of the chromate type. The chromate films are produced by immersing the plated article in a solution containing chromic acid or other chromates and catalytic agents. These films provide protection against initial corrosion through the inhibitive properties of the water-soluble chromium compounds present. However, the chromate finish must not be applied before stress relieving or baking, because its beneficial effect will be destroyed by the elevated temperature.

Chromate conversion coatings are used in some instances to improve the bond between paint and cadmium-plated surfaces and to provide the plate with resistance to corrosion if gaps should occur in the paint film. However, wash primers will not adhere to chromate finishes, and baking painted chromate finishes will produce poor bonding.

Plate Discoloration. Cadmium tarnishes easily from handling and, at a lesser rate, from normal oxidation. Both types of tarnish may be prevented by the use of chromate conversion coatings. For maximum prevention of tarnish, an unmodified chromate film should be applied, if the iridescence or the light yellow coloration it imparts is not objectionable. Such a surface film also provides resistance against salt spray and humidity, and its application for this purpose is frequently standard practice. The clear film obtained by bleaching a chromate coating affords much poorer protection, but it is superior to an as-plated cadmium surface with respect to resistance to tarnishing, humidity, and salt spray.

With a plate thickness of 13 to 18 μm (520 to 720 μin.) and a chromate conversion coating, cadmium will provide adequate service in marine and humid tropical atmospheres. When long-term exposure is anticipated, a paint coating is desirable.

If a chromate treatment is used, only two cold-water rinse tanks are necessary after plating. The first may be for reclaiming the cadmium solution or for the treatment of water. The second rinse should be provided with sufficient flow and agitation to prevent carryover of cyanide into the chromate solution. After chromate dipping, three rinse tanks are required. Again, the first tank may be for reclaiming or waste treatment.

Yellow chromate finish is obtained by dipping in acidified sodium or potassium dichromate. Excellent corrosion protection and a superior base for organic finishing are obtained.

Clear chromate finish consists of 117 g (0.258 lb) of chromic acid and 1.2 g (2.6×10^{-3} lb) of sulfuric acid per liter (gallon) of water and provides good passivation and attractive appearance. Although the protective film is very thin, it prevents the formation of a white, powdery corrosion product on cadmium-plated parts in indoor or internal-component use.

Olive green coating is obtained in an acidified dichromate solution and is easily colored by any of the acid dyes.

Other Postplating Processes

Bright Dipping. The solution for bright dipping consists of $\frac{1}{4}$ to 1% of commercial-grade nitric acid (1.41 sp gr) and is used at room temperature. The acid neutralizes any alkaline salts on the surface and provides some passivation. It is used extensively because it does not interfere with solderability. Immersion times vary from 2 to 30 s.

A solution of acidified hydrogen peroxide is also used for bright dipping. It consists of 6 to 7% commercial-grade (35%) hydrogen peroxide acidified with about 0.25% H_2SO_4. It produces a bright luster and uniform finish but adversely affects resistance to atmospheric corrosion, ultimately resulting in the formation of a white powder. The solution is rather expensive and has a short life.

Phosphate treatment produces a supplementary conversion coating. The solution consists of 3 to 4% equivalent phosphoric acid at a pH of 3.5 to 4.2. The solution is maintained at a temperature of 71 to 88 °C (160 to 190 °F); immersion time ranges from 3 to 5 min. Following the acid dip, parts are water rinsed and then passivated for 2 to 3 min in a solution of sodium dichromate (0.8 to 1.5 g/L, or 0.1 to 0.2 oz/gal) or chromic acid (pH, 3.5 to 4.0) at a temperature of 66 to 77 °C (150 to 170 °F). The coating provides a good basis for organic finishes.

Molybdenum coating is performed in a proprietary bath containing molybdenum salts dissolved in a highly concentrated solution of ammonium chloride at 54 to 66 °C (130 to 150 °F). An attractive, adherent black finish is obtained.

Zinc Plating

Revised by A. Sato, Lea Ronal Inc.

Introduction

ZINC is anodic to iron and steel and therefore offers more protection when applied in thin films of 7 to 15 μm (0.3 to 0.5 mil) than similar thicknesses of nickel and other cathodic coatings, except in marine environments where it is surpassed by cadmium (which is somewhat less anodic than zinc to iron and steel). When compared to other metals it is relatively inexpensive and readily applied in barrel, tank, or continuous plating facilities. Zinc is often preferred for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective. Electroplated zinc without subsequent treatment becomes dull gray in appearance after exposure to air. Bright zinc that has been subsequently given a chromate conversion coating or a coating of clear lacquer (or both) is sometimes used as a decorative finish. Such a finish, although less durable than heavy nickel chromium, in many instances offers better corrosion protection than thin coatings of nickel chromium, and at much lower cost.

Much recent attention has been focused on the development of techniques for electroplating alloys such as zinc-iron, zinc-nickel, and zinc-cobalt. The operating parameters and applications of these coatings is very similar to those for unalloyed zinc. More detailed information about these techniques is provided in the article "Zinc Alloy Plating" in this Volume.

Plating Baths

Commercial zinc plating is accomplished by a number of distinctively different systems: cyanide baths, alkaline noncyanide baths, and acid chloride baths. In the 1970s, most commercial zinc plating was done in conventional cyanide baths, but the passage of environmental control laws throughout the world has led to the continuing development and widespread use of other processes. Today, bright acid zinc plating (acid chloride bath) is possibly the fastest growing system in the field. Approximately half of the existing baths in developed nations use this technology and most new installations specify it.

The preplate cleaning and postplate chromate treatments are similar for all zinc processes; however, the baths themselves are radically different. Each separate system is reviewed in detail in this article, giving its composition and the advantages and disadvantages.

Cyanide Zinc Baths

Bright cyanide zinc baths may be divided into four broad classifications based on their cyanide content: regular cyanide zinc baths, midcyanide or half-strength cyanide baths, low-cyanide baths, and microcyanide zinc baths. Table 1 gives the general composition and operating conditions for these systems.

Table 1 Composition and operating conditions of cyanide zinc baths

Constituent	**Standard cyanide bath**(a)				**Mid or half-strength cyanide bath**(b)			
	Optimum		**Range**		**Optimum**		**Range**	
	g/L	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**
Preparation								
Zinc cyanide	61	8.1	54-86	7.2-11.5	30	4.0	27-34	3.6-4.5

Sodium cyanide	42	5.6	30-41	4.0-5.5	20	2.7	15-28	2.0-3.7
Sodium hydroxide	79	10.5	68-105	9.0-14.0	75	10.0	60-90	8.0-12.0
Sodium carbonate	15	2.0	15-60	2.0-8.0	15	2.0	15-60	2.0-8.0
Sodium polysulfide	2	0.3	2-3	0.3-0.4	2	0.3	2-3	0.3-0.4
Brightener	(g)	(g)	1-4	0.1-0.5	(g)	(g)	1-4	0.1-0.5
Analysis								
Zinc metal	34	4.5	30-48	4.0-6.4	17	2.3	15-19	2.0-2.5
Total sodium cyanide	93	12.4	75-113	10.0-15.1	45	6.0	38-57	5.0-7.6
Sodium hydroxide	79	10.5	68-105	9.0-14.0	75	10.0	60-90	8.0-12.0
Ratio: NaCN to Zn	2.75	0.37	2.0-3.0	0.3-0.4	2.6	0.3	2.0-3.0	0.2-0.4

Constituent	**Low-cyanide bath(c)**				**Microcyanide bath(d)**			
	Optimum		**Range**		**Optimum**		**Range**	
	g/L	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**
Preparation								
Zinc cyanide	9.4(b)	1.3(e)	7.5-14(b)	1.0-1.9	(f)	(f)	(f)	(f)
Sodium cyanide	7.5	1.0	6.0-15.0	0.8-2.0	1.0	0.1	0.75-1.0	0.4-0.13
Sodium hydroxide	65	8.7	52-75	6.9-10.0	75	10.0	60-75	8-10
Sodium carbonate	15	2.0	15-60	2.0-8.0	. . .	. . .	. . .	. . .
Sodium polysulfide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Brightener	(g)	(g)	1-4	0.1-0.5	(g)	(g)	1-5	0.1-0.7
Analysis								

Zinc metal	7.5	1.0	. . .	0.8-1.5	7.5	1.0	6.0-11.3	0.8-1.5
Total sodium cyanide	7.5	1.0	6.0-15.0	0.8-2.0	1.0	0.1	0.75-1.0	0.1-0.13
Sodium hydroxide	75	10	60-75	8.0-10.0	75	10.0	60-75	8-10
Ratio: NaCN to Zn	1.0	0.1	1.0	0.1	. . .	. . .	. . .	. . .

Note: Cathode current density: limiting 0.002 to 25 A/dm^2 (0.02 to 250 A/ft^2); average barrel 0.6 A/dm^2 (6 A/ft^2); average rack 2.0 to 5 A/dm^2 (20 to 50 ft^2). Bath voltage: 3 to 6 V, rack; 12 to 25 V, barrel.

(a) Operating temperature: 29 °C (84 °F) optimum; range of 21 to 40 °C (69 to 105 °F).

(b) Operating temperature: 29 °C (84 °F) optimum; range of 21 to 40 °C (69 to 105 °F).

(c) Operating temperature: 27 °C (79 °F) optimum; range of 21 to 35 °C (69 to 94 °F).

(d) Operating temperature: 27 °C (79 °F) optimum; range of 21 to 35 °C (69 to 94 °F).

(e) Zinc oxide.

(f) Dissolve zinc anodes in solution until desired concentration of zinc metal is obtained.

(g) As specified

Cyanide baths are prepared from zinc cyanide (or zinc oxide sodium cyanide), and sodium hydroxide, or from proprietary concentrates. Sodium polysulfide or tetrasulfide, commonly marketed as zinc purifier, is normally required in standard, midcyanide, and occasionally low-cyanide baths, to precipitate heavy metals such as lead and cadmium that may enter the baths as an anode impurity or through drag-in.

Standard cyanide zinc baths have a number of advantages. They have been the mainstay of the bright zinc plating industry since the early 1940s. A vast amount of information regarding standard cyanide bath technology is available, including information on the technology of operation, bath treatments, and troubleshooting.

The standard cyanide bath provides excellent throwing and covering power. The ability of the bath to cover at very low current densities is greater than that of any other zinc plating system. This capability depends on the bath composition, temperature, base metal, and proprietary additives used, but it is generally superior to that of the acid chloride systems. This advantage may be critical in plating complex shapes. This bath also tolerates marginal preplate cleaning better than the other systems.

Cyanide zinc formulas are highly flexible, and a wide variety of bath compositions can be prepared to meet diverse plating requirements. Zinc cyanide systems are highly alkaline and pose no corrosive problems to equipment. Steel tanks and anode baskets can be used for the bath, substantially reducing initial plant investment.

The cyanide system also has a number of disadvantages, including toxicity. With the possible exception of silver or cadmium cyanide baths, the standard cyanide zinc bath containing 90 g/L (12 oz/gal) of total sodium cyanide is potentially the most toxic bath used in the plating industry. The health hazard posed by the high cyanide content and the cost for treating cyanide wastes have been the primary reasons for the development of the lower-cyanide baths and the switch to alkaline noncyanide and acid baths. Although the technology for waste treatment of cyanide baths is well developed, the cost for the initial treatment plant may be as much as or more than for the basic plating installation.

Another disadvantage is the relatively poor bath conductivity. The conductivity of the cyanide bath is substantially inferior to that of the acid bath, so substantial power savings may be had by using the latter.

The plating efficiency of the cyanide system varies greatly, depending on such factors as bath temperature, cyanide content, and current density. In barrel installations at current densities up to 2.5 A/dm^2 (25 A/ft^2), the efficiency can range within 75 to 90%. In rack installations, the efficiency rapidly drops below 50% at current densities above 6 A/dm^2 (60 A/ft^2).

Although the depth of brilliance obtained from the cyanide zinc bath has increased steadily since 1950, none of the additives shows any degree of the intrinsic leveling found in the acid chloride baths. The ultimate in depth of color and level deposits reached in the newer acid baths cannot be duplicated in the cyanide bath.

Midcyanide Zinc Baths. In an effort to reduce cyanide waste as well as treatment and operating costs, most cyanide zinc baths are currently at the so-called midcyanide, half-strength, or dilute cyanide bath concentration indicated in Table 1. Plating characteristics of midcyanide baths and regular cyanide baths are practically identical. The only drawback of the midcyanide bath, compared with the standard bath, is a somewhat lower tolerance to impurities and poor preplate cleaning. This drawback is seldom encountered in practice in the well-run plant. Greater ease of rinsing, substantially less dragout, and savings in bath preparation, maintenance, and effluent disposal costs are responsible for the prominence of this type of bath.

Low-cyanide zinc baths are generally defined as those baths operating at approximately 6 to 12 g/L (0.68 to 1.36 oz/gal) sodium cyanide and zinc metal. They are substantially different in plating characteristics from the midcyanide and standard cyanide baths. The plating additives normally used in regular and midstrength cyanide baths do not function well with low metal and cyanide contents. Special low-cyanide brighteners have been developed for these baths.

Low-cyanide zinc baths are more sensitive to extremes of operating temperatures than either the regular or midcyanide bath. The efficiency of the bath may be similar to that of a regular cyanide bath initially, but it tends to drop off more rapidly (especially at higher current densities) as the bath ages. Bright throwing power and covering power are slightly inferior to those of a standard midcyanide bath. However, most work that can be plated in the higher cyanide electrolytes can be plated in the low-cyanide bath. Despite the fact that low-cyanide baths have significantly lower metal and cyanide contents, they are less sensitive to impurity content than the standard or midcyanide bath. Heavy metal impurities are much less soluble at lower cyanide contents. The deposit from a low-cyanide bath is usually brighter than that from a regular or midcyanide system, especially at higher current densities. These baths are used extensively for rack plating of wire goods. Unlike the other cyanide systems, low-cyanide baths are quite sensitive to sulfide treatments to reduce impurities. Regular sulfide additions may reduce the plating brightness and precipitate zinc.

Microcyanide zinc baths are essentially a retrogression from the alkaline noncyanide zinc process discussed in the following section. In the early history of alkaline baths it was often difficult to operate within its somewhat limited parameters; many platers used a minimal amount of cyanide in these baths, 1.0 g/L (0.13 oz/gal), for example. This acted essentially as an additive, increasing the overall bright range of the baths. However, it negated the purpose of the alkaline noncyanide bath, which is to totally eliminate cyanide.

Preparation of Cyanide Zinc Baths

Bath may be prepared with cyanide zinc liquid concentrates that are diluted with water, and to which sodium hydroxide is normally added, or they may be prepared as follows:

1. Fill the makeup and/or plating tank approximately two-thirds full of tap water.
2. Slowly stir in the required amount of sodium hydroxide.
3. Add the required amount of sodium cyanide and mix until dissolved.
4. Prepare a slurry of the required amount of zinc oxide or zinc cyanide and slowly add to the bath. Mix until completely dissolved. Instead of zinc salts, the bath may be charged with steel baskets of zinc

anode balls that are allowed to dissolve into the solution until the desired metal content is reached.

5. Add an initial 15 g/L (2.0 oz/gal) sodium carbonate for rack plating baths.
6. Add approximately 0.25 to 0.50 g/L (0.03 to 0.06 oz/gal) of sodium polysulfide or zinc purifier for regular and midcyanide baths.
7. Run plating test panels and add the necessary amount of brightener to the bath. If a satisfactory deposit is obtained, place anodes for production.

Zinc baths prepared from impure zinc salts may require treatment with zinc dust and/or low-current-density dummying (the process of plating out bath impurities). Zinc dust should be added at the rate of 2 g/L (0.26 oz/gal) and the bath should be agitated for about 1 h. After settling, the bath should be filtered into the plating tank. Dummying is preferably done on steel cathode sheets at low current densities of 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2) for 12 to 24 h.

Cyanide Zinc Plating Brighteners

Zinc plating bath brighteners are almost exclusively proprietary mixtures of organic additives, usually combinations of polyepoxyamine reaction products, polyvinyl alcohols, aromatic aldehydes, and quaternary nicotinates. These materials are formulated for producing brightness at both low- and high-density areas and for stability at elevated temperatures. Metallic brighteners based on nickel and molybdenum are no longer commercially used in zinc systems, because their concentration in the deposit is highly critical. Proprietary additives should be used following the manufacturer's recommendations for bath operation. Some incompatibility between various proprietary additives may be encountered, and Hull Cell plating tests should always be used to test a given bath and evaluate new brighteners.

Alkaline Noncyanide Baths

Alkaline noncyanide baths are a logical development in the effort to produce a relatively nontoxic, cyanide-free zinc electrolyte. Approximately 15 to 20% of zinc plated at present is deposited from these baths. Bath composition and operating parameters of these electrolytes are given in Table 2. The operating characteristics of an alkaline noncyanide system depend to a great extent on the proprietary additives and brightening agents used in the bath, because the zinc deposit may actually contain 0.3 to 0.5 wt % C, which originates from these additives. This is ten times as much carbon as is found in deposits from the cyanide system.

Table 2 Composition and operating characteristics of alkaline noncyanide zinc baths

Constituent	**Optimum**[a]		**Range**[b]	
	g/L	**oz/gal**	**g/L**	**oz/gal**
Preparation				
Zinc oxide	9.4	1.3	7.5-21	1-2.8
Sodium hydroxide	65	8.6	65-90	8.6-12
Proprietary additive	[c]	[c]	3-5	0.4-0.7
Analysis				
Zinc metal	7.5	1.0	6.0-17.0	0.8-2.3

Sodium hydroxide	75.0	10.0	75-112	10.0-14.9

(a) Operating conditions: temperature, 27 °C (81 °F) optimum; cathode current density, 0.6 A/dm^2 (6 A/ft^2); bath voltages, 3 to 6 rack.

(b) Operating conditions: temperature, 21 to 35 °C (69 to 94 °F) range; cathode current density, 2.0 to 4.0 A/dm^2 (20 to 40 A/ft^2); bath voltages, 12 to 18 barrel.

(c) As specified

Alkaline noncyanide baths are inexpensive to prepare and maintain, and they produce bright deposits and cyanide-free effluents. An alkaline noncyanide zinc bath with a zinc metal content of 7.5 to 12 g/L (1.0 to 1.6 oz/gal) used at 3 A/dm^2 (30 A/ft^2) produces an acceptably bright deposit at efficiencies of approximately 80%, as shown in Fig. 1. However, if the metal content is allowed to drop 2 g/L (0.26 oz/gal), efficiency drops to below 60% at this current density. Raising the metal content much above 17 g/L (2.3 oz/gal) produces dull gray deposits, lower-current-density plating areas, and poor distribution; however, additives have been developed to address this problem. Increasing sodium hydroxide concentration increases efficiency, as shown in Fig. 2. However, excessively high concentrations will cause metal buildup on sharp-cornered edges. Alkaline noncyanide zinc is a practical plating bath having hundreds of thousands of gallons in use in large captive plating installations.

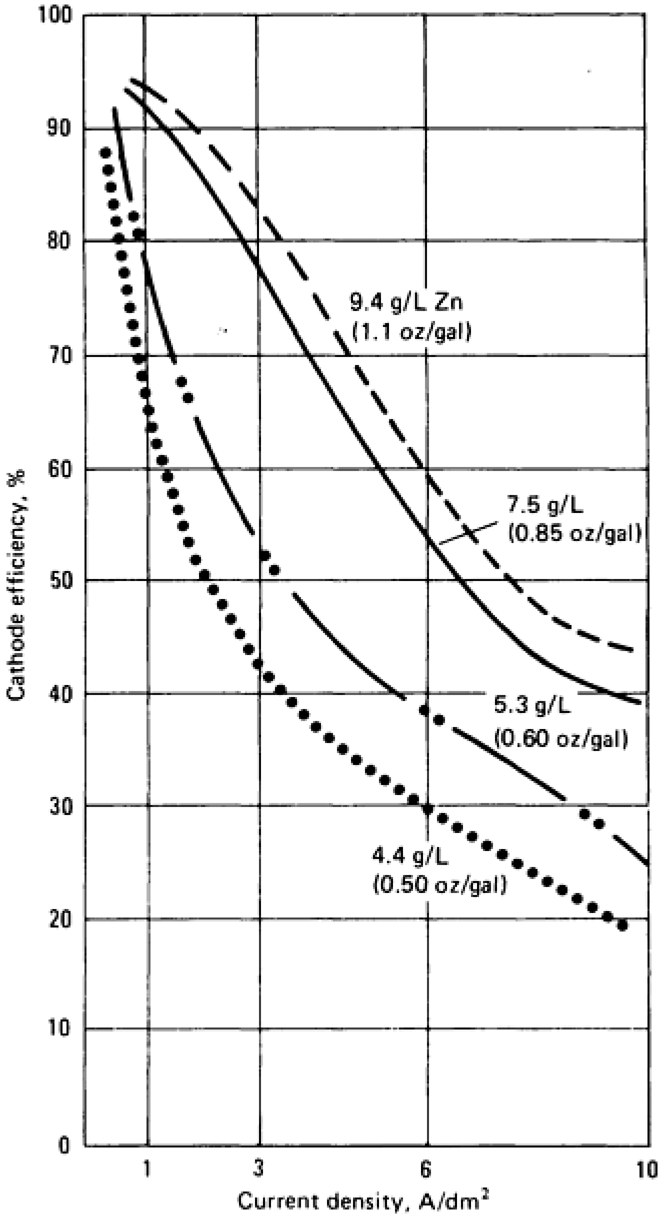

Fig. 1 Cathode current efficiency of alkaline noncyanide zinc baths as related to zinc metal contents. NaOH, 80 g/L (11 oz/gal); Na_2CO_3, 15 g/L (2 oz/gal)

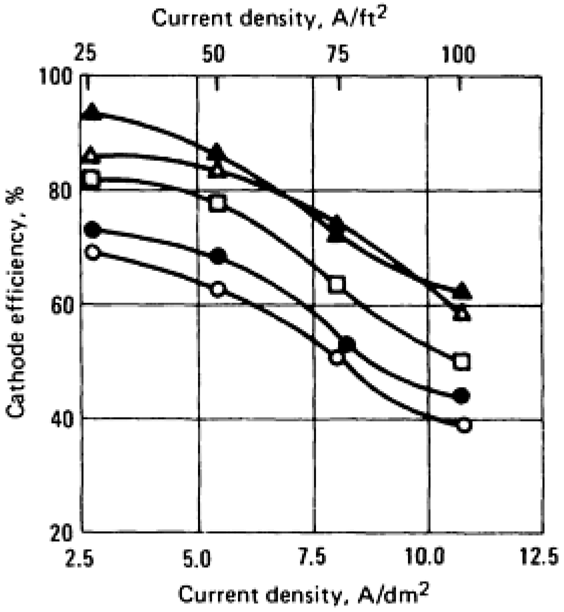

Fig. 2 Effect of zinc and sodium hydroxide concentration on the cathode efficiency of noncyanide zinc solutions. Temperature: 26 °C (77 °F). d : 7.5 g/L (1 oz/gal) Zn, 75 g/L (10 oz/gal) NaOH; •: 7.5 g/L (1.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; V : 11 g/L (1.5 oz/gal) Zn, 110 g/L (15 oz/gal) NaOH; ▲: 15 g/L (2.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; W : 11 g/L (1.5 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH.

Operating Parameters of Standard Cyanide and Midcyanide Zinc Solutions

Anodes. Almost every physical form of zinc anode material has been used in cyanide zinc plating, the type and prevalence varying from country to country. In the United States, cast zinc balls approximately 50 mm (2 in.) in diameter, contained in spiral steel wire cages, are by far the most common anode material. A practical variation of this is the so-called flat top anode, with a flat surface to distinguish it from cadmium ball anodes. The use of ball anodes provides maximum anode area, ease of maintenance, and practically complete dissolution of the zinc anodes with no anode scrap formation.

One of the most economical forms of anode material is the large cast zinc slabs that form the prime material for subsequent ball or elliptical anode casting. Although these have the disadvantage of bulky handling and the need for specially fabricated anode baskets, their lower initial cost makes their use an important economic factor in the larger zinc plating shop.

Three grades of zinc for anodes are conventionally used for cyanide zinc plating: prime western, intermediate, and special high-grade zinc. The zinc contents of these are approximately 98.5%, 99.5%, and 99.99%, respectively. The usual impurities in zinc anodes are all heavy metals, which cause deposition problems unless continuously treated. Nearly troublefree results can consistently be obtained through the use of special high-grade zinc. A typical composition of special high-grade zinc is:

Constituent	Amount, %
Zinc	99.9930
Lead	0.0031

Cadmium	0.0017
Iron	0.0010
Copper	Trace

Control of Zinc Metal Content. Zinc anodes dissolve chemically as well as electrochemically in cyanide baths, so effective anode efficiency will be above 100%. This causes a buildup in zinc metal content, because cathode efficiencies are usually substantially less than 100%. A number of procedures have been developed to control this tendency.

In a conventional new zinc cyanide installation, approximately ten spiral anode ball containers should be used for every meter of anode rod. These should be filled initially, and after 1 or 2 weeks of operation they should be adjusted to compensate for anode corrosion and dragout losses so that the metal content remains as constant as possible. During shutdown periods in excess of 48 h, most cyanide zinc platers remove anodes from the bath. In large automatic installations, this may be done by using a submerged steel anode bar sitting in yokes that can be easily lifted by hoist mechanisms.

One of the prime causes of zinc metal buildup is the very active galvanic cell between the zinc anodes and the steel anode containers. This is evidenced by intense gassing in the area of anodes in a tank not in operation. Zinc buildup from this source can be eliminated by plating the anode containers with zinc before shutdown, which eliminates the galvanic couple.

Temperature. Probably no operating variable is as important and as often overlooked in the operation of cyanide zinc baths as operating temperature. Cyanide zinc solutions have been reported operating between the rather wide limits of 12 to 55 °C (54 to 130 °F), with the vast majority of baths operating between 23 to 32 °C (73 to 90 °F). The exact operating temperature for a given installation depends on the type of work processed, the finish desired, and the engineering characteristics of the plating system. Bath temperature has an effect on a great many variables in the cyanide zinc systems, so the optimum temperature is generally a compromise. Increasing the bath temperature:

- Increases cathode efficiency
- Increases bath conductivity
- Increases anode corrosion
- Produces duller deposits over a broad range of current densities
- Reduces covering power
- Reduces throwing power
- Increases breakdown of cyanide and addition agents

Lowering the bath temperature has the opposite effects. Thus, if a plater is primarily concerned with plating of pipe or conduit where deposit brilliance is not of great importance and covering and throwing power are not critical, operating the bath at the highest practical temperature to give optimum conductivity and plating efficiency would be preferred. For general bright plating of fabricated stampings, a lower bath temperature should be used, permitting the required excellent covering and throwing power and bright deposits.

The effects of higher bath temperature can be compensated to a substantial extent by increasing the total-cyanide-to-zinc ratio of the solution. The exact optimum ratio varies slightly for a given proprietary system, as shown in Table 3.

Table 3 Effect of bath temperature on total-cyanide-to-zinc ratio

Temperature	Total-NaCN-to-Zn ratio	Total-NaCN-to-Zn ratio

°C	°F	(standard cyanide bath)	(midcyanide bath)
22	72	2.6	2.2
26	79	2.7	2.3
30	86	2.8	2.4
34	93	2.9	2.5
38	100	3.0	2.6
42	108	3.2	2.7
46	115	3.3	3.0

Cathode Current Densities. Bright cyanide zinc solutions operate at wide-ranging cathode current densities varying from extremely low, less than 0.002 A/dm^2 (0.02 A/ft^2), to above 25 A/dm^2 (250 A/ft^2) without burning (i.e., the formation of dark, coarse electrodeposits). Current density limits depend on bath composition, temperature, cathode film movement, and addition agents used.

Average current densities vary but are approximately 0.6 A/dm^2 (6 A/ft^2) in barrel plating and 2 to 5 A/dm^2 (20 to 50 A/ft^2) in still or rack plating. Barrel zinc plating is a complex phenomenon in which a large mass of parts is constantly tumbled in the plating cylinder at varying distances from the cathode contact surfaces. At any given time, a part may have an infinitesimally low current density or it may even be deplating, and in another instant, near the outer surface of the tumbling mass, current density may approach 20.0 A/dm^2 (200 A/ft^2). In general, the bulk of deposition takes place in the lower current density range of 0.2 to 1 A/dm^2 (2 to 10 A/ft^2).

Average cathode current densities are generally easier to maintain in rack and still line operations and range from approximately 2 to 5 A/dm^2 (20 to 50 A/ft^2). However, the actual current density of any particular area of a given part will vary greatly, depending on part configuration, anode-to-cathode distance, bath shape, and other factors affecting the primary and secondary current distribution characteristics. In most cases, with proper attention to racking and work shape, current density variations can be kept within practical limits on fabricated parts so that if a minimum average thickness of 4 µm (0.15 mil) is required on a specific part, variations from approximately 2.5 to 8 µm (0.09 to 0.3 mil) occur at various areas on the part.

Cathode current efficiencies in barrel cyanide zinc plating vary between 75 and 93%, depending on temperature, formulation, and barrel current densities. In rack or still plating, however, there is quite a wide variation in current efficiencies when higher current densities are used, especially above 3 A/dm^2 (30 A/ft^2). The effects of zinc metal content, sodium hydroxide content, and the cyanide-to-zinc ratio on cathode current efficiency are shown in Fig. 3. As can be seen from the graphs, the current efficiency in the most commonly used baths drops dramatically from approximately 90% at 2.5 A/dm^2 (25 A/ft^2) to 50% at 5 A/dm^2 (50 A/ft^2). An improvement in current efficiency can be obtained by using a high-strength bath; however, this is offset by the relatively poor throwing power of the solution, higher brightener consumption, higher operating costs, and maintenance difficulties. The lower standard bath concentration, which gives practically identical results, is used for practically all plating installations except a selected few rack tanks that plate conduit or large flat surfaces with no critical recessed areas.

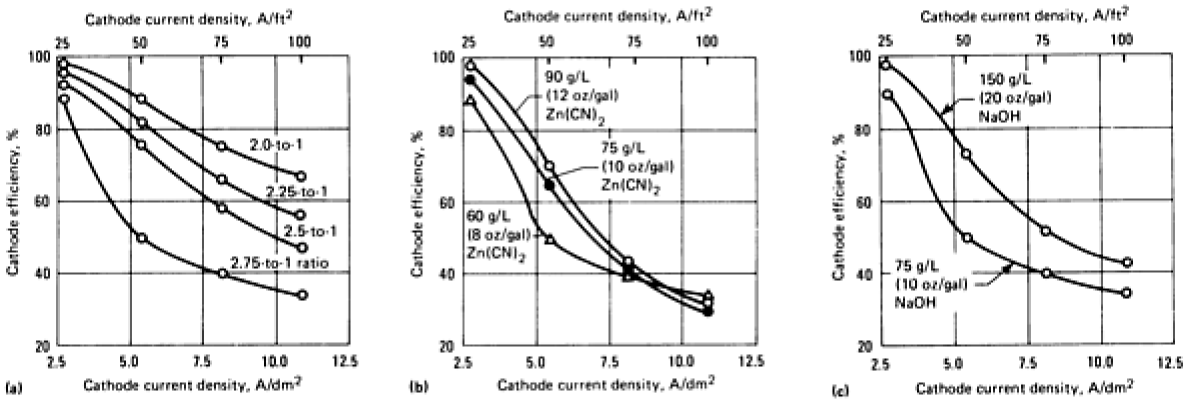

Fig. 3 Effects of bath composition variables and cathode current density on cathode efficiency in cyanide zinc plating. (a) Effect of NaCN/Zn ratio. 60 g/L (8 oz/gal) Zn (CN); 17.5 to 43.7 g/L (2.33 to 5.82 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.0-to-1 to 2.75-to-1 ratios of NaCN to zinc. Temperature: 30 °C (86 °F). (b) Effect of zinc metal content. 60.1, 75.2, and 90.2 g/L (8, 10, and 12 oz/gal) Zn (CN); 43.7, 54.6, and 65.5 g/L (5.82, 7.27, and 8.72 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.75-to-1 ratio of NaCN to zinc. Temperature: 30 °C (86 °F). (c) Effect of NaOH content. 60.1 g/L (8 oz/gal) Zn(CN); 43.6 g/L (5.8 oz/gal) NaCN; 150.4 and 75.2 g/L (20 and 10 oz/gal) NaOH; 2.75-to-1 ratio of NaCN to zinc. Temperature: 30 °C (86 °F)

Sodium carbonate is present in every cyanide and alkaline zinc solution. It enters the bath as an impurity from the makeup salts (sodium hydroxide and sodium cyanide may contain anywhere from 0.5 to 2% sodium carbonate) or as a deliberate addition to the initial bath (15 to 30 g/L, or 2.0 to 4 oz/gal).

The harmful effects of sodium carbonate in cyanide zinc plating are not as critical as in cyanide cadmium plating. Sodium carbonate does not begin to affect normal bath operation until it builds to above 75 to 105 g/L (10 to 14 oz/gal). Depending on overall bath composition and the type of work being done, a carbonate content in this range results in a slight decrease in current efficiency, especially at higher current densities, decreased bath conductivity, grainier deposits, and roughness, which becomes visible when the carbonate crystallizes out of cold solutions.

The carbonate content of zinc baths builds up by decomposition of sodium cyanide and absorption of carbon dioxide from the air reacting with the sodium hydroxide in the bath. Carbonates are best removed by one of the common cooling or refrigeration methods rather than by chemical methods, which are simple in theory but extremely cumbersome in practice. When an operating cyanide zinc bath has reached the point that excessive carbonates present a problem, it undoubtedly is contaminated with a great many other dragged-in impurities, and dilution is often a much quicker, although expensive, method of treatment. Alkaline noncyanide baths do not suffer from the effects of carbonate buildup.

Operating Parameters of Low-Cyanide Zinc Systems

Temperature control is as critical, if not more critical, in the low-cyanide bath as in the regular or midcyanide bath. The optimum operating temperature for most proprietary baths is 29 °C (84 °F), and the permissible range is more restricted than for the standard cyanide bath. Adequate cooling facilities are therefore mandatory and are more critical for low-cyanide than for the standard system.

Cathode Current Density. The average cathode current densities used in most low-cyanide processes are the same as in the standard cyanide bath. However, some proprietary baths do not have the extreme high-current-density capabilities of the standard cyanide bath, and burning on extremely high-current-density areas may be more of a problem with the low-cyanide bath than with the conventional baths.

Agitation. Unlike the standard cyanide bath, where agitation is usually nonexistent, air or mechanical agitation of the low-cyanide bath is common and is often quite useful in obtaining the optimum high-current-density plating range of the bath.

Filtration. Most low-cyanide baths appear to operate much more cleanly than the standard or midcyanide bath. The bath is a poor cleaner, and soils that may be removed and crystallized out of high-cyanide baths are not as readily affected by the low-cyanide bath.

Efficiency. The efficiency of the low-cyanide bath on aging is much more dependent on the particular addition agent used than the standard cyanide bath, because there is a substantial difference in various proprietary systems. In a new low-cyanide bath, current efficiency is slightly higher than that of a standard or midcyanide system. However, as the bath ages, current efficiency tends to drop, possibly because of the formation of additive breakdown products, and the efficiency of a bath after 2 or 3 months of operation may be as much as 30% below that of a higher cyanide system, especially at higher current densities. As in the standard cyanide bath, increasing the sodium hydroxide content, zinc metal content, and operating temperature increases the efficiency of the low-cyanide bath. However, increasing these variables has markedly harmful effects on the bright operating range of a low-cyanide bath that usually override the benefit of increased efficiency. The effects of bath constituents and temperature on the plating characteristics of the bright low-cyanide zinc systems are given in Table 4. Figure 4 shows the effect of sodium cyanide concentration on cathode efficiency.

Table 4 Effect of bath constituents and temperature on plating characteristics of bright, low-cyanide zinc plating

Variable	**Cathode efficiency**	**Bright plating range**	**Bright low-current-density throwing power**
Increasing sodium hydroxide	Increases	Slightly decreases	Negligible
Increasing zinc metal	Increases	Decreases	Decreases
Increasing sodium cyanide	Decreases	Increases	Increases
Increasing brightener	Increases	Increases	Increases
Increasing temperature	Increases	Decreases	Decreases

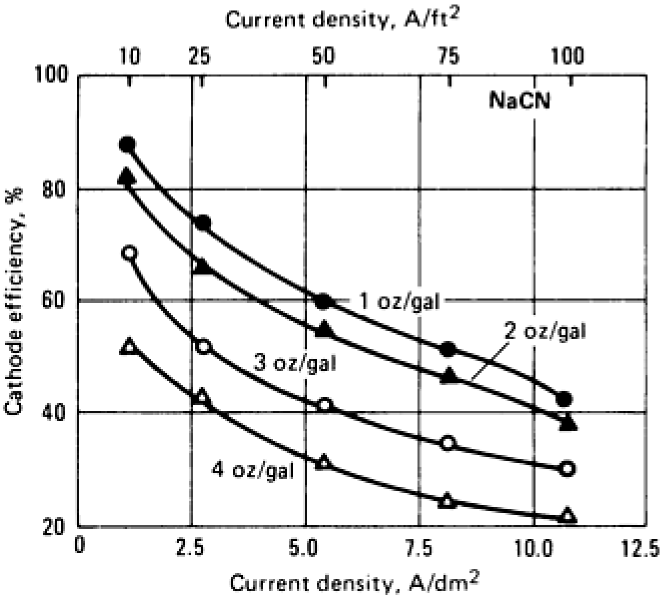

Fig. 4 Effect of sodium cyanide concentration on the cathode efficiency of low-cyanide zinc solutions. d :20 g/L

(2.5 oz/gal) NaCN; •:8 g/L (1 oz/gal) NaCN; ∨:30 g/L (4 oz/gal) NaCN; ▲:15 g/L (2 oz/gal) NaCN

Bright Throwing Power and Covering Power. The bright covering power of a low-cyanide bath operated at low current density is intrinsically not as good as that of a standard or midcyanide bath. In most operations, however, the difference is negligible except on extremely deep recessed parts. The vast majority of parts that can be adequately covered in a standard cyanide bath can be similarly plated in a low-cyanide bath without any production problems, such as excessively dull recessed areas or stripping by subsequent bright dipping.

Increasing the brightener and cyanide contents, within limits, improves the bright low-current-density deposition to a visible degree. Problems with bright throwing power at extremely low current densities are often solved by raising the cyanide content to approximately 15 g/L (2 oz/gal), which in effect returns the system to the lower range of the midcyanide bath.

Operating Parameters of Alkaline Noncyanide Zinc Baths

Temperature control is more critical in noncyanide zinc baths than in cyanide baths. The optimum temperature for most baths is approximately 29 °C (84 °F). Low operating temperatures result in no plating or, at most, very thin, milky white deposits. High operating temperatures rapidly narrow the bright plating current range, cause dullness at low current densities, and result in very high brightener consumption. However, because these temperature limitations for noncyanide zinc are within those commonly used in regular cyanide zinc, no additional refrigeration or cooling equipment is required for conversion to the process.

Operating Voltages. Normal voltages used in standard cyanide zinc plating are adequate for the noncyanide zinc bath, in both rack and barrel range. Normal voltage will be approximately 3 V with a range of 2 to 20 V, depending on part shape, anode-to-cathode relationship, temperature, barrelhole size, and variables that are unique to each operation.

Cathode Current Densities. The maximum allowable cathode current densities of the noncomplexing noncyanide bath closely approximate those of a standard cyanide bath. Current density ranges from 0.1 to more than 20 A/dm^2 (1 to 200 A/ft^2) can be obtained. This extremely wide plating range permits operation at an average current density of 2 to 4 A/dm^2 (20 to 40 A/ft^2) in rack plating, which makes a noncyanide system practical for high-production work.

Anodes. Standard zinc ball or slab anodes in steel containers are used in the noncyanide electrolyte. During the first 2 or 3 weeks of installation of noncyanide zinc baths, the anode area should be watched carefully to determine the appropriate anode area to maintain a stable analysis of zinc in the system. Whenever possible, zinc anodes should be removed during weekend shutdown periods to avoid excessive metal buildup.

Filtration of noncyanide baths is not an absolute necessity. However, the occurrence of roughness in these baths presents a greater potential problem than in regular cyanide baths. This is due to the nature of the deposit, which may become amorphous at very high current densities if the brightener is not maintained at an optimum level, and to anode polarization problems, which result in sloughing off of anode slimes, a more common occurrence in these baths. Carbon filtration may be required to remove organic contamination caused by marginal preplate cleaning practices. Filtration is also the preferred method for removing zinc dust used to treat metallic impurities in the system.

The bright plating range of the alkaline, noncyanide zinc bath is totally dependent on the particular additive used. Without any additive, the deposit from an alkaline, noncyanide bath is totally useless for commercial finishing, with a powdery, black amorphous deposit over the entire normal plating range.

Proper maintenance of the addition agent at the recommended level is extremely important in noncyanide alkaline zinc baths. A plater does not have the liberty of maintaining low levels of brightener in the bath and still obtaining passably bright deposits, as is the case in cyanide systems. Low brightener content rapidly leads to high- and medium-current-density burning, because in the noncyanide bath, as in the low-cyanide bath, burning and brightness are interdependent.

Cathode current efficiency of a noncyanide bath is a very critical function of the metal content (Fig. 1). At lower metal concentrations of approximately 4 g/L (0.5 oz/gal), efficiency is less than that of a standard cyanide bath, whereas at a metal content of approximately 9 g/L (1.2 oz/gal), efficiency is somewhat higher than in either regular or low-cyanide baths. Thus, if a plater can maintain metal content close to the 9 g/L (1.2 oz/gal) value, there will be no problem in obtaining deposition rates similar to those obtained with cyanide baths.

Acid Baths

The continuing development of acid zinc plating baths based on zinc chloride has radically altered the technology of zinc plating since the early 1970s. Acid zinc plating baths now constitute 40 to 50% of all zinc baths in most developed nations and are the fastest growing baths throughout the world. Acid zinc formulas and operating limits are given in Table 5. Bright acid zinc baths have a number of intrinsic advantages over the other zinc baths:

- They are the only zinc baths possessing any leveling ability, which, combined with their superb out-of-bath brightness, produces the most brilliant zinc deposits available.
- They can readily plate cast iron, malleable iron, and carbonitrided parts, which are difficult or impossible to plate from alkaline baths.
- They have much higher conductivity than alkaline baths, which produces substantial energy savings.
- Current efficiencies are 95 to 98%, normally much higher than in cyanide or alkaline processes, especially at higher current densities, as shown in Fig. 5.
- Minimal hydrogen embrittlement is produced than in other zinc baths because of the high current efficiency.
- Waste disposal procedures are minimal, consisting only of neutralization, at pH 8.5 to 9, and precipitation of zinc metal, when required.

The negative aspects of the acid chloride bath are that:

- The acid chloride electrolyte is corrosive. All equipment in contact with the bath, such as tanks and superstructures, must be coated with corrosion-resistant materials.
- Bleedout of entrapped plating solution occurs to some extent with every plating process. It can become a serious and limiting factor, prohibiting the use of acid chloride baths on some fabricated, stamped, or spot welded parts that entrap solution. Bleedout may occur months after plating, and the corrosive electrolyte can ruin the part. This potential problem should be carefully considered when complex assemblies are plated in acid chloride electrolytes.

Table 5 Composition and operating characteristics of acid chloride zinc plating baths

Constituent	**Ammoniated bath Barrel**		**Ammoniated bath Rack**	
	Optimum	**Range**	**Optimum**	**Range**
Preparation				
Zinc chloride	18 g/L (2.4 oz/gal)	15-25 g/L (2.0-3.8 oz/gal)	30 g/L (4.0 oz/gal)	19-56 g/L (2.5-7.5 oz/gal)
Ammonium chloride	120 g/L (16.0 oz/gal)	100-150 g/L (13.4-20.0 oz/gal)	180 g/L (24.0 oz/gal)	120-200 g/L (16.0-26.7 oz/gal)
Potassium chloride	. . .	. . .	. . .	. . .
Sodium chloride	. . .	. . .	. . .	. . .
Boric acid	. . .	. . .	. . .	. . .

Carrier brightener[(a)]	4 vol%	3-5%	3.5%	3-4%
Primary brightener[(a)]	0.25%	0.1-0.3%	0.25%	0.1-0.3%
pH	5.6	5.5-5.8	5.8	5.2-6.2
Analysis				
Zinc metal	9 g/L (1.2 oz/gal)	7.5-25 g/L (1.0-3.8 oz/gal)	14.5 g/L (1.9 oz/gal)	9-27 g/L (1.2-3.6 oz/gal)
Chloride ion	90 g/L (1.2 oz/gal)	75-112 g/L (10.0-14.9 oz/gal)	135 g/L (18.0 oz/gal)	90-161 g/L (12.0-21.5 oz/gal)
Boric acid	. . .	. . .	. . .	. . .
Operating conditions				
Temperature	24 °C (75 °F)	21-27 °C (69-79 °F)	24 °C (75 °F)	21-27 °C (69-79 °F)
Cathode current density	. . .	0.3-1.0 A/dm^2 (3-10 A/ft^2)	. . .	2.0-5 A/dm^2 (20-50 A/ft^2)
Voltage	. . .	4-12 V	. . .	1-5 V

Constituent	**Potassium bath**		**Mixed sodium ammonium Barrel bath**	
	Optimum	**Range**	**Optimum**	**Range**
Preparation				
Zinc chloride	71 g/L (9.5 oz/gal)	62-85 g/L (8.3-11.4 oz/gal)	34 g/L (4.5 oz/gal)	31-40 g/L (4.1-5.3 oz/gal)
Ammonium chloride	. . .	. . .	30 g/L (4.0 oz/gal)	25-35 g/L (3.3-4.7 oz/gal)
Potassium chloride	207 g/L (27.6 oz/gal)	186-255 g/L (24.8-34.0 oz/gal)	. . .	. . .
Sodium chloride	. . .	. . .	120 g/L (16.0 oz/gal)	100-140 g/L (13.3-18.7 oz/gal)
Boric acid	34 g/L (4.5 oz/gal)	30-38 g/L (4.0-5.1 oz/gal)	. . .	. . .

Carrier brightener(a)	4%	4-5%	4%	3-5%
Primary brightener(a)	0.25%	0.1-0.3%	0.2%	0.1-0.3%
pH	5.2	4.8-5.8	5.0	4.8-5.3
Analysis				
Zinc metal	34 g/L (4.5 oz/gal)	30-41 g/L (4.0-5.5 oz/gal)	16.5 g/L (2.2 oz/gal)	15-19 g/L (2.0-2.5 oz/gal)
Chloride ion	135 g/L (18.0 oz/gal)	120-165 g/L (16.0-22.0 oz/gal)	110 g/L (14.7 oz/gal)	93-130 g/L (12.4-17.4 oz/gal)
Boric acid	34 g/L (4.5 oz/gal)	30-38 g/L (4.0-5.1 oz/gal)	. . .	. . .
Operating conditions				
Temperature	27 °C (79 °F)	21-35 °C (69-94 °F)	27 °C (79 °F)	25-35 °C (76-94 °F)
Cathode current density	. . .	2.0-4 A/dm^2 (20-40 A/ft^2)	. . .	0.3-1 A/dm^2 (3-10 A/ft^2)
Voltage	. . .	1-5 V	. . .	4-12 V

(a) Carrier and primary brighteners for acid chloride are proprietary, and exact recommendations of manufacturer should be followed. Values given are representative.

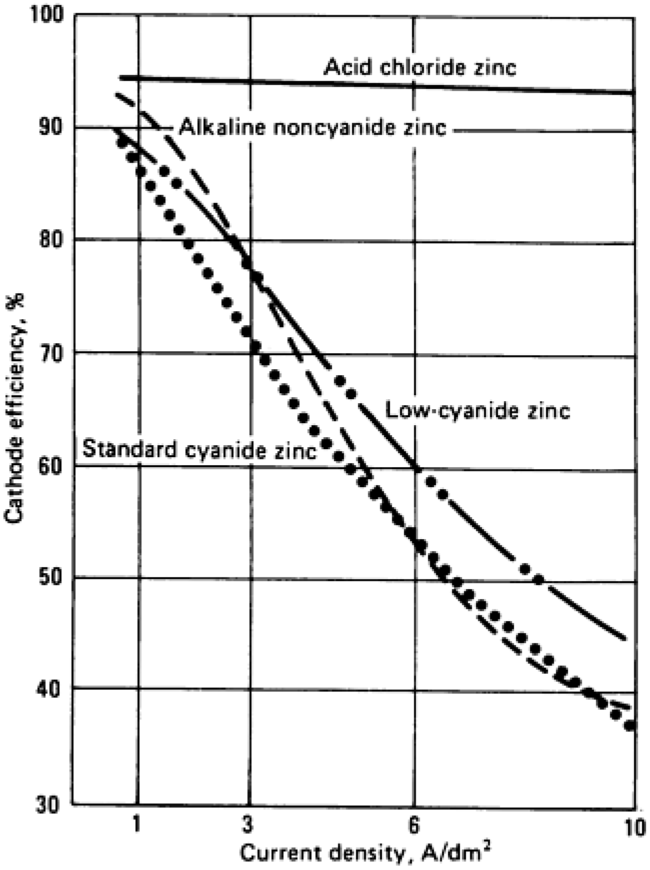

Fig. 5 Comparison of cathode current efficiencies of bright zinc plating electrolytes

Acid chloride zinc baths currently in use are principally of two types: those based on ammonium chloride and those based on potassium chloride. The ammonium-based baths, the first to be developed, can be operated at higher current densities than potassium baths. Both systems depend on a rather high concentration of wetting agents, 4 to 6 vol%, to solubilize the primary brighteners. This is more readily accomplished in the ammonia systems, which makes bath control somewhat easier. Ammonium ions, however, act as a complexing agent in waste streams containing nickel and copper effluents, and in many localities they must be disposed of by expensive chlorination. This was the essential reason for the development of the potassium chloride bath.

All bright acid chloride processes are proprietary, and some degree of incompatibility may be encountered between them. Conversion from an existing process should be done only after a Hull Cell plating test evaluation. Preplate cleaning, filtration, and rack designs for acid chloride baths should be equivalent to those required for nickel plating.

The latest acid chloride zinc baths to become available to the industry are those based on salt (sodium chloride) rather than the more expensive potassium chloride. In many of these baths, salt is substituted for a portion of either ammonium or potassium chloride, producing a mixed bath. Sodium acid chloride baths at present are generally restricted to barrel operation, because burning occurs much more readily in these baths at higher current densities. However, with the continuing development of additive technology, sodium acid chloride baths may challenge the widely used nonammoniated potassium bath in the near future.

Acid chloride zinc baths are now being explored as the basis of zinc alloy plating incorporating metals such as nickel and cobalt, to improve corrosion for specific applications and possibly eliminate standard chromate treating.

A number of zinc baths based on zinc sulfate and zinc fluoborate have been developed, but these have very limited applications. They are used principally for high-speed, continuous plating of wire and strip and are not commercially used for plating fabricated parts. Table 6 shows the compositions and operating conditions for some typical fluoborate and sulfate baths.

Table 6 Fluoborate and sulfate electroplating bath compositions

Constituent	Fluoborate[(a)]		Sulfate[(b)]	
	g/L	oz/gal	g/L	oz/gal
Zinc	65-105	9-14	135	18
Zinc fluoborate	225-375	30-50	. . .	. . .
Zinc sulfate	. . .	. . .	375	50
Ammonium fluoborate	30-45	4-6	. . .	. . .
Ammonium chloride	. . .	. . .	7.5-22.5	1-3
Addition agent	(c)	(c)	(c)	(c)

(a) At room temperature; 3.5 to 4 pH; at 20 to 60 A/dm^2 (200 to 600 A/ft^2).

(b) At 30 to 52 °C (85 to 125 °F); 3 to 4 pH; at 10 to 60 A/dm^2 (100 to 600 A/ft^2).

(c) As needed

Operating Parameters of Acid Chloride Zinc Baths

Anodes for acid chloride zinc should be special high grade, 99.99% Zn. Most installations use zinc ball or flat top anodes in titanium anode baskets. Baskets should not be used if the applied voltage on an installation exceeds 8 V, because there may be some attack on the baskets. Baskets should be kept filled to the solution level with zinc balls. Slab zinc anodes, drilled and tapped for titanium hooks, may also be used. Any areas of hooks or splines exposed to solution should be protective coated. Anode bags are optional but recommended for most processes, especially for rack plating where they are useful to minimize roughness. Bags may be made of polypropylene, Dynel, or nylon. Before being used they should be leached for 24 h in a 5% hydrochloric acid solution containing 0.1% of the carrier or wetting agent used in the particular plating bath.

Chemical Composition. Zinc, total chloride, pH, and boric acid, when used, should be controlled and maintained in the recommended ranges (see Table 5) by periodic replenishment using chemically pure materials. Excess zinc causes poor low-current-density deposits, and insufficient zinc causes high-current-density burning. Excess chloride may cause separation of brighteners, and insufficient chloride reduces the conductivity of solutions. Excessively high pH values cause the formation of precipitates and anode polarization, and excessively low pH values cause poor plating. Insufficient boric acid reduces the plating range.

Brighteners also have to be replenished by periodic additions. Because the chemical compositions of brighteners are proprietary, the suppliers specify concentrations and control procedures.

Agitation is recommended in acid chloride baths to achieve practical operating current densities. Solution circulation is recommended in barrel baths to supplement barrel rotation. In rack baths, solution circulation is usually accomplished by locating the intake and discharge of the filter at opposite ends of the plating tank. Cathode rod agitation is suitable for many hand-operated rack lines.

Air agitation is the preferred method for most installations. A low-pressure air blower should be used as a supply source.

Temperature control is more critical in acid zinc baths than in cyanide zinc baths, and auxiliary refrigeration should be provided to maintain the bath at its maximum recommended operating temperature, usually 35 °C (95 °F). Cooling coils in the bath itself should be Teflon or Teflon-coated tubing. Titanium coils may be used if they are isolated from the direct current source.

Operating an acid chloride bath above its maximum recommended temperature causes low overall brightness, usually beginning at low current densities and rapidly progressing over the entire part. High temperatures may also bring the bath above the cloud point of the brightener system. As the acid bath gets hot, additives start coming out of solution, giving the bath a milky or cloudy appearance and causing bath imbalance. Conversely, low temperatures, usually below 21 °C (70 °F), cause many baths to crystallize and cause organic additives to separate out of solution. This produces roughness and, in extreme cases, a sticky globular deposit on the bath and work, which clogs filters and completely curtails operations.

Cathode Current Efficiency. The high cathode current efficiency exhibited by acid chloride zinc baths is one of the most important properties of these baths. As shown in Fig. 5, the average cathode current efficiency for these baths is approximately 95 to 98% over the entire range of operable current densities. No other zinc plating system approaches this extremely high efficiency at higher current densities, which can lead to productivity increases of 15 to 50% over those obtainable with cyanide baths. In barrel plating, barrel loads can often be doubled in comparison with those for cyanide baths, and equivalent plating thickness can often be achieved in half the time.

pH control of acid zinc baths is usually monitored on a daily basis. Electrometric methods are preferred over test papers. The pH of a bath is lowered with a hydrochloric acid addition; when required, the pH may be raised with a potassium or ammonium hydroxide addition.

Iron contamination is a common problem in all acid chloride zinc baths. Iron is introduced into the bath from parts falling into the tank during operation, from attack by the solution on parts at current densities below the normal range, such as the inside of steel tubular parts, and from contaminated rinse waters used before plating. Iron contamination usually appears as dark deposits at high current densities; in barrel plating it appears as stained dark spots reproducing the perforations of the plating barrel. A high iron content turns the plating solution brown and murky.

Iron can be readily removed from acid chloride baths by oxidizing soluble ferrous iron to insoluble ferric hydroxide. This is accomplished by adding concentrated hydrogen peroxide to the bath, usually on a daily basis. Approximately 10 mL (0.34 fl oz) of 30% hydrogen peroxide should be used for every 100 L (26.4 gal.) of bath. The peroxide should be diluted with 4 to 5 parts water and dispersed over the bath surface. Dissolved potassium permanganate can be used instead of peroxide. The precipitated iron hydroxide should then be filtered from the bath using a 15 μm (0.6 mil) or smaller filter coated with diatomaceous earth or a similar filter aid.

Control of Plate Thickness

This section discusses the thicknesses of zinc specified for service in various indoor and outdoor atmospheres. Many combinations of variables must be considered in attempting to plate to a given thickness. To hold each variable at a steady value is virtually impossible under production conditions, so as one variable changes spontaneously, others must be adjusted to maintain uniformity of plate thickness. In automatic plating this is impractical, so the process is set up to give a certain minimum thickness under a great variety of conditions. This accounts for much of the thickness variation normally encountered in automatic plating of a run of identical pieces.

The shape and size of parts that may be plated all over, with or without the use of conforming anodes to attain uniformity of plate thickness, are essentially the same in zinc plating as in cadmium plating (see the article "Cadmium Plating" in this Volume).

Normal Variations. Preferred thicknesses in automatic zinc plating are usually minimum specified thicknesses, and there is little concern regarding the maximum thicknesses obtained. Thickness variations encountered should therefore be over the established minimum thickness.

For example, as shown in Fig. 6, tests were made on 75 samples, over a one-week period, of parts 100 mm (4 in.) long and 39 g (1.375 oz) that were automatically plated to a minimum specified thickness of 3.8 μm (0.15 mil). Although actual plate thicknesses ranged from 2.5 to 7.5 μm (0.1 to 0.3 mil), over 80% of the parts examined exceeded the target minimum.

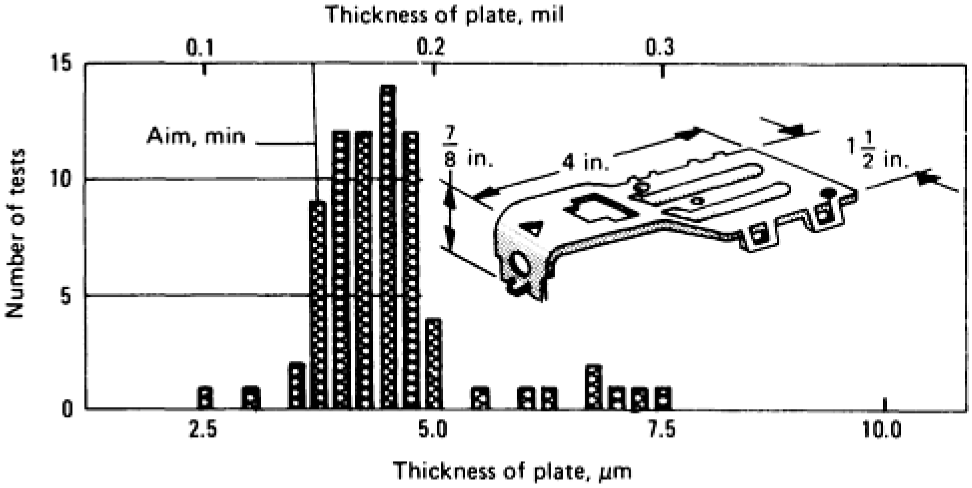

Fig. 6 Variation in thickness of zinc plate obtained in automatic plating in cyanide zinc bath, 75 tests

Thickness variations obtained in barrel plating are markedly affected by the tumbling characteristics of the part and by the density of the load in the plating barrel. Parts that can be tumbled readily are more likely to develop a uniform coating. As shown in Fig. 7, a minimum plate thickness of 12.5 μm (0.5 mil) was the target in barrel plating a 0.12 kg (0.26 lb) S-shape part made of 3 mm (0.125 in.) flat stock. Of 75 parts examined, all were found to be plated to thicknesses that exceeded the target minimum, and a few had thicknesses in excess of 34 μm (0.9 mil).

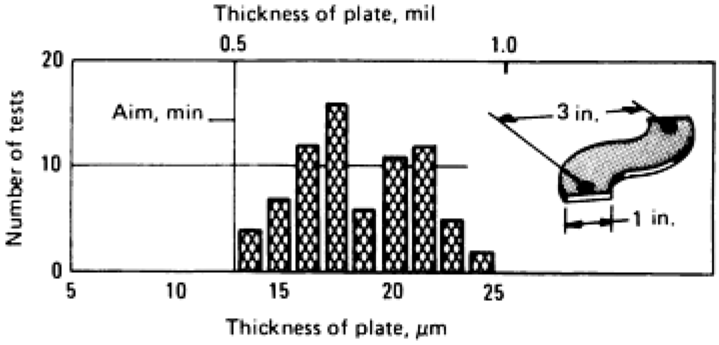

Fig. 7 Variation in thickness of zinc plate obtained in barrel plating a 3.2 mm ($\frac{1}{8}$ in.) thick part in a cyanide zinc

Similarities Between Cadmium and Zinc Plating

Except for differences in plating baths and in such operational details as current density and rates of deposition, alkaline cadmium and zinc plating are essentially similar processes. See the article "Cadmium Plating" in this Volume for a detailed discussion of plating methods, equipment, and processing. Exceptions with respect to equipment and processing are described below.

Plating Equipment. The equipment requirements for zinc plating are the same as those noted for cadmium plating, except for the following:

- In barrel plating, zinc solutions require higher voltage and current density and therefore must be provided with greater cooling capacity to prevent overheating. Also, because the cyanide zinc bath generates much larger amounts of hydrogen, barrel design should incorporate safety features to prevent explosions.
- Fume hoods should be used on cyanide, low-cyanide, and, especially, alkaline noncyanide baths to exhaust caustic spray and toxic fumes.
- Barrels, tanks, and all superstructures coming into contact with acid chloride zinc plating baths should be coated with material able to resist acid corrosion. Polypropylene, polyethylene, polyvinyl chloride, and fiberglass are commonly used materials. Lead-lined tanks should never be used in these systems. Heating and cooling coils should be built of titanium that is electrically isolated from the tank, or of high-temperature Teflon.

Hydrogen embrittlement of steels is a major problem in all types of cyanide zinc plating. These formulas should not be used for spring tempered parts or other parts susceptible to this type of embrittlement. Spring-tempered parts and other susceptible parts should be plated in acid chloride electrolyte. When no embrittlement whatsoever can be tolerated, mechanically deposited zinc is the preferable alternative.

Processing Steps. Time requirements for various operations involved in still tank, barrel, and automatic methods of plating zinc to a thickness of less than 12.5 μm (0.5 mil) are given in Table 7.

Table 7 Process steps and time requirements for zinc plating operations

Times listed are for plating zinc to a thickness of less than 12.5 μm (0.5 mil).

Processing cycle	Time for each operation
Hand- or hoist-operated still tank	
Electrolytic cleaning	1-3 min
Cold water rinse	10-20 s
Acid pickle	30 s-2 min
Cold water rinse	10-20 s
Cold water rinse	10-20 s
Zinc plate	6-8 min
Cold water rinse	10-20 s

Cold water rinse	10-20 s
Chromate conversion coat	15-30 s
Cold water rinse	10-20 s
Hot water rinse	20-30 s
Air dry	1 min
Hand- or hoist-operated barrel line	
Soak clean	4 min
Electroclean	4 min
Cold water rinse	1-2 min
Acid pickle	2-3 min
Zinc plate	20-30 min
Cold water rinse	1-2 min
Cold water rinse	1-2 min
Chromate conversion coat	30 s-1 min
Cold water rinse	1-2 min
Hot water rinse	2-3 min
Centrifugal dry	3-5 min
Automatic barrel line	
Soak clean	6 min
Electroclean	3 min
Cold water rinse	2 min

Cold water rinse	2 min
Acid pickle	1 min
Neutralize dip	3 min
Cold water rinse	2 min
Zinc plate	30-40 min
Dragout rinse	2 min
Neutralize rinse	2 min
Cold water rinse	2 min
Nitric acid dip	30 s
Cold water rinse	2 min
Chromate dip	30 s
Cold water rinse	2 min
Hot water rinse	2 min
Centrifugal dry	3 min

Applications

In the presence of moisture, zinc becomes a sacrificial protecting agent when in contact with iron and other metals that are below zinc in the galvanic series. Attack is most severe when the electrolyte has high electrical conductivity (as in marine atmospheres) and when the area ratio of zinc to the other metals is small.

Plate Thickness. The life of a zinc coating in the atmosphere is nearly proportional to the coating thickness. Its rate of corrosion is highest in industrial areas, intermediate in marine environments, and lowest in rural locations. Corrosion is greatly increased by frequent dew and fog, particularly if the exposure is such that evaporation is slow.

Table 8 gives the estimated life of different thicknesses of unprotected zinc coatings on steel in different outdoor atmospheres. The majority of zinc-plated parts are coated with a thickness of 7.5 to 12.5 μm (0.3 to 0.5 mil). Typical applications employing thicknesses less than or greater than usual are given in Table 9.

Table 8 Estimated average service life of unprotected zinc coatings on steel in outdoor service

Condition	Coating thickness	Service, yr

	µm	**mil**	
Rural	5	0.2	3
	13	0.5	7
	25	1.0	14
	38	1.5	20
	50	2.0	30
Temperate marine	5	0.2	1
	13	0.5	3
	25	1.0	7
	38	1.5	10
	50	2.0	13
Industrial marine	5	0.2	1
	13	0.5	2
	25	1.0	4
	38	1.5	7
	50	2.0	9
Severe industrial	5	0.2	0.5
	13	0.5	1
	25	1.0	3
	38	1.5	4
	50	2.0	6

Table 9 Applications of zinc plating at thicknesses below or above 7 to 13 µm (0.3 to 0.5 mil)

Application	**Plate thickness**	
	µm	**mil**
Less than 7 µm (0.3 mil) of zinc		
Automobile ashtrays(a)	5-7	0.2-0.3
Birdcages(b)	5	0.2
Electrical outlet boxes(c)	4-13	0.15-0.5
Tacks	5	0.2
Tubular rivets(d)	5	0.2
More than 13 µm (0.5 mil) of zinc		
Conduit tubing(e)	30	1.2

(a) Chromated after plating.

(b) Chromated after plating; some parts dyed and lacquered.

(c) Bright chromated after plating.

(d) Chromated, clear or colored, after plating.

(e) Dipped in 0.5% HNO_3 or chromated after plating

Supplementary Coatings. Because corrosion is rapid in industrial and marine locations, zinc-plated parts that must endure for many years are usually protected by supplementary coatings. Steel with 5 µm (0.2 mil) of electroplated zinc is often painted to obtain a coating system for general outdoor service; a phosphate or chromate post-plating treatment ensures suitable adherence of paint to zinc.

In uncontaminated indoor atmospheres, zinc corrodes very little. A 5 µm (0.2 mil) coating has been known to protect steel framework on indoor cabinets for more than 20 years. Atmospheric contaminants accelerate corrosion of zinc if condensation occurs on cooler parts of structural members inside buildings. In 10 years or less, 12.5 µm (0.5 mil) of zinc may be dissipated. Zinc-plated steel in such locations is usually given a protective coating of paint.

A satisfactory coating for parts such as those on the inside of an office machine must afford protection in storage, assembly, and service. The cost is also important. Gears, cams, and other parts of the working mechanism can be plated with 3.8 to 6.3 μm (0.15 to 0.25 mil) of zinc to meet these requirements.

Chromate conversion coatings, colored or clear, are almost universally applied to zinc-plated parts for both indoor and outdoor use to retard corrosion from intermittent condensation, such as may occur in unheated warehouses. Chromate films minimize staining from fingerprints and provide a more permanent surface appearance than bare zinc.

Limitations. Zinc-plated steel is not used for equipment that is continually immersed in aqueous solutions. It must not be used in contact with foods and beverages because of dangerous health effects. Although zinc may be used in contact with gases such as carbon dioxide and sulfur dioxide at normal temperatures if moisture is absent, it has poor resistance to most common liquid chemicals and to chemicals of the petroleum and pharmaceutical industries.

Fasteners. Steel fasteners, such as screws, nuts, bolts, and washers, are often electroplated for corrosion resistance and appearance. If protection against atmospheric corrosion is the sole objective, zinc is the most economical coating metal. Coatings of 5 to 7.5 μm (0.2 to 0.3 mil) give protection for 20 years or more for indoor applications in the absence of frequent condensation of moisture. Chromate coatings are used to retard corrosion from condensates, provide a more permanent surface appearance, and prevent staining from fingerprints. For indoor use in industrial areas and in locations where condensation is prevalent, as in unheated buildings, corrosion may be rapid, and the zinc surface should be phosphated and then painted to extend its service beyond the few years that would be obtained by the unpainted coating. Unprotected zinc-plated screws should not be used to fasten bare parts if the service is to include marine exposure.

The dimensional tolerance of most threaded articles, such as nuts, bolts, screws, and similar fasteners with complementary threads, does not permit the application of coatings much thicker than 7.5 μm (0.3 mil). The limitation of coating thickness on threaded fasteners imposed by dimensional tolerance, including class or fit, should be considered whenever practicable, to prevent the application of thicker coatings than are generally permissible. If heavier coatings are required for satisfactory corrosion resistance, allowance must be made in the manufacture of the threaded fasteners for the tolerance necessary for plate buildup. If this is not practicable, phosphating before assembly and painting after assembly will increase service life. The approximate durability of 5 μm (0.2 mil) untreated coatings is given in Table 8.

Appearance. The appearance of electrodeposited zinc can be varied over a wide range, depending on bath composition, current density, the use of brighteners, and postplating treatments. The appearance of electroplated zinc is bright and silvery, and the deposit from the acid chloride baths is often initially indistinguishable from bright nickel chrome when plated.

Currently, nearly all zinc plating is followed by some type of chromate dip. These preserve the appearance of the part and vastly increase the bright shelf life of the surface. The cost of chromating is so minimal that its use has become practically universal. Presently, bright zinc deposits are used for a wide variety of low-cost consumer goods such as children's toys, bird cages, bicycles, and tools. Refrigerator shelves are commonly bright zinc plated, chromated, and lacquered. Without lacquer protection, even chromated bright zinc will tarnish and discolor quite rapidly when handled, and unlacquered bright zinc plate is not a good substitute for nickel chrome when a longlasting bright finish is desired. However, the vast majority of zinc plate is deposited primarily to impart corrosion resistance; brightness is not the primary factor for these applications.

Additional information about applications of electroplated zinc is provided in the article "Surface Engineering of Carbon and Alloy Steels" in this Volume.

Indium Plating

Allen W. Grobin, Jr., Grobin Associates, Inc.

Introduction

INDIUM is a soft, low-melting-point, silvery white metal with a brilliant metallic luster and a color resembling that of platinum. It alloys with most other metals to form a series of unique alloys, many of which are used as solders. It is soft enough to be readily marked by light fingernail pressure. Indium can be easily extruded at very low pressures: solders containing 50% In can be extruded as 1 mm (0.04 in.) wire at a pressure of 83 MPa (12 ksi). The hardness of indium is

0.9 to 1.0 on the modified Brinell scale, and it has a melting point of 156.7 °C (314.1 °F), a boiling point of 2000 °C (3632 °F), and a low vapor pressure.

Indium is ductile, malleable, crystalline, and diamagnetic. The pure metal gives a high pitched "cry" when bent. It wets glass and finds application in low-melting alloys and solders. It is used in making alkaline batteries, automotive trim, bearing alloys, electronic assemblies, germanium transistors, photoconductors, rectifiers, thermistors, vacuum seals, and group III-V compound semiconductors such as indium phosphide and indium arsenide. When rubbed together, two indium-plated parts will "cold weld" (autogenously join). This can be easily accomplished with freshly plated parts, but as surface oxides build up with time, more vigorous rubbing is required. This cold welding phenomenon is being explored for use in the surface mount technology of the electronics industry. Indium is electropositive to iron and steel and electronegative to tin. In an aqueous 3% sodium chloride solution of pH 6.7 to 7.2, indium has a half-cell static potential of -0.56 V referenced to that of a silver electrode given the value of zero. This places indium between cadmium and tin in the electromotive series of metals, which is used by materials and design engineers to identify and avoid potential galvanic corrosion problems.

Indium is particularly useful in making reliable electrical contact to aluminum. When indium-plated steel wire terminals are secured to aluminum, the high-resistance surface aluminum oxide cracks under the pressure and the indium extrudes into the oxide cracks, making direct metal-to-metal contact with the underlying aluminum. This application, which was widely used in the telephone industry, has diminished in use with that industry's switch to fiber optics. However, it is used for aluminum wire terminals in the electronics industry, particularly where the use of terminal fluids is undesirable. One relatively new use is for the plating of steel internal dished-tooth star-washer-ring-lug terminals for attachment to aluminum capacitors.

Acknowledgements

Special thanks are due to Joseph Mazia, Mazia Tech-Com Services, Inc., and James Slattery, Indium Corporation of America, for their helpful review comments and suggestions.

Indium Electrodeposits

Indium electrodeposits provide excellent solderability, low electrical contact resistance, friction resistance, and atmospheric corrosion resistance when plated on aluminum, copper-base alloys, and steel, which are typically selected for their engineering properties. Indium can be readily electrodeposited from either acid or alkaline solutions. It is particularly useful for coating aluminum and other amphoteric metals; its alkaline corrosion resistance provides a wider measure of corrosion protection for these metals than that provided by cadmium, tin, or zinc.

Indium can be plated without special apparatus. Any shop or laboratory that has plating equipment can set up an indium plating tank without costly equipment. Any technician familiar with the plating of silver, copper, and so on finds indium plating quite easy to handle. However, barrel plating of small, lightweight items (e.g., ring lugs, wire terminations, and threaded fasteners and washers) may present a problem on occasion. This type of part may cold weld during the tumbling action of the barrel and end up as a solid indium-plated mass. The problem is easily overcome by adding gelatin or glue to the bath to increase its viscosity.

Plating Baths. The four most commonly used indium plating baths are indium cyanide, indium fluoborate, indium sulfamate, and indium sulfate. Table 1 compares these processes. The details of the processes are shown in Tables 2, 3, 4, and 5.

Table 1 Comparison of indium plating baths

Parameter	Bath salt			
	Cyanide	Fluoborate	Sulfamate	Sulfate
Throwing power	Excellent	Good	Excellent	Poor

Quality of plate	Excellent	Good	Excellent	Passable
Ease of solution analysis	Difficult	Easy	Easy	Easy
Critical temperature	No	21-32 °C (70-90 °F)	No	Controlled
Color of solution	Clear	Clear	Clear	Clear
Wettability	Easy	Difficult	Easy	Difficult
Anode	Insoluble	Indium	Indium	Indium
Cathode efficiency	40-50%	40-50%	90%	30-70%
Tendency to pit	No	No	No	Yes
Control of solution	Cyanide and metal	Metal and pH	Metal and pH	Metal and pH

Table 2 Indium cyanide plating bath

Constituent or parameter	**Value or condition**
Indium as metal	33 g/L (4.4 oz/gal)
Dextrose	33 g/L (4.4 oz/gal)
Total cyanide (KCN)	96 g/L (12.7 oz/gal)
Potassium hydroxide (KOH)	64 g/L (8.5 oz/gal)
Temperature (static)	Room temperature
Cathode efficiency	50-75%
Anodes	Plain steel
Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Difficult

Critical temperature (working)	None, with or without agitation
Color of solution	Clear, pale yellow to dark amber
Wettability	Easy
Tendency to pit	None
Control of solution	Cyanide and metal by additions
Use	General
Current	162-216 A/m^2 (15-20 A/ft^2)
pH	High

Notes: (1) Because insoluble anodes are used, it is necessary to replace the indium metal content of this alkaline bath. Under normal conditions, addition of cyanide will not be required; however, it is best to keep the cyanide concentration at about 100 g/L (13.4 oz/gal) for efficient operation. (2) Plating efficiency of the bath will be maintained within a range suitable for normal plating until the indium content is reduced. The plating rate should be checked at regular intervals, because as the bath is depleted a decrease in rate of deposition is to be expected.

Table 3 Indium fluoborate plating bath

Constituent parameter	**Value or condition**
Indium fluoborate	236 g/L (31.5 oz/gal)
Boric acid	22-30 g/L (2.9-4.0 oz/gal)
Ammonium fluoborate	40-50 g/L (5.3-6.7 oz/gal)
pH (colorimetric)	1.0
Temperature (static)	21-32 °C (70-90 °F)
Cathode efficiency	40-75%
Anode efficiency	Indium, 100%
Throwing power	Good
Quality of plate	Good

Ease of solution analysis	Easy
Critical temperature (working)	21-32 °C (70-90 °F), with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	None
Control of solution	Metal and pH
Use	Experimental
Current density	540-1080 A/m^2 (50-100 A/ft^2)

Notes: (1) The pH of this bath is controlled by the addition of 42% fluoboric acid. (2) Some insoluble anodes (platinum or graphite) should be used because the anode and cathode efficiency are not in good relation.

Table 4 Indium sulfamate plating bath

Constituent or parameter	**Value or condition**
Indium sulfamate	105.36 g/L (14 oz/gal)
Sodium sulfamate	150 g/L (20 oz/gal)
Sulfamic acid	26.4 g/L (3.5 oz/gal)
Sodium chloride	45.84 g/L (6 oz/gal)
Dextrose	8.0 g/L (1 oz/gal)
Triethanolamine	2.29 g/L (0.3 oz/gal)
pH	1-3.5(a)
Temperature (static)	Room temperature
Cathode efficiency	90%
Anode efficiency	Indium, 100%

Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Easy
Critical temperature (working)	None, with or without agitation
Color of solution	(b)
Wettability	Fairly easy
Tendency to pit	None
Control of solution	Metal and pH(a)
Use of solution	Experimental
Current density	108-216 A/m^2 (10-20 A/ft^2)(c)

(a) 1.5-2 preferred. The pH of this bath is controlled by the addition of sulfamic acid.

(b) Clear when new; after use will darken due to organic material breakdown. This has no effect on deposit. Filtering of bath can be done through activated charcoal to maintain clarity of bath.

(c) Optimum. If metal is increased, current density can be increased up to 1080 A/m^2 (100 A/ft^2).

Table 5 Indium sulfate plating bath

Constituent or parameter	**Value or condition**
Indium (as sulfate)	20 g/L (2.67 oz/gal min)
Sodium sulfate	10 g/L (1.3 oz/gal)
pH	2.0-2.5
Temperature (static)	Room temperature
Cathode efficiency	30-70%

Anode efficiency	Indium, 100%
Throwing power	Poor
Quality of plate	Passable
Ease of solution analysis	Easy
Critical temperature (working)	Controlled, with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	Yes
Control of solution	Metal and pH
Use	Experimental
Current density	216-432 A/m^2 (20-40 A/ft^2)

Notes: (1) The pH of this bath is controlled by the addition of sulfuric acid or sodium hydroxide as needed. (2) Some insoluble anodes (platinum or graphite) should be used because the anode and cathode efficiency are not in good relation.

Diffusion Treatment. The plating of indium on a clean, nonferrous surface does not necessarily end the operation. For some applications, such as bearing plating, the indium deposit is diffused into the base metal, forming a surface alloy. This is accomplished by placing the plated part in an oven or hot oil bath and heat treating it for about 2 h at a temperature slightly above the melting point of indium. Indium melts at 156.7 °C (314.1 °F), and the diffusion treatment is carried out at about 175 °C (350 °F). The processing time may be shortened by increasing the temperature, but only after the diffusion has actually begun. Failure to observe the proper temperature at the beginning of the diffusion process may lead to the formation of surface bubbles or droplets of indium, which are undesirable, particularly on a decorative finish. A number of factors govern the depth of diffusion:

- The amount of indium plated on the surface
- Temperature of heat treatment
- Time of diffusion treatment
- The diffusion coefficient for indium in the base metal

Indium Alloy Electrodeposits

A variety of indium alloy deposits have been reported in the literature. Included are alloys with antimony, arsenic, bismuth, cadmium, copper, gallium, lead, tin, and zinc. Of these, only indium-lead has had any degree of commercial importance.

Indium-lead electroplated alloy was developed as an improvement over the diffusion alloy that is formed by plating a thin layer of indium over lead on lead-containing bearings and diffusing the indium into the lead in a hot, 150 °C (300 °F) oil bath. The alloy reduces the corrosion of the lead-containing bearings by lubricating oils. An alloy containing an average of about 4% In had high resistance to corrosion and was harder and had better antifriction properties than lead. However, the composition of the thermally diffused alloy was nonuniform. The electrodeposited indium-lead alloy provided greater uniformity of composition and showed only one-fourth the corrosion compared to the thermally diffused alloy.

Plating Baths. The two most successful indium-lead plating baths are indium-lead fluoborate and indium-lead sulfamate. Table 6 compares these processes. The details of the processes are shown in Tables 7 and 8.

Table 6 Comparison of indium-lead plating baths

Parameter	**Bath salt**	
	Fluoborate	**Sulfamate**
Indium content of deposit	11%	5%
Microhardness of deposit	2.5 kg/mm^2	(a)

(a) Not reported

Table 7 Indium-lead fluoborate plating bath

Constituent or parameter	**Value or condition**
Indium fluoborate	25 g/L (3.4 oz/gal)
Lead fluoborate	90 g/L (12.0 oz/gal)
Free fluoboric acid	15 g/L (2.0 oz/gal)
Glue	1.5 g/L (0.2 oz/gal)
Current density	100-300 A/m^2 (9-28 A/ft^2)
Temperature	20 °C (70 °F)

Table 8 Indium-lead sulfamate plating bath

Constituent or parameter	**Value or condition**
Indium sulfamate	20 g/L (2.67 oz/gal)
Lead sulfamate	1 g/L (0.13 oz/gal)

Soluble coffee[a]	5 g/L (0.67 oz/gal)
pH	1.5
Current density	100-300 A/m^2 (9-28 A/ft^2)

(a) Regular instant coffee powder

Nonaqueous Indium Plating Baths

The literature has reported the electrodeposition of indium and alloys such as indium-antimony, indium-gallium, and indium-bismuth from solutions of the metals dissolved in distilled ethylene glycol or glycerin. High-quality deposits have been reported with good current efficiencies.

Stripping Indium Plating

Diffused indium plate cannot be stripped from bronze. Undiffused indium on bronze can be removed with hydrochloric acid. Lead-indium plating, either diffused or undiffused, can be removed by immersion in a mixture of 9 parts glacial acetic acid and 1 part 30% hydrogen peroxide at room temperature. Indium and silver-indium alloy can be removed from steel by reversing the current in 30 g/L (4 oz/gal) solution of sodium cyanide at approximately 50 to 55 °C (122 to 131 °F). The silver-indium alloy can be removed in 1:1 nitric acid, but care must be taken to remove it from the bath before the steel is etched.

Specifications and Standards

No ASTM, ISO, or U.S. government specifications exist for indium plating. ASTM initiated a draft standard several years ago, but work was suspended due to lack of interest. The thickness ranges initially proposed were identical to those for tin (ASTM B 545). The SAE/AMS series has a specification for indium-lead plating, AMS 2415.

Hazards

The toxicity of indium and its compounds has not been extensively investigated. Animal tests indicate some degree of hazard, but for normal electroplating applications, usual good housekeeping practices should be sufficient. Indium should not be used in contact with food products because its solubility in food acids is high.

Tin Plating

Revised by Arthur J. Killmeyer, Tin Information Center of North America

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Introduction

TIN IS A VERSATILE, low-melting point, nontoxic metal that has valuable physical properties. It alloys readily with most other metals, and it forms many useful inorganic and organic chemical compounds because it is amphoteric. It has the largest melting point to boiling point range (from 232 to 2370 °C, or 450 to 4300 °F) of any metal. In conventional metallurgical applications, evaporation from a pot of liquid tin does not occur. Tin is used in a multitude of products, although the amount in which it is present is usually relatively small as a percentage of the total. Most manufacturers use some tin, and it is an essential material in industries such as communications, transportation, agriculture, food processing, and construction.

Electrodeposits

A thin coating of electrodeposited tin provides beneficial properties, such as excellent solderability, ductility, softness, and corrosion or tarnish resistance. In this way, the stronger materials that are required for their engineering properties can be enhanced by the desirable properties of tin on their surfaces. A tin deposit provides sacrificial protection to copper, nickel, and many other nonferrous metals and alloys. Tin also provides good protection to steel. However, because tin is normally cathodic to iron, the coating must be continuous and effectively pore-free. (This requirement does not apply to tinplate used for food packaging because the absence of oxygen inside tin-plated food containers prevents the electrochemical cell reactions that lead to corrosion.)

Thick, nonporous coatings of tin provide long-term protection in almost any application. The required coating thickness is established by the application. Thickness recommendations for tin coatings on metallic materials are given in Table 1. Tin coatings can be applied at thicknesses of less than 1 to 250 μm or greater.

Table 1 Recommended thicknesses for typical applications of tin deposits on metal substrates (ASTM B 545-92)

Class	**Minimum thickness**		**Typical applications**
	μm	**μin.**	
A	2.5	100	Mild service conditions, particularly where the significant surface is shielded from the atmosphere (as in electronic connector housings). Provides corrosion and tarnish resistance where greater thicknesses may be detrimental to the mechanical operation of the product (for example, small electrical spring contacts and relays). Class A often used for tin coatings that are not to be soldered, but must function as low-resistance electrical contact surfaces.
B	5	200	Mild service conditions with less severe requirements than grade C. Used as a precoating on solderable base metals to facilitate soldering of electrical components, surface preparation for protective painting, antigalling agent, and a stopoff in nitriding. Also found on baking pans after reflow.
C	8(a)	320(a)	Moderate exposure conditions, usually indoors, but more severe than class B. Used on electrical hardware (such as cases for relays and coils, transformer cans, screened cages, chassis, frames, and fittings) and for retention of the solderability of solderable articles during storage.
D	15(b)	600(b)	Severe service conditions, including exposure to dampness and mild corrosion from moderate industrial environments. Used with fittings for gas meters, automotive accessories (such as air cleaners and oil filters), and in some electronic applications.
E	30	1200	Very severe service conditions, including elevated temperatures, where underlying metal diffusion and intermetallic formation processes are accelerated. Thicknesses of 30 to 125 μm (0.0012 to 0.005 in.) may be required if the coating is subjected to abrasion or is exposed to slowly corrosive liquids or to corrosive atmospheres or gases. Thicker coatings are used for water containers, threaded steel couplings of oil-drilling

(a) 10 μm (400 μin.) for steel substrates.

(b) 20 μm (800 μin.) for steel substrates

Applications. The largest use of tin electrodeposits occurs at steel mills that produce tinplate, primarily as food-preservation containers. A thin tin coating protects the steel inside a tin can, as long as an oxygen-free environment is maintained. The second largest use of tin electrodeposits occurs in the electronics industry, where coatings are applied to the surfaces that require good solderability and corrosion or tarnish resistance.

These include radio and television chassis, computer frames, integrated circuit chip leads, tags, connectors, lead frames, printed wiring boards, and copper wire. Electrodeposited tin is also used on food handling equipment, such as steel baking pans, sieves, can openers, and fasteners. In general, tin electrodeposits are used to protect surfaces and render them usable in applications for which they would otherwise be unsuited.

Types of Electrolytes

Tin can be deposited from either alkaline or acid solutions. Electrolyte compositions and process operating details are provided in Ref 1, 2, and 3, as well as in publications of the International Tin Research Institute. Table 2 gives the basic details of electrolyte composition and operating conditions for alkaline solutions, and Tables 3 and 4 provide this information for acid solutions. Tin ions in the alkaline electrolytes have a valence of +4, whereas those in the acid electrolytes have a valence of +2. Consequently, the alkaline systems require the passage of twice as much current to deposit one gram-molecule of tin at the cathode.

Table 2 Composition and operating conditions for stannate (alkaline) tin plating electrolytes

Values of composition are for electrolyte startup; operating limits for the electrolyte composition are approximately -10 to + 10% of startup values

Solution	Composition										Operating conditions			
	Potassium stannate		Sodium stannate		Potassium hydroxide		Sodium hydroxide		Tin metal(a)		Temperature		Cathode current density	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	°C	°F	A/dm^2	A/ft^2
A	105	14	. . .	. . .	15(b)	2(b)	. . .	. . .	40	5.3	66-88	150-190	3-10	30-100
B	210	28	. . .	. . .	22	3	. . .	. . .	80	10.6	77-88	170-190	0-16	0-160
C	420	56	. . .	. . .	22	3	. . .	. . .	160	21.2	77-88	170-190	0-40	0-400
D	. . .	. . .	105(c)	14	. . .	. . .	10(b)	1.3(b)	42	5.6	60-	140-	0.5-3	6-30

(a) As stannate.

(b) Free alkali may need to be higher for barrel plating.

(c) $Na_2SnO_3 \cdot 3H_2O$; solubility in water is 61.3 g/L (8.2 oz/gal) at 16 °C (60 °F) and 50 g/L (6.6 oz/gal) at 100 °C (212 °F)

Table 3 Composition and operating conditions for sulfate (acidic) tin plating electrolyte

Constituent	Amount	Operating limits

	g/L	oz/gal	g/L	oz/gal
Stannous sulfate	80	10.6	60-100	8-13
Tin metal, as sulfate	40	5.3	30-50	4-6.5
Free sulfuric acid	50	6.7	40-70	5.3-9.3
Phenolsulfonic acid(a)	40	5.3	30-60	4-8
β-naphthol	1	0.13	1	0.13
Gelatin	2	0.27	2	0.27

Note: Temperature range for sulfate electrolytes is 21 to 38 °C (70 to 100 °F), and they do not require heating. Cooling can be considered if temperature rises to reduce adverse effects of heat on the electrolyte constituents. Cathode current density is 1 to 10

(a) Phenolsulfonic acid is most often used. Cresolsulfonic acid performs equally well and is a constituent of some proprietary solutions.

Table 4 Composition and operating conditions for fluoborate tin (acidic) plating electrolyte

Constituent or condition	Standard	High-speed	High throwing power
Electrolyte, g/L (oz/gal)			
Stannous fluoborate	200 (26.7)	300 (39.7)	75 (9.9)
Tin metal(a)	80 (10.8)	120 (16.1)	30 (4.0)
Free fluoboric acid	100 (13.4)	200 (26.8)	300 (40.2)
Free boric acid	25 (3.35)	25 (3.35)	25 (3.35)
Peptone(b)	5 (0.67)	5 (0.67)	5 (0.67)
β-naphthol	1 (0.13)	1 (0.13)	1 (0.13)
Hydroquinone	1 (0.13)	1 (0.13)	1 (0.13)
Temperature, °C (°F)	16-38(c) (60-100)(c)	16-38 (60-100)	16-38 (60-100)

Cathode current density, A/dm^2 (A/ft^2)	2-20 (20-200)	2-20 (20-200)	2-20 (20-200)

Note: The standard electrolyte composition is generally used for rack or still plating, the high-speed composition for applications like wire plating, and the high-throwing-power composition for barrel plating or applications where a great variance exists in cathode current density as a result of cathode configuration.

(a) As fluoborate.

(b) Dry basis.

(c) Electrolytes do not require heating. Cooling may be considered if temperature rises to reduce adverse effects of heat on the electrolyte constituents.

Alkaline electrolytes usually contain only a metal stannate and the applicable hydroxide to obtain satisfactory coatings. Unlined mild steel tanks are satisfactory. These can be heated by electrical immersion heaters, steam coils, or external gas burners. If steam coils are used, they should be supported 5 to 10 cm (2 to 4 in.) above the bottom of the tank to allow sediment to remain undisturbed. It is not necessary to filter still baths of this type, except at infrequent intervals. The electrical equipment is the same as that used in other plating operations. A rectifier for converting alternating current to direct current or a pulse-plating rectifier, which allows more precise control of electrical parameters, can be used. Factors such as operating temperature, solution constituent concentration, and operating current density all affect the efficiency and plating rate of the system and must be properly balanced and controlled.

Unusual operating conditions of the alkaline electrolytes involve:

- Tin anode control and electrochemical solution mode (discussed below)
- Cathodic deposition occurring from Sn^{+4}
- Solubility of the alkaline stannate in water

Ninety percent of the problems encountered in alkaline tin plating result from improper anode control. Conversely, operating the alkaline electrolytes is simple if one understands anode behavior, because there are no electrolyte constituents except the applicable stannate and hydroxide.

Tin anodes must be properly filmed, or polarized, in alkaline solutions to dissolve with the tin in the Sn^{+4} state. Once established, the anode film continues to provide the tin as Sn^{+4}. The anodes can be filmed either by subjecting them for about 1 min to a current density considerably above that normally used, or by lowering them slowly into the bath with the current already flowing.

Three reactions are possible at tin anodes in alkaline solutions:

$$Sn + 6OH^- \rightarrow Sn(OH)_6^{2-} + 4e^- \qquad \textbf{(Eq 1)}$$

$$Sn + 4OH^- \rightarrow Sn(OH)_4^{2-} + 2e^- \qquad \textbf{(Eq 2)}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad \textbf{(Eq 3)}$$

Equation 1 represents the overall process occurring at the anodes when the film is intact and the tin is dissolving as stannate ion, with tin in the Sn^{+4} state. Film formation is confirmed by a sudden increase in the electrolyte cell voltage, a drop in the amperage passing through the cell, and the observation of a yellow-green film for pure tin anodes. High-speed anodes (containing 1% Al), used for tinplate production, turn darker. Because the anodes do not function at 100% efficiency when filmed, moderate gassing occurs as the result of the generation of oxygen, as in Eq 3.

Equation 2 is the process occurring if there is no film and the tin is dissolving as stannite ion, with tin in the Sn^{+2} state. The presence of stannite in the electrolyte produces unsatisfactory plating conditions, and the deposit becomes bulky, rough, porous, and nonadherent. The addition of hydrogen peroxide to the electrolyte oxidizes the Sn^{+2} to Sn^{+4}, returning it to a usable condition. If this remedy is required frequently, it indicates other problems that must be addressed. The concentration of caustic may be too high. This can be remedied with the addition of acetic acid.

Equation 3 shows the decomposition of hydroxyl ion with the formation of oxygen. While this is a normal reaction at the anode, it should not be permitted to become the dominant reaction, as occurs when the anode current density is too high. Under this condition, no tin dissolves and the anodes take on a brown or black oxide film. The anode current density should be reduced until the normal film color returns. If this is allowed to become thick enough, it is removable only by the action of strong mineral acids. Stannate baths normally appear colorless to straw colored, and clear to milky, depending on the quantity of colloidal material present. If an appreciable quantity of stannite builds up in the bath, it will appear light to dark gray, depending on the quantity of stannite that has formed. The gray color is caused by the precipitation of colloidal tin as a result of the disproportionation of stannite:

$$2Sn(OH)_4^{2-} \rightarrow Sn(OH)_6^{2-} + Sn + 2OH^-$$

This tin will codeposit with tin from the stannate ions, causing the rough spongy deposits mentioned above.

In the alkaline systems, two factors tend to restrict the usable current density range and limit the deposition rate. One factor is the solubility of the stannates in hydroxide solutions. With the sodium formula, the normal increase is not possible, because sodium stannate is one of the unusual salts that have a reverse temperature coefficient of solubility. An example of this process is given in Table 2. Less sodium stannate dissolves as the electrolyte temperature increases, which reduces the usable current density and the plating rate. Potassium stannate is more soluble with increasing temperature, but as the stannate increases, the potassium hydroxide must also increase. Stannate solubility decreases as the hydroxide content increases.

The second factor is that cathode efficiency decreases as current density increases. Eventually, a point is reached at which these factors become offset, and a further increase in current density does not increase the deposition rate. This limits the rate at which tin can be deposited.

In specialized applications, such as plating the inside of oil-well pipe, it is not possible to have an anode surface sufficient enough to avoid passivity. A higher current density can be used if insoluble anodes are utilized, but tin deposited on the cathode must then be replaced by the addition of chemicals. The addition of stannate to provide the tin cations also adds sodium or potassium hydroxide to the electrolyte. Although the resulting additional alkalinity can be neutralized by adding a calculated amount of an acetic acid, the sodium or potassium ion concentration continues to increase and the alkaline stannate solubility is reduced. This, in turn, reduces the available Sn^{+4} ion to a low enough concentration that the plating rate decreases rapidly, and the electrolyte must be discarded. A potassium-base composition has been developed, in which the necessary Sn^{+4} ions are added to the electrolyte as a soluble, colloidal, hydrated tin oxide (Ref 2). Because the potassium ion concentration builds up more slowly in this composition, electrolyte life is nearly indefinite. The throwing power of alkaline stannate solutions is quite high, allowing the coating of intricate shapes and interior parts of cathodes.

Acid Electrolytes. Several acid electrolytes are available for tin plating. Two of these--stannous sulfate and stannous fluoborate--are general systems that are adaptable to almost any application. Electrolytes such as halogen (a chloride-fluoride base system) and Ferrostan (a special sulfate-base system) have been developed for tin coating cold-rolled steel strip traveling at high speed for the production of tinplate. The acid electrolytes differ from alkaline electrolytes in many respects. A stannous salt that is dissolved in a water solution of the applicable acid does not produce a smooth, adherent deposit on a cathode. Therefore, a grain-refining addition agent (such as gelatin or peptone) must be used. Usually, such materials are not directly soluble in a water solution, and a wetting-agent type of material (such as β-naphthol) is also necessary.

Organic brighteners can be added if a bright-as-coated electrodeposit is desired. This produces a coating that looks the same as a reflowed tin coating. Over time, these brighteners will decompose in the bath and must be replenished. The composition of these organic brighteners has been the subject of considerable research over the years. The earliest substance studied, in the 1920s, was wood tar dispersed with a wetting agent. Other materials were studied in later years, especially pure compounds such as cresol sulfonic acid and various aromatic sulfonates. These were seen to have more of a stabilizing effect, preventing the hydrolysis and precipitation of tin as tin(II) and tin(IV) salts. Later work has shown that a "cruder" material is more effective as a brightener. Such a material is obtained by the sulfonation of commercial cresylic acid. The implication here is that by-products of the sulfonation and not the cresol sulfonic acid itself are responsible for the brightening of the tin coating. Various proprietary brightening systems have been produced over the years. Very little of the development work on brightening agents has been published outside the patent literature. A comprehensive discussion of the topic is beyond the scope of this article. It is usually most convenient to purchase a packaged system from a plating supply house.

The organic materials will co-deposit with the tin, resulting in a higher than normal carbon content in the electrodeposit. This does not create a problem, unless the tin coating is to be soldered or reflowed. The supplier of the proprietary bath should be consulted for directions on controlling this problem.

To retard the oxidation of the stannous tin ions to the stannic form, either phenolsulfonic or cresolsulfonic acid is added to a sulfate-base system, and hydroquinone is added to a fluoboric acid-base system. Although the acid electrolytes can contain large amounts of stannic ions without affecting the operation of the system, only the stannous ions are deposited at the cathode. As a result, oxidation depletes the available stannous ions, which must be replaced by adding the corresponding stannous salt to the bath. To limit the oxidation of stannous ions, a sufficient anode area must be maintained, and the operating temperature must be kept as low as possible. In addition, one must avoid introducing oxygen into the solution, either by a filter leak or air agitation. Usually, an antioxidant is added to the solution.

In terms of operating characteristics, the basic differences between acid and alkaline electrolytes are related to the type of tin ion that is present in the electrolyte. In acid systems, the stannous ions must not be oxidized to the stannic form, and operation must occur at lower temperatures. The acid electrolytes require only half as much current to deposit one gram-molecule of tin. The tin dissolves directly from the metallic anodes, and the control of an anode film is not involved. Acid electrolytes are nearly 100% efficient, both anodically and cathodically, which avoids the necessity of regularly adding chemicals for tin. The problems of oxygen gas evolution at the anode surface and hydrogen gas at the cathode surface are reduced. Some particulate matter is produced as sludge from three sources: anode slime products, the precipitation of addition agents and their breakdown products, and basic tin compounds formed by oxidation. These materials must be removed during operation. In a still tank, the precipitates gradually settle, but agitated solutions require continuous filtration.

Acid-resistant equipment must be used. Lead-lined plating tanks were formerly used, but stoneware, rubber- or plastic-lined steel, or plastic tanks are now more common. Filtration equipment should be available, because solid particles of precipitated matter in the solution will cause deposit porosity and roughness. With still baths, suspended matter can be allowed to settle without filtration, but with agitated baths, continuous filtration is advisable. Cathode bar movement is often recommended.

The stannous sulfate electrolyte is most popular because of its general ease of operation. The rate of deposition is somewhat limited by optimum metal concentration in the electrolyte. A still bath is operated at a cathode current density of 1 to 2 A/dm^2 (10 to 20 A/ft^2). Current densities of up to 10 A/dm^2 (100 A/ft^2) are possible with suitable electrolyte agitation. Higher current densities will result in burned deposits. The anode surface area must be increased when higher current densities are used, otherwise the anodes will become passive. Addition agent control is not quantitative in nature, but deficiencies are easily recognized by the experienced plater. An electrolyte can be prepared from readily available chemicals, or a proprietary system can be purchased from suppliers. Most commercial bright acid tin processes and the more recent matte acid tin systems are based on the stannous sulfate solution. Precise information on operation and control should be obtained directly from the specific supplier.

The stannous fluoborate electrolyte is a good general-purpose electrolyte. It can operate at higher current densities because of the conductivity provided by the fluoboric acid. Cathode current densities of 20 A/dm^2 (200 A/ft^2) and higher are possible with suitable solution agitation. The need to increase anode surface area at high current densities and the control of the addition agents parallel the requirements associated with using stannous sulfate. Table 4 gives standard, high-speed, and high-throwing-power electrolyte compositions, because each meets a specific need. The solution conductivity that is lost because of the lower metal content in the high-throwing-power bath is compensated for by the higher concentration of fluoboric acid. The lower total metal in the solution reduces the variance in deposit thickness that is usually associated with varying areas of cathode current density. Boric acid is listed as a constituent of the fluoborate solutions because of its presence in the stannous fluoborate and fluoboric acid used to prepare the solutions. It is not a necessary ingredient in the electrolyte.

References cited in this section

1. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley-Interscience, 1974
2. S. Hirsch, Tin-Lead, Lead, and Tin Plating, *Metal Finishing Guidebook and Directory Issue,* Vol 91 (No. 1A), Jan 1993, p 269-280
3. J.W. Price, *Tin and Tin Alloy Plating,* Electrochemical Publications Ltd., Ayr, Scotland, 1983

Lead Plating

Revised by George B. Rynne, Novamax Technology

Introduction

LEAD has been deposited from a variety of electrolytes, including fluoborates, fluosilicates, sulfamates, and methane sulfonic acid baths. Fluoborate baths are the most widely used because of the availability of lead fluoborate and the simplicity of bath preparation, operation, and stability. Fluoborate baths provide finer grained, denser lead deposits. Fluosilicate baths, although less costly to use for large operations, are difficult to prepare for small-scale plating. They are not suitable for plating directly on steel and are subject to decomposition, which produces silica and lead fluoride. Use of sulfamate baths is almost nonexistent in the United States, because neither lead silicofluoride nor lead sulfamate is available commercially. These salts must be prepared by the plater using litharge (PbO) and the corresponding fluosilicic or sulfamic acids. Sulfamate baths are subject to decomposition, which produces lead sulfate.

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Applications

The appearance and properties of lead limit its commercial use in electroplating largely to corrosion protection and bearing applications-two fields in which the physical and chemical properties of lead render it unique among the commercially plated metals. Lead has not been extensively electroplated because its low melting point of 325 °C (620 °F) facilitates application by hot dipping. Electrodeposited lead has been used for the protection of metals from corrosive liquids such as dilute sulfuric acid; the lining of brine refrigerating tanks, chemical apparatus, and metal gas shells; and barrel plating of nuts and bolts, storage battery parts, and equipment used in the viscose industry.

Electroplated lead has been used for corrosion protection of electrical fuse boxes installed in industrial plants or where sulfur-bearing atmospheres are present. Lead is also codeposited with tin for wire plating, automotive crankshaft bearings, and printed circuits.

Nonporous lead deposits with thicknesses of 0.01 to 0.025 mm (0.4 to 1 mil) give good protection against corrosion, although the coating may be subject to breaking during abrasion due to the soft nature of lead. Better mechanical properties and improved durability are obtained with coating deposits with thicknesses greater than 0.025 mm (1 mil). Depositing more than 0.08 mm (3 mils) of lead is relatively easy, in that a deposit of about 0.1 mm (4 mils) can be produced in about 1 h at 2 A/dm^2 (19 A/ft^2) (Ref 1).

Reference cited in this section

1. H. Silman, G. Isserlis, and A.F. Averill, *Protective and Decorative Coatings for Metals,* Finishing Publications Ltd., 1978, p 443-448

Process Sequence

Low-Carbon Steel. Lead can be plated directly on steel from the fluoborate bath using the following cycle:

- Degrease with solvent (optional)
- Alkali clean (anodic)
- Water rinse
- Dip in 10% fluoboric acid (*Caution: Hydrochloric or sulfuric acid should not be used because they can precipitate insoluble lead sulfate or chloride on the work in the event of poor rinsing*)
- Water rinse
- Lead plate
- Rinse

Lead can be plated on steel from fluosilicate and sulfamate baths using the following cycle:

- Degrease with solvent (optional)
- Alkali clean (anodic)
- Rinse
- Dip in 5 to 25% hydrochloric acid
- Rinse thoroughly
- Dip in 30 to 75 g/L (4 to 10 oz/gal) sodium cyanide
- Rinse
- Copper cyanide strike
- Rinse thoroughly
- Dip in 10% fluoboric acid (see caution above)
- Rinse
- Lead plate
- Rinse

Copper. Lead can be plated directly on copper from fluoborate, fluosilicate, or sulfamate baths using the following cycle:

- Alkali clean (anodic or cathodic/anodic)
- Rinse
- Dip in 10% fluoboric acid (see caution above)
- Rinse
- Lead plate
- Rinse

Fluoborate Baths

Lead fluoborate baths are prepared by adding the required amount of lead fluoborate concentrate and fluoboric acid to water followed by peptone as the preferred addition agent.

Until methane sulfonic acid (MSA) baths became widely used in the past few years, fluoroborate baths were the most important bath for lead plating. Good lead deposits up to 1.5 mm (60 mils) in thickness can be achieved with a fluoroborate bath of the following composition:

Basic lead carbonate, $2PbCO_3 \cdot Pb(OH_2)$	300 g/L (40 oz/gal)

Hydrofluoric acid (50% HF)	480 g/L (64 oz/gal)
Boric acid, H_3BO_3	212 g/L (28 oz/gal)
Glue	0.2 g/L (0.03 oz/gal)

A bath of half the above concentration is suitable for thinner deposits at low current densities, but the lead concentration should be kept high if smooth deposits and good throwing power are required (Ref 1). More detailed information on fluoroborate formulations and performance for lead plating is covered in Ref 2, 3, 4, and 5.

Many different types of glue and gelatin additives are available, but no one type is manufactured specifically for lead plating. Depending on the method of manufacture, each can exhibit different levels of solubility and impurities that may be of concern to the plater.

Glue and gelatin addition agents must be swelled and dissolved in water by the plater just prior to addition to the bath. The resultant colloidal solution has a limited shelf-life and is prone to bacterial degradation on standing. Glue and hydroquinone are relatively expensive. Often, it is a by-product of an industrial process and can contain organic and inorganic impurities detrimental to the lead plating process. No grade is manufactured and sold specifically for lead plating.

Concentrates of lead fluoborate and fluoboric acid contain free boric acid to ensure bath stability. An anode bag filled with boric acid in each corner of the plating tank is recommended to maintain a stable level of boric acid in the bath solution. The concentration of boric acid in the bath is not critical and can vary from 1 g/L (0.13 oz/gal) to saturation. The water used in the bath preparation must be low in sulfate and chloride, as these lead salts are insoluble.

Table 1 provides the compositions and operating conditions of high-speed and high-throwing-power fluoborate plating baths. The high-speed bath is useful for plating of wire and strip where high current densities are used. The high-throwing-power formulation is used in applications such as barrel plating of small parts or where thickness distribution on intricate or irregularly shaped parts is important. The high-throwing-power bath should be operated at a lower current density because of the lower lead content of the bath.

Table 1 Compositions and operating conditions of lead fluoborate baths

Anode composition, pure lead; anode/cathode ratio, 2:1

Bath	**Bath composition**							**Temperature**		**Cathode current density**[a]	
	Lead		**Fluorobic acid (min)**		**Peptone solution, vol%**	**Free boric acid**					
	g/L	**oz/gal**	**g/L**	**oz/gal**		**g/L**	**oz/gal**	**°C**	**°F**	**A/dm^2**	**A/ft^2**
High-speed	225	30	100	13.4	1.7	1 to saturation	0.13 to saturation	20-41	68-105	5	50
High-throwing-	15	2	400	54	1.7	. . .	. . .	24-71	75-	1	10

(a) Values given are minimums. Current density should be increased as high as possible without burning the deposit; this is influenced by the degree of agitation.

Fluoborate baths rank among the most highly conductive plating electrolytes and thus require low voltage for the amperage used.

Maintenance and Control. The very high solubility of lead fluoborate in solution with fluoboric acid and water accounts for its almost universal use for lead plating. In the high-speed bath formulation of Table 1, neither the lead nor acid content is critical, and the bath can be operated over a wide range of lead and acid concentrations.

The high-throwing-power bath formulation of Table 1 must be operated fairly close to the guidelines given. Lowering the lead concentration improves the throwing power characteristics; however, a reduction in lead concentration must be followed by a corresponding decrease in the cathode current density. On the other hand, an increase in lead content above the optimum permits the use of higher current densities, with a corresponding decrease in throwing power.

Sludge may form in the fluoborate bath as a result of the use of impure lead anodes that contain bismuth or antimony or as a result of the drag-in of sulfates. Fluoborate baths should be constantly filtered through dynel or polypropylene filter media to remove any sludge that may form. Anodes must be bagged in dynel or polypropylene cloth. Absence of gas bubbles at the cathode or anode while plating indicates all electric energy is theoretically being used to transfer lead from the anode to the workpiece; in other words, the process is operating at 100% anode and cathode efficiency. The plating bath concentration therefore remains unchanged except for changes due to evaporation and dilution from placing wet parts in the bath in combination with dragout when the parts are removed from the bath.

Methods are available for analyzing lead and fluoboric acid concentrations. Additive concentration can be adequately evaluated through the use of the Hull cell. Low concentration of additive results in loss of throwing power, coarse-grained deposits, and treeing. (*Treeing* is the formation of irregular projections on a cathode during electrodeposition, especially at edges and other high-current-density areas).

References cited in this section

1. H. Silman, G. Isserlis, and A.F. Averill, *Protective and Decorative Coatings for Metals,* Finishing Publications Ltd., 1978, p 443-448
2. S. Hirsch, Tin-Lead, Lead and Tin Plating, *Metal Finishing Guidebook and Directory,* Elsevier Science, 1992, p 262-278
3. F.A. Lowenheim, *Modern Electroplating,* 2nd ed., John Wiley & Sons, 1963, p 242-249
4. A. Graham, *Electroplating Engineering Handbook,* 3rd ed., Van Nostrand Reinhold, 1971, p 238, 246, 266
5. *The Canning Handbook,* 23rd ed., Canning, 1982, p 742-746

Fluosilicate Baths

Fluosilicic acid is formed by the action of hydrofluoric acid on silicon dioxide. The lead fluosilicate ($PbSiF_6$) electrolyte is formed when fluosilicic acid is treated with litharge. No great excess of silicic acid can be held in solution; therefore, the fluosilicate solution is less stable than the fluoborate solution. Table 2 lists compositions and operating conditions for two lead fluosilicate baths.

Table 2 Compositions and operating conditions of lead fluosilicate baths

Temperature, 35-41 °C (95-105 °F); cathode current density, 0.5-8 A/dm^2 (5-80 A/ft^2); anode current density, 0.5-3 A/dm^2 (5-30 A/ft^2); anode composition, pure lead

Bath	Lead		Animal glue		Peptone equivalent		Total fluosilicate	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	10	1.3	0.19	0.025	5	0.67	150	20

2	180	24	5.6	0.75	150	20.1	140	18.75

Although at low current densities it is possible to secure smooth deposits of lead from the fluosilicate bath without additive agents, higher current densities are likely to produce treeing, especially in heavy deposits. Therefore, an additive agent, such as peptone glue or other colloidal materials or reducing agents, is always used. The use of excess glue in lead plating baths, however, may result in dark deposits. Maintenance and control procedures for the fluosilicate baths are similar to those described for the fluoborate baths.

Sulfamate Baths

Sulfamate baths consist essentially of lead sulfamate with sufficient sulfamic acid to obtain a pH of about 1.5. Sulfamic acid is stable and nonhygroscopic, and is considered a strong acid. Compositions and operating conditions of two typical sulfamate baths are given in Table 3.

Table 3 Compositions and operating conditions of lead sulfamate baths

pH, 1.5; temperature, 24-49 °C (75-120 °F); cathode current density, 0.5-4 A/dm^2 (5-40 A/ft^2); anode current density, 0.5-4 A/dm^2 (5-40 A/ft^2); anode/cathode ratio, 1:1; anode composition, pure lead

Bath	Lead		Animal glue		Peptone equivalent		Free sulfamic acid	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	140	18.75	5.6	0.75	150	20.1	. . .	. . .

Because the acid and the salt used in the solutions in Table 3 are highly soluble in water, sulfamate baths can be prepared either by adding constituents singly or as formulated salts to water. Solutions are usually formulated to concentrations that allow bath operation over a wide range of current densities. Lead concentration can vary from 112 to 165 g/L (15 to 22 oz/gal), while the pH is held at about 1.5. As in other lead plating solutions, additive agents (peptone gelatin or other colloids, alkyl or alkyl aryl polyethylene glycols) are required to produce smooth, fine-grained deposits.

Spongy deposits are obtained if the lead concentration is too low, the current density is too high, or the concentration of additive agent is too low. At low pH or high temperature, sulfamate ions hydrolyze to ammonium bisulfate to form insoluble lead sulfate. Ordinarily, this hydrolysis presents no problem, provided the bath is correctly operated.

Maintenance and Control. Sulfamate baths do not require much attention other than maintenance of the correct proportion of additive agents to produce the desired deposit quality. Additive agent content is evaluated by the use of the Hull cell. The pH is easily adjusted with sulfamic acid or ammonia and can be measured with a glass electrode. Lead concentration can be determined with sufficient accuracy by hydrometer readings or an occasional gravimetric analysis.

Methane Sulfonic Acid Baths

Methane sulfonic acid (MSA) baths consist essentially of MSA-lead concentrate mixed with MSA to arrive at a total acid concentration of 300 mL/L. The overall system is stable and is considered to be a strong acid. Compositions and operating conditions for two MSA baths are given in Table 4.

Table 4 Compositions and operating conditions of lead methane sulfonic acid (MSA) baths

Temperature, 45 °C (110 °F); anode composition, pure lead; anode/cathode ratio, 1:1

Bank	Lead		MSA, mL/L	Additive, vol%	Cathode current density	
	g/L	oz/gal			A/dm^2	A/ft^2
Rack/barrel	30	4	300	4	0.5-5	5-50
High-current	100	13.3	300	4	0.5-20	5-200

The materials used to formulate MSA baths are highly soluble liquids. The baths listed in Table 4 are metal concentrations and, as such, are sensitive to current density. A lead concentration of 30 g/L (4 oz/gal) supports a maximum current density of 5 A/dm^2 (50 A/ft^2); an increase in the lead concentration to 100 g/L (13.3 oz/gal) allows a corresponding increase in the maximum current density to 20 A/dm^2 (200 A/ft^2). The use of a proprietary additive (4% of bath composition) is required to produce the smooth, fine-grained deposits usually provided by colloidal agents in fluoborate systems.

The principal advantage of MSA baths, in addition to their overall chemical stability, is the absence of the fluoride and borate ions present in other lead plating baths. These ions are heavily regulated or prohibited in many states because of their deleterious effects on fruit-bearing trees when released to the environment. An additional advantage of MSA baths is that when they are applied to 60Pb-40Sn solder alloys, these eutectic alloys can be plated over an extremely broad range of current densities. MSA baths are easily operated and controlled, but they are more expensive to make up.

Maintenance and Control. The MSA system is extremely stable and requires little or no maintenance other than control of the metal, acid, and additive concentrations within relatively broad ranges. Of these, it is of greatest importance to control the acid concentration in actual production situations. Additive concentration is evaluated using the Hull cell; metal and acid concentrations can be evaluated through simple titrations. Deionized water must be used for rinsing the part prior to immersion in the plating bath because MSA is sensitive to chloride ions in the makeup water.

Anodes

Lead of satisfactory purity for anodes may be obtained either as corroding lead or chemical lead. Chemical lead anodes generally are preferred. Impurities in the anodes such as antimony, bismuth, copper, and silver cause the formation of anode slime or sludge and can cause rough deposits if they enter the plating solution. These impurities can also cause anode polarization if present in the anode, especially at higher anode current densities. Small amount of tin and zinc are not harmful. Anode efficiency in acid baths is virtually 100%.

Anodes should be bagged in dynel or polypropylene cloth to prevent sludge from entering the plating bath. These bags should be leached in hot water to remove any sizing agents used in their manufacture before use in the plating bath. Nylon and cotton materials deteriorate rapidly and should not be used in any of the baths.

Equipment Requirements

Fluoborate and fluosilicate baths attack equipment made of titanium, neoprene, glass, or other silicated material; thus, these materials should not be used in these solutions. Anode hooks should be made of Monel metal.

Tanks or tank linings should be made of rubber, polypropylene, or other plastic materials inert to the solution. Pumps and filters of type 316 stainless steel or Hastelloy C are satisfactory for intermittent use; for continuous use, however, equipment should be made from or lined with graphite, rubber, polypropylene, or other inert plastic. Filter aids used for the fluoborate solution should be made of cellulose rather than asbestos or diatomaceous earth.

Stripping of Lead

Table 5 identifies solutions and operating conditions for stripping lead from steel. Method C, at about 16 °C (60 °F), strips 25 μm (1 mil) of lead in 6 or 7 min with very slight etching of the steel. With Method B, voltage increases suddenly when the lead coating has been removed; at room temperature and 9.3 A/dm^2 (92 A/ft^2), the voltage may be about 2.7 V during stripping, but increases to 4.6 V when stripping is complete.

Table 5 Solutions and operating conditions for stripping lead from steel

Method A	
Sodium hydroxide	100 g/L (13.4 oz/gal)
Sodium metasilicate	75 g/L (10 oz/gal)
Rochelle salt	50 g/L (6.7 oz/gal)
Temperature	82 °C (180 °F)
Anode current density	1.9-3.7 A/dm^2 (18.5-37 A/ft^2)
Method B	
Sodium nitrite	500 g/L (67 oz/gal)
pH	6-10
Temperature	20-82 °C (68-180 °F)
Anode current density	1.9-18.5 A/dm^2 (18.5-185 A/ft^2)
Method C[(a)]	
Acetic acid (glacial)	10-85 vol%
Hydrogen peroxide (30%)	5 vol%
Method D[(a)][(b)]	
Fluoboric acid (48-50%)	4 parts
Hydrogen peroxide (30%)	1 part
Water	2 parts

Temperature	20-25 °C (68-77 °F)

(a) Formulations should be made up fresh daily.

(b) Alternate method for stripping lead or lead-tin deposits. Work must be removed as soon as the lead is stripped; otherwise, the base metal will be attacked.

With the solutions used in Method A or B, a stain occasionally remains on the steel after stripping. The stain can be removed by immersion for 30 s in the solution used in Method C, leaving the steel completely clean and unetched (unless the nitrate solution of Method B was used at less than about 2 V).

Silver Plating

Alan Blair, AT&T Bell Laboratories

ELECTROPLATED SILVER--which was developed primarily for use on holloware, flatware, and tableware--has proven its usefulness in both decorative and functional applications in both engineering and electrical/electronic applications. Decorative applications of silver plating still predominate; however, silver has been successfully substituted for gold in some functional uses in electronics. Its greatest success has been the virtually complete replacement of gold on metallic leadframes, the devices that support the majority of silicon chips. Here the development of new silicon-to-silver bonding techniques and ultimate encapsulation of the silver allow for the replacement of a much more expensive precious metal without loss of performance. In electrical contact applications, where the long-term integrity of the surface is of paramount importance, silver has been less successful as a gold substitute due to its tendency to form oxides and sulfides on its surface and the resultant rise in contact resistance. Silver has been employed as a bearing surface for many decades. It is particularly useful where the load-bearing surfaces are not well lubricated (e.g, in kerosene fuel pumps on gas turbine engines.)

Solution Formulations. The first patent concerning electroplating was filed in 1840 and reported a process for plating silver from a cyanide solution. To this day, silver is plated almost exclusively with cyanide-based solutions, despite the considerable research effort that has been expended on evaluating less toxic alternatives. A formulation for such a solution is given in Table 1. This type of electrolyte would be used for plating decorative or functional deposits of silver in a conventional way (i.e., on a rack or in a barrel). It is possible to produce fully bright deposits that require no further buffing or polishing. This is achieved by including a brightening agent in the solution formula, (one of several sulfur-bearing organic compounds, or selenium or antimony added as soluble salts). Antimony containing silver deposits are harder than pure silver. A typical antimony content might be 0.1 to 0.2% by weight. However, it should be noted that antimony content will vary with the current density employed during deposition; lower current densities will produce a deposit with higher antimony content.

Table 1 Plating solutions for silver

Component/Parameter	Rack	Barrel
Silver as $KAg(CN)_2$, g/L (oz/gal)	15-40 (2.0-2.5)	5-20 (0.7-2.5)
Potassium cyanide (free), g/L (oz/gal)	12-120 (1.6-16)	25-75 (3.3-10)
Potassium carbonate (min), g/L (oz/gal)	15 (2.0)	15 (2.0)

Temperature, °C (°F)	20-30 (70-85)	15-25 (60-80)
Current density, A/dm^2 (A/ft^2)	0.5-4.0 (5-40)	0.1-0.7 (1-7.5)

Anodes of pure silver are readily soluble in the excess or "free"cyanide of these solutions. Carbonate is a natural byproduct of atmospheric oxidation of cyanide, but this adds to the solution conductivity, and some carbonate is included when preparing a new solution. Silver metal concentration is normally maintained by anode dissolution, but occasional small additions of the metal salt may be needed. This is facilitated by adding either silver cyanide (80% silver) or potassium silver cyanide (54% silver, sometimes referred to as the double salt). Additions of the former will lower the free cyanide concentration, whereas additions of the double salt will not.

Silver is usually more noble than the metal over which it is being plated, and because of this it has a tendency to form "immersion deposits." These are poorly adherent films of silver that form due to a chemical reaction between the base metal substrate and the silver ions in solution before true electrodeposition can commence. In order to avoid this phenomenon a silver strike should always be used. (A *strike* is a low-concentration bath operated at high cathode current density.) The following gives a typical silver strike solution formulation.

Component/Parameter	**Value**
Silver, as $KAg(CN)_2$, g/L (oz/gal)	1.0-2.0 (0.13-0.27)
Potassium cyanide (free), g/L (oz/gal)	80-100 (10-13)
Potassium carbonate (minimum), g/L (oz/gal)	15 (2.0)
Temperature, °C (°F)	15-25 (60-80)
Current density, A/dm^2 (A/ft^2)	0.5-1.0 (5-10)

Stainless steel anodes should always be used in a silver strike solution to avoid an increase in silver metal concentration.

High-speed, selective plating of leadframes or similar electronic components requires the use of extremely high current densities and short plating times. Typical thicknesses range from 1.5 to 5.0 μm deposited in less than 2 s. Under these conditions, solutions containing free cyanide decompose very rapidly, the cyanide polymerizes and codeposits through electrophoresis, and the deposits cease to provide the desired properties. Solutions that use phosphate or nitrate salts as conducting media and use insoluble platinum or platinized titanium or niobium anodes have been developed to meet this requirement. Silver is present as potassium silver cyanide, and its concentration must be maintained by making periodic additions of this double salt. Careful attention must be paid to buffering because of the tendency to produce low pH values at the insoluble anodes. If this occurs, an insoluble silver salt will rapidly coat the anode and plating will cease. A typical formula is shown below.

Component/Parameter	Value
Silver, as $KAg(CN)_2$,g/L (oz/gal)	40-75 (5-10)
Conducting/buffering salts,g/L (oz/gal)	60-120 (8-16)
pH	8.0-9.5
Temperature, °C (°F)	60-70 (140-160)
Current density, A/dm^2(A/ft^2)	30-380 (275-3500)

Noncyanide formulas that have been reported include those based on simple salts such as nitrate, fluoborate, and fluosilicate; inorganic complexes such as iodide, thiocyanate, thiosulfate, pyrophosphate, and trimetaphosphate; and organic complexes such as succinimide, lactate, and thiourea. A succinimide solution and a thiosulfate/metabisulfite solution have been commercialized, but the volumes used are very small compared with the cyanide solutions.

Specifications. Federal specification QQ-S-365D gives general requirements for silver plating. Using this specification it is possible to define the type of finish needed: matte (type I), semibright (type II), or bright (type III), and with chromate film for added tarnish resistance (grade A), or with no film (grade B). A minimum thickness of 13 μm (0.0005 in.) is required for functional coatings.

ASTM B 700 specifies electrodeposited coatings of silver for engineering uses and defines purity (types 1, 2, and 3: 99.9, 99.0, and 98.0%, respectively); degree of brightness or mechanical polish (grades A, B, and C: matte, plated bright, and mechanically polished, respectively); and absence or presence of a chromate film (class N or S). Thickness must be specified by the purchaser.

The aerospace industry refers to four aerospace material specifications: AMS 2410G, AMS 2411D, and AMS 2412F, each of which applies to specific undercoats and bake temperatures; and AMS 2413C, which defines requirements for silver and rhodium plating on microwave devices.

International standard ISO 4521 defines silver coatings on metallic and nonmetallic substrates. Thicknesses are not specified but preferred thicknesses are quoted.

Users of silver plating for decorative purposes will find guidance in "Guides for the Jewelry Industry," originally issued by the Federal Trade Commission.

Gold Plating

Alfred M. Weisberg, Technic Inc.

Introduction

GOLD PLATING is similar to other metal plating in most chemical and electrochemical ways. Gold differs from other metals primarily in that it is much more expensive. Within recent memory, the price of gold metal has gone from $35 per ounce to $850 per ounce and at the time of this writing is characteristically unstable at about $375 per ounce. Thus the cost of a gallon of gold plating solution is quite high.

This price level and the daily variability of its price have required chemists and engineers to severely limit the concentration of gold in the plating solution. Nickel, alkaline copper, and silver are typically plated from solutions that contain 37 g of metal per liter of plating bath. Acid copper is plated from a solution that contains 60 g of metal per liter, and a chromium solution can contain over 240 g of metal per liter. Gold, because of its price and the cost of the dragout losses, is rarely plated from a solution that contains more than 1 troy ounce per gallon (8.2 g/L). Some gold baths used for striking, decorative use, and barrel plating use as little as 0.8 or 0.4 g/L of gold.

These very low metal concentrations, or "starved" solutions, present problems to the gold plater that are quite different from those of other metal plating solutions. With a starved solution, every control parameter in the plating process becomes more critical. Gold concentration, electrolyte concentration, pH, impurity level, and additive level must all be monitored and controlled. Temperature, current density, agitation, and the current efficiency must be accurately known and controlled beyond the degree necessary for copper, nickel, or even silver plating. If any factor changes, even 2 to 3%, the cathode gold deposition efficiency changes. If the efficiency decreases, items being plated under standard conditions will be underplated and the specified thickness will not be attained. Similarly, if the cathode efficiency increases, the plate will be too thick and result in increased cost because of using excess gold.

The engineer and plater of gold must tread the narrow line between not depositing enough gold and giving away too much gold. In addition, those concerned with gold plating must not only keep the chemistry of the process and the peculiarities of electrodeposition in mind, as do other platers, but also be aware of the market price of gold. The plater must be an economist in order to realize when the operating conditions of the solution should be altered or the entire process changed to reflect the changes in the price of gold. Economics also determines the total consumption of gold. In the recent past, when the price of gold vaulted above $500 per troy ounce, many electronics companies replaced some of the total thickness of gold with undercoats of palladium or palladium-nickel alloys. Others abandoned gold completely. Economics is a more important factor in the plating and metallurgy of gold than in the plating of nonprecious metals.

General Description

Gold electroplating was invented in 1840. During the first 100 years electrodeposited gold was used primarily for its aesthetic appeal as a decorative finish. Because decorative appeal is a matter of fashion and personal whim, hundreds of different formulations are recorded in the literature. Each was the favorite color and finish of a master plater. In their time and place, each was good. Today, however, many factors have changed, especially the price, and the old formulas should be used for historical reference only.

With the development of electronics and radar during World War II, gold had to become a functional utilitarian coating. Low voltages, milliamp currents, dry circuits, and microwave frequencies required the very best low resistance surfaces for contacts, connectors, and waveguides. The stability of the contact resistance was of paramount importance. Nontarnishing and low-resistance 24K gold surfaces were the logical choice for connectors. Later, as the demands on the gold surface increased, it was found necessary to change the metallurgy of the gold deposit. Initially, wear resistance was increased by hardening the deposit to 150 to 250 HK. Later, wear resistance was increased by altering the crystal orientation of the gold deposit from the (100) plane to the slip plane, (111). Both of these results were achieved by the addition of controlled amounts of metallic and nonmetallic additives.

At virtually the same time, transistors required high-purity gold that could be doped with antimony or indium to give n- or p-type junctions. The printed circuit industry required gold electroplates that could be produced from solutions of lower pH (actually on the acid side) and from solutions that contained no free cyanide. The alkalinity of free cyanide lifted the resist and sometimes even lifted the laminate itself. It was rediscovered that potassium gold cyanide was stable at acidic pH. Under these conditions of mild acidity, hard, bright, and even solderable coatings could be achieved. This led to the development of perhaps another 100 formulations that could meet all of the requirements mentioned above as well as the different purities and hardnesses of the military gold plating standard MIL-G-45204 with its various modifications. The multiplicity of gold electroplating formulations was further augmented by the addition of baths for high-speed deposition that were used for continuous strip, stripe, or spot plating. Some of these plated at up to 215 A/dm^2 (2000 A/ft^2). Recently, numerous formulations have been developed to allow immersion and/or electroless gold plating. As additional requirements develop, there will be a continuing introduction of new gold plating formulations to meet these needs. All of the many formulations work, and each one has its own special advantages, but care must be taken to pick the best one for a particular application.

Decorative Plating

The traditional gold electroplating solution (Table 1) for decorative use required:

- A source of gold

- A complexing agent for the gold
- A conducting salt to help carry the current and broaden the conditions of operation
- An alloying metal or metals for color and/or hardness

The source of gold was historically gold cyanide. The complexing agent was sodium or potassium cyanide (Table 1). The conducting salts were cyanides, phosphates, carbonates, hydroxides, and occasionally but rarely citrates, tartrates, and so forth.

Table 1 Typical flash formulations for decorative gold plating

Component or parameter	**Type of jewelry plating**						
	English (24K)	**Hard (18K)**	**Hamilton**[(a)]	**White**	**Rose**	**Green**	**Barrel flash**
Gold as potassium gold cyanide, g/L (oz/gal)	2 (0.3)	1.6 (0.2)	1.25 (0.15)	0.4 (0.05)	4.1 (0.5)	2 (0.3)	0.8 (0.1)
Free potassium cyanide, g/L (oz/gal)	7.5 (1)	7.5 (1)	7.5 (1)	15 (2)	3.75 (0.5)	7.5 (1)	7.5 (1)
Dipotassium phosphate, g/L (oz/gal)	15-30 (2-4)	15-30 (2-4)	15-30 (2-4)	15-30 (2-4)	. . .	15-30 (2-4)	60-90 (8-12)
Sodium hydroxide, g/L (oz/gal)	. . .	. . .	. . .	. . .	15 (2)	. . .	. . .
Sodium carbonate, g/L (oz/gal)	. . .	. . .	. . .	. . .	30 (4)	. . .	. . .
Nickel as potassium nickel cyanide,g/L (oz/gal)	. . .	0.15-1.5 (0.02-0.2)	0.3 (0.04)	1.1 (0.15)	. . .	. . .	0.3 (0.04)
Copper as potassium copper cyanide, g/L (oz/gal)	. . .	. . .	1.5 (0.2)	. . .	. . .	. . .	. . .
Silver as potassium silver cyanide, ppm	. . .	. . .	. . .	. . .	. . .	200	. . .
Temperature, °C (°F)	60-70 (140-158)	60-70 (140-158)	65-70 (150-158)	. . .	65-82 (150-180)	54-65 (130-150)	49-60 (120-140)
Current density, A/dm^2 (A/ft^2)	1-4 (10-40)	1-4 (10-40)	1-3 (10-30)	. . .	2-5.5 (20-55)	1-2 (10-20)	0.5-10 (5-10)

(a) *Hamilton* is a term that has been applied to white, pink, green, and brown golds. It is practically meaningless today, but is still widely used.

If any four numbers are randomly assigned to the concentrations of the four constituents of the gold electroplating solution, plating conditions can be found that will yield a satisfactory deposit. The four numbers chosen would determine the necessary temperature of operation, the degree of agitation, the current density for producing a good deposit, and the time of plating needed for different thicknesses. The fact that any four numbers could be used explains why hundreds of formulations appear in the literature. Given the proper operation conditions, any of the formulas will work, and at one time or another each cited formula was optimum and economic for a given plant and a given plater. Variations in the price of gold, the size of the item to be plated, the necessary rate of production, the desired deposit thickness, and the desired color resulted in almost every plater designing the "best bath."

Today, most jewelry is flash plated or strike plated from a hot-cyanide alloy (color) bath. The deposit is usually applied over a bright nickel deposit. Occasionally, the gold is flash plated over a palladium deposit over a bright acid-copper deposit, where nickel-free deposits are desired. (The European Common Market is concerned about nickel dermatitis from costume jewelry, snap fasteners, and other items that contact the skin.) Occasionally, the flash gold deposit is applied over a karat gold or rolled-gold plated item. This is done to give an even color to jewelry items made of several different findings. (Some jewelry is flashed from an acid bath directly over stainless steel for hypoallergenic jewelry.)

Typical flash formulations are given in Table 1. Although broad ranges are given for the decorative flash baths, it is absolutely essential that each parameter be closely and tightly controlled within its range if consistency of color is desired. The time of plating is quite short, usually 5 to 30 s. For minimum porosity and subtle color matches, even a 30 s plate may be duplex plated from two different solutions. For flash barrel plating the gold concentration can be as low as 0.8 g/L, the free cyanide is 7.5 g/L, the dipotassium phosphate should be 75 g/L or above, and nickel, as a brightener, should be added at 2 g/L or higher as potassium nickel cyanide.

The deposit is generally 0.05 to 0.1 μm (2 to 4 μin.) and *cannot*be marketed as gold electroplate. If the jewelry is to be marketed as gold electroplate the deposit must be 0.175 μm (7 μin.). If the jewelry is to be marketed as heavy gold electroplate the deposit must be 2.5 μm (100 μin.). Most deposits in this range are plated from an acid gold formulation (Table 2) or from a sulfite gold bath (Table 3).

Table 2 Acid gold color plating baths for heavy deposits

Component or parameter	1N Color(a)	2N Color(a)	Yellow 24K	Yellow 22K
Gold, g/L (oz/gal)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)
Conducting salt(b), g/L (oz/gal)	120 (16)	120 (16)	120 (16)	120 (16)
Nickel as chelate, g/L (oz/gal)	11 (1.5)	3.7-6 (0.5-0.8)	. . .	200 ppm
Cobalt as chelate, ppm	. . .	. . .	250	1000
pH	4-4.5	4-4.5	4.4-4.8	4.5
Temperature, °C (°F)	50-60 (120-140)	38-50 (100-120)	26-32 (80-90)	32-38 (90-100)
Current density, A/dm^2 (A/ft^2)	1-2 (9-19)	1-2 (9-19)	1-2 (9-19)	1-2 (9-19)
Agitation	Yes	Yes	Yes	Yes

(a) European color standards.

(b) The conducting salt can be a phosphate or an organic acid such as citric or malic.

Table 3 Sulfite gold decorative plating baths

Component or parameter	24K	Flash green	Pink	Heavy plating
Gold as sulfite, g/L (oz/gal)	1.25-2 (0.17-0.27)	1.25-2 (0.17-0.27)	1.25-2 (0.17-0.27)	8-12 (1.0-1.6)
Conducting sulfite salt, g/L (oz/gal)	90 (12)	90 (12)	90 (12)	45-75 (6-10)
Nickel as chelate, g/L (oz/gal)	. . .	1.1 (0.15)	0.5 (0.07)	. . .
Copper as chelate, g/L (oz/gal)	. . .	. . .	0.5 (0.07)	. . .
Cadmium as chelate, ppm	. . .	760	. . .	. . .
Brightener, often arsenic, ppm	20	20	20	20
Current density, A/dm^2 (A/ft^2)	3-5 (28-46)	3-5 (28-46)	3-5 (28-46)	0.1-0.4 (1-4)
Temperature, °C (°F)	50-65 (120-150)	50-65 (120-150)	50-65 (120-150)	50-60 (120-140)
Time, s	10-20	15-30	10-20	(a)

(a) 12.5 min at 0.3 A/dm^2 (3 A/ft^2) gives 100 μin.

As with cyanide gold plating, to achieve consistent good color control it is necessary to regulate each chemical and physical variable within its range given in Table 2. It is also necessary to analyze for metallic impurities and control their concentrations. Drag-in of metallic impurities can have a disastrous effect on color control.

Sulfite gold plating solutions (Table 3) have several unique and advantageous characteristics. First, they contain no cyanide, so the normal safety precautions used when working with or handling cyanide are not necessary when using sulfite gold. In addition, of course, there is no cyanide to destroy in the dragout, rinse stream or old solutions shipped for recovery. The second unique property is exceptional microthrowing power; the bath will actually build brightness during plating. The deposit is essentially featureless with exceptionally fine crystal structure.

Industrial Gold Plating

The printed circuit industry of the late 1950s led to the rediscovery of the stability of potassium gold cyanide on the acid side (below a pH of 7). This was first hinted at in a Ruolz French patent of addition of 1840-45. The stability was described in the English edition of *Cyanogen Compounds* by H.E. Williams in the 1890s. Finally, the Lukens patent of 1938 made use of low-pH gold cyanide plating to ensure good adhesion on stainless steel. Lukens referred to this bath, made up with sodium gold cyanide, sodium cyanide, and hydrochloric acid as *acid gold plating.*

The alkaline gold plating solutions in use in the early 1950s caused lifting of printed circuit resists, especially the wax-based resists introduced in an attempt to speed board preparation. The pH of the gold solutions was progressively lowered to minimize this effect. In one case, an accident resulted in too low a drop in the pH. It was not noticed at first because the bath continued to plate and there was no lifting of the resist. However, a drop in cathode current efficiency and a decrease in the thickness of the gold deposit alerted the operator. On investigation it was found that the pH had fallen to 4.0.

Separately, it was discovered by Duva that at a pH of 3.5 to 5, it was possible to add small amounts of cobalt, nickel, iron, and other metals to harden the gold deposit and cause it to plate bright. The purity of the deposit was still over 98% gold, but the hardness could be as high as 230 HK. Later, it was also noticed that the crystal structure of the surface could be plated to yield a (111) crystal plane, which greatly increased the wear resistance of the contact surface. Depending on the added metal or metals, the chemical form of the addition, and the pH of the electrolyte, deposits of various hardnesses and other characteristics could be made (Table 4).

Table 4 Acid gold industrial plating baths

Component or parameter	**Bright, hard acid**	**Weak acid**
Regular baths		
Gold as potassium gold cyanide g/L (oz/gal)	4-16 (0.5-2)	4-8 (0.5-1)
Potassium citrate, citric acid, g/L (oz/gal)	180 (24)	. . .
Mono- and dipotassium phosphate, g/L (oz/gal)	. . .	180 (24)
Brightener	(a)	. . .
pH	3.5-5.0	5.5-7.0
Temperature, °C (°F)	20-50 (68-122)	65-74 (150-165)
Current density, A/dm^2 (A/ft^2)	1-10 (9-90)	0.1-0.5 (1-5)
Current efficiency, %	30-40	85-100
High-speed baths		
Gold as potassium gold cyanide, g/L (oz/gal)	4-24 (0.5-3)	8-32 (1-4)
Citrates, g/L (oz/gal)	90 (12)	. . .
Phosphates/citrates, g/L (oz/gal)	. . .	90 (12)
Brighteners	(a)	(a)
Temperature, °C (°F)	49-60 (120-140)	71-82 (160-180)

Current density(b), A/dm^2 (A/ft^2)	10-200 (93-1860)	5-50 (46-460)
Current efficiency, %	40-50	50-60

(a) As required.

(b) Values given are typical; they depend on agitation and the individual machine.

At the same time that the above developments took place, the semiconductor industry developed a need for high-purity golds at increased thicknesses. This led to a series of formulations by Ehrheart that plated gold from mild acid solutions. Raising the pH resulted in better covering power and higher current efficiency. At first the hardness and brightness of the acid golds was lost, but it was found that by modifying the neutral electrolytes, these properties could be partially restored (Table 4). So many different solutions were developed that a standard was needed. The most recent MIL-G-45204C (1984) and ASTM B 488-86, the military specification defines the purity, hardness, and thickness of the deposit. Purity is described as:

- Type I: 99.7% gold min
- Type II: 99.0% gold min
- Type III: 99.9% gold min

Hardness is specified as:

- A, 90 HK max
- B, 91-129 HK max
- C, 130-200 HK max
- D, 201 + HK

Thickness is specified as:

- Class 00, 0.5 μm (20 μin.)
- Class 0, 0.75 μm (30 μin.)
- Class 1, 1.25 μm (50 μin.)
- Class 2, 2.5 μm (100 μin.)
- Class 3, 5.0 μm (200 μin.)
- Class 4, 7.5 μm (300 μin.)
- Class 5, 12.5 μm (500 μin.)
- Class 6, 37.5 μm (1500 μin.)

Type I purity cannot have hardness D, and Type II purity cannot have hardness A. Type III purity can only be hardness A.

Strike Plating. Gold is a noble metal and deposits at a very low applied potential. These characteristics can cause nonadherence of the gold deposit if the substrate is either passive or not perfectly clean. Poor adhesion can be prevented by using a gold strike bath. A *strike* is generally a solution with very low metal concentration that is operated at high voltage and high current density for a very short period of time. For rack plating, the strike plating time is less than 1 min at a current density of 1 to 3 A/dm^2 (9 to 28 A/ft^2). A gold strike generally is not needed when plating from an acid gold solution unless the gold concentration is greater than 8 g/L or the substrate is passive.

Noncyanide Gold Plating Solutions. Sulfite gold industrial baths are used for their unique physical properties in addition to the desirable property of being noncyanide. As discussed above, sulfite golds have exceptional microthrowing power, which makes them the only gold formulations that build brightness. Furthermore, they have the best infrared reflectivity of any gold plating solution. The following table shows the composition and operating parameters of sulfite gold industrial baths:

Component or parameter	**Value**
Gold as sodium gold sulfite, g/L (oz/gal)	4-16 (0.5-2)
Sodium sulfite and sulfate, g/L (oz/gal)	90 (12)
pH	8.5-10.0
Temperature, °C (°F)	50-60 (122-140)
Brightener	As required
Current density, A/dm^2 (A/ft^2)	0.1-0.4 (1-4)
Current efficiency, %	100

Electroplating Calculations. Factors to use with gold electroplating calculations are:

- The price of gold, as given in newspapers and on the radio, is expressed in dollars per troy ounce (1 troy ounce = 31.1 g).
- A deposit of gold that is 1 μm thick = 19.58 g/m^2 (1.82 g/ft^2).
- At 100% cathode current efficiency, 7.35 g of gold can be electrodeposited in 1 ampere-hour, or 0.123 g in 1 ampere-minute.
- At 100% cathode current efficiency, 160.5 ampere-minutes are required for a gold deposit that is 1 μm thick and covers 1 m^2.

Time, temperature, and amperage can be accurately measured and controlled in gold electroplating. The largest errors that can affect gold calculations are the inaccuracies in the current density and the current efficiency. Current density is determined by calculating the area measurement, which is not always an easy task. Outside surface areas may be correctly calculated, but inside surfaces and holes, such as solder cups, must be calculated and then their effective plating area must be estimated.

Current efficiency is determined by current density, metal concentration, electrolyte concentration, and impurity content. The impurities that change the current efficiency are the metallic impurities, the organic impurities from masking materials and resists, and airborne dust. Current efficiency can be measured with a weighed coupon plated in the laboratory using a sample of the solution.

In practice, a good way to measure the efficiency of a solution is to estimate the required amperage and time based on theory, increase the amount by, say, 10%, and then plate a load under these conditions. The thickness of the gold on the plated work can be measured by microsection, x-ray diffraction, beta-ray backscatter, or other means. The thickness actually measured should be used to correct the estimated efficiency and to modify the plating conditions. It is best to measure the thickness periodically, because the cathode current efficiency of a gold bath will change not only with the variability of all the chemical constituents but also with the age of the bath. Periodic monitoring of the thickness ensures consistent quality control.

Dragout

Minimizing the dragout of gold solutions is of both economic and environmental concern. It is an economic advantage to decrease the cost of gold loss, and it is an environmental advantage to reduce the amount of processing needed to purify the waste stream before discharge.

Many factors affect dragout:

- The thickness of the gold plated
- The shape of the part to be plated
- The number of holes or other solution-trapping structures
- The speed of removing the plated part from the plating tank
- Provisions for air jets or wiper blades to return the drippings to the plating tank

In some cases the dragout is from 30 to 50% of the gold actually deposited. Typically, however, it is 10 to 20%. It is far better to limit the dragout than to expend effort in processing the cyanide and recovering the gold from the dragout.

Minimizing the dragout can be done with simple procedures such as training the operator to remove the rack slowly and to "nudge" or shake the withdrawn rack over the gold tank so droplets return to the tank. Barrels should be allowed to drip over the gold tank and should be rotated one-half turn or more before being dipped into the dragout recovery tank. Continuous plating machines should have an air knife or a synthetic sponge to remove excess gold solution.

All gold-plated work should be rinsed in a stagnant gold recovery tank that is treated frequently to recover the dragged-out gold. The gold can be recovered by passing the dragout solution through an appropriate ion exchange resin, or it may be recovered by plating out, in which the dragout is circulated and continuously electroplated on a carbon or wire-mesh cathode. The gold-plated cathode should periodically be sent to a refiner.

Platinum-Group Metals Plating

Ch.J. Raub, Forschungsinstitut für Edelmetalle und Metallchemie

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Introduction

THE SIX PLATINUM-GROUP METALS (PGMs), listed in order of their atomic numbers, are ruthenium, rhodium, palladium, osmium, iridium, and platinum. The PGMs are among the scarcest of metallic elements, and thus their cost is high. Their most exceptional trait in the metallic form is their excellent corrosion resistance. The electroplating of PGMs from aqueous electrolytes for engineering applications is limited principally to palladium and, to a much lesser extent, to platinum, rhodium, and thin layers of ruthenium. There are practically no electrolytes on the market for the deposition of osmium or iridium. While solution formulations have been published for these last two metals, they have not proven themselves in practical use for any significant applications, and thus will be discussed only briefly in this article.

Detailed information about the general availability, properties, and applications of PGMs is provided in *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Volume 2 of *ASM Handbook.* Good overview coverage of plating of these metals is available in Ref 1, 2, and 3.

Acknowledgement

The section on anode materials was prepared by Ronald J. Morrissey, Technic, Inc.

References

1. F.H. Reid, Platinum Metal Plating-A Process and Application Survey, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 112-123
2. F.H. Reid, Electrodeposition of Platinum-Group Metals, *Met. Rev.,* Vol 8, 1963, p 167-211
3. Ch.J. Raub, Electrodeposition of Platinum-Group Metals, *GMELIN Handbook of Inorganic Chemistry,* Platinum Supplement, Vol A1, 1982

Ruthenium Plating

Ruthenium in the solid form is hard and brittle; furthermore, it oxidizes rather easily. These factors limit its use, even as its low price relative to the other PGMs provides impetus for its application. Despite extensive research work on electroplating of ruthenium, it has obtained a small market share in only two areas: for decorative applications such as eyeglass frames and for layers on electrical contacts used in sealed atmospheres.

All ruthenium plating electrolytes are based on solutions of simple ruthenium salts or ruthenium nitrosyl derivatives. Typical examples are ruthenium sulfate, ruthenium phosphate, ruthenium sulfamate, or ruthenium chloride (Ref 4). These electrolytes are all essentially based on those described in Ref 5 and 6. They work in a wide range of current densities from 1 to 10 A/dm^2 (9 to 93 A/ft^2) at temperatures between 50 and 90 °C (120 and 195 °F), and at current efficiencies of 50 to 90%. Compositions and operating conditions for two ruthenium plating solutions are given in Table 1.

Table 1 Ruthenium electroplating solutions

Constituent or condition	**Amount or value**
General-purpose solution	
Ruthenium (as sulfamate or nitrosyl sulfamate), g/L (oz/gal)	5.3 (0.7)
Sulfamic acid, g/L (oz/gal)	8 (1.1)
Anodes	Platinum
Temperature, °C (°F)	
Sulfamate solution	27-60 (80-140)
Nitrosyl sulfamate solution	21-88 (70-190)
Current density, A/dm^2 (A/ft^2)	1-3 (10-30)
Current efficiency, %	20
Time to plate thickness of 0.003 mm (0.0001 in.)	30-40 min at 2 A/dm^2 (20 A/ft^2)
Flash-plating solution for decorative deposits	

Ruthenium (as nitroso salt), g/L (oz/gal)	2.0 (0.3)
Sulfuric acid, g/L (oz/gal)	20 (2.7)
Current density, A/dm^2 (A/ft^2)	2-3 (20-30)
Temperature, °C (°F)	50-80 (120-180)

Note: Both solutions require a flash-plated undercoat of gold or palladium. Source: Ref 7

The preparation of the electrolyte constituents is rather critical. Deposits are hard and highly stressed, making it difficult to obtain crack-free layers at higher thicknesses. For electrical contact applications, a layer of gold flash plated on top of the ruthenium is recommended to ensure excellent wear and good contact resistant on a long-term basis (Ref 8, and 9). Smooth and bright deposits can be obtained from cyanide melts (Ref 10, 11). Microhardness of such layers is between 600 and 900 HK.

References cited in this section

4. F.H. Reid and J.C. Blake, *Trans. Inst. Met. Finish.,* Vol 38, 1961, p 45-51
5. H.C. Angus, *Trans. Inst. Met. Finish.,* Vol 43, 1965, p 135-142
6. T.A. Palumbo, *Plat. Surf. Finish.,* Vol 66, 1979, p 42-44
7. A.M. Weisberg, Ruthenium Plating, *Met. Finish.,* Vol 90 (No. 1A), 1992, p 257
8. R.G. Baker and T.A. Palumbo, *Plat. Surf. Finish.,* Vol 69, 1982, p 66-68
9. A.F. Bogenschütz, J.L. Jostan, and W. Mussinger, *Galvanotechnik,* Vol 67, 1976, p 98-105
10. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
11. G.S. Reddy and P. Taimsalu, *Trans. Inst. Met. Finish.,* Vol 47, 1969, p 187-193

Rhodium Plating

Rhodium in its solid form is hard (microhardness about 800 to 1000 HV) and tough. It is nearly as tarnish resistant as platinum and palladium. However, because of its rare occurrence in PGM ores and market speculation, it is much more expensive, limiting its engineering use. Like silver, it has one of the highest reflectivities of all metals, making it ideal for use as a counterpoint to cut diamonds in jewelry and as a nontarnishing reflective coating for mirrors. Its excellent wear resistance and its superb contact resistance prompt its frequent use for rotating electrical contacts.

The electrolytes for deposition of rhodium from aqueous solutions are similar to those for ruthenium insofar as they are either based on simple rhodium salts or on special rhodium complexes (Ref 12, and 13). Because, in most cases, only layer thicknesses of 1 μm or less are specified, most commercial electrolytes have been developed to produce layers in this thickness range. The deposits have a high concentration of nonmetallic impurities (e.g., up to 1000 ppm H and/or O) (Ref 14), which causes high hardnesses and internal stresses, which easily lead to cracks. This thin and highly porous layer of rhodium, coupled with the high electrochemical nobility of the metal, limits its use as a corrosion protection layer. Therefore, an electroplated base coating must be used. Silver and silver-tin alloys (with varying concentrations of tin) have exhibited excellent field service behavior and are now applied for decorative as well as engineering purposes. Nickel is not recommended for use as a base coating. For decorative use the color (better reflectivity) is most important. It changes from electrolyte to electrolyte, many of which are commercial solutions. Deposition conditions must be carefully controlled for best results.

The complex rhodium salts of solutions cited in the literature are based on sulfate, phosphate, sulfate-phosphate, sulfate-sulfite, sulfamate, chloride, nitrate, fluoroborate, or perchlorate systems. Properties of the layers are strongly influenced by the chemistry of their salts as well as by impurities present (Ref 15). Three solutions for decorative rhodium plating are given in Table 2.

Table 2 Solutions for decorative rhodium plating

Solution type	**Rhodium**		**Phosphoric acid (concentrate) fluid**		**Sulfuric acid (concentrate) fluid**		**Current density**		**Voltage, V**	**Temperature**		**Anodes**
	g/L	**oz/gal**	**mL/L**	**oz/gal**	**mL/L**	**oz/gal**	**A/dm^2**	**A/ft^2**		**°C**	**°F**	
Phosphate	2(a)	0.3(a)	40-80	5-10	. . .	. . .	2-16	20-160	4-8	40-50	105-120	Platinum or platinum-coated(b)
Phosphate-sulfate	2(c)	0.3(c)	. . .	. . .	40-80	5-10	2-11	20-110	3-6	40-50	105-120	Platinum or platinum-coated(b)
Sulfate	1.3-2(c)	0.17-0.3(c)	. . .	. . .	40-80	5-10	2-11	20-110	3-6	40-50	105-120	Platinum or platinum-

(a) Rhodium as metal, from phosphate complex syrup.

(b) Platinum-coated products are also known as platinized titanium.

(c) Rhodium, as metal, from sulfate complex syrup

A typical, widely used production bath is based on rhodium sulfate (Ref 15). With use of proper additives, especially sulfur-containing compounds, crack-free layers may be obtained in thicknesses of about 10 μm and microhardnesses of 800 to 1000 HV (Ref 15). The deposition temperature of such baths is about 50 °C (120 °F), the current density is between 1 and 10 A/dm^2 (9 to 93 A/ft^2), and current efficiency is approximately 80%. Insoluble anodes are normally used.

For electronic applications where undercoatings are undesirable, special low-stress compositions have been developed. One electrolyte contains selenic acid and another contains magnesium sulfamate (Table 3). Deposit thickness obtained from these solutions range from 25 to 200 μm (1 to 8 mils), respectively. The low-stress sulfamate solution is used for barrel plating of rhodium on small electronic parts. Operating conditions for various plating thicknesses using this solution are given in Table 4.

Table 3 Solutions for electroplating low-stress rhodium deposits for engineering applications

Solution	**Selenic acid process**	**Magnesium sulfamate process**
Rhodium (sulfate complex)	10 g/L (1.3 oz/gal)	2-10 g/L (0.3-1.3 oz/gal)
Sulfuric acid (concentrated)	15-200 mL/L (2-26 fluid oz/gal)	5-50 mL/L (0.7-7 fluid oz/gal)
Selenic acid	0.1-1.0 g/L (0.01-0.1 oz/gal)	. . .

Magnesium sulfamate	. . .	10-100 g/L (1.3-13 oz/gal)
Magnesium sulfate	. . .	0-50 g/L (0-7 oz/gal)
Current density	1-2 A/dm^2 (10-20 A/ft^2)	0.4-2 A/dm^2 (4-22 A/ft^2)
Temperature	50-75 °C (120-165 °F)	20-50 °C (68-120 °F)

Table 4 Plating parameters for producing low-stress deposits from a rhodium sulfamate solution

Required thickness		**Thickness of plate**		**Apparent current density**(a)		**Calculated current density**(a)		**Plating time**
µm	**mil**	**µm**	**mil**	**A/dm^2**	**A/ft^2**	**A/dm^2**	**A/ft^2**	
1	0.04	0.5-1.5	0.02-0.06	0.55	5.5	1.6-2.2	16-22	35 min
2.5	0.1	1.75-3.25	0.07-0.127	0.55	5.5	1.6-2.2	16-22	$1\frac{1}{4}$ h

(a) Calculated current density is an estimate of the amount of current being used by those parts that are making electrical contact and are not being shielded by other parts in the rotating load in the barrel. Calculated current density is considered to be about three times the apparent current density, that is, the actual current used for the load divided by the surface of that load.

Rhodium also can be electroplated from fused-salt electrolytes. This deposition process is interesting because the requirements are that the coatings must be highly ductile for high-temperature use (e.g., coatings on molybdenum for combustion engine parts or glass-making equipment). For fused-salt electrolysis, a variety of mixtures have been tested, ranging from cyanide to chloride melts (Ref 16).

Thickness class designations for engineering applications of electroplated rhodium are given in Table 5.

Table 5 Thickness classifications for rhodium plating for engineering use

Specification	**Class**	**Minimum thickness**	
		µm	**mil**
ASTM B 634-78	0.2	0.2	0.008
	0.5	0.5	0.02
	1	1	0.04

	2	2	0.08
	4	4	0.16
	5	6.25	0.25
MIL-R-46085A	1	0.05	0.002
	2	0.3	0.01
	3	0.5	0.02
	4	2.5	0.10
	5	6.4	0.25

Source: Ref 17

References cited in this section

12. G.R. Smith, C.B. Kenahan, R.L. Andrews, and D. Schlain, *Plating,* Vol 56, 1969, p 804-808
13. W.B. Harding, *Plating,* Vol 64, 1977, p 48-56
14. Ch. J. Raub, unpublished research
15. F. Simon, Degussa-Demetron, Information Sheet, and article in *GMELIN Handbook of Inorganic Chemistry,* Platinum Supplement, Vol Al, 1982
16. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
17. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold, 1984, p 276

Palladium Plating

Palladium has been electroplated since before the turn of the 20th century. However, it stirred little interest until the 1960s and 1970s, when the price of gold peaked, prompting a search for alternatives. Palladium plating is currently used for jewelry and electrical contacts; however, the decorative applications of palladium are limited due to the dark color of the metal. Three typical palladium plating solutions are listed in Table 6.

Table 6 Palladium electroplating solutions

Constituent or condition	**Amount or value**
Solution A	
Palladium (as tetraamino-palladous nitrate, g/L (oz/gal)	10-25 (1-3)(a)
pH	8-10

Temperature, °C (°F)	40-60 (100-140)
Current density, A/dm^2 (A/ft^2)	0.5-2.2 (5-20)$^{(b)}$
Cathode efficiency, %	90-95
Anodes	Insoluble; palladium, platinum, or platinized titanium
Tank lining	Glass or plastic
Solution B	
Palladium (as diamino-palladous nitrite), g/L (oz/gal)	10 (1)
Ammonium sulfamate, g/L (oz/gal)	110 (15)
Ammonium hydroxide	To pH
pH	7.5-8.5
Temperature	Room
Current density, A/dm^2 (A/ft^2)	0.5-2.2 (5-20)$^{(b)}$
Cathode efficiency, %	70
Anodes	Insoluble; platinum or platinized titanium
Tank lining	Glass or plastic
Solution C	
Palladium (as palladous chloride), g/L (oz/gal)	50 (7)
Ammonium chloride, g/L (oz/gal)	30 (4)
Hydrochloric acid	To pH
pH	0.1-0.5
Temperature, °C (°F)	40-50 (100-120)

Current density, A/dm^2 (A/ft^2)	0.5-1.1 (5-10)
Anodes	Soluble palladium
Tank lining	Rubber, plastic, or glass

Source: Ref 18

(a) Normally 10-15 g/L (1-2 oz/gal).

(b) Normally 0.5 A/dm^2 (5 A/ft^2).

Palladium alloys such as palladium-nickel, palladium-iron, and, to a lesser extent, palladium-cobalt are also electroplated. The plating solutions for palladium alloys are generally based on the same or similar complexes as the ones for palladium alone. The main application at present for these alloy electrodeposits is for electrical connectors (Ref 19, 20, 21, 22). A solution composition for depositing palladium-nickel is given in Table 7.

Table 7 Palladium-nickel electroplating solutions

Constituent or condition	**Amount or value**
Palladium as $Pd(NH_3)_2(NO_2)_2$, g/L (oz/gal)	6 (0.8)[a]
Nickel sulfamate concentrate, mL/L (fluid oz/gal)	20 (2.6)[b]
Ammonium sulfamate, g/L (oz/gal)	90 (12)
Ammonium hydroxide	To pH
pH	8-9
Temperature, °C (°F)	20-40 (70-100)
Current density, A/dm^2 (A/ft^2)	0.5-1.0 (5-9)
Anodes	Platinized

Note: Formulation is for plating an alloy of about 75 wt% Pd. A strike of gold or silver is recommended for most base metals prior to plating.

Source: Ref 23

(a) Palladium metal, 3 g/L (0.4 oz/gal).

(b) Nickel metal, 3 g/L (0.4 oz/gal).

The properties of palladium electrodeposits are generally similar to those of gold, but it has higher receptivity and hardness. Soldering, crimping, and wire wrapping present no serious problems. The sliding and wear behavior of palladium are similar to those of hard gold. Palladium coatings may be slightly less porous than gold coatings, and they resist tarnish and corrosion. On the other hand, the chemical properties of palladium are quite different from those of gold, which may explain why an effective agent for stripping palladium and palladium alloy electrodeposits has not yet been developed.

In service, palladium and palladium alloys tend to exhibit what is called a *brown powder effect,* in which a "brown polymer" catalytically forms on the contact surface upon exposure to organic compounds in the environment. This effect can be minimized by application of flash plating a layer of fine gold on top of the palladium surface. The biggest challenge when electrodepositing palladium is avoiding hydrogen embrittlement. Palladium in electrodeposition may dissolve fairly large amounts of hydrogen, and this expands the palladium lattice, especially if the so-called β-Pd/H phase is formed. However, this hydrogen diffuses out of the palladium during storage at room temperature, and the lattice contracts again. This expansion/contraction generates stresses in the deposit that cause cracks and pores. Furthermore, palladium promotes diffusion of atomic hydrogen, which may cause secondary reactions (e.g., hydrogen embrittlement of underlying steel bases or blister) if the base material does not take up the diffused hydrogen.

Electrolytes have been developed that effectively solve the problem of hydrogen embrittlement. The most economical are based on palladium chloride. In these solutions, the palladium ion is complexed by ammonia or amines. Other systems using other complexes have also been developed (Ref 19, 20, 21, 22, 24). Currently, no electrolyte for the deposition of palladium-silver or palladium-copper alloys is available. The influence of organic and inorganic impurities on palladium-nickel deposits has been studied extensively (Ref 19).

Thickness class designations for engineering applications of electroplated palladium are given in Table 8.

Table 8 Thickness classifications for palladium plating for engineering use

Specification	Class	Minimum thickness	
		μm	mil
ASTM B 679-80	5.0	5.0	0.20
	2.5	2.5	0.10
	1.2	1.2	0.05
	0.6	0.6	0.02
	0.3	0.3	0.01
	F	0.025	0.0010

MIL-P-45209	. . .	1.3[(a)]	0.05[(a)]

Source: Ref 17

(a) Unless otherwise specified.

References cited in this section

17. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold, 1984, p 276
18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205
19. Ch.J. Raub, *Platinum Met. Rev.,* Vol 28, 1992, p 158-166
20. F.H. Reid, *Plating,* Vol 52, 1965, p 531-539
21. M. Antler, *Platinum Met. Rev.,* Vol 26, 1982, p 106-117
22. H. Grossmann, M. Huck, and G. Schaudt, *Galvanotechnik,* Vol 71, 1980, p 484-488
23. R.J. Morrissey, Palladium and Palladium-Nickel Plating, *Metal Finishing,* Vol 90 (No. 1A), 1992, p 247-248
24. German Society for Electroplating and Surface Technology, Precious Metals Working Group, Electroplating of Palladium and Palladium Alloys, *Galvanotechnik,* Vol 84, 1993, p 2247-2938

Osmium Plating

Currently, no practical applications exist for electrodeposited osmium, primarily because the metal oxidizes readily at room temperature, forming poisonous and volatile osmium tetroxide. The metal itself is hard and brittle and has few industrial uses. For a review of the existing literature on electrodeposition of osmium, see Ref 25, 26, and 27.

References cited in this section

25. J.M. Nutley, *Trans. Inst. Met. Finish.,* Vol 50, 1972, p 58-62
26. L. Greenspan, *Plating,* Vol 59, 1972, p 137-139
27. J.W. Crosby, *Trans. Inst. Met. Finish.,* Vol 54, 1976, p 75-79

Iridium Electroplating

The electroplating of iridium has up to now not found any widespread application. Essentially, no electrolytes are available that can deposit iridium from aqueous electrolytes at reasonable thicknesses and with satisfactory properties.

Known electrolytes are mostly based on the chloro-iridic acid. The bath is highly acidic and works at a temperature of about 80 °C (176 °F) and at a current density of 0.15 A/dm^2 (1.4 A/ft^2). The microhardness of deposits is 900 DPN, and their total reflectivity is about 61% that of silver. At thicknesses of more than 1 μm, the layers are cracked. The current efficiency of these processes approaches 50%. At low current densities, the plating rate is close to 1 μm/h (Ref 28, 29, 30, 31).

Iridium has been deposited from fused salts. The solution was prepared by passing alternating current between two electrodes suspended in the melt, which was a eutectic of NaCN or KCN/NaCN, with melting points of 564 and 500 °C (1050 and 930 °F), respectively (Ref 32). However, these electrolytes have not proven to be usable in commercial practice.

References cited in this section

28. F.H. Reid, *Met. Rev.,* Vol 8, 1963, p 167, 211
29. C.J. Tyrell, *Trans. Inst. Met. Finish.,* Vol 43, 1965, p 161-166
30. F.H. Reid, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 115-123
31. G.A. Conn, *Plating,* Vol 52, 1965, p 1256-1261
32. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71

Platinum Plating

The electrodeposition of platinum from aqueous electrolytes is of limited engineering value. The metal is very expensive, and the currently available plating solutions are not capable of consistently producing ductile and pore-free deposits at thicknesses above a few microns. Today, most of the deposits produced are less than 1 μm thick and are used primarily for decorative applications.

The main challenge when electroplating platinum from aqueous electrolytes is to obtain a clean, ductile platinum coating with a minimum of nonmetallic impurities, which act as hardeners and embrittle the platinum. This is rather difficult because platinum compounds tend to hydrolyze even at rather low pH levels. Therefore, close control of plating parameters is very important.

The three most common electrolytes used today are platinum chloride, diamino-dinitroplatinum (platinum "P" salt), and alkali hydroxy platinate. The current efficiency of the highly acidic baths is close to 90%, but the electrolytes are difficult to handle. Two platinum plating solutions are listed in Table 9.

Table 9 Platinum electroplating solutions

Constituent or condition	**Amount or value**
Solution A	
Platinum (as sulfatodinitrito-platinous acid), g/L (oz/gal)	5 (0.7)
Sulfuric acid	To pH
pH	1.5-2.0
Temperature, °C (°F)	Room to 40 (100)
Current density, A/dm^2 (A/ft^2)	5-20 (5-20)
Anode	Platinum or platinized titanium
Cathode efficiency	10-20%
Solution B	
Platinum (as diaminodinitrito salt), g/L (oz/gal)	10 (1.3)
Ammonium nitrate or phosphate, g/L (oz/gal)	100 (13.4)

Sodium nitrite, g/L (oz/gal)	10 (1.3)
Ammonium hydroxide (28% solution), mL/L (fluid oz/gal)	50 (6.4)
Temperature, °C (°F)	90-100 (190-210)
Current density, A/dm^2 (A/ft^2)	3-10 (30-100)(a)
Anode	Platinum (insoluble)
Tank lining	Glass or plastic
Cathode efficiency	Low(b)

Source: Ref 18

(a) Normally 4 A/dm^2 (40 A/ft^2).

(b) 10% at 6 A/dm^2 (60 A/ft^2).

A commercial process gaining more and more importance for engineering applications in the chemical, electronics, and glass industries is the electrodeposition of platinum from salt melts, because the process forms highly dense and ductile platinum layers. The platinum compound can be formed by electrolytic dissolution with alternating current in a NaCN/KCN fused-salt mixture, melting at 500 °C (930 °F). For deposition, a cyanide/cyanate mixture operating at about 450 °C (840 °F) is recommended.

For decorative platinum deposits, the use of a flash-plated base coat is recommended. Suitable layers include palladium-iron, silver, and copper-tin systems. Detailed information on platinum electroplating is available in Ref 33, 34, 35, 36, 37, and 38.

References cited in this section

18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205
33. F.H. Reid, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 115-123
34. F.H. Reid, *Met. Rev.,* Vol 8, 1963, p 167-211
35. K. Wundt, *Oberfl. Surf.,* Vol 25, 1984, p 207-212
36. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
37. H.H. Beyer and F. Simon, *Metall.,* Vol 34, 1980, p 1016-1018
38. C. Hood, *Plat. Met. Rev.,* Vol 20, 1976, p 48-52

Anodes for PGM Plating

In most aqueous or oxygen-bearing environments, the platinum-group metals are coated with a very thin layer of the appropriate metal oxide. This film is referred to as a *passive layer,* and it serves to prevent the underlying metal from corroding. Thus, anodes fabricated from PGMs are insoluble (inert) in most environments. The anode processes are mainly

$$2H_2O \rightarrow O_2 + 4H^+ + 4E^-$$

in acid solutions, or

$$4OH^- \rightarrow O_2 + 2H_2O + 4E^-$$

in alkaline solutions.

There are exceptions to this rule. The platinum metals are soluble in hot halogen acids (HF, HCl, HBr) and will dissolve anodically under these conditions. Similarly, oxidizing ligands such as nitrate and nitrite tend to dissolve PGMs, particularly in the presence of halogen acids. Plating solutions based on such systems are highly corrosive, and it is usually necessary to protect the work to be plated by prestriking with gold. Platinum-group metal anodes are also soluble in molten cyanide systems, from which PGMs can be deposited to very heavy thicknesses. Molten cyanide systems operate under an argon atmosphere at temperatures of about 600 °C (1100 °F), and for these reasons are not widely used. They are useful for heavy deposition because the high temperature provides some degree of stress-relief annealing during the plating operation.

Because anodes fabricated from PGMs are inert in most aqueous environments, they are useful not only for the electrodeposition of PGMs but also for plating of other metals, such as gold. Platinum is the metal of choice for such applications and is available in the form of wire mesh, or plated onto anodizable metals such as titanium, or clad onto passive-prone metals such as niobium or tantalum. In the plated and clad configurations, the required mechanical strength is provided by the substrate, and the actual amount of platinum used is quite small.

Reference 39 is a good general resource of information about anode selection and general plating practices.

Reference cited in this section

39. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley, 1974

Copper Alloy Plating

Henry Strow, Oxyphen Products

Introduction

COPPER ALLOYS are widely used as electroplated coatings, and they can be used with practically any substrate material that is suitable for electroplating. While alloys such as copper-gold and copper-gold-nickel are commonly electroplated, these are usually considered as part of gold plating technology. The most frequently electroplated copper alloys are brass (principally alloys of copper and zinc) and bronze (principally alloys of copper and tin). Brass and bronze are both available in a wide variety of useful compositions that range in content practically from 100% Cu to 100% Zn or Sn.

The history of brass and bronze plating dates back at least as far as the 1840s. Early work that was commercially exploited occurred in Russia, France, and England. All of the early copper alloy plating solutions were cyanide based and used batteries for power. Progress was slow, with much of the work being of an academic nature. A major advance was made in 1938 when patents on a high-speed copper plating process by DuPont were extended to a high-speed process for plating of both yellow and white brass (alloys containing about 70 to 80% Cu). The solution was cyanide based with a relatively high hydroxide content.

Brass Plating

Decorative Applications. The largest use of brass plating is for decorative applications. Copper-zinc alloys that contain more than 60% Cu have distinct colors, depending on the composition. The 60Cu-40Zn alloys are pale yellow, sometimes with a brown cast. Alloys with compositions from 70Cu-30Zn to 80Cu-20Zn are yellow, with only slight color variations over this range. The 85Cu-15Zn alloys are darker and resemble gold. The 90Cu-10Zn alloys are darker still, with a reddish, bronze-like cast. With proper control of plating parameters, the variation of the alloy composition of brass plate can be kept within 1%, and consistency in color can be achieved. Plated alloys have the same color as wrought alloys of the same composition and surface treatment. Brass darkens with age due to the formation of copper oxide on the surface, so the appearance of old samples will not match that of newly plated items.

Yellow brass plate (normally a 75Cu-25Zn alloy) is frequently flash plated over bright nickel plating to maintain its bright appearance; the surface is subsequently lacquered to preserve the finish. (*Flash plating* is the electrodeposition of a thin layer of material; plating times are usually under 1 min.) This type of flash plating is accomplished in both rack plating and barrel plating operations. Heavy brass plate can be buffed to a bright finish or oxidized to a dark finish; dark finishes can be *relieved* (selectively buffed) for an antique appearance. Brass plated items can also be burnished in tumbling barrels to give a uniform bright finish. Cosmetic cases are frequently plated with an 85Cu-15Zn alloy to impart a golden appearance; the alloy can be applied as a flash plate or as a heavier plate that is subsequently burnished. Builders hardware plated with a 90Cu-10Zn alloy called *architectural bronze* uses these same techniques.

Engineering applications for brass plating are also important. Brass plate on sheet steel and wire performs a lubricating function in deep drawing and wire drawing operations. Brass plating is used to promote adhesion of rubber bonded to steel. For example, the wire in steel-belted radial tires is plated with a brass alloy containing between 63 and 70% Cu (to secure the best adhesion, it is important that composition limits of the alloy be kept within 1%). After plating, the wire is drawn from 1.2 mm (0.049 in.) to approximately 0.15 mm (0.006 in.) without a break in the coating. The wire bonds to rubber so that blistering of the tires does not occur. Brass is also plated on sheet steel from which parts are stamped.

Equipment. Brass plating can be done in all the standard plating equipment, including barrel, rack, and continuous wire and strip machines. Steel is a suitable material for tanks, coils, and filters. However, rubber- or plastic-lined tanks with stainless or titanium coils are preferred because the iron in the steel can form ferrocyanides that precipitate as zinc ferrocyanide, resulting in the formation of a gray-colored sludge.

Surface Preparation. Brass can be plated on most metallic surfaces (e.g., zinc castings, steel, nickel, and aluminum) after only standard preplating procedures. Direct brass plating of zinc castings requires the use of relatively heavy coatings to prevent diffusion of the brass into the zinc and a resulting loss of color; an intermediate layer of plate is often used for this purpose. One method of brass plating uses this diffusion interaction to produce brass by plating separate layers of copper and zinc of appropriate thickness and then heating the plate to create the alloy by diffusion.

Plate thickness can be varied as required from very thin flash deposits for decorative purposes to deposits over 0.02 mm (0.001 in.) thick. The heavier plates are needed to withstand buffing, bright dipping antiquing, and other post-treatments that require heavier plate to maintain coverage.

Solution Composition and Operating Conditions. The majority of currently used brass plating solution are based on cyanide complexes. No other material brings the deposition potential of copper and zinc so close together. Solutions using a pyrophosphate base have been used commercially with limited success. Brass solutions using polyhydroxy aliphatic chemicals have also been used commercially with limited success. Formulas for low-pH brass plating solutions are given in Table 1.

Table 1 Low-pH brass plating conditions

Constituent or condition	Standard brass solution	High-copper brass solution
Makeup		
Sodium cyanide, g/L (oz/gal)	50 (6.7)	75 (10.0)
Copper cyanide, g/L (oz/gal)	35 (4.7)	45 (6.0)

Zinc cyanide, g/L (oz/gal)	10 (1.3)	7.5 (1.0)
Sodium carbonate, g/L (oz/gal)	10 (1.3)	10 (1.3)
Sodium bicarbonate, g/L (oz/gal)	7.5 (1.0)	7.5 (1.0)
Ammonia (aqua), %	0.5	0.1
Analysis		
"Total" sodium cyanide, g/L (oz/gal)	22 (2.9)	33 (4.4)
Copper (as metal), g/L (oz/gal)	23 (3.1)	22 (2.9)
Zinc (as metal), g/L (oz/gal)	6 (0.8)	4.2 (0.6)
pH	9.8-10.2	9.8-10.5
Operating conditions		
Temperature, °C (°F)	24-35 (75-95)	27-45 (80-113)
Current density, A/dm^2 (A/ft^2)	≤ 3 (≤ 28)	≤ 2.5 (≤ 23)
Sodium cyanide to zinc		
Ratio	3.5:1	7.0:1
Range	3-5:1	6-9:1

The formulas for standard brass plating solution can be varied to suit various uses while maintaining the ratios of components. The solution listed in Table 1 is well suited for barrel plating, where high efficiency is needed and good conductivity enables the use of maximum current. (Barrel plating is carried out at a voltage of 6 to 14 V.) Where flash plating is used, the solution should be operated with the cyanide constituents at approximately half the amounts shown in Table 1. This reduced cyanide concentration allows the use of a wider range of current densities and results in excellent covering power. The plating efficiency at the reduced cyanide concentration is lower, but this is not a significant factor in flash plating. For rack plating, the optimum cyanide concentration is about two-thirds of that shown in Table 1; this level provides improved efficiency (compared to flash plating) while still allowing use of a wide range of current densities.

Formulas for high-alkalinity brass plating solutions are given in Table 2. The solutions listed in Table 2 may be varied to meet specific applications. The functions of the solution constituents are somewhat different than in the low-pH solutions. In the high-alkalinity solutions, the hydroxide and cyanide can work together so that a higher hydroxide content increases the zinc content of the deposit; thus, the ratio of cyanide to zinc is not applicable. The high-alkalinity solutions have high efficiencies and can be used at high current densities; the use of additives is needed to secure uniform color at low current densities. Thus they are difficult to use in barrel plating operations.

Table 2 High-alkalinity brass plating solutions

Constituent or condition	Original (potassium)	High-speed strip plating	Modern
Makeup			
Sodium cyanide, g/L (oz/gal)	. . .	120 (16.1)	125 (16.8)
Potassium cyanide, g/L (oz/gal)	125 (16.8)	. . .	. . .
Copper cyanide, g/L (oz/gal)	44 (5.9)	100 (13.4)	75 (10.1)
Zinc cyanide, g/L (oz/gal)	17.3 (2.3)	. . .	5 (0.7)
Sodium hydroxide, g/L (oz/gal)	. . .	11 (1.5)	45 (6.0)
Potassium hydroxide, g/L (oz/gal)	30 (4.0)	. . .	. . .
Analysis			
Copper (as metal), g/L (oz/gal)	31 (4.2)	70 (9.4)	50 (6.7)
Zinc (as metal), g/L (oz/gal)	9.6 (1.3)	7 (0.9)	3 (0.4)
"Total" cyanide, g/L (oz/gal)	80 (10.7)	50 (6.7)	53 (7.1)
Sodium hydroxide, g/L (oz/gal)	. . .	11 (1.5)	45 (6.0)
Potassium hydroxide, g/L (oz/gal)	30 (4.0)	. . .	. . .
Operating conditions			
Temperature, °C (°F)	45 (113)	80 (176)	70 (158)
Current density, A/dm^2 (A/ft^2)	1-4 (9-37)	3-16 (28-149)	1-8 (9-74)

The copper cyanide content of the plating solution serves as a source of copper for the plating deposit, but also is a major factor in plating efficiency. Cyanide is necessary to form the complexes that enable the copper and zinc to plate together to form brass. The ratio of cyanide to zinc in a conventional brass solution is the major determinant of the resulting composition of the plated alloy. The zinc can form a complex with either cyanide or hydroxide, depending on the hydroxide content of the solution. Cyanide is also necessary for solubility of the anodes. While zinc is usually added as cyanide, a very pure grade of zinc oxide can also be used.

The carbonate content of a brass solution is usually regarded as an impurity. It is formed by breakdown of the cyanide. Small amounts (15-20 g/L) are necessary in low-pH solutions to buffer the solution. Without carbonate, the solution is unstable and will give inconsistent plating. Hydroxide acts as a stabilizer in the solutions in which it is present, and thus carbonate is not essential in these solutions. The carbonate in the low-pH solutions exists as an equilibrium between carbonate and bicarbonate, making the use of both necessary to secure the proper pH. Carbonates in sodium baths can be frozen out; potassium baths can be treated with barium cyanide or barium hydroxide to precipitate the carbonate. It should be noted, however, that the use of barium cyanide or barium hydroxide creates insoluble sludges that are poisonous and cannot be destroyed, so that a hazardous waste is created. The use of calcium salts is recommended.

Hydroxide is used in the high-speed solutions to complex the zinc and increase efficiency. Increasing the hydroxide content increases the zinc content in the plated alloy.

Ammonia is a very important constituent in the low-pH brass plating solutions. Ammonia serves as a brightener and improves the appearance of plating accomplished at both high and low current densities. Ammonia is formed during plating by the decomposition of cyanide and is usually stable at temperatures up to 30 °C (86 °F). Higher temperatures (and the high hydroxide content of high-speed solutions) drive off ammonia faster than it is formed, making regular additions necessary to maintain color. Amines may be used to secure the benefit of ammonia at higher temperatures. An excess of ammonia causes the alloy to become richer in zinc; large excesses may result in white plate. Additions of ammonia do not change the pH level of the solution.

The temperature of the plating solution should be controlled to give constant alloy composition. A rise in temperature increases the copper content of the plate and also increases the plating efficiency.

Impurities in the solution affect the quality of the plating. Soluble oils and soaps will cause a brown smutty plate; they can be removed by carbon filtration. Tin is not usually troublesome but can cause dullness and white plate in recesses. Treatment is by dummy plating. Iron is not troublesome because it forms ferrocyanides, which precipitate out of the solution (but, as noted above, may result in the formation of sludge). Lead is by far the most troublesome impurity. As little as 10 ppm Pb will result in red recesses in the plate, especially in barrel-plated parts. Higher amounts of lead will cause dullness, black areas, and blistering. The source of lead is usually the anodes, although lead pipe and other lead-containing objects in the solution can cause contamination.

Anodes for brass plating may be forged, cast, extruded, or rolled, and differences in performance are minimal. Balls or nuggets (chopped rod) are frequently used with steel or titanium baskets; these furnish a uniform high current area, which is especially good for barrel plating where a relatively high current is used. Brass anodes should be used at low current densities because high current densities will cause polarization. The anodes should be of high purity and contain less than 0.02% Pb and less than 0.1% Fe or other metals. The optimum composition of yellow brass anodes is 70% Cu and 30% Zn. Use of anodes with higher copper contents will necessitate frequent additions of zinc to the solution. Deposition of brass with higher copper content requires the use of 85Cu-15Zn or 90Cu-10Zn anodes; the composition of the anodes should approximate that of the alloy being plated. Anodes of the composition types mentioned above are readily available. Steel anodes can be used in place of some of the brass anodes in order to lower the metal concentration in the solution.

Solution Analysis. Analysis and close control of the plating solution are essential for maintaining control of the alloy composition and color of the plated deposit. Analysis of copper and zinc content can be done by several methods, ranging from simple titrations to x-ray fluorescence. The results of these methods are generally accurate and reproducible.

Analysis of cyanide content is not so simple. Many methods analyze the "free" cyanide content, which is applicable to copper cyanide solutions but of dubious value when zinc is present, as in brass plating solutions. A simple and reproducible method is that used to determine the total cyanide content in zinc cyanide plating solutions: The cyanide is titrated with silver nitrate using a small amount of hydroxide in the sample being analyzed. This makes all of the cyanide in the brass solution available except that which is combined with the copper. A meaningful number is the ratio of this "total" cyanide to the zinc content of the solution. Another method for analyzing cyanide content involves distilling the cyanide from an acidified sample. This method is used to determine the cyanide content of waste solutions. Its results include cyanide present in the solution as ferrocyanide, so this method may indicate relatively high cyanide contents.

The pH level can be determined by meters, pH papers, or colorimetric comparison with suitable indicators. Hydroxide content can be determined by titration with acid using a high pH indicator. Carbonate content is easily determined by standard methods involving precipitation of the carbonate, separation, and titration.

Ammonia content can be determined by using a specific ion electrode, but is more commonly determined by using a plating cell and checking the effects of ammonia additions. For the standard Hull cell, a total current of 1 A for 10 min. can be used. The plating cell panel will also indicate the effect of impurities and additions determined by analysis. For high-speed solutions, a current of 2 A for 10 min. is recommended. Effects at various current densities can also be determined by reading the panels. For flash plating, a Hull cell preplated with bright nickel and a total current of 1A for 1 min is preferred.

Bronze Plating

Applications of bronze plating are varied. Alloys containing from 10 to 15% Sn are attractive and are used for decorative wares. These alloys have gold color that is browner than true gold; equivalent copper-zinc alloys are pinker in color.

Bronze plating is used on builders hardware, locks, and hinges to provide an attractive appearance and excellent corrosion resistance. Bronze-plated steel or cast iron bushings replace solid bronze bushings for many uses. Bronze plating is used where improved lubricity and wear resistance against steel are desired. Its good corrosion resistance makes it desirable as an undercoat on steel for bright nickel and chromium plate. Speculum alloys (45Sn-65Cu) are similar in appearance to silver and are used almost entirely for decorative purposes.

Solution Composition and Operating Conditions. Copper-tin alloys are plated from a simple system containing copper as a cyanide complex and tin as a stannate complex. A typical formula is given in Table 3. Because there are no interrelated complexes in the bronze plating solution, the alloy composition is controlled by the relative amounts of copper and tin in the solution (i.e., raising the tin content of the solution produces a higher tin content in the bronze plate). Alloys with very high tin contents, such as speculum, can be produced by simply increasing the tin content of the solution. Additives can be used to produce a bright plate. These additives usually contain lead, which acts as a brightener in bronze plating solutions.

Table 3 Composition and operating conditions for a typical bronze plating solution

Composition of plated deposit, 88Cu-12Sn

Constituent or condition	Amount
Makeup	
Potassium cyanide, g/L (oz/gal)	64 (8.6)
Copper cyanide, g/L (oz/gal)	29 (3.9)
Potassium stannate, g/L (oz/gal)	35 (4.7)
Potassium hydroxide, g/L (oz/gal)	10 (1.3)
Rochelle salt, g/L (oz/gal)	4.5 (6.0)
Analysis	
"Free cyanide," g/L (oz/gal)	22 (2.9)
Copper (as metal), g/L (oz/gal)	20 (2.7)

Tin (as metal), g/L (oz/gal)	14 (1.9)
Hydroxide, g/L (oz/gal)	10 (1.3)
Operating conditions	
Temperature, °C (°F)	65 (149)

The temperature of the solution is an important plating variable. Temperatures below 40 °C (105 °F) generally produce poor deposits that are almost always higher in copper content. Higher temperatures create higher efficiencies and allow the use of a wide range of current densities. Normal temperatures are from 60 to 80 °C (140 to 175 °F). Barrel plating solutions usually use lower temperatures.

Equipment requirements for bronze plating are similar to those for brass plating; however, the tanks should be built to withstand the higher temperatures that are generally used for bronze plating.

Anodes. The choice of anodes for bronze plating is complicated by a number of factors. The tin in bronze plating solutions is present as stannate, and when bronze alloy anodes are used, the tin dissolves as stannite; thus bronze anodes are not suitable for use. Dual anodes of copper and tin, where each type of anode has a separate current source, have been used. To eliminate the need for separate current sources, it is customary to use oxygen-free copper anodes and to add stannate tin as stannic oxide, potassium stannate, or a slurry of stannate oxide to replace the tin being plated. The presence of stannite is indicated by a dark color in the solution. The stannite is oxidized to stannate by the use of hydrogen peroxide, which must be added slowly and with constant stirring to prevent reaction with cyanide. Other impurities are not of major concern in bronze plating solutions.

Waste Water Treatment

The treatment of waste water from brass and bronze plating operations is relatively simple. Normal procedures for eliminating cyanide (i.e., treating the waste water with chlorine and adjusting pH to precipitate the metals) are all that is required. The metallic limits and allowance for chemicals in the final discharge are fixed by federal, state, and local regulations. Waste water treatment systems are usually designed by engineers who are conversant with local regulations and can make sure the equipment meets the necessary requirements.

Tin Alloy Plating

Reginald K. Asher, Sr., Motorola Semiconductor Product Sector

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Introduction

ELECTRODEPOSITION of tin alloys is used to protect steel against corrosion or wear, to impart resistance to etching, and to facilitate soldering. Four types of tin alloys are available in commercial processes.

Tin-lead is the most commonly used of these processes because of its simplicity and low cost. It is especially popular in the electronics industry because of its excellent solderability, resistance to tin whisker growth, and resistance to tin pest (formation of a gray powder on the surface, also called *tin disease*). These properties make it a valuable coating for integrated-circuit leads, surface-mount (small outline transistor) components, and circuit board connections.

Tin-bismuth processes have been developed in recent years as a substitute for tin-lead. Bismuth as an alloying agent prevents the whiskering and tin pest that can occur in tin coatings.

Tin-nickel is used for corrosion-resistant coatings, especially in seawater environments. It has an attractive chromelike appearance and high lubricity when plated over bright nickel.

Tin-zinc provides outstanding corrosion protection, comparable to cadmium, and is a possible replacement for cadmium at a lower cost.

Acknowledgement

Portions of this article were adapted from Nicholas J. Spilotis, Tin-Lead Plating, *Metals Handbook,* 9th Edition, Volume 5, ASM, 1982, p 276-278.

Tin-Lead Plating

Tin-lead plating is a relatively simple process because the standard electrode potentials of tin and lead differ by only 10 mV. Tin-lead alloys have been deposited from electrolytes such as sulfonates, fluosilicates, pyrophosphates, chlorides, fluoborates, and, infrequently, phenosulfonates or benzenesulfonates. Of these, fluoborate and sulfonates (methane sulfonic acid, or MSA, also known as nonfluoborates, or NF) are available commercially. Tin-lead plating has traditionally been done with fluoborate solutions, but MSA solutions have become popular in the electronics industry because they are less corrosive to plating equipment, more uniform in deposition, easier to control, and more acceptable environmentally.

Fluoborate and methane sulfonate solutions plate tin from the stannous valance state. The term *stannous valence state* refers to the valence of tin in solution. In the case of fluoborate and MSA solutions, the tin is in the +2 valence state as Sn^{+2}. Tin will plate only from the +2 state in acid solution. Alkaline stannate solutions plate tin from the +4 valence state. In fluoborate and MSA solutions, the stannous tin requires only two electrons to reduce it to metal:

$$Sn^{+2} + 2e \rightarrow Sn^{0} \text{ (metal)} \qquad \textbf{(Eq 1)}$$

Stannous fluoborate, along with lead fluoborate, fluoboric acid, and an addition agent, comprises the plating solution. The ingredients of the nonfluoborate MSA solution are stannous methane sulfonate with lead methane sulfonate, MSA, grain refiners (wetting agents), antioxidants, and fungicides. These components, as well as various addition agents, are available in commercial quantities. The solution operates at 100% cathode and anode efficiency.

Uses of Tin-Lead. Electrodeposition of tin-lead alloys was first patented in 1920, when these alloys were used to protect the interiors of torpedo air flasks against corrosion. When air was pumped into a flask under pressure, moisture in the air condensed and corroded the flask, weakening it. Lead coatings had been used to protect the interior against corrosion, but tin-lead alloy was found to be more corrosion resistant.

Today, tin-lead deposits are used as corrosion-resistant protective coatings for steel. The deposits usually contain 4 to 15% Sn, but the composition varies with the application. Automotive crankshaft bearings are plated with tin-lead or tin-lead-copper alloys containing 7 to 10% Sn, whereas an alloy containing 55 to 65% Sn is plated onto printed circuit boards. Tin-lead plating on circuit boards acts as an etch-resistant coating and facilitates soldering of board components after they have been inserted into the board. Copper alloys and alloy 42 (42Ni-58Fe) substrates are ordinarily plated with 80% Sn/20% Pb ± 10% MSA solutions in the manufacture of electronic components such as integrated circuits and surface mounts for postsoldering requirements. The shelf life, storage, and thickness of this composition have been proven by some Taguchi fractional multivariable experiments.

MSA Plating Solutions for Tin-Lead

In the electronics industry, MSA solutions are replacing fluoborate solutions for tin-lead plating of contacts on integrated circuits, surface-mount devices, radio-frequency components, and similar devices. The tin-lead MSA solution is well-established worldwide for rack, vibratory bowl, barrel, reel-to-reel, and especially high-speed cut-strip plating. Rack plating of components is being replaced where possible by semiautomated cut-strip lines.

Advantages. The MSA process is preferred over fluoborate solution for several reasons. First, it produces a better-quality, more uniform finish. For a typical specification of a coating thickness of 7 to 20 μm (300 to 800 μin.) with a composition of 80% Sn + 20% Pb ± 10%, it can maintain 6-sigma reliability (fewer than 3.4 rejects per million). MSA solutions are faster and have higher throwing power than fluoborate solutions, and they are able to produce a finer grain size. A recently developed, patented process is able to produce a semibright solderable finish. Because of low levels of occluded codeposited organic substances (<500 ppm C), coatings are suitable for soldering as-plated or after standard thermal excursions. Coatings produced from MSA solutions have excellent storage life and pass the bake and steam age solderability requirements of MIL-883, Method 2003.7. They also pass MIL-38510 requirements for surface finish on electronic components.

Second, the MSA process is environmentally more acceptable. MSA is less corrosive than fluoborate solutions, and because there is no boron or fluorine in the solution, it is more acceptable for wastewater treatment and water reuse. The electrolyte is safer to handle, and the MSA activator (10 to 20 vol%) can be recycled. The latter consideration offsets the higher initial cost and higher operating cost of MSA.

Third, the MSA process is easily automated. Cut strips of electronic components are loaded into high-speed plating equipment by magazine or cassette for easy handling. Deposition rates are two to five times higher than for fluoborate solutions, ranging from 5.4 to 21.5 A/dm^2 (50 to 200 A/ft^2). Table 1 lists deposition rates for a high-speed solution. There are high-speed fluoborate baths operating at from 500 to 1000 A/ft^2.

Table 1 Time required to plate 2.54 μm (100 μin) of 80Sn-from high-speed methane sulfonic acid (MSA) solution

Total metal content		**Time required at indicated current density, min**				
g/L	**oz/gal**	**10.8 A/dm^2 (100 A/ft^2)**	**13.5 A/dm^2 (125 A/ft^2)**	**16.1 A/dm^2 (150 A/ft^2)**	**18.8 A/dm^2 (175 A/ft^2)**	**21.5 A/dm^2 (200 A/ft^2)**
20	2.7	0.78	0.72	0.65	0.59	0.56
30	4.0	0.70	0.64	0.56	0.52	0.47
40	5.3	0.62	0.63	0.44	0.40	0.37
50	6.7	0.55	0.47	0.40	0.36	0.33
60	8.0	0.54	0.46	0.38	0.34	0.30
70	9.3	0.53	0.46	0.37	0.33	0.28
80	10.7	0.52	0.45	0.36	0.32	0.27
90	12.0	0.51	0.43	0.35	0.31	0.26
100	13.4	0.50	0.42	0.34	0.29	0.25

Source: Ref 1

Experimental modified MSA tin-lead plating solutions are being evaluated for semiautomatic plating of leaded-glass sealed integrated-circuit packages, with excellent results.

A minimum of 2% Pb in a tin deposit is reported to prevent whiskering, eliminating the need for reflow as required by MIL-38510 for integrated-circuit devices. The electrolyte will accommodate any tin-lead composition.

Automation. Commercially available automated process lines for electronic devices are loaded manually or from a magazine or cassette. The process operations include deflashing, deoxidation, activation, tin-lead plating, neutralization (if necessary), final rinse, hot deionized water rinse, hot air dry, and automatic reloading into the magazine or cassette. Rinses are pressure spray, with air knives to remove the maximum water for recovery and reuse.

At the time of this writing, equipment for electronic components is limited to strips 23 cm (9 in.) long and 6.4 cm (2.5 in.) wide. A contact rail 3 mm (0.12 in.) wide for light strips and 5 mm (0.20 in.) wide for heavy strips is necessary for gripping the top edge of the strip.

Substrates. The MSA process is generally used for electronic solderable leads on integrated circuits, surface-mount devices, radio-frequency components, and similar devices. The materials used are typically copper or alloy 42 (42Ni-58Fe). Silicon and zirconium copper alloys require special, proprietary preparations for plating.

Properties of the Coated Surface. The deposit usually has a smooth matte finish. Some newly developed solutions give a semibright finish with dense deposits and excellent solderability.

Health and Safety Considerations. Local exhaust is required for fumes from the electrolyte. This is generally provided in the commercial equipment. Chemical goggles, a face shield, rubber gloves, and an acid-resistant apron should be worn when handling the electrolyte. Ordinarily, exhaust fans eliminate the problem of lead fumes in the air (Ref 2), and there should be no problem with meeting Occupational Safety and Health Administration requirements OSHA Standard 1910.1025.

Parameters. Any desired tin-lead alloy composition can be plated from an MSA solution. The composition of the deposit depends on the amount of stannous tin and lead in the solution, the type and amount of addition agent, the current density, and the tin-lead content of the anodes (usually 85Sn-15Pb for high-speed plating). Solution temperature and degree of agitation affect composition, especially in high-speed solutions.

Multivariable fractional factorial experiments have shown that the 80Sn-20Pb (80/20) coating has a slightly higher solderability quality than 90/10 or 60/40 compositions, and much better than rack 100% Sn.

Solution Components. Concentrated solutions of stannous and lead nonfluoborates, MSA, and additives are available commercially, so alloy plating solutions are made by mixing and diluting concentrates. Additives are wetting agents, antioxidants, and fungicides.

80Sn-20Pb high-speed MSA solution (Ref 3) is used for high-speed automated plating of leads for electronic components, including dual-inline-pin and surface-mount integrated circuits, radio-frequency components, and similar devices where highly consistent coating thickness, surface finish, and solderability are required, along with high production rates. The solution composition is:

- Stannous tin: 52±7 g/L (7.0±1.0 oz/gal)
- Lead: 13.0±1.9 g/L (1.73±0.25 oz/gal)
- Free MSA: 255±15 g/L (34.0±2.0 oz/gal)
- Mixed nonionic surfactant: 5 to 10 g/L
- Antioxidant: 0.5 to 1.5 g/L

The operating conditions are:

- Temperature: 21±2.8 °C (70±5 °F)
- Current density: 10.8±5.4 A/dm^2 (100±50 A/ft^2) with less than 1% current ripple on the plating rectifiers
- Agitation: very rapid, mechanical pump and hydraulic pressure
- Anodes: 85Sn-15Pb
- Filtration: continuous through polypropylene or acrylic filter cartridges

80Sn-20Pb MSA solution (Ref 4) is used for barrel plating of electronic components and applications requiring higher throwing power than the high-speed solution. The solution composition is:

- Stannous tin: 14±2 g/L (1.9±0.3 oz/gal)
- Lead: 2.0 to 4.0 g/L (0.27 to 0.54 oz/gal), 3.4 g/L (0.45 oz/gal) optimum
- Free MSA: 165±32 g/L (22.0±4.3 oz/gal)
- Proprietary additive: 5 to 10%

The operating conditions are:

- Temperature: 21±2.8 °C (70±5 °F)
- Current density: 0.32 to 0.64 A/dm^2 (3 to 6 A/ft^2)
- Agitation: mechanical (sparger)
- Anodes: 80Sn-20Pb
- Filtration: continuous through polypropylene or acrylic filter cartridges

Table 2 is a troubleshooting guide to MSA plating solutions.

Table 2 Troubleshooting guide for tin alloy plating with methane sulfonic acid (MSA) solutions

Problem	**Possible cause**	**Solution**
Burn (dark, rough deposit) at high current density	Low metal content	Analyze metal content and adjust if necessary.
	Current density too high	Lower rectifier settings.
	Temperature of plating solution too high	Check and adjust to 19-21 °C (66-70 °F).
	Lack of solution circulation	Check to be sure all circulating pumps are operating.
	Excessive copper in plating solution	Analyze and remove contamination by dummy plating.
	Additive low	Analyze and adjust.
Dark, nonuniform deposit at low density	Low acid content of the plating solution	Analyze and adjust.
	Plating current density too low	Check and adjust current setting.
	Poor cleaning or inadequate activation	Check parts going out of descale/activator. Adjust to proper operating conditions if necessary.
Poor throwing power or plating distribution	Metal content too high	Analyze and adjust.

distribution	Plating current density too low	Check and adjust current setting.
Pitting	Organic contamination	Check for carbon and treat if necessary.
	Oil or grease in solution	Check and dump if positive.
	Poor cleaning	Check/analyze descale and activation for proper operating conditions.
	Insufficient solution agitation	Check circulating pump.
Rough deposits	Particles (anode sludge, dirt) in solution	Check filter for proper operating condition. Replace cartridge.
	Excessive current setting	Check and adjust.
	Insufficient solution agitation	Check circulation.
Alloy composition in deposit out of specification	Incorrect bath composition	Analysis and adjust
Poor solderability	Low thickness	Check and adjust.
	Organic contamination in the bath	Analyze for carbon and treat if necessary.
	Copper contamination in the bath	Check and do low-current dummy plating if necessary.
	Incorrect alloy composition	Check and adjust.
	Insufficient/poor cleaning of base metal	Check parts going out of descale. Check descale and activator for proper operating conditions.
Excessive foaming	Air being drawn into filter	Check for line leaks.
	Imbalance of system circulation	Set discharge line flow. Close down on drain back valves.
	Excessive additive concentration	Analyze and dilute if necessary.
	Air blow offset too high	Reduce air wipe flows.

Poor adhesion	Poor pretreatment	Adjust to proper operating range. Makeup new when necessary.
	Poor rinsing	Check and adjust rinse flow.
	Excessive additive	Analyze and adjust.
Staining or discoloration	Air blower nozzle offset	Check and reset.
	Poor/insufficient rinse	Check and adjust flows.
	Air wipe blocked or offset	Check and reset.
	Insufficient additive	Analyze and adjust.

References cited in this section

1. Techni-Solder NF Acid process information sheet, Technic, Inc., Cranston, RI
2. Techni-Solder NF Acid material safety data sheet, Technic, Inc., Cranston, RI, 1991
3. Techni-Solder NF 80/20 Alloy High Speed Matte product data sheet, Technic, Inc., Cranston, RI
4. Techni-Solder NF 1957 product data sheet, Technic, Inc., Cranston, RI

Fluoborate Plating Solutions for Tin-Lead

Any desired tin-lead alloy composition can be plated from a fluoborate solution. The composition of the deposit depends on the amount of stannous tin and lead in the solution, the type and amount of addition agent, the current density, and the tin-lead content of the anodes. Bath temperature and degree of agitation also affect the composition, especially in high-speed solutions.

Solution Components. Concentrated solutions of stannous and lead fluoborates and fluoboric acid are available commercially, so alloy plating solutions are made by mixing and diluting concentrates. Some compositions of concentrates are given in Table 3. The fluoborates of tin and lead contain free or excess fluoboric and boric acids for stability, and fluoboric acid contains free boric acid for the same reason.

Table 3 Composition of fluoborate alloy plating solution concentrates

Constituent	**Amount**		
	wt%	**g/L**	**oz/gal**
Lead fluoborate			
Lead fluoborate, $Pb(BF_4)_2$	51.0	893	119
Lead, Pb[(a)]	27.7	485	65

Fluoboric acid, free HBF_4	0.6	10.5	1.4
Boric acid, free H_3BO_3	1.0	18	2.4
Stannous (tin) fluoborate			
Stannous fluoborate, $Sn(BF_4)_2$	51.0	816	109.0
Tin, $Sn^{-2(a)}$	20.7	331	44.3
Fluoboric acid, free HBF_4	1.8	29	3.9
Boric acid, free H_3BO_3	1.0	16	2.1
Fluoboric acid			
Fluoboric acid, HBF_4	49	671	89.9
Boric acid, free H_3BO_3	0.6	8.3	1.1
Hydrofluoric acid, free HF	None	. . .	. . .

(a) Equivalent

The reason that excess boric and fluoboric acids provide stability in the fluoborate concentrates can best be shown by the reactions described below, with lead fluoborate used as an example, although the same is true for all other fluoborate concentrates. In the absence of boric acid, the metal fluoride will form. To stabilize the lead fluoborate, the following reaction takes place:

$$4PbF_2 + 2H_3BO_3 \rightarrow Pb(BF_4)_2 + 3Pb(OH)_2 \qquad \textbf{(Eq 2)}$$

The reaction is incomplete unless fluoboric acid is added to produce the result:

$$3Pb(OH)_2 + 6HBF_4 \rightarrow 3Pb(BF_4)_2 + 3H_2O \qquad \textbf{(Eq 3)}$$

The overall reaction is then:

$$4PbF_2 + 2H_3BO_3 + 6HBF_4 \rightarrow 4Pb(BF_4)_2 + 6H_2O \qquad \textbf{(Eq 4)}$$

Commercially, fluoboric acid is made by reacting hydrofluoric acid with boric acid:

$$4HF + H_3BO_3 \rightarrow HBF_4 + 3H_2O \qquad \textbf{(Eq 5)}$$

When excess boric acid is added beyond the amount required to react stoichiometrically with the hydrofluoric acid present, the reaction is driven far to the right, thus stabilizing the fluoboric acid and preventing the formation of fluorides.

A tin-lead plating solution deficient in free boric acid can precipitate insoluble lead fluoride. To guard against this possibility, anode bags filled with boric acid should be hung in corners of the plating tank and immersed in solution. Bags should be refilled when the boric acid has dissolved.

Addition agents are important for the production of dense, fine-grain deposits and the improvement of throwing power in a tin-lead solution operation. Many organic addition agents have been used in tin-lead solutions, including bone glue, gelatin, peptone, aldehyde condensation products, glycols, sulfonated organic acids, beta-naphthol, hydroquinone, and resorcinol. Peptone is the addition agent most frequently used because of its commercial availability as a stabilized solution specifically prepared for tin-lead plating solutions.

Solution Compositions and Operating Conditions. Listed below are the tin-lead fluoboric bath compositions that are used most frequently.

7Sn-93Pb solution is used for bearings and corrosion protection of steel. The solution composition is:

- Stannous tin: 6.0 g/L (0.80 oz/gal)
- Lead: 88.0 g/L (11.8 oz/gal)
- Fluoboric acid: 100 g/L (13.4 oz/gal) min
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.67 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 3.2 A/dm^2 (30 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 7Sn-93Pb

60Sn-40Pb solution is used for printed circuit boards, barrel plating of small parts, and applications requiring high throwing power. The solution composition is:

- Stannous tin: 15 g/L (2 oz/gal)
- Lead: 10 g/L (1.3 oz/gal)
- Fluoboric acid: 400 g/L (53.4 oz/gal)
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.7 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 2.1 A/dm^2 (20 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 60Sn-40Pb

60Sn-40Pb high-speed solution is used for high-speed wire and strip plating, or for general plating where throwing power is not of prime importance. The solution composition is:

- Stannous tin: 52 g/L (7.0 oz/gal)
- Lead: 30 g/L (4.0 oz/gal)
- Fluoboric acid: 100 g/L (13.4 oz/gal) min
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.7 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 3.2 A/dm^2 (30 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 60Sn-40Pb

When this solution is used to deposit 60Sn-40Pb on wire or strip, current densities in excess of 32 A/dm^2 (300 A/ft^2) can be used if the wire or strip is moved continuously through the plating solution at a relatively high speed.

$HBF_4$60Sn-40Pb solution (Ref 5) provides high throwing power. The solution composition is:

- Fluoboric acid 48%: 350 mL/L
- Tin fluoborate 50%: 46.2 mL/L
- Lead fluoborate 50%: 25.2 mL/L
- Proprietary additive: 20 mL/L
- Boric acid: 26 g/L
- Tin-lead salt No. 1: 2 g/L

The optimum operating conditions are:

- Temperature: 21 °C (70 °F)
- Current density: 2.5 A/dm^2 (25 $A/ft^{2)}$
- Agitation: mechanical, slow to moderate
- Filtration: continuous through polypropylene or Dynel

Table 4 is a troubleshooting guide for this solution.

Table 4 Troubleshooting guide for $HBF_4$60Sn/40Pb high-throw bath

Problem	**Possible cause**	**Remedy**
Treeing	Low addition agent	Replenish.
Edge feathers	Too high a current density	Lower current density.
Grainy deposit	Organic contamination	Replenish addition agent. As a last resort, carbon treat.
Burning	Too high a current density	Lower amperage.

	Too low a metal content	Add stannous fluoborate or lead fluoborate.
	Low acid content	Add fluoboric acid.
Wrong alloy composition	Incorrect bath composition	Adjust bath composition.
	Wrong current density	Plate at 2.5-3 A/dm^2(25-30 A/ft^2).
	Insufficient addition agent	Replenish.
	Improper agitation	Use cathode rod agitation.
Poor throwing power	High pH	Add fluoboric acid.
	Too high an anode-to-cathode ratio	Remove some anodes.
	Low agitation agent	Replenish.
Precipitate in bath, roughness	Chloride or sulfate drag-in	Improve rinsing.
	Torn anode bags	Replace anode bags.
	Oxidation of tin from excessive agitation	Look for air leak in filter, if used.
Poor reflow	Insufficient deposit. Minimum should be 0.00025 in.	Do not reflow unless thickness is above minimum.
	Wrong alloy	Check reason for wrong alloy as described above.
	Organic contamination	Carbon treat.
	Metallic contamination	Dummy the bath.
	Copper substrate not active or clean	Check cleaning cycle.

Compositions of anodes and solutions for deposits up to 50% Sn are listed in Table 5. The composition of the anode should be the same as that desired in the deposit. If deposits do not have the desired composition, anode composition should be maintained as indicated and adjustments should be made to the solution formula.

Table 5 Composition of anode and fluoborate solution for deposits up to 50% Sn

Plated 3.2 A/dm^2(30 A/ft^2); compositions of all baths contains a minimum of 100 g/L (13.3 oz/gal) of free HBF_4, 25 g/L. (3.3 oz/gal) of free H_3BO_3, and 5.0 g/L (0.7 oz/gal) of peptone

Composition of deposit and anode, %		Composition of bath			
		Stannous tin		Lead	
Tin	Lead	g/L	oz/gal	g/L	oz/gal
5	95	4	0.5	85	11.3
7	93	6	0.8	88	11.8
10	90	8.5	1.1	90	12.0
15	85	13	1.7	80	10.7
25	75	22	2.9	65	8.7
40	60	35	4.8	44	5.8
50	50	45	6.0	35	4.7

Table 5 is based on an operating density of 3.2 A/dm^2 (30 A/ft^2). Higher or lower current densities may result in deposition of alloys of compositions differing from those given in the table. It is then necessary to make compensating corrections in solution composition. Deposition rates of tin-lead coatings can be controlled by current density. Table 6 shows that as the current density of a fluoborate solution is increased, the rate of 60Sn-40Pb deposition also increases.

Table 6 Rate of 60Sn-40Pb deposition from the fluoborate solution

100% cathode efficiency

Current density		Time in bath, min, at thickness of:			
A/dm^2	A/ft^2	25µm (0.0001 in.)	7.5µm (0.0003 in.)	12.5µm (0.0005 in.)	25µm (0.001 in.)
1.0	10	4.5	13.5	22.5	45
1.5	15	3.0	9.0	15.0	30
2.0	20	2.3	6.8	11.3	22.5
2.5	25	1.8	5.4	9.0	18
3.0	30	1.5	4.5	7.5	15

Temperature. Tin-lead fluoborate solutions operate efficiently in a temperature range of 18 to 38 °C (65 to 100 °F). Upper temperatures slightly increase tin in deposits, and lower temperatures can decrease tin.

Current densities below the specified amount for a particular solution formula can decrease the tin content of deposits. Higher current densities can increase tin content.

Agitation is an important factor in tin-lead plating. Optimum conditions exist when mild agitation is used. Use of a still bath results in nonuniform deposits because of local exhaustion of the solution at the cathode surface. Vigorous agitation may increase the stannic tin content of a solution, resulting in a decrease of tin in deposits. Cathode rod agitation or circulation through an outside pump provides suitable agitation for a tin-lead plating solution. Air agitation should not be used because it can oxidize stannous tin.

Boric acid is added to maintain solution stability. Approximately 25 g/L (3.4 oz/gal) of boric acid has been found desirable, but its concentration is not critical. An anode bag filled with boric acid may be hung in a corner of the tank to maintain the required concentration. Excess boric acid prevents fluoride precipitates, which can deplete lead from the solution. This is based on the following formula:

$$4HF + H_3BO_3 \ \text{€} \ HBF_4 + 3H_2O \qquad \textbf{(Eq 6)}$$

where $HBF_4$is the resultant fluoboric acid. The reaction is reversible if the stoicheiometric amount of boric acid (H_3BO_3)is used to react with the hydrofluoric acid (HF) present. As the amount of boric acid in the above reaction is increased, the reaction is driven far to the right so that the reaction becomes irreversible and no free hydrofluoric acid is regenerated. This is important because if free hydrofluoric acid were present, then insoluble fluorides, especially lead fluoride, would precipitate. Thus, all fluoborate concentrates and plating baths contain free boric acid. Although 25 g/L of boric acid is optimum (close to its solubility), any amount of free boric acid is acceptable to prevent the formation of fluorides.

Free fluoboric acid is maintained in the solution to provide the requisite acidity and to raise conductivity. In conjunction with peptone, it can prevent "treeing" and give a fine-grain deposit. Free fluoboric acid can be added in amounts ranging between 100 to 500 g/L (13.4 to 67 oz/gal), depending on the solution formula used.

Peptone is added to the plating bath to promote formation of fine-grain adherent deposits and prevent treeing. Peptone solution is available commercially, and proper amounts can be measured and poured directly into the plating bath. The bath can then be used immediately, after it is gently stirred to ensure complete mixing of peptone. During the operation of the plating bath, a loss of peptone can result because of dragout, chemical breakdown, and codeposition with the metal. As peptone is depleted, it must be replenished. Replenishment amounts should be determined by experience. As a guide, 1 L (2.1 pints) of peptone solution per 380 L (100 gal) of plating bath can be used per week. A Hull cell operated at 1 A for 10 min can be used to control the peptone content of a plating solution.

Tin-lead fluoborate solutions containing peptone should be filtered through activated carbon at least four times per year to ensure removal of organic breakdown products and avoid buildup of peptone from indiscriminate additions. The plating bath should be treated with about 4.5 kg. (10 lb) of activated carbon per 380 L (100 gal) of bath until, after filtration, the solution is water white. The bath should not be heated during carbon treatment, because stannous will be oxidized to stannic tin. Fresh peptone is added after carbon treatment. Because there is no simple analytical method for determining peptone concentration in this solution, carbon treatment and replenishment of peptone every 3 or 4 months ensures proper amounts of peptone in a solution.

Proprietary synthetic wetting agents can be purchased for grain refinement, as a substitute for peptone. Because these components are synthetic, they are less susceptible to algae and bacterial growth.

Metallic impurities are removed by low-current-density electrolysis, but in a tin-lead bath, low current density favors deposition of lead, which may unbalance the solution. Metallic impurities can be removed by dummying a bath at a current density of 0.2 A/dm^2 (2 A/ft^2) for at least 8 h. The solution should then be analyzed and brought up to specification with stannous or lead fluoborate. Iron, nickel, and other metals above hydrogen in the electromotive series are not removed by dummying, although copper is easily removed.

Filtration. A tin-lead fluoborate plating solution should be filtered constantly, to keep the bath clear. If constant filtration is not used, a bath can turn cloudy because of sulfates entering the solution and precipitating as lead sulfate.

Stannic salts can also precipitate out of the solution. Anode sludge or breakdown products from peptone solutions can contribute to a cloudy appearance as well. Polypropylene filter spools or cartridges can be used as filters, but they must first be leached in hot water (65 °C, or 150 °F) to remove organic agents used in their manufacture. The end of the return hose from the filter must be submerged in the bath to prevent aeration of the bath.

Anodes. Tin-lead alloy anodes of at least 99.9% purity must be used. The most objectionable anode impurities are arsenic, silver, bismuth, antimony, copper, iron, sulfur, nickel, and zinc. Extruded anodes are preferred over cast anodes, because cast anodes have a larger grain size and suffer from intergranular corrosion, which causes large pits or depressions to form on the anode surface. The finer grain size of extruded anodes provides uniform and efficient corrosion during plating. Tin-lead anodes should be left in an idle tin-lead fluoborate bath because they exercise a reducing effect on tin in solution, thus helping to maintain the bath in a stannous valence state. Tin-lead anodes should be bagged with acrylic or polypropylene cloth to contain any anode sludge that may form. Anode sludge suspended in solution can cause rough deposits.

Materials of construction for tin-lead plating equipment include:

- Steel lined with rubber or polypropylene or made entirely of polypropylene, used for tanks and pumps
- Monel metal, used for anode hooks
- Polypropylene, used for anode bags and filter spools
- Pure paper pulp (alpha cellulose), used for filter aid

The following materials should not be used in contact with fluoborate solutions: glass; quartz or other silicated materials; nylon; neoprene; or titanium. Equipment in contact with fluoborates should have the recommendation of the manufacturer for use in a fluoborate solution.

Lead disposal for fluoborate and MSA solutions is most commonly accomplished by diverting the lead-containing rinse water (or dilute concentrate) to a pH-controlled holding tank, filtering the solution, and then running it through an ion exchanger. The fluoborate rinse will have to be regenerated with MSA before going to a holding tank and then to electrowinning. The MSA rinse can go directly to electrowinning, where the lead is plated out on a reusable cathode. The water can then be carbon treated, ion exchanged, and reused for certain rinses.

Reference cited in this section

5. Techni HBF_4 60/40 High Throw PC product data sheet, Technic, Inc., Cranston, RI

Other Tin Plating

Tin-Bismuth Plating. A small amount of bismuth or antimony added to tin helps to eliminate whiskering and tin pest in tin coatings that are subjected to temperatures below 13.2 °C (55.8 °F). MIL-QQS-571 recommends 0.27% Sb to prevent tin pest. Several processes for tin-bismuth plating have been patented (Ref 6, 7, 8) and commercialized. Experimental processes using inert anodes, such as platinized titanium, have been used to produce printed circuit board prototypes with tin-bismuth coatings on parts. An MSA solution similar to that used for tin-lead plating has been developed, and solutions are being developed for commercial sales by chemical suppliers. Tin methane sulfonate and bismuth methane sulfonate are used in the solution. Plating is done at room temperature with mild agitation.

Tin-Zinc Plating. In most environments, tin-zinc alloys approach the corrosion resistance and solderability of cadmium. Because cadmium can release toxic fumes when heated, and because it is a strategic element and therefore relatively expensive and subject to availability concerns, tin-zinc coatings are often used as substitutes. Compositions ranging from 10Sn-90Zn to 85Sn-15Zn have been used. Electrolytes are made from a mixture of potassium stannate, zinc cyanide, potassium cyanide, and potassium hydroxide. The amount of potassium cyanide determined by analysis is higher than that added to the bath initially, because the analysis also detects the cyanide in zinc cyanide.

80Sn-20Zn solution is the most commonly used. The solution compositions are:

Still tank

- Stannous tin: 38 to 53 g/L (5.1 to 7.1 oz/gal)
- Zinc: 4.5 to 7.5 g/L (0.60 to 1.0 oz/gal)
- Potassium cyanide: 38 to 53 g/L (5.1 to 7.1 oz/gal)
- Free potassium hydroxide: 4.9 to 8.3 g/L (0.65 to 1.1 oz/gal)

Barrel

- Stannous tin: 32 to 40 g/L (4.3 to 5.3 oz/gal)
- Zinc: 6.8 to 10 g/L (0.91 to 1.3 oz/gal)
- Potassium cyanide: 41 to 60 g/L (5.5 to 8.0 oz/gal)
- Free potassium hydroxide: 8.3 to 11.3 g/L (1.1 to 1.51 oz/gal)

The operating conditions are:

- Temperature: 65 ± 2 °C (149 ± 4 °F)
- Anode current density: 1.5 to 2.5 A/dm^2 (14 to 23 A/ft^2)
- Cathode current density: 0.1 to 0.9 A/dm^2 (1 to 8 A/ft^2)
- Agitation: none for still tanks, or barrel agitation
- Anodes: 80Sn-20Zn
- Equipment: mild steel

Anodes must be filmed. (An oxide film is deposited on the anode by plating it at a high current density.) Unfilmed anodes cause formation of stannite (Cu_2FeSnS_4), which inhibits plating.

Temperature. Temperatures in the high end of the range increase the tin content and cause the cyanide to break down. Low temperatures decrease cathode efficiency and lower the percentage of tin.

Current densities at the low end of the range result in tin-rich deposits.

Electrolyte Concentrations. The proportions of zinc and tin in the deposit vary with the amounts in the solution. Higher concentrations of zinc in solution result in higher levels in the deposit, and likewise with tin. Higher levels of free potassium hydroxide increase the percentage of zinc in the deposit. Small changes in free cyanide content have little effect, because the solution contains more cyanide than is necessary. Excessively low levels of cyanide decrease tin content (Ref 9).

Tin-Nickel Plating. The intermetallic compound 65Sn-35Ni can be plated from several commercial electrolyte solutions. The finish has high lubricity and a bright, chromelike appearance with excellent corrosion resistance, especially in seawater environments. It is used more often for general industrial applications than for electronic components, because it is more difficult to solder than other tin-alloy coatings. The solution composition is:

- Nickel chloride: 250 g/L (33 oz/gal)
- Stannous chloride: 50 g/L (6.7 oz/gal)
- Ammonium chloride: 50 g/L (6.7 oz/gal)
- Starter (makeup and additives containing surfactants and grain refiners): 20% by volume

The operating conditions are:

- Temperature: 60 to 70 °C (140 to 160 °F), 66 °C (151 °F) optimum
- Current density: 0.1 to 3.2 A/dm^2 (1 to 30 A/ft^2), 1.6 A/dm^2 (15 A/ft^2) optimum

- Agitation: cathode rod, solution, or barrel. Still racks may be used at low current densities.
- Anodes: high-purity nickel in polypropylene bags
- Filtration: continuous through polypropylene or chlorinated polyvinyl chloride (CPVC) above 60 °C (140 °F)

Preparation. Metallic substrates should be cleaned. A common acid cleaning procedure is a 10 to 20% HCl bath immediately before plating. Steel substrates should be plated with an alkaline copper or acid nickel strike coating.

Equipment. All equipment in contact with the plating solution should be nonmetallic. Tanks and filters should be polypropylene or CPVC. Heaters should be fluorocarbon coated.

Handling Precautions. Gloves, protective clothing, and goggles should be worn when handling electrolyte solution or its components.

Environmental Considerations. Electrolyte solutions and their components should be treated according to procedures for fluoride- and cyanide-containing wastes. They should not be mixed with metal-bearing waste streams, because they contain metal chelators (Ref 10, 11).

Table 7 is a troubleshooting guide to tin-nickel plating solutions.

Table 7 Troubleshooting guide for tin-nickel plating solutions

Problem	**Possible cause**	**Remedy**
Powdery gray deposit	Current density too high	Use a lower current density.
	Nickel content too low	Analyze nickel content, add nickel chloride if necessary.
Dull or black deposit	Tin content too low	Analyze tin content, add stannous chloride if necessary (starter concentrate must be added at the same time as stannous chloride).
Brittle or milky deposit	Low replenisher	Add replenisher.
	Metallic contamination	Remove metal by electrolyzing solution.
Dark or black deposits in low-current-density plating areas	Copper contamination	Eliminate source of contamination, remove copper by electrolyzing.
Dark deposit with standard current density or burn with high current density	Organic contamination	Filter solution through activated carbon. Never add hydrogen peroxide, potassium permanganate, or other oxidizing agents.
Incorrect alloy composition	Incorrect solution composition	Analyze tin and nickel contents of bath and adjust.
Nickel content increases during operation	Excess anode area	Decrease anode area.

Source: Ref 10

References cited in this section

6. T.I. Murphy and B.R. Reynolds, "Low Temperature Tin-Bismuth Electroplating System," International Patent Application PCT/US92/08485, April 1993
7. H.P. Wilson, "Bismuth Composition, Method of Electroplating a Tin Bismuth Alloy and Electroplating Bath Therefor," U.S. Patent 4,331,518, May 1982
8. H.P. Wilson, "Electrodeposited Eutectic Tin-Bismuth Alloy on a Conductive Substrate," U.S. Patent 5,039,576, Aug 1991
9. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley, 1974, p 531-533
10. Nicostan product data sheet, LeaRonal, Freeport, NY
11. Techni Tin-Nickel product data sheet, Technic, Inc., Cranston, RI

Zinc Alloy Plating

Nabil Zaki, Frederick Gumm Chemical Company, Inc.

Introduction

ZINC ALLOY PLATING has found significant use since about 1980 in Japan and Europe, and more recently in the United States. The driving force behind the development of this technology was the quest for higher-performance coatings, especially in the automotive industry. Another driver was the urgent need to find an adequate replacement for cadmium plating; cadmium is highly toxic and has been banned in many industrial countries.

The use of zinc alloys provides several advantages. Electrochemically, alloys have different corrosion potentials from their alloying elements. Alloys of zinc, for example, can be designed to maintain anodic protection to steel, but remain less electrochemically active than pure zinc. Thus, a zinc alloy coating can still be sacrificial to steel components, but corrodes much more slowly than zinc when exposed to a corrosive environment.

Several zinc alloy processes are currently in commercial use. The choice of a particular process depends on the end-product requirements and conditions of use. Available alloys are zinc-iron, zinc-cobalt, zinc-nickel, and tin-zinc. As in unalloyed zinc plating, chromate conversion coating post-treatments are used to improve the overall corrosion resistance of the alloy, and especially to retard the bulky "white rusting" characteristic of unalloyed zinc. Specialty chromating processes designed to work with these alloys are used for this purpose. See the article "Zinc Plating" in this Volume for more information.

Zinc-Iron Plating

Zinc-iron plating produces alloys containing 15 to 25% Fe as-plated. Advantages of this alloy are good weldability and ductility. It is electroplated on steel coil and strip for auto bodies. Strip for the manufacture of automotive components is also plated in baths that produce 1% Fe in the alloy deposit; a special feature of this alloy is its suitability for deep black chromating.

The corrosion resistance of zinc-iron is generally lower than that of the other zinc alloys, especially after exposure to high temperatures such as those encountered by under-the-hood automotive components. A typical zinc-iron solution composition used in strip line plating is:

Constituent	Content	
	g/L	oz/gal
Ferric sulfate	200-300	27-40
Zinc sulfate	200-300	27-40
Sodium sulfate	20-40	2.7-5.3
Sodium acetate	10-30	1.3-4
Organic additive	1-5	0.1-0.66

Zinc-Cobalt Plating

Zinc-cobalt coatings contain 0.6 to 2% Co. Zinc-cobalt alloys find extensive use for relatively inexpensive components in applications that require improved abrasion resistance and corrosion protection. Typically, an 8 μm film with 1% cobalt will last up to 500 h in a neutral salt spray test before red rust if the proper chromate is applied. Some reduction in corrosion resistance is experienced after exposure to high temperature, but not as much as with zinc-iron alloys. A unique attribute of zinc-cobalt is its corrosion resistance to sulfur dioxide in accelerated corrosion tests. This suggests that these coatings may be suitable for use in sulfur-containing corrosive environments.

There are two types of zinc-cobalt plating baths; acid and alkaline. Alkaline baths are preferred for tubes and other configurations with internal unplated areas. Exposure to acidic electrolyte reduces the corrosion resistance of such parts. Available chromates include clear, yellow, iridescent and black.

Typical zinc-cobalt bath compositions and process parameters are given in Table 1.

Table 1 Compositions and process parameters for zinc-cobalt plating solutions

Constituent or parameter	Amount or value
Acid baths	
Zinc chloride, g/L (oz/gal)	80-90 (10-12)
Potassium chloride, g/L (oz/gal)	150-200 (20-27)
Ammonium chloride(a), g/L (oz/gal)	50-70 (7-9)
Boric acid(a), g/L (oz/gal)	20-30 (3-4)
Cobalt chloride, g/L (oz/gal)	1-20 (0.1-2.7)

Organic additive, g/L (oz/gal)	5-20 (0.66-2.7)
pH	5.0-6.0
Temperature, °C (°F)	20-40 (70-100)
Anodes	Zinc
Alkaline baths	
Zinc oxide, g/L (oz/gal)	10-20 (1.3-2.7)
Sodium hydroxide, g/L (oz/gal)	80-150 (10-20)
Cobalt salt complex, g/L (oz/gal)	1.0-2.0 (0.1-0.3)
Organic additive, g/L (oz/gal)	5-10 (0.66-1.3)
Temperature, °C (°F)	25-40 (77-100)
Anodes	Zinc

(a) Used only in some compositions

Zinc-Nickel Plating

Zinc-nickel alloys produce the highest corrosion resistance of electroplated zinc alloys. These alloys contain from 5 to 15% Ni. Corrosion resistance improves with nickel content up to 15 to 18%. Beyond this range the alloy becomes more noble than steel and loses its sacrificial protection property. An alloy containing 10 to 13 wt% Ni is electroplated on steel strip and coil as an alternative to zinc-iron or electrogalvanizing. An advantage of this composition is the formability of the steel after coiling. For components, chromatizing is required; however, best results are achieved on alloys containing 5 to 10% Ni. For alloys in this range of nickel content, corrosion resistance to neutral salt spray reaches 1000 h or more before red rust. An advantage of zinc-nickel alloys is their retention of 60 to 80% of their corrosion resistance after forming and after heat treatment of plated components. This attribute makes these alloys suitable for automotive applications such as fasteners, brake and fuel lines, and other under-the-hood components.

Zinc-nickel alloys plated from alkaline baths have shown potential as substitutes for cadmium coatings in aircraft and military applications. Available chromates are clear, iridescent, bronze, and black. Typical zinc-nickel bath compositions and process parameters are given in Table 2. Alkaline formulations are preferred for their ease of operation and because they provide more uniform alloy composition and better overall corrosion resistance, especially on tubing and on internal configurations of parts.

Table 2 Compositions and process parameters for zinc-nickel plating solutions

Constituent or parameter	**Amount or value**

Acid baths	
Zinc chloride, g/L (oz/gal)	120-130 (16-17)
Nickel chloride, g/L (oz/gal)	110-130 (15-17)
Potassium chloride, g/L (oz/gal)	200-250 (27-33)
Ammonium chloride(a), g/L (oz/gal)	100-200 (13-27)
Organic additives, g/L (oz/gal)(a)	5-10 (0.66-1.3)
pH	5-6
Anodes	Zinc and nickel connected to two separate rectifiers
Alkaline baths	
Sodium hydroxide, g/L (oz/gal)	100-130 (13-17)
Zinc, g/L (oz/gal)	6-15 (0.8-2.0)
Nickel, g/L (oz/gal)	0.5-1.5 (0.07-0.20)
Organic additives, g/L (oz/gal)	2-5 (0.25-0.66)
Anodes	Zinc and steel, one rectifier
Temperature, °C (°F)	20-35 (70-95)

(a) Used only in some compositions

Tin-Zinc Plating

Tin-zinc alloys contain 70 to 90% Sn and 10 to 30% Zn. Cyanide, acid, and neutral commercial baths are available. Tin-zinc baths are expensive to operate because they require the use of special cast tin-zinc anodes. Tin-zinc alloys exhibit excellent solderability, ductility, and corrosion resistance.

Chromate posttreatments are limited to yellow or clear. The tin-zinc deposit is semibright as-plated and is used primarily as a functional coating. Tin-zinc is finding increasing application in the automotive and electronic industries and as a substitute for cadmium plating.

Additional information about tin-zinc coatings is contained in the article "Tin Alloy Plating" in this Volume.

Corrosion Protection

Corrosion rates for zinc alloy coatings as demonstrated by the neutral salt spray test are:

Coating[(a)]	**Hours to red rust**
Zinc	200-250
Zinc-iron (1% Fe)	350
Zinc-cobalt (0.8% Co)	500
Zinc-nickel (8% Ni)	1000
Tin-zinc (70% Sn)	1000

(a) Coating thickness, 8 μm; iridescent yellow chromate post-treatment

Nickel Alloy Plating

S. Alec Watson, Nickel Development Institute

Introduction

NICKEL ALLOYS electroplated for engineering applications include nickel-iron, nickel-cobalt, nickel-manganese, and zinc-nickel. Zinc-nickel plating is covered elsewhere in this Volume; see the article "Zinc Alloy Plating." Iron is a cheap metal, and solutions for plating nickel-iron alloys were developed mainly in order to reduce the cost of the metal used to form a layer of given thickness, but they were also developed for special magnetic purposes. Cobalt and manganese are used to increase the hardness and strength of nickel plating. Additionally, nickel-manganese alloys have improved resistance to sulfur embrittlement when heated. Alloy layers 20 to 30 μm thick of nickel with about 15% Mo exhibit higher hardness and resistance to corrosion than pure nickel but at the expense of a reduction in ductility to around 1% (Ref 1). Coatings of nickel-tungsten show very high resistance to corrosion, but they are believed not to be true alloys (Ref 2) and have not been used in practice. This article will discuss the alloys nickel-iron, nickel-cobalt, and nickel-manganese that are of practical interest, plus a few paragraphs on nickel-chromium binary and ternary alloys.

References

1. E. Chassaing, K. Vu Quang, M.E. Baumgärtner, M. Funk, and Ch.J. Raub, High Temperature Ni-Mo Electrodeposited Alloys--Structure and Properties, *Plating and Surface Finishing,* Vol 77 (No. 8), Aug 1990, p 60-65
2. G. Raucher, V. Rogoll, M.E. Baumgärtner, and Ch.J. Raub, Investigation of the Dissolution Behaviour of Electrodeposited Ni-W Layers in Concentrated Hydrogen Chloride Solution, *Transactions of the Institute of Metal Finishing,* Vol 71 (Part 3), Aug 1993, p 95-98

Nickel-Iron

Bright nickel-iron plating was strongly promoted as a substitute for bright nickel plating in the period from 1970 to the early 1980s when the relative price of nickel was high (Ref 3, 4, 5, 6).

Advantages. The main advantage of the alloy is the significant saving in the cost of metal, because up to 35% of the nickel is replaced by iron. An additional advantage is that iron entering the plating solution through chemical dissolution of steel substrates, which is highly detrimental in straight nickel plating solutions, is readily dissolved and subsequently plated out. This feature is particularly relevant during plating onto tubular steel parts. Ductility is usually higher for the alloy coatings than for bright nickel, which may be advantageous if the plated parts are subject to deformation.

Disadvantages. The organic addition agents are more expensive than those needed for bright nickel, substantially negating the saving on metal. The addition agent system is also more complex so that electrolyte control is more difficult. At equal thickness, nickel-iron plating is less resistant to corrosion than nickel, and the higher the iron content, the lower its resistance. The corrosion product is rust-colored, and there is no international standard for the alloy coatings.

Process Description. Preferred solutions for plating bright nickel-iron are slightly more dilute than nickel plating solutions in order to obtain a high-iron alloy without using a high iron concentration in the solution. A typical solution is given in Table 1 (Ref 4). Addition agents include stabilizers for the ferrous iron, organic brighteners, leveling agents, and wetting agents. Total iron includes ferrous and ferric ions, and it is important to control the ratio, with ferric usually below 20%. Solution temperature is typically 54 to 60 °C (130 to 140 °F), and solution pH must be kept low at 2.8 to 3.6. The solution is preferably used with air agitation rather than cathode-rod movement, because higher plating rates can be used, a higher iron content can be obtained in the deposits, and iron content can be altered at will by increasing or reducing the rate of air bubbling.

Table 1 Typical nickel-iron solution composition

Constituent	Amount, g/L (oz/gal)
Ni^{+2}	56 (7.46)
Iron (total)	4 (0.53)
$NiSO_4 \cdot 6H_2O$	150 (20.00)
$NiCl_2 \cdot 6H_2O$	90 (12.00)
$FeSO_4 \cdot 7H_2O$	20 (2.67)
H_3BO_3	45 (6.00)
Stabilizer(a)	15 (2.00)

(a) Concentration will vary between 10-25 g/L (1.3-3.3 oz/gal), depending on the type of stabilizer used.

Properties of the alloy deposits that are of interest include ductility, deposit hardness, internal stress, and magnetic properties.

Ductility depends on iron content, brightener concentration, solution temperature, and pH.

Deposit hardness varies with iron content. With iron content increasing from zero to about 10%, microhardness rises from 490 to 560 HK, then falls to around 510 HK with 49% Fe for coatings plated at standard conditions of 4 A/dm^2 (40 A/ft^2), 60 °C (140 °F), pH 3.5, and air agitation. Changes in solution pH and brightener concentration also influence deposit hardness, enabling values exceeding 700 HV to be achieved.

Internal stress is tensile, in contrast to that of most bright nickel deposits. It is influenced by iron content and, more sharply, by solution pH. Increasing iron content from 10.8 to 27.6% raises stress from 93 to 154 MN/m^2 (13,500 to 22,400 psi). Increasing pH from 2.8 to 4.5 raises stress from 17.5 to 230 MN/m^2 (2500 to 33,600 psi) (Ref 4).

Magnetic properties of nickel-iron are not important in the application of bright decorative coatings. Similar alloys are, however, deposited for magnetic applications from solutions not containing brightening additions (Ref 7). The alloys with 18 to 25% Fe are soft magnetic materials with low coercive force, low remanence, and high maximum permeabilities (Ref 8). They can be used as coatings or as electroformed parts (i.e., freestanding electrodeposited shapes detached from the substrate after being deposited).

References cited in this section

3. R.J. Clauss, R.A. Tremmell, and R.W. Klein, Decorative Nickel-Iron Alloy Electrodeposits: Present Status and Future Possibilities, *Transactions of the Institute of Metal Finishing,* Vol 53 (No. 1), Spring Conference 1975, p 22-27
4. R.A. Tremmell, Decorative Nickel-Iron Coatings: An Acceptable and Economic Alternative to Bright Nickel--No. I, *Plating and Surface Finishing,* Vol 68, Jan 1981, p 22-26
5. R.A. Tremmell, Decorative Nickel-Iron Coatings: An Acceptable and Economic Alternative to Bright Nickel-No. II, *Plating and Surface Finishing,* Vol 68, Feb 1981, p 30-33
6. J.S. Hadley and J. O'Grady, Corrosion Studies on Nickel-Iron Electrodeposits, *Transactions of the Institute of Metal Finishing,* Vol 59 (No. 3), Autumn 1981, p 89-92
7. P.J. Boden, D.E. Eastham, and M.E. Henstock, Recent Developments in the Electrodeposition of Permalloy Films, *Transactions of the Institute of Metal Finishing,* Vol 50 (No. 3), Summer 1972, p 117-118
8. H.H. Law, C.A. Holden, C.A. Mattoe, J. Sapjeta, Y. Degani, and T.H. Tiefel, Prototype Manufacture of Miniature Nickel/Iron Alloy Magnetic Sleeves for Optical Switching, *Plating and Surface Finishing,* Vol 79 (No. 8), Aug 1992, p 50-54

Nickel-Cobalt

Some of the earliest solutions for bright nickel plating contained cobalt, formate, and formaldehyde additions, but with the development of modern bright nickel solutions based on organic addition agents only, the cobalt-containing solutions have fallen into disuse. Today, the cobalt additions are used when it is necessary to increase the hardness and strength of nickel plating, especially in electroforming applications.

Advantages. Compared with nickel itself, nickel-cobalt alloys are harder and stronger. In contrast to nickel hardened with conventional organic addition agents such as naphthalene 1:3:6 trisulfonic acid, nickel-cobalt alloys can be heated to high temperatures without embrittlement by sulfur incorporated from addition agents.

Disadvantages. Compared with nickel alone, the need to maintain the level of cobalt ions in solution introduces an additional maintenance requirement. Also, deposit internal stress is moved in the tensile direction, and there is a practical limit to the level of cobalt that can be used. Hence the maximum hardness of about 400 HV is less than the 600 HV that can be attained using conventional organic additives.

Process Description. Most of the published data about nickel-cobalt plating were determined using the 600 g/L nickel sulfamate solution of the Ni-Speed process (Ref 9, 10, 11). The initial charge of cobalt is added to the base solution as cobalt sulfamate. Replenishment during operation of the solution is usually made by metered additions of cobalt sulfamate. It can, however, be achieved by dividing the anodic current between a nickel anode and a cobalt anode, so that the percentage of total current passing to the cobalt is the same as the percentage of cobalt required in the alloy deposited at the cathode. Good control of solution cobalt content by analysis is needed.

Processing Variables and Properties of the Alloy from 600 g/L Nickel Sulfamate Solution. With solution composition and pH standardized, the cobalt content and the properties of the alloys depend on solution temperature and deposition current density. The properties are modified by subsequent heat treatment (Ref 12, 13, 14) and by simultaneous use of sulfur-free organic addition agents (Ref 15). The main results of various studies were drawn together in 1989 (Ref 16).

Alloy Hardness. The relationship between cobalt content and deposit hardness is shown in Fig. 1. The broken curve shows microhardness versus cobalt content in the deposits formed at 5.4 A/dm^2 (50 A/ft^2), and the solid curve shows microhardness versus cobalt content in the solution. A peak hardness of about 520 HV is attained with 6 g/L Co in the solution, which gives an alloy containing about 34% Co. At peak hardness, internal tensile stress is too high for electroforming applications, although the alloy can be used as a coating on a solid substrate. For electroforming purposes, the limit of tolerable deposit stress is reached with alloys containing about 15% Co that have hardnesses around 350 to 400 HV.

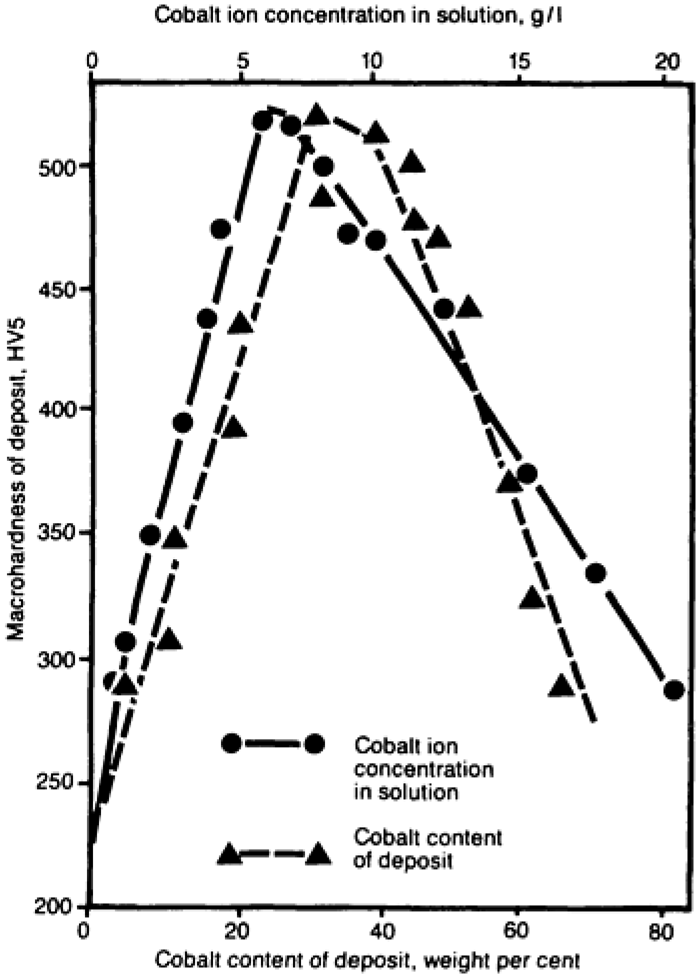

Fig. 1 Relationship between deposit hardness and cobalt concentration in the sulfamate solution and in the deposit

Alloy hardness depends on both the cobalt content of the solution and the deposition current density. Figure 2 shows hardness plotted against current density for different concentrations of cobalt in a solution operated at 60 °C(140 °F), pH 4.0. Deposit stress also depends on deposition current density, and moving left to right along any one of the curves, deposit stress changes from compressive through zero to tensile. The superimposed dotted line is a zero-stress contour linking the combinations of cobalt ion concentration and current density for zero-stress alloys. The corresponding value of deposit hardness can be read from the graph for each combination. The overall relationship is that the higher the cobalt ion concentration, the lower the current density that can be used for zero-stress alloys, but the higher the hardness of the alloy.

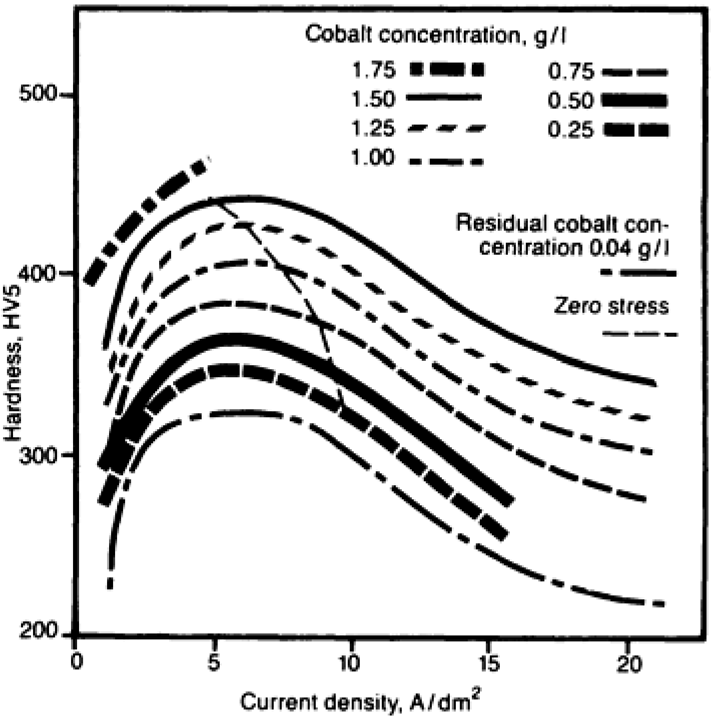

Fig. 2 Relationship between current density and alloy deposit hardness for various cobalt concentrations in solution with superimposed zero stress contour

Effect of Heat. Heating at temperatures up to 300 °C (570 °F) has little effect on the mechanical properties of the alloys. At higher temperatures deposit hardness falls, but nickel-cobalt alloys still retain greater hardness than that of nickel deposits similarly heat treated (Fig. 3).

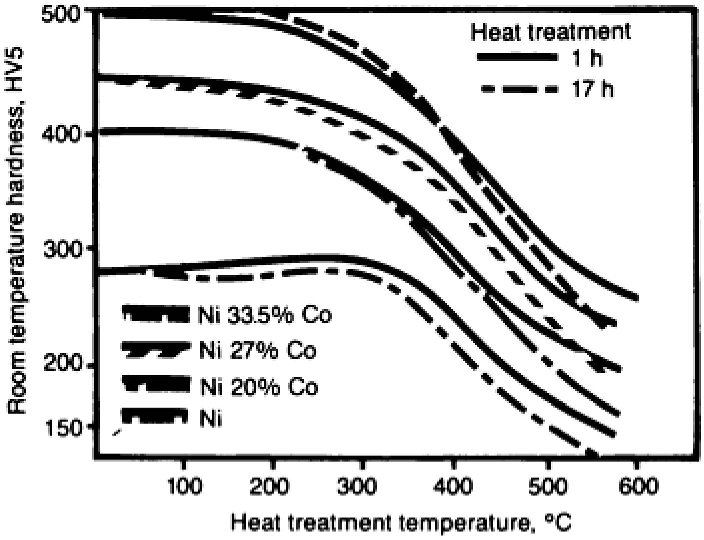

Fig. 3 Room-temperature hardness of electroformed nickel and nickel-cobalt alloys after heating

Tensile strength, 1034 MN/m^2 (150,000 psi) for a 15% Co alloy and 745 MN/m^2 (108,000 psi) for a 10% Co alloy (Ref 14), falls progressively as heat-treatment temperature is increased above 300 °C (570 °F) (Fig. 4). The effect is similar with proof stress, 677 MN/m^2 (98,000 psi) for an as-deposited 15% Co alloy and 531 MN/m^2 (77,000 psi) for a 10% Co alloy (Ref 14).

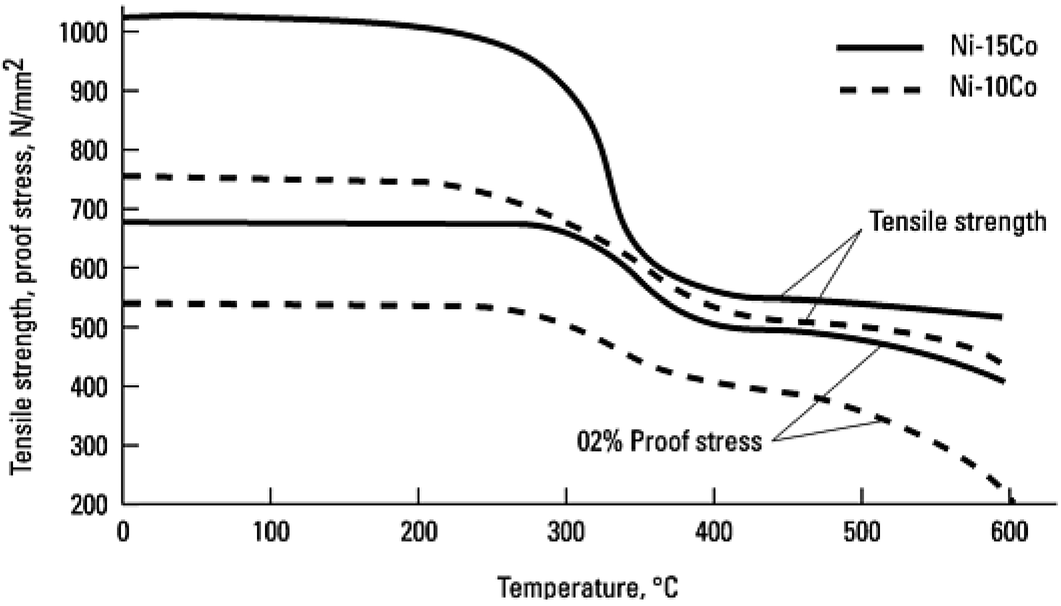

Fig. 4 Effect of heat treatment on the mechanical properties of Ni-10Co and Ni-15Co alloys

Deposit ductility increases on heating above about 300 °C (570 °F), from a value of 5% elongation as-deposited to about 40% after heating at 600 °C (1100 °F) for both 10% and 15% Co alloys (Fig. 5).

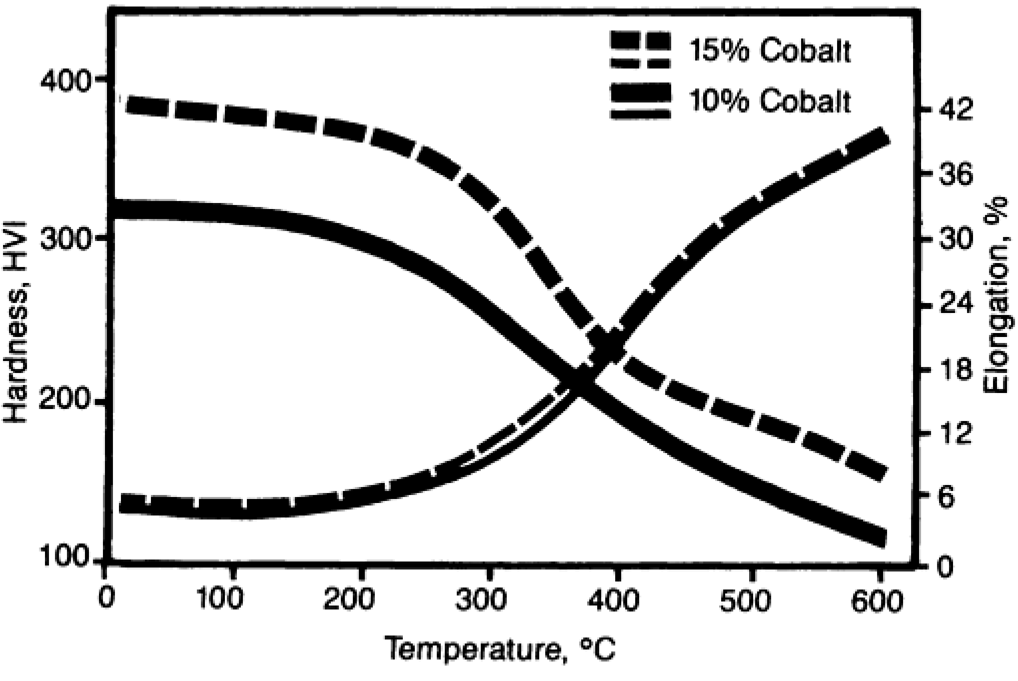

Fig. 5 Hardness and elongation of Ni-10Co and Ni-15Co alloys after heating to various temperatures

Properties of Alloys from Other Nickel Solutions. The above data apply to alloys from a 600 g/L nickel sulfamate solution. A Ni-14Co alloy deposited from a 450 g/L solution without chloride or organic additions, operated at 52 °C (126 °F), pH 4.0, and cathodic current density 2.5 A/dm^2 (23 A/ft^2) has a hardness of 350 to 400 HV, ductility less than 5%, and internal tensile stress of 50 to 60 MN/m^2 (7000 to 9000 psi) (Ref 17).

Measurements of the effects of heat treatment at 204 °C (400 °F) on alloys containing 53 to 55% Co indicate a small increase in yield strength, from 1062 MN/m^2 (154,000 psi) to 1124 MN/m^2 (163,000 psi), and a substantial increase in elongation, from 10 to 16% (Ref 18). Heat treatment at 260 °C (500 °F) or more reduces yield strength, as with alloys from the 600 g/L nickel sulfamate solution. Prior heat treatment of the 53 to 55% Co alloys at 204 °C (500 °F), 371 °C (700 °F), or 427 °C (800 °F) improves subsequent mechanical properties measured at a test temperature of 260 °C (500 °F). Thus pretreatment for 4 h at 427 °C (800 °F) increases yield strength from 372 to 448 MN/m^2 (54,000 to 65,000 psi) and elongation from 28 to 32%.

Alloys deposited from a sulfosalicylate-based solution exhibit a maximum hardness value above 700 HV (Ref 19). To date, this solution has not been used industrially.

References cited in this section

9. R.J. Kendrick, High Speed Nickel Plating from Sulphamate Solutions, *Transactions of the Institute of Metal Finishing,* Vol 41 (Advance Copy, International Conference), 1964; also Inco Publication 2782
10. R.J. Kendrick and S.A. Watson, Plating with Nickel Sulphamate, *Electrochimica Metallorum,* Symposium on Sulfamic Acid and Its Electrometallurgical Applications (Milan), 25-27 May 1966; also Inco Publication 4055
11. "The Ni-Speed Electrodeposition Process: Operating Conditions," Inco Publication 2902a
12. K.C. Belt, J.A. Crossley, and S.A. Watson, Nickel-Cobalt Alloy Deposits from a Concentrated Sulphamate Electrolyte, *Transactions of the Institute of Metal Finishing,* Vol 48 (No. 4), Autumn 1970, p 132-139
13. W.R. Wearmouth and K.C. Belt, The Mechanical Properties and Electroforming Applications of Nickel-Cobalt Electrodeposits, *Transactions of the Institute of Metal Finishing,* Vol 52 (No. 3), Summer 1974, p 114-118
14. W.R. Wearmouth, Application of New Developments in Electroforming Technology in the Toolmaking Industry, *Plastics and Rubber: Processing,* Vol 2 (No. 4), Dec 1977, p 131-138
15. W.R. Wearmouth and R.C.E. Bishop, Hard Smooth Stress-Free Electroformed Nickel for Video Discs, *Transactions of the Institute of Metal Finishing,* Vol 62 (No. 3), Autumn 1984, p 104
16. S.A. Watson, Additions to Sulphamate Nickel Solutions, Nickel Development Institute Technical Series, Publication 10053, 1989, p 1-7
17. W. Metzger and L. Läser, Electrolytic Manufacture of Line Gratings, *Galvanotechnik,* Vol 77 (No. 12), Dec 1986, p 2985-2986
18. R.J. Walter, Tensile Properties of Electrodeposited Nickel-Cobalt, *Plating and Surface Finishing,* Vol 73 (No. 10), Oct 1986, p 48-53
19. J. Vitec, J. Neuman, and P. Nejedly, Some Properties of Nickel-Cobalt Alloys Electrodeposited from Sulphosalicylate Solutions, *Transactions of the Institute of Metal Finishing,* Vol 69 (No. 3), Aug 1991, p 86-89

Nickel-Manganese

Embrittlement of nickel by incorporated sulfur when heated above 200 °C (390 °F) can arise by formation of brittle grain boundary films. In electrodeposits, the sulfur incorporation can result from the use of organic addition agents put into the solution in order to control internal stress in the plating. In these circumstances, manganese ions can be added to the solution so as to allow deposition of a nickel-manganese alloy resistant to sulfur embrittlement.

Manganese ions are also added in the absence of sulfur-bearing addition agents in the solution in order to produce nickel-manganese alloys that are stronger than plain nickel. There are both actual and potential applications of nickel-manganese alloy deposition in electroforming.

Advantages. The ability to neutralize the harmful effect of sulfur is not shared by iron or cobalt. Harder, stronger nickel alloys can be attained with manganese than with cobalt.

Disadvantages. Manganese does not codeposit as readily as iron or cobalt with nickel, and so nickel-manganese alloys contain much less manganese for a given concentration in solution of the second metal. Nickel-manganese alloys containing a useful amount of manganese tend to have high tensile internal stress and to be brittle.

Process Variables and Properties of the Alloys from Solutions with Stress Reducer. The percentage of manganese in the alloy at a fixed level of manganese in solution rises as deposition current density is increased, whether the solution is Watts-type, conventional sulfamate, or 600 g/L nickel sulfamate Ni-Speed (Ref 20). Manganese content rises from 0.02 to 0.03% at 4.3 A/dm^2 (40 A/ft^2) to 0.17 to 0.22% at 12.9 A/dm^2 (120 A/ft^2). These data were obtained in a solution that contained 15 g/L Mn and 0.25 g/L soluble saccharin to control deposit stress. Although sulfur uptake in the deposit also rises with increasing current density, by a half in the Watts and Ni-Speed solutions, the ratio of manganese content to sulfur content rises much more, from 1.1 to 6.2. Measurements of deposit ductility after heat treatment at various temperatures show that a higher ratio is required to avoid embrittlement for higher temperatures: 1.1 for 200 °C (390 °F) and 5.1 for 500 °C (930 °F) (Ref 20).

Alloy Hardness. As-deposited hardness of alloys plated with 15 g/L Mn and 0.25 g/L saccharin rises with an increase in percentage manganese in the alloy, from 287 HV at 0.02% Mn to 420 HV at 0.27% Mn when the base solution is Watts, and from 338 HV at 0.04% Mn to 445 HV at 0.23% Mn when the base solution is conventional sulfamate (Ref 21). Heat treatment for 22 h at 200 °C (390 °F) increases room-temperature hardness about 10% for all alloys with 0.1% Mn or more. Similar periods of heat treatment at 300 °C (570 °F) drastically reduce hardness to about 170 HV for all alloys irrespective of manganese content. Further increase in temperature to 400 °C (750 °F) or 500 °C (930 °F) has little further effect.

Internal stress in deposits from the 15 g/L Mn plus 0.25 g/L saccharin system is compressive for alloys deposited at up to 10.8 A/dm^2 (100 A/ft^2), whether the base solution is Watts, conventional sulfamate, or 600 g/L nickel sulfamate. Values lie in the range of 43 to 62 MN/m^2 (6200 to 9000 psi) for Watts, 62 to 91 MN/m^2 (9000 to 13,200 psi) for 600 g/L nickel sulfamate, and 94 to 100 MN/m^2 (13,600 to 14,500 psi) for conventional sulfamate (Ref 20). At the highest current density, 12.9 A/dm^2 (120 A/ft^2), the Watts deposit remains in its compressive range while the conventional and 600 g/L nickel sulfamate deposits show small tensile stress values, respectively 17 MN/m^2 (2500 psi) and 36 MN/m^2 (5200 psi). These low-stress deposits produced at 12.9 A/dm^2 (120 A/ft^2), with hardness values 420 to 443 HV, are harder than any low-stress alloys produced with the nickel-cobalt system.

Properties of Alloys from Solutions without Stress Reducer. Alloys deposited from straight nickel plating solutions with only manganese additions can have tensile strengths exceeding 1000 MN/m^2 (145,000 psi) and yield strengths up to 800 to 950 MN/m^2 (116,000 to 138,000 psi) (Ref 22). However, ductility is low when more than a small percentage of manganese is alloyed with the nickel, deposit internal stress is tensile, and the alloys may crack during formation. Nonetheless, such alloys have been used as rigid electroforms (Ref 23). Heat treatment of the alloys increases ductility and relieves stress, the values depending on heat-treatment temperature and manganese content, and deposit properties can be further modified using pulse plating during deposition of the alloys (Ref 22).

References cited in this section

20. W.R. Wearmouth and K.C. Belt, Electroforming with Heat-Resistant Sulfur-Hardened Nickel, *Plating and Surface Finishing,* Vol 66, Oct 1979, p 53-57
21. W.R. Wearmouth, Nickel Alloy Electrodeposits for Non-Decorative Applications, *Transactions of the Institute of Metal Finishing,* Vol 60 (No. 2), Summer 1982, p 68-73
22. G.A. Malone, New Developments in Electroformed Nickel-Based Structural Alloys, *Plating and Surface Finishing,* Vol 74 (No. 1), Jan 1987, p 50-56
23. G.A. Malone, Multi-Stage Electroforming of High Energy Chemical and Excimer Laser Components, *Plating and Surface Finishing,* Vol 75 (No. 7), July 1988, p 58-62

Nickel-Chromium

There are many references in the published literature to the deposition of nickel-chromium and iron-nickel-chromium alloys from simple salt solutions, but these solutions have not achieved commercial application except for a proprietary process used for depositing thin decorative coatings (Ref 24).

Alloys of nickel with 22% Cr can be prepared by codepositing chromium carbide particles with nickel followed by heat treatment for 24 h at 1000 °C (1800 °F) in hydrogen. Hardness of the alloy after the heat treatment is 223 HV, compared with 55 HV for similarly treated plain nickel (Ref 21, 25).

Alloys containing 19% Co or 20% Fe in addition to chromium are produced by codepositing chromium carbide from nickel-cobalt or nickel-iron base solutions and heat treating (Ref 21).

Heat treatment in hydrogen gives almost complete decarburization with the nickel-cobalt-chromium alloy, and hardness after heat treatment is 215 HV. Approximately 0.8% C remains in the nickel-iron-chromium alloy, however, which might account for its higher hardness, 332 HV.

References cited in this section

21. W.R. Wearmouth, Nickel Alloy Electrodeposits for Non-Decorative Applications, *Transactions of the Institute of Metal Finishing,* Vol 60 (No. 2), Summer 1982, p 68-73
24. M. Law, Electrodeposition of a Ternary Alloy of Chromium, *Finishing,* Vol 8 (No. 7), July 1984, p 30-31
25. A.C. Hart and W.R. Wearmouth, U.K. Patent 1,476,099, 10 June 1977

Environmental, Health, and Safety Considerations

For practical purposes, the environmental, health, and safety considerations for these nickel-base alloys and their production are the same as those for nickel and nickel plating.

Environmental Considerations. Nickel is a naturally occurring constituent of our day-to-day environment. The soil worldwide contains 5 to 500 ppm Ni, with an average of 100 ppm. Food is grown and consumed in areas with higher levels still, without leading to any health problems for the inhabitants (e.g., 661 ppm in Hawaii) (Ref 26). Nickel has been determined to be an essential trace element for plant life, and some plants that accumulate nickel are regularly eaten by people with no harmful effects. Nickel is also present naturally in the atmosphere, rivers, seas, and oceans. Nonetheless, the desire to maintain the natural environment as it is has led to the establishment of maximum permitted levels for the discharge of nickel and other metals by industry. In nickel plating, the levels are attained by measures to reduce spray emission, process solution dragout, and effluent treatment. Details of all necessary techniques are available from suppliers to the metal finishing industry.

Health and Safety Considerations. Some 1.2% of men and 10 to 15% of women are sensitized to nickel and, when exposed to prolonged skin contact with nickel metal, certain nickel alloys, or nickel-containing solutions, may develop dermatitis at the point of contact. The occurrence of nickel contact dermatitis was first observed as a result of exposure to nickel-containing solutions in electrorefining of nickel. Today most electroplaters are aware of "nickel itch" but have never seen a case of it. The reason is that, despite increasing use of nickel-containing products, industry has adopted work practices that prevent occurrence of contact dermatitis. Today, nickel contact dermatitis occurs most frequently as a result of domestic exposures from close and persistent contact of the skin with nickel-plated articles or with certain nickel alloys. Accordingly, legislation in Europe will control the use of nickel metal, nickel alloys, and nickel-containing materials that come in contact with the skin. The main problem is with those articles that come into direct and prolonged contact, such as earrings, necklaces, bracelets, watch cases and straps, buttons, and rivets. It is important to note that nickel alloys that do not react with sweat do not cause dermatitis. Transient contact with nickel or nickel alloys is not damaging because there is insufficient time for reaction with sweat to form the soluble products that can penetrate the skin (Ref 27).

In nickel plating, plant design, exhaust ventilation, and methods of operation should be such as to avoid any risk of skin contact with the solutions. Protective clothing should be inspected regularly for leaks and tears. Where protective gloves are necessary it is recommended that cotton inner gloves be worn to reduce perspiration. The outer gloves should be rinsed off before removal to prevent process solution transfer to the hands or the inside of the gloves on removal (Ref 28).

A few cases of asthma, claimed to be nickel-induced, have reportedly arisen from aerosols of soluble nickel salts. The content of nickel in the atmosphere should be kept below the occupational exposure limit.

There is evidence that inhalation of some nickel compounds (nickel oxide, nickel subsulfide) occurring in the atmosphere associated with certain nickel refining operations may cause respiratory cancers in humans. There is no good evidence that occupational exposure to metallic nickel or nickel oxide, sulfate, or chloride during plating or polishing is associated with increased mortality due to cancer (Ref 29).

References cited in this section

26. B.K. Davison, BKD Consulting, personal communication, 1994
27. "Nickel and Nickel Alloy Articles That Come into Contact with the Skin," Nickel Development Institute Status Report, Toronto, Sept 1992
28. "Nickel: Meeting the Control Limits for Nickel and Its Inorganic Compounds," Health and Safety Bulletin 1, The Metal Finishing Association, Birmingham, England, June 1991
29. The Toxicity of Nickel and Its Inorganic Compounds, Toxicity Review 19, Her Majesty's Stationery Office, London, 1987

Chromium Alloy Plating

Eric W. Brooman, Concurrent Technologies Corporation

Introduction

CHROMIUM ALLOYS, which are relatively difficult to deposit, yield alloy coatings with properties that range from completely satisfactory to marginally acceptable, depending on the end use. The idea of depositing a thin, stainless steel type of coating has been receiving renewed interest since the 1970s. Stainless steel coatings would conserve strategic metals, facilitate the manufacturing process, and lower cost if they could be applied to strip or sheet, or to a component that has been fabricated to the required size and shape. This would also mean that a component could be made from a material that is more easily worked than stainless steel.

For both chromium and stainless steel types of alloys, the most important properties to develop in a coating are corrosion resistance, abrasion and wear resistance, hardness, surface texture, and luster. Thickness requirements can range from a few microns up to a few hundred microns. Thicker coatings are rarely specified, primarily because the relatively poor throwing power of the plating solution gives an uneven surface coverage. Further, the low plating efficiencies can lead to high internal stresses from hydrogen uptake. The resulting microcracking has a detrimental effect on coating properties.

It is difficult to deposit chromium from aqueous solutions because of its low hydrogen overvoltage. As a result, cathodic coulombic efficiency typically ranges from 10 to 20% for commercial processes. In order to deposit chromium-containing alloys, it is usually necessary to implement the approaches summarized below and described more fully in Ref 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11:

- Complexing agents are needed to bring the deposition potentials of the alloying metals (e.g., nickel and iron) closer together.
- The plating solution should contain a greater proportion of chromium salts, relative to the alloy addition, in order to obtain significant amounts of chromium in the deposits.
- Care must be taken to deposit metallic coatings rather than hydrated, chromium-containing salts, especially if chloride-base solutions are used.
- Close control of temperature, agitation, current density, and pH is necessary with most of the reported solution chemistries, in order to obtain reproducible alloy compositions and properties, as well as reasonable plating rates.
- Trivalent chromium-base solution chemistries provide better prospects for depositing satisfactory alloy coatings from aqueous solutions. An additional benefit is that waste-treatment requirements are less stringent than they are for hexavalent chromium-base solutions.
- The chromium concentration in the alloy should be limited in order to avoid microcracking.
- Aqueous solutions with a low pH value (between 1 and 3) seem to produce better deposits than solutions with pH values outside this range.
- Nonaqueous solutions, especially those based on molten salts, can provide useful alloy deposits.

However, these tend to be relatively thick.

- Thin deposits offer the best prospect for providing lustrous finishes.
- Post-plating heat treatments can sometimes improve the mechanical properties and corrosion resistance of the deposits.

References to chromium alloy plating date back to the mid-1950s, when corrosion- and wear-resistant coatings were first developed for the inside of gun barrels used in military applications, and patents date back to circa 1970. This article will emphasize just the work performed since the 1980s. Those chromium alloys that contain nickel or iron or both are discussed first, because of their importance. Other alloying elements that have been deposited with chromium are discussed as a group, in less detail.

The variables and techniques available to apply coatings based on chromium and other alloys are extensive (Table 1). Because of space limitations, many of these variables or options are mentioned only briefly, where appropriate, and the discussion of deposit properties is similarly limited.

Table 1 Technology options for the deposition of chromium-base alloys

Type of bath Aqueous Acid Alkaline Nonaqueous Organic Molten salt
Applied current None (electroless) Conventional direct current Pulsed direct current Periodic reversed direct current High-speed direct current High-speed pulsed direct current
Composition Alloy Mixture Amorphous
Structure Homogeneous Multilayer Composite

- Dispersed

Post treatments

- Heat treatment
    - Diffusion
    - Laser glazing

References

1. V.M. Dokras, Codeposition of Nickel and Chromium, *Symp. Electroplat. Met. Finish.,* Vol 5, 1952, p 134-139
2. C. Levy, Electrodeposition of Chromium Alloys, *Met. Finish.,* Vol 57 (No. 8), 1962, p 59-62
3. A. Brenner, Electrodeposition of Chromium Alloys, in *Electrodeposition of Alloys,* Vol II, Academic Press, Inc., 1963
4. M. Sarojamma and T.L. Rama Char, Electrodeposition of Stainless Steel, *Electroplat. Met. Finish.,* Vol 23 (No. 10), 1970, p 13-20
5. R. Sivakumar and T.L. Rama Char, Electrodeposition of Ternary Alloys: 1964-1969 Developments, *Electroplat. Met. Finish.,* Vol 24 (No. 1), 1971, p 14-27
6. M. Bonnemay and J. Royon, "Electrolytic Deposition of Chromium Alloys: Factors of Electrolysis," Bulletin of the Information Center for Hard Chromium, June-July 1973, p 12-22
7. H. Benninghoff, Functional Electroplating: Properties of Electrodeposited Metal and Alloy Coating, II--Chromium, Chromium-Iron-Nickel Alloys, Copper Plus Nickel Plus Chromium Systems, Nickel Plus Chromium Systems, Dispersion Systems, *Metalloberfläche,* Vol 33 (No. 9), 1979, p 361-371
8. S.C. Srivastava, Electrodeposition of Ternary Alloys: Developments in 1972-1978, *Surf. Technol.,* Vol 10, 1980, p 237-257
9. M.A. Shulgar and L.D. Tok, New Electrolytes for Chromium and Chromium Alloy Plating, *Zh. Vses. Khim, Ova. im D.I. Mendeleeva,* Vol 33 (No. 3), 1988, p 297-305
10. V.V. Bondar et al., Electrodeposition of Amorphous Chromium and Alloys Based on It, *Itogi Nauki Tekh., Ser.-Electrokhhim.,* Vol 33, 1990, p 37-49
11. "Electroplating of Chromium (Latest Citations from the Compendex Database)," NTIS Accession No. PB93-873412/XAB, NERAC, Inc., June 1993

Chromium-Iron, Chromium-Nickel, and Chromium-Iron-Nickel Alloys

Chromium-Iron Alloys. In contrast to nickel-iron alloys, which have been investigated to replace materials based on iron-nickel alloys in magnetic applications, relatively little work has been done on the chromium-iron analog. No well-defined, large-volume manufacturing application exists for the latter.

Chromium-iron alloys have been deposited from sulfate solutions. Early work in India favored a mixed sulfate-citrate solution (Ref 12), but more recent work used sulfates (Ref 13). Deposits were obtained at low pH levels, near-ambient temperatures, and low current densities (~10 A/dm^2, or 100 A/ft^2). In Japan, the emphasis has been on using modified, commercial trivalent chromium solutions (Ref 14, 15). One patent specifically calls for the presence of divalent chromium ion (Ref 16). The divalent chromium solution also operates at a pH less than 2.0, but at higher temperatures (30 to 80 °C, or 80 to 175 °F) and higher current densities (10 to 80 A/dm^2, or 100 to 800 A/ft^2). In the United States, some work has been performed with a mixed trivalent/hexavalent solution (Ref 17, 18, 19). These efforts focused on using organic additives, such as alcohol, to improve deposit properties. However, solution chemistry and plating efficiencies changed with time, and the deposits tended to be lamellar (banded). Different bands contained different amounts of chromium (up to 90 wt%). The addition of barium carbonate was said to give crack-free coatings.

If suitable additives are used, then chromium can be deposited as an amorphous coating with excellent properties (Ref 19). Recently, it has been shown that amorphous coatings containing chromium, iron, and other minor elements (such as phosphorus and carbon) also can be electrodeposited. Corrosion-resistant amorphous alloys have been obtained from an acid-citrate-base solution containing sodium hypophosphite (Ref 20). Unfortunately, deposits from this solution with greater than 10 wt% Cr are rough and porous. Also, a semipermeable membrane is needed to prevent oxidation of trivalent chromium at the anode.

Other investigators have reported on the use of a chromic acid/formic acid solution containing ferrous chloride and sulfuric acid (Ref 21), or a sulfate-base solution containing organic additives such as sodium citrate and several organic acids (Ref 22). Deposition conditions were similar to those described above for chromium-iron alloys plated from trivalent chromium-type solutions. The sulfate-base solution type also required the use of a semipermeable membrane.

Chromium-Nickel Alloys. The early work on the deposition of chromium-nickel alloys from aqueous and nonaqueous (organic) plating solutions is summarized in Ref 23. Most of the solutions referenced gave poor deposits, and plating efficiencis were low. Deposit quality decreased as plating time increased and as the solution aged. As a result, banded deposits were often obtained, and each band had a slightly different composition. Subsequent work in the United States and Europe gave similar results.

For example, a patented process (Ref 24) calls for using a solution comprising chromous (trivalent) chloride, nickelous chloride, formic acid, boric acid, and sodium nitrate. The solution is operated at 20 to 60 °C (70 to 140 °F), and the chromium content in the deposit is a function of current density and the duty cycle of the pulsed current used. Low duty cycles and high current densities (>70 A/dm^2, or 700 A/ft^2) yield the highest chromium contents (about 60 to 70 wt%). The layered alloy structures are more corrosion resistant in acidic and chloride environments than sulfamate nickel, hard chromium deposits, or conventional stainless steels.

Continued interest has been shown in dimethylformamide-base solutions containing between 10 and 50% water (Ref 25, 26). Water content, temperature, and current density exert a strong influence on deposit quality and composition with such solutions. At low temperatures (7 to 15 °C, or 45 to 60 °F) and high current densities, chromium-rich alloys can be obtained. At higher temperatures (20 to 35 °C, or 70 to 95 °F), nickel-rich deposits are produced. Thicker deposits were cracked and layered in those solutions that contained chromic (hexavalent) chloride, nickelous chloride, ammonium chloride and boric acid, with vanadyl sulfate in some cases. Agitation helps to minimize the banding effect (Ref 26).

Two problems to avoid when plating chromium-nickel alloys are localized pH changes at the cathode surface, which can lead to the precipitation of a hydrated chromium compound, and excessive amounts of divalent chromium in trivalent chromium solutions (Ref 27). Divalent chromium is a strong reducing agent and can precipitate nickel as metal, leading to dark, powdery deposits. In some sulfate-base solutions, commercial nickel-chromium alloy anodes are not satisfactory (Ref 28) because they passivate, or dissolve, to produce hexavalent chromium, which interferes with the alloy deposition process. A plating cell that can alleviate this problem incorporates an ion-exchange membrane (Ref 29). If chloride ions are present in the solution, the problem with passivation can be overcome (Ref 28).

A Japanese patent (Ref 30) claims that satisfactory alloy deposits can be obtained from an organic (imide base) electrolyte containing boric acid and nickel and chromium sulfates. Bright deposits are said to be obtained at a pH equal to 2.5, a temperature of 50 °C (120 °F), and a current density of about 25 A/dm^2 (250 A/ft^2). A nickel-chromium alloy anode can be used.

Amorphous chromium-nickel deposits, which are similar to chromium-iron coatings, also can be obtained, either by electroless (Ref 31, 32) or electrolytic (Ref 33, 34) techniques. These amorphous coatings contain either phosphorus or boron as a minor alloying element, and they provide excellent corrosion resistance if they do not contain any microdiscontinuities, such as pores and cracks.

Chromium-Nickel-Iron Alloys. Although electrodeposited stainless steel type alloys have been deposited, they have had limited commercial success. These coatings did not exhibit comparable corrosion resistance, unless a significant thickness of nickel was first deposited. Although lustrous coatings can be obtained, they tend to be darker in color than the "blue-white" color traditionally associated with decorative chromium or polished stainless steel.

Several patents exist for depositing chromium-nickel-iron alloys (Ref 35, 36, 37), but only one process has been made available commercially. It is known as the "Oztelloy" process, originally promoted in the United Kingdom in the early 1980s (Ref 38). The coating consists of two layers. The first layer is a thick deposit of nickel, and the second layer is an alloy of 55Cr-10Ni-35Fe (wt%). To obtain good corrosion resistance, at least 8 wt% Ni is necessary. The solution is a complexed chloride-base electrolyte operating at a pH of 2.4, a temperature of 25 °C (77 °F), and a current density ranging from 12 to 22 A/dm^2 (120 to 220 A/ft^2). Carbon rods are used as anodes. The deposition rate is slow for the alloy layer (~0.2 to 0.3 μm/min, or 8 to 12 μin./min), and chlorine gas is evolved at the anode. Therefore, proper ventilation above the plating tank is required. Other investigators (Ref 39, 40) have attempted to use complexed, mixed chloride solutions to deposit ternary alloys, but with less success.

Ternary chromium-nickel-iron alloys have been obtained by some Japanese researchers (Ref 41), who used a mixed sulfamate electrolyte with an excess of the iron salt and a high concentration of the chromium salt. The solution also contained potassium citrate and potassium fluoride. It was operated at temperatures ranging from 30 to 50 °C (85 to 120 °F) and a current density ranging from 1.0 to 2.5 A/dm^2 (10 to 25 A/ft^2). The cathode efficiency ranged from 20 to 40%, and bright, fine-grained, homogeneous deposits were said to have been obtained. Fine-grained, semibright to fully bright deposits also have been obtained from a mixed sulfate solution containing boric acid and glycine (Ref 42). However, in chloride solutions, the corrosion resistance of those deposits was not as good as that of comparable conventional stainless steels.

In an effort to obtain homogeneous, crack-free deposits, techniques based on high-speed interrupted current (Ref 43) and periodically reversed current (Ref 44) have been tried, but their success also has been limited. Both pulsed current approaches used a trivalent chromium solution as the base electrolyte, with various additives. With the periodically reversed current approach, low-carbon steel anodes and a semipermeable membrane were used. The pulse frequency was 10 to 15 Hz, and the current density was approximately 20 A/dm^2 (200 A/ft^2). In the former approach, a semipermeable membrane was not necessary because a flowing electrolyte was used. Ternary iron-chromium-nickel alloys (stainless steels) were used as anodes. Deposits with low internal stress were obtained, but only thick coatings provided good corrosion resistance. Heat treating the highly stressed coatings obtained with the periodically reversed current technique did not improve their properties.

In the United States, a novel approach to producing chromium-nickel-iron coatings has been developed specifically for applications that require thick coatings or electroforms (Ref 45). The technique consists of codepositing chromium particles from a nickel-iron sulfate-base alloy plating solution. Subsequent heat treatment of the deposit at 1100 °C (2010 °F) for 8 h in a vacuum or under an inert gas yields a homogeneous, ternary, stainless steel type alloy coating. When depositing the coating, care must be exercised to prevent oxidation of the ferrous ions in the solution. When ferric ions are present, they prevent the occlusion of the chromium particles. The deposited coatings can be polished to provide a lustrous finish.

Other Chromium-Base Alloys. Attempts to deposit chromium-cobalt alloys have been made using fluoborate and dimethylformamide/water solutions (Ref 46). Like many chromium alloys that were plated from similar solutions, it was difficult to sustain a reasonable rate of deposition. Consequently, only thin films (with controlled composition) could be obtained.

Chromium-molybdenum alloy coatings have been used on automobile wheels (Ref 47). The plating solution for this alloy consisted of sulfuric acid, chromous oxide, ammonium molybdate, and sodium hexafluosilicate. It was operated at a temperature of 48 °C (120 °F) and a current density of 25 A/dm^2 (250 A/ft^2).

The literature (Ref 48, 49) also contains a number of references to the deposition of chromium-zinc coatings, with zinc being the major alloying element. Russian workers have used an acidic glycine-base solution, both with and without the application of a pulsed current. Some Japanese steel companies have developed techniques for depositing a chromium-zinc alloy on steel sheets to improve either the subsequent bonding of a (modified) polyethylene film (Ref 50, 51) or the corrosion resistance of the alloy (Ref 52, 53). A chloride-base solution has been used to deposit a ternary zinc-nickel-chromium alloy for similar applications (Ref 54).

Other alloying elements that have been deposited with chromium include gold, molybdenum, rhenium, selenium, tellurium, titanium, vanadium, and zirconium.

The bath compositions and operating parameters for depositing binary and ternary chromium-base alloys are summarized in Table 2. A discussion of the properties of some of these and other electrodeposited alloys is provided in Ref 55.

Table 2 Summary of bath compositions and plating parameters for deposition of selected chromium-base alloys

Alloy	Bath composition	pH	Operating temperature		Current density		Anode	Comments	Ref
			°C	°F	A/dm^2	A/ft^2			
Chromium-iron	250 g/L CrO_3; 72.2 g/L $CrCl_3$; 62.6 g/l $FeCl_2$; 1 ml/L H_2SO_4; 20 ml/L CH_3OH	. . .	40	105	25	250	Lead	Current efficiency 55% (max), decreased as bath aged; shiny deposits	18
Chromium-iron	250 g/L CrO_3; 72.2-143 g/L $FeCl_2$; 1 ml/L H_2SO_4; 20 ml/L CH_3OH	. . .	40	105	11-35	110-350	Lead	Composition and current efficiency changed as bath aged; shiny deposits	18
Chromium-iron	100 g/L CrO_3; 5 g/L H_2SO_4; 60 g/L $FeCl_2$; 20 ml/L (85%) HCOOH	. . .	50	120	40	400	Lead-5% antimony	Amorphous deposits, gray, slightly bright deposits; 6% current efficiency	21
Chromium-iron	167 g/L $Cr_2(SO_4)_3$; 40 g/L $Fe(NH_4)(SO_4)_2$; 80 g/L $(NH_4)_2SO_4$; 10 g/L NaH_2PO_2; 20 g/L K_2SO_4	1-2	30	85	20-90	200-900	Platinum	Nafion membrane used lowered chromium content in deposit; current efficiency ~10% (max), deposits contained phosphorus and were amorphous	22
Chromium-nickel	100 g/L CrO_3; 250 g/L nickel fluoborate; plus CH_3COOH	. . .	20	70	50	500	. . .	Alloys contained 9-10% Cr	23
Chromium-nickel	300 g/L $CrCl_3$; 100 g/L $NiCl_2$	. . .	20	70	20	200	. . .	Alloy contained 9% Cr; cathode efficiency 25%	23
Chromium-nickel	400 g/L $CrCl_3$; 100 g/L nickel fluoborate; plus CH_3OH	. . .	20	70	50-100	500-1000	. . .	Alloys contained 15-30% Cr	23
Chromium-nickel	100 g/L $CrCl_3$; 30-40 g/L $NiCl_2$; 30-40 H_3BO_3; 80 g/L sodium citrate; 35-40 g/L HCOOH; plus other organic additives	~3.5	35	95	10-100	100-1000	. . .	Pulsed current; alloys contained 1-60% Cr; hydrogen bromide optional additive	23
Chromium-nickel	270 g/L $CrCl_3$; 100 g/L $NiCl_2$; 30 g/L NH_4Cl; 10 g/L boric acid; 1 g/L vanadium chloride	2.4	7-20	45-70	1	10	. . .	Electrolyte was dimethylformamide with 10% water; higher temperatures decreased chromium content	25
Chromium-nickel	0.8M $CrCl_3$; 0.2M $NiCl_2$; 0.5M NH_4Cl; 0.5M NaCl;	. . .	25	75	4	40	Graphite	Electrolyte was dimethylformamide with 25% water; composition changed	27

	0.15M H_3BO_3							as bath aged	
Chromium-nickel	0.5M $Cr_2(SO_4)_3$; 0.5M $NiCl_3$; 1M lactic acid; 1.4M NaCl	. . .	60	140	20-50	200-500	Nichrome	Nichrome not satisfactory if chloride not present	28
Chromium-nickel-iron	0.15-0.3M chromium sulfamate; ~0.01M nickel sulfamate; 0.4-0.8 iron sulfamate; 0.25-0.5 potassium citrate; plus potassium fluoride	2-4	30-50	85-120	1-25	10-250	. . .	Current efficiency 24-40%; excellent brightness	41
Chromium-nickel-iron	36.4 g/L $Cr_2(SO_4)_3$; 1.47 g/L $NiSO_4$; 2.7 g/L $FeSO_4$; 147 g/L sodium citrate; 50 g/L H_3BO_3; plus sodium and potassium sulfates, sodium disulfite	. . .	25	75	5-20	50-200	Steel	Semipermeable membrane and pulsed current used	44
Chromium-nickel-iron	0.8M $CrCl_3$; 0.2M $NiCl_2$; 0.03M $FeCl_2$; 0.5M NH_4Cl; 0.5M NaCl; 0.15M H_3BO_3	~2	25	75	4	40	Graphite, steel	Electrolyte was dimethylformamide with 50% water; semibright to bright deposits	39
Chromium-nickel-iron	0.2M $KCr(SO_4)_2$; 0.45M $NiSO_4$; 0.35M $FeSO_4$; 0.5M H_3BO_3; 1M glycine	2	20-30	70-85	15-20	150-200	Platinum	Glass frit separator, current efficiency 50-55%; bright deposits	42

References cited in this section

12. P. Elsie et al., Iron-Chromium Alloy Deposition, *Met. Finish.,* Vol 68 (No. 11), 1970, p 52-55, 63
13. R. Murti et al., Electrodeposition of Iron-Chromium Alloy from Sulfate Solutions, *J. Electrochem. Soc. India,* Vol 38 (No. 1), 1989, p 6-10
14. T. Yoshida et al., Electrochemical Behavior of Electrodeposited Iron-Chromium Alloys, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokaku,* Vol 17, 1970, p 195-209
15. T. Hayashi and A. Ishihama, Electrodeposition of Chromium-Iron Alloys from Trivalent Chromium Baths, *Plat. Surf. Finish.,* Vol 66 (No. 9), 1979, p 36-40
16. H. Kagechika et al., "Chromium Alloy Bath," U.S. Patent 4,673,471, June 1987
17. A.M. Kasaaian and J. Dash, "Effects of Chromium Electroplating Solution Composition on Properties of the Deposits," paper presented at Sur/Fin '85 (Detroit, MI), AESF Society, July 15-18, 1985
18. A.M. Kasaaian and J. Dash, "Chromium-Iron Alloy Plating Using Hexavalent and Trivalent Chromium Ion Solutions," U.S. Patent Application, May 1986
19. S. Hoshino et al., The Electrodeposition and Properties of Amorphous Chromium Film Prepared from Chromium Acid Solutions, *J. Electrochem. Soc.,* Vol 133 (No. 4), 1986, p 681-685
20. P.K. Ng, "Iron-Chromium-Phosphorus Bath," U.S. Patent 4,758,314, July 1988
21. R.Y. Tsai and S.T. Wu, Amorphous Chromium Electroplating with Iron as an Alloying Agent, *J. Electrochem. Soc.,* Vol 137 (No. 9), 1990, p 2803-2806
22. J.C. Kang and S.B. Lalvani, Electrodeposition and Characterization of Amorphous Fe-Cr-P-C Alloys, *J.*

Appl. Electrochem., Vol 22, 1992, p 797-794

23. C.H. Chisholm, Electrodeposition of Nickel-Chromium Alloys from Solvent Based Electrolytes--I: Review, Abstract No. 238, *Extended Abstr.,* Vol 83 (No. 2), 1983, p 374-375
24. D.S. Lashmore, "Process and Bath for Electroplating Nickel-Chromium Alloys," U.S. Patent 4,461,680, July 1984
25. C.H. Chisholm and M.R. El-Sharif, Deposition of Chromium-Nickel Alloys from Dimethylformamide/Water Electrolytes, *Plat. Surf. Finish.,* Vol 72 (No. 8), 1985, p 58-61
26. C.H. Chisholm and M.R. El-Sharif, Chromium-Nickel Codeposits from Dimethylformamide Baths Containing 10 Percent Water, *Plat. Surf. Finish.,* Vol 72, 1985, p 82-84
27. A. Watson et al., "The Role of Chromium II and VI in the Electrodeposition of Chromium-Nickel Alloys from Trivalent Chromium-Amide Electrolytes," paper presented at Annual Tech. Conf. (Bournemouth, UK), IMF, April 15-19, 1986
28. I.A. Polunina and A.J. Falicheva, Nichrome Soluble Anode for Electrodeposition of Nickel-Chromium Alloys, *Z. Metallov.,* Vol 24 (No. 2), 1988, p 258-261
29. H. Ariga, Chromium Alloy Plating by Ion Exchange Membrane, *Jpn. Kokai Tokkyo Koho,* No. 86/00594, 1986
30. M. Kamata and A. Shigeo, Electroplating of Nickel-Chromium Alloys Using Chromic Complexes, *Jpn. Kokai Tokkyo Koho,* No. 86/113,788, 1986
31. I. Nakayama et al., A Study of Electroless Nickel-Chromium Alloy Plating Baths, *Hyomen Gijutsu,* Vol 43 (No. 9), 1992, p 835-838
32. C.E. Cedarleaf, Solution for Electroless Chromium Alloy Plating, U.S. Patent 4,028,116, June 1977
33. J. Gruberger et al., A Sulfate Solution for Deposition of Nickel-Chromium-Phosphorus Alloys, *Surface Coat. Technol.,* Vol 53 (No. 3), 1992, p 203-213
34. K.L. Lin and J.K. Ho, Electrodeposited Nickel-Chromium and Nickel-Chromium-Phosphorus Alloys, *J. Electrochem. Soc.,* Vol 39 (No. 5), 1992, p 1305-1310
35. B.A. Shenoi et al., "Electrodeposition of Iron-Chromium-Nickel Alloy," Indian Patent 114,867, 1970
36. E. Terada, Improvement of Stainless Steel Plating Method, *Jpn. Kokai Tokkyo Koho,* No. 55-148,794, 1980
37. G.R. Schaer, "High Rate Chromium Alloy Plating, " World Patent 82103095, September 1982
38. L. Free, "Electrodeposition of a Stainless Steel Finish," paper presented at Annual Tech. Conf. (Bournemouth, UK), IMF, April 15-19, 1986
39. C.H. Chisholm and M.R. El-Sharif, Sustained Electrodeposition of Chromium-Nickel-Iron Ternary Alloys by Control of Transient Trivalent Chromium Levels, *Proc. Sur./Fin. '87* (Chicago, IL), AESF Society, July 13-16, 1987
40. M. Yasuda et al., Electroplating of Iron-Chromium-Nickel Alloys from the Chloride-Glycine Baths, *Kinzuku Hyomen Gijutsu,* Vol 39, 1988, p 19
41. T. Ishiguro and H. Ochiai, Studies on the Electrodeposition of Iron-Chromium-Nickel Alloys from Sulfamate Solution - Part I, *Puretingu to Kotingu,* Vol 6 (No. 2), 1986, p 79-90
42. M. Matsuoko et al., Electrodeposition of Iron-Chromium-Nickel Alloys, *Plat. Surf. Finish.,* Vol 74 (No. 10), 1987, p 56-60
43. M.F. El-Shazly et al., "The Development of Electrodeposited Stainless Steel Type Alloys," Final Report of Multiclient Research Project, Battelle National Laboratory, December 30, 1986
44. J. Krüger and J.P. Nepper, Galvanic Deposition of Iron-Chromium-Nickel Alloy Using Modulated Current, *Metalloberfläche,* Vol 40, 1986, p 107-111
45. G.R. Smith and J.E. Allison, Jr., "Alloy Coating Method," U.S. Patent 4,601,795, July 22, 1986
46. C.U. Chisholm, Cobalt-Chromium Coatings by Electrodeposition: Review and Initial Experimental Studies, *Electrod. Surf. Treat.,* Vol 3 (No. 5-6), 1975, p 321-333
47. L. Herbansky, Czechoslovakia Patent 214,553, 1985
48. N.B. Berezin et al., Role of Complex Formation During the Cathodic Deposition of Zinc-Chromium

Electroplates from Acidic Glycine-Containing Baths, *Zashch. Met.,* Vol 28 (No. 6), 1992, p 961-966

49. N.B. Berezin et al., Electrodeposition of Zinc-Chromium Alloy with a Pulsed Current, *Zashch. Met.,* Vol 29 (No. 1), 1993, p 99-105
50. M. Matsumoto et al., Manufacturing of Corrosion-Resistant Steel Laminates, *Jpn. Kokai Tokkyo Koho,* No. 92/357439, 1992
51. M. Kimoto et al., Electroplating of Zinc-Chromium Alloy on Steel Sheet, *Jpn. Kokai Tokkyo Koho,* No. 93/09779, 1993
52. T. Komori et al., Manufacture of Steel Sheet Electroplated with Zinc-Chromium Alloy, *Jpn. Kokai Tokkyo Koho,* No. 92/36495, 1992
53. H. Sakai et al., Manufacture of Steel Sheet Electroplated with Zinc-Chromium Alloy, *Jpn. Kokai Tokkyo Koho,* No. 91/120393, 1991
54. C. Kato et al., Alloy Electroplated Steel Sheet with High Corrosion Resistance, and its Manufacture, *Jpn. Kokai Tokkyo Koho,* No. 90/031394, 1990
55. W.H. Safranek, *The Properties of Electrodeposited Metals and Alloys,* 2nd ed., The AESF Society, 1986

Multiple-Layer Alloy Plating

Daniel T. Schwartz, University of Washington

Introduction

MULTIPLE-LAYER ALLOY PLATING is an emerging technology for engineering desirable properties into thin surface layers through the use of carefully controlled deposit microstructures. As implied by the name, multiple-layer alloy electrodeposition involves the formation of an inhomogeneous alloy consisting of lamellae of different composition, as shown schematically in Fig. 1 for a binary alloy composed of species A and B. Each lamella of species A (or species B) in the film has a nearly uniform thickness λ_A (or λ_B). The modulation wavelength ($\lambda = \lambda_A + \lambda_B$) characterizes the imposed compositional microstructure and typically takes a value anywhere from angstroms to microns in thickness. Multiple-layer thin films with spatially periodic compositional microstructures of the type shown in Fig. 1 are sometimes referred to in the literature as composition-modulated alloys (CMAs) or as superlattice alloys. A wide variety of binary and ternary alloy systems have been electroplated as multiple-layer films, including Ni/Cu, Ag/Pd, Cu/Ni-Fe, Cu/Ag, Cu/Co, Cu/Pb, Cu/Zn, Ni-P/Ni-Co-P, and Ni/Ni-P, to name a few. In many cases these alloys can be electroplated from a single electrolyte bath using either current or potential pulsing schemes. A common feature to many single-bath electroplating strategies is the use of hydrodynamic modulation that is synchronized in some manner with the pulsed plating. Multiple-layer alloys are often found to exhibit unusual (and sometimes highly desirable) mechanical, magnetic, electrical, and chemical properties, especially when the modulation wavelength λ is of the order of nanometers.

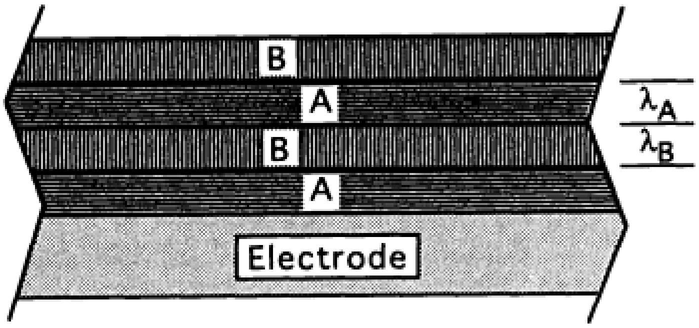

Fig. 1 Schematic representation of a multiple-layer alloy consisting of alternating lamellae of species A and species B. The thicknesses of the A and B layers are given by λ_A and λ_B, respectively. The modulation wavelength that characterizes the multiple-layer superlattice structure is $\lambda = \lambda_A + \lambda_B$. Multiple-layer alloys often exhibit a spatially periodic compositional wave throughout the film, rather than the discrete interface depicted between each lamella.

In short, multiple-layer alloy plating combines the best attributes of electroplating--high throughput, low cost, and simple equipment--with an extra degree of freedom to engineer surface film properties. The potential impact of multiple-layer plating on the performance and economics of engineered surface layers appears to be large, although most commercial applications of the technology are still being developed. This article is focused mainly on the science and engineering of multiple-layer metallic alloys with nanometer-scale modulation wavelengths, because these are the materials that have gained the most attention for surface engineering. Throughout this chapter a solidus, or virgule (/) is used to denote the two materials that are spatially modulated to form a superlattice structure, whereas a dash between elements indicates that the species is an alloy. Using this nomenclature, Fig. 1 shows an A/B alloy. If species A happens to be copper and species B is a Ni-Fe alloy, then the figure denotes a Cu/Ni-Fe multiple-layer alloy.

Applications

For the most part, applications that take advantage of the material properties of nanometer-scale multiple-layer films are still in the development stage. Within the past few years, however, a number of promising applications have emerged that seem especially well suited for multiple-layer alloy plating.

The magnetic properties of electroplated multiple-layer alloys have received a great deal of attention for applications related to magnetic recording. For example, Ref 1 shows that multiple-layer thin films of Cu/Ni-Fe ($\lambda_{Cu} \approx 10$ nm and $\lambda_{Ni\text{-}Fe} \approx 50$ nm) eliminate the classical edge-closure domains that give rise to noise in thin-film inductive heads. At the same time, the remaining magnetic properties of the multiple-layer Cu/Ni-Fe alloy are comparable to homogeneous Ni-Fe alloy properties. The combination of reduced domain noise in the multiple-layer alloy with excellent magnetic properties makes these materials extremely attractive for thin-film inductive heads with very narrow track width. It is also likely that electroplated multiple-layer alloys will soon affect the performance of magnetoresistive head technology, given the recent discovery of giant magnetoresistance in electroplated Cu/Co-Ni-Cu multiple-layer alloys with $\lambda_{Cu} < 1$ nm (Ref 2).

Electroplated multiple-layer foils of Ni/Cu alloy (with $\lambda_{Cu} \approx 2$ nm and $\lambda_{Ni} \approx 18$ nm) exhibit tensile strengths that exceed homogeneous nickel or copper foil strengths by more than a factor of three (Ref 3), and steel that is coated with an electroplated Ni/Cu multiple-layer film ($\lambda_{Cu} \approx 3.8$ nm and $\lambda_{Ni} \approx 3.8$ nm) exhibits a high resistance to sliding wear (Ref 4). Because of these enhanced mechanical properties, electroplated Ni/Cu multiple-layer surface coatings are being used to extend the lifetime of printing press components that are subject to sliding-wear damage.

Other applications of electroplated multiple-layer thin films that are being explored include the use of Cu/Ag and Cu/Co alloys for high-temperature applications in rocket thrust aligners, where protective surface films are used to minimize hydrogen embrittlement.

References cited in this section

1. L.T. Romankiw and J.D. Olsen, Electroplated Laminated Cu/Ni-Fe Films from a Single Plating Bath for Inductive Recording Heads and Magnetic Shields, *Proceedings of the Symposium on Magnetic Materials, Processes, and Devices,* L.T. Romankiw and D.A. Herman, Jr., Ed., Electrochemical Society, 1990, p 339-345
2. M. Alpers, K. Attenborough, R. Hart, S.J. Lane, D.S. Lashmore, C. Younes, and W. Schwarzacher, Giant Magnetoresistance in Electrodeposited Superlattices, *Applied Physics Letters,* Vol 63, 1993, p 2144
3. S. Menezes and D.P. Anderson, Wavelength-Property Correlation in Electrodeposited Ultrastructured Cu/Ni Multilayers, *Journal of the Electrochemical Society,* Vol 137, 1990, p 440
4. A.W. Ruff and D.S. Lashmore, Effects of Layer Spacing on Wear of Ni/Cu Multilayer Alloys, *Wear,* Vol 151, 1991, p 245

Process Description and Engineering Parameters

Nanometer-wavelength multiple-layer alloys were initially fabricated in the late 1960s using vapor-phase evaporation to test theories on the thermodynamic stability and interdiffusion of layered materials. Although vacuum evaporation techniques have been used to form reproducible multiple-layer thin films, sputtering and electroplating techniques are currently the preferred fabrication methods. Multiple-layer alloys can be electroplated from a single bath that contains ions of all of the species to be deposited, or plating can take place sequentially by moving the electrode between multiple plating baths that contain individual species of interest. From a throughput standpoint, single bath plating techniques are preferred, although not all electrolyte chemistries and species redox properties are compatible with single-bath plating.

Multiple-layer alloy plating from a single bath typically requires that the deposition of each species in the multiple-layer pair occur at potentials that differ by more than 100 mV. The more noble component of the alloy is normally plated at the mass transfer limited rate, and the less noble component is plated under kinetics limited conditions. Figure 2 is a schematic showing deposition rate versus potential for an ideal multiple-layer alloy plating bath. The more noble species A plates readily at potentials that are negative of V_A, and the less noble species B plates at potentials negative of V_B. Within the potential window between V_A and V_B, it is possible to electroplate a film that is essentially pure in the noble component A. Conversely, the less noble component B is always codeposited with the more noble species A to form a B-A alloy. Periodically switching the potential (or current) between the region where pure A deposits and the region where B-A alloy deposits results in an A/B-A multiple-layer film. The thickness of each lamella is related to the deposition charge through Faraday's law (a knowledge of the current efficiency is also needed). Figure 2 suggests that species A is codeposited with species B at the mass transfer limited rate ($R_{A.MT}$). The mole percent of species B (in the B-A alloy) is dictated largely by the potential (or current) at which deposition occurs, the strength of agitation in the cell, and the relative concentrations of reducible species A and B that are dissolved in the electrolyte. Decreasing the agitation during species B deposition serves to reduce the rate of which species A ($R_{A.MT}$) is added to the film, and increasing the concentration ratio of B to A in the electrolyte directly affects the ratio of $R_{B.MT}$ to $R_{A.MT}$. The formulation of a multiple-layer plating bath normally begins with an electrolyte that is known to work well for plating the less noble component B at high rates. A small concentration of the more noble species A ($\approx$1% of B) is then added to the bath in an effort to minimize the amount of A that codeposits with B. Using this strategy, it is possible to make an A/B alloy in which each lamella is nearly pure (>95%).

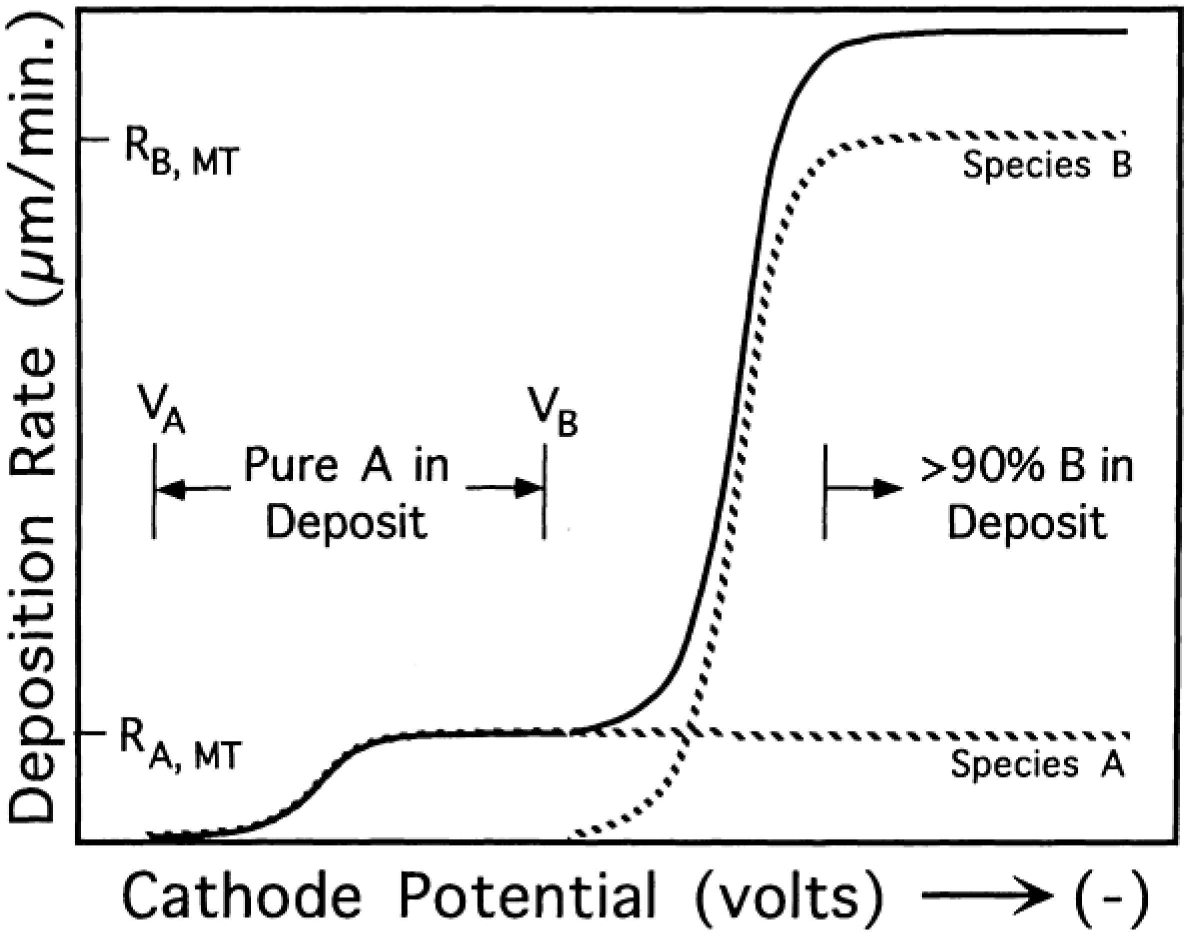

Fig. 2 Schematic of ideal deposition rate vs. applied cathodic potential characteristics for electroplating an A/B multiple-layer alloy. The dashed lines denote deposition rates for plating each individual species, and the solid line represents the total deposition rate. Note that pure A is deposited in the potential window between the reversible potential for species A (V_A) and the reversible potential for species B (V_B), whereas an impure A-B

alloy forms at potentials cathodic of V_B.

The ideal deposition conditions represented in Fig. 2 are nearly matched in reality by some alloy systems. For example, a variety of bath chemistries and deposition conditions have been found for plating Ni/Cu multiple-layer alloys, where copper is more noble than nickel by nearly 600 mV. For the case of Ni/Cu alloy plating, one often starts with a nickel-sulfate-based electrolyte (Watts nickel bath) or a nickel sulfamate bath. Small amounts of copper sulfate (50 to 1000 ppm Cu^{+2}) are then added to the bath. Table 1 shows typical sulfate and sulfamate plating baths for making Ni/Cu multiple-layer alloys. The deposition protocols for creating multiple-layer Ni/Cu alloys from these baths are nearly identical.

Table 1 Characteristic plating baths for making nanometer-scale Ni/Cu multiple-layer alloys

Plating bath	**Typical bath composition**	**Temperature, °C**
Nickel sulfate	330 g/L $NiSO_4 \cdot 6H_2O$, 45 g/L $NiCl_2 \cdot 6H_2O$, 35 g/L H_3BO_4, 0.05-0.1 g/L Cu^{+2}, 0.1 g/L coumarine, 0.1 g/L sodium dodecyl sulfate, pH ≈ 2	≈ 60
Nickel sulfamate	70-90 g/L Ni, 0.3-0.9 g/L Cu (as sulfate), 30-45 g/L boric acid, 0.15 g/L sulfamate nickel anti-pit, pH ≈ 3.5	≈ 50

Pulsed-potential plating of Ni/Cu multiple layers from either bath listed in Table 1 requires the copper lamella to be deposited at a potential near -0.4 V (referenced against a saturated calomel electrode, SCE) and each nickel lamella to be plated at a potential between -1.0 and -1.5 V versus SCE. Under these conditions, the copper deposition rate is controlled by the rate of Cu^{+2} mass transfer, and the nickel deposition rate is controlled by either electrode kinetics or by mixed mass transfer and kinetics. Copper plating proceeds with nearly 100% current efficiency, but the nickel plating has a lower current efficiency due to the simultaneous evolution of hydrogen. The electrolyte is often strongly agitated during copper plating so that higher mass transfer limited copper deposition rates are achieved. Conversely, the agitation rate is often reduced when the nickel is deposited so that the purity of the nickel layer can be increased by reducing the rate of copper codeposition. An important feature of the single-plating bath formulations described here is that the more noble species, copper, has a low deposition rate compared to nickel and therefore requires a longer duration pulse to achieve a comparable layer thickness. Reference 4 provides an example of pulsed-potential plating of Ni/Cu multiple-layer alloys from a sulfamate bath.

Pulsed-current plating is somewhat more common for making high-quality multiple-layer alloys than is pulsed-potential plating. Moreover, the best results are achieved using a triple-current-pulsing scheme that employs a brief high-current nickel deposition pulse, followed by a brief zero-current pulse and then a long-duration, low-current copper deposition pulse. The size and duration of each pulse depend on details of the electrolyte agitation, the bath formulation, and the modulation wavelength desired. The two triple-pulse-plating protocols given in Table 2 are representative of conditions that lead to coherent nanometer-wavelength Ni/Cu multiple-layer alloys (both studies used plating baths that fall in the range of the sulfamate formulations given in Table 1). The triple-pulse protocol given in Ref 3 results in a high plating rate and a high nickel alloy. The high plating rate is achieved, in part, by agitating the cell using a rotating cylinder cathode. Also contributing to the high plating rate is the formation of a high-nickel-content alloy (recall that the less noble component normally plates at high rates compared to the more noble component). The triple-pulse protocol given in Ref 5 results in lower plating rates and higher-copper-content alloys than the protocol used in Ref 3. The low overall deposition rate reported in Ref 5 is a direct result of forming a high-copper alloy using a quiescent plating bath. In the protocol given in Ref 3, the strength of agitation is modulated during each stage of current pulsing. The use and synchronization of a time-periodic agitation scheme should be carefully considered when developing a multiple-layer alloy plating protocol (Ref 6). Additional information is available in the article "Pulsed-Current Plating" in this Volume.

Table 2 Two representative triple-current-pulsing schemes for plating coherent, nanometer-scale Ni/Cu multiple-layer alloys from sulfamate electrolytes

Characteristic triple-pulse condition	**Bath agitation**	**Growth rate (μm/h)**	**λNi/λCu**	**Reference**

Nickel pulse: 90 mA/cm^2 for ≈0.7 s	60 rpm			3
"Rest" pulse: 0 mA/cm^2 for 0.25 to 1 s		≈7	≈10	
Copper pulse: 1.5 mA/cm^2 for ≈4 s	600 rpm			
Nickel pulse: 12-20 mA/cm^2 for ≈0.5 s	None			5
"Rest" pulse: 0 mA/cm^2 for ≈0.5 s		≈1	≈2	
Copper pulse: 0.3 mA/cm^2 for ≈11 s	None			

Multiple-layer alloys that are plated using two baths are not limited to species with widely separated deposition potentials, nor is it necessary to modify well-established bath chemistries. However, plating a multiple layers using two baths requires the substrate cathode to be periodically moved between the baths. If transferring the cathode between baths takes substantial time, then forming nanometer-wavelength multiple-layer alloys with appreciable total film thickness becomes prohibitively slow. Reference 7 describes the use of a novel dual-bath plating cell that provides nanometer-wavelength Ni/Ni-P multiple-layer alloys at a high deposition rate (2 to 4 μm/h). The cell employs a disk-shape cathode substrate that rotates with an angular velocity of 12 to 20 rpm. The rotating substrate is exposed to each plating bath once per revolution. After each exposure to a plating bath, the cathode is mechanically wiped free of electrolyte to avoid cross-contamination of the electrolytes. A voltage divider is used with a single power supply to control the current flowing through each bath (each bath contains a separate nickel anode). Conventional nickel and nickel phosphorous bath formulations are used in the dual-bath cell to deposit each lamella of the multiple layer. Compared to single-bath strategies, the dual-bath approach substitutes a mechanically complex plating apparatus for a much simpler electrolyte formulation.

A new two-bath electroplating strategy for making multiple-layered materials with molecular-level compositional control is described in Ref 8. The technique, called electrochemical atomic layer epitaxy (ECALE), takes advantage of the underpotential deposition (UPD) phenomenon that occurs when the first monolayer (or partial monolayer) of a surface film is formed. The energetics of the first atomic layer of a deposit is often favorable compared to bulk material deposition, thus resulting in deposition at potentials that are noble of bulk deposition. The ECALE concept has been tested for Cd/Te electrodeposition. The chemistry of each bath was manipulated to provide cathodic UPD of cadmium and anodic UPD of tellurium (at potentials that did not strip the cadmium monolayer from the surface). Low-energy electron diffraction verified the formation of ordered cadmium deposits on tellurium and ordered tellurium deposits on cadmium (Ref 8). Despite the initial verification of the ECALE concept, practical applications of the technique await further development.

References cited in this section

3. S. Menezes and D.P. Anderson, Wavelength-Property Correlation in Electrodeposited Ultrastructured Cu/Ni Multilayers, *Journal of the Electrochemical Society,* Vol 137, 1990, p 440
4. A.W. Ruff and D.S. Lashmore, Effects of Layer Spacing on Wear of Ni/Cu Multilayer Alloys, *Wear,* Vol 151, 1991, p 245
5. D.S. Lashmore and M.P. Dariel, Electrodeposited Cu/Ni Textured Superlattices, *Journal of the Electrochemical Society,* Vol 135, 1988, p 1218
6. D.T. Schwartz, P. Stroeve, and B.G. Higgings, Electrodeposition of Composition-Modulated Alloys in a Fluctuating Flow Field, *AIChE Journal,* Vol 35, 1989, p 1315
7. L.M. Goldman, B. Blanpain, and F. Spaepen, Short Wavelength Compositionally Modulated Ni/Ni-P Films Prepared by Electrodeposition, *Journal of Applied Physics,* Vol 60, 1986,p 1374

8. B.W. Gregory, D.W. Suggs, and J.L. Stickney, Conditions for the Deposition of CdTe by Electrochemical Atomic Layer Epitaxy, *Journal of the Electrochemical Society,* Vol 138, 1991, p 1279

Characterization of Multiple-Layer Alloys

One of the most common methods for characterizing nanometer-wavelength multiple-layer alloys is x-ray diffraction (XRD), which provides information about the crystalline texture and superlattice structure of a multiple-layer material. The superlattice structure of the alloy is revealed as satellite peaks located at low and high angles around the crystallographic Bragg peaks in the diffraction pattern. The dispersion angle of the satellite peaks provides the modulation wavelength of the multiple layer, and the number and amplitude of the satellite peaks provide a measure of the interfacial "sharpness" between each lamella. The wavelength of a multiple-layer alloy (λ) is quantitatively related to the first-order satellite peak locations through the relationship

$$l = \frac{l_x}{\sin(q^+) - \sin(q^-)}$$

where λ_x is the x-ray source wavelength, θ^+ is the high-angle satellite peak location, and θ^- is the low-angle satellite peak location. Transmission electron microscopy and Auger electron spectroscopy (used with sputtering) have both been employed to study nanometer-scale structure in multiple-layer alloys, but these techniques require significantly more sample preparation and handling than XRD. Moreover, the sample preparation for these techniques requires destructive treatment of the multiple-layer material.

Once the structural characteristics of a multiple-layer alloy are known, then the material properties are normally analyzed using conventional techniques. Relationships have been observed between the superlattice structure of multiple-layer alloys and their mechanical properties (e.g., tensile strength, moduli), their electrical properties (e.g., conductivity), their magnetic properties (e.g., magnetoresistance, magnetostriction, saturation magnetization), and their chemical properties (e.g., corrosion resistance).

The growing technological need for inexpensive, high-performance thin-film materials is propelling academic and industrial research efforts to understand the processing-structure-property relationships in a wider range of plated multiple-layer alloys. The degree to which plated multiple-layer films will ultimately meet the technological challenges that face surface engineers remains to be answered.

Selective (Brush) Plating

Introduction

SELECTIVE PLATING, also known as brush plating, differs from traditional tank or bath plating in that the workpiece is not immersed in a plating solution (electrolyte). Instead, the electrolyte is brought to the part and applied by a hand-held anode or stylus, which incorporates an absorbent wrapping for applying the solution to the workpiece (cathode). A direct current power pack drives the electrochemical reaction, depositing the desired metal on the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating, and so on. A schematic of the selective plating process appears in Fig. 1.

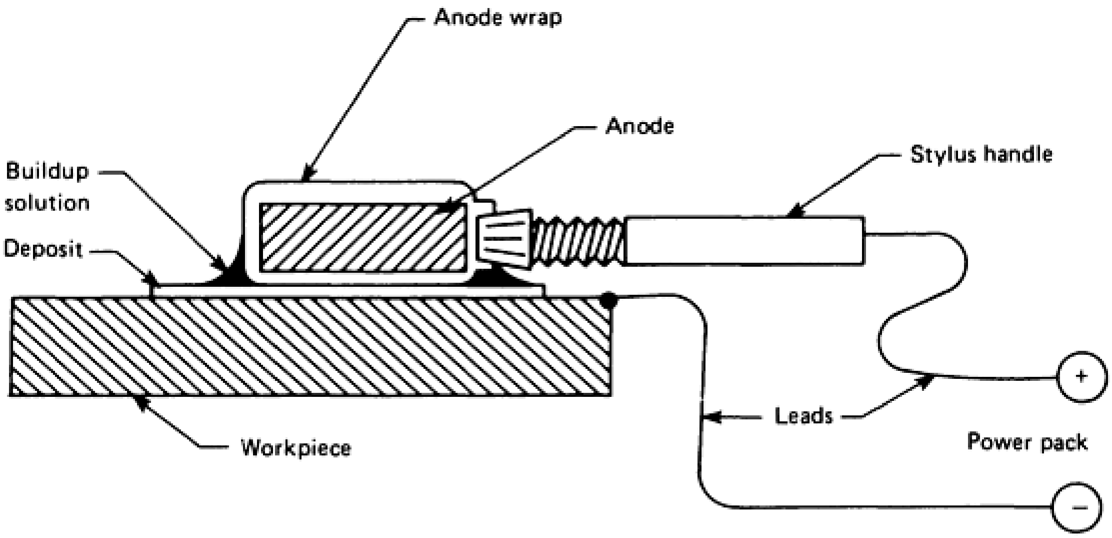

Fig. 1 Manual operation of selective plating process. Source: Ref 1

Currently, a broad range of elements and alloys can be brush plated; the majority are listed in Table 1. Even though selective plating can be done in a tank, labor-intensive masking and subsequent removal often make this option impractical.

Table 1 Energy factors for selective plating

Element or alloy	Energy factor
Cadmium	0.006
Chromium	0.200
Cobalt	0.014
Copper	0.013
Gallium	0.014
Gold	0.006
Indium	0.009
Iridium	0.069
Iron	0.025

Lead	0.006
Mercury	0.008
Nickel acid	0.047
Nickel alkaline	0.017
Nickel, black	0.025
Nickel, natural	0.025
Palladium	0.019
Platinum	0.015
Rhodium	0.030
Silver, noncyanide	0.750
Silver, pure	0.004
Babbitt	0.006
Brass	0.017
Bronze	0.017
Cobalt-nickel	0.019
Cobalt-tungsten	0.015
Nickel-cobalt	0.020
Nickel-tungsten	0.020
Tin-cadmium	0.007
Tin-indium	0.008
Tin-lead (90/10)	0.006

Tin-lead (60-40)	0.007
Tin-nickel	0.010

Note: The energy factor is the ampere-hours required to produce a deposit thickness of 0.003 mm (0.0001 in.) on a square inch of area.

Acknowledgements

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Reference

1. M. Rubinstein, *Electrochemical Metallizing,* Vinmar Press, 1987

Advantages and Limitations

The key advantage of selective plating is portability. Many systems can be moved to various locations in a production facility or be transported to the job site. Selective plating is also versatile; it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, steel, stainless steel, high-temperature nickel-base alloys, aluminum, and zinc are commonly plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials, such as titanium, tungsten, and tantalum.

Selective plating allows higher current densities than tank plating, which translate into higher deposition rates, up to 0.010 mm/min (0.0004 in./min). In addition, inherently precise thickness control permits plate buildup or repair without the need for subsequent machining. In regard to deposit hardness, a 70 HRC trivalent chrome is available for selective plating of thick deposits, which places selective plating on a par with hexavalent tank chrome. The exceptions are the harder deposits of cobalt and gold (Table 2). Table 3 provides a point-by-point comparison of selective plating with competitive processes, including tank plating.

Table 2 Deposit hardness attainable with selective plating versus bath plating

Metal type	**Microhardness, DPH**	
	Bath plating	**Selective plating**
Cadmium	30-50	20-27
Chromium	750-1100[(a)]	850-1100
Cobalt	180-440	510
Copper	53-350	140-210
Gold	40-100	140-150

Lead	4-20	7
Nickel	150-760	280-580
Palladium	85-450	375
Rhodium	550-1000	800
Silver	42-190	70-140
Tin	4-15	7
Zinc	35-125	40-54

Source: Ref 2

(a) Usual range, but hardnesses of 280-1200 DPH are possible.

Table 3 Selective plating versus other processes

Characteristic	**Selective plating**	**Welding**	**Flame spray or plasma metallizing**	**Electroplating**
Precision buildup capability	Excellent	Poor	Poor	Fair to good
Quality of bond	Excellent	Excellent	Fair to good	Good
Heat distortion or stresses	None	Frequently	Sometimes	None
Heat cracking	None	Frequently	Sometimes	None
Speed of deposit	Fast	Very fast	Very fast	Slow
Density of deposit (porosity)	Very dense[(a)]	Very dense, but with blowholes	70-90% of theoretical density	Moderately dense
Portability	Yes	Yes	Sometimes, but over-spray precludes its use	No
Requirement for post-machining	Not required on thicknesses up to 0.254 mm (0.010 in.) on smooth surface	Always required	Almost always required	Usually required

Hydrogen embrittlement	No[(b)]	No	No	Yes

Source: Ref 1

(a) Generally 25% less porous than electroplating and 70% less porous than flame spray or plasma metallizing.

(b) Specific cadmium, nickel, and nickel-tungsten deposits have been tested on high-strength steel and were found to be nonembrittling. Other deposits may not cause embrittlement.

Besides electroplating, selective plating systems can perform several other ancillary operations:

- *Electrostripping* for deplating of many metals and alloys
- *Anodizing* for protecting aluminum and alloys
- *Electromilling* for removing base metal, as in chemical milling
- *Electroetching* for permanently identifying parts
- *Electropolishing* for refining a surface chemically

Depending on part size, dimensional considerations, and required surface characteristics, all of these operations can be done with the same equipment and similar electrodes. Only the solutions are different.

Selective plating of small parts is more the exception than the rule, and large volumes of small parts are more economically plated by high-production-rate processes, such as barrel plating. Plating of entire components with complex geometries is better left to processes such as tank plating, which is more economical because solutions are less costly and throughput is higher. Another limitation is deposit rate; both flame spraying and welding deposit metal at a considerably faster rate.

References cited in this section

1. M. Rubinstein, *Electrochemical Metallizing,* Vinmar Press, 1987
2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

Applications

In many cases, an operator brush plates only one part at a time. Nevertheless, selective plating is an effective and economical electroplating process when used in application for which it is designed. These include plating of parts that are too large to immerse in solution, plating a small area of a larger component, and touchup and repair of components, large or small, that would cost too much to strip and remanufacture. The largest parts ever plated are building domes and church steeples, up to about 1390 m^2 (15,000 ft^2), in copper, nickel, and gold. The smallest are cells on rotogravure rolls, 0.076 by 0.038 mm (0.003 by 0.0015 in.). The process can also perform at high production volumes, such as 4,000,000 parts/day for nickel-plated brass electrical contacts on alkaline batteries.

Cosmetic or decorative applications involve parts that range in size from jewelry to large exterior structural domes and lobby interiors.

Corrosion protection applications allow touchup of small rusted or corroded areas without disassembly. Examples include aircraft landing gears, virtually all kinds of machinery, mixing vats, and tanks. Parts too large to fit into plating tanks are almost always good candidates.

Repair of electronic parts is usually done with precious metals, such as gold, silver, and rhodium. Typical applications are repair of broken circuits and small circuit board contacts, and application of conductive coatings on high-voltage sources. Selective plating minimizes scrap, allows immediate repair on site, and does not require immersion of the entire part in solution.

Restoration of large parts is a natural application for selective plating if the parts are permanent fixtures that cannot be removed or disassembled. The process makes it possible to repair and restore dimensions or apply a wear-resistant or corrosion-resistant surface to just about any part. Portable systems allow access to parts at great elevations and in remote areas, such as protecting the inside surface of a large mixing vessel and repairing critical equipment on ships at sea.

Specialized applications of selective plating involve unusual environments or the need for certain properties, such as conductivity or impact resistance. Examples include blocking radio frequency interference with a soft, radiowave-resistant material such as tin; plating aluminum to facilitate soldering; plating machinery components to ensure initial lubrication; and even plating test probes to resist extreme environmental conditions.

Following are examples of specific applications of selective plating and anodizing:

- *Adhesive-bonded aircraft parts:* anodizing (phosphoric acid) used to prepare aluminum skins and frames for adhesive repair of damaged skins
- *Aircraft engine components:* sulfamate nickel on high-temperature nickel alloys used as a prebrazing operation for second-stage turbine vanes, blades, and stator segments; also used for restoration of bearing area on turbine exhaust case, bearing housing and support, and cooling air duct
- *Aircraft landing gears:* cadmium touchup; on 2014 aluminum, hard coat on inner diameter of oil air strut used to accommodate press fit of bronze bearing
- *Aircraft skins:* anodizing (chromic acid or sulfuric acid) used to repair damaged chromic-acid and sulfuric-acid coatings, respectively
- *Aircraft wheel:* anodizing (sulfuric acid) used to correct a mismachined bearing bore
- *Bus bars:* silver on copper or aluminum used for electrical contacts
- *Electric motors:* nickel and copper used for dimensional restoration of motor shafts and bearing end caps; tin used for low-power motors to reduce vibration; and platinum, gold, or rhodium used to increase wear life and reduce arcing of commutators and slip rings
- *Hydraulics:* copper, nickel, cobalt, or chrome used to repair steel- or chrome-plated hydraulic components, often without disassembly
- *Metal recovery systems:* platinum coating used on titanium permanent anodes
- *Missile launch rail:* hard coat used on a 6061-T6 surface to bring dimensions into tolerance and provide wear resistance and corrosion resistance
- *Mold repair:* gold plating used on plastic molds where corrosive gases attack existing chrome; final plating of chrome used to repair rubber molds; copper, nickel, and cobalt used to repair other types of molds
- *Printed circuit boards:* gold over copper used on contact tabs, fingers, etc.
- *Printing presses:* copper, silver, nickel, cobalt, or chrome plating used to repair cylinders; in-press overhaul plating of side frame used for bearing retention and to correct out-of-concentricity condition
- *Railroad axles:* nickel used for dimensional restoration on bearing journals and sealing wear ring grooves
- *Space shuttle manifolds:* up to 0.5 mm (0.20 in.) of copper used to increase wall strength of a nickel-electroformed hydrogen-oxygen manifold for the prototype "Columbia" engine
- *Steel mill coating line:* cadmium, zinc, or nickel-zinc used to increase the thickness of the protective coating on steel sheet moving at 137 m/min (450 ft/min)
- *Submarines:* rhodium and gold used on copper slip rings
- *Turbines:* cobalt, nickel, nickel/cobalt, or chrome used to restore dimensions on bearing and seal surfaces; silver used to repair steam cuts on horizontal seal surfaces

Equipment

Typical selective plating systems include a power pack, plating tools (called *styli* or *anodes*), anode covers, specially formulated plating solutions, and any auxiliary equipment required for the particular application. To achieve optimum deposits, equipment should be designed expressly for selective plating. Although tank plating solutions and rectifiers are occasionally used, they are not usually recommended because the resultant deposits are thin and quality is typically below par.

Power packs (rectifiers) supply the direct current and are specially designed with the features and/or controls required by the process. Output voltage can typically be varied from 0 to between 25 and 30 V, compared to the usual 6 to 12 V for tank-plating power packs. Power packs are available in a variety of ratings to suit specific applications (Table 4).

Table 4 Commercially available power packs

Alternating current input, V	Phase	Maximum output current, A[(a)]
115 or 230	1	30
115 or 230	1 or 3	60
230 or 460	1 or 3	100
230 or 460	1 or 3	150
230 or 460	1 or 3	200
230 or 460	3	500

Source: Ref 2

(a) At 25 V dc.

Voltage control is extremely important because it regulates the current supplied to the process. In turn, the amount of current consumed over time, measured in ampere-hours (A · h), determines the deposit thickness. Ampere-hour requirements vary widely for different types of electroplates, as indicated by the energy factors in Table 1.

Stepless voltage control is a typical feature of selective plating power packs; most can be adjusted from 0 to 100%. The magnitude of power required depends on the part size, the deposit thickness required, and the plating type. For example, for delicate electronics parts, an output of 5 A and 12 V should be ample, whereas plating of large areas with thick buildups requires a much larger source.

A voltmeter and an ammeter should be available and should show 0 to 100% ranges. The voltmeter permits monitoring of the voltage required to plate a given part. The ammeter displays the amount of current flowing between the anode and the cathode, allowing calculation of the current density.

A polarity-reversing switch allows the operator to automatically change current flow direction, which is necessary in preparatory operations (e.g., etching and desmutting) and in stripping, when the current must run opposite to the direction used in electroplating. Otherwise, the connections to the anode and cathode must be changed manually, slowing down the entire process. Indicator lights to show polarity direction may also be incorporated.

Safety circuit breakers instantly shut off the current should a short circuit occur between the anode and the workpiece. Typically, shutdown is within one-half cycle (1/120 s), preventing workpiece damage and injury to the operator.

Energy counters (ampere-hour meters) are required by many industrial and government specifications. Besides keeping track of the energy being used, these meters make it possible to control the thickness of the deposit. Counters may incorporate set points with visual and/or audio warnings to indicate when the desired thickness has been reached.

Optional microprocessor-controlled systems reduce the chance of miscalculation and allow continuous monitoring of the process via an alphanumeric readout. The amount of energy required for an area to be plated to the desired thickness and the applicable parameters are determined by a microprocessor, not the operator. Such equipment is also of merit for plating multiple parts to the same specifications. In some systems, the software prompts the operator for data entry for a particular operation, then displays the correct process parameters.

The plating tool (stylus) must have an insulating handle and an anode material that is inert, insoluble in plating solutions, and able to carry high current. Graphite is by far the most practical choice for anode material. High purity is preferred; any additive used to harden the graphite or give it a different physical characteristic interferes with its beneficial qualities. Graphite can be machined or shaped to fit the contour of the part being processed. Stainless steel is much more durable, but it dissolves in some plating solutions, and after a short time it changes the characteristics of the electrolyte being used. Platinum-iridium, platinum-clad niobium, and platinum-clad titanium are inert to all of the electrolytes used in selective plating operations, and they are used for smaller-diameter anodes. Their disadvantages are increased cost and high hardness, which makes shaping difficult.

The anode covers (wrapping materials) serve as an insulator between the anode and cathode and help ensure smooth deposits at high current densities. Because they hold the electrolyte, they must be absolutely free of oil and foreign materials. Any substance that contaminates the electrolyte has a detrimental effect on the plating. For example, any oil contamination whatsoever results in poor adhesion. Consequently, in a machine shop or other environment where oil is widely used, the work area should be carefully selected. When necessary, applicable part surfaces can be solvent or vapor degreased or go through a separate cleaning cycle.

Various fiberlike materials make suitable covers. Cotton works very well if it is sterile, long fiber. Synthetic fibers, such as polyester and nylon, do not wet or hold electrolytes as well as cotton, but this does not preclude their use. Polyester felt is typically selected when the same anode will be used for numerous parts or for heavy deposits. Most of these materials work well in the form of tube gauze ("bandage covers") as covers over cotton. Scotch-Brite has been used when heavy/hard deposits are required, and it can also function as a burnishing tool, improving the surface as plating continues. If a surface is soft and easily scratched, a different wrap should be chosen.

Reference cited in this section

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

Key Process Elements

Anode-Cathode Motion. Controlling continuous movement between the anode and the workpiece, or cathode, is a key element in obtaining high-quality brush-plated deposits. However, quality also depends on plating within a specific current density range, so both variables affect ultimate deposit quality. This relationship is illustrated in Fig. 2. Solution suppliers routinely recommend ranges of anode-cathode speeds and current density values for each solution; a representative list is given in Table 5.

Table 5 Anode-cathode motion and current density for selective plating solutions

Selective plating solution	Anode-cathode motion		Current density	
	m/s	ft/min	A/dm^2	A/ft^2
Cadmium (acid)	0.26-0.561	50-110	86.4	864
Cadmium LHE (low hydrogen embrittlement formula)	0.20-0.41	40-80	86.4	864

Chromium	0.02-0.03	4-6	86.4	864
Cobalt (machinable)	0.13-0.26	25-50	115.2	1152
Copper (high speed, acid)	0.20-0.51	40-100	144.0	1440
Gold	0.15-0.31	30-60	28.8	288
Lead	0.15-0.26	30-50	86.4	864
Nickel (acid)	0.10-0.26	20-50	86.4	864
Nickel (high speed)	0.20-0.41	40-80	144.0	1440
Nickel-tungsten alloy	0.10-0.15	20-30	72.0	720
Rhodium	0.03-0.05	5-10	43.2	432
Silver (heavy build)	0.10-0.31	20-60	72.0	720
Tin (alkaline)	0.10-0.41	20-80	86.4	864
Zinc (alkaline)	0.15-0.612	30-120	115.2	1152

Data courtesy of SIFCO Selective Plating

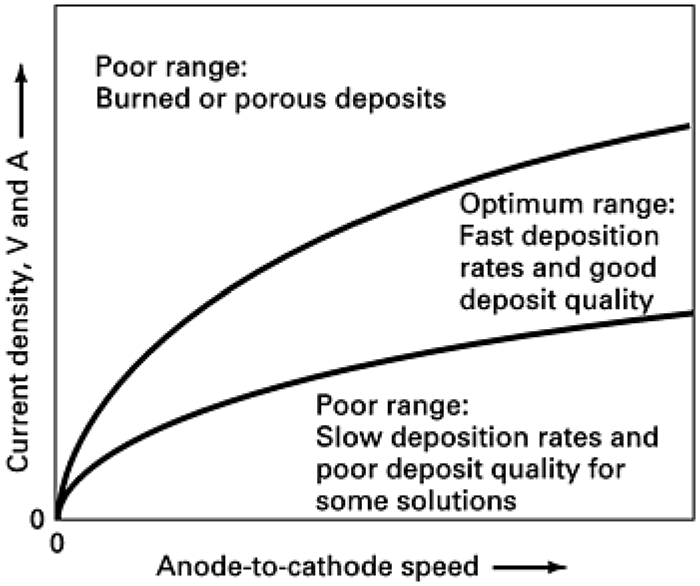

Fig. 2 Relationship between current density and anode-to-cathode speed. Source: Ref 3

The visual appearance of the electroplate is also an indicator of quality. A dark gray or black color usually corresponds to a burnt deposit, which results from too high a current density or insufficient movement. In contrast, inadequate current density or too much movement produces a generally shiny surface.

Anode-to-cathode movement may be achieved manually or mechanically, such as by using turning equipment to provide a constant rotational speed for cylindrical parts (Fig. 3) or by using specially designed tilting turntables to rotate large parts at controlled speeds. Another option is the rotostylus (Fig. 4), which rotates the anode instead of the workpiece.

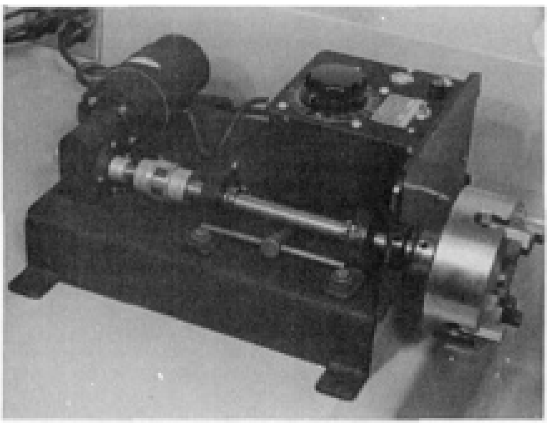

Fig. 3 Turning head. Courtesy of SIFCO Selective Plating

Fig. 4 Rotostylus. Courtesy of SIFCO Selective Plating

Anodes and Flowthrough. For the plating process to be efficient, the plating solution must flow between the anode and the area being plated. Solution can be supplied by periodically dipping the plating tool into the electrolyte. However, the most efficient method is to pump the solution through the block anode and into the interface between the anode and the workpiece (Fig. 5). Plating of large areas at high currents *requires* the use of a pump to recirculate the solution. This keeps the solution from overheating, results in thicker buildups on large areas, and allows the use of higher current densities. In addition, the entire process is faster. Various types of pumps can be used, depending on the amperage and on whether preheating and/or filtering is necessary for the solution used.

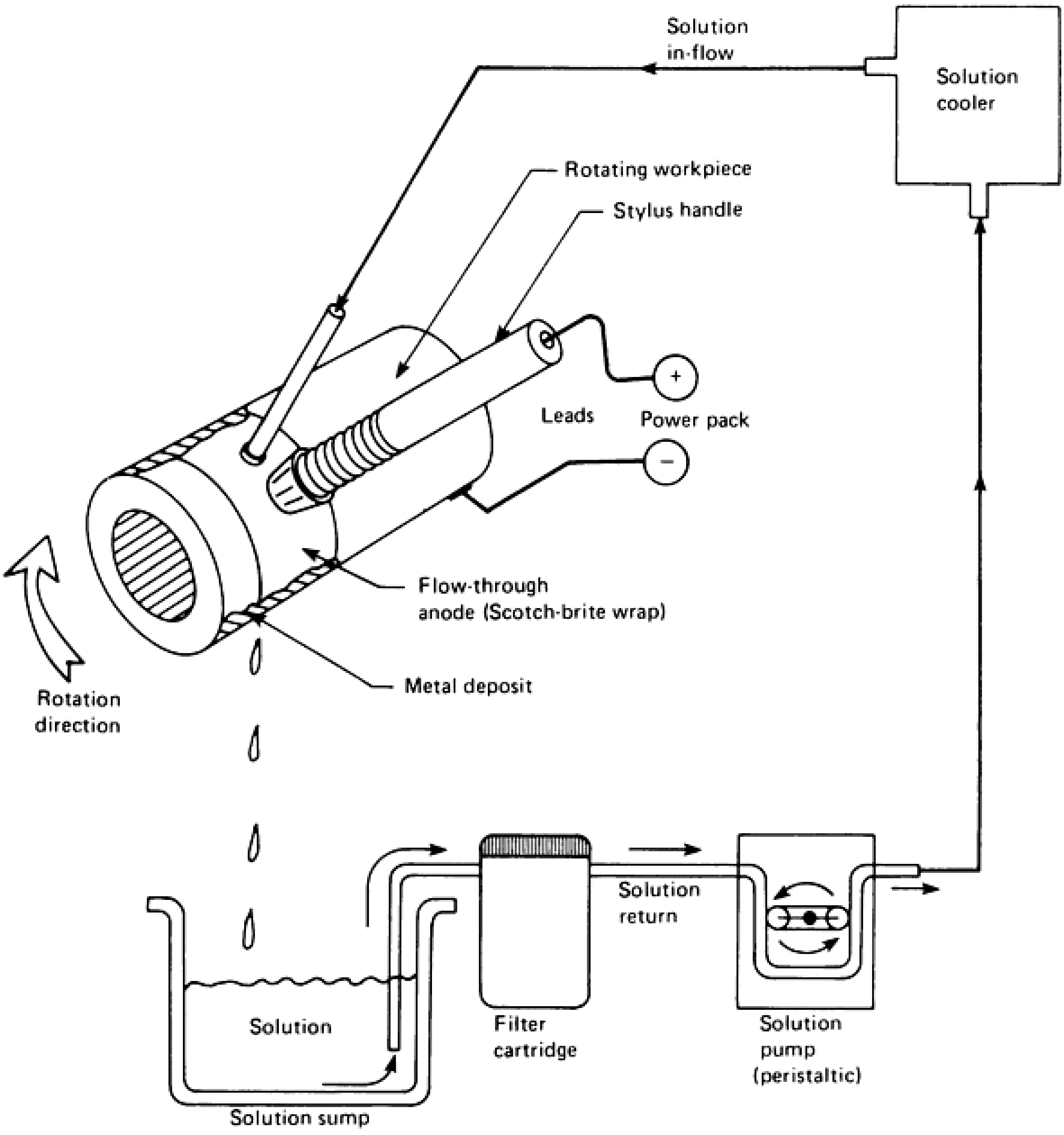

Fig. 5 Flow-through deposition. Courtesy of Vanguard Pacific, Inc.

Solutions. Three basic types of solutions are used in selective plating: preparatory, plating, and special-purpose. Table 6 shows the most common solutions and their uses. The base metal and the type of plating generally dictate which solutions are appropriate.

Table 6 Typical selective plating solutions

Preparatory solutions
Activating (for industrial hard chromium)
Cadmium activator
Chromium activator (for decorative applications)
Cleaning (for most materials)

- Desmutting (for cast iron, carbon and alloy steels, copper alloys)
- Etching (for aluminum alloys, steels, cast iron)
- Etching and activating (for high-temperature nickel-base alloys and stainless)

Plating solutions for ferrous and nonferrous metals

- Nickel (acid strike)
- Nickel (alkaline)
- Nickel (dense)
- Nickel (ductile, for corrosion protection)
- Nickel (neutral, for heavy buildup)
- Nickel (sulfamate, hard, low stress)
- Nickel (sulfamate, moderate hardness)
- Nickel (sulfamate, soft, low stress)
- Antimony
- Bismuth
- Cadmium (acid)
- Cadmium (alkaline)
- Cadmium (no-bake)
- Chromium (hexavalent)
- Chromium (trivalent)
- Cobalt (for heavy buildup)
- Copper (acid)
- Copper (alkaline)
- Copper (high-speed acid)
- Copper (high-speed alkaline for heavy buildup)
- Copper (neutral)
- Iron
- Lead (alkaline)
- Lead (for alloying)
- Tin (alkaline)
- Zinc (acid)
- Zinc (alkaline)
- Zinc (bright)
- Zinc (neutral)

Plating solutions for precious metals

- Gallium
- Gold (acid)
- Gold (alkaline)
- Gold (neutral)
- Indium
- Palladium
- Platinum
- Rhenium
- Rhodium
- Silver (hard)
- Silver (noncyanide)
- Silver (soft)

Plating solutions for alloys

- Babbitt Navy Grade 2
- Babbitt SAE 11
- Brass
- Cadmium-tin
- Cobalt-tungsten
- Nickel-cobalt
- Nickel-tungsten

Tin-indium
Tin-lead-nickel

Special-purpose solutions

Anodizing (chromic)
Anodizing (hard coat)
Anodizing (sulfuric)
Chromate treatment
Electropolishing solution

Source: Ref 2

Preparatory solutions clean the substrate surface so that it can effect a better bond with the electroplate. Preparation typically involves precleaning, electrocleaning, and electroetching; some base materials also require desmutting, activation, and preplate operations. Parts with heavy corrosion, lubricants, oil, and so on ordinarily require more aggressive cleaning, such as vapor/solvent degreasing or grit blasting, prior to precleaning.

Plating solutions used for selective plating have a much higher concentration of metal, usually as organometallic salts, than do solutions used for tank plating. This higher metal content permits the use of higher current densities, which results in faster deposition, better bond strength, and less porosity than in tank plating.

Two basic kinds of plating solutions are used. One deposits a thin preplate ("strike") that boosts adhesion on certain metals and alloys, and the other builds up the coating to its functional thickness. Suppliers usually offer a choice of solution for each type of electroplate, because different properties are required for different applications (e.g., high hardness and wear resistance for one, ductility for another).

Special-purpose solutions include those used for post-treatment, anodizing, and electropolishing.

Thickness Control. The thickness of a deposit can be controlled by monitoring the ampere-hour meter. Each solution has a prescribed energy factor, which indicates how many ampere-hours are required to deposit a given metal thickness on a given area:

$$\mathrm{A} \cdot \mathrm{h} = F \times A \times T$$

where $\mathrm{A} \cdot \mathrm{h}$ is the ampere-hours required, F is the energy factor, A is the area to be plated (in square centimeters), and T is the thickness of the deposit (in microns). The calculation yields a fixed value that can be monitored on the meter (or set on the ampere-hour counter, if the power pack is so equipped). If needed, simple additional calculations can also be performed to determine the optimum current, plating time, volume of plating solution, and even rotational speed (Ref 4).

References cited in this section

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48
3. DALIC Process Instruction Manual, 5th ed., SIFCO Selective Plating, 1990
4. J.C. Norris, Brush Plating: Part II, *Metal Finishing,* Aug 1988, p 45-47

Specifications

Since the mid 1950s, when the first commercial selective plating specification was introduced, the number of specifications has surpassed 100. The following list includes some of the more important industrial, government, and military specifications:

- MIL-STD-865C (U.S. Air Force)
- MIL-STD-2197SH (U.S. Navy)

- BAC 5849, 5854 (Boeing)
- DPS 9.89 (Douglas Aircraft)
- MPS 1118A (Lockheed Aircraft)
- SS 8413, 8494 (Sikorksy Aircraft)
- BPSFW 4312 (Bell Helicopter)
- FPS 1046 (General Dynamics)
- HA 0109-018 (North American Rockwell)
- GSS PO60B (Grumman)
- Standard Practice Manual 70-45-03 and T.M. No. 72-191 (General Electric)
- PS 137, Issue 1 (Dowty Rotol Ltd., England)
- ITF 40-839-01 (Messier-Hispano, France)
- TCMK-5 (Saab-Scania, Sweden)
- Report NAEC-AML 1617 (Naval Air Engineering Center, Philadelphia)
- M-967-80 (Association of American Railroads)
- AC 43.13-1A, Chg. 1 (Federal Aviation Administration)
- AMS 2439, 2441, 2424C
- SPOP 321 (Pratt & Whitney)

In addition to the above specifications, many U.S. Navy and U.S. Air Force activities have generated instructions for selective plating of specific hardware or components at specific military facilities.

In the electronics field, the repair of printed circuit boards for military applications is authorized by MIL-STD-865C. For commercial applications, the Institute for Interconnecting and Packaging Electronic Circuits approves the use of selective plating for repair of both bare and assembled printed circuit boards (Ref 5). In addition, many electronics companies have issued their own specifications for in-house repair of circuit boards and other electronic components.

Reference cited in this section

5. *Modification and Repair for Printed Boards and Assemblies,* Manual IPC-R700B, Institute for Interconnecting and Packaging Electronic Circuits

Health and Safety Considerations

There are two safety issues in selective plating: the chemicals and the equipment used to apply the chemicals. Overall, the process meets the safety requirements set by the Occupational Safety and Health Administration (OSHA) for in-plant use. Electrical protection of the power pack, workpiece, and operator are provided by a direct current circuit breaker within the power pack. This circuit breaker trips when an overload occurs. If the anode shorts out by contacting the part, or if the power pack exceeds its amperage rating, the breaker almost instantly stops power flow.

Today, manufacturers provide material safety data sheets (MSDS) with solutions, in conformance with OSHA requirements. The solutions are industrial chemicals and should be handled as such. Ventilation to remove fumes is recommended, and conventional safety guidelines, including the use of safety glasses and rubber gloves, should be routinely followed. Reviewing the MSDS will alert personnel to any special handling or other safety precautions required.

Pulsed-Current Plating

Chuck VanHorn, Enthone-OMI, Inc.

Introduction

CONVENTIONAL PULSED-CURRENT PLATING (commonly referred to as *pulse plating*) can be defined simply as metal deposition by pulsed electrolysis. In its simplest form, it involves using interrupted direct current to electroplate parts. This is accomplished with a series of pulses of direct current, of equal amplitude and duration in the same direction, separated by periods of zero current. The pulse rate (frequency) and "on" and "off" times (duty cycle) can be controlled to meet the needs of a given application. The ideal shape of the pulsed current is shown in Fig. 1(a). An oscilloscope should be used to reveal how well the equipment controls the output (Fig. 1b).

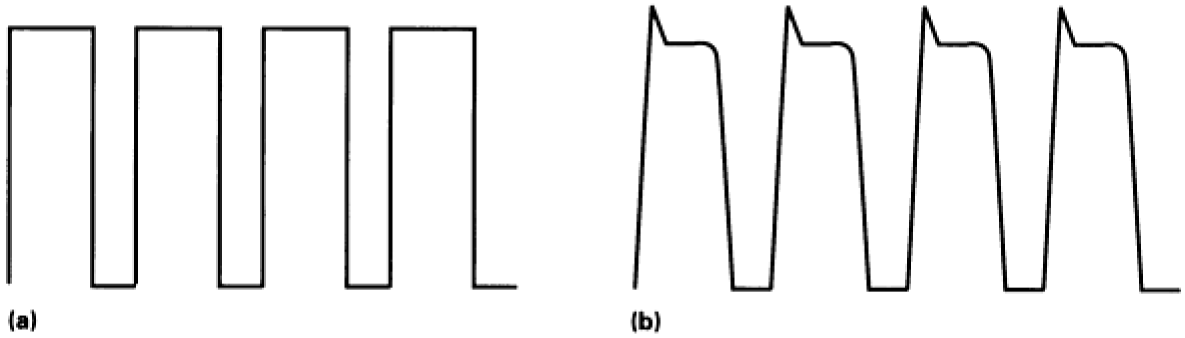

Fig. 1 Current patterns in conventional pulsed-current plating. (a) Ideal pattern. (b) Typical pattern as seen using an oscilloscope

Pulse plating has gained acceptance in a number of metal finishing industries, especially the electronics industry. With the advent of solid state pulse plating power supplies, the imprecision has been taken out of the process. The amount of time the current is on and off is set directly on digital thumb-wheel switches or via programmable software. Two different modes of operation are used: constant current and constant voltage. Figure 2 illustrates the constant-current mode of operation. The tops of the current pulses are kept flat by allowing the voltage to vary during the pulse on-time. In the constant-voltage mode (Fig. 3), the tops of the voltage pulses are kept flat by varying the current. Because of the shape of the current pulse in the constant-voltage mode, the peak current is not useful for controlling the plating rate. An amp-minute controller is needed to accurately control the plating thickness.

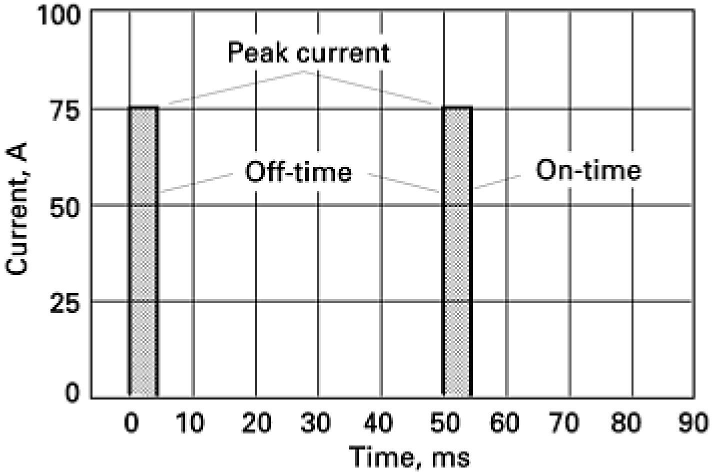

Fig. 2 Constant-current pulse plating with an on-time of 5 ms, an off-time of 45 ms, and a peak current of 75 A. Because the current is on one-tenth of the time, the average current is 7.5 A.

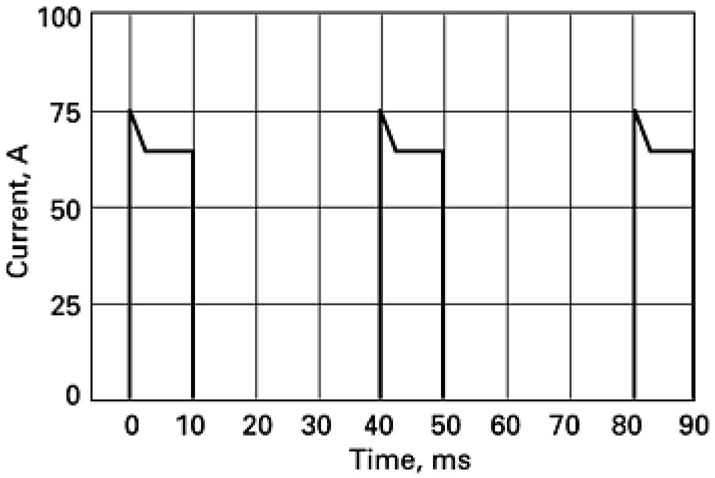

Fig. 3 Typical current pattern for constant-voltage pulse plating. The current falls during the on-time because of the increasing resistance of the cathode. On-time, 10 ms; off-time, 30 ms

Metals that are commonly deposited using pulsed current include gold and gold alloys, nickel, silver, chromium, tin-lead alloys, and palladium. Pulsed current is also used for anodizing and, in select cases, for etching, electrocleaning, and electroforming.

The advantages of pulse plating vary from one application to the next. The most common (relative to plating with conventional continuous current) include the following:

- Deposits are smooth, dense, fine-grained, and almost completely free of pinholes.
- Variation in plate thickness from one part to the next is considerably reduced.
- Plating speeds can normally be increased.
- Current efficiency generally is improved.
- Use of organic additives, in most cases, can be reduced by 50 to 60%. Deposits are free from dendritic growth even if additives are not used.
- For some electrodeposits, such as gold, less metal is required in the plating solution to meet end-use specifications.

The limitations of pulse plating include the fact that the cost of a pulsed-current rectifier is greater than that of a conventional dc unit. Also, optimization of results requires planning and experimentation, and plating equipment may need to be redesigned or upgraded.

Process Principles

The theory behind pulse plating is simple (Ref 1, 2). The cathode film is kept as rich in metal ions as possible and as low in impurities as possible. During the period when the current is on, the metal ions next to the cathode are depleted and a layer rich in water molecules is left. During the portion of the cycle when the current is off, the metal ions from the bulk of the plating solution diffuse into the layer next to the cathode. Then the process is repeated again. Also during the time the current is off, gas bubbles and impurities that have been adsorbed on the cathode have a chance to desorb.

Typical on-time range from 0.1 to 9.9 ms, and typical off-times range from 1 to 99 ms. If an ammeter is inserted into a pulsed-current plating circuit, it responds to the average current. In order to have the same plating rate using pulsed current as with conventional continuous current, the average current must be the same. This can be achieved by adjusting the peak current, the on-time, or the off-time. The physical and chemical properties of deposits can be very precisely controlled through the careful selection of pulse-plating parameters.

Concepts and Terminology. Selected terms that have special meaning when applied to pulse plating are defined as follows:

- *Cathodic (forward) and anodic (reverse)* are used to describe current direction; *cathodic* indicates flow is in the normal (plating) direction, *anodic* indicates flow is in the reverse (deplating) direction. In normal operation of a reversing pulse unit, current direction alternates in a controllable forward and reverse pattern.
- *Envelope* is the time span during which current may flow in only one direction. The time spans of the forward envelope and the reverse envelope are set individually.
- *Pulse train* is a regularly interrupted current flow in either the cathodic or anodic direction. A pulse train exists within the envelope.
- *Pulse* is the individual interval in a pulse train, consisting of one "on and off" period.
- *Pulse rate* is the number of times the current is switched on in a given period of time (usually 1 *s*).
- *Duty cycle* is the ratio of time an individual pulse is on compared to the total (on and off) pulse time. For example, 5 ms on and 5 ms off is a 50% duty cycle, 4 ms on and 1 ms off is an 80% duty cycle, and so on. (*Note:* if the duty cycle is 100%, there is no off time; the current is on for the duration of the envelope and there is no pulse or frequency.)
- *Frequency* is the pulse rate expressed as hertz units (e.g., 100 Hz = 100 pulses/s).
- *Pulse width* is the time span of the on portion of a pulse. Pulse width is a function of both frequency and duty cycle. For example, a 1000 Hz pulse with a duty cycle of 50% has a pulse width of 0.5 ms.

References cited in this section

1. H.Y. Chen, *J. Electrochem. Soc.,* Vol 118, 1971, p 551
2. R.J. Tedeschi, *Met. Finish.,* Nov 1971, p 49

Process Control

Microprocessor-controlled modulation of applied direct current to improve the electrodeposition process has found use in reel-to-reel selective plating, automatic tab plating, barrel line plating, still plating, electroforming, anodizing, electrocleaning, electropolishing, and electromachining. It recently has been adapted for use with semiconductor bump and wafer plating technologies.

The use of this sophisticated power control can result in greatly increased plating speeds, improved deposit distribution, lower deposit stress, finer grain structure, increased ductility, improved adhesion, increased micro-throwing power, reduced susceptibility to hydrogen embrittlement, and a markedly decreased need for additives.

The use of modulated dc power supplies with advanced electronic circuitry enables the user to control output patterns with extreme precision. A high-quality unit will superimpose periodic reverse on a high-frequency pulse. The power pattern that results is quite complex, with a wide range of profiles. The output--a series of pulses with controllable amplitude, frequency, duration, and polarity--influences the deposition characteristics of any solution. The characteristics obtained with modulated power supplies are quite different from those obtained with conventional pulse or periodic-reverse equipment. By "tuning" or shaping the output power pattern to a given plating application, the operator can dramatically enhance the rate of deposition and the character of the deposit.

In periodic-reverse plating, the polarity of a constant dc output is switched back and forth in a regular pattern. Figure 4(a) depicts the ideal output; Figure 4(b) shows the actual output from a slow-response control unit.

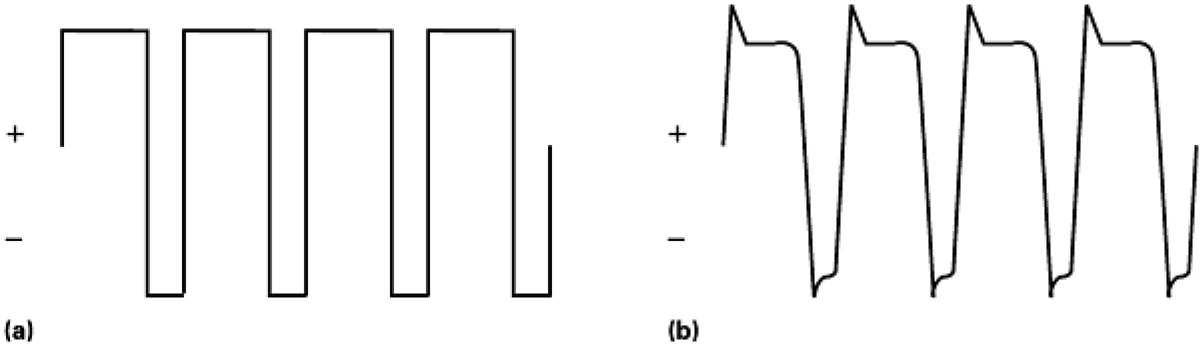

Fig. 4 Current patterns in periodic-reverse pulsed-current plating. (a) Ideal pattern. (b) Pattern of a slow-response control unit as seen using an oscilloscope

The sharpness of the output current pattern as revealed by an oscilloscope depends on the degree of ripple in the rectifier output and the quickness of response in the internal switching circuitry of the controller. High-quality units produce extremely sharp square-wave patterns (Fig. 3 and 4). Figure 5 illustrates the wave form of the forward (cathodic) and reverse (anodic) output of a high-quality unit.

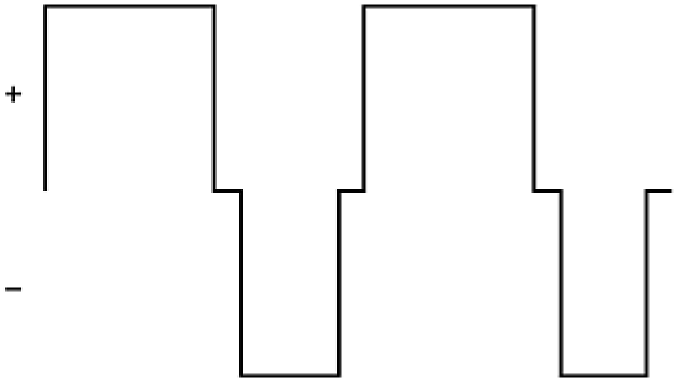

Fig. 5 Square-wave current pattern of the forward and reverse envelopes in periodic-reverse pulse plating

The duration of the current in each direction (the forward and reverse envelopes) can be individually controlled from 0.1 ms to 99.99 s. (A zero current delay of less than 0.1 ms between forward and reverse is a design feature of high-quality units that serves to prevent transistor failure due to "shoot through.") The simple, square-wave pattern shown in Fig. 5 is the result of a precisely controlled periodic-reverse output; pulse frequencies can then be superimposed upon this output pattern. Within each envelope, a square-wave pulse is generated (Fig. 6). The frequency and the duration of the pulses are set independently for the forward and reverse envelopes; frequencies range from 10 to 9999 Hz. Duty cycle settings in percentages determine the on and off times for each pulse.

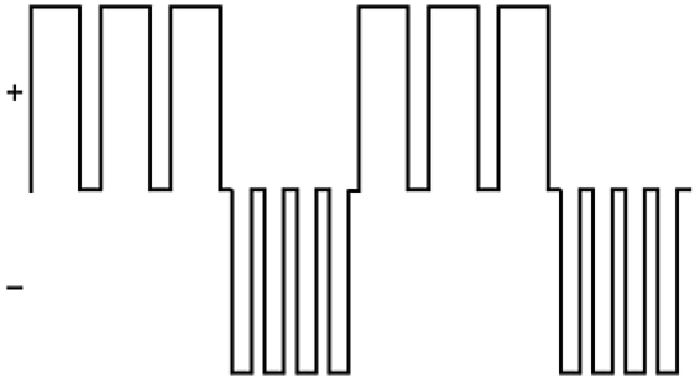

Fig. 6 Current pattern for periodic-reverse pulse plating in which pulse frequencies have been superimposed on the forward and reverse envelopes

On some models, forward and reverse amplitude can be controlled individually (Fig. 7). This permits, for example, a higher current density in the reverse (deplating) stage than in the forward (plating) stage, which is highly desirable for some applications. (More complete explanation of output control with specific units is available in the operation manuals supplied by their manufacturers.)

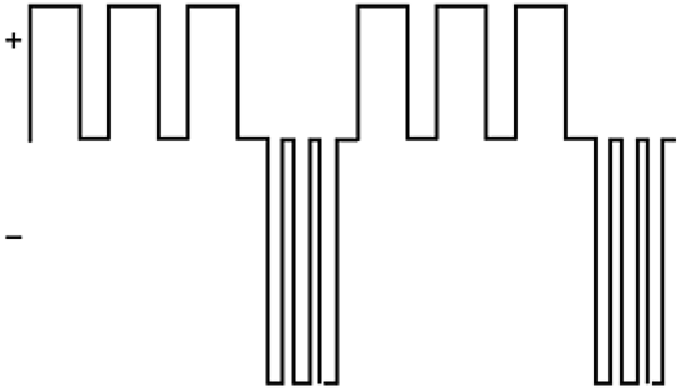

Fig. 7 Current pattern for periodic-reverse pulse plating in which pulse frequencies of different current densities have been superimposed on the forward and reverse envelopes

Solution Composition and Operating Conditions

With the changes that take place in the plating tank when a modulated periodic reverse pulse is impressed on the electrolyte, changes in the other operating conditions or even in the formulation may be required. Generally speaking, better results are obtained with simple, rather than sophisticated, formulations (Ref 3). Typical solutions used in pulse plating are given in Table 1.

Table 1 Typical solutions used in pulsed-current plating

Constituent or condition	Amount or value
Watts nickel solution for reel-to-reel plating	
Nickel sulfate, g/L (oz/gal)	650 (87)

Boric acid, g/L (oz/gal)	50 (7)
Temperature, °C (°F)	60 (140)
pH	3-4
Anodes[(a)]	Platinized niobium (insoluble)
Organic additives	None
Pure gold	
Potassium citrate, g/L (oz/gal)	150 (20)
Citric acid, g/L (oz/gal)	15 (2)
Potassium phosphate, g/L (oz/gal)	26 (3)
Boric acid, g/L (oz/gal)	72 (10)
Gold metal, g/L (oz/gal)	8.2 (1)
Temperature, °C (°F)	60 (140)
pH	3.5-4.0
Anodes	Platinized titanium
Hard gold	
Citric acid, g/L (oz/gal)	65 (9)
Potassium citrate, g/L (oz/gal)	50 (7)
Cobalt, g/L (oz/gal)[(b)]	0.5-0.6(0.07-0.08)
Gold, g/L (oz/gal)	8.2 (1)
pH	3.8-4.0
Temperature, °C (°F)	32-38 (90-100)

(a) When using soluble nickel anodes with reversing pulse modes, the use of an anode activator such as chloride is not required because the reversing current keeps the anode active and soluble.

(b) The higher voltage of pulse plating relative to continuous dc plating favors the deposition of the alloying agent. The operator should analyze the deposits to determine if the amount of cobalt in the solution should be adjusted. In most cases, the amount of available cobalt (or other alloying agent) should be reduced (from the amount used with continuous current) to obtain the desired properties.

Additives. The polarization imposed by the power pattern on the bath reduces, or even eliminates, the need for some addition agents. In many cases, additives can actually inhibit the effectiveness of the pulsed-current pattern. For example, large-molecule additives do not respond as they do under conventional power; in a high-frequency pulse field, their molecular size is a disadvantage. Small-molecule organics or inorganics will generally function well as additives. In many cases, the use of brighteners can be reduced as much as 90% without diminishing the brightness of the deposit because of the improved grain structures. If brightener levels are not reduced, longer pulses--i.e., lower frequencies and/or higher duty cycles--may be required (Ref 3).

Electrolyte conductivity must be maintained at a high level to allow the peak pulse current to be completely effective. If the conductivity is not high enough, an excess in voltage will be required to attain the desired peak current. Such peaks are power-inefficient and less effective.

Anode-to-cathode ratios for pulse plating are rarely the same as those for conventional power applications. Generally speaking, in acid or alkaline nonchelating formulations, the anode area should be reduced. In cyanide or other chelating formulations, the reverse is generally the case, and a greater anode area is required.

Temperature and agitation conditions for conventional processes may also have to be altered for modulated power pattern plating. Unfortunately, no general rule applies; each application has its own requirements, and optimum conditions must be established on a case-by-case basis.

Reference cited in this section

3. J. Padden, J. Lochet, and C. VanHorn, "Improvement of Electrodeposition through Modulated dc Power Patterns," 1981

Equipment Modification

One factor that should always be checked when planning a change from conventional to pulsed-current power is the tank electrical contact system. Some anode and/or cathode contacts that may be perfectly suitable for conventional plating may present unwanted resistance to high-frequency peak currents. Overlooking this factor may prevent the realization of the full benefits of a modulated power supply.

The major consideration, of course, is the power system itself. Existing rectifiers may or may not be suitable for use with modulated periodic reverse or direct pulse units. For pulse plating, a high-voltage, quick-response rectifier is required, and the lower the ripple, the more precise and predictable the output. Although pulse units are available for use with existing power supplies, models with self-contained rectifiers give greater assurance that full benefit of the control system will be realized.

Pulse units with self-contained power can be operated in either a constant-average-current or constant-voltage mode. The significance of this option is illustrated in Fig. 8. Figure 8(a) depicts a pulse train with a 50% duty cycle. The *average* current delivered is 50% of the *peak* value. Figure 8(b) shows the effect of reducing the duty cycle to 25% when in a constant-voltage mode. The peak current remains the same, but the average current changes directly with the duty cycle, in this case dropping to half its former value. The current density of the pulsed current remains the same, but twice as much real time is required to deliver the same amp-minutes of current. Figure 8(c) shows the effect of reducing the duty cycle from 50 to 25% when operating in constant-average-current mode. In this case, the peak current changes inversely to the duty cycle, increasing in value to maintain the same average current delivered as before but in shorter pulses.

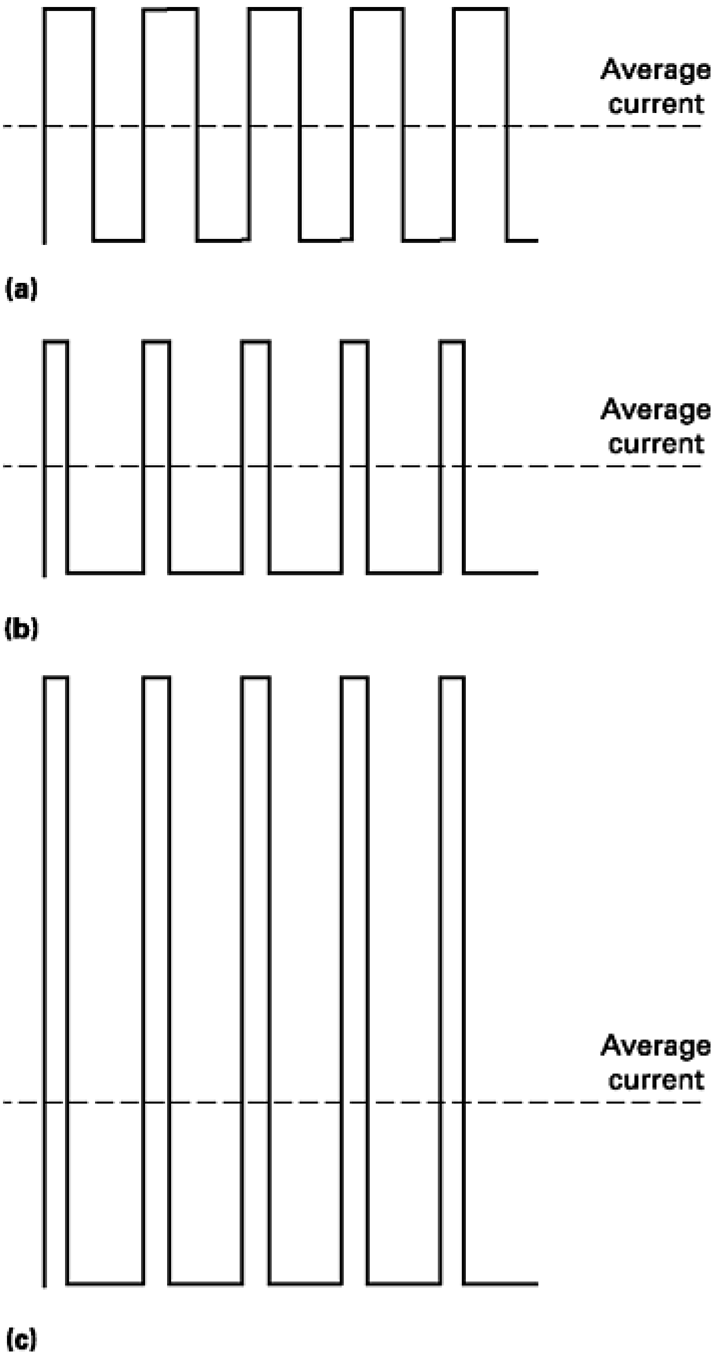

Fig. 8 Effect of changes in the duty cycle on constant-average-current and constant-voltage pulsed-current plating. (a) 50% duty cycle, with average current 50% of the peak value. (b) Duty cycle reduced to 25% in constant-voltage mode; average current drops with duty cycle. (c) Duty cycle reduced to 25% in constant-current mode; the peak current changes inversely to the duty cycle.

Although a change in frequency also changes the pulse width, it does not effect either peak or average current, regardless of output mode (Fig. 9). Unlike conventional plating rectifiers, which are rated by average current capacity (ignoring the ripple), modulated periodic reverse pulse units are normally rated by their peak current capacity. Because both peak and average current values are intrinsic to modulated power pattern plating, both output capacities must be considered. Depending on the internal circuitry of the unit, the average current output capacity of some models can be as low as 25 or 30% of the peak capacity. With such a low value for average current, the rated peak current output would be attained even at average current capacity only if a duty cycle as low as 25 or 30% was used. Attempting to push average current up would drastically shorten the life of the unit. Experience has shown that effective duty cycles are usually not less than 50% (although they can be as low as 10% for pure precious metals), and most units are designed to deliver an average current capacity of 50 to 60% of the peak current capacity rating. However, any desired duty cycle can be used or specified, but the operator must keep in mind that the average current is the percentage (duty cycle) of the peak rating.

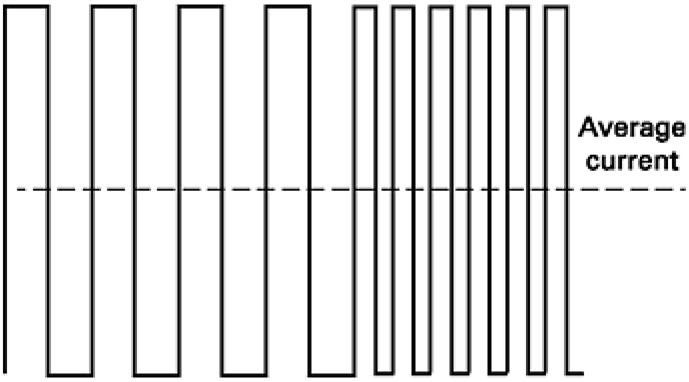

Fig. 9 Effect of change of frequency on current pattern in pulsed-current plating. Only pulse width is altered; peak current, average current, and duty cycle remain constant.

Electroforming

Glenn Malone, Electroformed Nickel, Inc.; Myron E. Browning, Matrix Technologies

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Introduction

ELECTROFORMING is the process by which articles or shapes can be exactly reproduced by electrodeposition on a mandrel or form that is later removed, leaving a precise duplicate of the original. In certain applications, the mandrel is designed to remain as an integral part of the final electroformed object. Electroforms themselves may be used as parents or masters, usually with special passivating treatments so the secondary electroform can be easily removed. The same or similar electrodeposition additives as those used for electroplating are required for electroforming to control deposit stress, grain size, and other resultant mechanical properties in order to produce high-quality electroforms.

Early Applications

Electroforming was developed by a Prof. Jacobi of the Academy of Sciences in St. Petersburg, Russia in 1838 while working with an engraved copper printing plate. While Prof. Jacobi had much difficulty in trying to separate the replicated layer, he did note that once it was released the copper piece gave a perfect match of the original.

Prof. Boettger of Germany used nickel plating in the 1840s to produce exacting replicates of art objects by the electroforming process. Electroformed articles, including sculpture, bas-reliefs, and statues from nickel, iron, or copper were produced prior to 1870. Of special interest were the huge electroformed street lamps found in downtown Paris, the production of which might be considered an enormous world-record accomplishment for electrodeposition. Iron electroforming had early applications in the duplication of printing plates for coinage and currency because of its facility to produce the highest accuracy in copying engraved masters.

Modern Applications

Today, the electroforming industry sees a number of high-tech uses for nickel, copper, iron, and alloy deposits to electrofabricate exceedingly important components such as the main combustion chamber for the Space Shuttle, heart pump components, body joint implants (prosthetic devices), high-precision optical scanners and holographic masters (for credit cards, etc.), and recording masters. Fabrication of duplicating plates such as electrotypes, video disc stampers, and currency embossing plates is manufacturing technology of today that employs electroforming. High-precision parts such as molds and dies, where tolerances of internal surfaces are critical, are pieces for which electroforming can be used advantageously. Optical memory disc mold cavities, including those for compact discs (CD and video discs) rely on the virtually perfect surface reproduction found with the electroforming process. The average optical disc requires impressions having a mean diameter of about 0.2 μm, which is well within the range of the electroforming processes practiced today. One of the most widely used applications today is nickel disc mold electroforming.

Examples of electroforming applications are almost limitless, but a few of the more exacting examples are:

- Delicate, thin-wall components such as lightweight heat or cold shields for aerospace applications, hypodermic needles, foil, fine-mesh screen, and seamless tubing
- Parts that would be difficult to make by any other means, such as electronic waveguides, regeneratively cooled thrust chambers for rocket engines, musical instruments, Pitot tubes, surface roughness gages, and complex metal bellows
- Electroform joining (cold welding) of dissimilar metals that are difficult, if not impossible, to join by thermal means

Electroforming provides unique production advantages for precision operation in the textile, medical, aerospace, communication, electronics, photocopying, automotive, and computer industries, and a number of other industries and is used in the manufacturing of items such as textile printing screens, molds and dies, mesh products, bellows, compact disc stampers, radar wave guides, and optical components.

Electroforming Determinants

Once the conceptual design for a part or component is developed, it is necessary to determine the fabrication process that best meets the functional requirements of the hardware with least cost impact. The following advantages of electroforming might be weighed:

- Parts can be mass produced with identical tolerances from one part to the next, provided that mandrels can be made with adequate replication.
- Fine detail reproduction is unmatched by any other method of mass fabrication. Examples are the electroforming of microgroove masters and stampers for the record and compact disc industries, surface roughness standards, and masters and stampers for holographic image reproduction.
- Mechanical properties of electroformed articles can be varied over a wide range by selecting a suitable plating electrolyte and adjusting operating conditions. In some instances properties can be created in electroformed metals that are difficult, if not impossible, to duplicate in wrought counterparts.
- Some shapes, particularly those with complex internal surfaces or passages, cannot be made by any other method without excessive machining costs and scrap losses. These shapes are often easily electroformed. Examples of such hardware are regeneratively cooled thrust chambers and waveguides with compound curves.
- Gearing up to high-volume production is relatively easy in many electroforming applications. For example, a number of first-generation positive replicas can be made from which a large number of second-generation negatives can be electroformed. Such technology lends itself to many molds, stamping devices, and optical surfaces requiring volume production.
- The size and thickness of parts electroformed is not limited. Larger size can be accommodated by increasing the tank volume in which the electrolyte is contained. Thickness may vary from micrometers, as in foils, to one or more centimeters, as is common in rocket thrust chamber shells.
- Without the use of thermal joining techniques, metal layers can be applied by electroforming to provide sandwich composites having a variety of functional properties. Waveguides having an inner silver electroformed layer for high electrical conductivity and an outer electroformed structural layer of copper, nickel, nickel-cobalt, or other electrodepositable alloys are examples.

There are also some disadvantages of electroforming that must be considered, such as:

- Electroforming is generally an expensive manufacturing method and is chosen when other methods are more expensive or impractical to produce the desired hardware.

- Thick electroforming is very time-consuming. Some deposits require days, or even weeks, to produce the desired thickness. However, unlike precision machining, which is also very time-consuming, electroforming is not labor-intensive once the deposition process is started.
- Design limitations exist in that deep or narrow recesses and sharp angles cause problems. Sudden and severe change in cross section or wall thickness must be avoided unless subsequent machining can be permitted.
- Most electrodeposits have some degree of stress in the as-deposited condition that may cause distortion after the mandrel is separated. Stress relieving and special attention to electrolyte chemistries and operating parameters can lessen this problem.
- Any degradation in the mandrel surface quality will be reproduced in the electroform made from it.

The Electroforming Process

Electroforming is very similar to conventional electroplating as far as facilities and electrolytes are concerned. However, the controls are more stringent, because the process consumes much more time and the product must be mechanically sound and have low internal stress for dimensional acceptance. With long deposition times, high current densities at edges and surfaces closer to the anodes result in significant buildup, leading to nodules and uncontrolled growth. This results in further current density variations that can seriously affect the mechanical properties of the deposit.

In electroforming nickel, cobalt, or iron there is significant hydrogen codeposition that, if not removed, causes pits in the deposit surface. Pumping filtered electrolyte through sprays over the surfaces being electroformed will minimize the problem and aid in maintaining a smooth deposit. Areas of high current density showing excessive and rough buildup can be corrected by using nonconducting shields as baffles to improve the current distribution. Where recessed areas exist, low current density will be experienced. Undesired trace metal impurities will codeposit in such locales, leading to inferior mechanical properties and surface appearance. Auxiliary or bipolar anodes may be necessary to overcome the low-current problem.

Electroforming solutions may be used with one or more additives to control stress, brightness, leveling (smoothness), and microstructure. When mechanical properties (including high ductility) or good electrical or thermal conductivity are important in the deposit, it is advisable to use nonadditive electrolytes. Because most additives are organic compounds, they are subject to decomposition if the deposit is subjected to elevated temperatures.

Stress-reducing agents are often used in nickel, iron, and cobalt plating baths to produce neutral or compressive residual stresses. Such agents are usually grain-refining compounds also. These deposits are generally harder, have higher yield strength, and exhibit less ductility than conventional deposits of the same metal. Advantages in neutral or compressively stressed deposits are ease of removal of electroforms from mandrels and inhibition of growth of cracks in deposits should they occur from impact. A problem with stress reducers in nickel is that sulfur codeposits form when the agent reacts at the cathode, because most stress reducers contain sulfur. Brazing or welding such deposits causes sulfur to react with nickel to form a nickel sulfide liquidus in the range of 483 °C (901 °F) to about 650 °C (1200 °F). This leads to the effect known as "hot shortness" experienced in wrought nickels. Such deposits can be alloyed with as little as 1500 ppm Mg to counter the problem.

Copper Electroforming. Acid sulfate electrolytes are the industry standard for copper electroforming. Additives are usually employed for grain refining, leveling, and brightening. The mechanical property improvements achieved are mostly a result of grain refining. Organic compounds capable of reducing copper oxides at the cathode may also be used to produce an oxygen-free, high-conductivity copper equivalent (<10 ppm oxygen). Decomposition products from copper bath additives will codeposit to degrade ductility. Without additives, acid sulfate baths produce copper with grain size increasing proportionally to deposit thickness. Intergranular voids are created that seriously degrade mechanical properties. A plating technique known as periodic current reversal will promote deposition of a copper deposit having uniform grain size and excellent mechanical properties for thicknesses of 0.5 cm (0.2 in.) or greater. This procedure requires plating in a conventional direction for a given period of time, followed by a reversal of current direction for a lesser period of time. Although the process results in a slow rate of deposition, the benefits of good mechanical properties, relatively smooth deposit surfaces, and ability to plate dense, thick deposits make this technique most useful.

Mandrel Types and Selection

Mandrels are either permanent or expendable. Permanent mandrels are usually metallic, but they can also be made of a conductive plastic. They can be used repeatedly until surface wear or scratching renders them useless. The most widely used permanent mandrels are made of metals that are resistant to adherent bonding by the metal being electroformed. The 300-series stainless steels are the preferred materials for permanent mandrels because of the naturally passive surfaces. Substrates such as copper, brass, or steel may also be used, but these must be plated with chromium to provide a passive surface for ease of separation. It is also possible to use copper or brass for engravure mandrels if they are chemically passivated to prevent electroform bonding. Nickel is frequently employed for producing multiple first-generation replicas for mass production of second-generation electroforms. Adherence on nickel is unpredictable, so it is advisable to passivate the surfaces chemically.

Plastics are suitable for permanent mandrels where flat electroforms are involved and separation is relatively simple. Such mandrels are made conductive by the silver reduction method (Ref 1) or by use of silver-filled paint. Plastic mandrels are often used for the electroforming of Fresnel lenses. Glass plates can also be used as permanent mandrels containing holographic imagery.

Expendable mandrels may consist of cast fusible metals, plaster, plastics, waxes, soluble metals, or wood. Fusible metals are commonly alloys of tin, lead, bismuth, antimony, and cadmium. Aluminum is a popular expendable mandrel material because it is easily machined and polished to close surface and dimensional tolerances. It is also easy to dissolve in caustic solutions.

Reference cited in this section

1. H. Narcus, *Metallizing of Plastics,* Reinhold Publishing Company, 1960

Mandrel Design and Preparation

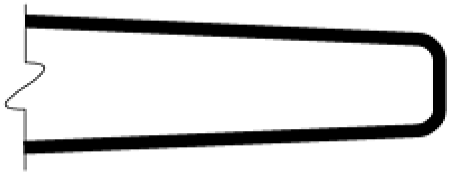
Mandrels may be made to reproduce accurately external or internal surfaces. The reproduced surface will be precisely the same as the surface upon which plating is initiated. The final plated surface will be rougher as the plated thickness increases. Design features of importance are avoidance of deep grooves or recesses, avoidance of sharp internal angles, and maintenance of liberal radii on corners. Figure 1 illustrates mandrel design considerations that should be followed.

Electrodeposited metal builds up on outside corners and thins out on inside corners, a. Breaking sharp corners and providing fillets, b, minimizes variations in metal deposit thickrness.

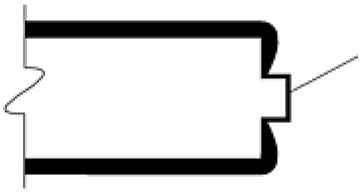
Recesses should be wider than deep. It is difficult and sometimes impossible to electrodeposit into deep, narrow recesses.

Use fillets at least equal to metal deposit thickness for strong inside corners.

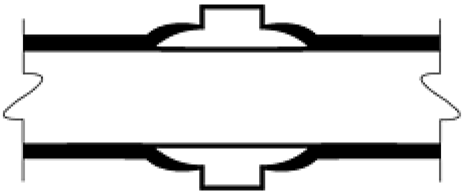
Holes can be "spotted" for subsequent drilling by providing depressions in pattern.



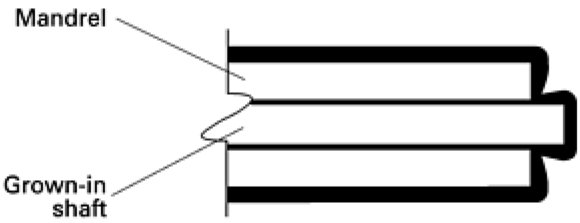
When feasible provide slight taper (0.001 in. per ft) to aid mandrel removal.



Eliminate drilling and reaming operations by providing masked or nonconductive studs on pattern. Hole diameters can be held to ±0.0002 in. and have excellent surface finish.



Flanges and bosses should fit tightly and be flared or tapered to mandrel diameter.



Extend internal piece beyond end of surrounding part to assure deposition on sides as well as end of internal "grow-in" piece. This provision assures bonding of internal shaft to outside cylinder.

Fig. 1 Factors to consider in electroforming mandrel design. Source: Ref 2

Permanent mandrels for electroforming concentric shapes must be designed with a draft or taper to permit removal of the mandrel without damaging the electrodeposit or the mandrel. If this is not possible, expendable mandrels must be considered. ASTM B 450 provides more guidelines in the design of electroformed articles (Ref 3). Preparation of mandrels for electroforming is detailed in ASTM B 431 (Ref 4). Special design considerations are often given to permanent mandrels being developed for complex parts that are to be produced in mass quantities or are of a complex nature, requiring speedy release from the mandrel. In these cases, knockout blocks or key release sections are designed into the mold, mandrel, or matrix to ensure quick and positive release and multiple uses of the master form.

References cited in this section

2. A. Squitero, Designing Electroformed Parts, *Machine Design,* 9 May 1963
3. ASTM B 450, "Standard Practice for Engineering Design of Electroformed Articles," ASTM
4. ASTM B 431, "Standard Practice for Processing of Mandrels for Electroforming," ASTM

Electroforming Solutions and Operating Variables

Nickel Electroforming Solutions. Nickel, the most commonly electroformed metal, is plated from Watts, fluoborate, and sulfamate solutions. The last is the most widely used due to lower stresses in the deposits and ease of operation. Nickel is deposited from most baths with moderate to high tensile stress. If uncontrolled, this stress can make removal of the mandrel difficult, can result in distorted parts after mandrel separation, and can even result in deposit cracking. In general, the chloride-free sulfamate bath produces the lowest internal stresses of all the nickel baths. Typical nickel sulfamate electrolyte compositions, operating conditions, and deposit mechanical properties are shown in Table 1. Effects of changes in operating variables on mechanical properties of nickel sulfamate deposits are described in Table 2. Similar information for all commonly used nickel electroforming baths is given in ASTM B 503 (Ref 5).

Table 1 Nickel electroforming solutions and selected properties of the deposits

Parameter	Watts nickel	Nickel sulfamate
Electrolyte composition, g/L (oz/gal)	$NiSO_4 \cdot 6H_2O$--225-300 (30-40)	$Ni(SO_3NH_2)_2$--315-450 (42-60)
	$NiCl_2 \cdot 6H_2O$--37.5-52.5 (5-7)	H_3BO_3--30-45 (4-6)
	H_3BO_3--30-45 (4-6)	$NiCl_2 \cdot 6H_2O$--0-22.5 (0-3)
Operating conditions		
Temperature, °C (°F)	44-66 (115-150)	32-60 (90-140)
Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2 (A/ft^2)	270-1075 (25-100)	50-3225 (5-300)
Anodes	Soluble nickel	Soluble nickel
pH	3.0-4.2	3.5-4.5
Mechanical properties		

Tensile strength, MPa (ksi)	345-482 (50-70)	410-620 (60-90)
Elongation, %	15-25	10-25
Hardness, HV_{100}	130-200	170-230
Internal tensile stress, MPa (ksi)	125-186 (18-27)	0-55 (0-8)

Table 2 Variables affecting mechanical properties of deposits from nickel sulfamate electrolytes

Property	Operational effects	Solution composition effects
Tensile strength	Decreases with increasing temperature to 49 °C, then increases slowly with further temperature increase. Increases with increasing pH. Decreases with increasing current density.	Decreases slightly with increasing nickel content.
Elongation	Decreases as the temperature varies in either direction from 43 °C. Decreases with increasing pH. Increases moderately with increasing current density.	Increases slightly with increasing nickel content. Increases slightly with increasing chloride content.
Hardness	Increases with increasing temperature within operating range suggested. Increases with increasing solution pH.Reaches a minimum at about 13 A/dm^2.	Decreases slightly with increasing concentration of nickel ion. Decreases slightly with increasing chloride content.
Internal stress	Decreases with increasing solution temperature. Reaches a minimum at pH 4.0-4.2. Increases with increasing current density.	Relatively independent of variation in nickel ion content within range. Increases significantly with increasing chloride content.

Copper electroforming solutions of significance are the acid sulfate and fluoborate baths. Table 3 lists typical compositions, operating conditions, and mechanical properties for these baths. Changes in operating variables will affect mechanical properties of copper sulfate deposits, as noted in Table 4. Similar information for effects of variable changes on copper fluoborate deposits are found in ASTM B 503 (Ref 5).

Table 3 Copper electroforming solutions and selected properties of deposits

Parameter	Copper sulfate	Copper fluoborate
Electrolyte composition, g/L (oz/gal)	$CuSO_4 \cdot 5H_2O$--210-240 (28-32)	$Cu(BF_4)_2$--225-450 (30-60)
	H_2SO_4--52-75 (7-10)	HBF_4--To maintain pH at 0.15-1.5
Operating conditions		
Temperature, °C (°F)	21-32 (70-90)	21-54 (70-129)

Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2 (A/ft^2)	1-10 (9.3-93)	8-44 (75-410)
Anodes	Oxygen-free, high-conductivity copper or phosphorized copper	Soluble copper
Mechanical properties		
Tensile strength, MPa (ksi)	205-380 (30-55)	140-345 (20-50)
Elongation, %	15-25	5-25
Hardness, HV_{100}	45-70	40-80
Internal tensile stress, MPa (ksi)	0-10 (0-1.45)	0-105 (0-15)

Table 4 Variables affecting mechanical properties of deposits from acid copper sulfate electrolytes

Property	**Operational effects**	**Solution composition effects**
Tensile strength	Decreases slightly with increasing solution temperature. Increases significantly with increase in cathode current density.	Relatively independent of changes in copper sulfate concentration within the range suggested. Relatively independent of changes in sulfuric acid concentration within the range suggested.
Elongation	Decreases with increasing solution temperature. Increases slightly with increasing cathode current density.	High acid concentrations, particularly with low copper sulfate concentration, tend to reduce elongation slightly.
Hardness	Decreases slightly with increasing solution temperature. Relatively independent of change in cathode current density.	Relatively independent of copper sulfate concentration. Increases slightly with increasing acid concentration.
Internal stress	Increases with increasing solution temperature. Increases with increasing cathode current density.	Relatively independent of copper sulfate concentration. Decreases very slightly with increasing acid concentration.

Iron Electroforming Solutions. Iron electroforming, while not in major industrial production today, is technically usable if precautions are followed. Three types of electroforming baths exist as slightly acidic systems: sulfate, fluoborate, and sulfamate systems. A fourth system is the highly acidic chloride system, which uses ferrous chloride/calcium chloride operating between 88 and 99 °C (190 and 210 °F). Table 5 presents condensed details of the four baths and primary operating conditions. Except for deposits from the chloride bath, all other baths produce iron deposits brittle in nature and not usable without special thermal treatment, stress-reducing additives, or backup deposits to protect the brittle nature of the iron films. The chloride deposits can be best used with a postplating heat treatment of 260 °C (500 °F) or above to ensure ductility.

Table 5 Iron electroforming solutions and operating conditions

Parameter	**Value**
Chloride bath	
Ferrous chloride (dihydrate), g/L (oz/gal)	300-450 (40-60)
Calcium chloride, g/L (oz/gal)	150-185 (20-25)
Temperature, °C (°F)	90-99 (190-210)
pH (HCl)	0.2-1.8
Current density, A/dm^2 (A/ft^2)	
Without agitation	2-8.5 (20-80)
With agitation	2-21 (20-200)
Sulfate bath	
Ferrous sulfate, g/L (oz/gal)	240 (32)
pH	2.8-3.5
Temperature, °C (°F)	32-65 (90-150)
Current density, max, A/dm^2 (A/ft^2)	
at 32 °C (90 °F)	4.3 (40)
at 65 °C (150 °F)	10 (100)
Surface tension, dynes/cm	40
Cathode agitation	Desirable
Fluoborate bath	
Iron fluoborate, g/L (oz/gal)	227 (30.3)

Metallic iron, g/L (oz/gal)	55.2 (7.37)
Sodium chloride, g/L (oz/gal)	10.0 (1.34)
Baumé, degrees, at 27 °C (80 °F)	19-21
pH (colorimetric)	3.0-3.4
Temperature, °C (°F)	57-63 (135-145)
Current density (cathode-average), A/dm^2 (A/ft^2)	2-10 (20-90)
Tank voltage, avg	2-6
Sulfamate bath	
Ferrous iron, g/L (oz/gal)	75 (10)
Ammonium sulfamate, g/L (oz/gal)	30-37 (4-5)
Sodium chloride, g/L (oz/gal)	37-45 (5-6)
Temperature, °C (°F)	50-60 (120-140)
Current density, A/dm^2 (A/ft^2)	5.4 (50)
pH	2.7-3.0

Reference cited in this section

5. ASTM B 503, "Standard Practice for Use of Copper and Nickel Electroplating Solutions for Electroforming," ASTM

Process Controls

Because of the exacting products desired during electroforming, the controls are apt to be more stringent. Controlling metal distribution, internal stress, nodular growth, and roughness are among the potential problems that are often found in electroforming. Some of these problems are handled by using various addition agents, but special attention is often required to monitor conditions during deposition. Other significant aspects of the electroforming process that demand special consideration include the following.

Metal distribution relates to nonuniform deposition due to changes in mandrel configuration, throwing power of the bath selected, placement in the plating tank, and other features of the deposits being produced. Attempting to retain the best properties of the metal being deposited and at the same time maintain excellent throwing power is most difficult. One can improve metal distribution by using proper racking designs, employing "thieves," "robbers," shields, or auxiliary or conforming anodes, and completely mapping out the electrical requirements of the mandrel. Computer software programs exist that aid in the design of cathode distribution systems.

Internal deposit stress is most important to control during, before, and after deposition. Before deposition it may develop within the mandrel, resulting in unwarranted partial liftoff of the electroform before it is complete. During deposition, symptoms of internal deposit stress are problems trying to separate the electroform from the mold, buckling or blistering of the deposits, and cracking of the deposit during deposition or while it is separated from the master. Most of these manifestations come from either the bath itself, impurities permitted in the bath (incomplete filtration), or lack of control of the additives needed for the bath. Careful monitoring of all operating conditions is also important for deposit stress control.

Roughness and "treeing" are conditions that may appear during electroforming if care is not taken. To minimize roughness, the electroformer must watch the filtration rates, because even small dirt particles can be the nucleation sites for rough deposits. Filtration rates may need to be as high as whole-solution-volume recycling once or more per hour. Other aids in preventing roughness include using positive pressure of an inch or so with filtered air, plus keeping the electroforming room in extra-clean condition.

The phenomenon of treeing occurs near the edges or corners of the mandrel or attachment areas. These can be minimized by the use of shields, improved racking, or "thieving" to prevent excess current in unwanted areas. Leveling agents and nodule suppressants may also be useful to reduce treeing. Often it becomes necessary to stop the electroforming, remove the part, and machine off the excess deposit. One must remember to reactivate the electroform when replacing it in the plating tank.

One other factor worthy of considering in minimizing roughness, pitting, burning, and sometimes treeing is to constantly check solution agitation, whether by air, mechanical, cathode rod, or other means. Make sure that no grease, wear particles, or other outside dirt enters the electroforming system by virtue of the agitation system.

Alloy Electroforming

Alloy electroforming using high-strength materials, such as nickel-cobalt, cobalt-tungsten, and even more complex alloys involving tungsten and the iron group metals, has made some inroads for special applications. Microfabrication of sensors, maskless jet systems, miniature computer components, and a host of newer devices rely on the properties of many electrodeposited alloys and the precision of electroforming to produce such items. Bath chemistries, deposition parameters (in some cases requiring pulse plating control), and fixturing are all very critical to control for optimal production of these advanced products.

Future Applications

Such developments as composition-modulated alloys, nanophase composites, nonaqueous plating baths, and advanced pulsed current controls are expected to open the field of electroforming to more complex and innovative applications.

Electroless Nickel Plating

Revised by Donald W. Baudrand, MacDermid Inc.

Introduction

ELECTROLESS NICKEL PLATING is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by hypophosphite, aminoborane, or borohydride compounds. Two other methods have been used commercially for plating nickel without electric current, including (1) immersion plating on steel from solutions of nickel chloride and boric acid at 70 °C (160 °F) and (2) decomposition of nickel carbonyl vapor at 180 °C (360 °F). Immersion deposits, however, are poorly adherent and nonprotective, while the decomposition of nickel carbonyl is expensive and hazardous. Accordingly, only electroless nickel plating has gained wide acceptance.

Since gaining commercial use in the 1950s, electroless nickel plating has grown rapidly and now is an established industrial process. Currently, hot acid hypophosphite-reduced baths are most frequently used to plate steel and other metals, whereas warm alkaline hypophosphite baths are used for plating plastics and nonmetals. Borohydride-reduced baths are also used to plate iron and copper alloys, especially in Europe.

Electroless nickel is an engineering coating, normally used because of excellent corrosion and wear resistance. Electroless nickel coatings are also frequently applied on aluminum to provide a solderable surface and are used with molds and dies to improve lubricity and part release. Because of these properties, electroless nickel coatings have found many applications, including those in petroleum, chemicals, plastics, optics, printing, mining, aerospace, nuclear, automotive, electronics, computers, textiles, paper, and food machinery (Ref 1). Some advantages and limitations of electroless nickel coatings include:

Advantages

- Good resistance to corrosion and wear
- Excellent uniformity
- Solderability and brazeability
- Low labor costs

Limitations

- Higher chemical cost than electroplating
- Brittleness
- Poor welding characteristics due to contamination of nickel plate with nickel phosphorus deposits
- Need to copper strike plate alloys containing significant amounts of lead, tin, cadmium, and zinc before electroless nickel can be applied
- Slower plating rate, as compared to electrolytic methods

Reference

1. K. Parker, "Recent Advances in Electroless Nickel Deposits, 8th Interfinish Conference," 1972 (Basel)

Bath Composition and Characteristics

Electroless nickel coatings are produced by the controlled chemical reduction of nickel ions onto a catalytic surface. The deposit itself is catalytic to reduction, and the reaction continues as long as the surface remains in contact with the electroless nickel solution. Because the deposit is applied without an electric current, its thickness is uniform on all areas of an article in contact with fresh solution.

Electroless nickel solutions are blends of different chemicals, each performing an important function. Electroless nickel solutions contain:

- A source of nickel, usually nickel sulfate
- A reducing agent to supply electrons for the reduction of nickel
- Energy (heat)
- Complexing agents (chelators) to control the free nickel available to the reaction
- Buffering agents to resist the pH changes caused by the hydrogen generated during deposition
- Accelerators (exultants) to help increase the speed of the reaction
- Inhibitors (stabilizers) to help control reduction
- Reaction byproducts

The characteristics of an electroless nickel bath and its deposit are determined by the composition of these components.

Reducing Agents

A number of different reducing agents have been used in preparing electroless nickel baths, including sodium hypophosphite, aminoboranes, sodium borohydride, and hydrazine.

Sodium Hypophosphite Baths. The majority of electroless nickel used commercially is deposited from solutions reduced with sodium hypophosphite. The principal advantages of these solutions over those reduced with boron compounds or hydrazine include lower cost, greater ease of control, and better corrosion resistance of the deposit.

Several mechanisms have been proposed for the chemical reactions that occur in hypophosphite-reduced electroless nickel plating solutions. The most widely accepted mechanism is illustrated by the following equations:

$$(H_2PO_2)^- + H_2O \frac{Catalyst}{Heat} \rightarrow H^+ + (HPO_3)^{-2} + 2H_{abs} \qquad \textbf{(Eq 1)}$$

$$\mathrm{Ni_2 + 2H_{abs} \rightarrow Ni + 2H^+} \qquad \textbf{(Eq 2)}$$

$$\mathrm{(H_2PO_2)^- + H_{abs} \rightarrow H_2O + OH^- + P} \qquad \textbf{(Eq 3)}$$

$$\mathrm{(H_2PO_2)^- + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2} \qquad \textbf{(Eq 4)}$$

In the presence of a catalytic surface and sufficient energy, hypophosphite ions are oxidized to orthophosphite. A portion of the hydrogen given off is absorbed onto the catalytic surface (Eq 1). Nickel at the surface of the catalyst is then reduced by the absorbed active hydrogen (Eq 2). Simultaneously, some of the absorbed hydrogen reduces a small amount of the hypophosphite at the catalytic surface to water, hydroxyl ion, and phosphorus (Eq 3). Most of the hypophosphite present is catalytically oxidized to orthophosphite and gaseous hydrogen (Eq 4) independently of the deposition of nickel and phosphorus, causing the low efficiency of electroless nickel solutions. Usually 5 kg (10 lb) of sodium hypophosphite is required to reduce 1 kg (2 lb) of nickel, for an average efficiency of 37% (Ref 2, 3).

Early electroless nickel formulations were ammoniacal and operated at high pH. Later, acid solutions were found to have several advantages over alkaline solutions. Among these are higher plating rate, better stability, greater ease of control, and improved deposit corrosion resistance. Accordingly, most hypophosphite reduced electroless nickel solutions are operated between 4 and 5.5 pH. Compositions for alkaline and acid plating solutions are listed in Table 1 (Ref 2, 3, 4, 5).

Table 1 Hypophosphite-reduced electroless nickel plating solutions

Constituent or condition	**Alkaline**			**Acid**		
	Bath 1	**Bath 2**	**Bath 3**	**Bath 4**	**Bath 5**	**Bath 6**
Composition						
Nickel chloride, g/L (oz/gal)	45 (6)	30 (4)	30 (4)	. . .	. . .	. . .
Nickel sulfate, g/L (oz/gal)	. . .	. . .	. . .	21 (2.8)	34 (4.5)	45 (6)
Sodium hypophosphite, g/L (oz/gal)	11 (1.5)	10 (1.3)	10 (1.3)	24 (3.2)	35 (4.7)	10 (1.3)
Ammonium chloride, g/L (oz/gal)	50 (6.7)	50 (6.7)	. . .	. . .	. . .	. . .
Sodium citrate, g/L (oz/gal)	100 (13.3)	. . .	. . .	. . .	. . .	. . .

Ammonium citrate, g/L (oz/gal)	. . .	65 (8.6)	. . .	. . .	. . .	. . .
Ammonium hydroxide	To pH	To pH	. . .	. . .	. . .	. . .
Lactic acid, g/L (oz/gal)	. . .	. . .	. . .	28 (3.7)	. . .	. . .
Malic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	35 (4.7)	. . .
Amino-acetic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	. . .	40 (5.3)
Sodium hydroxyacetate, g/L (oz/gal)	. . .	. . .	10 (1.3)	. . .	. . .	. . .
Propionic acid, g/L (oz/gal)	. . .	. . .	. . .	2.2 (0.3)	. . .	. . .
Acetic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	. . .	10 (1.3)
Succinic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	10 (1.3)	. . .
Lead, ppm	. . .	. . .	. . .	1	. . .	. . .
Thiourea, ppm	. . .	. . .	. . .	. . .	1	. . .
Operating conditions						
pH	8.5-10	8-10	4-6	4.3-4.6	4.5-5.5	4.5-5.5
Temperature, °C (°F)	90-95 (195-205)	90-95 (195-205)	88-95 (190-205)	88-95 (190-205)	88-95 (190-205)	88-95 (190-205)
Plating rate, μm/h (mil/h)	10 (0.4)	8 (0.3)	10 (0.4)	25 (1)	25 (1)	25 (1)

Aminoborane Baths. The use of aminoboranes in commercial electroless nickel plating solutions has been limited to two compounds: N-dimethylamine borane (DMAB)-$(CH_3)_2$ $NHBH_3$, and H-diethylamine borane (DEAB)--$(C_2H_5)_2$ $NHBH_3$. DEAB is used primarily in European facilities, whereas DMAB is used principally in the United States. DMAB is readily soluble in aqueous systems. DEAB must be mixed with a short chain aliphatic alcohol, such as ethanol, before it can be dissolved in the plating solution.

Aminoborane-reduced electroless nickel solutions have been formulated over wide pH ranges, although they are usually operated between 6 and 9 pH. Operating temperatures for these baths range from 50 to 80 °C (120 to 180 °F), but they can be used at temperatures as low as 30 °C (90 °F). Accordingly, aminoborane baths are very useful for plating plastics and nonmetals, which is their primary application. The rate of deposition varies with pH and temperature, but is usually 7 to 12 μm/h (0.3 to 0.5 mil/h). The boron content of the deposit from these baths varies between 0.4 and 5%. Compositions and operating conditions for aminoborane baths are listed in Table 2 (Ref 2, 5, 6).

Table 2 Aminoborane- and borohydride-reduced electroless nickel plating solutions

Constituent or condition	Aminoborane		Borohydride	
	Bath 7	Bath 8	Bath 9	Bath 10
Composition				
Nickel chloride, g/L (oz/gal)	30 (4)	24-48 (3.2-6.4)	. . .	20 (2.7)
Nickel sulfate, g/L (oz/gal)	. . .	. . .	50 (6.7)	. . .
DMAB, g/L (oz/gal)	. . .	3-4.8 (0.4-0.64)	3 (0.4)	. . .
DEAB, g/L (oz/gal)	3 (0.4)	. . .	. . .	. . .
Isopropanol, mL (fluid oz)	50 (1.7)	. . .	. . .	. . .
Sodium citrate, g/L (oz/gal)	10 (1.3)	. . .	. . .	. . .
Sodium succinate, g/L (oz/gal)	20 (2.7)	. . .	. . .	. . .
Potassium acetate, g/L (oz/gal)	. . .	18-37 (2.4-4.9)	. . .	. . .
Sodium pyrophosphate, g/L (oz/gal)	. . .	. . .	100 (13.3)	. . .
Sodium borohydride, g/L (oz/gal)	. . .	. . .	. . .	0.4 (0.05)
Sodium hydroxide, g/L (oz/gal)	. . .	. . .	. . .	90 (12)
Ethylene diamine, 98%, g/L (oz/gal)	. . .	. . .	. . .	90 (12)
Thallium sulfate, g/L (oz/gal)	. . .	. . .	. . .	0.4 (0.05)
Operating conditions				
pH	5-7	5.5	10	14
Temperature, °C (°F)	65 (150)	70 (160)	25 (77)	95 (205)
Plating rate, μm/h (mil/h)	7-12 (0.5)	7-12 (0.5)	. . .	15-20 (0.6-0.8)

Sodium Borohydride Baths. The borohydride ion is the most powerful reducing agent available for electroless nickel plating. Any water-soluble borohydride may be used, although sodium borohydride is preferred.

In acid or neutral solutions, hydrolysis of borohydride ions is very rapid. In the presence of nickel ions, nickel boride may form spontaneously. If the pH of the plating solution is maintained between 12 and 14, however, nickel boride formation is suppressed, and the reaction product is principally elemental nickel. One mol of sodium borohydride can reduce approximately one mol of nickel, so that the reduction of 1 kg (2 lb) of nickel requires 0.6 kg (1 lb) of sodium borohydride. Deposits from borohydride-reduced electroless nickel solutions contain 3 to 8 wt% B.

To prevent precipitation of nickel hydroxide, complexing agents, such as ethylene diamine, that are effective between 12 to 14 pH must be used. Such strong complexing agents, however, decrease the rate of deposition. At an operating temperature of 90 to 95 °C (195 to 205 °F), the plating rate of commercial baths is 25 to 30 μm/h (1 to 1.2 mil/h). Compositions of a borohydride-reduced electroless nickel bath are also shown in Table 2 (Ref 6).

During the course of reduction, the solution pH decreases, requiring constant additions of an alkali hydroxide. Spontaneous solution decomposition may occur if the bath pH is allowed to fall below 12. Because of the high operating pH, borohydride plating baths cannot be used for aluminum substrates (Ref 2, 5, 7).

Hydrazine Baths. Hydrazine has also been used to produce electroless nickel deposits. These baths operate at 90 to 95 °C (195 to 205 °F) and 10 to 11 pH. Their plating rate is approximately 12 μm/h (0.5 mil/h). Because of the instability of hydrazine at high temperatures, however, these baths tend to be very unstable and difficult to control.

Whereas the deposit from hydrazine-reduced solutions is 97 to 99% N, it does not have a metallic appearance. The deposit is brittle and highly stressed with poor corrosion resistance. The stress and brittleness are likely due to codeposition of small amounts of basic nickel salts, $Ni(OH)_2$, and nitrogen. Unlike hypophosphite- and boron-reduced nickels, hardness from a hydrazine-reduced electroless nickel has very little commercial use (Ref 2).

Energy

The amount of energy or heat present in an electroless nickel solution is one of the most important variables affecting coating deposition. In a plating bath, temperature is a measure of its energy content.

Temperature has a strong effect on the deposition rate of acid hypophosphite-reduced solutions. The rate of deposition is usually very low at temperatures below 65 °C (150 °F), but increases rapidly with increased temperature (Ref 5). This is illustrated in Fig. 1, which gives the results of tests conducted using bath 3 in Table 1 (Ref 7). The effect of temperature on deposition in boron-reduced solutions is similar. At temperatures above 100 °C (212 °F), electroless nickel solutions may decompose. Accordingly, the preferred operating range for most solutions is 85 to 95 °C (185 to 205 °F).

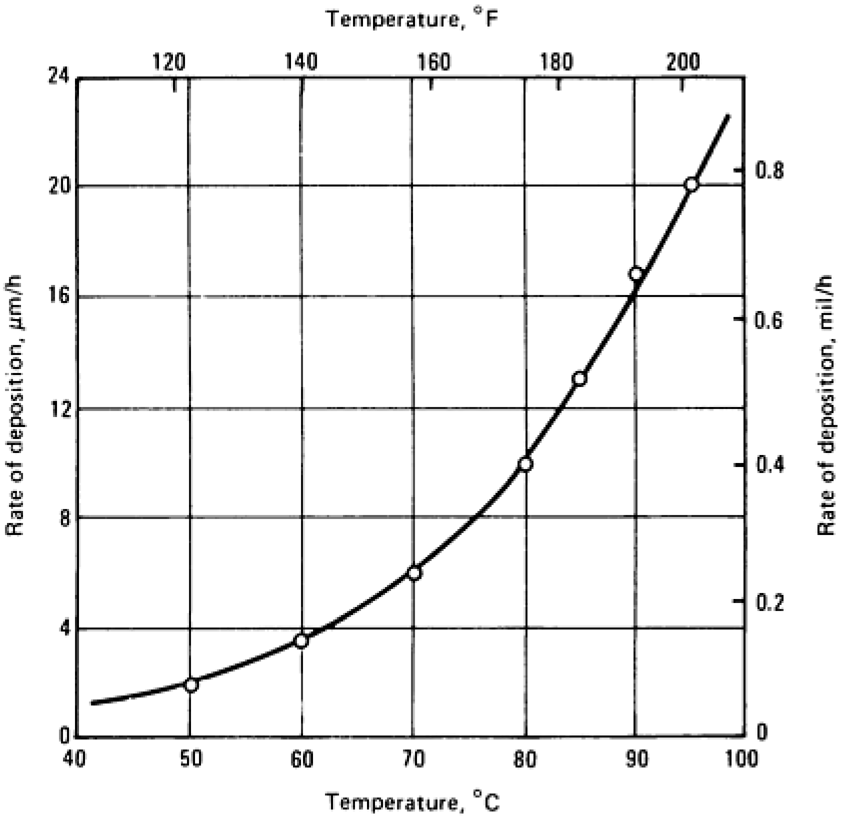


Fig. 1 Effect of solution temperature on the rate of deposition. Tests conducted on bath 3 at 5 pH

Complexing Agents

To avoid spontaneous decomposition of electroless nickel solutions and to control the reaction so that it occurs only on the catalytic surface, complexing agents are added. Complexing agents are organic acids or their salts, added to control the amount of free nickel available for reaction. They act to stabilize the solution and to retard the precipitation of nickel phosphite.

Complexing agents also buffer the plating solution and prevent its pH from decreasing too rapidly as hydrogen ions are produced by the reduction reaction. Ammonia, hydroxides, or carbonates, however, may also have to be added periodically to neutralize hydrogen.

Original electroless nickel solutions were made with the salts of glycolic, citric, or acetic acids. Later baths were prepared using other polydentate acids, including succinic, glutaric, lactic, propionic, and aminoacetic. The complexing ability of an individual acid or group of acids varies, but may be quantified by the amount of orthophosphite that can be held in solution without precipitation (Ref 2, 8). This is illustrated in Fig. 2, which shows the maximum solubility of orthophosphite in solutions complexed with citric and glycolic acids as a function of pH (Ref 9). The complexing agent used in the plating solution can also have a pronounced effect on the quality of the deposit, especially on its phosphorus content, internal stress, and porosity (Ref 8).

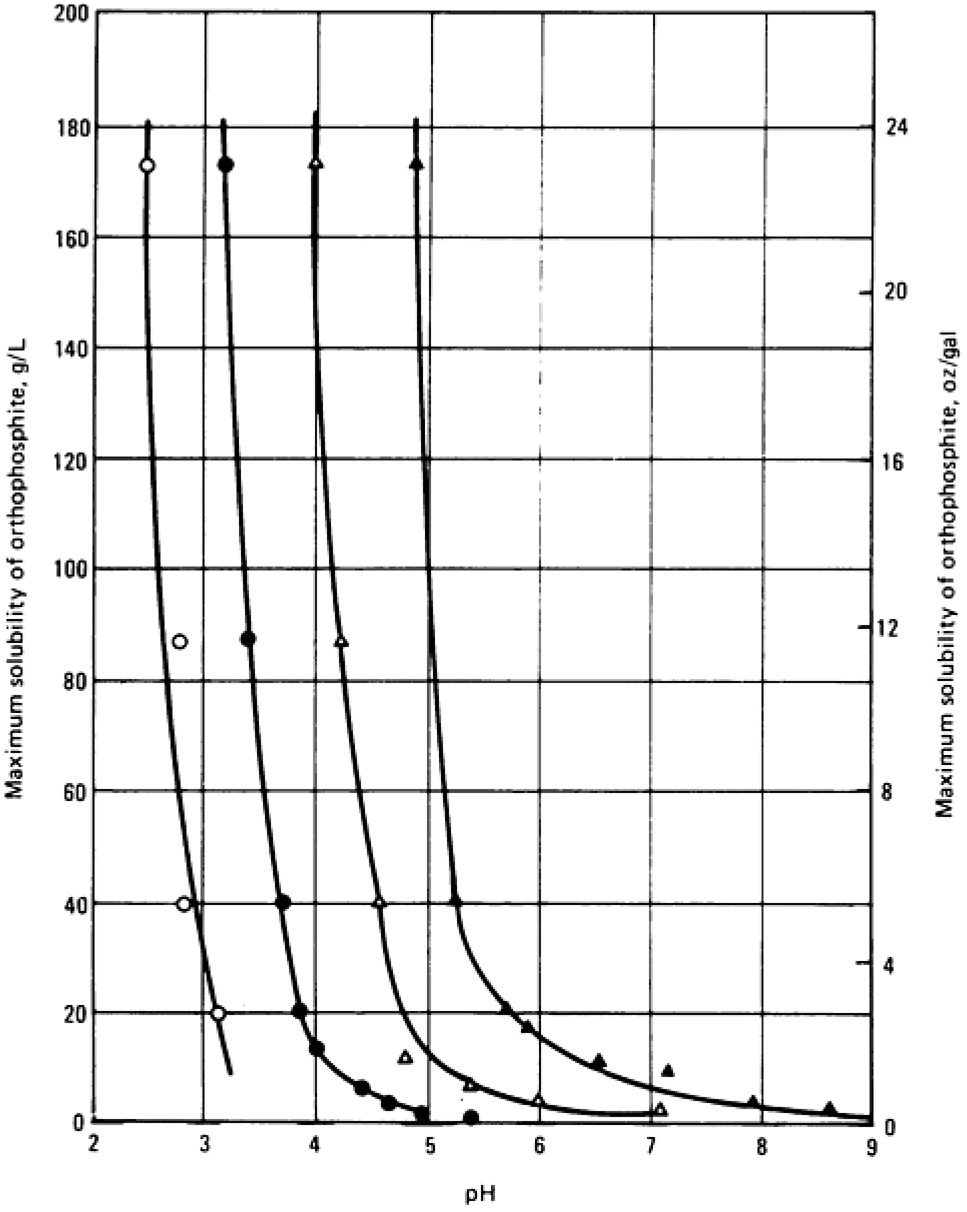


Fig. 2 Limits of solubility for orthophosphite in electroless nickel solutions. Solutions contain 30 g/L (4 oz/gal) nickel chloride ($NiCl_2$) and 10 g/L (1.3 oz/gal) sodium hypophosphite (NaH_2PO_2). d , without a complexing agent; •, with 15 g/L (2 oz/gal) citric acid; V , with 39 g/L (5.2 oz/gal) glycolic acid; ▲, with 78 g/L (10 oz/gal) glycolic acid.

Accelerators

Complexing agents reduce the speed of deposition and can cause the plating rate to become uneconomically slow. To overcome this, organic additives, called accelerators or exultants, are often added to the plating solution in small amounts. Accelerators are thought to function by loosening the bond between hydrogen and phosphorous atoms in the hypophosphite molecule, allowing it to be more easily removed and absorbed onto the catalytic surface. Accelerators activate the hypophosphite ion and speed the reaction shown in Eq 1 (Ref 2, 3). In hypophosphite-reduced solutions, succinic acid is the accelerator most frequently used. Other carbonic acids, soluble fluorides, and some solvents, however, have also been used (Ref 2). The effect of succinate additions upon deposition rate is illustrated in Fig. 3 (Ref 3).

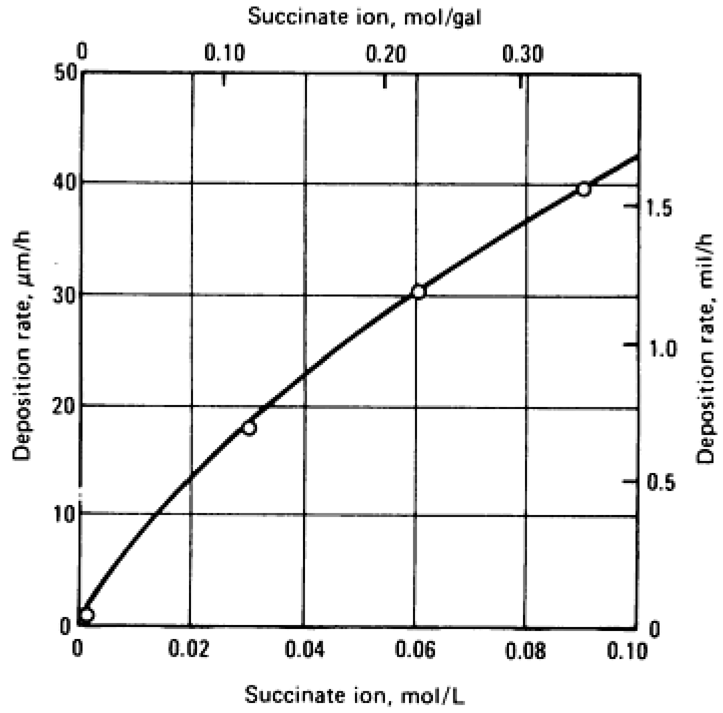


Fig. 3 Effect of succinate additions on the plating rate of an electroless nickel solution. Solutions contain 16 g/L (2.1 oz/gal) nickel chloride ($NiCl_2$) and 24 g/L (3.2 oz/gal) sodium hypophosphite (NaH_2PO_2). 5 g/L (0.7 oz/gal) ammonium hydroxide (NH_4OH) and 1 mg/L (4 mg/gal) lead at 5 pH and 95 °C (205 °F).

Inhibitors

The reduction reaction in an electroless nickel plating bath must be controlled so that deposition occurs at a predictable rate and only on the substrate to be plated. To accomplish this, inhibitors, also known as stabilizers, are added. Electroless nickel plating solutions can operate for hours or days without inhibitors, only to decompose unexpectedly. Decomposition is usually initiated by the presence of colloidal, solid particles in the solution. These particles may be the result of the presence of foreign matter (such as dust or blasting media), or may be generated in the bath as the concentration of orthophosphite exceeds its solubility limit. Whatever the source, the large surface area of the particles catalyzes reduction, leading to a self-accelerating chain reaction and decomposition. This is usually preceded by increased hydrogen evolution and the appearance of a finely divided black precipitate throughout the solution. This precipitate consists of nickel and either nickel phosphide or nickel boride.

Spontaneous decomposition can be controlled by adding trace amounts of catalytic inhibitors to the solution. These inhibitors are absorbed on any colloidal particles present in the solution and prevent the reduction of nickel on their surface. Traditionally, inhibitors used with hypophosphite-reduced electroless nickel have been of three types: sulfur compounds, such as thiourea; oxy anions, such as molybdates or iodates; and heavy metals, such as lead, bismuth, tin, or cadmium. More recently, organic compounds, including oleates and some unsaturated acids, have been used for some functional solutions. Organic sulfide, thio compounds, and metals, such as selenium and thallium, are used to inhibit aminoborane- and borohydride-reduced electroless nickel solutions.

The addition of inhibitors can have harmful as well as beneficial effects on the plating bath and its deposit. In small amounts, some inhibitors increase the rate of deposition and/or the brightness of the deposit; others, especially metals or sulfur compounds, increase internal stress and porosity and reduce ductility, thus reducing the ability of the coating to resist corrosion and wear (Ref 2, 3, 5).

The amount of inhibitor used is critical. The presence of only about 1 mg/L (4 mg/gal) of HS^- ion completely stops deposition, whereas at a concentration of 0.01 mg/L (0.04 mg/gal), this ion is an effective inhibitor. The effect of lead additions on a hypophosphite-reduced succinate bath at pH 4.6 and 95 °C (205 °F) is shown in Fig. 4 (Ref 3). The tests illustrated in Fig. 4 also showed that baths containing less than 0.1 mg/L (0.4 mg/gal) Pb^{2+} decomposed rapidly, whereas baths containing higher concentrations were stable. Excess inhibitor absorbs preferentially at sharp edges and corners, resulting in incomplete coverage (edge pull back) and porosity.

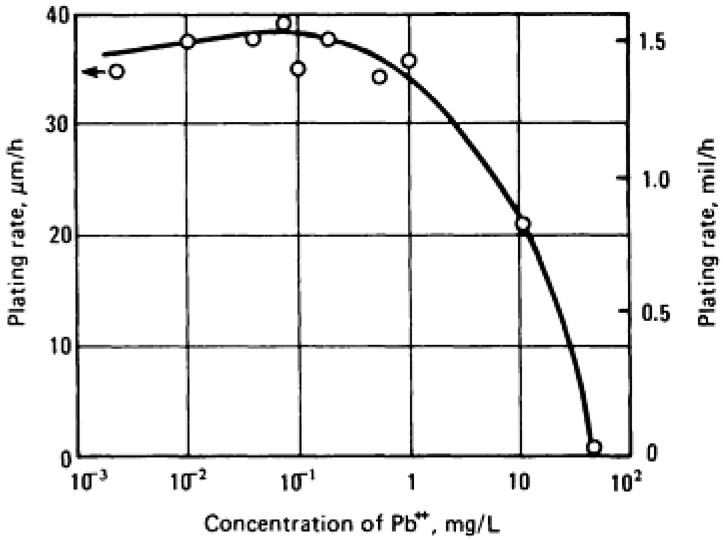


Fig. 4 Effect of lead additions on plating rate in a hypophosphite-reduced succinate-based bath. Bath at 4.6 pH and 95 °C (205 °F). Solutions containing less than 0.1 mg (0.4 mg/gal) Pb^{2+} were unstable.

Reaction Byproducts

During electroless nickel deposition, the byproducts of the reduction, orthophosphite or borate and hydrogen ions, as well as dissolved metals from the substrate accumulate in the solution. These can affect the performance of the plating bath.

Orthophosphite. As nickel is reduced, orthophosphite ion (HPO_3^{2-}) accumulates in the solution and at some point interferes with the reaction. As the concentration of orthophosphite increases, there is usually a small decrease in the deposition rate and a small increase in the phosphorus content of the deposit. Ultimately the accumulation of orthophosphite in the plating solution results in the precipitation of nickel phosphite, causing rough deposits and spontaneous decomposition. Orthophosphite ion also codeposits with nickel and phosphorus, creating a highly stressed, porous deposit.

The solubility of phosphite in the solution is increased when complexing agents, such as citric or glycolic acids, are added. This effect is shown in Fig. 2. However, the use of strong complexors, in other than limited quantities, tends to reduce the deposition rate and increase the porosity and brittleness of the deposit (Ref 8).

Borates. The accumulation of metaborate ion (BO_2^-) from the reduction of borohydride or of boric acid (H_3BO_3) from the reduction of aminoboranes has little effect on electroless nickel plating baths. Both borohydride and aminoborate baths have been operated through numerous regenerations with only a slight decrease in plating rate and without decomposing. With aminoborane-reduced solutions, the solubility of boric acid is probably increased by the presence of amine through the formation of a complex aminoborate (Ref 10).

Hydrogen ions (H^+), produced by the reduction reaction, cause the pH of the bath to decrease. The amount of hydrogen produced, however, depends on the reducing agent being used. Because they are less efficient, hypophosphite-reduced solutions tend to generate more hydrogen ions than those reduced with boron compounds.

The pH of the bath has a strong effect on both solution operation and the composition of the deposit. This is illustrated in Fig. 5, which shows the plating rate and deposit phosphorus content resulting from varying solution pH values in a bath containing 33 g/L (4.4 oz/gal) of nickel sulfate and 20 g/L (2.7 oz/gal) of sodium hypophosphite at 82 °C (180 °F) (Ref 11).

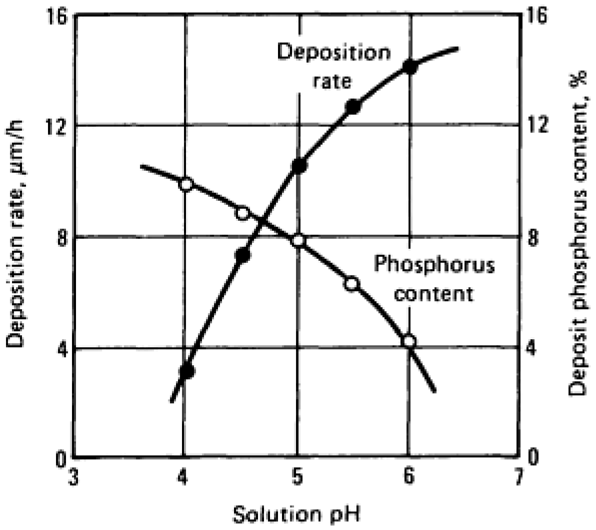


Fig. 5 Effect of solution pH on deposition rate and deposit phosphorus content

To retard pH changes and to help keep operating conditions and deposit properties constant, buffers are included in electroless nickel solutions. Some of the most frequently used buffers include acetate, propionate, and succinate salts. Additions of alkaline materials, such as hydroxide, carbonate solutions, or ammonia, are also required periodically to neutralize the acid formed during plating.

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating*, Portcullis Press, Redhill, England, 1979
3. G. Gutzeit, An Outline of the Chemistry Involved in the Process of Catalytic Nickel Deposition from Aqueous Solution, *Plat. Surf. Finish.*, Vol 46 (No. 10), 1959, p 1158
4. A. Brenner and G. Riddell, Deposition of Nickel and Cobalt by Chemical Reduction, *J. Res. Natl. Bur. Stand.*, Vol 39 (No. 11), 1947, p 385
5. G.O. Mallory, The Electroless Nickel Plating Bath, Electroless Nickel Conference, Cincinnati, Nov 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.*, Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating*, Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
8. G.O. Mallory, Influence of the Electroless Plating Bath on the Corrosion Resistance of the Deposits, *Plating*, Vol 61 (No. 11), 1974, p 1005
9. C.E. deMinjer and A. Brenner, Studies on Electroless Nickel Plating, *Plating*, Vol 44 (No. 12), 1957, p 1297
10. G.O. Mallory, The Electroless Nickel-Boron Plating Bath; Effects of Variables on Deposit Properties, *Plating*, Vol 58 (No. 4), 1971, p 319
11. C. Baldwin and T.E. Such, The Plating Rates and Physical Properties of Electroless Nickel/Phosphorus Alloy Deposits, *Trans. Inst. Met. Finish.*, Vol 46 (No. 2), 1968, p 73

Properties of Electroless Nickel-Phosphorus Coatings

Hypophosphite-reduced electroless nickel is an unusual engineering material, because of both its method of application and its unique properties. As applied, nickel-phosphorus coatings are uniform, hard, relatively brittle, lubricious, easily solderable, and highly corrosion resistant. They can be precipitation hardened to very high levels through the use of low-temperature treatments, producing wear resistance equal to that of commercial hard chromium coatings. This combination of properties makes the coating well suited for many severe applications and often allows it to be used in place of more expensive or less readily available alloys.

Structure. Hypophosphite-reduced electroless nickel is one of the very few metallic glasses used as an engineering material. Depending on the formulation of the plating solution, commercial coatings may contain 6 to 12% P dissolved in nickel, and as much as 0.25% of other elements. As applied, most of these coatings are amorphous; they have no crystal or phase structure. Their continuity, however, depends on their composition. Coatings containing more than 10% P and less than 0.05% impurities are typically continuous. A cross section of one of these coatings is shown in Fig. 6.

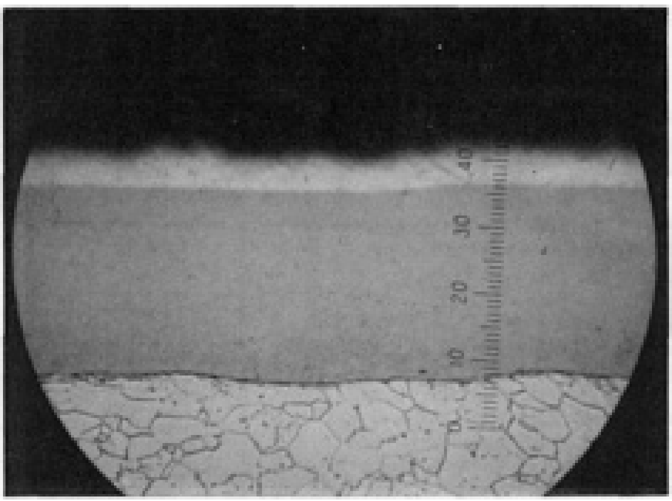


Fig. 6 Cross section of a 75 μm (3 mils) thick electroless nickel deposit. Contains approximately 10% phosphorus and less than 0.05% other elements. 400×

Coatings with lower phosphorus content, especially those applied from baths stabilized with heavy metals or sulfur compounds, are often porous. These deposits consist of columns of amorphous material separated by cracks and holes. The presence of such discontinuities has a severe effect on the properties of the deposit, especially on ductility and corrosion resistance.

As electroless nickel-phosphorus is heated to temperatures above 220 to 260 °C (430 to 500 °F), structural changes begin to occur. First, coherent and then distinct particles of nickel phosphite (Ni_3P) form within the alloy. Then, at temperatures above 320 °C (610 °F), the deposit begins to crystallize and lose its amorphous character. With continued heating, nickel phosphite particles conglomerate and a two-phase alloy forms. With coatings containing more than 8% P, a matrix of nickel phosphite forms, whereas almost pure nickel is the predominant phase in deposits with lower phosphorus content. These changes cause a rapid increase in the hardness and wear resistance of the coating, but cause its corrosion resistance and ductility to be reduced (Ref 2, 12, 13, 14).

Internal stress in electroless nickel coatings is primarily a function of coating composition. As illustrated in Fig. 7, stress in coatings used on steel containing more than 10% P is neutral or compressive (Ref 15). With lower phosphorus deposits, however, tensile stresses of 15 to 45 MPa (2.2 to 6.5 ksi) develop because of the difference in thermal expansion between the deposits and the substrate. The high level of stress in these coatings promotes cracking and porosity (Ref 12).

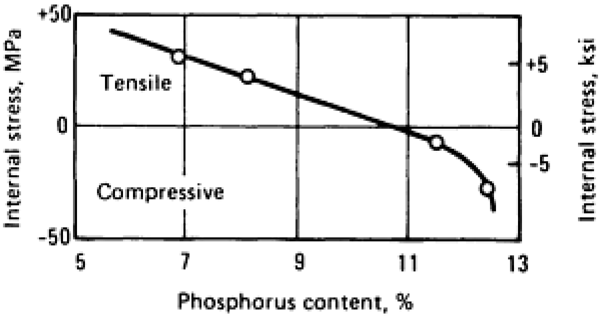


Fig. 7 Effect of phosphorus content on the internal stress of electroless nickel deposits on steel

The structural changes during heat treatment at temperatures above 220 °C (430 °F) cause a volumetric shrinkage of electroless nickel deposits of up to 4 to 6% (Ref 16). This increases tensile stress and reduces compressive stress in the coating.

Deposit stress can also be increased by the codeposition of orthophosphites or heavy metals, as well as by the presence of excess complexing agents in the plating solution. Even small quantities of some metals can produce a severe increase in stress. The addition of only 5 mg/L (20 mg/gal) of bismuth and antimony to most baths can cause the deposit tensile stress to increase to as much as 350 MPa (50 ksi). High levels of internal stress also reduce the ductility of the coating and increase cracking (Ref 2, 16).

When using reported values for stress, it is important to know how the stress was measured. There are several methods that may yield different results. It is important to know whether intrinsic stress (internal stress of the deposit independent of basis material) or total stress of the plated system is reported. Total stress includes the effect of differences in coefficient of thermal expansion of the basis metal and the plated deposit (Ref 17).

Intrinsic stress (Fig. 8) is measured using a spiral contractometer covered by ASTM B 636. Intrinsic stress is found by taking the initial and final readings at the operating temperature of the plating solution. Reading at room temperature provides the total stress, but only for the specific basis metal used for the test. It is best to specify intrinsic stress so that comparison between deposit characteristics can be made (Ref 17).

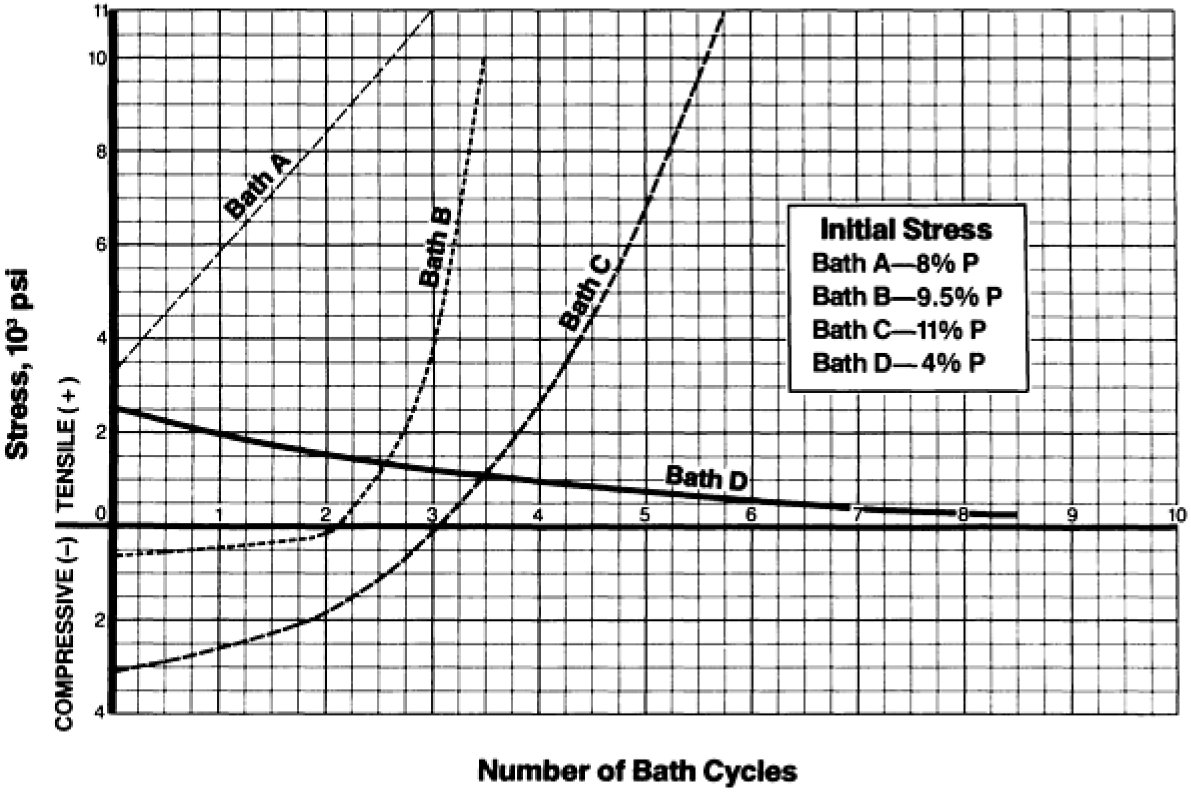


Fig. 8 intrinsic stresses as related to bath cycles for four amounts of phosphorus in deposits from acid nickel-phosphorus solutions. A *bath cycle* is defined as one complete replacement of nickel in the solution (sometimes called *bath turnover*). Nickel content, 6 g/L (0.8 oz/gal); pH, 4.8

The thickness must be constant since stress readings vary with deposit thickness. The ASTM thickness standard is 0.0006 in. (15 μm).

Uniformity. One especially beneficial property of electroless nickel is uniform coating thickness. With electroplated coatings, thickness can vary significantly depending on the shape of the part and the proximity of the part to the anodes. These variations can affect the ultimate performance of the coating, and additional finishing may be required after plating. With electroless nickel, the plating rate and coating thickness are the same on any section of the part exposed to fresh plating solution. Grooves and blind holes have the same amount of coating as the outside of a part.

With electroless nickel, coating thickness can be controlled to suit the application. Coatings as thin as 2.5 μm (0.1 mil) are applied for electronic components, whereas those as thick as 75 to 125 μm (3 to 5 mils) are normally used in corrosive environments. Coatings thicker than 250 μm (10 mils) are used for salvage or repair of worn or mismachined parts (Ref 12).

Adhesion of electroless nickel coatings to most metals is excellent. The initial replacement reaction, which occurs with catalytic metals, together with the associated ability of the baths to remove submicroscopic soils, allows the deposit to establish metallic as well as mechanical bonds with the substrate. The bond strength of the coating to properly cleaned steel or aluminum substrates has been found to be at least 300 to 400 MPa (40 to 60 ksi).

With noncatalytic or passive metals, such as stainless steel, an initial replacement reaction does not occur, and adhesion is reduced. With proper pretreatment and activation, however, the bond strength of the coating usually exceeds 140 MPa (20 ksi) (Ref 2, 12, 13). With metals such as aluminum, parts baked after plating for $1\frac{1}{2}$ h at 190 to 210 °C (375 to 410 °F) to increase the adhesion of the coating. These treatments relieve hydrogen from the part and the deposit and provide a very minor amount of codiffusion between coating and substrate. Baking parts is most useful where pretreatment has been less than adequate and adhesion is marginal. With properly applied coatings, baking has only a minimal effect on bond strength (Ref 2, 12, 14).

The adhesion of electroless nickel deposits depends on the quality of the cleaning and preparation steps prior to plating. Procedures for cleaning and preparation for electroless nickel plating are generally the same as those for electroplating. One exception is that electrocleaners sometimes cannot be used because of fixturing restraints, making soak cleaning more critical. See the section "Pretreatments for Electroless Nickel Coatings" in this article for more information.

Physical Properties. The density of electroless nickel coatings is inversely proportional to their phosphorus content. As shown in Fig. 9, density varies from about 8.5 g/cm^3 for very low phosphorus deposit to 7.75 g/cm^3 for coatings containing 10 to 11% P (Ref 2, 13, 18, 19, 20).

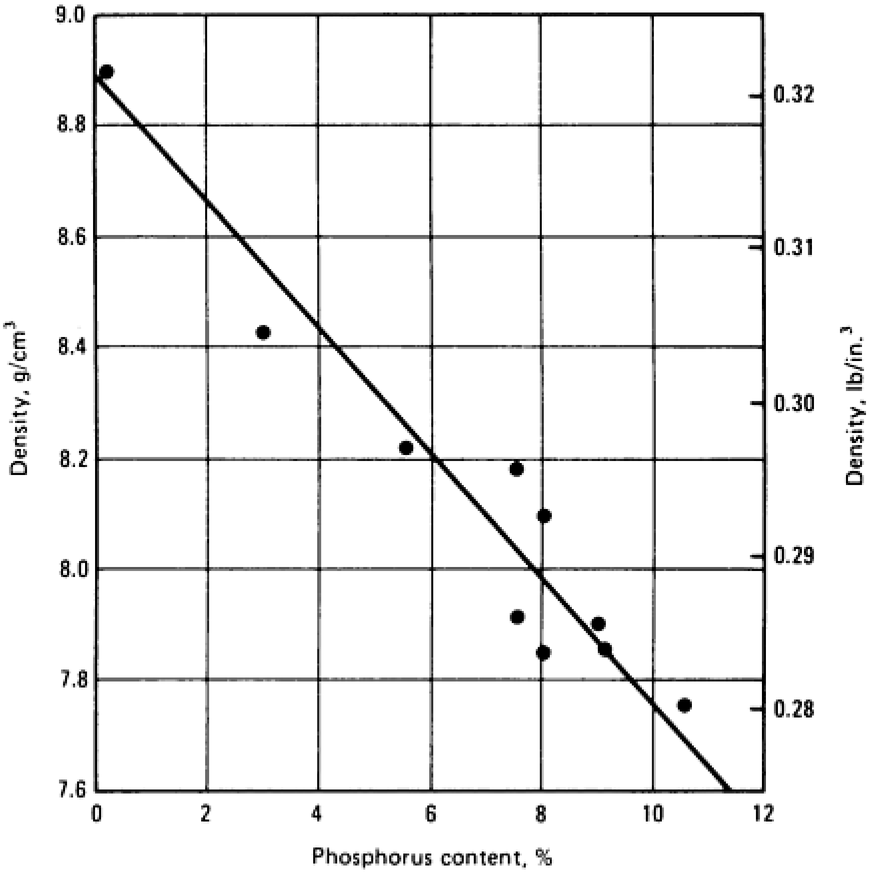


Fig. 9 Effect of phosphorus content on coating density

The thermal and electrical properties of these coatings also vary with composition. For commercial coatings, however, electrical resistivity and thermal conductivity are generally about 50 to 90 μΩ· cm and 0.010 to 0.013 cal/cm · s · °C (2.4 to 3.1 Btu/ft · h · °F), respectively. Accordingly, these coatings are significantly less conductive than conventional conductors such as copper or silver.

Heat treatments precipitate phosphorus from the alloy and can increase its conductivity by three to four times (Ref 2, 13). The formulation of the plating solution can also affect conductivity. Tests with baths containing sodium acetate and succinic acid showed electrical resistivities of 61 and 84 μΩ· cm, respectively (Ref 2).

Phosphorus content also has a strong effect on the thermal expansion of electroless nickel. This is shown in Fig. 10, which shows data for deposit stress measurements on different substrates (Ref 15). The coefficient of thermal expansion of high phosphorus coatings is approximately equal to that of steel. As deposited, coatings containing more than 10% P are completely nonmagnetic. Lower phosphorus coatings, however, have some magnetic susceptibility. The coercivity of 3 to 6% P coatings is about 20 to 80 Oe (1592 to 6366 A/m), while that of deposits containing 7 to 9% P is typically 1 to 2 Oe (80 to 160 A/m). Heat treatments at temperatures above 300 °C (570 °F) improve the magnetic response of electroless nickel and can provide coercivities of about 100 to 300 Oe (7958 to 23,873 A/m) (Ref 11, 21).

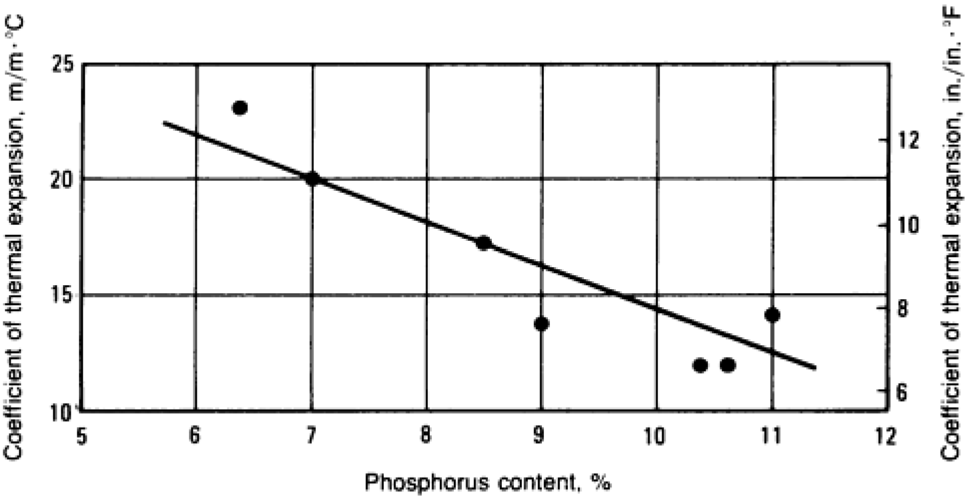


Fig. 10 Effect of deposit phosphorus content on coefficient of thermal expansion

Mechanical Properties. The mechanical properties of electroless nickel deposits are similar to those of other glasses. They have high strength, limited ductility, and a high modulus of elasticity. The ultimate tensile strength of commercial coatings exceeds 700 MPa (102 ksi) and allows the coating to withstand a considerable amount of abuse without damage. The effect of phosphorus content on the strength and strain at fracture of electroless nickel deposits is shown in Fig. 11 (Ref 22).

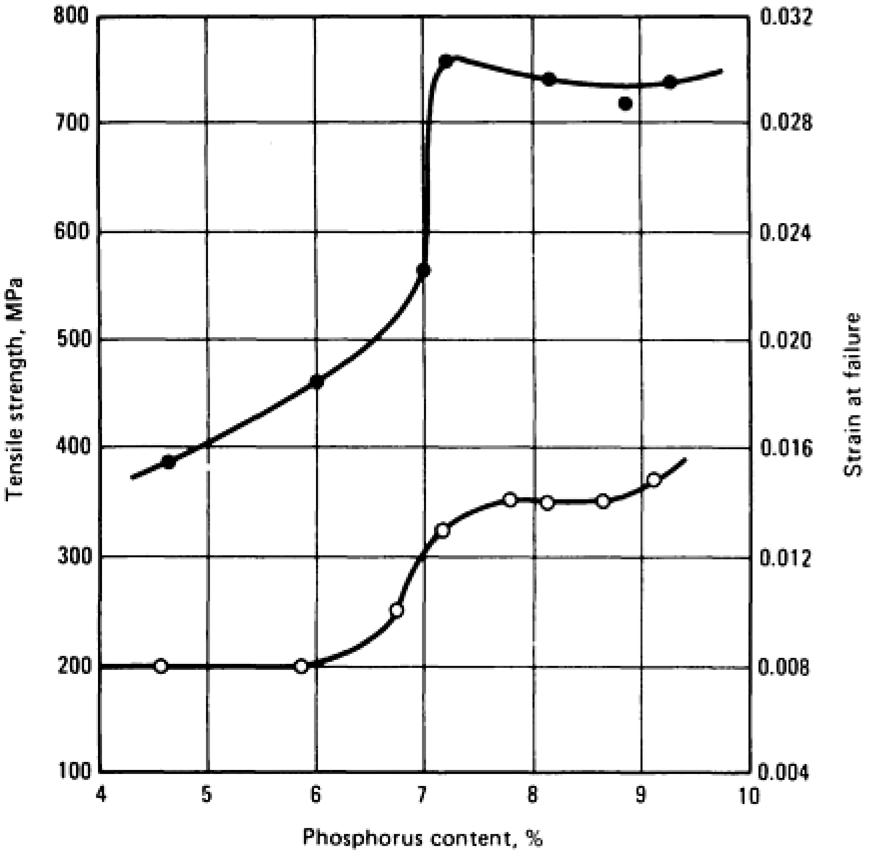


Fig. 11 Effect of deposit phosphorus content on strength and strain at fracture

The ductility of electroless nickel coatings also varies with composition. High phosphorus, high purity coatings have a ductility of about 1 to $1\frac{1}{2}$% (as elongation). Although this is less ductile than most engineering materials, it is adequate for most coating applications. Thin films of deposit can be bent completely around themselves without fracture. With lower phosphorus deposits, or with deposits containing metallic or sulfur impurities, ductility is greatly reduced and may approach zero (Ref 12, 14).

Hardening type heat treatments reduce both the strength and ductility of electroless nickel deposits. Exposure to temperatures above 220 °C (428 °F) causes an 80 to 90% reduction in strength and can destroy ductility. This is illustrated by Fig. 12, which shows the effect of different 1 h heat treatments on the elongation at fracture of brass panels coated with 6% P electroless nickel (Ref 11). The modulus of elasticity of electroless nickel coatings containing 7 to 11% P is about 200 GPa (29,000 ksi) and is very similar to that of steel.

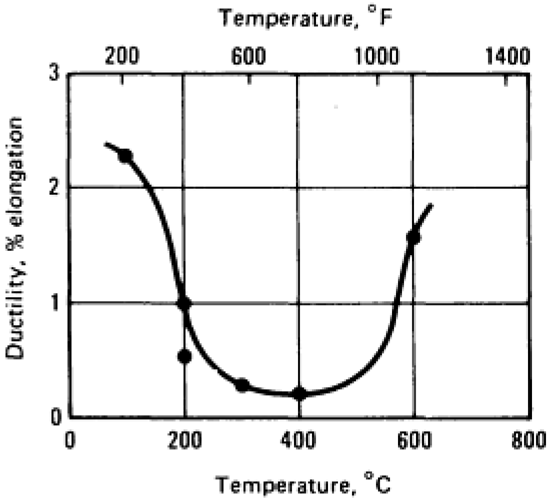


Fig. 12 Effect of heat treatment on the ductility of a 6% P electroless nickel coating

Hardness and wear resistance are extremely important properties for many applications. As deposited, the microhardness of electroless nickel coatings is about 500 to 600 HV_{100}, which is approximately equal to 48 to 52 HRC and equivalent to many hardened alloy steels. Heat treatment causes these alloys to age harden and can produce hardness values as high as 1100 HV_{100}, equal to most commercial hard chromium coatings (Ref 2, 12). Figure 13 shows the effect of different 1-h heat treatments on the hardness of electroless nickel containing $10\frac{1}{2}$% P (Ref 2).

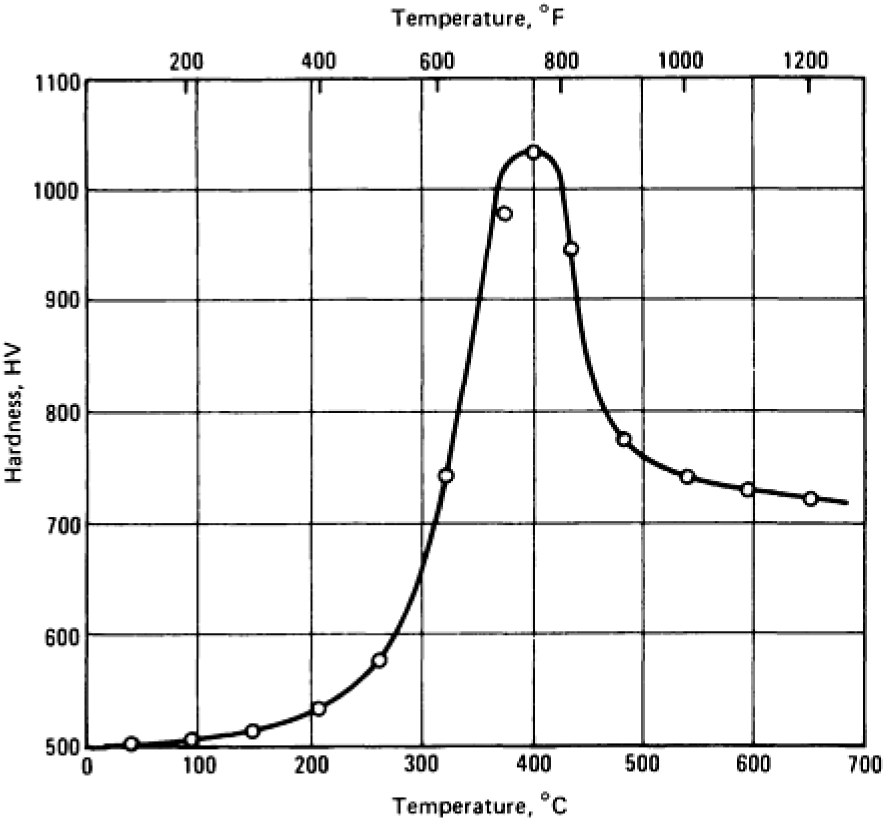


Fig. 13 Effect of heat treatment on hardness of $10\frac{1}{2}$% P electroless nickel coating

For some applications, high-temperature treatments cannot be tolerated because parts may warp, or the strength of the substrate may be reduced. For these applications, longer times and lower temperatures are sometimes used to obtain the desired hardness. This is illustrated in Fig. 14, which shows the effect of different treatment periods on the hardness of a coating containing $10\frac{1}{2}$% P (Ref 12). ASTM specification B 578 requires that the Knoop hardness method be used for plated deposits. However, Vickers hardness numbers have been widely used (Ref 23, 24, 25).

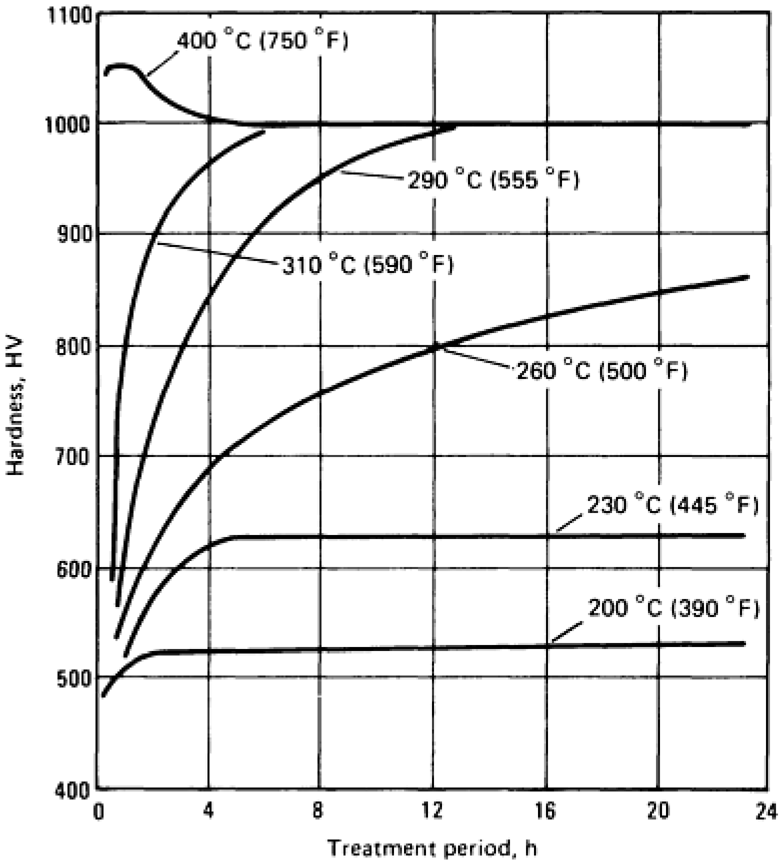


Fig. 14 Effect of different heat treatment periods on hardness of a high-phosphorus electroless nickel coating

Electroless nickel coatings also have excellent hot hardness. To about 400 °C (750 °F), the hardness of heat-treated electroless nickel is equal to or better than that of hard chromium coatings. As-deposited coatings also retain their hardness to this temperature, although at a lower level. The effect of elevated temperature on a 10% P coating is shown in Fig. 15 (Ref 26, 27).

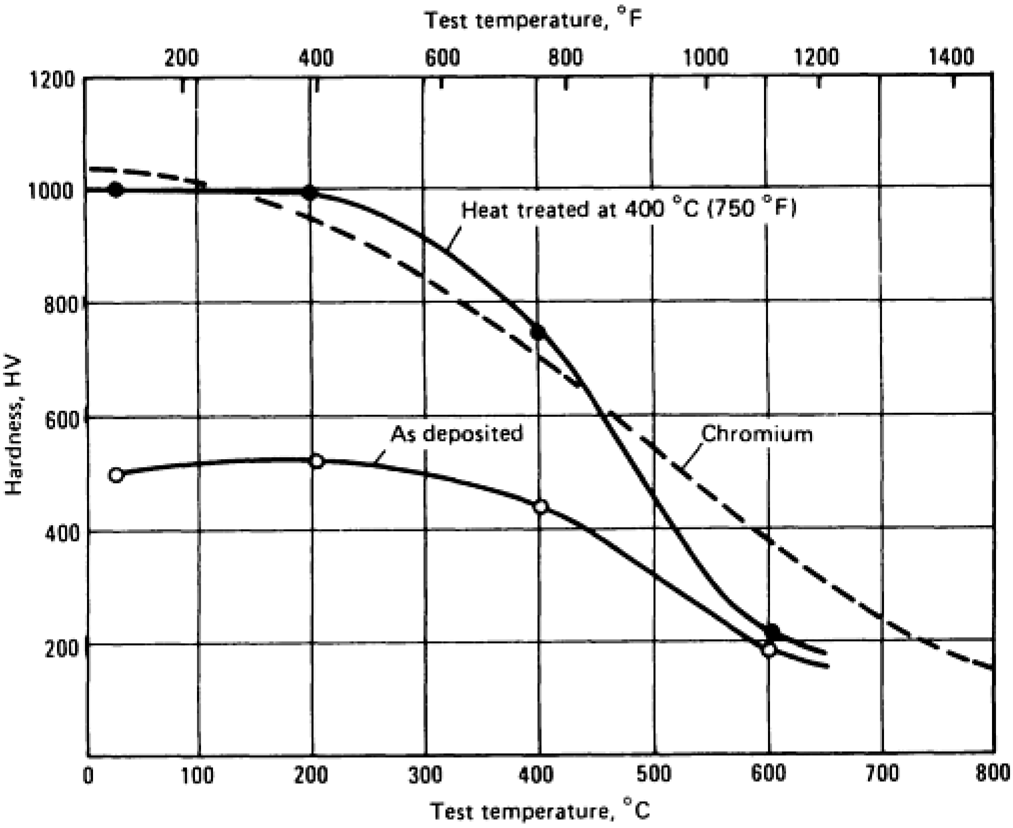


Fig. 15 Effect of temperature on the elevated-temperature hardness of a 10% P electroless nickel coating

Because of their high hardness, electroless nickel coatings have excellent resistance to wear and abrasion, both in the as-deposited and hardened conditions. Taber Abraser Index values for electroless nickel and for electrodeposited nickel and chromium are summarized in Table 3 (Ref 28, 29, 30).

Table 3 Comparison of the Taber abraser resistance of different engineering coatings

Coating	Heat treatment for 1 h		Taber wear index, mg/1000 cycles[a]
	°C	°F	
Watts nickel	None	None	25
Electroless Ni-P[b]	None	None	17
Electroless Ni-P[b]	300	570	10
Electroless Ni-P[b]	500	930	6
Electroless Ni-P[b]	650	1200	4

Electroless Ni-B[(c)]	None	None	9
Electroless Ni-B[(c)]	400	750	3
Hard chromium	None	None	2

(a) CS-10 abraser wheels, 1000 g load, determined as average weight loss per 1000 cycles for total test of 6000 cycles.

(b) Hypophosphite-reduced electroless nickel containing approximately 9% P.

(c) Borohydride-reduced electroless nickel containing approximately 5% B

Tests with electroless nickel-coated vee-blocks in a Falex Wear Tester have shown a similar relationship between heat treatment and wear and confirmed the coating to be equal to hard chrome under lubricated wear conditions (Ref 14, 28). The effect of phosphorus content on the wear experienced by electroless nickel coatings under lubricated conditions is summarized in Fig. 16. These rotating ball tests showed that after heat treatment, high phosphorus deposits provide the best resistance to adhesive wear (Ref 6, 31).

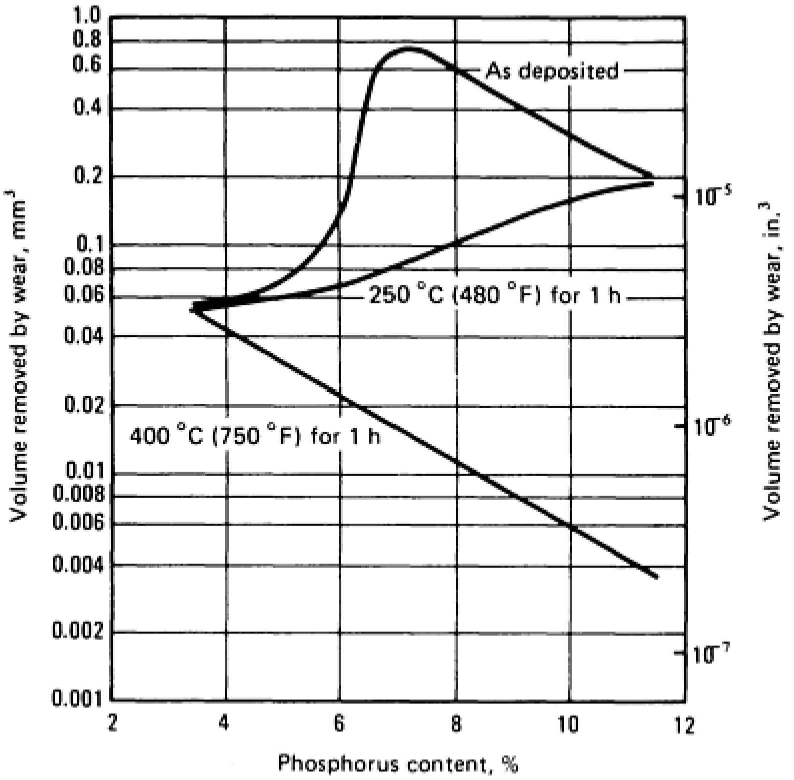


Fig. 16 Effect of phosphorus content on the wear of electroless nickel coatings in rotating ball tests

Frictional properties of electroless nickel coatings are excellent and similar to those of chromium. Their phosphorus content provides a natural lubricity, which can be very useful for applications such as plastic molding. The coefficient of friction for electroless nickel versus steel is about 0.13 for lubricated conditions and 0.4 for unlubricated conditions. The frictional properties of these coatings vary little with either phosphorus content or with heat treatment (Ref 2, 28, 31).

Solderability. Electroless nickel coatings can be easily soldered and are used in electronic applications to facilitate soldering such light metals as aluminum. For most components, rosin mildly activated (RMA) flux is specified along with conventional tin-lead solder. Preheating the component to 100 to 110 °C (212 to 230 °F) improves the ease and speed of joining. With moderately oxidized surfaces, such as those resulting from steam aging, activated rosin (RA) flux or organic acid is usually required to obtain wetting of the coating (Ref 2, 32).

Corrosion Resistance. Electroless nickel is a barrier coating, protecting the substrate by sealing it off from the environment, rather than using sacrificial action. Therefore, the deposit must be free of pores and defects. Because of its amorphous nature and passivity, the coating's corrosion resistance is excellent and, in many environments, superior to that of pure nickel or chromium alloys. Amorphous alloys have better resistance to attack than equivalent polycrystalline materials, because of their freedom from grain or phase boundaries, and because of the glassy films that form on and passivate their surfaces. Some examples of the corrosion experienced in different environments are shown in Table 4 (Ref 2, 16, 30, 33). The resistance to attack in neutral and acidic environments is increased as the phosphorus content is increased in the deposit. The reverse is true in alkaline corrosive environments.

Table 4 Corrosion of electroless nickel coatings in various environments

Environment	Temperature		Corrosion rate			
			Electroless nickel-phosphorus(a)		Electroless nickel-boron(b)	
	°C	°F	µm/yr	mil/yr	µm/yr	mil/yr
Acetic acid, glacial	20	68	0.8	0.03	84	3.3
Acetone	20	68	0.08	0.003	Nil	Nil
Aluminum sulfate, 27%	20	68	5	0.2	. . .	. . .
Ammonia, 25%	20	68	16	0.6	40	1.6
Ammonia nitrate, 20%	20	68	15	0.6	(c)	(c)
Ammonium sulfate, saturated	20	68	3	0.1	3.5	0.14
Benzene	20	68	Nil	Nil	Nil	Nil
Brine, $3\frac{1}{2}$% salt, CO_2 saturated	95	205	5	0.2	. . .	. . .
Brine, $3\frac{1}{2}$% salt, H_2S saturated	95	205	Nil	Nil	. . .	. . .
Calcium chloride, 42%	20	68	0.2	0.008	. . .	. . .
Carbon tetrachloride	20	68	Nil	Nil	Nil	Nil

Citric acid, saturated	20	68	7	0.3	42	1.7
Cupric chloride, 5%	20	68	25	1	. . .	. . .
Ethylene glycol	20	68	0.6	0.02	0.2	0.008
Ferric chloride, 1%	20	68	200	8	. . .	. . .
Formic acid, 88%	20	68	13	0.5	90	3.5
Hydrochloric acid, 5%	20	68	24	0.9	. . .	. . .
Hydrochloric acid, 2%	20	68	27	1.1	. . .	. . .
Lactic acid, 85%	20	68	1	0.04	. . .	. . .
Lead acetate, 36%	20	68	0.2	0.008	. . .	. . .
Nitric acid, 1%	20	68	25	2	. . .	. . .
Oxalic acid, 10%	20	68	3	0.1	. . .	. . .
Phenol, 90%	20	68	0.2	0.008	Nil	Nil
Phosphoric acid, 85%	20	68	3	0.1	(c)	(c)
Potassium hydroxide, 50%	20	68	Nil	Nil	Nil	Nil
Sodium carbonate, saturated	20	68	1	0.04	Nil	Nil
Sodium hydroxide, 45%	20	68	Nil	Nil	Nil	Nil
Sodium hydroxide, 50%	95	205	0.2	0.008	. . .	. . .
Sodium sulfate, 10%	20	68	0.8	0.03	11	0.4
Sulfuric acid, 65%	20	68	9	0.4	. . .	. . .
Water, acid mine, 3.3 pH	20	68	7	0.3	. . .	. . .
Water, distilled, N_2 deaerated	100	212	Nil	Nil	Nil	Nil

Water, distilled, O_2 saturated	95	205	Nil	Nil	Nil	Nil
Water, sea ($3\frac{1}{2}$% salt)	95	205	Nil	Nil	. . .	. . .

(a) Hypophosphite reduced electroless nickel containing approximately $10\frac{1}{2}$% P.

(b) Borohydride reduced electroless nickel containing approximately 5% B.

(c) Very rapid. Specimen dissolved during test

Effect of Composition. The corrosion resistance of an electroless nickel coating is a function of its composition. Most deposits are naturally passive and very resistant to attack in most environments. Their degree of passivity and corrosion resistance, however, is greatly affected by their phosphorus content. Alloys containing more than 10% P are more resistant to attack than those with lower phosphorus contents (Ref 16, 18) in neutral or acidic environments. Alloys containing low phosphorus (3 to 4%) are more resistant to strong alkaline environments than high phosphorus deposits.

Often the tramp constituents present in an electroless nickel are even more important to its corrosion resistance than its phosphorus content. Most coatings are applied from baths inhibited with lead, tin, cadmium, or sulfur. Codeposition of these elements in more than trace amounts causes the corrosion resistance to be decreased by 5 to 40 times (Ref 16).

Effect of Heat Treatment. One of the most important variables affecting the corrosion of electroless nickel is its heat treatment. As nickel-phosphorus deposits are heated to temperatures above 220 °C (430 °F), nickel phosphide particles begin to form, reducing the phosphorus content of the remaining material. This reduces the corrosion resistance of the coating. The particles also create small active/passive corrosion cells, further contributing to the destruction of the deposit. The deposit also shrinks as it hardens, which can crack the coating and expose the substrate to attack. The effect of these changes is illustrated in Table 5, which shows the results of tests with a $10\frac{1}{2}$% P deposit heat treated to represent different commercial treatments and then exposed to 10% hydrochloric acid at ambient temperature (Ref 16). Baking at 190 °C (375 °F), similar to the treatment used for hydrogen embrittlement relief, caused no significant increase in corrosion. Hardening, however, caused the corrosion rate of the deposit to increase from 15 μm/yr (0.6 mil/yr) to more than 900 μm/yr (35 mils/yr). Tests in other environments showed a similar reduction in resistance after hardening. Where corrosion resistance is required, hardened coatings should not be used (Ref 16).

Table 5 The effect of heat treatment on the corrosion of a $10\frac{1}{2}$% P electroless nickel deposit in 10% hydrochloric acid

Heat treatment	**Deposit hardness, HV_{100}**	**Corrosion rate**	
		μm/yr	**mil/yr**
None	480	15	0.6

190 °C (375 °F) for $1\frac{1}{2}$ h	500	20	0.8
290 °C (550 °F) for 6 h	900	1900	75
290 °C (550 °F) for 10 h	970	1400	55
340 °C (650 °F) for 4 h	970	900	35
400 °C (750 °F) for 1 h	1050	1200	47

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
11. C. Baldwin and T.E. Such, The Plating Rates and Physical Properties of Electroless Nickel/Phosphorus Alloy Deposits, *Trans. Inst. Met. Finish.,* Vol 46 (No. 2), 1968, p 73
12. R.N. Duncan, Properties and Applications of Electroless Nickel Deposits, *Finish. Manage.,* Vol 26 (No. 3), 1981, p 5
13. W.H. Metzger, Characteristics of Deposits, *Symposium on Electroless Nickel Plating,* STP 265, ASTM, 1959
14. K. Parker, Effects of Heat Treatment on th Properties of Electroless Nickel Deposits, *Plat. Surf. Finish.,* Vol 68 (No. 12), 1981, p 71
15. K. Parker and H. Shah, Residual Stresses in Electroless Nickel Plating, *Plating,* Vol 58 (No. 3), 1971, p 230
16. R.N. Duncan, Performance of Electroless Nickel Coatings in Oil Field Environments, CORROSION/82 Conference, National Association of Corrosion Engineers, March 1982
17. J. Horner and B. Durkin, "Experiences with Measuring Properties of Electroless Nickel Deposits," Electroless Nickel Conf. (Sulihill, UK), British Electroless Nickel Society, 1991
18. G.D.R. Jarrett, Electroless Nickel Plating, *Ind. Finish.* (London), Vol 18 (No. 218), 1966, p 41
19. L.G. Fitzgerald, Chemical Nickel Plating Products, *Finishing* (London), Vol 13 (No. 5), 1960, p 68
20. W.H. Roberts, "Coating Beryllium with Electroless Nickel," Report RFP478, U.S. Atomic Energy Commission, 1964
21. L.F. Spencer, Electroless Nickel Plating--A Review, *Met. Finish.,* Vol 72 (No. 12), 1974, p 58
22. A.H. Graham, R.W. Lindsay, and H.J. Read, The Structure and Mechanical Properties of Electroless Nickel, *J. Electrochem. Soc.,* Vol 112 (No. 4), 1965, p 401
23. J. Horner, Microhardness Testing of Plated Coatings; Recent Round Experiences, STP947, ASTM, 1987
24. J. Horner, "Microhardness Testing of Plated Coatings; Defining Precision and Bias," Int. Tech. Conf. Proc, AESF Surf./Finish., 1992
25. L. Weisenberger and J. Greene, "Hardness versus Wear Resistance of Electroless Nickel Alloys," Electroless Nickel Conf. Proc. on Products Finishing, 1989
26. K. Nemoto et al., The Study on Hardness of Non-Electrolytically Plated Ni-P Deposits at High Temperatures and Effects Given by Heat Treatments, *J. Met. Finish. Soc. Jpn.,* Vol 16 (No. 3), p 106
27. L. Domnikov, Chromium and Electroless Nickel Deposits, Hardness at High Temperatures, *Met. Finish.,* Vol 60 (No. 1), 1962, p 67

28. K. Parker, Hardness and Wear Resistance Tests of Electroless Nickel Deposits, *Plating,* Vol 61 (No. 9), 1974, p 834
29. Industrial Nickel Plating and Coating, International Nickel Company, New York, 1976
30. H.G. Klein et al., *Metalloberfl.; Angew. Elektrochem.,* Vol 25 (No. 9), 1971; Vol 26 (No. 1), 1972
31. J.P. Randin and H.E. Hintermann, Electroless Nickel Deposited at Controlled pH; Mechanical Properties as a Function of Phosphorus Content, *Plating,* Vol 54 (No. 5), 1967 p 523
32. D.W. Baudrand, Use of Electroless Nickel to Reduce Gold Requirements, *Plat. Surf. Finish.,* Vol 68 (No. 12), 1981, p 57
33. R.N. Duncan, "Corrosion Control with Electroless Nickel Coatings," Electroless Plating Symposium, American Electroplaters' Society, March 1982 (St. Louis, MO)

Properties of Electroless Nickel-Boron Coatings

The properties of deposits from borohydride- or aminoborane-reduced baths are similar to those of electroless nickel-phosphorus alloys with a few exceptions. The hardness of nickel-boron alloys is very high, and these alloys can be heat treated to levels equal to or greater than that of hard chromium. Nickel-boron coatings have outstanding resistance to wear and abrasion. These coatings, however, are not completely amorphous and have reduced resistance to corrosive environments; furthermore, they are much more costly than nickel-phosphorus coatings. The physical and mechanical properties of borohydride-reduced electroless nickel are summarized in Table 6 (Ref 2, 6, 34). For comparison, the properties of a hypophosphite-reduced coating containing $10\frac{1}{2}$% P are also listed (Ref 12).

Table 6 Physical and mechanical properties of electroless nickel-boron and nickel-phosphorus deposits

Properties are for coatings in the as-deposited condition, unless noted.

Property	**Electroless nickel-boron**(a)	**Electroless nickel-phosphorus**(b)
Density, g/cm^3 (lb/in.^{3})	8.25 (2.98)	7.75 (2.8)
Melting point, °C (°F)	1080 (1980)	890 (1630)
Electrical resistivity, μΩ· cm	89	90
Thermal conductivity, W/m · K (cal/cm · s · °C)	. . .	4 (0.01)
Coefficient of thermal expansion (22-100 °C, or 72-212 °F), μm/m · °C (μin./in. · °F)	12.6 (7.1)	12 (6.7)
Magnetic properties	Very weakly ferromagnetic	Nonmagnetic
Internal stress, MPa (ksi)	110 (16)	Nil
Tensile strength	110 (16)	700 (100)
Ductility, % elongation	0.2	1.0
Modulus of elasticity, GPa (10^6 psi)	120 (17)	200 (29)

As-deposited hardness, HV_{100}	700	500
Heat-treated hardness, 400 °C (750 °F) for 1 h, HV_{100}	1200	1100
Coefficient of friction vs steel, lubricated	0.12	0.13
Wear resistance, as-deposited, Taber mg/1000 cycles	9	18
Wear resistance, heat treated 400 °C (750 °F) for 1 h, Taber mg/1000 cycles	3	9

(a) Borohydride-reduced electroless nickel containing approximately 5% B.

(b) Hypophosphite-reduced electroless nickel containing approximately $10\frac{1}{2}$% P.

Structure and Internal Stress. The boron content of electroless nickel reduced with DMAB or DEAB can vary from 0.2 to 4% depending on bath formulation and operation. Commercial borohydride-reduced coatings typically contain 3 to 5% B. Unlike nickel-phosphorus coatings in the as-deposited condition, electroless nickel-boron contains crystalline nickel mixed with nickel-boron (typically Ni_2B) glass. These coatings also are not totally homogeneous and consist of phases of different composition (Ref 2, 7, 35).

During heating, electroless nickel-boron age hardens in the same manner as nickel-phosphorus alloys. At temperatures over 250 °C (480 °F), particles of nickel boride (Ni_3B) form, and at 370 to 380 °C (700 to 715 °F), the coating crystallizes. The final structure of hardened nickel-boron coatings consists of nickel-boron intermetallic compounds (principally Ni_3B and Ni_2B) and about 10% Ni (Ref 2, 7, 34).

The internal stress level of nickel-boron deposits is generally high. The effect of boron content and complexing agent on the stress in DMAB-reduced electroless nickel coatings is shown in Table 7 (Ref 10). The internal stress of borohydride-reduced coatings is typically 110 to 200 MPa (16 to 29 ksi) tensile (Ref 34).

Table 7 Effect of boron content and complexing agent on internal stress in DMAB-reduced deposits

Complexing agent	**Boron content, %**	**Internal stress**(a)	
		MPa	**ksi**
Malonate	4.3	120	17.4
Malein-glycine	1.2	310	44.9

(a) Based on tests with $12\frac{1}{2}$ μm thick coatings on a Brenner-Senderoff Spiral Contractometer. Stresses are tensile.

Physical and mechanical properties of borohydride-reduced electroless nickel are summarized in Table 6 (Ref 2, 6, 34). For comparison, the properties of a hypophosphite-reduced coating containing $10\frac{1}{2}$% P are also listed (Ref 12). The density of electroless nickel-boron is very similar to that of nickel-phosphorus coatings of equal alloy content. The density of borohydride-reduced coatings containing 5% B is 8.25 g/cm^3 in both the as-deposited and heat-treated condition (Ref 2, 34).

The melting point of nickel-boron coatings is relatively high and can approach that of metallic nickel. Sodium borohydride reduced coatings melt at 1080 °C (1975 °F), while the melting point of DMAB-reduced coatings varies from about 1350 to 1390 °C (2460 to 2535 °F) (Ref 2, 34).

The electrical resistivity of 5% B coatings is similar to that of nickel-phosphorus alloys ranging from 89 μΩ· cm in the as-deposited condition to 43 μΩ· cm after heat treatment at 1100 °C (2010 °F). The resistivity of 0.5% B to 1% B ranges from 10 to 20 μΩ· cm. In the as-deposited condition, nickel-boron coatings are very weakly ferromagnetic, with coercivities about 10% of that of metallic nickel. Their magnetic susceptibility, however, can be increased by heat treatments at temperatures above 370 °C (700 °F) (Ref 2, 7, 34).

The strength and ductility of nickel-boron coatings containing 5% B is only about one-fifth that of high-phosphorus deposits. Guided bend tests of panels coated with 5% Ni-B showed it strain at fracture to be 2.5 mm/m (2.5 mils/in.). In the same test, the breaking strain of a hypophosphite-reduced electroless nickel containing approximately 9% P was 5.3 mm/m (5.3 mils/in.). Unlike nickel-phosphorus coatings, however, heat treatment has little effect on the ductility of nickel-boron. As illustrated by Fig. 17, even after 12 h at 400 °C (750 °F), strain at fracture declines by only 15% (Ref 7). The modulus of elasticity of borohydride-reduced coatings ranges from 120 GPa (17,000 ksi) in the as-deposited condition to 180 GPa (26,000 ksi) for coatings heat treated at 400 °C (750 °F) for 1 h (Ref 34).

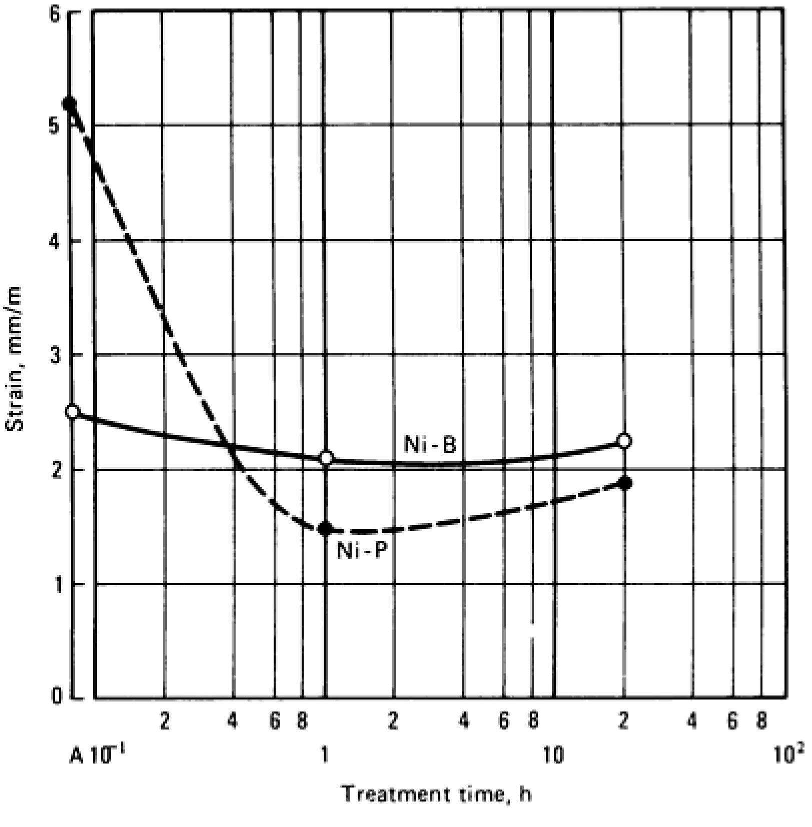


Fig. 17 Effect of heat treatments at 400 °C (752 °F) on the strain at fracture of electroless Ni-5% B and Ni-9% P coatings

Hardness and Wear Resistance. The principle advantage of electroless nickel-boron is its high hardness and superior wear resistance. In the as-deposited condition, microhardness values of 650 to 750 HV_{100} are typical for borohydride-and aminoborane-reduced coatings. After 1-h heat treatments at 350 to 400 °C (660 to 750 °F) hardness values of 1200 HV_{100} can be produced. This is illustrated by Fig. 18, which shows the effect of heat treatment temperature on hardness (Ref 2, 7, 34).

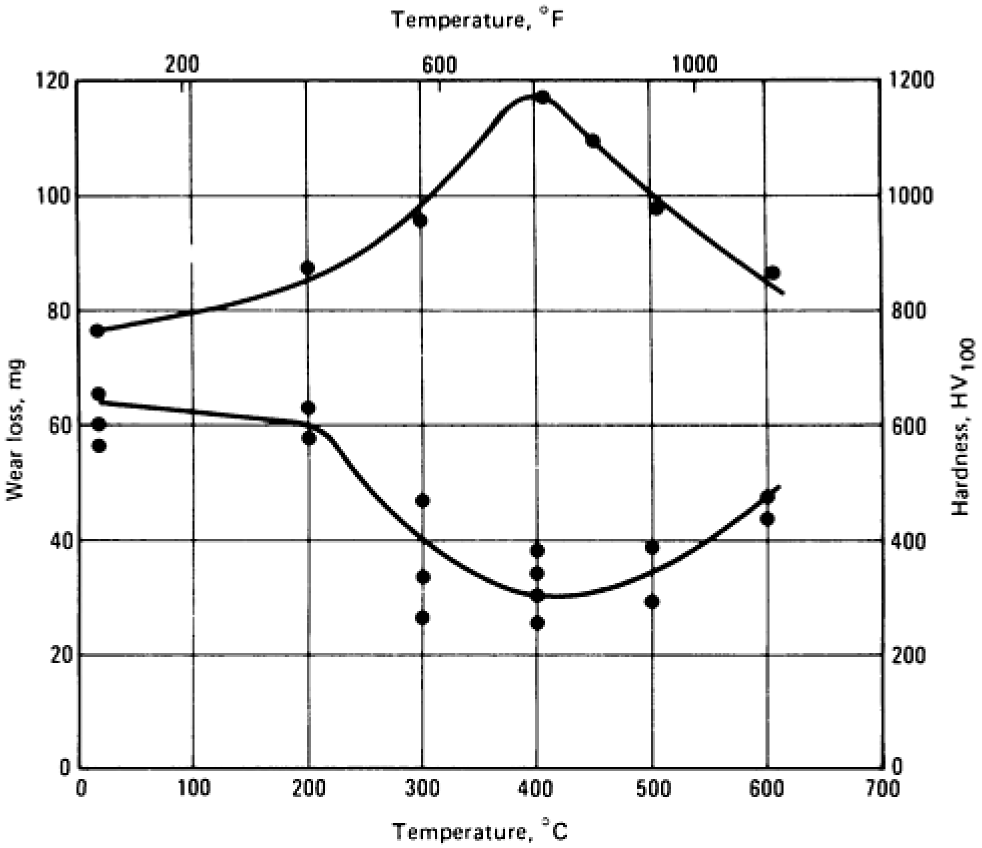


Fig. 18 Effect of different 1h heat treatments on the hardness and wear resistance of borohydride-reduced electroless nickel

Long-term treatments (30 to 40 weeks) at temperatures between 200 and 300 °C (390 and 570 °F) can produce hardness values of 1700 to 2000 HV_{100}. These low-temperature treatments result in a finer dispersion of nickel boride than do higher temperatures and in the formation of iron borides (such as Fe_2B and $Fe_3C_{0.2}B_{0.8}$) within the coating (Ref 2, 34).

The wear resistance of electroless nickel-boron is exceptional and after heat treatment equals or exceeds that of hard chromium coatings. Typical Taber wear test results for a 5% B coating is shown in Tables 3 and 6. The effect of heat treatment and hardness on the wear experienced in rotating ring and block tests (similar to the Alpha LFW-1 test described in ASTM D 2714) (Ref 35) under nonlubricated conditions is also shown in Fig. 18. Nickel-boron deposits containing 2.5 to 3% B exhibit similar wear characteristics.

Electroless nickel-boron coatings are naturally lubricious. Their coefficient of friction versus steel is typically 0.12 to 0.13 in the lubricating conditions, and 0.43 to 0.44 for dry wear (Ref 2, 34).

Corrosion Resistance. In general, the corrosion resistance of electroless nickel-boron coatings is less than that of high-phosphorus alloys. That is illustrated by Table 4, which compares the attack experience by hypophosphite- and borohydride-reduced coatings in different media. In environments that cause little corrosion of nickel-phosphorus, such as alkalis and solvents, electroless nickel-boron is also very resistant. In environments, however, that cause moderate attack of nickel-phosphorus, such as acids and ammonia solutions, nickel-boron coatings can be severely corroded. In strongly oxidizing media, of course, neither coating is satisfactory.

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating,* Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
10. G.O. Mallory, The Electroless Nickel-Boron Plating Bath; Effects of Variables on Deposit Properties, *Plating,* Vol 58 (No. 4), 1971, p 319
12. R.N. Duncan, Properties and Applications of Electroless Nickel Deposits, *Finish. Manage.,* Vol 26 (No. 3), 1981, p 5
34. "Technical Information about Electroless of Chemical Nickel Plating by the Nibodur Method," Paul Anke KG, Essen, West Germany
35. "Calibration and Operation of the Alpha Model LFW-1 Friction and Wear Testing Machine," Part 24, D 2714, *Annual Book of ASTM Standards,* ASTM, 1978

Effect of Electroless Nickel Coatings on the Fatigue Strength of Steel

Because of their tendency to crack under cyclic loads, electroless nickel coatings can cause a significant reduction in the fatigue strength of steel substrates. The magnitude of the reduction, however, depends on the composition, heat treatment, and thickness of the coating, as well as the original fatigue strength of the steel. Several investigations have shown that the use of electroless nickel coatings causes a 10 to 50% reduction in the fatigue strength and endurance limit of steel substrates (Ref 6, 7, 36, 37, 38). In these tests, fatigue strength of notched specimens was reduced by at least 15%, whereas unnotched samples showed relatively small reductions.

The loss of fatigue strength has principally been a problem with hypophosphite-reduced coatings containing less than 10% P, and with nickel-boron alloys. These deposits contain high levels of internal tensile stress and under cyclic stress conditions tend to crack and initiate fatigue failures. Other tests have implied that this is not a significant problem with high-phosphorus deposits (Ref 39, 40). Coatings containing $10\frac{1}{2}$% or more phosphorus are compressively stressed on steel and tend to resist cracking.

Heat treatment of electroless nickel coatings tends to exacerbate the decrease in fatigue strength. Heat-treated coatings tend to be more highly stressed than as-deposited coatings and have a greater tendency to crack. Heat treating a high phosphorus, compressively stressed coating can cause it to become tensilely stressed (Ref 14). Coatings heat treated at temperatures above 340 °C (650 °F) also tend to be cracked because of the shrinkage of the alloy. These cracks act as stress risers and further reduce fatigue resistance. Table 8 shows the effect of different 1-h heat treatments on the fatigue strength of a 0.42% C steel (C45, Werkstoff 1.0503) coated with 30 μ(1.2 mils) of borohydride-reduced electroless nickel (Ref 6). Heat treatments at very high temperatures, 650 to 800 °C (1200 to 1470 °F), produce a thick diffusion zone between the coating and the substrate, which may eliminate or at least greatly reduce the effect of the coating on fatigue strength.

Table 8 Effect of heat treatment of an electroless nickel-5% B coating on the fatigue strength of steel

Condition	**Fatigue strength**	
	MPa	**ksi**
Not coated	350	51
As-deposited	270	39
250 °C (480 °F) for 1 h	260	38

350 °C (660 °F) for 1 h	245	36
400 °C (750 °F) for 1 h	270	39

The reduction in fatigue strength produced by electroless nickel deposits is also affected by the thickness of the coating. Thicker deposits have the greatest effect on fatigue strength. This is illustrated in Fig. 19, which shows the reduction in strength of a carbon-manganese steel (St52, Werkstoff 1.0580) produced by different thicknesses of a 5% nickel coating (Ref 6).

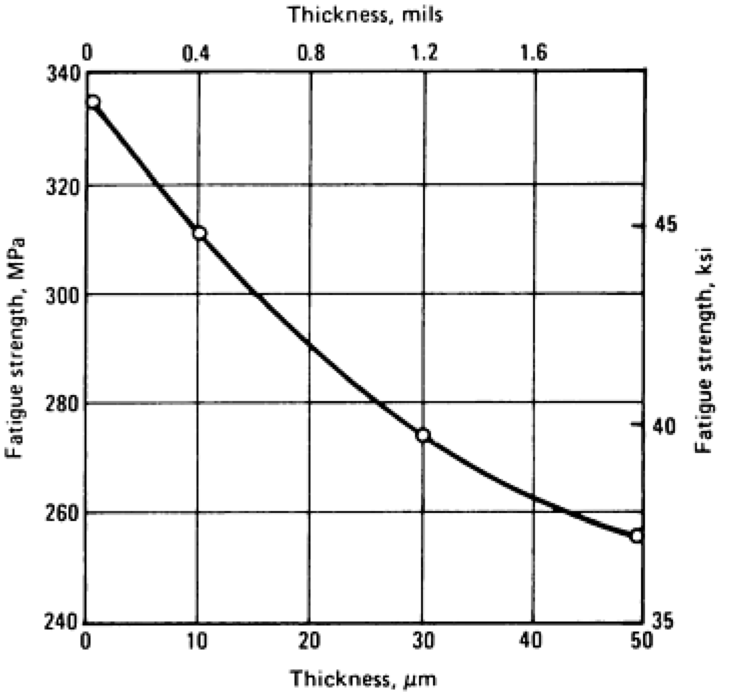


Fig. 19 Effect of coating thickness on the fatigue strength of a carbon-manganese steel

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References cited in this section

6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating,* Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
14. K. Parker, Effects of Heat Treatment on th Properties of Electroless Nickel Deposits, *Plat. Surf. Finish.,* Vol 68 (No. 12), 1981, p 71
36. H. Spahn, The Effect of Internal Stress on the Fatigue and Corrosion Fatigue Properties of Electroplated and Chemically Plated Nickel Deposits, Proc. 6th Int. Metal Finish. Conf., *Trans. Inst. Met. Finish.,* Vol 42, 1964, p 364
37. E.F. Jungslager, Electroless Deposition of Nickel, *Tijdschr, Oppervlakte Tech. Metalen,* Vol 9 (No. 1), 1965, p 2
38. E.W. Turns and J.W. Browning, Properties of Electroless Nickel Coatings on High Strength Steels, *Plating,* Vol 60 (No. 5), 1973
39. G. Reinhardt, "Potential Applications of Electroless Nickel in Airline Maintenance Operations," Electroless

Nickel Conference, 6-7 Nov 1979 (Cincinnati)

40. S. Izumi and Kondo, "The Fatigue Strength of Electroless Nickel Plated Steel," The 18th Japan Conf. Mater. Res., March 1975

Pretreatment for Electroless Nickel Coatings

Proper pretreatment can be as important to the successful application of an electroless nickel coating as the actual deposit. Inadequate cleaning can result in lack of adhesion, roughness, coating porosity, and early failure. The methods used to clean and prepare a metal surface for electroless nickel plating are similar to those used for conventional electroplating, although more care and control are required. One penetrant that is unique to electroless nickel plating is the application of a strike copper plate to alloys containing significant amounts of lead, tin, cadmium, or zinc. This ensures adequate coverage and prevents contamination of the electroless solution.

Pretreatment for Ferrous Alloys

To prepare ferrous alloys properly for electroless nickel plating, the combination of solvent and alkaline degreasing, acid activation, and electrocleaning are required, with intermediate water rinses. These steps are discussed in other articles in this Volume. Recommended pretreatment procedures for different ferrous alloys are summarized below:

Carbon and low-alloy steel

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in 30% HCl for 30 to 60 s. Alternatives: 10 to 20% sulfuric acid avoids leaving chloride ions in pores and thus can improve salt spray resistance. Sulfamic acid and citric acids are also used beneficially.
6. Rinse
7. Electroclean at 5 V for 30 to 60 s
8. Rinse
9. Plate to thickness

Alloy steel (Cr or Ni > $1\frac{1}{2}$%)

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in HCl acid for 30 to 60 s
6. Rinse
7. Electroclean at 5 V for 30 to 60 s
8. Rinse
9. Dip in 30% HCl for 30 to 60 s
10. Rinse
11. Nickel strike at 2 A/dm^2 (20 A/ft^2) for 60 s
12. Rinse
13. Plate to thickness

300 or 400 series stainless steel

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s

4. Rinse
5. Dip in 30% HCl for 60 s
6. Rinse
7. Nickel strike at 2 A/dm^2 (20 A/ft^2) for 60 s
8. Rinse
9. Plate to thickness

300 series stainless steel (complex shapes)

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in 30% HCl for 60 s
6. Rinse
7. 10% H_2SO_4 at 60 °C (140 °F) for 30 s. Alternative: nickel strike
8. Plate to thickness

400 series stainless steel (complex shapes)

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in 30% HCl for 60 s
6. Rinse
7. Dip in 20% HCl at 50 °C (120 °F) for 30 s. Alternative: nickel strike
8. Rinse with deionized water
9. Plate to thickness

In Step 1, all alkaline soak cleaners should be operated at their supplier's maximum recommended temperature, typically 60 to 80 °C (140 to 175 °F). Unless otherwise indicated, all other processes are at ambient temperature. In Step 3, electrocleaning is with at least three reversals of current (part, cathodic/anodic, three times) at 3 to 5 A/dm^2 (30 to 50 A/ft^2). Except for 300 series stainless steel, the final current cycle should be with the part anodic; with 300 series stainless steels, the final current cycle should be with the part cathodic to minimize the formation of an oxide film on its surface.

Activation for Alloy Steels. Before electroless plating, stainless and alloy steel parts must be chemically activated to obtain satisfactory adhesion. For this, a low pH nickel strike is normally used. Two common strike baths are listed below:

Nickel sulfamate strike	
Nickel sulfamate	165-325 g/L (22-43 oz/gal)
Nickel (as metal)	35-75 g/L (5-10 oz/gal)

Sulfamic acid (~20 g/L, or 2.7 oz/gal)	to pH 1-1.5
Boric acid	30-34 g/L (4-4.5 oz/gal)
Hydrochloric acid (20° Bé)	12 mL/L (1.5 fluid oz/gal)
Temperature	Room temperature
Cathode current density	1-10 A/dm^2 (10-100 A/ft^2)
Time	30-60 s
Anodes (bagged)	Sulfur depolarized nickel
Operating pH	0.8-1.5
Woods nickel strike	
Nickel chloride	240 g/L (32 oz/gal)
Hydrochloric acid	250 mL/L (32 fluid oz/gal)
Temperature	Room temperature
Cathode current density	2-10 A/dm^2(20-100 A/ft^2)
Time	30-120 s
Anodes	Rolled depolarized nickel

Caution: Insoluble anodes cannot be used. Chlorine gas would be liberated from insoluble anodes.

(a)

Nickel strikes should not be used to cover up improper pretreatment of plain or low-alloy steel. Nickel-strike activation should be considered, however, when processing steel with chromium or nickel contents of over 1.5% carburized or nitrided steels, and stainless steels. Nickel-strike processing should follow acid activation to avoid drag-in of alkaline materials into the strike (Ref 41, 42, 43, 44, 45, 46).

Pretreatment for Aluminum Alloys

Like steel, aluminum is catalytic to electroless nickel deposition and could be plated after only a simple cleaning. Aluminum is very reactive, however, and oxides form very rapidly on its surface during rinsing or exposure to air. The oxide films that develop prevent metallic bonds from forming between the coating and the substrate and can result in adhesion failure. To avoid this problem, special processing procedures are required, including deoxidizing and zincating or acid zinc immersion. Processing procedures for aluminum alloys are discussed in the article on cleaning and finishing of aluminum alloys in this Volume.

Pretreatment for Copper Alloys

Copper-base alloys are prepared for electroless nickel plating using procedures similar to those for steel, alkaline cleaning and acid deoxidizing. Two important differences exist, however:

- Copper is not catalytic to the chemical reduction of electroless nickel, and its alloys must be activated chemically or electrolytically before they can be plated.
- Lead in amounts of $\frac{1}{2}$ to 10% is often added to copper alloys to make them easier to machine. Unless the free lead present on the surface of the part is removed, adhesion failures and coating porosity result.

Processing procedures for copper alloys are given in the article on cleaning and finishing of copper and copper alloys in this Volume.

Activation. Once a copper alloy surface is clean and oxide-free, it must be activated before electroless nickel can deposit. To prevent reoxidation, this activation should be initiated without long intermediate delays. The preferred method for initiating deposition is an electrolytic strike in the electroless nickel bath. Using a nickel anode, the parts are made cathodic at 5 V for 30 to 60 s. This applies a thin, electrolytic nickel-phosphorus coating and provides a catalytic surface. After the current is removed, the electroless deposition can continue.

Another method for initiating electroless deposition on copper alloy surfaces is to preplate surfaces with electrolytic nickel. One disadvantage of this method is that blind holes, internal surfaces, or low current density areas may not be coated by the strike, resulting in incomplete coverage or unplated areas. The use of nickel chloride strikes also may result in chloride contamination of the electroless nickel bath through drag-in.

A third method of activating copper alloys in electroless nickel solutions is to touch them with a piece of steel or with another part already coated with electroless nickel after they have been immersed in the bath. This creates a galvanic cell, producing an electric current to initiate the electroless reaction. Deposition spreads until the whole part is covered with electroless nickel. However, two problems can occur with galvanic activation:

- Galvanic currents do not travel well around sharp curves, such as those on threads or corners, and can leave bare spots or areas of reduced thickness
- Passivation of the copper can occur before the deposit spreads across the entire surface leading to poor adhesion

Other methods include immersion for 15 to 30 s in dilute solutions of palladium chloride (0.05 to 0.1 g/L), and nickel-boron nickel strike processes that use DMAB reducing agent.

Leaded Alloys. Unlike other elements added to brass or bronze, lead does not combine with copper to form an alloy. Instead, it remains in the metal as globules. The lead exposed during cutting or machining acts as a lubricant by flowing or smearing across the surface. Electroless nickel does not deposit on lead. Unless lead smears are removed, the applied coating is porous with poor adhesion. Lead remaining on the surface of parts can also contaminate electroless nickel solutions, causing a rapid decline in plating rate and deposit quality.

Surface lead is best removed by immersing parts for 30 s to 2 min in a 10 to 30% solution of fluoboric acid at room temperature. Sulfamic acid, citric acid, and dilute nitric acid have also been reported to be effective solutions for removing lead. The removal of lead must occur before deoxidizing or bright dipping in the pretreatment cycle, and it is not a substitute for these steps (Ref 2, 41, 47).

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
41. S. Spring, *Industrial Cleaning,* Prism Press, Melbourne, 1974
42. J. Kuczma, How to Operate Electroless Nickel More Efficiently, *Prod. Finish. (Directory),* Vol 44 (No. 12A), 1980, p 158
43. " Autocatalytic Nickel Deposition on Metals for Engineering Use," Part 9, B 656, *Annual Book of ASTM Standards,* ASTM, 1981
44. "Preparation of Low-Carbon Steel for Electroplating," Part 9, B 183, *Annual Book of ASTM Standards,* ASTM, 1981
45. "Preparation of High-Carbon Steel for Electroplating, Part 9, B 242, *Annual Book of ASTM Standards,* ASTM, 1981
46. "Preparation of and Electroplating on Stainless Steel," Part 9, B 254, *Annual Book of ASTM Standards,* ASTM, 1981
47. "Preparation of Copper and Copper-Base Alloys for Electroplating," Part 9, B 281, *Annual Book of ASTM Standards,* 1981

Equipment for Electroless Nickel Plating

Because electroless nickel is applied by a chemical reaction rather than by electrolytic deposition, special attention to design and construction of the tanks and auxiliary equipment is required to ensure trouble-free operation and quality coatings.

Plating Tanks

Cylindrical or bell-shaped tanks have been used for electroless nickel plating, although rectangular tanks have been found to be the most convenient to build and operate. Rectangular tanks have been constructed from various materials in many different sizes. A common electroless nickel plating system is shown in Fig. 20.

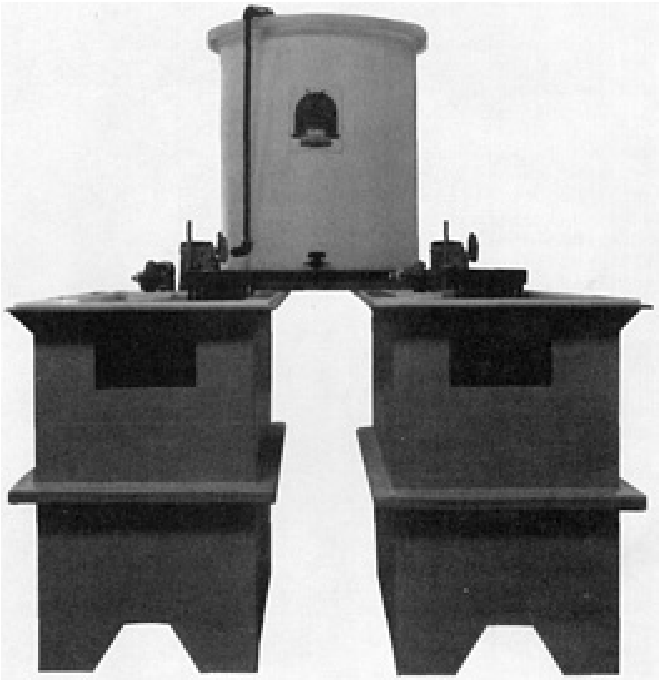

Fig. 20 Twin tank system for electroless nickel plating. Tanks are used alternately. While one tank is being used to plate, the second is being passivated. Cylindrical tank is used to store 30% nitric acid for passivation.

Physical Dimensions. The following factors should be considered when selecting the size of an electroless nickel plating tank:

- Size of the part to be plated
- Number of parts to be plated each day
- Plating thickness required
- Plating rate of the solution (most conventional electroless nickel solutions deposit between 12 and 25 μm/h, or 0.5 and 1 mil/h)
- Type of rack, barrel, or basket used to support parts
- Number of production hours available each day to process parts
- Nominal recommended work load of 1.2 dm^2/L (0.5 ft^2/gal) of working solution

The size of the part or the size of the supporting rack, barrel, or basket usually defines the minimum size tank that can be used. The minimum dimension of the tank should be at least 15 cm (6 in.) greater than the maximum dimension of the part or its support to allow proper agitation and the flow of fresh solution to all surfaces. The size of the tank may have to be increased, however, to accommodate the volume of the parts required or to provide a more suitable work area to solution volume ratio.

Construction Materials. The following factors should be considered when selecting construction materials for a plating tank:

- Operating temperature of the electroless nickel plating solution usually 85 to 95 °C (185 to 205 °F)
- Tendency of tank material to become sensitized to the deposition of electroless nickel
- Cost of tank material, including both initial construction cost and its life in a production environment

With continued exposure to heated electroless nickel solutions, almost any surface eventually becomes sensitized or receptive to deposition of the coating. The more inert or passive the material selected, the less likely that plate out can occur. All material in contact with the plating solution must be repassivated periodically with 30 vol% nitric acid to minimize deposition on its surface.

The most widely used materials for tank construction have been polypropylene, stainless steel, and steel or aluminum with a 635 μm (25 mil) thick polyvinyl chloride bag liner. Contamination from bleedout of oils or other plasticizers can have harmful effects on the plating solution. Leaching linings prior to use is recommended. However, the contaminants continue to migrate to the surface and enter the solution (Ref 48). Although all of these materials have been used successfully, a 6 to 12 mm (0.25 to 0.5 in.) thick polypropylene liner installed in a steel or fiberglass support tank, has proven to be the most troublefree material and has gained the widest acceptance. Polypropylene is relatively inexpesive and is very resistant to plate out. The smooth surface of polypropylene also reduces the possibility of deposit nucleation.

When constructing a polypropylene tank, only stress relieved, unfilled virgin material should be used. Welds should be made under an inert gas shield, such as nitrogen, to prevent oxidation of the polypropylene and incomplete fusion. All welds should be spark tested at 20,000 V before use to ensure integrity.

Heating the Solution

Steam and electricity are the two most common sources of power for heating plating solutions. Although the capital expenditures for steam or pressurized hot water are somewhat higher than that for electricity, the operating costs for steam are considerably less.

Steam. Heating with steam is accomplished using immersion coils or external heat exchangers. The most common immersion coils are those made of Teflon or stainless steel.

Teflon heat exchanger coils are made of many small diameter Teflon tubes looped into the tank between manifolds. Because of the poor conductivity of the plastic, a much larger coil surface area must be used than would be needed with a metal heater. Teflon tubes are delicate, and the tubes must be protected form mechanical damage.

Stainless steel panel coils are constructed of plates joined together with internal passages for the flow of heating medium. These coils are very efficient and economical. Their primary disadvantage is that they are easily galvanically activated and are prone to plate out. To prevent this, coils are often coated with Teflon. This, however, reduces their heat transfer and their efficiency.

Anodic passivation is also sometimes used to prevent stainless steel coils from plating. With this technique, a slight positive charge is applied to the coil preventing the deposition of electroless nickel. If the work is suspended too close to an anodically passivated coil, however, stray currents from the coil may affect the quality of the plating. Static electricity discharges from steam coils to the work can also cause nonuniform or pitted coatings. To avoid this, coils should be isolated from the steam piping with dielectric couplings.

Steam can also be used to heat the plating solution through a heat exchanger, which is mounted outside the tank. The heat exchangers are usually of shell and tube or plate coil design and are constructed of stainless steel. The solution is pumped through exchangers and returned to the tank, often through a filter. To prevent the inside of the exchanger from plating, the solution velocity must be maintained above $2\frac{1}{2}$ m/s (8 ft/s).

Electric. Heating with electricity is usually accomplished with tube immersion heaters. The resistance heating elements are sheathed in quartz, titanium, or stainless steel. Stainless steel is the most economical material and is usually preferred. Either type 304 or 316 stainless steel is acceptable. Occasionally electropolished stainless steel or Teflon-coated heaters are also used. The cost of these additions, however, cannot usually be justified for most applications. An electric immersion heater is shown in Fig. 21.

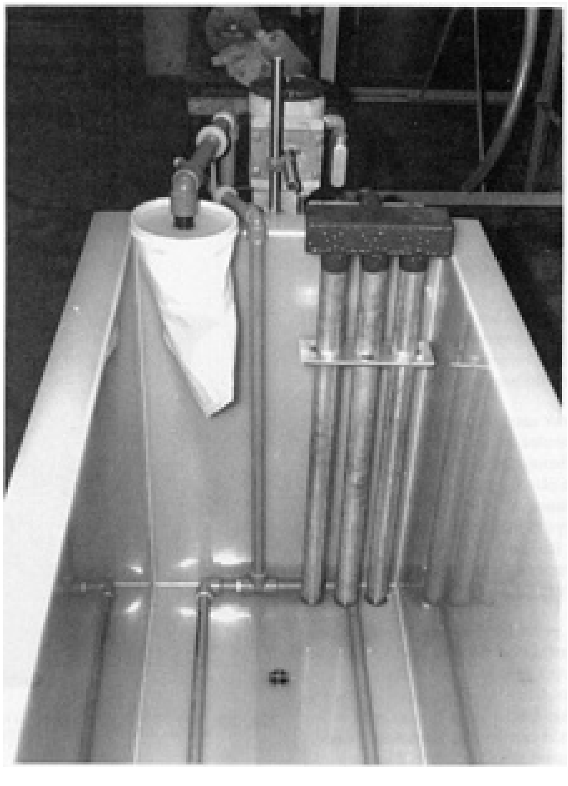

Fig. 21 Electric immersion heater. Heater mounted in a 200 L (50 gal) electroless nickel plating tank. A bag filter is mounted on the filtration pump discharge. 1000×

Pumps

Pumps are used in electroless nickel plating systems for solution transfer and filtration. The following factors should be considered when selecting pumps for electroless nickel plating systems:

- Operating temperature of the plating solution, usually 85 to 95 °C (185 to 205 °F)
- Chemicals being handled in both the electroless nickel plating solution and the 30% nitric acid solution used for passivation
- Volume flow rate (liters per minute) required to allow the total tank volume to be filtered approximately ten times each hour

Two materials, CPVC plastic and type 304 stainless steel, have been proven to be satisfactory for electroless nickel pumps. CPVC plastic is more resistant to plate out than stainless steel and is less expensive. However, large plastic pumps lack the capacity and mechanical strength needed to provide proper filtration in electroless nickel systems. Accordingly, plastic pumps are used for flow rates less than 300 L/min (80 gal/min), whereas stainless steel is used for higher flow applications.

Vertical Pumps. Vertical centrifugal pumps are now the most commonly used pumps for electroless nickel systems. These pumps can be mounted so only the impeller is below the solution level and shaft seals are not required. Consequently, maintenance of this pump is minimized. Some vertical pumps can also be mounted outside the tank, providing the maximum area for plating.

With CPVC plastic pumps, the impeller should be machined or molded; glued impellers should not be used. All gaskets and O-rings for electroless nickel systems should be fluorocarbon rubber.

The velocity of the solution through the pump should be at least $2\frac{1}{2}$ m/s (8 ft/min) to prevent the solution from plating out on the pump housing, especially when stainless steel is used. To accomplish this, a pump speed of 1750 rev/min is required.

Piping and Valves

Piping and valves available for electroless nickel systems are of four principal types: stainless steel, polyvinylidene fluoride, CPVC plastic, and polypropylene. The advantages and disadvantages of each of these materials are summarized in Table 9.

Table 9 Comparison of piping and valve materials for electroless nickel plating systems

Material	**Resistance to plating temperatures**	**Resistance to plate out**	**Relative cost**	**Availability**
Piping				
Stainless steel	High	Low	High	Good
Kynar	High	High	Moderate	Poor
CPVC	Moderate	Moderate	Low	Good
Polypropylene	Low	High	Low	Limited

Valves				
Stainless steel	High	Low	Moderate	Good
CPVC	Moderate	Moderate	Moderate	Good
Polypropylene	Moderate	High	Moderate	Good

Piping components in electroless nickel plating systems are used for air agitation spiders, tank outlet, pump inlet, and discharge pipes, solution manifolds, and deionized water fill lines. These pipes must be sized to minimize restrictions and provide proper agitation and filtration. The diameter of the tank outlet piping should be at least as large as the pump inlet connection to avoid cavitation and increased pump wear. CPVC plastic is normally used for pipe exposed to the plating solution.

Although CPVC or other plastic pipe may be joined by solvent welding, threaded joints are preferred. Threaded connections are easier to make and more trouble-free, allowing repairs or modifications to be accomplished quickly. When threading plastic pipe, a plug should be inserted inside the pipe end to support the pipe and prevent collapse or thread breakage. Threads should be wrapped with Teflon tape before joining to prevent potential leakage from the galling of the plastic.

Valves. Almost all of the valves used for electroless nickel systems are a ball and seat design. Because of prolonged exposure to stagnant plating solutions, inertness or resistance to deposit plate out is of primary importance with these valves. Accordingly, polypropylene is used most often. The reduced strength of polypropylene at plating temperatures is not a problem with valves, because of their compactness and greater thickness.

CPVC plastic valves are also used occasionally for electroless nickel systems, although their reduced resistance to deposit plate out makes them more prone to seizure and failure due to deposit buildup than polypropylene. Because of their somewhat higher cost and tendency to activation and deposition, stainless steel valves are not normally used. For valves in agitation air supply lines, plain PVC plastic valves may be used if they are mounted at least 200 mm (8 in.) away from hot plating solution. Valves and piping for steam services should be steel or stainless steel.

Agitation

Agitation of parts and solution is necessary during electroless nickel plating to provide a fresh supply of solution to the part and to remove the hydrogen produced during deposition. Without consistent renewal of plating solution, localized depleted areas can occur, resulting in nonuniform coating thickness. Hydrogen bubbles, if allowed to remain on the surface of the part, tend to mask plating and can cause pitting or fisheyes in the coating.

Agitation is accomplished by moving the part mechanically through the solution, by solution movement (preferably by discharge of solution from a suitable filter and distributed by a sparger throughout the tank), or by bubbling air through the bath to move the solution past the part. A typical air agitation spider is shown in Fig. 21. For air agitation, a clean low-pressure air source, such as is provided by centrifugal blowers, is preferred. High-pressure air from compressors can introduce oil or other contaminants into the bath and affect deposit quality.

Filtration

Two types of filtration are used for electroless nickel systems, cartridge filters and filter bags. Both require the use of an external circulation pump, and both should be capable of removing particles larger than 5 μm (0.2 mil) in size. Wound cartridge filters are supported in CPVC or polypropylene chambers located outside of the tank. The installation cost of these filters is high, however, and replacement of the cartridges is a large maintenance cost. Also the added back pressure of the filter can significantly reduce the flow of the pump and often its life.

Woven polypropylene bags are now being used to filter electroless nickel solutions. These bags are mounted above the plating tank itself, allowing the solution to flow through the bag by gravity. Filter bags are relatively inexpensive and result in only a minimum restriction on the discharge of the pump. When bags become soiled or begin to plate out, the change is obvious to the operator, and the bags can be quickly and easily replaced. Filter bags with stainless steel support rings rather than plated steel rings should be used. Plated rings can introduce cadmium or zinc into the bath and slow or stop deposition. A filter assembly is shown in Fig. 21.

Filter cartridges and bags should be washed using hot water prior to use for electroless nickel. Antistatic agents often found in these filter media can be harmful to the plating solution.

For extremely critical applications such as memory disks, filtration should be through a 1 μM filter cartridge followed by a 0.2 μM cartridge using flow rates sufficient to turn over the volume of plating solution 10 to 20 times per hour. Filter discharge is best done through a sparger to distribute the solution uniformly in the tank, and not impinge on the parts being plated.

Racking for Electroless Nickel Plating

Because electroless nickel is applied by chemical reduction, anode to cathode area relationships and current density considerations, usually of concern in electrolytical applications, are usually not important. This simplifies rack design.

Construction Materials. Racks for plating ferrous and copper alloys should be capable of carrying 3 to 6 A/dm^2 (30 to 60 A/ft^2) of part surface during electrocleaning and striking without overheating or excessive voltage loss. Suitable materials for racks include steel, stainless steel, copper, and titanium. Of these, steel or plastic coated steel is most often used. Stainless steel and titanium can be cleaned easily in the nitric acid, but are rarely used because of high cost and limited current carrying capability. The cost of copper racks is reasonable and current capacity is excellent. With copper, however, all submersed surface, except the contact points, should be coated to avoid copper contamination of the cleaning and plating solutions and to minimize stripping of the coating from the frame.

Because electrolytic steps are not required when processing aluminum alloys, plastics as well as metals can be used to support parts. The materials used for racks for aluminum alloys include polypropylene, CPVC, aluminum, and stainless steel. Polypropylene and CPVC are especially useful, because they are easily constructed, inexpensive, and highly resistant to plating. Iron, nickel, or copper alloys are not suitable, because they are rapidly attacked by the oxidizing and desmutting solutions used for aluminum alloys.

Coatings for racks and fixtures used in electroless nickel plating have only limited life. The high temperatures and harsh chemicals used during pretreatment and stripping can cause rapid degradation of vinyls, epoxies, and phenolics. Coatings, however, do reduce current requirements during cleaning and striking operations and can reduce unwanted deposition on the racks.

Fixturing. When fixturing and positioning a part, the following factors should be considered:

- *Hydrogen evolution:* During the deposition of electroless nickel, hydrogen gas is evolved at the surface of the part. As the hydrogen bubble grows and rises, it should be able to free itself from the part. If hydrogen becomes trapped in any area of the part, such as an inverted hole, it masks the surface and can reduce or prevent plating.
- *Electrical contact:* Good contact is needed between the support and the part to ensure adequate and uniform current for electrocleaning and striking. Proximity to anodes is not usually very important with these operations, although in extreme cases, such as deep holes, internal anodes may be required.
- *Rinsing:* Easy rinsing is necessary to minimize dragout of the pretreatment cleaners and to prevent drag-in of contaminants to the electroless nickel bath.

A rack should be designed to allow blind holes to drain easily or to allow holes to be rinsed thoroughly with a hose. Some racks are designed to be tipped or turned upside down to ensure rinsing and to control dragout. During plating, these holes must be positioned vertically to allow hydrogen gas to escape.

Reference cited in this section

48. C.P. Steinecker, Evaluation of PVC Tank Liners for Electroless Nickel Plating, *Met. Finish.,* Vol 90 (No. 5), May 1992

Bulk and Barrel Plating

The uniform plating thickness of electroless nickel coatings allows many parts that would have to be racked if they were finished electrolytically to be bulk plated. Because of the resulting labor savings, coatings such as chromium can sometimes be replaced with electroless nickel at a lower overall finished cost, although the chemical cost is higher. Four principal types of bulk plating are used:

- *Soldier-style racking:* Parts are placed so close together that complete coverage would be difficult, if not impossible, with an electrolytic process.
- *Baskets:* Many bulk plating jobs can be run efficiently in baskets made of polypropylene or stainless steel, especially in smaller electroless nickel tanks. Baskets occupy much less space than barrels and allow more loads to be run. When compared to using barrels, baskets have the disadvantage of not mechanically agitating parts during plating. Accordingly, baskets should be shaken and moved periodically to allow fresh plating solution to circulate around parts.
- *Trays:* Many jobs, such as small shafts and bars, can be run most easily using egg crate or test tube rack trays. In addition, many parts, because of their finish or design, must be separated during processing to keep them from touching or nesting. Separated trays accomplish this successfully and allow good solution transfer, minimizing the labor required for fixturing. Trays are most often constructed of polypropylene, steel, or stainless steel.
- *Barrels:* Where very large volumes of parts are to be plated or continuous mechanical agitation is necessary, barrels usually provide the most efficient and economical methods of processing.

Barrels for electroless nickel plating should be made from nonfilled, nonpigmented polypropylene. If added strength is required, glass-filled polypropylene construction is preferred. Polypropylene gears, rather than a belt drive, should be used to turn the barrel. Plastisol-coated steel barrels are not successful for electroless nickel plating, because they are prone to coating failures, plate out, possible contamination by bleedout of plasticizers or preplate preparation solutions, and occasional drive failures. For electroless nickel plating, the barrel speed should be 1 to 2 rev/min. Higher-speed barrels may be required, however, where the solution must be pumped through internal passages or holes in a part. The drive mechanism should allow the barrel to rotate, both in the processing tanks and in transfer stages, to ensure free rinsing and minimize dragout. To allow adequate solution transfer in and out of the barrel, the hole size should be as large as possible and should be just capable of containing parts.

All racks, baskets, trays, and barrels used for electroless nickel plating should be used exclusively for this operation. The use of equipment from other plating systems can result in contamination of the electroless nickel plating solution, in decomposition, or in reduced deposit quality.

Solution Control

To ensure a quality deposit and consistent plating rate, the composition of the plating solution must be kept relatively constant. This requires periodic analyses for the determination of pH, nickel content, and hypophosphite and orthophosphite concentrations, as well as careful temperature control. With modern premixed solutions, only checks of nickel content and pH are required. The frequency with which these analyses should be made depends on the quantity of work being plated and the volume and type of solution being used.

Hydrogen Embrittlement Relief

Hydrogen embrittlement is the failure that results from the absorption of hydrogen into metals. Hydrogen embrittlement usually occurs in combination with residual or applied stresses in a part, happening most frequently in high-strength steels and occasionally in other high-strength alloys.

Hydrogen can be introduced into a metal by processes such as pickling, electrocleaning, acid activation, electroplating, or electroless deposition. Although the hydrogen produced by electroless nickel plating is much less than that produced by an electrolytic process, such as cadmium or hard chrome plating, it can be enough to cause cracking of high-strength steels. To prevent this, components are baked at 200 ± 10 °C (390 ± 18 °F) to diffuse the absorbed hydrogen out of the steel. This usually restores the mechanical properties of the steel almost completely, helping to ensure against failure.

The time required to remove hydrogen from a steel and avoid embrittlement depends on the strength of the steel. Longer relief treatment periods or higher temperatures are needed as the strength of the steel increases. Recommendations for embrittlement relief of steels on different strength levels are summarized in Table 10. Longer times may be require for parts with deposit thickness greater than 1 mil. Deposits are amorphous, thus there are no grain boundaries for the hydrogen to follow. Shorter times may be used if unplated areas are present. Temperature ramp-up times should be longer than for hydrogen relief of other metal deposits. Hydrogen embrittlement relief treatment should begin within 4 h of the completion of electroless nickel plating (Ref 2, 49, 50).

Table 10 Heat treatment of steels to relieve hydrogen embrittlement

Maximum specified tensile strength		**Heat treatment at 190 to 210 °C (375 to 410 °F), h**
MPa	**ksi**	
≤ 1050	≤ 152	Not required
1051-1450	152-210	2
1451-1800	210-260	18

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating*, Portcullis Press, Redhill, England, 1979

49. *Metals Handbook*, 9th ed., Vol 1, American Society for Metals, 1978

50. "Autocatalytic Nickel-Phosphorus Coatings," ISO 4527, International Standards Organization

Applications

Electroless nickel is applied for five different applications: corrosion resistance, wear resistance, lubricity, solderability, or buildup of worn or overmachined surfaces. To varying degrees, these properties are used by all segments of industry, either separately or in combination. Applications of these coating are given in Table 11.

Table 11 Applications of electroless nickel plating

Application	**Base metal**	**Coating thickness[(a)]**		**Reason for use**
		µm	**mils**	
Automotive				
Heat sinks	Aluminum	10	0.4	Corrosion resistance, solderability, uniformity
Carburetor components	Steel	15	0.6	Corrosion resistance
Fuel injectors	Steel	25	1.0	Corrosion and wear resistance
Ball studs	Steel	25(b)	1.0(b)	Wear resistance
Differential pinion ball shafts	Steel	25(b)	1.0(b)	Wear resistance
Disc brake pistons and pad holders	Steel	25(b)	1.0(b)	Wear resistance
Transmission thrust washers	Steel	25(b)	1.0(b)	Wear resistance
Syncromesh gears	Brass	30	1.2	Wear resistance
Knuckle pins	Steel	38(b)	1.0(b)	Wear resistance
Exhaust manifolds and pipes and mufflers	Steel	25	1.0	Corrosion resistance
Shock absorbers	Steel	10	0.4	Corrosion resistance and lubricity
Lock components	Steel	10	0.4	Wear and corrosion resistance and lubricity
Hose couplings	Steel	5	0.2	Wear and corrosion resistance
Gears and gear assemblies	Carburized steel	25(c)	1.0(c)	Buildup of worn surfaces and wear resistance
Fuel pump motors	Steel	12	0.5	Corrosion, wear resistance
Aluminum wheels	Aluminum	25	1	Corrosion resistance
Water pump components	Steel	20	0.8	Corrosion resistance

Application	**Base metal**	**Coating thickness**[a]		**Reason for use**
		µm	**mils**	
Steering column tilt wheel components	Powdered metal	15	0.6	Ease of movement
Air bag hardware	Steel	10	0.4	Ease of movement
Air conditioning compressor components	Steel	25	1	Low friction
Decorative plastics	Plastics (ABS, etc)	2	0.1	Base coat
Slip yokes	Steel	15	0.6	. . .
Aircraft/aerospace				
Bearing journals	Aluminum	38[d]	1.5[d]	Wear resistance and uniformity
Servo valves	Steel	18	0.7	Corrosion resistance, uniformity and lubricity
Compressor blades	Alloy steel	25[e]	1.0[e]	. . .
Hot zone hardware	Alloy steel	25	1.0	Corrosion and wear resistance
Piston heads	Aluminum	25	1.0	Wear resistance
Engine main shafts and propellers	Steel	>38	>1.5	Buildup of worn surfaces and wear resistance
Hydraulic actuator splines	Steel	25[b]	1.0[b]	Wear resistance
Seal snaps and spacers	Steel	20[e]	0.8[e]	Wear and corrosion resistance
Landing gear components	Aluminum	>125	>5.0	Buildup of mis-machined surfaces
Struts	Stainless steel	>25	>1.0	Buildup of mis-machined or worn surfaces
Pitot tubes	Brass/stainless steel	12	0.5	Corrosion and wear resistance
Gyro parts	Steel	12	0.5	Wear resistance and lubricity

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Engine mounts	4140 Steel	25	1.0	Wear and corrosion resistance
Oil nozzle components	Steel	25	1.0	Corrosion resistance and uniformity
Turbine front bearing cages	Alloy steel	25	1	Corrosion, wear resistance
Engine mount insulator housing	Alloy steel	25	1	Corrosion resistance
Flanges	Alloy steel	20	0.8	Corrosion, wear resistance
Sun gears	Alloy steel	25	1	Wear resistance
Breech caps	Alloy steel	15	0.6	Corrosion, wear resistance
Shear bolts	Alloy steel	50	2	Corrosion resistance
Engine oil feed tubes	Steel, stainless steel	10	0.4	Corrosion resistance
Flexible bearing supports	Steel	25	1	Corrosion resistance
Break attach bolts	Alloy steel	25	1	Corrosion resistance
Antirotational plates	Alloy steel	25	1	Wear resistance
Wing flap universal joints	Alloy steel	20	0.8	Corrosion, low friction
Titanium thruster tracks	Titanium	25	1	Wear and corrosion resistance, low friction
Printing				
Printing rolls	Steel/cast iron	38	1.5	Corrosion and wear resistance
Press beds	Steel/cast iron	38	1.5	Corrosion and wear resistance
Textiles				

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Feeds and guides	Steel	50[(b)]	2.0[(b)]	Wear resistance
Fabric knives	Steel	12[(b)]	0.5[(b)]	Wear resistance
Spinnerettes	Stainless steel	25	1.0	Corrosion and wear resistance
Loom ratchets	Aluminum	25	1.0	Wear resistance
Knitting needles	Steel	12	0.5	Wear resistance
Molds and dies				
Zinc die cast dies	Alloy steel	25	1.0	Wear resistance and part release
Glass molds	Steel	50	2.0	Wear resistance and part release
Plastic injection molds	Alloy steel	15	0.6	Corrosion and wear resistance and part release
Plastic extrusion dies	Alloy steel	25	1.0	Corrosion and wear resistance and part release
Military				
Fuse assemblies	Steel	12	0.5	Corrosion resistance
Mortar detonators	Steel	10	0.4	Corrosion resistance
Tank turret bearings	Alloy steel	30	1.2	Wear and corrosion resistance
Radar wave guides	Aluminum	25	1.0	Corrosion resistance and uniformity
Mirrors	Aluminum/beryllium	>75	>3.0	Uniformity and reflectivity
Firearms				
Commercial and military firearms	Steel	8	0.3	Corrosion and wear resistance and lubricity

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Marine				
Marine hardware	Brass	25	1.0	Corrosion resistance
Pumps and equipment	Steel/cast iron	50	2.0	Corrosion and wear resistance
Electronics				
Heat sinks	Aluminum	10	0.4	Corrosion resistance and solderability
Computer drive mechanisms	Aluminum	18	0.7	Corrosion and wear resistance
Memory drums and discs	Aluminum	25	1.0	Corrosion and wear resistance and uniformity
Terminals and lead wires	Alloy steel	2	0.1	Solderability
Chassis	Aluminum/steel	12	0.5	Corrosion resistance and solderability
Connectors	Steel/aluminum	25	1.0	Corrosion and wear resistance and solderability
Diode and transistor cans	Steel	5	0.2	Corrosion resistance and solderability
Interlocks	Steel/brass	12	0.5	Corrosion and wear resistance
Junction fittings	Aluminum/plastic	10	0.4	Corrosion and wear resistance, solderability and conductivity
Printed circuit boards	Plastic	5	0.2	Solderability and weldability
Railroad				
Tank cars	Steel	90[(f)]	3.5[(f)]	Corrosion resistance
Diesel engine shafts	Steel	>25	>1.0	Wear and fretting resistance and buildup of worn surfaces
Car hardware	Powder iron	20	0.8	Corrosion and wear resistance

Application	**Base metal**	**Coating thickness**[(a)]		**Reason for use**
		µm	**mils**	
Electrical				
Motor shafts	Steel	12	0.5	Wear and corrosion resistance
Rotor blades	Steel/aluminum	25(b)	1.0(b)	Wear and corrosion resistance
Stator rings	Steel/aluminum	25	1.0	Wear and corrosion resistance
Chemical and petroleum				
Pressure vessels	Steel	50	2.0	Corrosion resistance
Reactors	Steel	100(f)	4.0(f)	Corrosion resistance and product purity
Mixer shafts	Steel	38	1.5	Corrosion resistance
Pumps and impellers	Cast iron/steel	75	3.0	Corrosion and erosion resistance
Heat exchangers	Steel	75	3.0	Corrosion resistance
Filters and components	Steel	25	1.0	Corrosion and erosion resistance
Turbine blades and rotor assemblies	Steel	75	3.0	Corrosion and erosion resistance
Compressor blades and impellers	Steel/aluminum	125(d)	5.0(d)	Corrosion and erosion resistance
Spray nozzles	Brass/steel	12	0.5	Corrosion and wear resistance
Ball, gate, plug, check and butterfly valves	Steel	75	3.0	Corrosion resistance and lubricity
Valves	Stainless steel	25(b)	1.0(b)	Wear and galling resistance and protection against stress-corrosion cracking
Chokes and control valves	Steel/stainless steel	75	3.0	Corrosion and wear resistance and protection against stress-corrosion cracking

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Oil field tools	Steel	75	3.0	Corrosion and wear resistance
Oil well packers and equipment	Alloy steel	75	3.0	Corrosion and erosion resistance
Oil well tubing and pumps	Steel	50	2.0	Corrosion and wear resistance
Drilling mud pumps	Alloy steel	75	3.0	Corrosion resistance and protection against stress-corrosion cracking
Hydraulic systems and actuators	Steel	75	3.0	Corrosion and wear resistance and lubricity
Blowout preventers	Alloy steel	75	3.0	Corrosion and wear resistance
Medical and pharmaceutical(g)				
Disposable surgical instruments and equipment	Steel/aluminum	12	0.5	Corrosion resistance and ease of operation
Sizing screens	Steel	20	0.8	Corrosion resistance and cleanliness
Pill sorters	Steel	20	0.8	Corrosion resistance and cleanliness
Feed screws and extruders	Steel	25	1.0	Corrosion and wear resistance and cleanliness
Food(g)				
Pneumatic canning machinery	Steel	25	1.0	Corrosion and wear resistance and cleanliness
Baking pans	Steel	25	1.0	High temperature resistance, cleanliness, and ease of release
Molds	Steel	12	0.5	Cleanliness, corrosion resistance and ease of release
Grills and fryers	Steel	12	0.5	Cleanliness, corrosion resistance and ease of release
Mixing bowls	Steel	25	1.0	Cleanliness and corrosion and wear resistance

Application	**Base metal**	**Coating thickness**[(a)]		**Reason for use**
		µm	**mils**	
Bun warmers	Steel	12	0.5	Cleanliness and ease of release
Feed screws and extruders	Steel	25	1.0	Cleanliness and corrosion and wear resistance
Material handling				
Hydraulic cylinders and shafts	Steel	25	1.0	Corrosion and wear resistance and lubricity
Extruders	Alloy steel	75[(b)]	3.0[(b)]	Wear and corrosion resistance
Link drive belts	Steel	12	0.5	Wear and corrosion resistance and lubricity
Gears and clutches	Steel	>25	>1.0	Wear resistance and buildup of worn surfaces
Mining				
Hydraulic systems	Steel	60	2.4	Corrosion and abrasion resistance
Jetting pump heads	Steel	60	2.4	Corrosion and erosion resistance
Mine engine components	Steel/cast iron	30	1.2	Corrosion and wear resistance
Piping connections	Steel	60	2.4	Corrosion resistance
Framing hardware	Steel	30	1.2	Corrosion resistance
Wood and paper				
Knife holder corer plates	Steel	30	1.2	Corrosion and abrasion resistance
Abrading plates	Steel	30	1.2	Corrosion and abrasion resistance
Chopping machine parts	Steel	30	1.2	Corrosion and abrasion resistance
Miscellaneous				

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Chain saw engines	Aluminum	25	1.0	Wear and corrosion resistance
Drill and taps	Alloy steel	12[(b)]	0.5[(b)]	Wear resistance and ease of use
Precision tools	Alloy steel	12	0.5	Wear resistance and cleanliness
Shaver blades and heads	Steel	8	0.3	Wear resistance and smoothness
Pen tips	Brass	5	0.2	Corrosion resistance

(a) Many components are heat treated at 190 to 210 °C (375 to 410 °F) for 1 to 3 h to improve adhesion or to relieve hydrogen embrittlement.

(b) Heat treated for 1 h at 400 °C (750 °F) for maximum hardness.

(c) Heat treated for 6 h at 135 °C (275 °F) for hydrogen embrittlement relief.

(d) Heat treated for 10 h at 290 °C (550 °F) for maximum hardness.

(e) Cadmium plated after electroless nickel and then heat treated for 2 h at 340 °C (640 °F) to diffuse cadmium into the nickel.

(f) Heat treated for 1 h at 620 °C (1150 °F) to diffuse coating into basis metal.

(g) For medical, pharmaceutical, and food applications, coatings must be free of toxic heavy metals such as lead, cadmium, mercury, or thallium.

Applications for electroless nickel-boron deposits in the electronics industry include wire bonding for IC chips, soldering, brazing, laser welding, low electrical resistivity, and as a diffusion barrier.

Specifications

The published specifications for electroless nickel-phosphorus currently available in the United States include:

- AMS 2404, Electroless Nickel Plating (Ref 51)
- ASTM B 656, Autocatalytic Nickel Deposition on Metals for Engineering Use (Ref 43)
- Military Specification Requirements for Electroless Nickel Coatings (Ref 52)

In addition, an international standard has been drafted by the International Standards Organization (Ref 50). Published standards for electroless nickel-boron coatings for engineering purposes are not available.

Although these standards are good guidelines for testing and quality control, none include any real requirements for structural quality, corrosion resistance, or wear resistance. The standards consist primarily of a visual examination and simple tests for thickness and adhesion. Often this forces industrial users to develop their own internal specifications for coating quality. These in-house specifications can be relatively simple with requirements for only a few desired properties, or very detailed with requirements for substrate pretreatment, bath operation, equipment design, deposit chemistry, and properties.

References cited in this section

43. " Autocatalytic Nickel Deposition on Metals for Engineering Use," Part 9, B 656, *Annual Book of ASTM Standards,* ASTM, 1981
50. "Autocatalytic Nickel-Phosphorus Coatings," ISO 4527, International Standards Organization
51. "Electroless Nickel Plating," AMS 2404B, Society of Automotive Engineers, 1977
52. "Military Specification-Coatings, Electroless Nickel, Requirements for," MIL-C-26074B, U.S. Government Printing Office, 1959 and 1971

Electroless Nickel Composite Coatings

Composites are one of the most recently developed types of electroless nickel coatings. These cermet deposits consist of small particles of intermetallic compounds, fluorocarbons, or diamonds dispersed in an electroless nickel-phosphorus matrix. These coatings have a high apparent hardness and superior wear and abrasion resistance.

Chemistry. Most composite coatings are applied from proprietary baths. Typically, they consist of 20 to 30 vol% of particles entrapped in an electroless nickel containing 4 to 11% P. Most commonly silicon carbide, diamond particles, fluorinated carbon powders and PTFE are used, although calcium fluoride is also occasionally codeposited. The particles are carefully sized and are normally 1 to 3 μm in diameter (Ref 53, 54, 55) for silicon carbide and diamonds and 0.35 μm for PTFE. A micrograph of a typical silicon carbide composite coating is shown in Fig. 22 (Ref 56). The baths used for composite plating are conventional sodium hypophosphite reduced electroless nickel solutions, with the desired particles suspended in them. These baths, however, are heavily stabilized to overcome or inhibit the very high surface area produced by the particles. The baths otherwise are operated normally and the nickel-phosphorus matrix is produced by the traditional hypophosphite reduction of nickel. The particles are merely caught or trapped in the coating as it forms. Their bond to the coatings is purely mechanical.

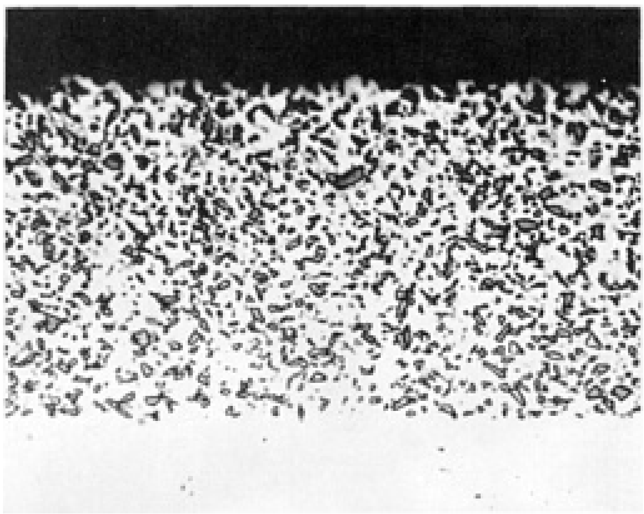

Fig. 22 Cross-sectional view of a typical silicon carbide composite coating.

Hardness and Wear. The primary use for electroless nickel composite coating is for applications requiring maximum resistance to wear and abrasion. The hardnesses of diamond and silicon carbide are 10,000 and 4500 HV, respectively. In addition, the coatings are normally heat treated to provide maximum hardness (1000 to 1100 HV_{100}) of the electroless nickel matrix. The resulting apparent surface hardness of the composite is 1300 HV_{100} or more (Ref 53, 56).

The wear surface of a composite coating consists of very hard mounds separated by lower areas of hard electroless nickel. During wear, the mating surface usually rides on the particles and slides over the matrix. Thus, the wear characteristics of these coatings approach that of the particle material (Ref 53). Typical wear test results for a silicon carbide composite coating are shown in Table 12 (Ref 56).

Table 12 Comparison of the Taber abraser resistance of silicon carbide composite coatings with other engineering materials

Material	**Hardness**	**Taber wear index, Mg 11,000 cycles**
400-C stainless steel	57 HRC	5.6
A2 tool steel	60-62 HRC	5.0
Electroless nickel (hardened)	900-1000 HV	3.7
Hard chromium	1000-1100 HV	3.0
Tungsten carbide	1300 HV	2.0
Electroless nickel and silicon carbide composite	1300 HV	0.18-0.22

Note: Taber wear index determined for an average of three 5000-cycle runs with 100 g load and CS17 abrasive test wheels

Frictional properties of composite coatings are similar to those of other electroless nickels. Typically, the coefficient of friction of these materials is about 0.13 in the lubricated condition and 0.3 to 0.4 in the unlubricated condition (Ref 53, 54).

Corrosion Resistance. In general, the corrosion resistance of composite coatings is significantly less than that of other electroless nickel coatings. The electroless nickel matrix contains large amounts of codeposited inhibitor, which reduces the alloy's passivity and corrosion resistance. Also, heat treated coatings are less protective than are as-applied coatings, both because of the conversion of the amorphous deposit to crystalline nickel and Ni_3P and because of cracking of the coating (Ref 53, 56). With composites, this problem is amplified because of the presence of the diamond or intermetallic particles. The mixture of phosphides, nickel, and particles creates a very strong galvanic couple accelerating attack. For applications requiring good corrosion resistance, electroless nickel composite coatings are not normally used.

References cited in this section

53. J.M. Scale, Wear Resistance of Silicon Carbide Composite Coatings, *Met. Prog.,* Vol 115 (No. 4), 1979, p 44

54. D.J. Kenton et al., "Development of Dual Particle Multifunction Electroless Nickel Composite Coatings," Electroless Plating Symposium, American Electroplaters' Society, 1982 (St. Louis, MO)

55. N. Feldstein et al., "The State of the Art in Electroless Composite Plating," Electroless Plating Symposium,

American Electroplaters' Society, 1982 (St. Louis, MO)

56. W.B. Martin et al., "Electroless Nickel Composites--The Second Generation of Chemical Plating," Electroless Nickel Conference, Nov 1979 (Cincinnati, OH)

Plating on Plastics

Except for ferrous alloys, plastics are probably the substrate most commonly electroless nickel plated. The coating is typically applied to nonmetallics as a conductive base for subsequent electroplating of both decorative and functional deposits. Occasionally, electroless nickel is used by itself for applications requiring resistance to abrasion or environmental attack (Ref 2). Because plastics are nonconductive and are not catalytic to the chemical reduction of nickel, special processing steps are required to ensure adequate adhesion and to initiate deposition. With synthetics, metallic bonds cannot form between the coating and the substrate. Thus, adhesion results only from mechanical bonding of the coating to the substrate surface. To improve adhesion, plastics are typically etched in acidic solutions or organic solvents to roughen their surface and to provide more bonding sites.

In order to initiate electroless nickel plating on plastics (or other nonmetals) their etched surfaces must first be catalyzed with stannous chloride and palladium chloride and then accelerated in acid. This produces palladium nucleation sites on the surface for deposition. A typical pretreatment sequence for plastics is:

- Degreasing
- Etching
- Neutralization
- Catalyzation
- Acceleration
- Electroless nickel deposition

Thorough rinsing after each processing step is essential. After the electroless nickel layer has been completed, the part may be plated conventionally with any desired electrolytic coating (Ref 2, 57).

Degreasing. When necessary, light soil or fingerprints can be removed from plastic parts by immersion in a mildly alkaline soak cleaner for 2 to 5 min. A typical degreasing solution contains 25 g/L each of sodium carbonate and trisodium phosphate and is operated at 50 to 70 °C (120 to 160 °F). Alkaline cleaning is not always required, provided the plastic is carefully handled after molding and is not allowed to become excessively soiled. Fingerprints and loose dust or dirt are normally removed by the etching solution.

Etching solutions for plastics are typically strongly oxidizing acids that cause a microscopic roughening of the part's surface. These solutions also alter the chemical character of the surface and cause it to become hydrophylic. Etching not only improves mechanical bonding and adhesion of the coating to the plastic substrate, but also improves access of subsequent processing solutions to the surface. Most commercially used etching solutions are formulated with either chromic acid or mixtures of sulfuric acid and chromic acid or dichromate salt. These solutions are typically operated at 50 to 70 °C (120 to 160 °F) with immersion times of 3 to 10 min. Chromic acid based solutions are particularly effective with ABS plastics, but are also used for polyethylene, polypropylene, PVC, polyesters, and other common polymers.

Neutralizing. After the plastic has been properly etched and rinsed, it should be neutralized to remove residual chromium ions, which may interfere with subsequent catalyzation. Neutralizers are rinsing aids and are typically dilute acid or alkaline solutions, often containing complexing and reducing agents. Ionic surfactants are sometimes added to increase the absorption of the catalyst on the surface. Neutralizing solutions are normally operated at 40 °C (105 °F) with immersion times of 1 to 2 min.

Catalyzing. In order to initiate deposition of the electroless nickel coating on plastics, their surfaces must be catalyzed. This is normally accomplished by chemically depositing small amounts of palladium. The original commercial catalyzing procedures required two processing steps. In the first step, stannous chloride was absorbed onto the surface from a solution of $SnCl_2$ and HCl. After rinsing, the part was immersed in a solution of $PdCl_2$ and HCl, and palladium chloride was absorbed onto the surface. The stannous ions then reduced the palladous ions leaving discrete sites of metallic palladium. Currently, a one-step catalyzing procedure is normally used. For this, a solution of stannous chloride and palladium chloride in hydrochloric acid is used. The solution consists of tin/palladium complexes and colloids stabilized by excess stannous chloride. The chloride content of the solution is critical and must be carefully controlled. During immersion, globules of tin/palladium colloid absorb onto the plastic surface. After rinsing, nuclei of metallic palladium surrounded by hydrolyzed stannous hydroxide, are left attached to the surface.

Acceleration. With one-step catalyzation, a further step is required to remove excess stannous hydroxide from the surface and to expose the palladium nuclei. This step is called acceleration and is accomplished by immersing the part in a dilute solution of hydrochloric acid or an acid salt. The acid reacts with the insoluble stannous hydroxide forming soluble stannous and stannic chloride. After rinsing, there surface is free of tin and active catalytic sites are present. Acceleration solutions are typically operated at a temperature of 50 °C (120 °F) and are agitated with air. The parts are normally immersed for 30 to 60 s.

Electroless Nickel Deposition. Most electroless nickel solutions operate at too high a temperature for plastics. High temperatures may cause plastics to warp. In addition, the large difference in coefficient of thermal expansion between plastics and electroless nickel may cause adhesion failures during cooling from bath temperatures. Electroless nickel solutions for plating on plastics, thus, are formulated to operate at low temperatures--typically 20 to 50 °C (70 to 120 °F). These solutions are normally alkaline and reduced with sodium hypophosphite, although some DMAB solutions are also used. Ammonia-based plating baths are preferred because of their ability to complex excess palladium dragged in with the part and to avoid spontaneous decomposition. While most of these solutions are proprietary, some typical formulations (Ref 2) are:

Composition	**Bath 1**		**Bath 2**	
	g/L	**oz/gal**	**g/L**	**oz/gal**
Nickel chloride	119	15	. . .	. . .
Nickel sulfate	. . .	. . .	50	6.5
Sodium hypophosphite	106	14	50	6.5
Sodium pyrophosphate	. . .	. . .	100	13
Ammonium citrate	65	8	. . .	. . .
Ammonia, mL/L (fluid oz/gal)	. . .	. . .	45	5.8
Sodium hydroxide	To pH		. . .	. . .

Operating conditions	**Bath 1**	**Bath 2**
pH	10	10
Temperature, °C (°F)	30-50 (85-120)	25 (77)

Typical plating rate, μm/h (mils/h)	3-11 (0.12-0.44)	3 (0.12)

Plastic parts are normally immersed in the electroless nickel solution for 5 to 10 min to provide a uniform metal film about 0.25 to 0.50 μm thick. This coating is sufficient to cover the surface of the plastics and to make them conductive for subsequent electroplating. These deposits typically contain 2 to 6% P. After proper treatment the peel strength of 25 mm (1 in.) width strips of these coatings on plastics like ABS and polypropylene is on the order of 50 to 100 N (Ref 2, 57).

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
57. J.K. Dennis and T.E. Such, *Nickel and Chromium Plating,* Newres-Butterworths, 1972, p 287

Electroless Copper Plating

Cheryl A. Deckert, Shipley Company, Inc.

Introduction

ELECTROLESS, OR AUTOCATALYTIC, METAL PLATING is a nonelectrolytic method of deposition from solution. The minimum necessary components of an electroless plating solution are a metal salt and an appropriate reducing agent. An additional requirement is that the solution, although thermodynamically unstable, is stable in practice until a suitable catalyzed surface is introduced. Plating is then initiated on the catalyzed surface, and the plating reaction is sustained by the catalytic nature of the plated metal surface itself. This definition of electroless plating thus eliminates both those solutions that spontaneously plate on all surfaces (homogeneous chemical reduction), such as silver mirroring solutions, and immersion plating solutions, which deposit by displacement a very thin film of a relatively noble metal onto the surface of a sacrificial, less noble metal.

The history of electroless plating began with the serendipitous discovery, by Brenner and Riddell, of electroless nickel-phosphorus, during a series of nickel electroplating experiments in 1946 (Ref 1). Electroless copper chemistry was first reported in the following year by Narcus (Ref 2). The first commercial applicability of electroless copper was reported in the mid-1950s with the development of plating solutions for plated-through-hole (PTH) printed wiring boards. Electroless copper solutions resembling today's technology were first reported in 1957 by Cahill (Ref 3) with the report of alkaline copper tartrate baths using formaldehyde as reducing agent. Copper baths of the 1950s were difficult to control and very susceptible to spontaneous decomposition. Over the years, continual advances in control and capabilities have taken place and continue to be recorded in a variety of reviews (Ref 4, 5). At present, not only are formulations extremely stable and predictable in behavior over long periods and under a wide variety of operating conditions, but they also provide copper deposits having excellent physical and metallurgical properties comparable with those of electrolytic deposits.

Electroless copper plates much more slowly, and is a much more expensive process, than electrolytic copper plating. However, electroless copper plating offers advantages over electrolytic plating that make it the method of choice in certain cases. Electroless copper plates uniformly over all surfaces, regardless of size and shape, demonstrating 100% throwing power; and it may be plated onto nonconductors, or onto conductive surfaces that do not share electrical continuity. The ability to plate large racks of substrates simultaneously is also an advantage in certain instances. These advantages have contributed to the choice of electroless copper in the applications to be discussed herein.

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References

1. A. Brenner and G.E. Riddell, *AES Proc.,* Vol 33, 1946, p 23
2. H. Narcus, *Met. Finish.,* Vol 45, Sept 1947, p 64
3. A.E. Cahill, *AES Proc.,* Vol 44, 1957, p 130
4. C.R. Shipley, *Plating,* Vol 71 (No. 6), 1984, p 94
5. G.O. Mallory and J.B. Hajdu, Ed., *Electroless Plating: Fundamentals and Applications,* American Electroplaters Society, 1990

Bath Chemistry

The theoretical basis of the electroless copper deposition process has been studied on numerous occasions and has recently been reviewed (Ref 6). As stated above, the minimum necessary components of an electroless plating solution are the metal salt and a reducing agent. The source of copper is a simple cupric salt, such as copper sulfate, chloride, or nitrate.

A number of common reducing agents have been suggested (Ref 7) for use in electroless copper baths: formaldehyde, dimethylamine borane, borohydride, hypophosphite (Ref 8), hydrazine, sugars (sucrose, glucose, etc.), and dithionite. In practice, however, virtually all commercial electroless copper solutions have used formaldehyde as reducing agent. This is due to the combination of cost, effectiveness, and ease of control of formaldehyde systems. It is particularly remarkable in view of the considerable and continual pressures exerted on the plating industry by environmental and regulatory agencies due to health concerns regarding formaldehyde exposure (see the section "Environmental and Safety Issues" in this article). Because of the overwhelming commercial importance, in this chapter we will confine discussion to formaldehyde-based systems.

For Cu(II), the relevant half-cell reaction for electroless deposition is:

$$\mathrm{Cu^{2+} + 2e^- \leftrightarrow Cu^0} \qquad E^0 = +0.340\,\mathrm{V}$$

For formaldehyde, the E^0 depends on the pH of the solution:

$$\mathrm{HCOOH + 2H^+ + 2}e^- \leftrightarrow \mathrm{HCHO + H_2O} \qquad \mathrm{pH} = 0 \qquad E^0 = +0.056$$

$$\mathrm{HCOO^- + 2H_2 + 2}e^- \leftrightarrow \mathrm{HCHO + 3OH^-} \qquad \mathrm{pH} = 14 \qquad E^0 = -1.070$$

Therefore, electroless copper solutions using formaldehyde as reducing agent employ high pH, above pH 12 (typical NaOH concentration is >0.1 *N*; theoretically 0.1 *N* = pH 13).

Because simple copper salts are insoluble at pH above about 4, the use of alkaline plating media necessitates use of a complexing, or chelating, component. Historically, complexing agents for electroless copper baths have almost always fallen into one of the following groups of compounds:

- Tartrate salts
- Alkanol amines, such as quadrol (N,N,N',N' tetrakis(2-hydroxypropyl)ethylenediamine) or related compounds
- EDTA (ethylenediamine tetraacetic acid) or related compounds

Glycolic acids and other amines have also been reported (Ref 7).

Tartrates were used in the earliest baths and continue to be used, particularly for low-plating-rate (≤ 0.5 μm/20 min), low-temperature (near ambient) applications. Tartrates are more easily waste-treatable than the other two classes of chelates, but they have not readily lent themselves to formulation of faster plating systems.

Alkanol amines came into wide use in electroless copper baths in the late 1960s, with the advent of faster plating systems. This type of chelate made it possible to achieve "high-build" (≥2 μm/20 min) electroless copper solutions, and it continues to have wide use even today. Because quadrol and its analogs are liquids, totally miscible with water, they are not easily removed from the waste solution, and hence they are resistant to many conventional waste treatment procedures.

EDTA salts are also widely used for complexing electroless copper solutions. EDTA has certain desirable characteristics versus those of quadrol, based on waste treatability. Specifically, EDTA can be more easily separated (precipitated) from waste solutions by pH adjustment. Starting in the late 1970s, bath additives for EDTA systems (see below) were developed that allowed excellent control of plating rate, grain structure, and other important factors. Because of the very high affinity of EDTA for any metal ions, even small residual amounts of dissolved EDTA can draw potentially toxic metals into the waste stream. This has led to increased legislative efforts (notably in Germany and Japan) against use of this chelate and its derivatives. However, at present, the most commonly used plating baths are based on EDTA.

Besides the copper salt, the reducing agent, the source of alkalinity, and the chelate, other important components are present in commercial electroless copper solutions. These components are generally considered the proprietary portion of the formulation, and they control such parameters as initiation and plating rate, stability (versus dragged-in catalyst; versus excessively high bath activity; versus long shutdown periods; versus Cu(I) oxide), deposit stress, color, ductility, and so on. Prior to development of well-characterized and controlled trace additives, electroless copper baths were prone to "triggering" (spontaneous decomposition of the bath), "plateout" (decomposition over a prolonged standing period), "second day startup" (inability to induce a controlled plating reaction when first stored after makeup), dark deposit color, rough deposit, coarse grain structure, and so on. Literally hundreds of papers and patents have been published relating to these additives. Useful summaries of this data are available (Ref 9, 10).

Additives that stabilize the bath against various manifestations of undesired plateout are referred to as *stabilizers.* Understanding their composition, mechanism, and optimal replenishment rate is key to successful operation of a bath. They are usually employed at low concentrations, typically 1 to 100 ppm. Principal among the materials reported are compounds such as mercaptobenzothiazole, thiourea, other sulfur compounds, cyanide or ferrocyanide salts, mercury compounds, molybdenum and tungsten, heterocyclic nitrogen compounds, methyl butynol, propionitrile, and so on. Pressure from environmental and regulatory groups over the years has led to near-elimination of cyanide- and mercury-type additives. It is noteworthy that perhaps the most common stabilizer for electroless copper baths is a steady stream of air (i.e., oxygen) bubbled through the solution.

Additives that increase the plating rate of the solution are variously referred to as *rate promoters, rate enhancers, exhaltants,* or *accelerators.* This last term is particularly unfortunate and confusing in view of the use of the term *accelerator* to describe a key process step in electroless copper processes (see the section "Processes" in this article). Materials that have been reported to function as rate promoters include ammonium salts, nitrates, chlorides, chlorates, perchlorates, molybdates, and tungstates. Rate promoters may be present in the electroless formulation at concentrations of 0.1 *M* or higher.

Other additives may also be incorporated in certain cases. For example, surfactants may be used to improve deposit characteristics (Ref 11), and incorporation of excess halide ion into the formulation permits elimination of the normal accelerator step (Ref 12) (see the section "Processes" in this article).

Typical examples of freshly made-up electroless copper baths are given in Table 1.

Table 1 Examples of electroless copper formulations

	Low build (tartrate)	**High build (quadrol)**	**High build (EDTA)**	**Full build (EDTA)**
Copper salt, as Cu(II)	1.8 g/L	2.2 g/L	2.0 g/L	3.0 g/L
	0.028 *M*	0.035 *M*	0.031 *M*	0.047 *M*

Chelate	Rochelle salt	Quadrol	Disodium EDTA dihydrate	Disodium EDTA dihydrate
	25 g/L	13 g/L	30 g/L	42 g/L
	0.089 *M*	0.044 *M*	0.080 *M*	0.11 *M*
Formaldehyde, as HCHO	10 g/L	3 g/L	3 g/L	1.5 g/L
Alkalinity, as NaOH	5 g/L	8 g/L	7 g/L	3 g/L
Additives[(a)]	<2 g/L	<2 g/L	<2 g/L	<2 g/L
Temperature, °C (°F)	20 (70)	43 (110)	45 (115)	70 (160)
Plating rate, μm/20 min	0.2	2.5	2	1

Note: The terms *low build, high build,* and *full build* are defined in the section "Deposit Properties" in this article.

(a) Examples of additives: 2-mercaptobenzothiazole, diethyldithiocarbamate, 2,2'-dipyridyl, potassium ferrocyanide, vanadium pentoxide, nickel chloride, polyethylene glycol

The overall electroless copper plating reaction is theoretically given as:

$$\begin{gathered}Cu^{2+} + 2HCHO + 4OH^- \rightarrow \\ Cu^0 + H_2 + 2\ H_2O + 2\ HCO_2^-\end{gathered}$$

This equation calls for the consumption of four hydroxide ions and two molecules of formaldehyde for each atom of copper deposited. However, certain side reactions may also take place, the most common being the Cannizzaro reaction, which consumes additional caustic and formaldehyde:

$$2HCHO + OH^- \leftrightarrow CH_3OH + HCOO^-$$

In addition, other side reactions also occur, consuming formaldehyde and producing unwanted byproducts such as cuprous oxide, which can lead to bath decomposition unless suitable stabilizers are present.

Once the bath begins to be used, copper, caustic, and formaldehyde are consumed and must be replenished. This is typically carried out by routine analysis, either manually or electronically, with back addition of appropriate replenishment chemistries (see the section "Controls" in this article). Ordinarily, some bailout of the plating solution must be done at this point, to allow for the volume of new chemistry to be added. Because the anion of the copper salt (usually sulfate or chloride) and the cation of the caustic component (usually sodium) are not consumed, a buildup of sodium sulfate or chloride occurs. This can cause deleterious effects such as "voiding" or high deposit stress over prolonged bath life, particularly when bailout volumes are very low. In addition, formate ion builds up as a byproduct of the plating reaction itself. The extent to which the Cannizzaro reaction takes place also contributes to the quantity of byproduct buildup. Byproduct buildup can cause deterioration of bath and deposit properties (Ref 13, 14), and it is now typically accounted for during the bath formulation. Steady-state performance is achieved after a specified number of bath turnovers (or "cycles"), depending on the recommended bailout volume, and is typically controlled through specific gravity.

References cited in this section

6. P. Bindra and J.R. White, *Electroless Plating: Fundamentals and Applications,* G.O. Mallory and J.B. Hajdu, Ed., American Electroplaters Society, 1990
7. E.B. Saubestre, *AES Proc.,* Vol 44, 1957, p 130
8. M. Gulla and O.B. Dutkewych, U.S. patent 4,482,596, 1984
9. J. McDermott, *Plating of Plastics with Metals,* Noyes Data, 1974
10. J. Bielinski and K. Kaminski, *Surf. Coat. Technol.,* Vol 31, 1987, p 223
11. R.M. Lukes, U.S. patent 2,996,408, 1961
12. G.M. Wilkinson, C.A. Deckert, and J.J. Doubrava, U.S. patent 4,751,106, 1988
13. C.I. Courduvelis and G. Sutcliffe, *Plat. Surf. Finish.,* Vol 67, Sept 1980, p 71
14. C.A. Deckert, G.E. Hutchins, and M. Abu-Moustafa, Paper T-2, *AES Proc.,* Vol 69, 1982

Deposit Properties

Plating Rate and Deposit Thickness. Not strictly a deposit property, plating rate is a key characteristic of an electroless copper plating bath. Plating rate and useful range of deposit thickness dictate the specific applicability of a formulation. Plating baths are typically categorized as *low build, high (heavy) build,* or *full build.*

Low build deposits about 0.5 μm (or less) in about 20 min and typically operates at ambient temperature. This was typical of the earliest stable bath formulations developed in the 1960s. These baths are traditionally tartrate-based; in fact, it has proven difficult to formulate stable, faster plating baths using a tartrate chelate system. These deposits are typically fine-grain and exhibit good deposit integrity. They are suitable for applications such as subtractive printed wiring boards, where an electrolytic plateup process follows immediately after copper deposition (see the section "Applications" in this article).

High (heavy) build deposits 2 to 3 μm in about 20 min and typically operates at elevated temperature (35 to 55 °C, or 95 to 130 °F), but room-temperature formulations are also available. These baths are usually based on EDTA or quadrol chemistry. Acceptable formulations of this type were first developed in the early 1970s. Earlier baths tended to give coarse-grain deposits and produced somewhat highly stressed deposits, especially at higher limits of deposit thickness. However, these formulations have been refined to a high degree and are readily controlled to give excellent deposit properties. Major applications for this type of bath are those where intervening process steps may occur prior to subsequent plateup, such as in pattern plate printed wiring boards (see the section "Applications" in this article).

Full build typically deposits 25 μm or more of copper over a more prolonged plating cycle of up to 15 h. (By comparison, a typical electroplating process would deposit 25 μm of copper in 35 to 50 min.) The typical temperature of operation is 55 to 80 °C (130 to 175 °F). A fundamental requirement in developing this type of bath has been the achievement and maintenance of deposit characteristics such as high ductility and tensile strength, fine grain structure, low intrinsic stress, and so on throughout the thick deposit. This type of bath was first reported in 1964 (Ref 15) and has been employed primarily for additive-type printed wiring board applications. EDTA has been the main chelate used. This deposit typically represents the full metal thickness required for the applications and hence eliminates the need for electroplating altogether (Fig. 1). The very high expense of building a thick copper deposit using an electroless versus electroplating process is warranted (or required) for certain applications, such as when absolutely uniform thickness is needed, when electrically discontinuous surfaces are to be plated, or when very high aspect ratio holes are to be plated. For example, processes for fabricating multichip modules require use of a full-build electroless copper (see the section "Applications" in this article). In this application the copper thickness requirement may be substantially less than 25 μm. A number of advances in the area of full-build copper plating have occurred over the past five years or so (Ref 15, 16, 17). The most critical deposit characteristics are ductility and tensile strength, particularly at the elevated temperatures (260 to 288 °C, or 500 to 550 °F) employed in the printed wiring board assembly processes. Current development activities in this area are aimed toward achievement of substantially higher plating rates without loss of deposit properties.

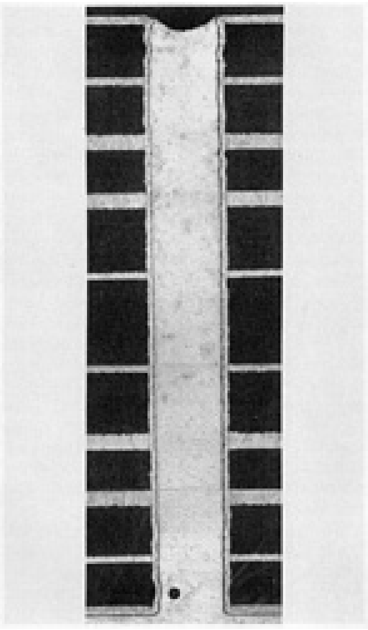


Fig. 1 Through-hole plated using full-build electroless copper

Other. Of course, intermediate thicknesses of copper are achievable by appropriate manipulation of the bath operating parameters. *Very slow* and *medium build* formulations are also applicable to some of the applications to be discussed.

Purity, Density, and Electrical Properties. Deposit purity of electroless copper films is somewhat lower than that of electrolytic films, due to codeposition of traces of electroless bath components. This affects several physical properties, including percent purity, density, and resistivity. Typical acid-copper electrolytic baths produce films of 99.9% purity, 8.92 g/cm^3 density, and 1.72 μΩ· cm volume resistivity (at 20 °C) (Ref 18), whereas the printed wiring board industry standard (Ref 19) for full-build electroless copper is 99.2% purity (min), 8.8 ±0.1 g/cm^3 density, and 1.90 μΩ· cm (at 20 °C) resistivity (max).

Grain Structure. Because electroless copper deposition is initiated on the randomly distributed catalyst particles on the substrate, initial grain structure is largely determined by that surface morphology. Bath formulation is of course a strongly determining factor as well, and it will control the grain structure as the deposit thickness increases. It is thought that fine-grain deposits, initiating at close proximity on the catalytic sites and coalescing to form a film early in the deposition process, offer superior copper quality in the early stages of film growth. Recently, full-build electroless copper grain structure was studied, correlated with etching rate in a variety of common copper foil etching solutions, and compared with typical electrolytic copper grain structure (Ref 17).

Tensile Strength and Ductility. Advances in electroless copper formulations, particularly for full-build applications in printed wiring board applications, have centered on achieving deposit mechanical properties, specifically tensile strength and ductility, that ensure the needed film reliability (Ref 20). Tensile strength of up to 490 MPa (70 ksi) and elongation of up to 15% can now be achieved (Ref 15), although these properties are not achieved from the same formulation. Improvement in the as-plated elongation values may be achieved with heat aging, at the expense of tensile strength. It has also been reported that ductility at thermal shock temperature (e.g., 260 to 288 °C, or 500 to 550 °F) may be significantly higher than as measured at ambient temperature. Some discussion is still in progress (Ref 15, 21) regarding the relative importance of these two properties in defining an ideal plated deposit.

Other Properties. Other deposit properties, such as hydrogen inclusion, are also of interest.

References cited in this section

15. D. Dinella and C. Mak, Paper B 5/1, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990

16. K. Minten and J. Toth, Paper B 5/2, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990; *Circuit World,* Vol 17, 1991, p 19
17. K. Minten, J. Seigo, and J. Cisson, *Circuit World,* Vol 18 (No. 4), 1992, p 5
18. F.E. Stone, *Electroless Plating: Fundamentals and Applications*, G.O. Mallory and J.B. Hajdu, Ed., American Electroplaters Society, 1990
19. IPC-AM-372, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL
20. V.A. Lamb, C.E. Johnson, and D.R. Valentine, *J. Electrochem. Soc.,* Vol 117, 1970, p 341c, 381c
21. A. Nakaso, K. Yamanoi, and T. Okamura, Paper WCIII-10, Proc. Printed Circuit World Convention III (Washington, D.C.), 1984

Applications

Printed Wiring Boards (PWBs)

By far the most important commercial application of electroless copper plating has been the PTH process for fabricating printed wiring boards (PWBs). Prior to the mid-1950s, mounting components onto PWBs relied on mechanical interlocking using inserted eyelets. The through-holes could not be electroplated directly because the base material of the circuit board (paper-phenolic, epoxy-glass, or other dielectric) did not provide the needed electrical conductivity. Development of electroless copper plating solutions (Ref 22), made practical by concurrent development of suitable selectively adsorbing catalytic materials (see the section "Processes" in this article), led to a dramatic improvement in the reliability of printed circuit boards and prompted the rapid growth of the PWB market during the 1960s through 1980s.

The vast majority of PWBs are made by a subtractive process using base material, typically epoxy-glass laminate, clad with electrolytic copper foil. The substrate is drilled, after which electroless copper is plated through the holes (and incidentally over the foil surface). Then electrolytic copper buildup and surface copper imaging (using dry film) take place; the order of these processes defines the fabrication process as either *panel* plating or *pattern* plating. In pattern plating, the plated areas are next overplated with a dissimilar metal (typically Sn/Pb), the dry film is removed, and all exposed copper is etched. In panel plating, no dissimilar metal plating is required; etching takes places immediately after imaging. The term *subtractive* processing arises from the fact that the circuitry is ultimately formed by removing base copper from the circuit board.

Although the basic overall process flow for fabricating a PWB has remained essentially constant for decades, the technology associated with every subprocess has undergone great improvement over that time period, and the electroless copper process is no exception. Improvements in electroless copper formulations, as discussed earlier, have greatly improved control of PWB processing and end product reliability. However, developments in PTH pretreatment have probably contributed even more greatly to end board reliability over that period. New hole preparation methods for multilayer boards provided such substantial benefits in terms of key criteria like copper coverage, adhesion (to laminate) and solderability (Ref 23) (see the section "Performance Criteria" in this article) that two-sided boards are now also frequently processed through these additional steps.

Careful integration of the steps immediately preceding catalyzation has also ensured that the optimal uniform, yet minimal, catalyst film is deposited in preparation for plating. This has provided the key to achieving interconnect bonds sufficiently strong (Ref 24) to withstand multiple thermal shocks, thus assuring very high end-product reliability (see the section "Performance Criteria" in this article). At present, the PWB market is under considerable environmental and cost pressure to replace electroless copper with a direct metallization process (see the section "Environmental and Safety Issues" in this article). Recent quality improvements, such as those described, present a formidable target for replacement technologies.

Additive processes for PWBs rely, as the name implies, on the buildup of the circuit copper over bare laminate. Variations on the fully additive process include semiadditive and partly additive processes. Description of these is documented in many published reports, which have been recently reviewed (Ref 25). Fully additive processes have been in use since 1964 and offer a number of advantages over conventional subtractive processing. Despite this, growth in the additive market has been slow; worldwide production in 1992 has been estimated at 2 to 5% of the world PWB production (Ref 26, 27). This slow growth is due partly to the more difficult adhesion and selectivity requirements and partly to the lack of adequate physical properties in the full-build electroless copper that is an integral component of the process. However, in recent years the quality of full-build electroless has become satisfactory, and this, coupled with improved process control and new automatic bath controllers, provides support for future growth of the additive PWB market (see the section "Equipment" in this article).

Decorative Plating-on-Plastic (POP) (Ref 28)

Since the 1950s, plastics have been substituted for metals in a multitude of applications and for a variety of reasons, including weight advantages, cost advantages, and the relative ease of creating complexly shaped substrates through molding. These factors prompted the development of suitable decorative finishing processes, specifically plating processes, starting in the early 1960s. Electroless metal deposition as a base for a thicker, decorative electrolytic deposit has proven extremely reliable and commercially successful. For lower-performance applications, electroless nickel is a suitable choice. However, ever since the demonstration in the 1970s that electroless copper provides better resistance to environmental exposure (Ref 29, 30), it has become the material of choice in the majority of higher-performance applications, especially automotive. The molded substrate is chemically treated to improve adhesion of the copper film (see the section "Processes" in this article), then about 0.5 to 0.75 μm of electroless copper is applied. Typically an electrolytic copper or Watts nickel strike follows, and then a thicker (12 to 25 μm) electrolytic bright acid copper deposit. Finishing coats of electrolytic nickel and/or chromium plating are then applied.

Substrate materials (Ref 28) for decorative plating-on plastic include acrylonitrile-butadiene-styrene (ABS), ABS/polycarbonate, polyphenylene oxide, polycarbonate, polysulfone, polyester, nylon, and so on. There are many grades for any given plastic, and these may differ considerably in plateability. Certain grades of foamed plastics may also be used. For decorative POP, ABS is by far the most commonly used plastic. ABS is a thermoplastic alloy with an acrylonitrile-styrene matrix that has butadiene rubber dispersed throughout. The butadiene is selectively etched by the pretreatment chemistry, creating a uniformly roughened surface suitable for plating.

In all POP applications, control of the molding process is critical. Care must be taken to avoid introducing stresses or strains, to avoid troublesome mold-release agents, to limit use of "regrind" resin, to ensure a resin-rich surface (in cases where fillers are used), and so on. The use of complexly shaped parts necessitates close attention to such details as mold design and maintenance, melt and mold temperatures, fill speed, and many other parameters. In designing or troubleshooting a plating-on-plastic process, it is critical to use molded parts of the exact grade and design to be used, as there is high interdependence between molding and plating processes.

Functional POP (Electromagnetic Interference Shielding)

Another commercially important application for electroless copper is electromagnetic interference (EMI) shielding of electronic components. The need to reduce (attenuate) electromagnetic signals (Ref 31) generated either internally or externally to a packaged component leads to the need to provide EMI shielding to the component. EMI shielding capability is directly related to the conductivity of the component; hence, metal cases are highly effective in attenuating EMI. However, the same factors (cost and weight) that led to the use of plastics as base materials for decorative applications have also led to their implementation in electronic cabinetry. Because plastic enclosures are poor at attenuating EMI signals, a variety of coating methods have been developed to address this need. Methods that address the requirements of EMI shielding of plastic enclosures include electroless copper plating, as well as various types of metal-filled paints, zinc arc/flame spray, sputtered or evaporated metals, and conductive foils/tapes. Table 2 summarizes and updates published data (Ref 32, 33) on the most common methods of shielding. Key in choosing a method is the attenuation (measured in decibels) over a desired frequency range (Ref 34). Note that decibels of shielding is a logarithmic term, so a difference of 20 dB equals 100 times the shielding effectiveness.

Table 2 Methods of EMI shielding

Material/ method	Shielding capability[(a)]	Process cost[(b)]	Advantages	Disadvantages
Zinc arc spray	H	H	Good conductivity; hard, dense coat; very effective	Special equipment needed; prone to flaking; may distort housing
Conductive paints				

Silver	VH	VH	Good conductivity; conventional equipment; resists flaking; easy to apply	Expensive
Nickel	L	M	Conventional equipment	Multiple coats needed; effectiveness not high; thickness causes problems
Copper	M-H	M	Conventional equipment	Multiple coats needed; thickness causes problems
Evaporated metal	M	H	Familiar technology	Size limited by vacuum chamber; expensive equipment
Sputtered metal	M	M	Good conductivity	Expensive equipment; may distort housing
Conductive foils/tapes	H	VH	Good conductivity; good for experimentation	Complex parts are difficult; labor intensive
Conductive plastics	L	L	No secondary process	Material expensive; poor attenuation
Electroless plating				
Copper (two-sided)	VH	M	Uniform thickness; good for all shape parts; resists chipping; good conductivity	Limited to certain plastics; two-sided process usually requires paint finish; prone to oxidation
Nickel (two-sided)	M	H	Same as above, except conductivity	High thickness required for effective shielding
Copper/nickel (two-sided)	VH	M	Same as copper only, plus corrosion resistant	Same as copper only, except no oxidation
Copper/nickel (one-sided)	H	M	Same as Cu/Ni two-sided; fewer chemical steps; allows molded-in color	Same as Cu/Ni two-sided, except no finish coat

Source: Updated from Ref 32, 33

(a) Attenuation: VH (very high), 90 to 120 dB+; H (high), 60 to 90 dB; M (moderate), 30 to 60 dB; L (low), 10 to 30 dB; VL (very low), 0 to 10 dB.

(b) Cost: VH (very high), $>\$3.25/\text{ft}^2$; H (high), $\$2.50$ to $\$3.25/\text{ft}^2$; M (moderate), $\$1.50$ to $\$2.50/\text{ft}^2$; L (low), $\$0.35$ to $\$1.50/\text{ft}^2$; VL (very low), $<\$0.35/\text{ft}^2$.

Clearly, electroless copper is a very effective method of EMI shielding over a wide range of radio frequencies, having been first suggested in 1966 (Ref 35) and subsequently developed in the early 1980s (Ref 36). Considerable commercial activity has taken place, as several large computer manufacturers anticipated that higher "clock speeds" of electronic devices would require rapid conversion to the most effective methods of EMI shielding, such as electroless copper. However commercial activity using electroless copper for EMI shielding applications has lagged versus the rate previously anticipated. Sustained growth in the use of electroless copper for EMI shielding is probable in the future, because the increased clock speeds of the devices emitting the signals accentuate the need for more effective shielding.

When electroless copper is employed for EMI shielding, the conductive film used typically consists of electroless copper plating to a thickness of about 0.7 to 2 μm, overplated with a thin film (0.25 to 0.5 μm) of electroless nickel. The parameter used to specify copper thickness is resistivity (Ref 37); normally less than 0.05 Ω/point-to-point over a set distance is readily achievable using electroless copper. The nickel contributes virtually nil to the shielding effectiveness (Ref 38), but it provides durability and corrosion resistance.

Specific substrate resins used in electronic enclosures include solid and/or foamed forms of ABS, polycarbonate, ABS/polycarbonate alloys, polyphenylene oxide, polystyrene, and polysulfone. A newly emerging, and potentially very large, market involves electroless copper for shielding fabric used in cable, military, and wall covering applications.

Electroless copper plating for EMI shielding may employ either a two-sided or single-sided process. In the two-sided process the entire cabinet is treated and plated; this approach generally requires a finish coat of paint. The single-sided process involves plating of the interior surface only; thus the molded plastic surface represents the final surface finish. These two processes involve totally different pretreatments, as discussed in the section "Processes" in this article.

Hybrid and Advanced Applications

Molded Interconnect Devices. Following advances in control and capability of imaging and plating technologies, and commercialization of high-performance injection molded plastics, a natural development was the molded circuit board, or molded interconnect device (MID). Adhesion promotion principles developed for the decorative POP industry have been applied to devising adhesion promotion processes for a variety of engineering thermoplastics (Ref 39), permitting deposition of adherent electroless copper deposits that could be built up in thickness and imaged similarly to conventional PWBs.

In certain cases, conventional plastics such as ABS have been used as MID substrates. However, in order to survive board assembly temperatures, more advanced plastics are often required. These include polyetherimide, polyethersulfone, polyarylsulfone, liquid crystal polymers, and so on. Molding requirements are even more critical than for decorative POP, due to the need for higher levels of adhesion (typically ≥1.1 kN/m, or 6 lb/in., peel strength, versus ~0.7 kN/m, or 4 lb/in., for decorative POP) and due to the stresses induced by plateup, imaging, and assembly processes. Certain of the plastics mentioned have proven more amenable than others to development of suitable adhesion promotion processes. Polyetherimide, in particular, has proven to be compatible with surface chemistry-altering pretreatments that produce very strongly adherent electroless copper (Ref 40), while not roughening the substrate surface excessively. The latter characteristic is particularly important when fine-line imaging processes are to be employed later in the process.

Depending on the MID design and process chosen, plateup of the initial electroless copper strike plate may employ either electrolytic copper or full-build additive copper (20 to 35 μmm). Imaging of three-dimensional substrates has necessitated development of inventive materials and processes (Ref 41). Electrodeposited photoresists, as well as novel methods of exposure and related equipment, have proven key in this effort.

At this time, the MID market has proven to be feasible and has achieved commercial success in several dedicated facilities. Many ingenious and cost-saving devices have been designed and are currently in production (Ref 39, 42). Figure 2 demonstrates a number of commercially produced MIDs. However, this market has not achieved the level of acceptance predicted in the late 1980s, due to the need for high volumes of a given design to amortize mold costs, the failure of materials costs to come down to required levels, and the tendency of electronic designers to employ more familiar methods, such as conventional PWBs, whenever possible.

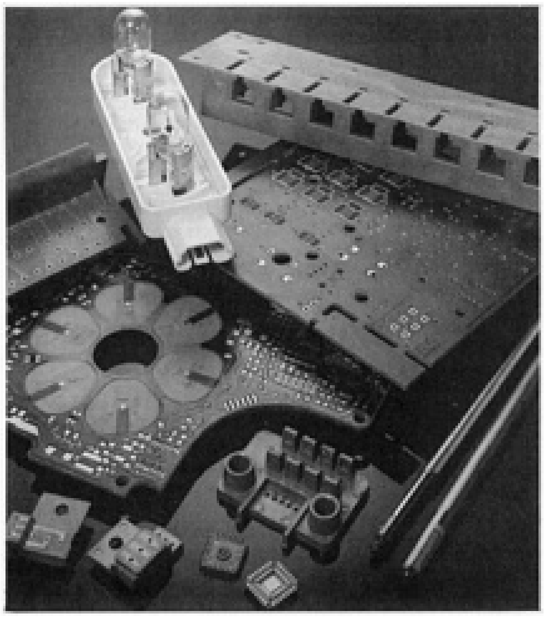


Fig. 2 Examples of commercially produced molded interconnect devices. Courtesy of Shipley Co.

Composite Connectors. The composite connector application is a hybrid of two-sided EMI shielding with molded interconnects. These parts are currently made of aluminum, and for all the usual reasons, considerable interest lies in replacing the aluminum with a lighter material such as plastic. The physical requirements of the connector are such that only advanced engineering plastics, such as those used in the MID market, are suitable. The parts must be plated, not to form circuitry but to provide EMI shielding. Fabrication of these devices employs the same plastics and pretreatments for electroless plating that are employed for molded interconnects. Due to the durability, lubricity, and hardness requirements of the finished parts, the electroless nickel overcoat is built up to a rather higher thickness (~5 μm) than for EMI shielding of electronic cabinetry. Examples of some plastic composite connectors, processed through electroless copper and nickel, are shown in Fig. 3.

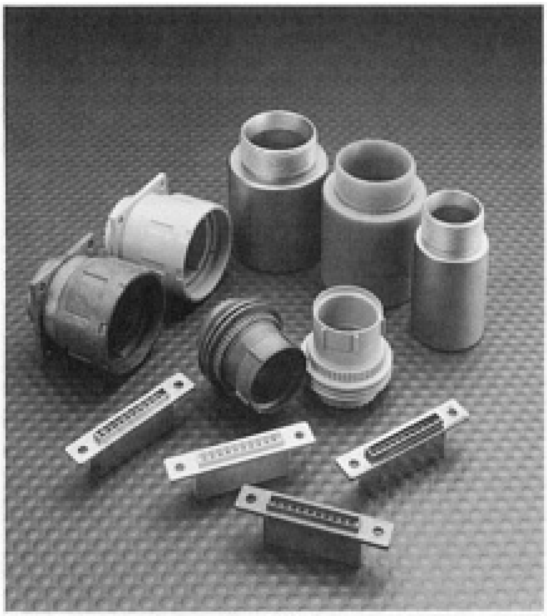


Fig. 3 Examples of plastic composite connectors plated with electroless copper and nickel. Courtesy of Shipley Co.

Multichip Modules. Progress in semiconductor technology continues to place increasing demands on interconnection and assembly technology. In the 1980s, the response to this demand on the PWB side was increasing numbers of layers and finer circuitry. However, this trend cannot be sustained at the needed rate (Ref 43), leading to the requirement for an intermediate level of interconnection onto which bare chips may be mounted (Ref 44). These devices, known as multichip modules (MCMs), may be fabricated using several approaches (Ref 45, 46, 47). However, a common feature is the use of full-build electroless copper (Ref 48) to build up the conductive traces.

An example of a fabrication process for an MCM is given in Fig. 4. The electroless copper subprocess generally follows along the lines of the PTH and POP processes (discussed in more detail in the section "Processes" in this article). Adhesion promotion for the metallization layer to the unique dielectric materials employed in MCMs can be a challenge in itself. Conventional "swell and etch" approaches are normally used; other approaches are also in development.

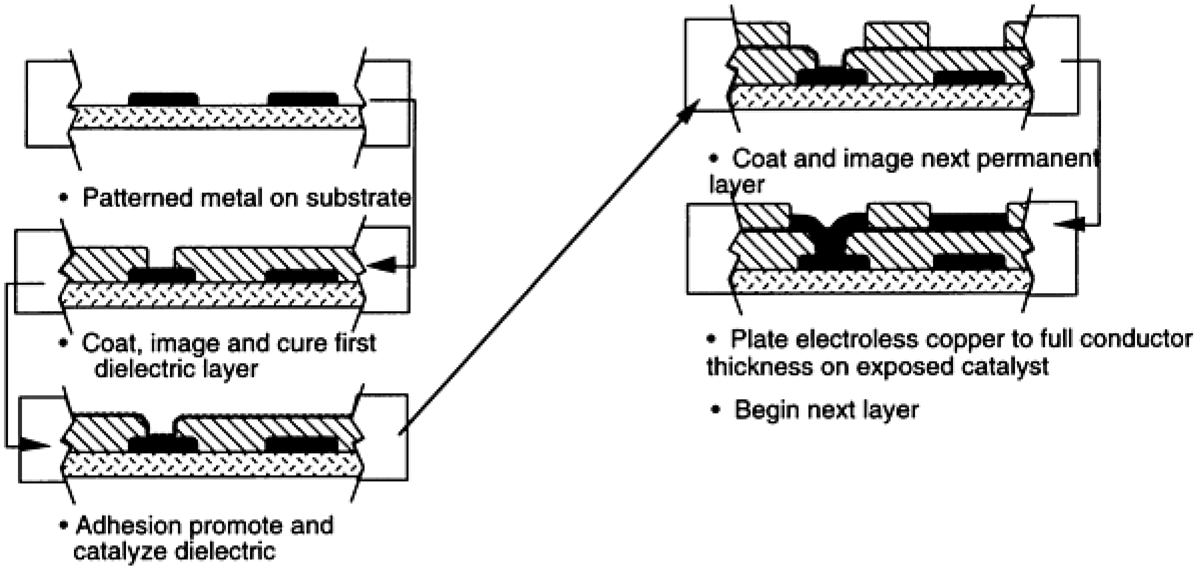


Fig. 4 A process flow chart for deposition of a multichip module on a conventional printed wiring board. Courtesy of Shipley Co.

Silicon Devices. Recently some interest has arisen in employing electroless copper for integrated circuit manufacture (Ref 49, 50, 51). It is felt that aluminum, which is used in providing the conductive path on chips, may not be sufficiently conductive at the very high resolutions required in future devices. Very thin films of electroless copper (~0.1 to 0.2 μm), deposited additively in channels between a photodefined temporary film, have been used.

References cited in this section

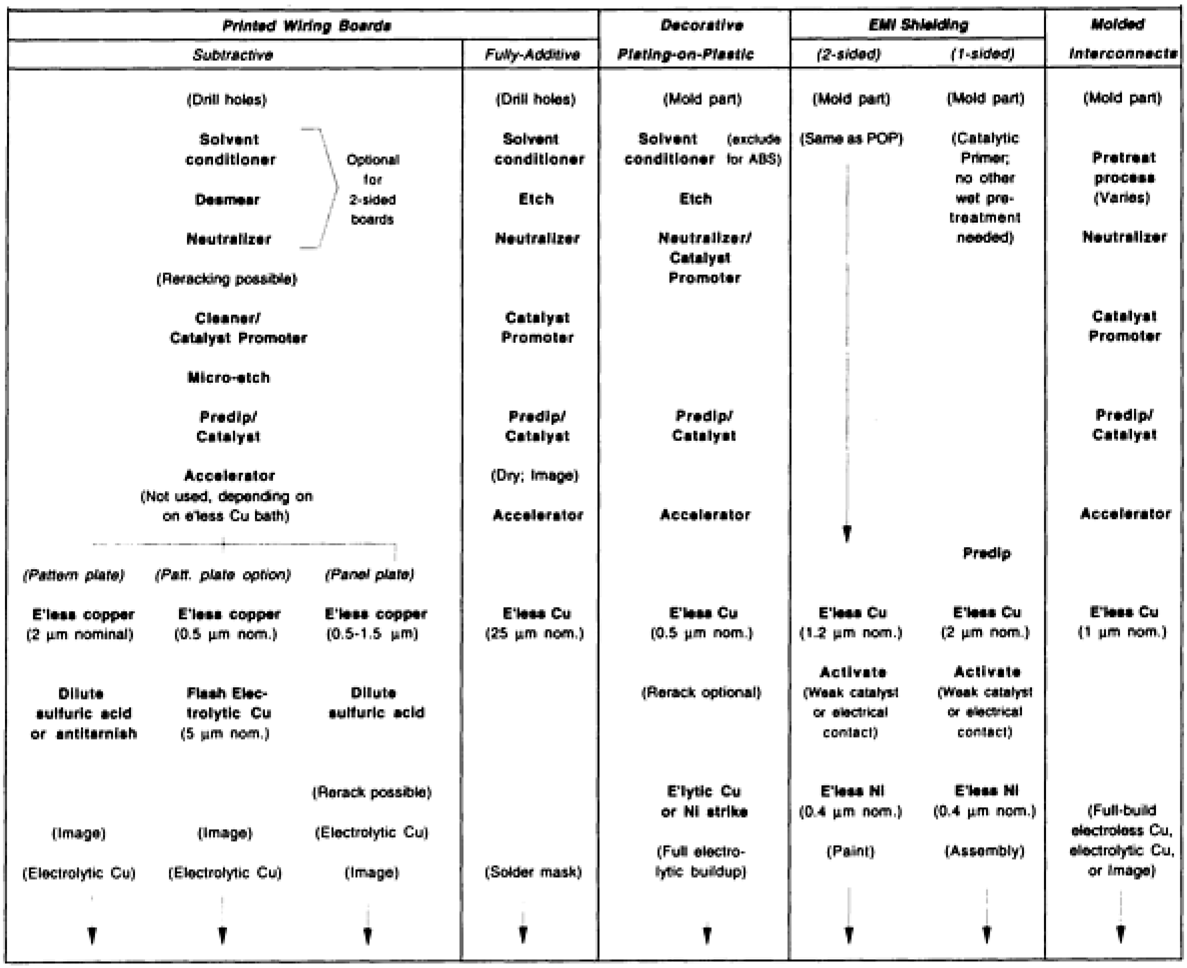
22. E.B. Saubestre, *AES Proc.,* Vol 46, 1959, p 264
23. C.A. Deckert, *Circuit World,* Vol 13 (No. 3), 1987, p 29
24. C.A. Deckert, IPC-TP-699, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, 1988
25. H. Nakahara, *Printed Circuits Handbook,* 3rd ed., C.F. Coombs, Ed., McGraw-Hill, 1988, and references therein
26. K. Nargi-Toth and J. Wynschenk, Paper P-16, Proc. Printed Circuit World Convention VI (San Francisco), 1993
27. D. Dinella, Paper P-17, Proc. Printed Circuit World Convention VI (San Francisco), 1993
28. *Standards and Guidelines for Electroplated Plastics,* 3rd ed., American Society of Electroplated Plastics, Prentice-Hall, 1984

29. R.L. Coombes, Proc. 2nd Annual Mtg, American Society of Electroplated Plastics, 1969, *Plating,* Vol 57, 1970, p 675
30. R.G. Wedel, *Plating,* Vol 62, 1975, p 40, p 235; *Int. Met. Rev.,* Vol 22, 1977, p 97
31. J.L.N. Violette, D.R.J. White, and M.F. Violette, *Electromagnetic Compatibility Handbook,* Van Nostrand Reinhold, 1987
32. G.A. Krulik, *Prod. Finish.,* Oct 1983, p 49
33. J.J. Kuzmik, *Electroless Plating: Fundamentals and Applications,* G.O. Mallory and J.B. Hajdu, Ed., American Electroplaters Society, 1990
34. ES 7-83 and D 4935-89, ASTM
35. G.A. Lordi, *Plating,* Vol 54, 1967, p 382
36. J. Hajdu and G. Krulik, *Plat. and Surf. Finish.,* Vol 70, July 1983, p 42
37. F 390, ASTM
38. G.A. Krulik, *Plastics Finishing and Decoration,* D. Satas, Ed., Van Nostrand Reinhold, 1986
39. J. E. Rychwalski, Paper A 7/2, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990
40. D.F. Foust and W.V. Dumas, U.S. patent 4,999,251, 1991
41. E.D. D'Ottavio, R.E. Hawkins, S.S. Rodriguez, and J.E. Rychwalski, U.S. patent 5,004,672, 1991
42. V.V. Zaderej, J. Mettler, R. McQueeney, and W. Kearney, Paper B 4/1, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990
43. E. Clark, *Printed Circuit Fab.,* Vol 16 (No. 20), 1993, p 69
44. Y. Tsukada, *Proc. 42nd Electronic Components and Technology Conference,* 1992, p 22
45. G. Messner et al., *Thin Film Multichip Modules,* The International Society for Hybrid Microelectronics, 1992
46. T.G. Tessier and P.E. Garrou, *Proc. International Society for Hybrid Microelectronics,* 1992, p 235
47. P.D. Knudsen, R.L. Brainard, and K.T. Schell, Proc. Surface Mount International (San Jose, CA), 1993
48. R. Enomoto and M. Asai, U.S. patent 5,055,321, 1991
49. C.H. Ting and M. Paunovic, *J. Electrochem. Soc.,* Vol 136, 1989, p 456
50. Y. Shacham-Diamand, *J. Micromech. Microeng.,* Vol 1, 1991, p 66
51. J.S.H. Cho, H.-K. Kang, S.S. Wong, and Y. Shacham-Diamand, Bull. 31, Materials Research Society, June 1993

Processes

Properties of the electroless copper bath and deposit are highly dependent on the pretreatment (and, to a lesser degree, the post-treatment) system used. Although the plating bath is the most visible and complex-to-operate solution in the process line, a mistake commonly made is to blame any process problem on the plating chemistry itself. In a majority of cases, this is not the case. Lack of correct attention to the details of the preplate chemistry is more likely to have caused the problem.

This section concentrates on the main commercial processes for electroless copper, namely PTH, decorative POP, and EMI. Other applications employ similar processes, some of which are shown in the overall process flow summary given in Fig. 5. Note that rinse steps are not shown; unless stated otherwise it should be assumed that one or more rinse steps intervene between every two process steps. This is not to minimize the importance of adequate rinsing; the adage of "it's the water" has been proven true in many troubleshooting situations. Specific requirements of water quality for PWB plating processes have been published (Ref 52) (see also the section "Controls--Miscellaneous" in this article).



Printed Wiring Boards				Decorative	EMI Shielding		Molded
Subtractive			Fully-Additive	Plating-on-Plastic	(2-sided)	(1-sided)	Interconnecte
(Drill holes)			(Drill holes)	(Mold part)	(Mold part)	(Mold part)	(Mold part)
Solvent conditioner	Optional for 2-sided boards		Solvent conditioner	Solvent conditioner (exclude for ABS)	(Same as POP)	(Catalytic Primer; no other wet pre-treatment needed)	Pretreat process (Varies)
Desmear			Etch	Etch			
Neutralizer			Neutralizer	Neutralizer/ Catalyst Promoter			Neutralizer
(Reracking possible)							
Cleaner/ Catalyst Promoter			Catalyst Promoter				Catalyst Promoter
Micro-etch							
Predip/ Catalyst			Predip/ Catalyst	Predip/ Catalyst			Predip/ Catalyst
Accelerator (Not used, depending on on e'less Cu bath)			(Dry; Image)				
			Accelerator	Accelerator			Accelerator
						Predip	
(Pattern plate)	(Patt. plate option)	(Panel plate)					
E'less copper (2 µm nominal)	E'less copper (0.5 µm nom.)	E'less copper (0.5-1.5 µm)	E'less Cu (25 µm nom.)	E'less Cu (0.5 µm nom.)	E'less Cu (1.2 µm nom.)	E'less Cu (2 µm nom.)	E'less Cu (1 µm nom.)
Dilute sulfuric acid or antitarnish	Flash Electrolytic Cu (5 µm nom.)	Dilute sulfuric acid		(Rerack optional)	Activate (Weak catalyst or electrical contact)	Activate (Weak catalyst or electrical contact)	
		(Rerack possible)		E'lytic Cu or Ni strike	E'less Ni (0.4 µm nom.)	E'less Ni (0.4 µm nom.)	(Full-build electroless Cu, electrolytic Cu, or Image)
(Image)	(Image)	(Electrolytic Cu)		(Full electrolytic buildup)	(Paint)	(Assembly)	
(Electrolytic Cu)	(Electrolytic Cu)	(Image)	(Solder mask)				

Fig. 5 Comparison of electroless copper processes. Unless otherwise stated, it should be assumed that one or more rinse steps intervene between each two process steps.

Pretreatment

Other than single-sided EMI, which will be discussed separately, electroless copper processes are similar in terms of functionality of pretreatment steps.

Gross Surface Preparation. The first steps of pretreatment, for either multilayer PWBs or bare plastic, employ fairly aggressive chemicals to remove debris and foreign matter from the substrate and etch the surface. These steps may change the topography and/or surface chemistry of the substrate significantly. The main objectives of this sequence of steps are to ensure good adhesion and eliminate the visible (gross) voiding that can result from a poorly prepared surface.

Printed Wiring Boards. This sequence of steps encompasses the desmear process for drilled holes in multilayer boards (MLBs). Drilling of the through-holes causes the laminate material (usually epoxy) to be smeared across hole wall surfaces. Reliable fabrication of multilayer boards requires that this drill smear be removed from the copper inner layers to ensure an effective copper-copper bond. The most common type of desmear process is based on a permanganate (Ref 53, 54, 55) oxidizing solution and involves three steps:

- *The MLB conditioner or pre-etch* is an aqueous-alkaline-oxygenated solvent solution that is operated at elevated temperatures (60 to 70 °C, or 140 to 160 °F) and penetrates slightly into the epoxy laminate so as to prepare it for optimal effect in the subsequent permanganate solution. Although analogous to the swell and etch system used in POP, this PWB analog does not penetrate deeply into the plastic; only surface layers (<5 µm) are thought to be affected. (Note that the term *conditioner* as used in this context must be differentiated from the PTH conditioner, or catalyst promoter, to be discussed below.)
- *The MLB etch or promoter* is a strongly alkaline permanganate solution that is operated hot (75 to 85

°C, or 165 to 185 °F) and actually dissolves a minute amount of epoxy, in particular removing any epoxy smeared on the copper inner layers. A microporous surface structure is also normally imparted to the resin. This results in an excellent surface upon which catalysis and plating can take place.

- *The neutralizer* is an acidic, mildly reducing solution that removes manganese (MnO_2) residues from all board surfaces. Typical chemistries include dilute sulfuric-peroxide solutions or acid solutions of hydroxylamine salts. It is noteworthy that, in contrast with the use of chromium-containing etchants, special care need not be taken to ensure total removal of all manganese residues, as manganese does not have a harmful effect on subsequent processing.

Figure 6 compares a typical multilayer board through-hole, after drilling, with a permanganate-desmeared through-hole that exhibits a clean hole wall and microroughened resin surface.

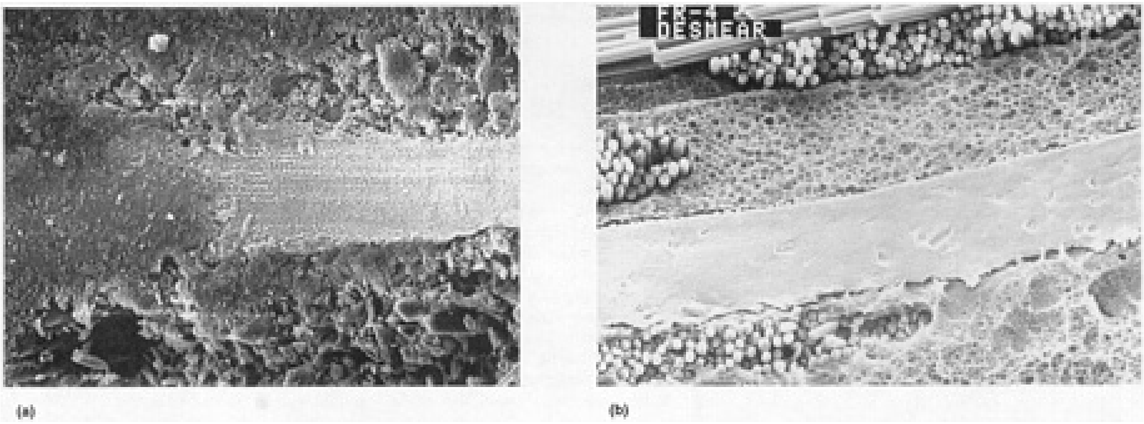


Fig. 6 Multilayer board through-holes. (a) After drilling. Note resin smear over copper inner layer surface, and loosely adherent debris covering surface. (b) After permanganate desmear. Note clean overall appearance and uniformly microroughened epoxy surface.

Chemistries alternative to permanganate that have been used for desmearing PWBs include chromic acid or concentrated sulfuric acid (each with appropriate pre- and/or post-treatment) or plasma treatment. These methods exhibit numerous shortcomings relative to permanganate in terms of safety, toxicity, reliability, cost, and/or control.

Following the desmear process, depending on the configuration of the plating equipment, it may be necessary to unrack the parts, and then rerack for treatment in the balance of the electroless process.

Plating-on-Plastic (Decorative and Two-Sided EMI Shielding). The corresponding process steps for POP applications also typically include three steps:

- *The conditioner or pre-etch* is an aqueous-organic solvent mixture. The specific solvent used will differ qualitatively depending on which plastic is being treated. In the case of ABS, this step is not needed.
- *The etch* is typically based on aqueous chromic acid (a sulfuric acid admixture is also commonly used).
- *The neutralizer* is a reducing solution that may be either acid or alkaline and which removes all hexavalent chromium residues. In comparison with the permanganate neutralizer used in PWB desmear, it is essential that every trace of hexavalent chromium be removed from the surface, as Cr(VI) is a poison for the subsequent catalyst step. The neutralizer chemistry may be modified to include in one step the catalyst promoter discussed below.

Immediate preparation for plating ensures the final cleanliness of the part (if necessary), ensures that the surface will be receptive to catalyst, deposits the catalytic film, and converts the catalyst to its active form, in preparation for electroless plating.

Cleaning (Optional). For substrates such as two-sided PWBs that do not require the gross surface preparation sequence above, a conventional cleaning step is needed. Also, in cases where equipment configuration forces a split between the gross surface preparation steps and the balance of the process, a cleaning step may be needed to remove any soils that were thereby introduced. It is common practice to incorporate this cleaning step together with the subsequent catalyst promotion step. A hot solution is typically used, ~55 to 70 °C (130 to 160 °F). The main constraints on the chemistry are that it be easily rinsable and that it be compatible with the rest of the process line. Waste treatment concerns are shifting cleaning chemistries away from the use of amine chelates and strongly acid or alkaline solutions.

Catalyst promotion (conditioning) imparts a uniform surface film to the substrate, which ensures uniform adsorption by the subsequent catalyst step and therefore promotes better plating. Because the most commonly used catalyst, the palladium-tin colloidal catalyst, is negatively charged, conditioning agents tend to bear a positive charge. The conditioning step may be combined with either the preceding cleaning step (two-sided PWBs) or the neutralizer (POP). The main issue is compatibility with subsequent steps. Specifically, in the case of PWBs, this means the ability to effectively remove any residual film from the copper during the intervening rinse and microetch steps. In the case of decorative POP, the need to achieve selectivity in the plating (i.e., no rack plating) favors the use of marginally effective catalyst promoters, whereas for PWB applications, the general difficulty of plating glass fibers in the laminate material leads to use of more effective conditioning chemistries, despite the resultant rack plating.

Microetching is required for PWBs only. It etches a thin film (0.75 to 2 μm) of the foil and inner-layer copper, thus ensuring cleanliness in preparation for plating. Any conditioning agent from the previous step is ideally removed from copper surfaces, as it could lead to a poor copper-copper bond if left in place. Normally either a mildly acidic sodium or potassium persulfate solution or a sulfuric acid-peroxide solution is used. If a persulfate solution is used, it may be followed by a dilute sulfuric acid dip.

A catalyst predip is normally employed just prior to the catalyst solution (no intervening rinses). This predip contains all components of the catalyst solution minus the catalyst itself. The purposes of the predip are to protect the expensive catalyst bath from contaminants and normalize the substrate surface chemistry prior to exposure to the catalytic species.

Catalyzation (Sensitization). Good catalyzation is the key to the entire electroless copper process. All the preceding steps are employed so as to optimize this step and ensure the uniformity and selectivity of the catalyst deposit. In theory, any of a wide range of metals, including copper, nickel, gold, silver, and all the other precious metals (Group VIIIB), may be used. In practice, because of a tradeoff between cost and selectivity (preferential adsorption of the catalyst to certain surfaces rather than others), only a few metals and physical/chemical forms of these have found acceptance in the electroless copper industry. These will be discussed roughly in chronological order of their development:

- *Binary precious metal salt:* Acidic solutions of simple precious metal salts, including $PdCl_2$, $PtCl_2$, and so on, may be used as catalyst for electroless plating in some instances. Because these salts are not tightly bound to the substrate surface, they may be removed by excessive rinsing. These solutions generally promote plating only on the most active surfaces, thus providing a good method of selectivity in certain applications.
- *Sequential tin, then palladium (so-called "two-step"):* An acidic Sn(II) solution, typically $SnCl_2$, dissolved in dilute hydrochloric acid, is first used to provide a uniform film of Sn^{2+} ions over the entire substrate surface. Because Sn(II) is inherently a strongly adherent material, the resultant film is tenaciously retained during rinsing. Then immersion in a dilute hydrochloric acid solution of $PdCl_2$ causes the more noble palladium ion to be reduced onto the substrate at the expense of the adsorbed Sn(II), which is oxidized to Sn(IV). This catalyst system was reported in 1955 (Ref 56) and has proven reliable and effective in metallizing nonconductive materials. However, a major disadvantage is the marked lack of selectivity: All exposed surfaces are heavily catalyzed. In the case of PWBs, use of the two-step catalyst often produces such a heavy catalyst film on the copper substrate that the resultant electroless copper deposit exhibits poor adhesion.
- *Palladium-tin colloid:* This type of catalyst system (Ref 57, 58) is by far the most prevalent type in commercial use. It is a stable reaction product of palladium and tin chlorides in acidic solution. The colloid is about 1 to 5 nm (10 to 50 Å) in size, consisting of a palladium-rich inner core and bearing hydrous Sn(IV) chlorides in the outer sphere. The overall colloid is negatively charged. Excess Sn(II) plays a key role in the stabilization of the catalyst solution. A high salt content is also present in modern versions of the colloidal catalyst. This system offers a number of advantages over earlier catalysts: it is

more stable, it is more active per unit of palladium, and it allows good selectivity. The catalyst as-deposited bears a high-tin-containing "sheath" surrounding the active catalytic species, and it is not optimally activated until the subsequent acceleration step.
- *Copper catalyst:* Because palladium is more expensive than the less noble metals (such as copper and nickel) that are known to be autocatalytic, there have been numerous attempts to develop a viable catalyst based on one of these metals. A copper-tin colloidal catalyst was first reported in 1976 (Ref 59) and has proven commercially successful in a number of installations. A major disadvantage is that because the catalyst is much less active catalytically, the accompanying electroless copper bath must be formulated as a much less stable solution than copper baths employed with the more active palladium-tin catalysts. This can result in process control problems.
- *Ionic (alkaline) complexed palladium:* In the mid-1970s an alkaline, ionic palladium catalyst system was developed (Ref 60) that demonstrated improved selectivity versus prior ionic palladium systems. This catalyst requires a subsequent activation step, namely immersion in a solution of a strong reducing agent such as dimethylamine borane, in order to become catalytically active. This catalyst system continues to have applicability (Ref 61) and is currently second in popularity to the colloidal palladium-tin catalyst system.

Acceleration (Activation). Discussion of this step will focus on the palladium-tin colloidal system, as it is the most commonly used catalyst. The tin-containing sheath surrounding the active palladium-rich catalytic core must be removed in order to initiate a strong plating reaction. Accelerating solutions typically are based on chemistries that dissolve and/or complex Sn(II) and Sn(IV) compounds. Commonly used formulations include dilute fluoboric acid or hydrochloric acid (or mixtures thereof), or other acidic or alkaline solutions. The catalyzation/acceleration process has been characterized in a number of studies (Ref 62). Proper control of accelerator parameters is needed to avoid an "overacceleration" condition wherein catalyst may actually be stripped, thus leading to voids in the electroless plating process. In recent years, particularly for PTH, the acceleration step has been eliminated altogether by incorporating excess chloride into the copper bath, thus causing it to be "self-accelerating" (Ref 12) without loss of stability.

Post-treatment

As Fig. 5 shows, post-treatments for electroless copper vary considerably, depending on the application.

Printed Wiring Boards. For conventional subtractive pattern plated boards, the panels may be treated in an antitarnish solution immediately after electroless copper. Afterward they are rinsed and dried, prior to unracking and going on to the imaging process. Antitarnish solutions are usually mildly acidic solutions, optionally containing a weakly chelating acid salt such as citrate or tartrate. Alternatively, a dilute solution of a specific antitarnish component such as benzotriazole may be used.

An optional pattern plate sequence, which employs very thin (≤0.5 μm) electroless copper, uses a post-treatment step of thin (flash) electrolytic copper, ~5 μm thick, prior to unracking.

For subtractive panel plating processes, electrolytic copper plating is carried out immediately after the electroless copper process. The electroplating may be either in-line (thus necessitating use of a single flight-bar throughout the entire electroless process) or in separate equipment (allowing more flexibility in electroless equipment and racking, but involving additional handling steps).

Decorative Plating-on-Plastic. After electroless copper deposition, the parts are usually treated with an electrolytic copper or nickel strike about 2.5 μm thick. The purpose of this step is to build up the initial thin electroless film so as to facilitate the subsequent buildup. Following the strike, bright acid copper plating is usually carried out to a thickness of 12 to 25μm. Next, depending on the final finish and physical characteristics desired, one to three different electrolytic nickel treatments may be employed, totaling up to ~33 μm thickness. The final finish is usually electrolytic chromium, 0.12 to 0.25 μm thick; however, the final finish may also be brass, gold, silver, or other finishes.

Single-Sided EMI Process

In order to plate electroless copper on the inside (only) of a cabinet, so that the molded plastic substrate needs no other finish, special pretreatment methods have been developed and commercialized. These take the form of catalytic spray paints (Ref 63) that can be applied selectively onto the plastic surface and, following a defined bake or cure step, allow direct deposition of electroless copper. In theory, any of the metals that catalyze electroless deposition may be used; in practice, the choice of metal is a tradeoff of catalytic activity versus cost. Typically, the single-sided EMI process requires no chemical pretreatment other than the paint. Other mechanical steps required include masking of the surfaces not to be plated, drying/baking of the paint, and racking for the plating process.

References cited in this section

12. G.M. Wilkinson, C.A. Deckert, and J.J. Doubrava, U.S. patent 4,751,106, 1988
52. E.F. Duffek, *Printed Circuits Handbook,* 3rd ed., C.F. Coombs, Ed., McGraw-Hill, 1988
53. E.J. Leech, J. Polichette, and J.G. Branigan, U.S. patent 4,054,693, 1977
54. C.A. Deckert, E.C. Couble, and W.F. Bonetti, U.S. patent 4,515,829, 1985
55. A.R. Del Gobbo and C.I. Courduvelis, IPC-TA-721, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL
56. F. Pearlstein, *Met. Finish.,* Vol 53, Aug 1955, p 59
57. C.R. Shipley, U.S. patent 3,011,920, 1961
58. E.D'Ottavio, U.S. patent 3,532,518, 1970
59. N. Feldstein, U.S. patent 3,993,799, 1976
60. H.J. Ehrich, W. Clauss, and H. Mahlkow, U.S. patent 4,248,632, 1981
61. H.J. Ehrich, Paper WCIII-06, Proc. Printed Circuit World Convention III (Washington, D.C.), 1984
62. R.L. Meek, *J. Electrochem. Soc.,* Vol 122, 1975, p 1177, 1478
63. J. Chen and P.D. Knudsen, U.S. patent 5,076,841, 1991; U.S. patent 5,120,578, 1992

Controls

Electroless Copper Solution. The electroless copper solution requires a variety of controls, all aimed toward maintaining steady-state performance in terms of plating rate, deposit physical properties, and bath stability (both during operation and on storage). First and foremost, the principal chemical parameters (copper, formaldehyde, and caustic content) must be kept within specification. Normally, by following replenishment and bailout instructions with respect to these primary components, all other bath chemical components will remain within the recommended ranges. However, occasionally chelate and stabilizer levels will also need independent control. Other than the chemistry, operating temperature is the most critical operating parameter. Too low a temperature will shut the plating off; too high may cause excessive plating rate and instability. Other key operating parameters include specific gravity (a measure of byproduct buildup (see the section "Bath Chemistry" in this article), air agitation, filtration, circulation, panel loading, and others. Specific methods for maintaining bath stability during periods of shutdown are also specified: plating down to 70 to 80% copper content in the case of room-temperature operating baths, or simply reducing the temperature for storage in the case of heated baths. Air agitation is usually employed to improve storage stability.

In general, baths providing higher film thicknesses have tighter requirements in terms of equipment parameters such as heaters, air agitation, circulation, filtration, replenishment mode, and so on. Full-build baths in particular have stringent requirements for agitation, circulation, and filtration, and they require close control over plating rate consistency. The needed controls are well characterized for all current electroless formulations, and most plating facilities can readily maintain the required controls on a regular basis. For a discussion of automatic bath controllers, see the section "Equipment--Control Equipment" in this article.

Other Process Solutions. General controls for other process solutions include the temperature and concentration of critical components, as specified by the supplier. Immersion time may also be critical in certain cases (e.g., PTH microetch), but not so long as a specified minimum immersion is attained (e.g., catalyst promoter). Supplier recommendations should be followed. Due to interaction between various pretreatment chemistries, as well as with the electroless chemistry, it is strongly recommended that a single supplier be used for the entire process. This practice also facilitates prompt resolution in troubleshooting situations.

In the gross pretreatment sequence, certain general controls must be considered. For PWB desmear, the permanganate (Mn^{7+}) to manganate (Mn^{6+}) ratio must be maintained at a specified level. Similarly, for POP adhesion promotion, the (Cr^{3+}) level must be controlled as specified. In POP it is strongly recommended that the temperature of the neutralizing solution be higher than that of the etch, to ensure that all hexavalent chromium residues are leached from any porous surfaces.

Adherence to specified chemistry controls is also necessary in the direct pretreatment sequence. In the PTH microetch, deviation from the prescribed parameters can lead to over- or underetching. In the catalyst solution, important parameters include specific gravity (to control salt content, which helps maintain colloid stability), Sn(II) level (which protects the colloid from oxidation and sedimentation), and colloid content (to control catalytic activity). In addition, certain metallic contaminants that can poison the catalytic activity (such as iron and chromium) must be monitored and controlled. Attention must be paid to the temperature and immersion time of the accelerator solution, to avoid under- or overacceleration. In addition, especially in chloride-containing accelerators, the dissolved copper content must be controlled to avoid formation of a rough deposit (believed to be CuCl) on the panel surface.

Miscellaneous. The importance of adequate rinsing, using good-quality water, can hardly be overemphasized. Heated rinses may be recommended after the catalyst promotion step to aid in removal of excess surfactant film. Rinsing after catalyzation requires maintenance of slightly acidic water containing no multiply charged cations, in order to prevent agglomeration of the negative colloid and surface roughness on the panel. Thorough rinsing in clean water is a general requirement in electroless copper processes, to prevent both panel surface defects and shortened bath life due to contaminated solutions.

Performance Criteria

The critical performance criteria for electroless copper processes vary somewhat, depending on the application. Two primary criteria that relate to all applications are coverage and adhesion. Other criteria have become increasingly important over the past decade or so, especially for PTH.

Coverage relates to the uniform and complete deposition of copper over the substrate. Coverage defects may be referred to as *voiding* (PWBs) or *skip plating* (POP). Gross coverage defects that are easily discerned by the naked eye are typically caused by an improperly prepared surface or major abnormality in the overall plating process parameters. Pinpoint defects, which may also be detectable to the eye, have long been a recognized problem in the POP industry, due to the importance of the appearance of the final product. Since about the late 1970s, microscopy has been widely used to detect minute defects in PTH, due to increasing demands on circuit integrity. Typically a panel is sliced so that half the plated hole is visible for microscopic examination. Rather than incident light, backlighting is often used (Ref 64), which provides a very sensitive measure of assessing coverage. Figure 7 demonstrates levels of coverage that can be discriminated. (Both these through-holes would appear totally covered when viewed using incident light.) Some debate has taken place regarding whether "total" backlight coverage is necessary, or even advisable. The critical importance of deposit adhesion, for instance, requires that any mechanism employed to promote coverage, such as use of strong catalyst promoters, be carefully controlled so as not to introduce weak boundary layers in the plated composite.

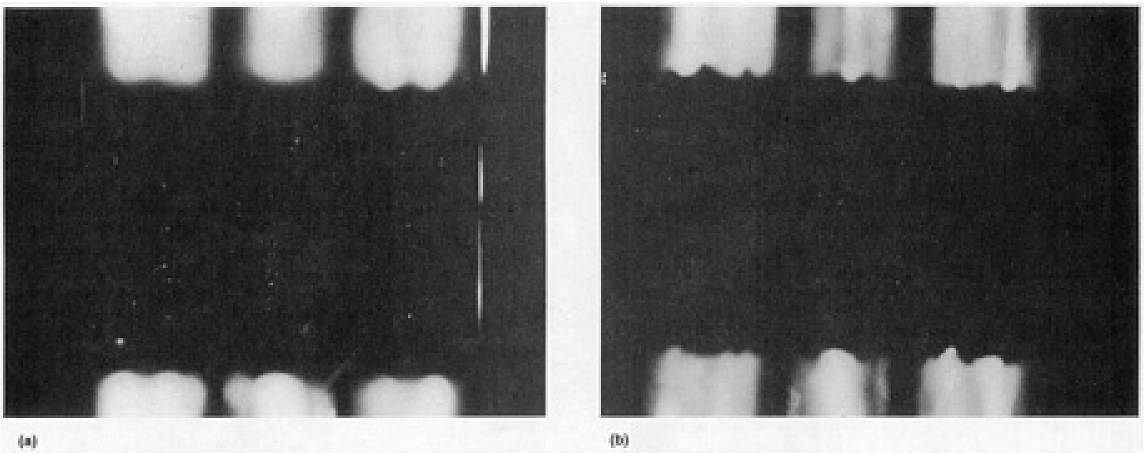


Fig. 7 Backlight test cuopons. (a) Showing pinpoints voids. (b) Showing total electroless copper coverage

Adhesion of the copper deposit to the substrate is typically controlled by proper surface preparation. Typically the first two or three steps in the plating process prepare the surface in a gross manner. The subsequent steps of conditioning, microetch (for PWBs), catalyzation, and acceleration ensure that a complete, yet minimal, catalyst film is present, so as to maximize adhesion. Adhesion requirements vary, depending on the application. For POP the adhesion requirement is ~0.7 kN/m (4 lb/in.) peel strength, as measured by the Jacquet test (Ref 65), with good integrity to be maintained under a variety of environmental test conditions. The important factor is maintenance of a durable, cosmetic film over the lifetime of the part. The primary failure mode is blistering of the deposit. For conventional PWBs, peel strength per se is not usually measured. Adhesion is typically ascertained by cross-sectioning the board after electroplating, optionally subjecting the sample to high thermal stress that simulates or exceeds the expected stress to be induced during assembly, and then mounting and polishing prior to microscopic examination for failure between the electroless film and any of the other surfaces. Adhesion failure to the epoxy surface is commonly referred to as *hole wall pullaway;* adhesion failure to a copper inner layer is referred to as an *interconnect defect (ICD).* Detection and elimination of ICDs by improved electroless copper plating processes has led to significant improvement in PWB reliability over the past several years. Current industry standard electroless copper processes stand up to significantly more severe test conditions than those defined in the industry specification (Ref 66) (Fig. 8). In EMI shielding, the standard adhesion test involves scratching a cross-hatch pattern into the metallized film, then applying a tape test under prescribed conditions (Ref 67). This test is often used following a variety of environmental storage conditions.

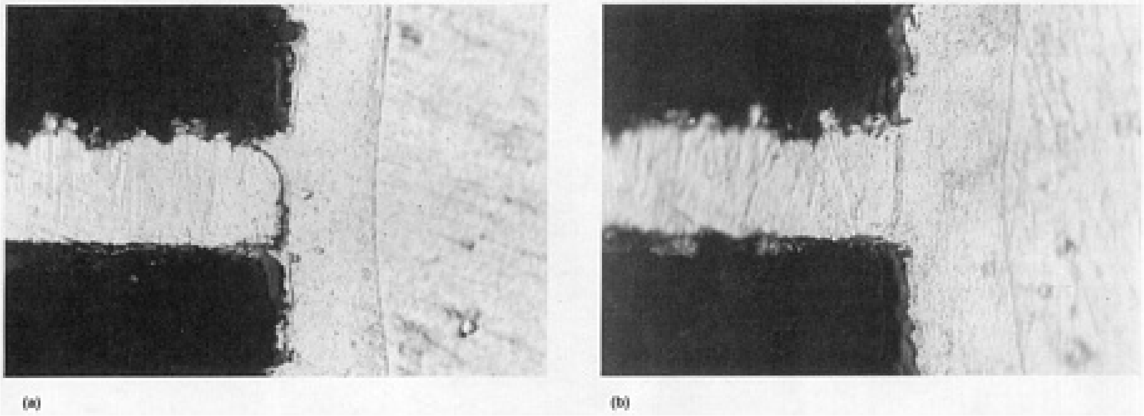


Fig. 8 Solder shock test coupons. (a) Showing interconnect defect. (b) Showing strong interconnect bond after multiple solder shock exposure. Courtesy of Shipley Co.

Deposit quality has become increasingly important over the past ten years. Controlled grain size, low intrinsic stress, and low electrical resistivity are some of the most important qualities sought. A method of PWB reliability testing using elevated-temperature fluid bed media has been employed to rapidly assess the long-term reliability of the copper deposit in through-holes (Ref 16).

Control of the copper bath is now routinely achieved, in contrast with the unstable and unpredictable formulations of the 1960s and 1970s. Plating rate, rate of depletion, deposit characteristics, and so on are all maintained consistently throughout the lifetime of the bath, allowing statistical control procedures to be readily implemented.

Solderability. The effect of the through-hole copper plating bath and process on solderability has been the subject of several studies (Ref 68), because outgassing or "blow holes" (Fig. 9) occurring during the assembly process can significantly affect PWB end-product reliability. It has been shown that outgassing is dramatically reduced by a permanganate-based surface preparation treatment used for desmearing multilayer boards in combination with a fine-grain, low-stressed copper deposit (Ref 24).

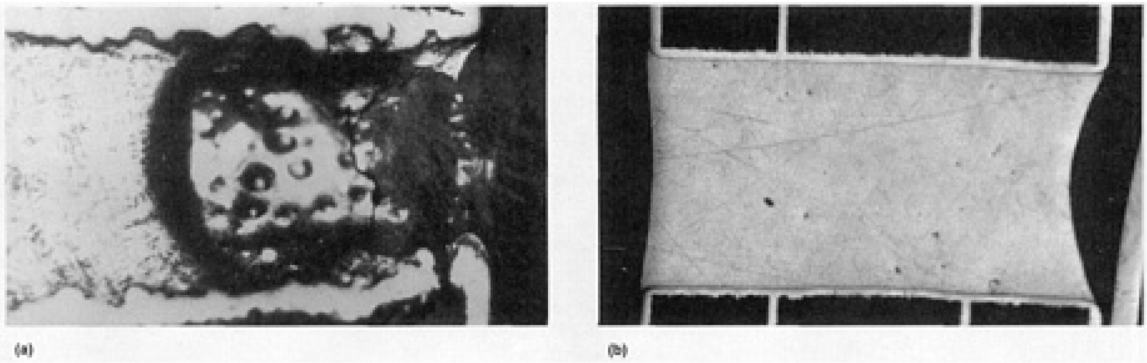


Fig. 9 (a) Solder blow hole induced during solder shock testing. (b) Through-hole showing good solder fill after solder shock testing

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References cited in this section

16. K. Minten and J. Toth, Paper B 5/2, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990; *Circuit World,* Vol 17, 1991, p 19
24. C.A. Deckert, IPC-TP-699, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, 1988
64. H.-J. Grapentin and J. Wolff, *Galvanotechnik,* Vol 70, 1979, p 958
65. B-533, ASTM
66. MIL-P-55110D, U.S. Government Printing Office
67. D3359-78B, ASTM
68. C. Lea et al, *Circuit World,* Vol 11 (No. 3), 1985, p 5; Vol 12 (No. 4), 1986, p 14, 20, 26; Vol 13 (No. 1), 1986, p 28, 43

Equipment

Processing Equipment

Printed Wiring Boards. Electroless copper process equipment consists essentially of a juxtaposed series of tanks, typically 380 to 1135 L (100 to 300 gal) in size (or as high as 3800 L, or 1000 gal), including process chemistry tanks, rinse tanks, and load/unload stations, with all associated heaters, chillers, air spargers, and so on. The panels are transported vertically through the system in a rack that typically holds panels representing a surface area of 25 to 735 cm^2/L (0.1 to 3 ft^2/gal) of copper bath. (Other process tanks may be sized appropriately to most efficiently hold the rack.) An automatic hoist system is used, except in the smallest installations.

In the past, electroless lines were designed for two-sided boards only. The multilayer desmear process was entirely separate, thus requiring additional unracking and reracking between segments. Most electroless copper plating lines now being built include tanks for the desmear process as well.

Recently, considerable interest has developed in applying conveyorized horizontal processing to part, or all, of the electroless copper process, as there are a number of technical and operational benefits to this approach. At present, horizontal desmear is being used in select facilities worldwide, and several facilities are also successfully operating in production using horizontal equipment for electroless copper itself (Ref 69).

Plating-on-Plastic. Plating equipment for POP typically involves tank volumes of about 3800 L (1000 gal), but tanks of up to 26,500 L (7000 gal) have been used. The plating process in decorative POP is carried out in one of two modes: designated straight-through or semibulk. Straight-through processing is carried out in a continuous system, where the preplate, electroless, and electroplating steps are carried out with no interruption for reracking. In semibulk processing, two separate fixtures are used, one for the pretreatment/electroless steps and the other for electroplating. There are numerous advantages for each type of system (Ref 28). Advantages of straight-through processing are evident: only one piece of equipment, fewer processing steps, less handling, and so on. Semibulk processing, however, offers a number of advantages, including much higher capacity, more degrees of freedom in choosing racking systems and chemicals, and flexibility in processing sequences.

Control Equipment

Due to rapid changes in the chemistry of an operating electroless plating bath, frequent analysis and replenishment are required. Hence, automatic control equipment has been of interest (Ref 70) almost since the baths were first commercially employed. A benchmark controller, developed in about 1980, measured and controlled copper, hydroxide, and formaldehyde contents. Copper content was determined by an optical absorbance method, hydroxide and formaldehyde contents by a titration method. Over the years, the simplicity and reliability of such equipment have undergone great improvement, but the basic techniques of analysis have remained essentially the same (Ref 71). Today these control systems are commonplace in all but the very smallest installations and are used to automatically replenish all bath components, as well as for bailout. Recently, to address the added control requirements of full-build electroless copper baths, a new, more accurate method of copper analysis and control has been developed and commercialized. This method is based on vibration of a quartz crystal that acts as a microbalance (Ref 72), thus measuring the mass of copper plated on its surface and providing real-time measurement and control of thickness.

References cited in this section

28. *Standards and Guidelines for Electroplated Plastics,* 3rd ed., American Society of Electroplated Plastics, Prentice-Hall, 1984
69. G. Allardyce, J. Bladon, S. Hirst, and J. Rasch, Paper P-18, Proc. Printed Circuit World Convention VI (San Francisco), 1993
70. H. Hirohata, M. Oita, and K. Honjo, U.S. patent 3,532,519, 1970
71. J.E. Harris and W.H. Rees, U.S. patent 4,774,101, 1988
72. K. Minten and J. Cisson, *Circuit World,* Vol 19 (No. 2), 1993, p 4

Environmental and Safety Issues

The electroless copper plating industry has come under increasing legislative control in recent years, due to a variety of environmental and safety concerns relative to the chemistry and processes. The main issues are quality of waste water discharged, volatile components discharged, and health and safety concerns about handling of the various chemicals.

Waste Water. Regulations regarding effluent vary dramatically, both globally and within single countries. This factor has probably contributed significantly to the relocation of numerous plating facilities to areas having less stringent regulations. Copper itself is probably the main concern; waste treatment equipment designed to plate residual copper from discarded plating solutions will normally reduce Cu^{2+} below the legal limit (typically 1 ppm). Strong chelates have become a concern recently due to their tendency to dissolve any metallic surfaces encountered, either before or after discharge. Certain plating bath additives used in the past, including mercury and cyanide compounds, have been virtually eliminated from use due to waste water restrictions. Adjustment of waste water pH to a neutral range is also usually required. Chromium, used in POP pretreatment, is particularly toxic to the environment, but virtually all current users recycle their chromic acid etchants internally, thus avoiding any discharge. Discharge of strong oxidizing or reducing agents is also typically regulated closely. The issue of waste water treatment is so key to operating a successful plating operation that considerable literature on designing and implementing waste treatment systems is available (Ref 73).

Handling of individual chemicals in the plating process presents a number of concerns. A significant concern is the use of formaldehyde, which has been shown to be a carcinogen for certain laboratory animals, although no direct link with cancer in humans has been demonstrated at this time. Limits by the Occupational Health and Safety Administration on airborne formaldehyde have recently been reduced from 1 to 0.075 ppm (8-h time-weighed average permissible exposure in air). Concerns about formaldehyde, as well as concerns about waste treatment of electroless copper, have contributed to ongoing development of direct electroplating (Ref 26, 69, 74, 75), which could eliminate the need for electroless copper, particularly in portions of the PWB market.

References cited in this section

26. K. Nargi-Toth and J. Wynschenk, Paper P-16, Proc. Printed Circuit World Convention VI (San Francisco), 1993
69. G. Allardyce, J. Bladon, S. Hirst, and J. Rasch, Paper P-18, Proc. Printed Circuit World Convention VI (San Francisco), 1993
73. P.G. Moleux, *Printed Circuits Handbook,* 3rd ed., C.F. Coombs, Ed., McGraw-Hill, 1988, and references therein
74. K.L. Minten and G. Pismennaya, U.S. patent 4,619,741, 1986
75. B. Bressl, H. Meyer, and L. Stamp, Paper P-20, Proc. Printed Circuit World Convention VI (San Francisco), 1993

Electroless Gold Plating

Jean W. Chevalier, Technic, Inc.

Introduction

THE DEPOSITION of a metal on a given substrate can be achieved by numerous conventional methods. Electrodeposition is extensively used because it is technically convenient to operate and is cost efficient. Other techniques, such as chemical vapor deposition and sputtering, are also used, but they require sophisticated equipment and are more expensive to operate. In recent years, an unconventional technique, electroless deposition, has become increasingly attractive, particularly in the electronics industry where the use of nonconductive substrates and the miniaturization of the circuitry presents difficulties in using conventional techniques.

By definition, electroless deposition is the controlled autocatalytic reduction of a dissolved metal by a dissolved reducing agent at an interface. This process requires a reducing agent to provide the electrons for the reduction of the metal ion to the metal to be deposited on the metal substrate. Chemical deposition can also be accomplished by galvanic reaction between a less noble metal and a more noble metal ion. The noble metal is deposited via this reaction. This form of the process is known as *immersion plating*.

Several metals can be deposited using the electroless plating technique. Electroless copper and electroless nickel are widely used (see the articles "Electroless Nickel Plating" and "Electroless Copper Plating" in this Volume). There is a growing interest in the electroless plating of gold and, to some extent, other precious metals such as palladium and silver. This article describes the electroless gold plating technique in terms of its advantages and limitations, applications, processing, and the properties of the plated deposits.

Advantages of electroless deposition of gold include the following:

- Uniform, thin gold films can be deposited over electrically isolated tracks and bonding pads.
- Gold can be uniformly deposited on complex shaped and hollow articles, provided there is adequate agitation of the solution and/or the articles to be coated.
- Gold can be deposited on nonconducting substrates such as glass, ceramics, polymeric materials, etc., provided the substrate is activated.
- Gold films resulting from electroless deposition are 99.9% pure; therefore, they have excellent electrical, soldering, and bonding properties.

Limitations of the process include:

- The electroless gold deposition rate is generally slow. The typical rate is 2 to 3 μm/h, compared to 10 or more μm/h for electroplating baths.
- The chemistry of electroless gold baths is complex; the baths require tight control because they are very sensitive to operating conditions as well as to organic and inorganic contaminants. Consequently, they have a shorter

lifetime and are more expensive to operate than conventional baths.

Applications. Electroless gold finds its application primarily in the electronics industry, where it is used for the metallization of conductors and insulators in printed circuit boards (Ref 1). It is particularly appropriate to use electroless gold on electrically isolated tracks and bonding pads that require uniform gold films, which are difficult to achieve by electrolytic gold deposition. Electroless gold is also recommended to achieve good ohmic contacts on III-V semiconductor materials such as n-GaAs, InP, etc. (Ref 2, 3). It can also be used in the fabrication of multilayer ceramic packages (Ref 4) to improve their brazing, soldering, and wire bonding properties. Another major application for electroless gold is for uniformly plating hollow articles that cannot be successfully plated by electrolytic deposition because their shape results in bad electric field distribution.

Properties of Electroless Gold Films. Depending on bath chemistry, the color of electroless gold films varies from pale yellow to dark brown; the surface texture can be matte, semibright, or reflective. The purity of electroless gold deposits is 99.9% or better. This results in a soft gold film of less than 90 Knoop hardness, suitable for soldering and bonding. The density of the deposited metal is about 19.3 g/cm^3. The grain structure, as observed by scanning electron microscopy (Fig. 1) exhibits a relatively tight distribution of fine particles. The porosity of such gold films depends on the thickness, but above 1.5 μm the deposit is generally pore-free.

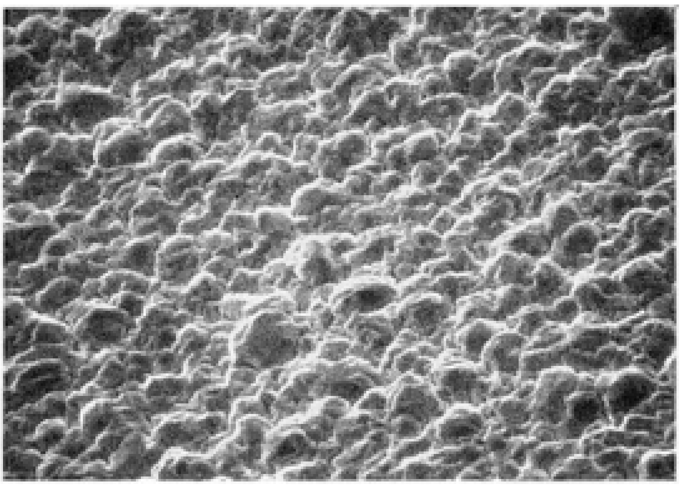

Fig. 1 SEM micrograph of an electroless gold film deposit obtained using a cyanide-base system with potassium borohydride as the reducing agent. Deposit thickness, 1.5 μm. 5000×

References

1. G.O. Mallory and J.B. Hajdu, Ed., *Electroless Plating: Fundamentals and Applications,* American Electroplaters and Surface Finishers Society, 1990
2. G. Stremsdoerfer, H. Perrot, J.R. Martin, and P. Clechet, *Proc. Electrochem. Soc.,* Vol 88 (No. 12), 1988, p 61
3. L. D'Asaro and Y. Okinaka, U.S. Patent 4,162,337, 1979
4. M.F. El-Shazly, U.S. Patent 4,374,876, 1983

Process Description

As mentioned earlier, the deposition of gold without an external source of current can occur by a simple displacement reaction between two metals:

$$\begin{array}{c} M_1^0 \rightarrow M_1^{n+} + ne^- \\ M_2^{n+} + ne^- \rightarrow M_2^0 \\ \hline M_1^0 + M_2^{n+} \rightarrow M_1^{n+} + M_2^0 \end{array} \qquad \textbf{(Eq 1)}$$

A typical immersion plating process is the displacement reaction between a less noble metal (nickel) and a more noble metal (gold) in an immersion gold bath:

$$\begin{array}{c} \mathrm{Ni} \rightarrow \mathrm{Ni}^{2+}\ 2e^- \\ 2\mathrm{Au}^+ + 2e^- \rightarrow 2\mathrm{Au} \\ \hline \mathrm{Ni} + 2\mathrm{Au}^+ \rightarrow \mathrm{Ni}^2+ + 2\mathrm{Au} \end{array} \qquad \textbf{(Eq 2)}$$

The immersion gold process is relatively slow, and it is limited by the decreasing availability of the nickel substrate as the thickness of deposited gold increases. A maximum gold bath thickness of 0.25 μm can be obtained (Fig. 2).

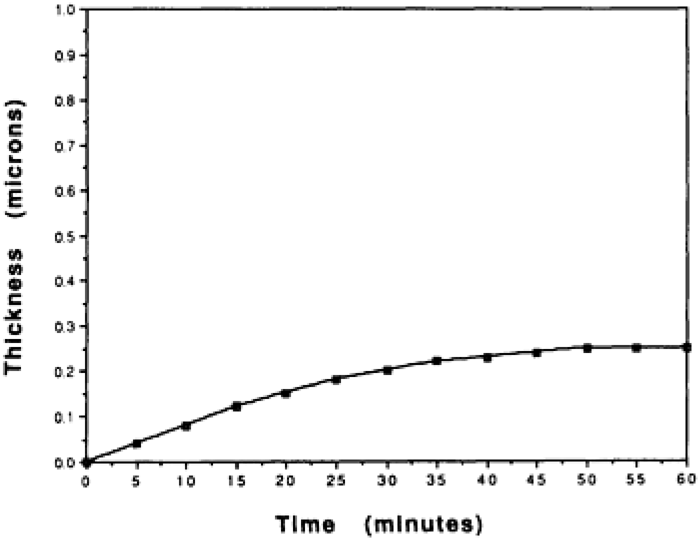

Fig. 2 Thickness of gold as a function of time for an immersion electroless gold plating bath

In order to achieve thicker gold deposits, the use of a true electroless gold bath is required. Such baths are based on a reducing agent that provides the electrons necessary for the reduction of gold ions absorbed on a gold substrate. The catalytic effect of metallic gold promotes the process. This deposition reaction is called an *autocatalytic* process:

$$\begin{array}{c} M^{n+} + ne^- \rightarrow M^0 \\ \mathrm{Red} \rightarrow O_x + ne^- \\ \hline M^{n+} + \mathrm{Red} \rightarrow M^0 + O_x \end{array} \qquad \textbf{(Eq 3)}$$

By definition, an autocatalytic system is substrate catalyzed. Consequently, there are no theoretical limitations to the thickness of gold that can be achieved with an electroless gold bath (Fig. 3).

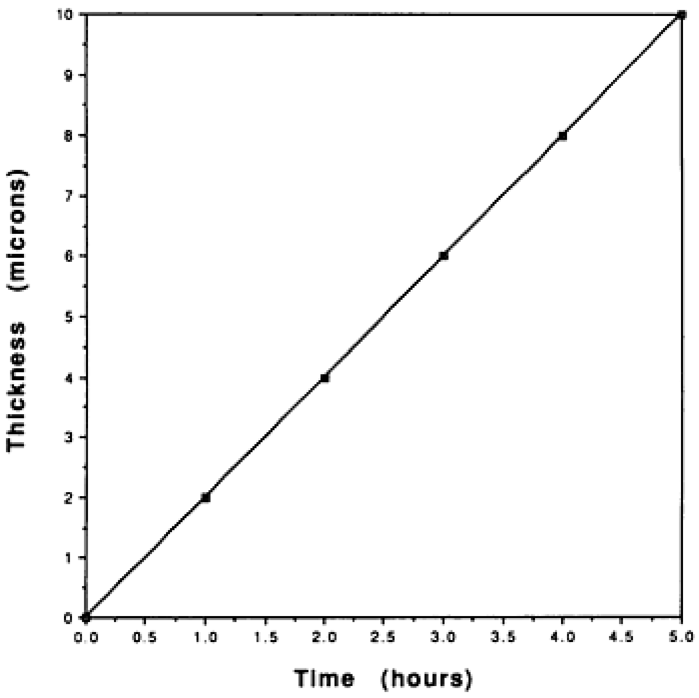

Fig. 3 Thickness of gold as a function of time for an autocatalytic electroless gold plating bath. Theoretical curve at optimum conditions

Many electroless gold bath compositions have been reported in the literature. A typical system, developed by Y. Okinaka (Ref 1), uses potassium gold cyanide as the source of gold and sodium borohydride or dimethylamine borane as reducing agents (Table 1). These baths operate in strongly alkaline media; the strong alkalinity is necessary for the activity of the reducing agent. The suggested reaction mechanism (Ref 5) for the electroless deposition of gold in the presence of sodium or potassium borohydride is:

$$\begin{array}{c} BH_4^- - H_2O \rightarrow BH_3OH^- + H_2 \\ BH_3OH^- + 3OH^- \rightarrow BO_2^- + 3/2H_2 + 2H_2O + 3e^- \\ 3Au(CN)_2^- + 3_e^- \rightarrow 3Au + 6CN^- \\ \hline BH_4^- + 3OH^- + 3Au(CN)_2^- \rightarrow BO_2^- + 5/2H_2 + H_2O \\ + 3Au + 6CN^- \end{array} \qquad \text{(Eq 4)}$$

In fact, according to this mechanism, the hydrolysis of potassium or sodium borohydride leads to the formation of BH_3OH^- species, which ultimately provide the electrons for the reduction of the gold complex.

Table 1 Compositions and operating conditions for cyanide-base electroless gold plating baths

Reported by Y. Okinaka (Ref 1)

Constituent or condition	**Bath A**	**Bath B**
Potassium gold cyanide	0.003 *M*	0.02 *M*
Potassium cyanide	0.10 *M*	0.10 *M*

Potassium hydroxide	0.20 *M*	0.20 *M*
Potassium borohydride	0.20 *M*	0.20 *M*
Temperature °C (°F)	70 (158)	70 (158)
Rate of deposition μm/h	1.5	0.5

A number of different gold salts are used in the formulation of electroless gold baths. In addition to the most commonly used--for example, potassium gold cyanide, $KAu(CN)_2$, and potassium chloroaurate, $KAuCl_4$--there is a growing interest in using sodium gold sulfite in the formulation of cyanide-free systems. Different reducing agents can also be used, and their activity influences both the rate of deposition and the stability of the bath. Other components of electroless gold baths include some chelating agents, stabilizers, buffers, accelerators, and wetting agents. Gold plating baths reported by H. Okudaira et al. (Ref 6) and C.D. Yacovangelo (Ref 7) are listed in Table 2 and Table 3, respectively.

Table 2 Composition and operating conditions for a sulfite-base electroless gold plating bath

Reported by H. Okudaira (Ref 6)

Constituent or condition	Amount
Sodium chloroaurate	0.20 *M*
Sodium thiosulfate	0.50 *M*
Sodium sulfite	0.05 *M*
N-Methylthiourea	0.0001 *M*
Pyrogallol	0.09 *M*
Ammonium chloride	0.20 *M*
Temperature, °C (°F)	70 (158)
pH	6.0
Rate of deposition, μm/h	1.8

Table 3 Composition and operating conditions for a cyanide-base electroless gold plating bath

Reported by C.D. Yacovangelo (Ref 7)

Constituent or condition	Amount
Potassium gold cyanide	0.005 *M*

Potassium cyanide	0.035 *M*
Potassium hydroxide	0.80 *M*
Potassium carbonate	0.45 *M*
Dimethylamine borane	0.05 *M*
Hydrazine	0.25 *M*
Lead acetate, ppm	15
Temperature, °C (°F)	80 (176)
Rate of deposition, μm/h	≤ 7.8

Process Variables and Parameters. Electroless gold baths are very sensitive to operating conditions; therefore, it is important to control all of the variables that can affect both the rate of deposition and the stability of these systems.

Gold Concentration. As the gold concentration decreases, the rate of deposition also decreases. In order to keep the rate of deposition constant, periodic addition of gold should be made in the form of a gold salt. Replenishment can be made based on analysis data and/or close monitoring of the quantity of metal deposited on the substrate.

Reducing Agent. The concentration of the reducing agent is almost as critical as the concentration of gold. The decrease in the reducing agent concentration is not only a function of the reduction of gold, but also is affected by possible degradation reactions, such as those that occur with sodium borohydride. The concentration level should be frequently analyzed and adjusted.

Stabilizers. The presence of stabilizers is necessary to the operation of most electroless gold baths. Free cyanide seems to have a beneficial effect on the stability of most cyanide-base electroless gold baths. However, excess amounts will overstabilize the bath and inhibit the deposition of gold. Other stabilizers can also be used to prevent the formation of gold particles and their accelerated growth, which can result in a significant drop in the ionic gold remaining in the solution.

Contaminants. Organic and inorganic contaminants can have very deleterious effects on electroless gold baths. For example, trace amounts of nickel ions are sufficient to cause a rapid decomposition of the borohydride bath reported by Okinaka. Because of the effects of nickel, the use of an immersion gold coating of about 0.25 μm over a nickel substrate is often recommended prior to electroless gold deposition. Some electroless gold baths (such as that given in Table 3) can deposit gold directly over nickel by combining an immersion process with a catalytic process. Traces of tin are also detrimental, whereas copper has no negative effect on bath stability.

Temperature. All electroless gold baths are temperature-dependent. In general, the higher the temperature, the faster the speed of deposition. An adverse effect of high temperature is bath decomposition. High temperatures also cause rapid consumption of reducing agents, creating the need for frequent replenishment.

Agitation. The rate of deposition of gold as well as the uniformity of the gold film will be influenced by the agitation. Both the solution and the workpiece can be moved to ensure good uniformity. Agitation is also required to prevent localized heating and possible decomposition of the solution.

The effect of pH is particularly important when plating on pH-sensitive substrates. For example, degradation of polyimide substrates will occur in very alkaline baths. Alumina-ceramic substrates are also incompatible with highly alkaline systems, and they should be treated in electroless gold baths operating at neutral pH (such as sulfite gold baths, which have a pH of 8.0).

Surface preparation is a key issue in any deposition process. Cleaning and activation of the gold substrate are necessary prior to plating in order to prevent contamination and to enhance adhesion. When plating gold directly over nickel or copper, the removal of the oxide layer is essential for achieving excellent adherence of the gold film. In this respect, a flash of nickel (electroless or electrolytic) may be beneficial.

Processing Equipment. Because of their sensitivity to high temperature and to contamination, electroless gold baths should be run in carefully controlled equipment. For operating very small units (3 gal or less), pyrex jars or jacketed beakers are practical. For larger units, polypropylene tanks or Teflon-coated stainless steel tanks are recommended.

The heat source plays a major role in controlling the stability and the performance of an electroless gold bath. Small water baths with thermostatic control are very practical for small-scale operations. For larger operations, heat-exchanger coil systems made of Teflon and operating with hot water or with steam are recommended. Teflon-coated immersion heaters can also be used, but care should be taken to prevent localized heating by vigorously circulating the solution in the vicinity of the heating coils.

In large-scale operations, pumping and filtration systems are also necessary. All pumps and filters should be made of chemically resistant materials, such as polypropylene or Teflon.

Environmental Considerations. Spent electroless gold baths should be treated both for environmental reasons and for gold recovery. All major suppliers of plating chemicals offer waste treatment guidelines that should be followed by their customers, particularly those operating the cyanide systems. In California, only cyanide solutions and IX resins are accepted by gold reclaimers. Aqua regia solutions are not accepted.

Health and Safety Considerations. All electroless gold baths contain chemicals that can be harmful to the user's health if not handled safely. The use of protective goggles, gloves, and lab coats is strongly recommended. The plating solutions should not be swallowed. They should be stored in cool and well-ventilated rooms and used under well-ventilated hoods. The Material Safety Data Sheets provided by the manufacturer should be read carefully before using any plating products.

References cited in this section

1. G.O. Mallory and J.B. Hajdu, Ed., *Electroless Plating: Fundamentals and Applications,* American Electroplaters and Surface Finishers Society, 1990
5. Y. Okinaka, *Plating and Surface Finishing,* Vol 57, 1970, p 914
6. H. Okudaira, T. Shimakazi, and H. Yokono, European Patent 0,418,715A2, 1990
7. C.D. Yacovangelo, *J. Electrochem. Soc.,* Vol 138 (No. 4), 1991, p 976

Electroless Alloy Deposition

Phillip D. Stapleton, Stapleton Technologies

Introduction

METALLIC NONELECTROLYTIC ALLOY COATINGS produced from aqueous solutions are commercially used in several industries, including electronics, aerospace, medical, oil and gas production, chemical processing, and automotive. These coatings provide unique material properties that expand the physical properties beyond those of pure metal coating systems. Table 1 lists many of the properties and the coatings capable of providing these properties.

Table 1 Features and types of metallic nonelectrolytic alloy coatings

Property or use	**Alloy types**	**Thickness range, μm**
Corrosion protection	Ni-P, Ni-P-Mo, Ni-Sn-P, Co-P, Co-P-Mo, Ni-Cu-P	12-125
Wear resistance	Ni-B, Ni-B-Tl, Ni-B-Mo, Ni-B-Sn, Co-P, Co-P-W, Co-B	30-120
	Ni-P + SiC, Ni-P + WC (dispersion)	30-125
	Au-Ni, Au-Co	0.5-3
Magnetic	Ni-Co-P, Ni-Co-B, Ni-Fe-P	<0.1
Catalyzation	Pd-Rh	<0.05
Solderability	Sn-Pb, Ni-P	0.5-10
Bondability	Ni-P	2-5
High temperature	Co-W-B, Ni-Re-P	1-125
Diffusion barrier	Ni-P	12-30

Nonelectrolytic coating systems use two types of reactions to deposit metal onto a part: electroless and displacement. The electroless or autocatalytic process uses reducing agents to convert the metal from its metal salt. Displacement reactions use oxidation and reduction of the base metal to deposit a thin coating of metal.

The advantage of using nonelectrolytic alloy coating systems over electrolytic is the uniformity of deposit in alloy composition and thickness, the ability to perform bulk processing, and the ability to produce unique catalytic coatings. These coatings are produced from aqueous chemical processes by conventional aqueous pretreatment procedures.

Nonelectrolytic processes can be used to deposit binary or ternary alloy coatings. The chemistries of ternary alloy plating can be very complex and involve several chelation and secondary reactions. The typical ternary system operates by having the primary metal reaction at the surface produce an electropotential greater than the half-wave potential of the complexed secondary metal. This induced surface potential is called an *overvoltage potential.* This causes the secondary metal to be included with the primary metal along with the cation portion of the reducing agent. Examples of this type of ternary system are alloys of nickel-copper-phosphorus or nickel-thallium-boron.

Nonelectrolytic processes generally operate at slightly elevated temperatures up to the temperature of boiling. These processing solutions contain the primary element and may contain other alloying metals. The operating parameters for pH can range from strong acid to strong base, depending on the metal system and the type of chelation and reducing agent being used.

With some processes, a secondary reducer is used to increase the efficiency and quantity of alloying metal incorporated. The secondary metals that are being galvanically plated at their overvoltage may limit the deposition of the primary metal. The secondary metals will generally be consumed at a high rate and require replenishment. Reducing agents may also be consumed at a higher rate than the primary metal and require more frequent replenishment.

Electroless (Autocatalytic) Alloy Coatings. Electrolessly produced metallic alloy coatings use a reducing agent to cause the metal salts to be reduced onto an oxide-free part surface. This reduction reaction proceeds until the part is removed from the process. During the reaction, metal and reducing agents are depleted and require replacement to continue the processing. The process is called *electroless* because no external electrical power is applied. The term *autocatalytic* is the technical term for the process.

The electroless process can be complex and involve several simultaneous reactions producing hydrogen and electrical charge at the interface. Through experience and good operating techniques the plating operation can produce a uniform alloy with specific phase structures and compositions.

Electroless dispersion alloy coatings use the conventional electroless reduction reaction process with a suspension of particles to produce a deposit with unique macroproperties. These particles fall into two categories: lubricants or hard load bearing particles. The soft particles contain powders of polytetrafluoroethylene (PTFE), fluorinated carbons (CF_x), and fluoride salts, whereas hard particles consist of carbides, ceramics, insoluble powders, and diamonds. Dispersion coatings contain particles in the concentration range of 5 to 30%, depending on the particle and wear system. These alloy coatings are used in applications in which significant wear is present or repair and service are difficult.

Displacement (immersion) alloy coatings use the corrosion (oxidation) of the base material to produce a galvanic (reduction) reaction producing a thin alloy coating. This process is self-limiting and will stop when the oxidation reaction of the base metal stops. Generally these coatings are very thin and contain elements of the base material. These coatings are used primarily in electronic applications.

Immersion alloy deposition processes are easy to control and require little metal replacement because of the very thin deposits produced. Displacement tin-lead solder processes are the exception, producing thicker deposits requiring more frequent additions.

Types of Electroless Alloy Plating Systems

Most electroless alloy systems are based on nickel alloys and have been developed from basic electroless nickel-plating technology. Many alloy systems are documented in the literature and several are commercially available. In the following section each coating type is summarized and its availability is indicated as either "production" or "laboratory."

Nickel-Phosphorus. Electroless nickel-phosphorus is the most common nonelectrolytic alloy coating system. Electroless nickel has been used since the early 1950s and continues to show the most growth and development.

These coatings are widely used for control of wear and corrosion. An important property is the amorphous structure in the as-plated condition and the ability to heat treat the deposit by precipitation hardening to produce a crystalline structure.

There are three nonequilibrium phases for the as-plated electroless nickel deposit: beta, beta + gamma, and gamma. The beta phase is present up to a phosphorus content of 4%; above 4%, there is a mix of beta and gamma. When the deposit has more than 11.2% P, the deposit is gamma-phase. Upon heat treating the deposit containing nickel and phosphorus, a precipitation occurs, producing an equilibrium mix of nickel phosphide and alpha-nickel. A coating of unique mechanical and physical qualities can be produced by controlling the phase of metal being deposited, the alloy of phosphorus, and the postheat treatment.

To help classify the different nickel-phosphorus coatings, a system has been developed that groups them into types. This system has been incorporated into national and international draft specifications. The scheme presented in Table 2 follows the current industry convention.

Table 2 Electroless nickel-phosphorus plating systems

Alloy	Hardness, HK_{100}	Environments in which plating has demonstrated corrosion resistance	Significant properties and applications	Availability

Type II: 1-3% P, bal Ni	435-680	Alkali, brine, strong caustics	Solderability, electrical conductivity[(a)], wire bonding	Production
Type III: 2-4% P, bal Ni	700-800	Alkali, brine, strong caustics	High as-plated hardness for wear application on aluminum, beryllium, copper, and other base materials that cannot be precipitation hardened	Production
Type IV: 5-9% P, bal Ni	520-650	Alkali, brine, caustic solutions	General wear and corrosion resistance applications, including application in industrial interior and exterior nonmarine environments, undercoatings. Thicknesses for these applications range from 1 to 125 μm (0.03 to 5 μin.).	Production
Type V: 10-14% P, bal Ni	430-530	Alkali, brine, mildly acidic solutions, marine environments	Wear and corrosion resistance applications in marine and corrosive industrial environments; nonmagnetic undercoating in memory discs; oil and gas environments	Production

(a) Conductivity, 10-30 $\mu\Omega \cdot cm^2$

Procedures for the electroless deposition of nickel, nickel-phosphorus, and nickel-boron are described in detail in the article "Electroless Nickel Plating" in this Volume.

Nickel-Boron. Another family of nonelectrolytic alloy coatings uses boron-based reducing agents (Table 3). These are classified by boron alloy content. Generally the low-boron coatings are used in electronic applications as a replacement for gold. The higher-boron coatings are used to provide a hard surface to prevent galling in iron and nickel wear applications.

Table 3 Electroless nickel-boron plating systems

Alloy	**Hardness, HK_{100}**	**Significant properties and applications**	**Availability**
0.1-1% B, bal Ni	520-620	Electronic applications, replacement for gold in microelectronic equipment and printed wire circuit boards	Production
2-4.5% B, bal Ni	750-800	Aircraft engines, landing gear, valves, and pumps; resistance to galling, fretting, and erosion wear	Production

In general, high-boron coatings use sodium borohydride as the reducing agent and operate at a pH of 12.5 and above. Low-boron coatings use dimethyl amino borane (DMAB) as the reducing agent and operate in a neutral pH of 5.5 to 7. These systems are commercially available and provide the chemical basis for many of the nonelectrolytic ternary alloy systems. Both DMAB and sodium borohydride are powerful reducing agents and provide energy to reduce many elements.

Hypophosphite-Reduced Cobalt Alloy Coatings. Nonelectrolytically produced cobalt alloy coatings have been used in a limited number of magnetic and wear applications. These coatings are produced from sodium hypophosphite-based solutions at a slightly alkaline pH range at elevated temperatures. Table 4 lists property and application information for a hypophosphite-reduced cobalt-phosphorus coating.

Table 4 Electroless cobalt alloy plating systems

Alloy	**Hardness, HK_{100}**	**Environments in which plating has demonstrated corrosion resistance**	**Significant properties and applications**	**Availability**
Hypophosphite-reduced cobalt-phosphorus (3-6% P, bal Co)	550-650	Alkali, brine solutions	Magnetic and medical applications	Production
Boron-reduced cobalt-boron (3-4% B, bal Co)	350-500[(a)]	. . .	Wear resistance in high-temperature applications	Laboratory; limited application

(a) As-plated; 800-1000 HK_{100} after 30 min at 400 °C (750 °F)

Boron-reduced cobalt alloy coatings (Table 4) are produced by a reduction reaction of sodium borohydride or DMAB reducing agents. The deposits are harder and have higher melting points than those alloyed with phosphorus. These coatings have not been commercially available. They could be used in wear applications where service at higher temperatures is required.

Ternary alloy coatings are used to provide higher performance in specific properties over conventional electroless coating systems. By incorporating a third element in significant or trace levels, the basic structure and physical properties of the coating can be altered. There are many possibilities and systems that have been investigated and are available (Table 5).

Table 5 Electroless ternary alloy plating systems

Alloy	**Hardness, HK_{100}**	**Environments in which plating has demonstrated corrosion resistance**	**Significant properties and applications**	**Availability**
Hypophosphite-reduced alloys				
Nickel-phosphorus-molybdenum (5-9% P, 0.5-1% Mo, bal Ni)	550-650	Alkali, brine, caustics, weak acid solutions	Pitting corrosion protection	Laboratory
Nickel-copper-phosphorus (4-8% P, 1-3% Cu, bal Ni)	430-520	Alkali, brine, caustic solutions	Nonmagnetic, conductive, high modulus	Production
Nickel-cobalt-phosphorus (15-40% Co, 3-8% P, bal Ni)	. . .	. . .	High-coercivity coating for use in magnetic memory applications	Laboratory, limited production
Nickel-iron-phosphorus (1-4% Fe, 2-4% P, bal Ni)	. . .	. . .	Magnetic applications in electronics	Laboratory
Nickel-rhenium-phosphorus (1-45% Re, 3-8% P, bal Ni)	. . .	. . .	High melting point (1700 °C, or 3090 °F); high-temperature wear resistance	Laboratory

Nickel-tungsten-phosphorus (4-8% P, 1-4% W, bal Ni)	550-620	. . .	High melting point (1550 °C, or 2820 °F); high-temperature wear resistance	Laboratory
Cobalt-tungsten-phosphorus (4-8% P, 1-5% W, bal Co)	570-640	. . .	High-temperature wear resistance	Production
Boron-reduced alloys				
Nickel-thallium-boron (3-5% Tl, 3-5% B, bal Ni)	650-850	. . .	Wear applications requiring resistance to galling, fretting, and erosion; coating is self-lubricating in contact with ferrous materials	Production
Nickel-tin-boron (3-5% B, 1-3% Sn, bal Ni)	650-850	. . .	Wear applications requiring resistance to galling, fretting, and erosion; this coating is also self-lubricating	Production
Cobalt-tungsten-boron (3-5% B, 1-5% W, bal Co)	750-850	. . .	Wear applications requiring resistance to galling; can be used at higher temperatures than phosphorus systems	Laboratory

Boron-reduced ternary alloy coatings are produced by a reduction reaction of sodium borohydride or DMAB reducing agents. The deposits are harder and have higher melting points than those alloyed with phosphorus. Some of these coatings have not been commercially available. Figure 1 shows the microstructure of an electroless nickel-thallium-boron plating deposit.

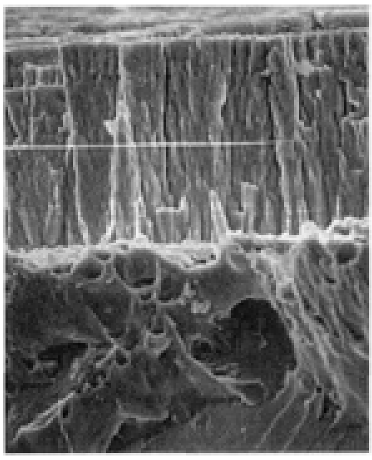

Fig. 1 Electroless nickel-thallium-boron deposit. The hard columnar structure increases resistance to fretting wear and the ability of the deposit to retain oil. Additional lubrication is provided with the presence of thallium, which interferes with the galling process between nickel and iron.

Types of Dispersion Alloy Coating Systems

Dispersion alloy coatings combine the finite microstructure of a dispersed particle into a macrostructure. These coatings can be categorized as composites containing lubricant particles or those containing hard particles. These dispersed particles are incorporated into a metal matrix of nickel phosphorus or cobalt phosphorus. In most applications an undercoat is used to increase the corrosion resistance and improve the coverage of the dispersion coating. An overplate is also used to seal particles into the surface and produce a more consistent initial wear.

Nonelectrolytic solid-lubricant dispersion alloys are produced from solutions that use lubricant powders suspended in an aqueous electroless nickel or cobalt system. The powders are sensitized by cationic surface agents and dispersed by other surfactants.

There are commercial processes that use PTFE and CF_x as well as fluorinated carbon and fluoride salts of lithium, calcium, and magnesium. Each of these lubricant particle systems has specific advantages. Generally PTFE is used where the loads are low. Fluorinated carbon powders can operate at higher temperatures and greater loads. Fluoride salts provide lubrication at temperatures near the melting point of the coating.

Nonelectrolytic Hard-Particle Dispersion Alloys. A wide range of hard particles can be incorporated into the deposits, including diamonds, silicon carbide, tungsten carbide, titanium carbide, silicon nitride, and others. The basic requirement for the process is that the particles remain passive while deposit is proceeding and at the same time come to rest on the surface and become incorporated into the coating. These particles are generally between 0.4 and 3 μm in diameter and are loaded into the deposit from between 15% and 25% by weight. Coatings using these particles are generally designed to support moderate to high loads.

Silicon carbide in a nickel phosphorus matrix is the most common of the dispersed particle coating systems. These coatings provide abrasion resistance in mining and chemical processing applications and are used in internal combustion engines because the deposit provides for the retention of oil on the surface. Deposits containing dispersed diamond particles have provided significant improvement in the performance of textile-weaving equipment by reducing abrasive wear caused by textile fibers.

Nonelectrolytic Displacement Alloys

Displacement alloys are applied without the use of a reducing agent and are deposited by a combination of oxidation and reduction reactions that occur as the base metal corrodes. The result of this chemical reaction is the formation of an alloy of two elements.

The displacement alloy coating is self-limiting in thickness, and the reaction will stop when the density of the corroding metal on the surface drops below the reduction potential of the primary metal. There are two coating systems used in electronic applications that incorporate this technique.

Displacement tin-lead alloys are available for limited use as solder deposits. Process control is critical in producing a consistent alloy and melting point in this system. The other system, which is also used on a limited basis, is an alloy of palladium and ruthenium used in the activation of copper for subsequent electroless nickel plating in printed circuit board applications. The addition of ruthenium reduces the number of palladium atoms on the surface and improves the adhesion of the nickel to the copper.

Processing of Parts

The electroless alloy coatings discussed in this article are produced from aqueous solutions following a specific base-metal-dependent cleaning and activation procedure. These procedures are generally similar to those employed for the electroless deposition of unalloyed nickel; see the article "Electroless Nickel Plating" in this Volume for more information.

Process Control. Nonelectrolytic alloy processes require more frequent sampling and analysis than conventional electrolytic plating processes. This is caused by metal salt consumption without the advantage of an anode to replace the metal, oxidation of reducing agents, lower metal concentrations, and the consumption of the alloying agent at a rate different from that of the primary metal.

The process control requires that the operator know the rate of consumption of all ingredients. After initial adjustment to optimum concentrations, the operator must replenish each of the ingredients at their individual rate of consumption.

Two types of control tests determine this replenishment on-line and off-line. On-line tests are performed during the process by analyzing for trace metals, alloying elements, reducing agents, and organics. By selecting specific organic chemistries that produce consistent alloys, maintaining these chemicals in balance, and controlling the conditions of the process, a consistent alloy can be produced. Off-line testing is performed on the alloy specimens after the plating process and is used to verify that the process control is valid.

By combined use of these control systems and scheduled replenishment during the plating process, uniform deposit properties can be achieved.

Deposit Analysis. There are several tests which can be performed on the alloy to determine its quality. They should be selected to measure a specific property in the application.

Composition is generally measured by inductively coupled plasma or atomic absorption for the major constituents. Alloys of dispersed particles require more complex procedures to ensure that the alloy as well as the percentage weight of the included particle is within specification.

Wear resistance is sometimes used to measure the quality of the deposit. The Taber abraser has been used to test abrasion resistance on dispersed hard-particle alloys. Other methods include the Falex pin-on-vee-block and LFW1 block-on-ring apparatus for testing adhesive wear. Other test methods for fretting and erosion wear are sometimes used. An important consideration in evaluating the wear rate is the number of samples required to produce statistically accurate results. Generally the most relevant test is in the field, where the parts are subjected to the actual wear system and the wear rate or service life is the measure of performance.

Uniformity of dispersed particles within the alloy may be measured to ensure consistent wear resistance. This is generally measured by examination of a metallographic cross section of a specimen processed with the parts.

Equipment for Nonelectrolytic Alloy Plating

Nonelectrolytic alloy plating processes use a variety of chemicals in their formulations. Some of the processes have high pH conditions, whereas others operate in the acid pH range. Still others are corrosive to polyvinylidene fluoride (PVDF) and other plastics. Because of this variability of chemistry a number of different materials are used in making the tanks and piping, including polypropylene, polyethylene, polyvinyl chloride, PVDF, PTFE, and stainless steel.

Nonelectrolytic alloy plating equipment is shown in Fig. 2. The plating solution is removed from the bottom of the tank and circulated through a pump, heat exchanger, and filter and then returned to the plating tank through an agitation manifold. Processes using dispersed particles require special fixturing and manifolds to ensure that the particles are distributed uniformly.

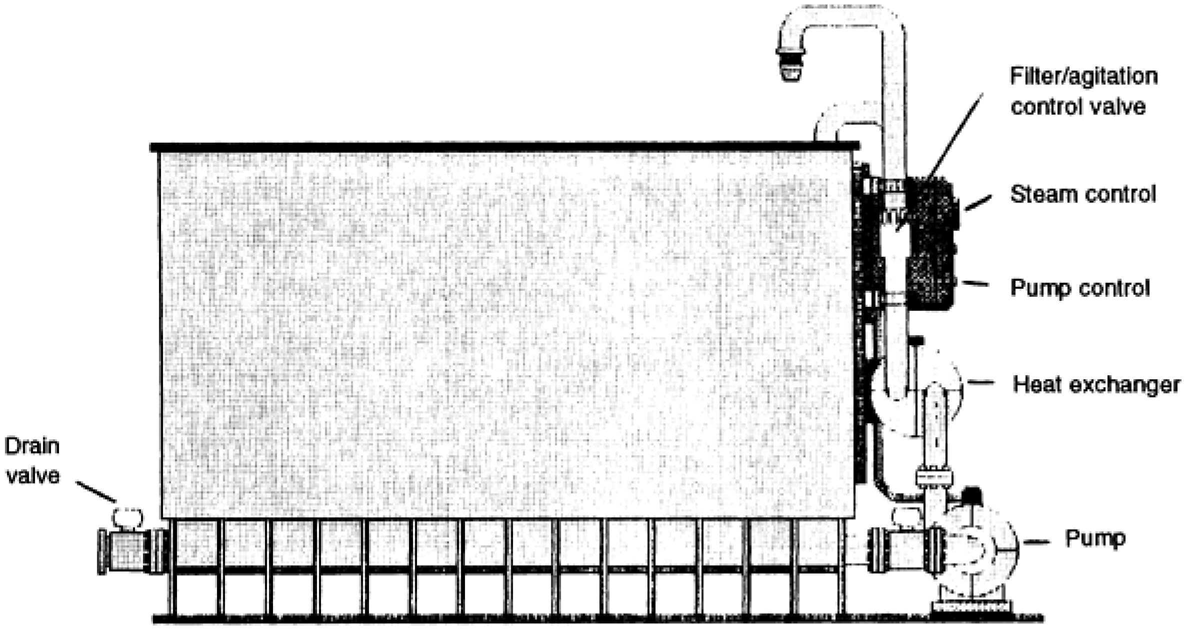

Fig. 2 Tank system for electroless alloy plating

In Fig. 2, the solution is heated with hot water or steam by a heat exchanger. A double mechanical, water-sealed pump is used to circulate the solution from a trough bottom tank that is constructed from natural, stress-relieved polypropylene and welded with inert gas. The piping is made of PVDF and is fuse welded to ensure years of leak-free service. Automatic equipment is used to add replenishment chemicals to maintain a consistent alloy by reducing variations in the process chemistry. Some processes require constant additions to ensure that the processes remain stable. For process volumes of less than 500 L, small chemical-feed pumps that deliver 10 to 20 L/h should be used. Racks, barrels, and baskets are used in the operations to move the parts through the processes. These items should be made of materials compatible with the system.

Safety and Environmental Concerns

Nonelectrolytic deposition processes contain metals that are generally considered toxic. Nickel is regulated in the sewer and ground water and should be controlled. Metals other than nickel may also be regulated and must therefore be controlled.

Processes should have secondary containment, ventilation, and exhaust blowers and recovery and recycling equipment to contain the metals and eliminate hazardous waste. Recycling equipment to remove the byproducts and return the metals to the process is available, thereby extending the operational life of the process.

Good finishing hygiene requires operators to use gloves, goggles, and aprons when mixing and handling chemicals used in these processes. The use of a mask is required on some processes, and careful study of the material safety data sheet is required.

Mechanical Plating

Arnold Satow, McGean-Rohco, Inc.

Introduction

MECHANICAL PLATING is a method for coating ferrous metals, copper alloys, lead, stainless steel, and certain types of castings. The process applies a malleable, metallic, corrosion-resistant coating of zinc, cadmium, tin, copper, or aluminum; combinations of metals can be applied as codeposits or as "sandwich" layered deposits. Mechanical plating has been used internationally for over 40 years and is referred to by a variety of names, including *peen plating, impact plating,* and *mechanical galvanizing.* Mechanical plating often can solve engineering, economic, and pollution-related plating problems. It offers a straightforward alternative method for achieving desired mechanical and galvanic properties with an extremely low risk of hydrogen embrittlement. In some circumstances, it offers a potential cost advantage over electroplating (Fig. 1).

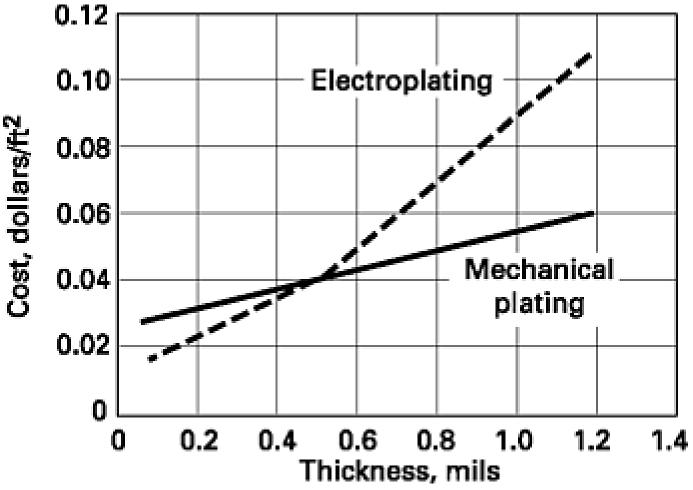

Fig. 1 Cost comparison of mechanical plating and electroplating. Approximate costs shown are for chemicals only and do not include labor or overhead.

Mechanical plating is accomplished at room temperature, without the electrical charge passing through the plating medium that is necessary with electroplating or electrocoating. The metallic coating is produced by tumbling the parts in a mixture of glass beads, metallic dust or powder, "promoter" or "accelerator" chemicals, and water. The glass beads provide impacting and hammering energy, which serves to pound the metallic particles against the surfaces of the parts. The result is a tight, adherent metallic coating produced by "cold welding" fine, powdered metallic particles to the surfaces of parts.

Recent improvements in deposit quality, cost-effectiveness, and ease of application have induced many finishing engineers to investigate and adopt mechanical plating for certain applications. Special advantages of the mechanical plating and galvanizing process are that it:

- Greatly reduces part susceptibility to hydrogen embrittlement
- Can be used to deposit a wide variety of metals in a broad range of coating thicknesses
- Consumes comparatively low amounts of energy
- Does not require the use of toxic chemicals
- Simplifies waste treatment
- Does not require baking in most cases
- Provides greater uniformity of coatings (when used for galvanizing)

Hydrogen Embrittlement

The need to prevent hydrogen embrittlement was one of the major reasons for the creation and use of mechanical plating. A critical concern in electroplating and other coating processes used on ferrous parts is the embrittling effects of hydrogen absorbed by the part. The current used in electroplating acts to enhance the possibility of hydrogen embrittlement--both because most electroplating generates hydrogen at the cathode and because the negative charge acts to pull hydrogen into the part. Hydrogen embrittlement can cause sudden development of breaks or cracks in highly stressed areas, with subsequent total rupture of the part or the assembly. The risk increases for parts that have high hardness from cold working or heat treating, especially those made of high-carbon steels.

In the normal electroplating process, an important source of hydrogen gas is the reaction between acids and metals present in the plating solution. The hydrogen migrates through the metallic substrate and concentrates at high stress points and grain boundaries. The trapped hydrogen builds internal pressures that can lower the tolerance to stresses applied in actual use. Dangerous failures in critical applications can result.

Other atmospheres that can potentially cause or contribute to hydrogen embrittlement include heat-treating furnaces, cleaning solutions, and pickling baths.

Advantage of Mechanical Plating in Avoiding Embrittlement. Mechanical plating deposits metals while eliminating or at least minimizing the risk of embrittlement caused by the coating process itself. A hydrogen-producing reaction does occur in mechanical plating:

$$\text{Zn metal} + 2\text{H}^+ \rightarrow \text{H}_2\text{(gas)} + \text{Zn}^{++}\text{(ion)} \qquad \textbf{(Eq 1)}$$

However, this reaction occurs essentially on the surface of the powdered zinc particles, which are approximately 5 to 10 μm in diameter. The reaction proceeds at a relatively slow rate and within a more porous, less oriented metallic grain structure than that produced by electroplating. Therefore, the hydrogen gas is not likely to be trapped or occluded within or under the metal particles in the coating. The effusion or escape of hydrogen gas through the deposit and away from the substrate is more likely than diffusion into the base metal. A substantial portion of the mechanical plating performed today is done on parts and metals that are predisposed to hydrogen embrittlement. These include spring steels, parts heat treated to 42 HRC or higher, cold-headed parts, or any part for which service application or structural integrity is highly critical.

Mechanical Plating Equipment

Mechanical plating is accomplished in mild steel or stainless steel variable-speed tumbling barrels. Because the entire process takes place at low (1 to 2) pH, the barrels must be lined with an inert, abrasion-resistant protective coating such as neoprene, polypropylene, polybutylene, or urethane. The lining is usually applied at a thickness of 19 to 25 mm (0.75 to 1 in.); thicker linings may be used in high wear areas such as the inner base of the barrel.

Typical tumbling barrels have capacities of 0.04 to 1.13 m^3 (1.5 to 40 ft^3), where *capacity* is the total available working volume, which is typically about 25 to 35% of the total volume. For example, a 0.57 m^3 (20 ft^3) plating barrel will hold approximately 910 kg (2000 lb) of 25 mm (1 in.) long steel threaded fasteners or about 680 kg (1500 lb) of 8d common nails. After the parts are loaded in the barrel, approximately 1000 kg (2200 lb) of glass beads are added with sufficient water to form a slurry.

The tumbling of part on part and glass bead on part creates kinetic energy that serves to cold weld the spheroidal metal particles to the substrate. The diameters of the most commonly used glass beads are nominally 5 mm (0.187 in.), 1.5 mm (0.056 in.), 0.7 mm (0.028 in.), and 0.25 mm (0.010 in.). The ratio of glass beads to parts is about 1.5:1 by weight, but varies depending on the part mass and geometry and on the coating thickness required (greater thicknesses sometimes require a higher ratio of beads to parts and the use of larger beads). The barrels rotate at a surface speed of 43 to 75 m/min (140 to 250 ft/min) and at a tilt angle of about 30° from horizontal.

The glass plating beads perform a number of functions. They:

- Assist cleaning and oxide removal through a mildly abrasive scrubbing action
- Facilitate mixing and displacement of the chemicals
- Consolidate the metallic coating
- Protect and separate parts from one another, thereby preventing edge damage and tangling
- Help push the plating metal into corners, recesses, and blind areas

Glass beads are constantly reused and recycled through a glass bead recovery and pumping system, which is part of the standard mechanical plating equipment package.

Process Steps

The mechanical plating process requires a series of chemical additions. The quantity depends on the total area of part surface. The total area must be determined prior to each cycle. All of the plating steps are performed in the same barrel, normally without rinsing or stopping the rotation. The only exception is removal of heavy oil or scale; these contaminants should be removed before parts enter the plating barrel.

The first process steps include a series of chemical and metal additions designed to mildly acid clean and activate the substrate and then to apply a thin, uniform copper strike. The copper strike provides a clean, galvanically receptive part surface. The next step involves adding an "accelerator" or "promoter" agent, which creates a chemical environment that controls the rate of deposition and subsequent bonding of the plating metals. A defoaming agent is used during the process to control foaming and to prevent any associated loss of plating solution.

The plating metal is added as a dry, fine powder or a water slurry containing the powder. Platers add metal in a series of steps and in amounts proportional to the coating thickness desired. Commercial plating thicknesses of 5 to 12.5 μm (0.0002 to 0.0005 in.) usually require two to three additions of metal, while greater thicknesses or "galvanized" coatings can demand eight or more.

The following represents a typical sequence of operations for mechanical plating:

1. Alkaline or acid preclean (if necessary)
2. Prepare surface
3. Copper strike

4. Add accelerator/promoter
5. Add plating metal
6. Add plating metal
7. Add plating metal

The plating cycle is carried out at temperatures between 15 and 32 °C (60 and 90 °F). A pH between 1 and 2 is required at all times to ensure proper adhesion and a high plating efficiency. The low pH level acts to maintain an oxide-free condition at all times on both the part surface and the surface of the plating metal particles. These temperature and pH conditions facilitate mechanical bonding ("cold welding"). The process has an efficiency of about 92%; that is, approximately 92% of the plating metal added is actually plated on the parts.

The mechanical plating process usually takes about 45 min. At the conclusion of the cycle, the slurry of glass beads, coated parts, and water discharges into a vibrating *surge hopper* under the plating barrel. The capacity of this hopper should be large enough to accept the entire load, thereby freeing the barrel to begin plating the next load. The slurry dumps onto a vibrating screen or magnetic separator. Water sprays are used to wash and remove glass beads from the parts. A glass bead handling system consisting of a sump, a double-diaphragm pump, and an overhead conical storage reservoir with a pinch valve at the bottom is used to recycle the beads. More than one batch of glass beads can be used to speed production.

As described above, the mechanical plating process can be used to apply a variety of metals and codeposits with varying coating thicknesses, all with the same equipment. This capability offers advantages in equipment cost and space utilization over other forms of plating.

Process Capabilities

Plating Thickness. The thickness of mechanical plating deposits ranges from 5 to 75 μm (0.2 to 3 mils). The heavier coatings are referred to as *mechanical galvanizing* or *cold-impact galvanizing* coatings. Because the coating thickness is somewhat independent of cycle time and is controlled by the plating metal additions, a heavy "galvanized" coating thickness can be applied in almost as little time as thinner commercial coating thicknesses. Mechanical galvanizing provides uniform, smooth, and adherent coatings, and the coated parts require no thread chasing. Extensive exposure and salt spray testing have confirmed that the corrosion resistance of mechanical galvanized parts is comparable to that of hot-dip galvanized parts and parts coated with other types of zinc deposits at equivalent coating weights (Table 1).

Table 1 Corrosion resistance of threaded bolts with various coatings

Coating	Coating thickness, μm	Hours to red rust(a)
Zinc-aluminum	50 25	5000 2200
Zinc galvanized	50	490
Cadmium plated	25	1100
Dacromet	. . .	1250
Zinc electroplated	12.5	144

Note: All parts except Dacromet were mechanically plated. Dacromet is a zinc flake/chromate dispersion coating applied like dip/spin paint with a double cure.

(a) ASTM B 117 salt spray test

Applicable Parts. Many parts for which coating options were formerly limited to electroplating or hot-dip galvanizing are now successfully being mechanically plated. Part types now universally accepted as candidates for mechanical plating or galvanizing include nails; chain and wire forms of all types; bolts, nuts, and washers; offshore drilling hardware; pole-line hardware for telephone and cable television lines; certain marine fasteners; ASTM A 325 structural bolts; aircraft hardware; and automotive hardware of all types.

Whether or not parts can be successfully coated using mechanical plating or galvanizing depends on their size, weight, and geometry. Parts that would tend not to withstand the vigorous tumbling action of the process are not suitable. Parts heavier than 1 to 2 kg (2.2 to 4.4 lb) or longer than 0.5 m (1.64 ft) are not usually coated using mechanical plating.

Specific Characteristics, Advantages, and Limitations. Because of the dust or powder form in which metals are deposited, the surfaces of mechanical coatings will have matte to medium-bright luster. It is possible to achieve very smooth surfaces, but the mirrorlike surfaces typical of electroplated parts cannot be obtained. For this reason, mechanical plating finishes are considered to be functional rather than decorative.

Parts with holes and recesses that are difficult to electroplate to the desired thickness usually can be properly plated via mechanical plating. Parts with hole diameters as small as 0.78 mm (0.03 in.)--even where the depth of the hole is greater than the diameter--frequently can be plated successfully. Mechanical plating is often more economical and more flexible for parts that require special racking or special anode configurations to electroplate recessed areas.

Powder metallurgy parts can be coated by mechanical plating without prior sealing of their surfaces. Because mechanical plating solutions are generally chemically consumed, little excess is available to be entrapped in the pores of the substrate. The initial galvanically deposited copper strike will permeate such pores, and the metal powder will fill and bridge them. Also, because the potential for hydrogen embrittlement is extremely low, any pores in the part should not accumulate significant amounts of hydrogen.

Quality Control. In order to ensure the quality of the mechanically plated parts, the operator must pay constant attention to the coating adhesion, weight and thickness, consolidation, uniformity, and general appearance and brightness. The main causes of nonuniform appearance include:

- Use of glass media in poor condition
- Insufficient cleanliness of parts prior to plating
- Insufficient burnishing time at the end of the plating cycle
- Wet parts kept in surge hopper too long
- Conductivity of water too high
- Zinc added to cycle too quickly or in incorrect amounts

Applicable Specifications. ASTM B 635, B 695, and B 696 are standard specifications for mechanical plating. The military standard is covered by MIL C 81562. Many large original equipment manufacturers have their own specifications, as do many state highway departments. Mechanical galvanizing conforms to the coating weight and general requirements specified in ASTM A 153, which is widely used in the hot-dip galvanizing industry.

Post Treatments

Mechanical plating post treatments are similar to those used in electroplating. The coating is most receptive to post treatment immediately after plating, while it is still wet. A mild acid dip (e.g., 1% nitric acid) will reactivate parts that have already been dried. Conversion coatings such as clear or blue, yellow, olive drab, or black chromates can be applied. Mechanically plated parts can also be painted. A chromate coating pretreatment will improve paint adhesion.

The color, luster, and iridescence obtained with colored or clear chromates are somewhat different than those obtained on electroplated surfaces, but are well within the normal range of acceptable appearance and performance. Waxes, lacquers, and silicates will satisfactorily adhere to the coating and will enhance the lubricity, durability, appearance, and corrosion resistance of the surface. No baking for embrittlement relief is required prior to or after supplementary treatment.

Waste Treatment

Before choosing a wastewater treatment system for mechanical plating, engineering and analytical data must be gathered. The preliminary work should determine:

- Treatment options for the metals in solution
- Present and future flow rates, and batch collection volume requirements
- Water conservation possibilities
- What is required to meet discharge limits
- Availability and type of treatment chemicals
- How sludge will be dewatered, dried, and disposed

In most cases, removal of heavy metals from mechanical plating effluent is accomplished by precipitating metal hydroxides. This is done routinely as long as the metal ions in the effluent are not complexed and the pH is high enough to ensure optimum precipitation. Zinc, for example, reaches minimum solubility at a pH between 9 and 10. A pH of 9.5 provides satisfactory precipitation in about 30 min. Although other metals reach minimum solubility at different pH levels, a pH of 9 to 10 will precipitate other residual metals associated with the process, such as copper, tin, iron, cadmium, and aluminum (but not the chromium present in certain post-treatment chromates). The chemical most commonly used in precipitation is 50% liquid sodium hydroxide. Magnesium hydroxide and lime slurry also can be used as a source of alkalinity. Lime tends to be less expensive but increases the precipitation time.

Chromium presents a special problem when present as a chromate (hexavalent state). Hexavalent chromium must first be reduced to the trivalent state before standard precipitation can proceed. Sodium metabisulfite or ferrous sulfate added at a pH of about 2 will reduce the hexavalent chromium and allow the resultant trivalent chromium to be combined with other wastes for regular precipitation.

Most mechanical plating systems capable of plating 1000 kg (2200 lb) of parts will discharge 22 to 45 1/min (6 to 12 gal/min) of solution; therefore, a batch system with a minimum of two collection tanks should be satisfactory. Each tank should be capable of holding the effluent from one shift, allowing one to fill while the other is being treated.

Flocculation is an important consideration. After pH adjustment of the effluent, it should flow to a tank for flocculation of the suspended metal hydroxides. Addition of a polyelectrolyte causes the small particles to agglomerate into larger, heavier particles, with improved settling characteristics.

After being flocculated and settled, the suspended solids enter a sludge dewatering device such as a filter press. Sludge drying further reduces the volume (by up to 75%) of the solid wastes released from the filter press. A standard mechanical plating and galvanizing system will produce approximately 0.028 m^3 (1 ft^3) of dewatered and dried sludge per 1000 to 2000 kg (2200 to 4400 lb) of plated parts.

Surface Preparation for Continuously Applied Coatings

Curtiss Dunbar, LTV Steel Company

Introduction

METALLURGICALLY CLEAN SURFACES are necessary to promote the proper bonding of continuously applied dip, barrier, and chemical conversion coatings on steel substrates. Surface preparation removes contaminants on the substrate that would prevent the optimal metallurgical bonding of the coating.

There are two basic types of contaminants. Carbonaceous materials, which include oils, represent one type. These materials are actually applied to the steel strip during the cold-reduction process to facilitate rolling. Normal, unavoidable surface oxidation is the other type. The surface of every processed steel strip has one or both of these contaminants, which must be removed before dip, barrier, or conversion coatings can be applied. These contaminants can be removed by using wet cleaning methods, furnace-atmosphere techniques, fluxes and other specialized methods, or a combination of these.

Although this article primarily describes techniques that prepare steel surfaces for hot-dip coatings, the same techniques can be used for electroplated and chemical conversion coatings. Modern continuous annealing lines use similar methods to clean steel strip before heat treatment. The term "line" refers to the sequenced operations in the coating process.

Surface preparation usually comprises separate cleaning steps, which can be used either alone or in combination, depending on the amount of soil on the incoming steel strip and the design layout for the coating line. Modern lines usually include several of these cleaning steps to meet the demanding quality requirements of the market in the 1990s.

A good example of modern surface-cleaning techniques, shown in Fig. 1, combines both wet and furnace surface-preparation methods in order to produce a clean steel strip. The incoming strip first contacts a dip alkaline cleaner and then a brush scrubber. The strip next contacts an electrolytic alkaline cleaner and then a second brush scrubber. The strip is then rinsed and dried. After this wet section of the process, the strip enters an unfired, or waste gas, preheater before entering a high-gradient, direct-fired furnace. Finally, it enters a high-temperature, radiant-tube, reducing/annealing furnace with a hydrogen-nitrogen atmosphere.

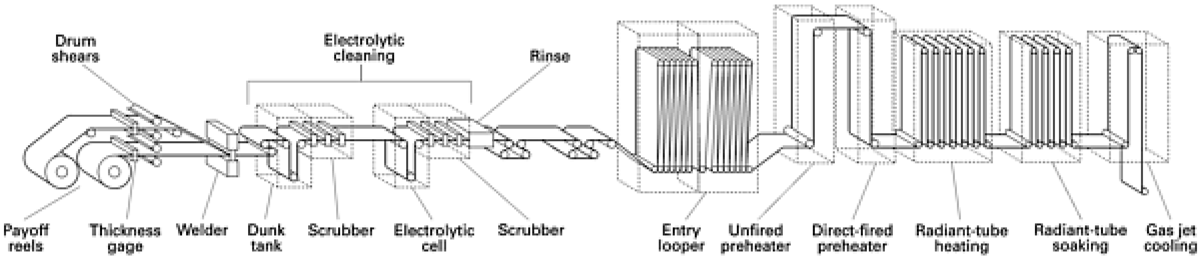

Fig. 1 Schematic of cleaning section of modern coating line that provides both wet and furnace types of surface preparation

Wet Cleaning Methods

Wet cleaning is a generic term that means aqueous solutions are used to prepare the surface of the strip. This term incorporates both alkaline and acid processes. The wet cleaning section of a coating line has a relatively low initial cost, compared with the cost of large, gas-fired furnaces, but requires a high degree of maintenance. In addition, the cost of the chemicals and of the disposal of spent chemicals results in high operating expenses.

Alkaline Cleaning. In the dip operation of continuous strip coating lines, alkaline cleaning is used to remove protective oils, soil, and the residues of rolling oils. Although it is possible to remove thin oxide layers using alkaline cleaning, these layers are usually removed during subsequent pickling operations.

Alkaline cleaners are blends of various inorganic salts with small amounts of inhibitors and surfactants to promote different cleaning mechanisms, such as saponification and emulsification.

Saponification refers to the chemical action whereby an oil is converted to a water-soluble soap. This reaction depends on concentration, temperature, pH, and time of immersion. This mechanism will clean the majority of light rolling oils and rust-preventative oils that are common on flat, rolled steel strip. Care must be taken to ensure that the soil level in the cleaner does not become high enough to cause redeposition of the soil or to interfere with proper rinsing.

Emulsification is the process whereby surfactants penetrate soils and break them into sufficiently small particles to allow dispersion and suspension in the cleaning solution.

The capabilities of the alkaline cleaner can be augmented by adding brushes to the continuous strip coating line in order to mechanically loosen and remove surface soil. An abrasive material can be bonded to these brushes to enhance their scouring or scrubbing action. The brushes are usually placed in the processing line with a steel roll on the opposite side of the strip. This arrangement allows the contact pressure of the brush to be increased without deflecting the pass-line of the strip. The cleaner is often applied through the brush to provide cooling at the contact area and to act as a medium for floating the loosened soil away and preventing its redeposition.

Electrolytic Cleaning. Cleaners can be designed to work with electric current. The strip can be either cathodic or anodic. The recommended practice for continuous lines is either the anodic configuration or a switching current, where the strip is switched between being positively and negatively charged. In anodic electrocleaning, the strip is positively charged and oxygen is discharged at the strip surface to create a mechanical scrubbing action. One disadvantage of anodic cleaning is the tendency to build up sludge on the electrodes. In cathodic electrocleaning, the strip is negatively charged, producing the release of a much larger volume of hydrogen and better mechanical scrubbing at the strip surface. This condition also increases the possibility of hydrogen being charged into the strip and the unwanted plating out of metallic contaminants onto the strip surface, which can cause quality problems with the subsequent coating operation. Periodic reversing, or switching, electrocleaning is a combination of both anodic and cathodic methods that produces a better cleaning of the strip surface without excessive contamination, hydrogen charging, or electrode buildup.

Maintenance. The concentration of the cleaner must be maintained and any additives that tend to be used up at a faster rate than the basic caustic components must be controlled in terms of proportion. The cleaner system should allow for the periodic settling and removal of solid soils, especially metallic particles such as the iron fines that form during cold rolling. Oil needs to be cleaned from the system by frequent or continuous skimming. Magnetic separators and other devices are effective in removing soil burden and prolonging the useful life of the cleaner.

Chemical Pickling. Most pickling operations use an acid to dissolve metal oxides. The resulting reactions are affected by concentration, temperature, and agitation. These reactions will naturally slow down as the acid solution becomes more concentrated in the metal being dissolved.

Sulfuric acid is the most common acid used in pickling iron-base materials because of its low cost. After the acid has removed the oxide scale, it will begin to attack the steel substrate. Therefore, inhibitors are commonly used to retard the attack of the base metal without affecting oxide scale removal. As with most chemical reactions, an increase in temperature increases the pickling rate. As the acid is consumed, the pickling time must be increased to achieve the same level of descaling. In continuous coating lines, it is not possible to simply increase the pickling time to compensate for the reduced effectiveness of the acid pickling. Pickling effectiveness is also decreased as iron builds up in the pickling bath. Therefore, both acid and iron contents must be adjusted by replenishment.

Hydrochloric acid is an excellent pickling agent for the removal of oxides from steel strip. Although it is more expensive and its fumes much more corrosive than sulfuric acid, it has a longer useful life, can be operated at lower temperatures, and is not affected by the iron concentration to the same degree experienced in sulfuric acid pickling.

Electrolytic Pickling. Electrolytic action can be used to increase the speed of pickling, which is a very important aspect of continuous coating lines (Fig. 2). The electric current can be either alternating or direct, and the strip can be either anodic or cathodic. Cathodic pickling is faster than anodic, but this advantage decreases with increasing concentration and bath temperature. Cathodic pickling charges the steel with hydrogen much faster than straight chemical pickling does. In modern continuous coating lines, the current is often switched, which makes the strip cathodic and then anodic.

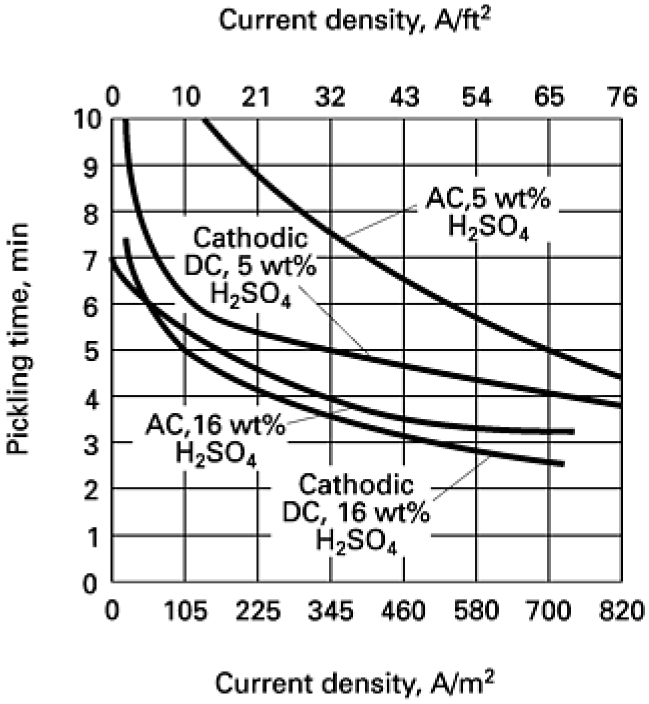

Fig. 2 Effect of current density on pickling time for anodic, cathodic, and alternating current electrolytic pickling. AC, alternating current; DC, direct current. Source: National Electric Products Corp.

Flame Cleaning and Furnace Preparation

Sendzimir Oxidation/Reduction Method. The original method for flame cleaning was proposed by Tadeusz Sendzimir in the 1930s. His invention involved heating a steel strip in a direct oxidizing flame to burn off the rolling oils and other contaminants. This step left an oxide on the steel surface, which was then cleaned by heating to a much higher temperature in a reducing furnace with a hydrogen-nitrogen atmosphere. This two-furnace cleaning method was converted into a coating line by cooling the strip and immersing it in molten zinc while it was still under the protective hydrogen-nitrogen atmosphere. An additional benefit was that the strip could be annealed while it was being cleaned for coating.

Oxidizing Furnace. In general, both the oxidizing furnace and the newer, nonoxidizing, direct-fired furnace can perform the same job. Both types of furnace configurations preheat the strip before it enters the radiant-tube furnace, and both flash off the volatile materials and oxidize the carbon compounds that are on the surface of the strip.

The role of the oxidizing furnace is to oxidize all of the carbonaceous products without leaving too thick an oxide layer for the reducing furnace to convert back to pure iron. All oxide that forms in the oxidizer *must* be reduced in the reducing furnace in order to prepare the strip for coating. Unreduced oxide is brittle and, if left on the strip, will result in poor coating adherence.

Oxidizing furnaces usually preheat the strip to approximately 480 °C (900 °F). This temperature, which is somewhat arbitrary, depends on the uniformity of heating and the reducing capability of the radiant-tube furnace that follows. Care should be exercised to avoid overheating the edges of the strip. Because the oxidizing furnace is not sealed, air can be drawn into the furnace, making the atmosphere within this furnace oxidizing to the steel strip, regardless of burner combustion practices. Burners are usually adjusted to perfect combustion for efficiency. If the combustion ratio of the burners is too rich, then carbon deposits (soot) can form on the strip and completely negate the cleaning purpose of the oxidizer. Carbon cannot be removed with a hydrogen atmosphere, and uncoated spots and poor coating adhesion will result.

Direct-Fired Furnace. The use of a nonoxidizing, high-gradient, direct-fired furnace is preferred for strip preparation. The direct-fired furnace is so named because there is direct flame impingement of the combustion products on the strip. This type of furnace is connected directly to a reducing or radiant-tube furnace. The large volume of combustion products that is produced in the direct-fired furnace acts as either a barrier or a seal to pressurize the rest of the reducing furnace, which minimizes the consequences of small furnace leaks.

Direct-fired furnaces usually have zones, or segments, that can be turned off to adjust for lighter-gage strip or lower annealing-temperature requirements. These zones are usually connected to a common flue near the entry of the furnace. This flue usually contains a damper that controls the furnace pressure to a predetermined value. Pressure that is too high can force combustion products into the reducing zones and contaminate the hydrogen-nitrogen atmosphere. The flue must be large enough and the pressure such that all combustion products will flow out of the flue.

The advantages of this type of furnace are that it preheats, removes volatiles and carbon without oxidizing the strip, and provides a much higher preheat temperature than an oxidizing furnace.

Although the direct-fired furnace is in many ways superior to the original oxidizing furnace, it does have negative aspects. Its major disadvantage is that it is expensive to operate and maintain. It also has a high initial cost because of the sophistication of the burners and burner controls, and because of the refractory requirements to operate at high temperatures. In addition, high operating temperatures and thermal shock can cause problems with the maintenance of the refractories. Controls for the fuel-to-air ratio and the furnace pressure are very critical and cannot be neglected. Because the gas feed on the individual burners can easily become plugged, it needs to be checked and cleaned. The ability of the positive pressure to overcome furnace leaks is not a cure-all for poor maintenance practices. Air can be aspirated into the furnace, even with positive furnace pressure.

Combustion Ratios. Because the furnace must rapidly heat a steel strip without oxidizing it, the correct ratio of air to gas must be ensured. Although the optimal amount will vary with the coating line, it should be in the 4 to 5% range for excess combustibles in the last zone of the direct-fired furnace, where the strip temperature is the highest. This ratio should be set without having the strip or any hydrogen in the furnace. This combustion ratio will increase when the coating line is running because of the addition of the hydrogen atmosphere to the furnace. After exiting from the furnace, the strip should be bright and oxide-free. Minor adjustments are often made using strip appearance only as a guide.

If the amount of excess combustibles are greater than 7 to 8%, then carbon can be deposited on the strip surface, resulting in uncoated spots and poor adhesion. In many mills, it is common practice to set the combustion ratios progressively leaner (closer to perfect combustion and, in some cases, excess air) in the zones closest to the furnace entry, where the strip temperatures are lower. Output will be increased and some of the wasted energy will be recovered by burning the hydrogen furnace atmosphere and the excess fuel from the preheater zones.

Strip Exit Temperature. If strip exit temperatures from the direct-fired furnace are too high, then the strip will be oxidized. Usually, the maximum indicated temperature without oxidation is approximately 730 °C (1350 °F). Higher temperatures almost always produce an oxide, regardless of burner ratios. Lower temperatures do not produce an oxide, but they defeat the powerful cleaning capability and lose the advantage of the rapid preheating. The maximum allowable temperature is also very dependent on furnace design, combustion ratios, and dwell time in the furnace.

Zone Temperature. If the zone temperatures of the direct-fired furnace are too low, then the strip will be oxidized. Usually, these zone temperatures are maintained at a minimum of 1100 °C (2000 °F). Control of the direct-fired furnace is best accomplished by turning zones off, rather than by turning them down. It is best to leave the last zone (the one next to the radiant-tube furnace) on full fire and then add or turn off the other zones in order, as needed. A relationship between strip exit temperature and zone temperature is critical to ensure proper cleaning.

Dwell Time. Even under perfect nonoxidizing conditions within a direct-fired furnace, strip will become oxidized if the residence time, or *dwell time,* is excessive. For any given coating line, the line speeds (dwell time in the direct-fired furnace) for each gage width and grade are predetermined to achieve the highest production rates consistent with producing the desired physical and mechanical properties. This virtually eliminates the possibility that well times will be used that are long enough to oxidize the strip.

A waste-gas preheater is an unfired section of furnace that is put ahead of the direct-fired furnace in the coating line. The exit gases pass through this furnace section before being exhausted through a damper. The incoming strip can be heated to approximately 200 °C (400 °F), just by contacting the very hot exhaust gases of the direct-fired furnace. Because this section of the furnace can be oxidizing if strip temperatures get too high, it is important not to make this section too large. Too much strip preheat will either oxidize or bake on the oils and carbonaceous material, which will seriously affect the ability of the direct-fired furnace to clean the strip. Direct-fired furnaces with waste-gas preheaters produce a tremendous amount of strip heating and cleaning in a relatively small amount of floor space. In addition to their cleaning capability, they produce a means to pressurize the rest of the furnace to negate the problem of small furnace leaks.

Radiant-Tube Furnace. Gas-phase surface preparation in a radiant-tube furnace allows surface iron oxide to be converted to pure iron, using heat and a hydrogen atmosphere. The radiant-tube furnace is so named because the insides of tubes that are positioned throughout the furnace are heated by external burners. These hot tubes radiate heat to the inside of the furnace without exposing the furnace to either air or combustion products.

Radiant-tube furnaces usually operate with an atmosphere mixture of hydrogen and nitrogen. The steel strip that enters the reducing, or radiant-tube, furnace will be heated under this reducing atmosphere. Hydrogen reacts with surface oxides to produce pure, nascent iron and water vapor (dew point). After the strip is cleaned and annealed to achieve the desired properties, its temperature is adjusted (cooled) to a level close to that of the molten coating bath. This is accomplished by passing the strip through an unheated furnace with cooling tubes that are similar to the radiant tubes, except that only air is blown through them.

A more efficient method of cooling the strip is to use gas-jet coolers, which remove the hot furnace atmosphere and pass it over a heat exchanger to cool, before returning the atmosphere to the furnace, where it contacts and cools the hot strip.

Process Variables. The atmosphere of the radiant-tube furnace must be maintained as reducing to steel, in order to achieve the desired surface preparation. This condition is controlled by the amount of hydrogen, the temperature of the strip, and the amount of water vapor in the furnace. Figure 3 shows the relationship of these variables as a function of temperature versus the water/hydrogen ratio.

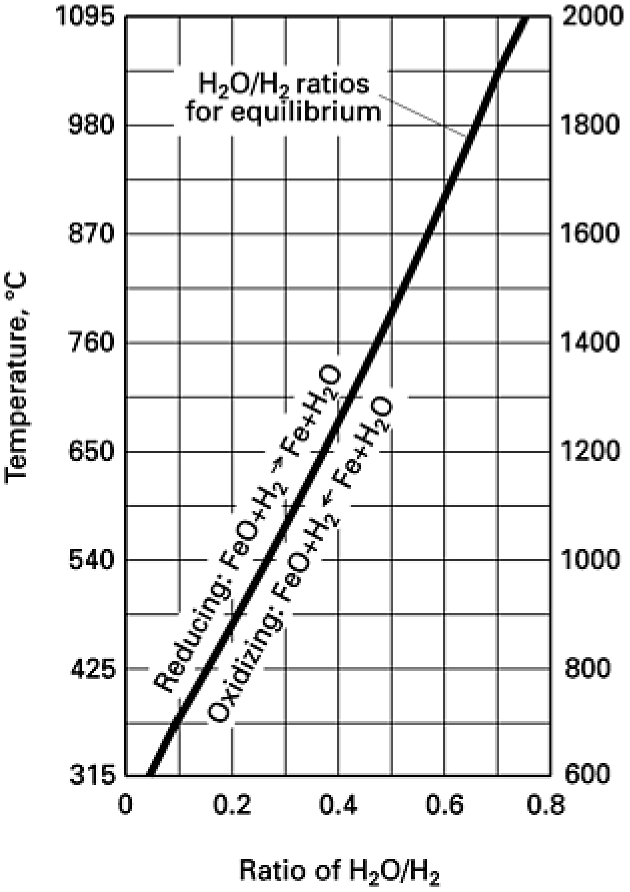

Fig. 3 Theoretical equilibrium relationship between iron, iron oxide, hydrogen, and water vapor

Another concern is the infiltration of free oxygen into this atmosphere. Oxygen levels between 50 and 100 ppm have been shown to be detrimental to proper surface preparation for hot-dip coatings.

Wet chemical precleaning and strip heating in a hydrogen-nitrogen atmosphere has certain advantages. The mechanical properties of the final product can be predetermined before coating, and then a low-temperature cycle can be used during coating to preserve these properties. This practice does have higher production costs than the in-line annealing processes. Advantages are that less furnace refractory maintenance is required and that there are many skilled builders of radiant-tube furnaces.

The relatively low-gradient heating that characterizes this method requires a long overall furnace length. Wet chemical precleaning requires higher overall maintenance of equipment and solutions. The cleaning section of the coating line must provide a properly dried and rinsed strip, or else problems can develop with alkaline carryover to ceramic-coated hearth rolls.

The maintenance of a radiant-tube furnace is higher, because tubes are fired harder than they are in a direct-fired furnace. There is greater vulnerability to furnace leaks, because it is difficult to maintain significant positive pressure of the hydrogen-nitrogen atmosphere.

The direct-fired preheating method provides positive and consistent thermal cleaning of cold-rolled strip. It is therefore the preferred combination for most modern coating lines. Direct-fired preheaters provide rapid, high-gradient heating, which requires a much shorter furnace length than radiant-tube furnaces with a wet cleaning capability. This system is less sensitive to furnace leaks, because a high positive furnace pressure is maintained by the controlled discharge of combustion products. Fewer radiant tubes are required, which is a factor that reduces the possibility of furnace leaks. In-line annealing is more economical and produces equivalent mechanical properties when modern stabilized substrates are used.

Refractory maintenance is much greater in a direct-fired section than in a radiant-tube furnace. The direct-fired section lends itself to both horizontal and vertical configurations. The steel strip is heated in the direct-fired section to temperatures that are high enough to effect positive shape correction by stretching before tracking difficulty can occur.

Other Specialized Cleaning Methods

Fluxes. One of the earliest methods of coating one metal with another incorporated the use of a flux. In modern methods, fluxing involves coating an incoming strip with a material that will chemically break down, thereby producing conditions that remove surface oxides. Modern continuous flux lines usually incorporate alkaline and acid wet cleaning steps ahead of the flux operation.

Fluxes are mixtures of acid salts with surfactants and other inert materials that float on the surface of the coating metal bath, helping to prevent oxidation. The most common fluxes are the zinc chloride plus ammonium chloride mixes that are used in the production of terne (92% Pb and 8% Sn) coatings and in Cook-Norteman continuous galvanizing lines. Ammonium chloride has the stronger fluxing action, whereas zinc chloride provides preheat thermal stability and acts as an inhibitor for steel surface oxidation. Steel strip is cleaned, pickled, and, as a final step, coated with an aqueous solution of the zinc and ammonium chloride flux. In the Cook-Norteman lines, the strip is then dried and preheated to minimize the impact of the cold, incoming strip in cooling the molten zinc bath. Because productivity is very important, it is desirable to preheat the strip to the maximum temperature possible without damaging the flux coating and oxidizing the strip. Upon entering the zinc bath, the flux breaks down, releasing a hydrogen chloride gas that acts as a chemical surface preparation. The balance of the spent flux floats to the surface of the bath, where it is removed. Under proper conditions, the flux will completely release from the strip surface and be replaced by a wetted layer of the coating metal.

Mechanical Cleaning. Other methods of cleaning also have been tried and used successfully in certain applications. These methods include mechanical alteration of the surface of a material, such as shot/grit blasting or abrasive/wire brushing, in order to remove particles before the surface is coated. Grit blasting can include sand, glass, and steel grit or shot. Brushes with embedded abrasive materials are commonly used as a surface preparation step in coil paint lines and in brush alkaline cleaners. Although these brushes appear to uniformly alter the strip surface, microstructural examination of a mechanically cleaned surface shows that a large portion of it never contacts the abrasive materials.

Ultrasonic cleaning methods loosen surface material by using ultrasonic energy to alternately compress and expand the cleaning solution. This pressure can "tear" the solution apart, producing cavitation bubbles. These bubbles have the effect of blasting solid soil away from the surface. Ultrasonic energy can be used with any of the standard cleaners if proper adjustments are made. The major disadvantage of using ultrasonic energy in a continuous line is the high cost associated with processing strip at high speeds.

Continuous Hot Dip Coatings

Herbert E. Townsend, Bethlehem Steel Corporation

Introduction

OWING TO its many favorable characteristics, steel is well suited and widely used for a broad range of engineering applications. It has a variety of excellent mechanical properties, such as strength, toughness, ductility, and dent resistance. Steel also offers good manufacturability, including formability, weldability, and paintability. Other positive factors include its availability, ferromagnetic properties, recyclability, and cost. Because steel is susceptible to corrosion in the presence of moisture, and to oxidation at elevated temperatures, successful use of these favorable characteristics generally requires some form of protection.

Methods of corrosion protection employed to protect steel include: altering the metal by alloying, changing the environment by desiccation or use of inhibitors, controlling electrochemical potential by application of cathodic or anodic currents, and applying organic and metallic coatings. Application of a metallic coating by a continuous hot dip process is one of the most widely used means of protecting steel. In continuous hot dip coating, long strands of sheet, wire, or tubing are fed through a bath of molten coating metal in a continuous process. In batch hot dip coating, fabricated parts, such as fasteners, poles, or beams, are dipped into a molten bath either individually or in discrete batches.

Metals and alloys that can be applied as coatings to steel in a continuous hot dip process are limited to those with a melting point low enough to allow steel to be pulled through a coating bath without tearing. These include the coatings described below, namely, zinc, zinc-iron alloy, aluminum, aluminum-silicon alloy, Zn-5Al alloy, 55Al-Zn alloy, and lead-tin alloy. Metals such as chromium and titanium cannot be applied to steel by hot dipping because of their high melting points. Tin, which prior to 1937 was applied only by hot dipping, is now almost always electrodeposited. This is because it is very difficult to produce the thin and uniform coatings required for tinplate by means of hot dipping.

Coating thickness is a key factor in determining coated product performance. In general, thicker coatings provide greater corrosion protection, whereas thinner coatings tend to give better formability and weldability. The amount of coating can also be expressed in terms of mass per unit area. This is determined by weighing a section of the coated product, stripping the coating in an acid solution, and weighing again. Tables 1 and 2 summarize coating thickness and mass called for by ASTM specifications for continuous hot dip coatings for sheet and wire (Ref 1, 2, 3, 4, 5, 6, 7, 8, 9). In the case of sheet, the coating thickness is usually expressed in terms of the coating on one side, whereas the mass is usually given as the sum of the coating on both sides.

Table 1 Nominal coating mass and thickness for continuous hot dip coatings on steel sheet

Type of coating[(a)]	Designation	Coating mass[(b)], g/m^2	Coating thickness[(c)], µm
Zinc (A 525)	Z1100	1100	78
	900	900	64
	700	700	50
	600	600	42
	450	450	32
	350	350	25

	275	275	19
	180	180	13
	90	90	6
	001	(d)	(d)
Zinc-iron (A 525)	ZF180	180	11
	120	120	9
	100	100	7
	75	75	5
	001	(d)	(d)
Aluminum (A 463) type 1	T1 40	120	20
	25	75	12
Aluminum (A 463) type 2	T2 100	305	48
	65	195	30
	LC	(d)	(d)
Zn-5Al (A 575)	ZGF 700	700	48
	600	600	41
	450	450	31
	350	350	24
	275	275	19
	225	225	15
	180	180	12

	135	135	9
	90	90	6
	001	(d)	(d)
Zn-55Al (A 792)	AZ 180	180	24
	165	165	22
	150	150	20
Lead-tin (A 308)	LT 110	336	15
	85	259	12
	55	168	8
	40	122	6
	35	107	5
	25	76	3
	01	(d)	(d)

Note: All values are based on specified triple-spot minima.

(a) ASTM specifications as given in *Coated Steel Products,* Vol 01.06, *Annual Book of ASTM Standards,* ASTM, 1993.

(b) Two sides.

(c) One side. Calculated from densities in g/cm^3 as follows: zinc and zinc-iron, 7.07; aluminum type 1, 3.017; aluminum type 2, 3.21; Zn-5Al, 6.87; Zn-55Al, 3.70; lead-tin, 11.08.

(d) No minimum

Table 2 Minimum coating mass and thickness ranges for continuous hot dip coatings on steel wire

Type of coating(b)	**Coating class**	**Range of minima(a)**	
		Coating mass(c), g/m^2	**Coating thickness(d), µm**

Zinc (A 641)	1	45-190	6-27
	A	180-300	25-42
	B	360-600	51-85
	C	540-900	76-127
Aluminum (A 809)	. . .	92-122	29-38
Zn-5Al (A 856)	1	45-190	7-28
	A	180-300	26-44
	B	360-600	52-87
	C	540-900	79-131

(a) Minimum coating increases with increasing wire diameter.

(b) ASTM specifications as given in *Coated Steel Products,* Vol 01.06, *Annual Book of ASTM Standards,* ASTM, 1993.

(c) Two sides.

(d) Calculated from densities in g/cm^3 as follows: zinc, 7.07; aluminum, 3.21; Al-5Zn, 6.87

Typical applications for hot-dip-coated steel sheet, wire, and tubing cover a wide range in the construction, automobile, utility, and appliance industries (Table 3). As the cost of lumber increases, additional large-scale applications of hot-dip-coated steel sheet are expected to develop in the residential construction markets for roofing, siding, and framing. Compared to conventional home building materials, steel has obvious advantages, such as price stability, dimensional stability, and better resistance to fire, earthquakes, hurricanes, and insects.

Table 3 Typical applications of continuous hot-dip-coated steel sheet, wire, and tubing

Coating	**Product**		
	Sheet	**Wire**	**Tubing**
Zinc and Zn-5Al	Roofing, siding, doors, culvert, ductwork, housings, appliances, autobody panels and structural components	Nails, staples, guy wires, strand, tension members, rope, utility wire, fencing	Electrical conduit

Zinc-iron	Autobody panels and structural components	. . .	. . .
Aluminum type 1	Mufflers, tailpipes, heat shields, ovens, toasters, flues, chimneys	Guy wires, strand, rope, utility wire, fencing	. . .
Aluminum type 2	Roofing, siding, ductwork, culvert, silo roofs	Guy wires, strand, rope, utility wire, fencing	. . .
Zn-55Al	Roofing, siding, ductwork, culvert, mufflers, tailpipes, heat shields, ovens, toasters, flues, chimneys, silo roofs	. . .	. . .
Lead-tin	Fuel tanks, radiator components, valve covers, air-filter housings	. . .	Fuel lines, hydraulic lines

Among all coated products, continuous hot-dip-coated steel sheet is the biggest in terms of tons produced and consumed. As shown in Fig. 1, over 9 million U.S. tons (8.2 million metric tons) of hot-dip-coated steel sheet were shipped in the United States in 1992 (Ref 10). This amounts to almost 12% of all steel products shipped in the United States.

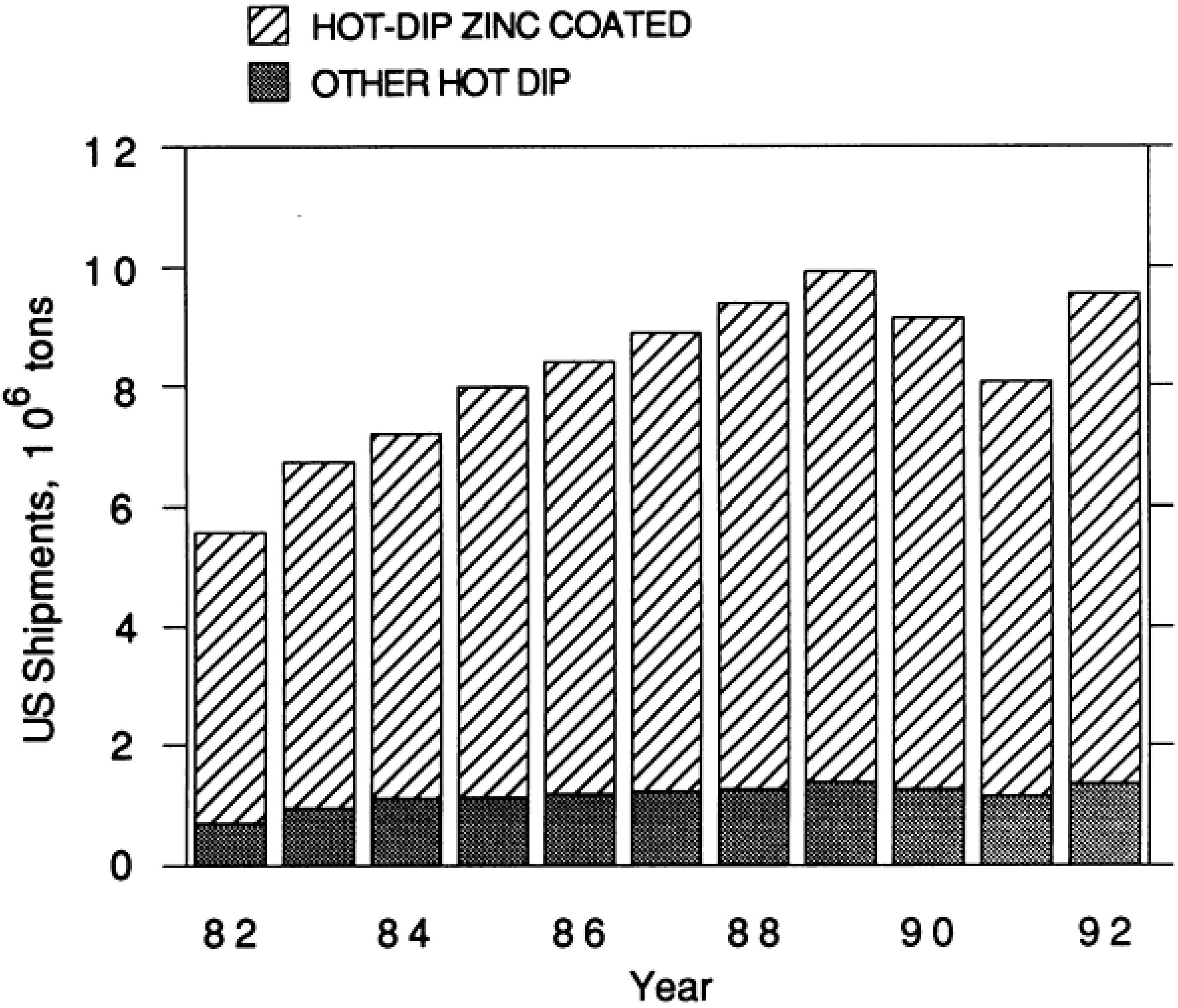

Fig. 1 U.S. shipments of coated steel sheet. Source: Ref 10

This chapter deals mainly with the processes and coatings used for the continuous hot-dip coating of steel sheet. Much of this information is also applicable to steel wire and tubing. Additional details can be found in a number of earlier reviews (Ref 11, 12, 13, 14, 15, 16).

Notwithstanding a lapse due to a sluggish economy during 1990-1991, hot-dip-coated steel sheet has shown substantial growth over the 11-year period shown in Fig. 1. This growth occurred largely because coated steel is replacing uncoated steel in order to satisfy consumer demands for improved durability, particularly in the automobile industry. In order to meet this increasing demand, producers in the United States and around the world are investing in more hot dip coating facilities. It is estimated that from 1990 to 1995, the total hot dip sheet-coating capacity of the Western World will grow from 49 to 63 million metric tons per year. Most of this capacity will be located in Japan (35%), North America (28%), and Europe (30%).

Hot-dip-coated, low-carbon steel sheet is available with a broad range of mechanical properties. As shown in Table 4, it can be produced with yield strengths in the range of 241 to 620 MPa (35 to 90 ksi). Compared to uncoated steel, hot-dip-coated, low-carbon steel sheet has slightly less ductility because of the thermal effects of the coating process on the precipitation of carbon in the steel and associated age hardening. Extra-deep-drawing-quality grades are made with steel that has been vacuum degassed to very low carbon levels and stabilized with additions of titanium and/or niobium. The stabilized substrates are relatively immune to the thermal effects of hot dipping and provide excellent formability. Low-alloy grades are also galvanized to meet the requirements of specific applications.

Table 4 Typical mechanical properties of continuous hot-dip-coated steel sheet

Grade	**Yield strength**		**Tensile strength**		**Elongation in 5 cm (2 in.), %**
	MPa	**ksi**	**MPa**	**ksi**	
Full hard	620	90	634	92	5
Commercial quality	255	37	338	49	35
Drawing quality	248	36	324	47	37
Drawing quality special killed	241	35	332	48	38

References

1. "Standard Test Method for Weight of Coating on Zinc-Coated (Galvanized) Iron or Steel Articles," ASTM A 90, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
2. "Standard Specification for Steel Sheet, Zinc-Coated (Galvanized) by the Hot-Dip Process," ASTM A 525, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
3. "Standard Specification for Zinc-Coated (Galvanized) Carbon Steel Wire," ASTM A 641, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
4. "Standard Specification for Steel Sheet, Cold-Rolled, Aluminum-Coated, Type 1 and Type 2," ASTM A 463, *Annual Book of ASTM Standards,* ASTM, 1993
5. "Standard Specification for Aluminum-Coated Carbon Steel Wire," ASTM A 809, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
6. "Standard Specification for Steel Sheet, Zinc-5% Aluminum Alloy Metallic-Coated by the Hot-Dip Process," ASTM 875, Vol 01.06, ASTM, 1993

7. "Standard Specification for Zinc-5% Aluminum-Mischmetal Alloy-Coated Carbon Steel Wire," ASTM A856, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
8. "Standard Specification for Steel Sheet, Aluminum-Zinc Alloy-Coated by the Hot-Dip Process, General Requirements," ASTM A 792, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
9. "Standard Specification for Steel Sheet, Long Terne (Lead-Tin Alloy) Coated by the Hot-Dip Process," ASTM A 308, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
10. "Annual Statistical Report," American Iron and Steel Institute, 1992
11. A.J. Stavros, Continuous Hot-Dip Coatings, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed. *Metals Handbook*), ASM International, 1987, p 432-436
12. H.E. Townsend, L. Allegra, R.J. Dutton, and S.A. Kriner, Hot-Dip Coated Sheet Steels--A Review, *Materials Performance,* April 1986, p 36-46
13. H.E. Townsend, Coated Steel Sheet for Corrosion Resistant Automobiles, *Materials Performance,* Oct 1991, p 60-65
14. V. Jagannathan, Emerging Technologies in the Hot-Dip Coating of Automotive Sheet Steel, *Journal of Metals,* Aug 1993, p 48-51
15. H.E. Townsend and L. Allegra, Precoated Sheet Steel for Automotive Applications, *Automotive Corrosion by Deicing Salts,* R. Baboian, Ed., National Association of Corrosion Engineers, 1981, p 337-351
16. H. Bablik, *Galvanizing (Hot-Dip),* Wiley, 1950

Continuous Hot Dip Sheet-Coating Processes

In continuous hot dip coating of steel sheet, coils of steel are welded end-to-end and are coated at speeds of up to about 200 m/min (650 ft/min). In general, continuous hot dip coating facilities are classified as either *hot* or *cold,* as described below.

Hot Lines. In hot processing, steel strip is cleaned and heated in a reducing gas atmosphere, typically a mixture of hydrogen and nitrogen, in order to prepare the surface for coating. Annealing of cold-rolled steel by heating above its recrystallization temperature of about 700 °C (1300 °F) is usually a part of this heating process. Combining the steps of cleaning, heat treating, and bringing the sheet to coating temperature into a continuous operation contributes to making the hot process economical. Hot processing at lower temperatures without recrystallization is also done to produce full-hard, coated, high-strength sheet. Lower temperatures are also used to coat hot-rolled sheet, or to coat cold-rolled sheet that has been previously annealed.

A state-of-the-art hot line capable of producing 450,000 metric tons per year and coating sheet up to 1830 mm (72 in.) wide is shown schematically in Fig. 2. Coils of steel sheet are first loaded onto reels at the entry end on the left. The leading end of each coil is resistance seam welded to the tail end of the preceding coil. This is made possible by the looping tower, which acts as a reservoir for sheet. Sheet previously stored in the looping tower is released downstream so that sheet at the entry point can be stationary long enough for a new coil to be loaded and welded without interrupting the continuity of the coating process.

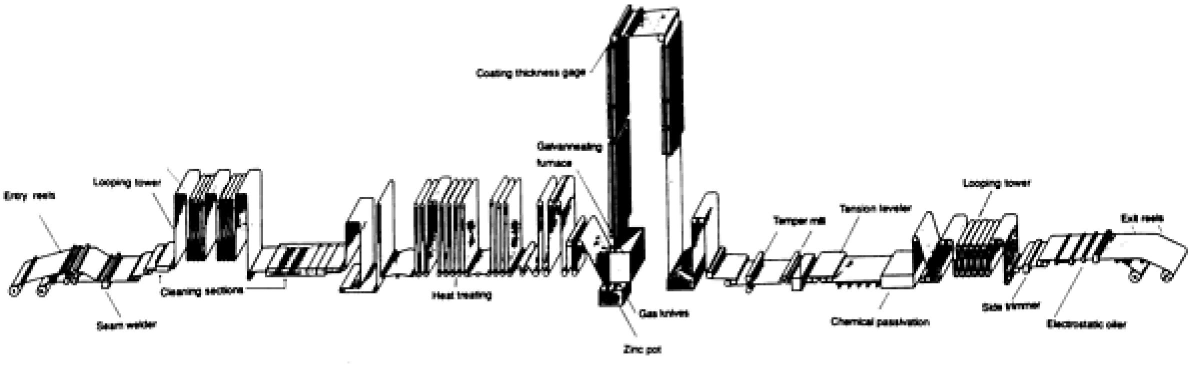

Fig. 2 Schematic diagram of a continuous galvanizing line. An example of a "hot" line with in-line annealing capability. See text for details.

After welding, the strip enters the first cleaning stage, an alkaline bath that removes oils, dirt, and residual iron fines from the rolling process. Upon exiting the looping tower, the strip surface is further cleaned by mechanical brushing and electrolytic alkaline cleaning. Older lines may rely solely on direct firing of gas burners on the strip surface in order to burn off residual oils.

Following cleaning, the sheet passes into a radiant tube furnace containing a mixture of hydrogen and nitrogen that reduces surface iron oxides. This atmosphere produces a very clean surface that can be easily wet by the coating metal. Heating of the steel also takes place in the furnace. Annealing of cold-rolled sheet is achieved by heating usually just above the temperature for subcritical recrystallization (about 720 °C, or 1330 °F). Following recrystallization, it is generally desirable to cool the sheet down to near the bath temperature (about 460 °C, or 860 °F in the case of zinc coatings) in order to avoid overheating of the metal bath. Most modern lines have jet coolers to convectively cool the strip before bath entry.

The steel strip next enters a pot containing a bath of the molten coating metal. Shown schematically in Fig. 3, the pot region is where the actual hot dip coating process takes place. The first coating pots were little more than steel tubs heated by gas flames. Modern pots are steel vessels lined with ceramic refractory and heated by electric induction. Any hardware in the bath, such as the rolls, bearings, and support members, is usually made of 316 stainless steel or a similar alloy in order to resist attack by the molten metal.

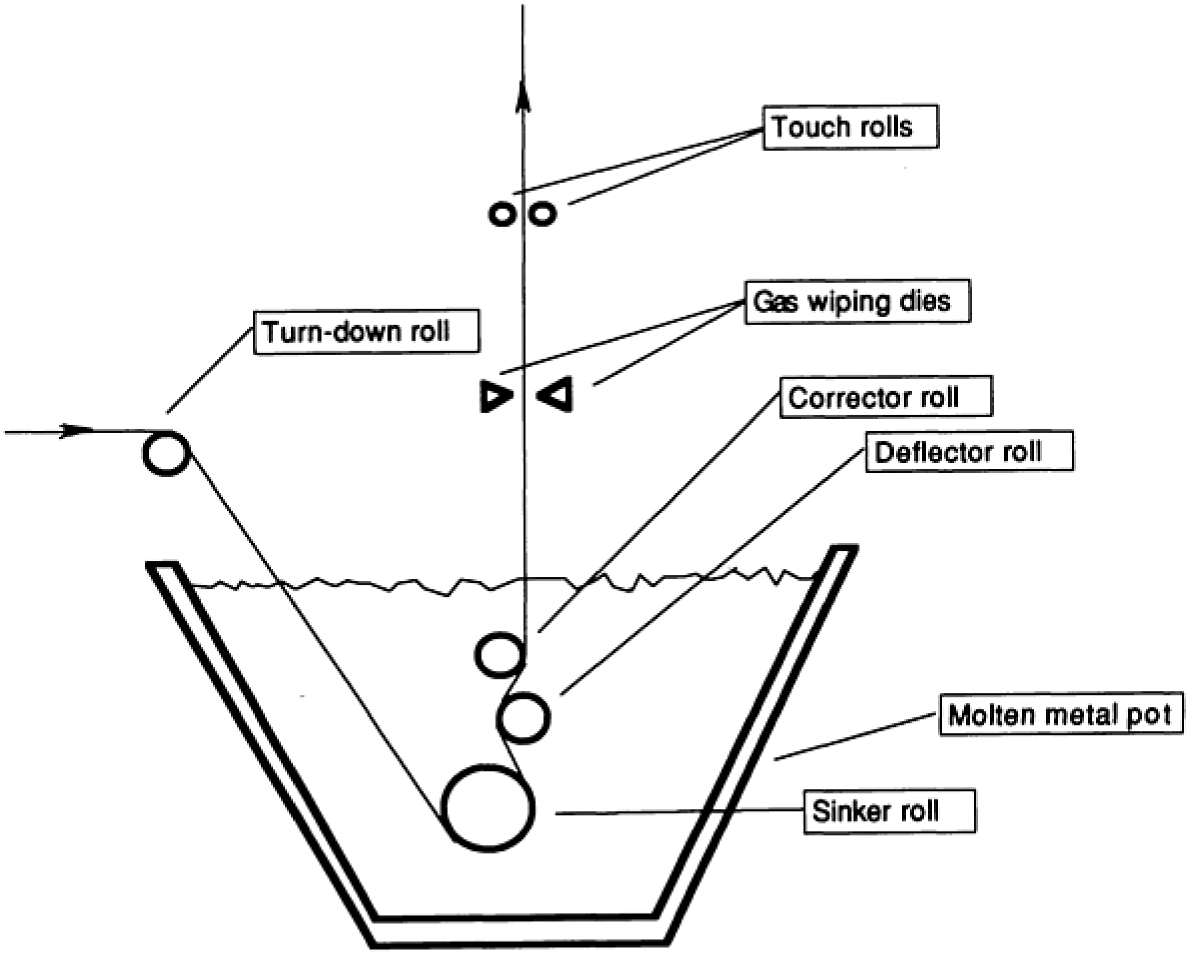

Fig. 3 Schematic of pot region in a typical continuous hot dip coating line

As the strip exits the pot, a film of molten coating adheres to the surface. The thickness of the molten film is controlled by passing the strip between gas wiping dies, which remove excess coating metal with a stream of gas. Coating thickness is determined by the geometry of the wipers, the velocity of the wiping gas, and the distance between the wiping dies and the sheet. The wiping gas may be steam, air, or nitrogen. On-line x-ray fluorescence or isotope gages continuously monitor the actual coating thickness and enable rapid adjustments to be made. Figure 4 shows the region of a typical hot dip coating line where the coated strip exits the pot.

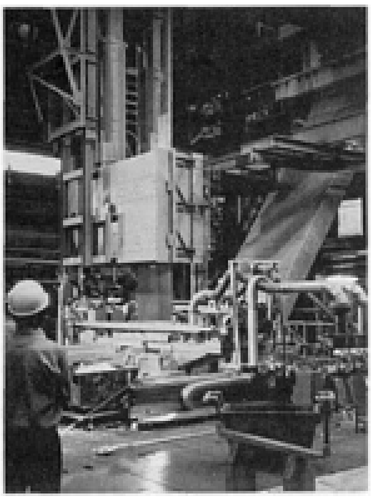

Fig. 4 Coated sheet exiting pot at a galvanizing line

In some coating facilities, the region above the pot and around the wipers is enclosed. The enclosed region is purged with the nitrogen wiping gas in order to reduce oxidation of the bath by air. This helps to reduce the incidence of surface defects and give a more uniform coating. In order to prevent fuming and copious clouds of zinc dust, it is also necessary to inject steam into the enclosure to form an oxide barrier on the surface of the molten metal.

Uniformity of coating thickness along and across the sheet surface is an important factor affecting the quality and performance of hot-dip-coated sheet. For this reason, it is critical to avoid fluctuations in the distance between sheet and wiping die that may result from poor sheet shape or vibrations. Shape-related difficulties are minimized by use of an adjustable deflector roll (see Fig. 3) that is submerged in the bath and pressed against the strip to reduce crossbow (i.e., excessive curvature in the plane of the sheet). The stationary corrector roll serves to keep the strip in alignment with the wiping dies. Variations in sheet-to-die distance resulting from sheet vibrations are minimized by use of the touch rolls located above the wipers. These reduce the amplitude of sheet vibration at the wiping dies by decreasing the unsupported length of sheet above the pot.

After coating, forced-air cooling is used to reduce sheet temperature. This prevents coating damage due to contact with the turnaround roll at the top of the upleg run. The sheet may be subjected to one or more post-treatments before being rewound into coil form, or sheared into cut lengths, at the exit end of the line.

Cold Lines. In cold processing, steel strip is cleaned, pickled, and fluxed in-line with no heating beyond that required to dry an aqueous flux solution on the sheet surface prior to entering the molten metal bath. Cold lines are also sometimes referred to as *flux* or *Cook-Norteman* lines. Because cold lines have limited heat-treating capability, incoming cold-rolled steel sheet requiring heat treatment will have been previously box annealed, or annealed on a separate continuous heat-treating line.

A typical cold line is shown schematically in Fig. 5. As with the hot line described above, this line is capable of producing 450,000 metric tons per year and coating sheet up to 1830 mm (72 in.) wide.

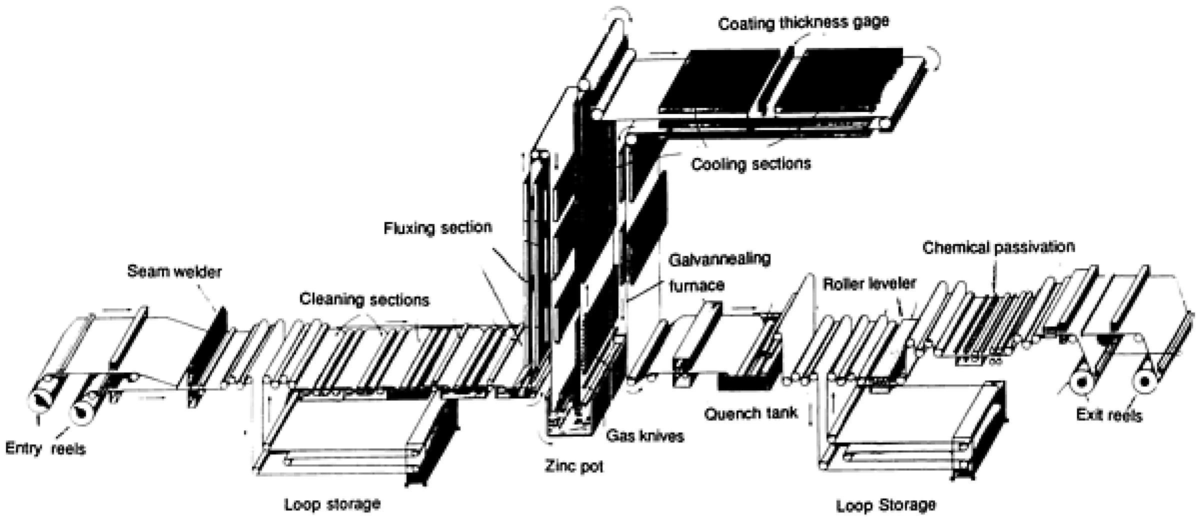

Fig. 5 Schematic diagram of a continuous galvanizing line. An example of a "cold" line without in-line annealing capability. See text for details.

Preparation of the sheet surface for coating includes alkaline and electrolytic cleaning, pickling in hydrochloric acid, and coating with flux, an aqueous solution of ammonium chloride and zinc chloride. After hot-air drying of the flux solution on the sheet surface, the strip enters the molten metal bath. Exhaust systems are essential to capture the fumes evolved when the fluxed sheet is submerged in the bath.

Because the sheet enters the bath at a relatively low temperature, considerable heat is transferred to the sheet by the bath. Consequently, cold lines generally have pots with a greater heating capacity in order to achieve the same throughput as an equivalent hot line. Downstream from the zinc pot, there is virtually no difference between hot and cold lines.

Post-Treatments. After the coating has been applied, several options are available for post-treatment of the strip. One possibility is galvannealing to produce zinc-iron alloy coatings, as discussed in the section "Zinc-Iron Alloy Coatings" in this article. Another is spangle minimizing, as described in the section "Zinc Coatings" in this article. Additional processing steps may be used to improve mechanical behavior, shape, corrosion resistance, and other properties as follows:

- Tension leveling or roller leveling to improve flatness
- Skin passing to make the surface smoother and to minimize yield-point behavior
- Overaging heat treatment to improve mechanical properties
- Slitting to narrower widths, shearing to produce cut lengths of sheet, and side trimming to remove nonuniform edges
- Chromate passivating to provide temporary protection against corrosion during shipment and storage. Passivation is done by spray or dip application of an acid chromate solution, removing excess solution by use of squeegee rolls, and drying the residue in hot air. Given the increasing environmental concerns about chromium, particularly in the hexavalent form, it is generally felt that other types of chemical passivation will eventually replace chromate.
- Oiling to provide lubricity during forming
- Oiling to provide temporary corrosion protection during shipment and storage. Inhibited oil is used in addition to chromate passivation to provide extra protection, or without chromate for applications in which chromate is inappropriate, such as those involving painting or contact with foodstuffs.
- Phosphating to improve formability
- Flash electroplating with iron to improve weldability

Some of these post-treatments are shown schematically in Fig. 2 and 5. Many could be done offline as separate operations, but in general they can be done more economically online as part of the continuous process, provided the necessary equipment is built into the line initially. Except in rare instances where unused space was deliberately left in a line, retrofit of the equipment for post-treating is problematic.

Zinc Coatings

Hot-dip-zinc-coated steel sheet, also called *galvanized*, is by far the most widely used coated sheet product. About 86% of the hot-dip-coated sheet produced in the United States (see Fig. 1) is zinc coated.

As evident in Table 1, hot dip zinc coatings for sheet are available in a broad range of coating thicknesses. For general-purpose galvanized sheet, 19 μm (0.75 mil) per side is the usual thickness. This corresponds to a two-side coating mass of 275 g/m^2 (0.9 oz/ft^2). Heavier coatings are used in applications requiring maximum corrosion resistance, such as highway drainage culverts. In the automotive industry, where formability and weldability are key considerations, lighter coatings such as 90 g/m^2 (0.3 oz/ft^2) are more typical.

Microstructure. The surface and cross section of a galvanized coating are shown in Fig. 6. Most of the coating is nearly pure zinc. Near to the steel-coating interface are prismatic particles of ζ-phase, a zinc-iron intermetallic compound containing about 6% Fe (see Fig. 7).

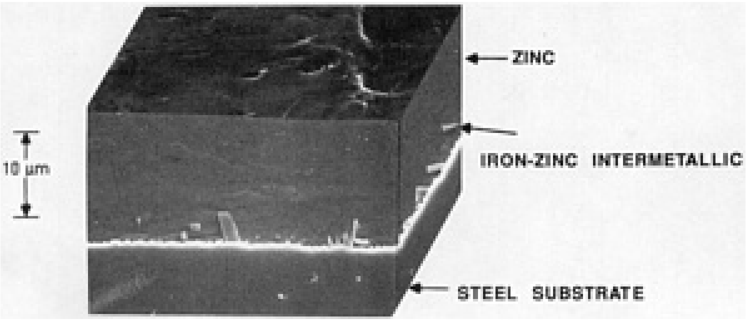

Fig. 6 Galvanized coating microstructure. Scanning electron microscope cross section

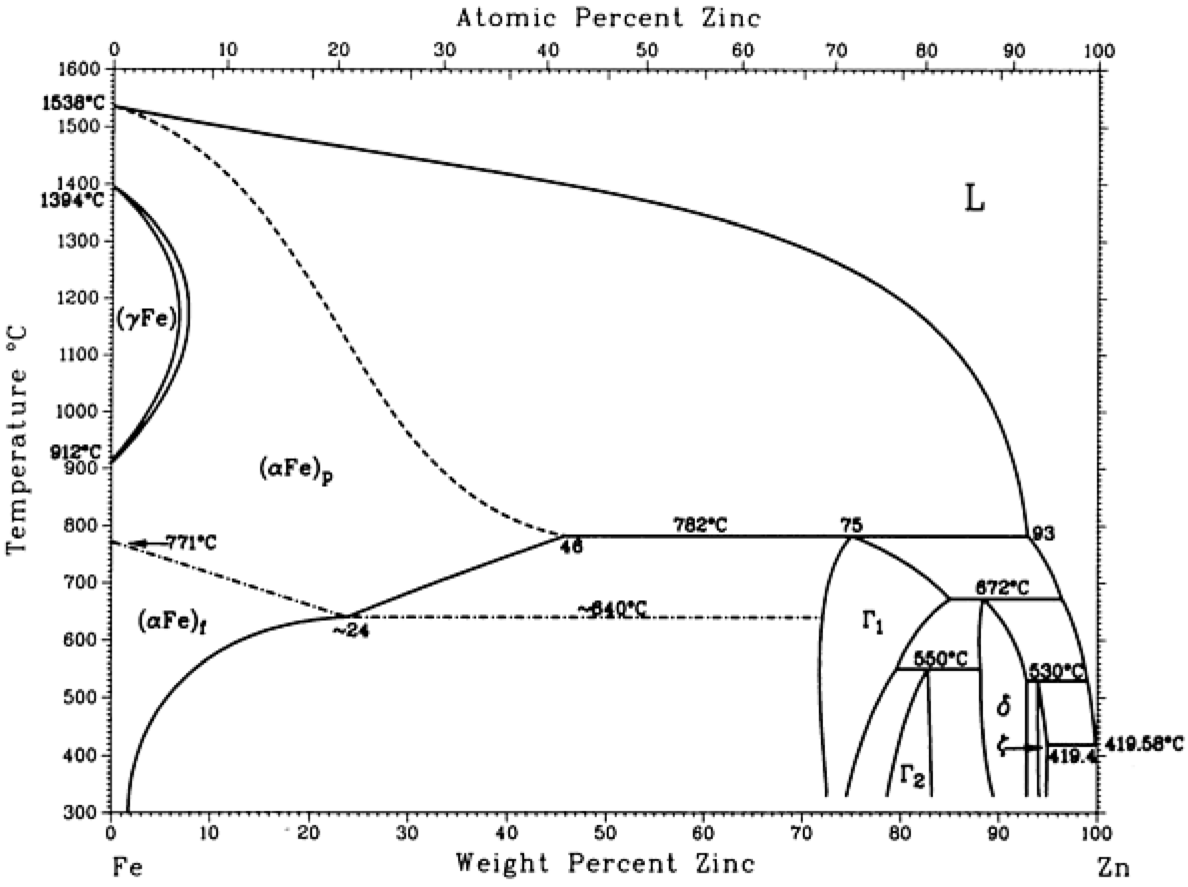

Fig. 7 Iron-zinc equilibrium phase diagram. Source: Ref 22

Alloy Additions. Aluminum, typically in the range of 0.1 to 0.2%, is added to the zinc bath in order to prevent formation of a thick, continuous layer of zinc-iron intermetallic that could lead to poor coating adhesion during forming. Aluminum reacts preferentially with the steel to form a thin layer of an iron-aluminum intermetallic that acts as a barrier and delays the growth of the zinc-iron intermetallic layer.

Lead was originally present in galvanized coatings as an impurity from the smelting process. The presence of lead causes the formation of spangles, the familiar dendritic surface pattern visible on galvanized ductwork and garbage cans. Historically, users relied on the spangled appearance to distinguish hot dip galvanized from less corrosion-resistant thin electroplated sheet. In order to maintain this distinction, it became common practice to add lead (typically about 0.1%) to keep the spangles, even after refining methods for producing lead-free zinc were developed. With increasing environmental concerns, however, the use of lead is declining. Antimony is now increasingly often used to produce spangled coatings without the environmental drawbacks of lead.

Spangles are also prone to spangle cracking, a phenomenon in which cracking occurs along certain crystallographic planes during forming of the coated sheet. For painted end uses, such as automobiles and metal buildings, a smoother, nonspangled surface is desirable for appearance purposes. When this is the case, lead or the other spangle-promoting elements can be omitted from the bath. When it is desirable to produce both spangled and nonspangled galvanized on the same line without having to change the composition of the zinc bath, an alternate approach is to spray the surface of the molten coating with steam, water, or fine zinc powder just after wiping. The spray increases the number of sites for spangle nucleation, which minimizes the spangle size so that the coating surface is smoother. Further increases in surface smoothness are achieved by a light temper roll of the coated product.

Corrosion Resistance. Zinc coatings protect steel in three ways:

- Initially, a continuous film of zinc at the surface of steel serves as a barrier to separate the steel from the environment.

- At voids in the coating, such as scratches and cut edges, the zinc behaves as a sacrificial anode to provide galvanic protection.
- After anodic dissolution of the zinc metal, zinc hydroxide can precipitate at the cathodic areas of exposed steel, thus forming a secondary barrier.

In order for a coating metal to serve as an effective corrosion barrier, it should corrode at a slower rate than the steel substrate. As shown in Table 5, the corrosion rate of zinc varies greatly, depending on the location of the exposure (Ref 17). Time of wetness and chloride and sulfate level are among the environmental factors that affect the corrosion rate of zinc. Nevertheless, zinc is generally one to two orders of magnitude more corrosion resistant than steel in a wide range of outdoor environments.

Table 5 Corrosion of zinc and steel at 45 locations (10 × 15 cm test specimens)

Location	**2-year exposure, grams lost**	
	Zinc	**Steel**
Norman Wells, N.W.T., Canada	0.07	0.73
Phoenix, AZ	0.13	2.23
Saskatoon, Sask., Canada	0.13	2.77
Esquimalt, Vancouver Island, Canada	0.21	6.50
Fort Amidor Pier, Panama, Canal Zone (C.Z.)	0.28	7.10
Melbourne, Australia	0.34	12.70
Ottawa, Ontario, Canada	0.49	9.60
Miraflores, Panama, C.Z.	0.50	20.9
Cape Kennedy, 0.8 km (0.5 mile) from ocean	0.50	42.0
State College, PA	0.51	11.17
Morenci, MI	0.53	7.03
Middletown, OH	0.54	14.00
Potter County, PA	0.55	10.00

Bethlehem, PA	0.57	18.3
Detroit, MI	0.58	7.03
Manila, Philippine Islands	0.66	26.2
Point Reyes, CA	0.67	244.0
Trail, B.C., Canada	0.70	16.90
Durham, NH	0.70	13.30
Halifax (York Redoubt), N.S.	0.70	12.97
South Bend, PA	0.78	16.20
East Chicago, IN	0.79	41.1
Brazos River, TX	0.81	45.4
Monroeville, PA	0.84	23.8
Daytona Beach, FL	0.88	144.0
Kure Beach, NC, 240 m (800 ft) lot	0.89	71.0
Columbus, OH	0.95	16.00
Montreal, Quebec, Canada	1.05	11.44
London (Battersea), Eng.	1.07	23.0
Pittsburgh, PA	1.14	14.90
Waterbury, CT	1.12	11.00
Limon Bay, Panama, C.Z.	1.17	30.3
Cleveland, OH	1.21	19.0
Dungeness, Eng.	1.60	238.0

Newark, NJ	1.63	24.7
Cape Kennedy, 55 m (60 yd) from ocean, 9 m (30 ft) elevation	1.77	80.2
Cape Kennedy, 55 m (60 yd) from ocean, ground level	1.83	215.0
Cape Kennedy, 55 m (60 yd) from ocean, 18 m (60 ft) elevation	1.94	64.0
Bayonne, NJ	2.11	37.7
Pilsey Island, Eng.	2.50	50.0
Kure Beach, NC, 25 m (80 ft) lot	2.80	260.0
London (Stratford), Eng.	3.06	54.3
Halifax (Federal Building), N.S.	3.27	55.3
Widness, Eng.	4.48	174.0
Galeta Point Beach, Panama, C.Z.	6.80	336.0

Source: Ref 17

The corrosion loss of a hot dip zinc coating is generally considered to be linear. Because of this, the life of a zinc coating is proportional to its thickness. In the industrial environment of Bethlehem, PA (see Fig. 8), the corrosion loss is approximately linear with time at an average rate of about 2 μm/year (Ref 18). Near-linear behavior is also observed in marine and rural environments.

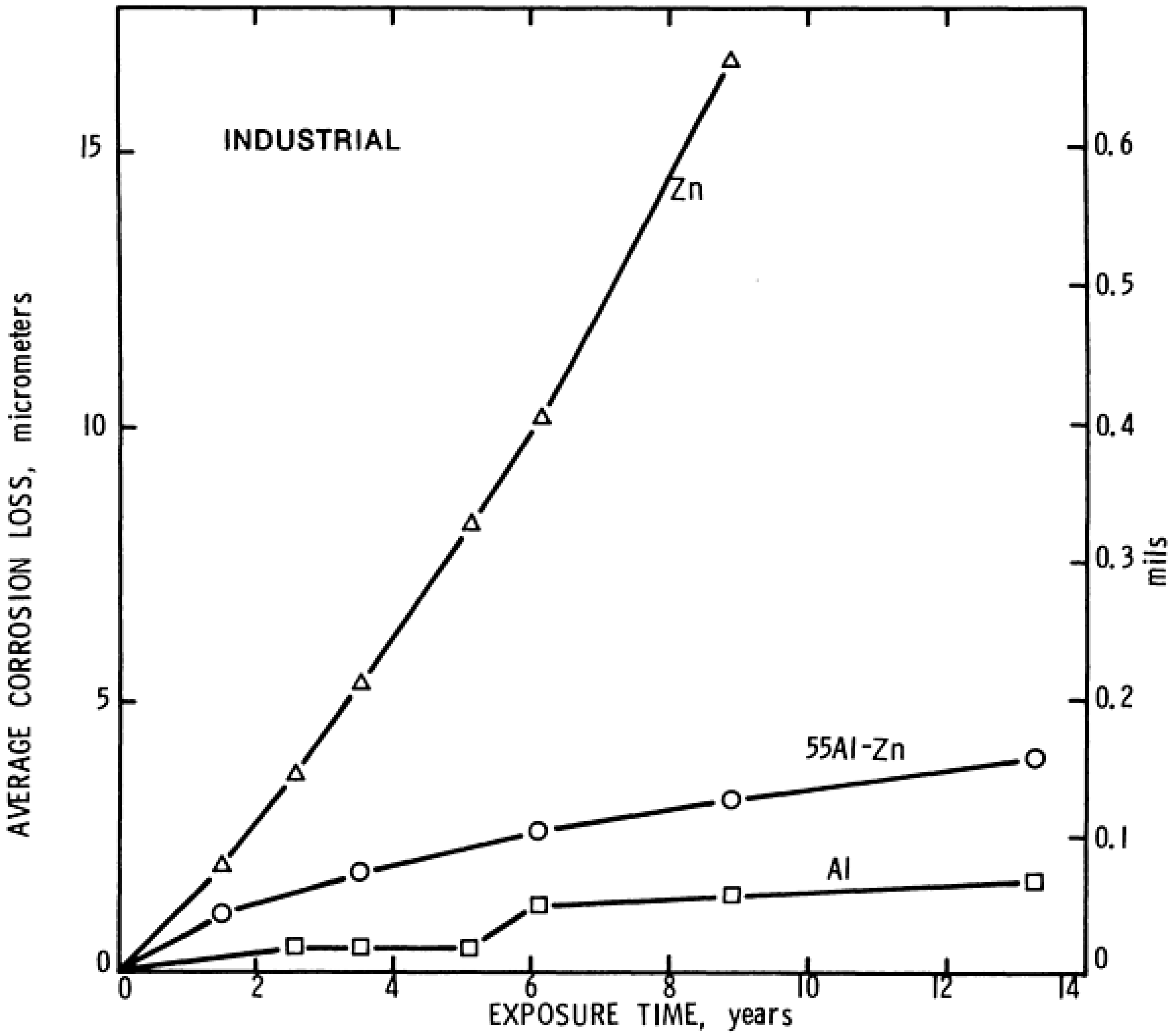

Fig. 8 Corrosion losses of hot dip coatings in the industrial environment of Bethlehem, PA. Source: Ref 18

The sacrificial properties of zinc coatings derive from the position of zinc relative to steel in the galvanic series. The corrosion potential of zinc is usually about 0.4 V less noble than steel in most environments at normal ambient temperatures. Thus, zinc will sacrifice itself to provide galvanic protection to steel exposed at voids in the coating. The effective distance of the sacrificial protection increases with the conductivity of the environment, but it is generally limited to a few millimeters in most atmospheres.

Other Properties. Zinc coatings provide some protection to steel against high-temperature oxidation. However, their usefulness for this purpose is limited to a maximum temperature of about 260 °C (500 °F) because of the tendency of zinc at higher temperatures and long exposure times to diffuse into the grain boundaries of the steel and cause embrittlement.

Zinc coatings may impair the formability of steel sheet under certain conditions. For example, in stretch-forming operations, the increased frictional coefficient of the zinc coating against the punch tends to concentrate the strain within a smaller area and thus result in less total stretch before fracture. Galling and coating pickoff can also occur in severe forming operations. The buildup of particulate material on die surfaces may cause impressions and poor appearance on the surface of formed parts.

The life of spot welding electrodes is reduced by zinc coatings, as shown in Table 6. This reduction occurs as a result of alloying of the copper electrode with zinc, which leads to higher local resistance, greater heating, and increased pitting and erosion of the electrode contact surface. Lower tip life reduces productivity and increases manufacturing costs because of more frequent interruptions to the welding operation to redress tips.

Table 6 Effects of hot dip coatings on tip life during spot welding of steel sheet

Type of coating	Coating mass, g/m^2	Electrode tip life, number of spots
None	. . .	>10,000
Zinc	197	2,500
Zinc-iron	110	6,000
Zn-55Al	150	700
Aluminum type 1	120	500

Source: Ref 15, 19

Galvanized sheet is used in both bare and painted conditions. In order for paint to have good adhesion to a hot-dip-zinc-coated surface, it is important that the surface is properly pretreated. Zinc phosphate or complex oxide pretreatments are the usual pretreatments for coil-line prepainted sheet. For galvanized components that are painted after fabrication, such as automobile body components, zinc phosphate or zinc phosphates modified with nickel or manganese are commonly used.

In the automotive industry, resistance to electrophoretic paint (e-coat) cratering is an important property. After phosphating, most automobile bodies produced today are primed with cathodic e-coat. In the e-coating process, the phosphated automobile body is immersed in an aqueous bath containing suspended, positively charged paint particles. A negative potential of several hundred volts is applied to the part, and the positively charged paint particles are attracted to the metal surface. Here the paint particles contact hydroxyl ions produced by the cathodic breakdown of water and coalesce to form a paint film. At higher voltages, the dielectric properties of the deposited paint film may be exceeded, with the result that sparking occurs. The heat generated by the sparks causes localized film disruption and premature curing of the paint. After overall curing of the paint, the sparked areas form pinpoint-size craters that are detrimental to the appearance of the painted surface.

Resistance to e-coat cratering can be expressed in terms of a threshold voltage below which cratering does not occur. As shown in Table 7, zinc-coated surfaces have a lower cratering threshold voltage than bare steel and hence are more prone to cratering (Ref 20). Although cratering can be avoided by reducing the voltage applied during e-coating to a level below the threshold, this may result in less productivity due to lower rates of coating deposition and slower line speeds.

Table 7 Effects of hot dip coatings on threshold voltages for cratering of cathodic electrophoretic primer

Type of surface	Cratering threshold, V
Uncoated bare steel	>400
Zinc	275
Zinc-iron	225
Zn-55Al	375

Aluminum	>400

Additional information about galvanized coatings is available in the article "Batch Hot Dip Galvanized Coatings" in this Volume.

References cited in this section

15. H.E. Townsend and L. Allegra, Precoated Sheet Steel for Automotive Applications, *Automotive Corrosion by Deicing Salts,* R. Baboian, Ed., National Association of Corrosion Engineers, 1981, p 337-351
17. D.C.H. Nevinson, Corrosion of Zinc, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed. *Metals Handbook*), ASM International, 1987, p 758
18. H.E. Townsend and J.C. Zoccola, *Materials Performance,* Vol 10, 1979, p 13-20
19. P. Howe and S.C. Kelley, "A Comparison of the Resistance Spot Weldability of Bare, Hot-Dipped, Galvannealed, and Electrogalvanized DQSK Sheet Steels," Paper 880280, Society of Automotive Engineers, 1988
20. R.G. Hart and H.E. Townsend, "Mechanism of Cathodic Electrocoat Primer Cratering," Paper 831818, *Proceedings of the Second Automotive Corrosion and Prevention Conference, P-136,* Society of Automotive Engineers, 1983
22. H. Baker, Ed., *Alloy Phase Diagrams,* Vol 3, *ASM Handbook,* ASM International, 1992, p 2·56, 2·206

Zinc-Iron Alloy Coatings

Also known as *galvanneal,* zinc-iron alloy coatings produced by the thermal diffusion and alloying of a galvanized coating with a steel substrate were developed during the 1970s, primarily for painted applications. Today, galvanneal is used increasingly often by the automobile industry because of its improved paintability and spot weldability (see Table 6) relative to a pure hot dip zinc coating of equal thickness. The iron content of the alloyed coating is usually in the range of 9 to 12%. For automotive body panels, the typical coating thickness for galvanneal is 7 μm (0.275 mil) with a coating mass of 50 g/m^2 (0.16 oz/ft^2).

In galvannealing, galvanized sheet is heated in-line just after coating and wiping in order to allow interdiffusion of iron from the substrate with zinc from the coating to form an iron-zinc alloy coating. Both gas-fired and induction furnaces are used for galvannealing. Heating to temperatures in the range of 500 to 550 °C (930 to 1020 °F) for about 10 s is sufficient to produce a 50 g/m^2 (0.16 oz/ft^2) coating with an iron content of about 10%.

Actual alloying time is influenced by coating thickness and the compositions of both zinc bath and steel substrate (Ref 21). More time is required to alloy a thicker coating. Alloying time also increases with increasing aluminum content of the bath, but it decreases for ultra-low-carbon, titanium- or titanium-niobium-stabilized steels as compared to ordinary low-carbon grades.

The galvannealing process is usually controlled by the "cook and look" method, in which the operator sets the initial galvannealing furnace conditions based on prior experience for the particular combination of steel thickness, line speed, bath composition, coating thickness, and steel composition. The operator then looks at the surface of the sheet as it exits the galvanneal furnace and adjusts the heat input to the furnace temperature until the sheet surface changes from the bright and shiny appearance of a pure zinc coating to the dull gray of an alloyed coating, except at the very edges of the strip where the coatings tend to be slightly thicker and take longer to alloy. Once this condition is attained, edge heaters can be employed in order to complete the alloying of the strip edges. The operator is also assisted in controlling the galvannealing process by information on the iron content of the coating provided by on-line x-ray fluorescence gages. Ideally, it would be desirable to have a fully automated galvanneal process based on actual measurement and control of strip temperature. However, this has been an elusive goal because of the difficulties inherent in temperature measurement by use of radiation pyrometry when surface emissivity changes as alloying proceeds.

The corrosion resistance of galvanneal is similar to that of a pure zinc coating. However, because of the iron in the coating, the galvanic potential is not as great as that of pure zinc. Also, the corrosion products are reddish brown. As a result, protection against rust stain at edges and scratches is not as good as with pure zinc.

Compared to ordinary galvanized metal, galvanneal is generally easier to paint without the use of special pretreatments. This is believed to result at least in part from the microscopically rougher surfaces of galvanneal (as seen when Fig. 6 is compared to Fig. 9 and 10). However, galvanneal coatings are more prone to cratering during e-coating, as shown in Table 7.

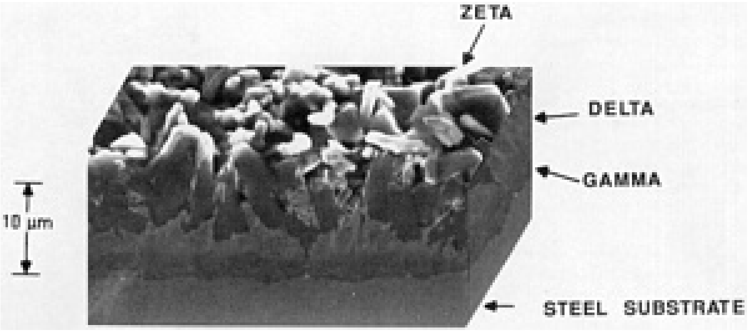

Fig. 9 Galvanneal coating microstructure composed of zeta, delta, and gamma phases. Scanning electron microscope cross section

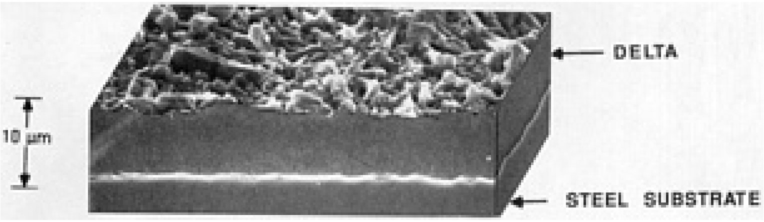

Fig. 10 Galvanneal coating microstructure composed of mostly delta phase. Scanning electron microscope cross section

Microstructure. As shown on the iron-zinc phase diagram, Fig. 7, a number of intermetallic compounds are possible in a galvanneal coating. In Fig. 9, a galvanneal coating composed of several phases is shown. The ζ-phase at the outer surface has a monoclinic crystal structure and contains about 6% Fe. It is believed that the ζ-phase has a relatively high friction coefficient and is thus undesirable for some forming and stamping operations. The intermediate δ-layer has a hexagonal close-packed structure and contains iron in the range of 8 to 12%. Next to the steel is a layer labeled simply Γ. In a galvanneal coating containing a mixture of these phases, it is difficult to distinguish between Γ_1 and Γ_2, both of which are cubic phases with iron contents in the range of roughly 16 to 28%. Thus, the Γ-layer shown in Fig. 9 could be Γ_1, Γ_2, or a mixture of the two.

The cubic Γ-phases have a large number of atoms per unit cell and limited ductility. Their presence is more likely with thicker coatings and higher iron contents. They also lead to powdering of the coating during forming. Powdering is undesirable because it results in a loss of coating and can lead to the buildup of coating debris on die surfaces, which in turn causes print-through and poor appearance on the surfaces of formed parts.

Because of the problems noted above with the zeta and gamma phases, galvanneal process conditions are ideally aimed at producing coatings composed of mostly δ-phase (see Fig. 10). However, as the thickness of the coating increases above about 9 μm, it becomes more difficult to make an all-δ coating.

Reference cited in this section

21. V. Jagannathan, The Influence of Coating Characteristics on Powdering and Corrosion Resistance of Galvanneal Coated Steel Sheet, *Proceedings of the Second International Conference on Zinc and Zinc Alloy Coated Steel Sheet,* Verlag Stahleisen, 1992, p 127-131

Aluminum Coating, Type 2

Two kinds of aluminum coating are produced. Type 2 is a thicker coating (typically 30 to 50 μm) that is applied by dipping in an unalloyed aluminum bath. This product is used for outdoor construction applications such as roofing, culverts, and silos that require resistance to atmospheric corrosion and have limited formability requirements.

As shown in Fig. 11, the microstructure of a Type 2 coating consists of an aluminum overlay and a thick iron-aluminum intermetallic layer. The formability and adhesion of the coating are limited by the poor ductility of this intermetallic layer.

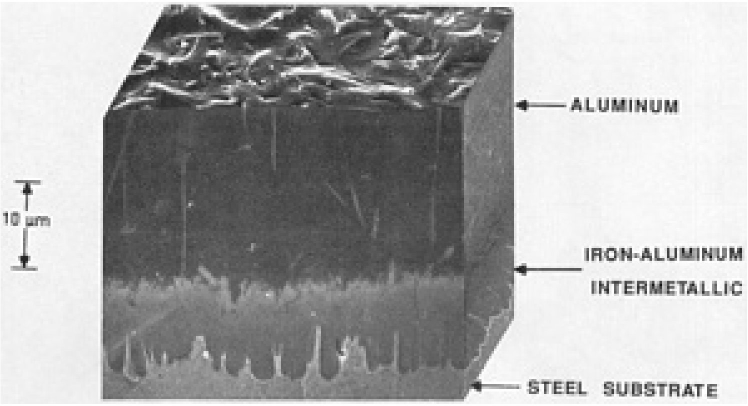

Fig. 11 Type 2 aluminum coating microstructure. Scanning electron microscope cross section

The outdoor durability of the Type 2 aluminum coating is excellent in most atmospheres because of the good barrier properties of the thick coating and its relatively low corrosion rate, as given in Fig. 8. However, except in severe salt environments, the aluminum coating does not provide sacrificial protection to steel. As a result, Type 2 tends to show rusting at cut edges and rust staining of adjacent surfaces in rural and industrial environments. In marine environments, the aluminum coating is susceptible to crevice corrosion.

Aluminum Coating, Type 1 (Aluminum-Silicon Alloy)

Type 1 aluminum coating is a thinner, aluminum-silicon alloy coating intended primarily for applications requiring formability and resistance to high temperatures, such as automobile exhaust components. Type 1 aluminum coatings are also applied to improve appearance. For most uses, the usual thickness of a Type 1 coating (Class 40) is about 20 to 25 μm (0.8 to 1 mil). When maximum formability is a critical requirement, a thinner 12 μm (Class 25) coating is specified.

Silicon is present in a Type 1 coating in the range of 5 to 11% in order to prevent formation of a thick iron-aluminum intermetallic layer, which would impair coating adherence and formability. Instead, a thinner iron-aluminum-silicon alloy layer is formed (Fig. 12).

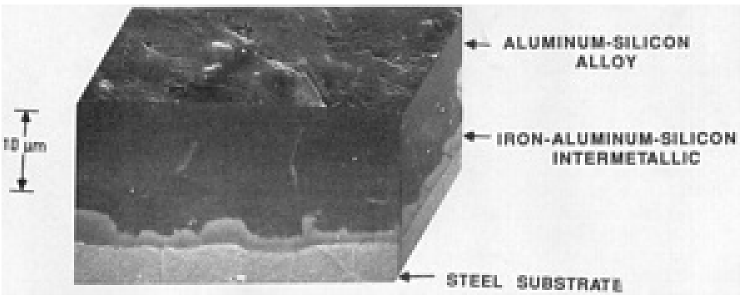

Fig. 12 Type 1 aluminum coating microstructure. Scanning electron microscope cross section

Aluminum has a more detrimental effect than zinc on the spot weldability of steel sheet. Accordingly, aluminum Type 1 and Zn-55Al alloy coatings show the lowest tip lives among the hot-dip-coated products listed in Table 6.

Zn-5Al Alloy Coatings

According to the aluminum-zinc equilibrium phase diagram (Fig. 13), a low-melting eutectic alloy occurs at 5% Al. Steel sheet coated with alloy coatings near to this composition (i.e., 4 and 7% Al) are more corrosion resistant than an equal-thickness galvanized coating when tested in accelerated laboratory tests or in severe marine atmospheres. However, the same alloy coatings perform no better than pure zinc in moderate marine, industrial, and rural environments, as shown in Table 8.

Table 8 Lifetimes of hot dip zinc and zinc-alloy coatings

Environment	**Years to first rust**			
	Zn	**Zn-4Al**	**Zn-7Al**	**Zn-55Al**
Severe marine				
25 m from ocean, Kure Beach, NC	4	9	9	15
Moderate marine				
250 m from ocean, Kure Beach, NC	16	15	14	>25
Rural				
Saylorsburg, PA	14	14	14	>25
Industrial				
Bethlehem, PA	10	10	9	>25

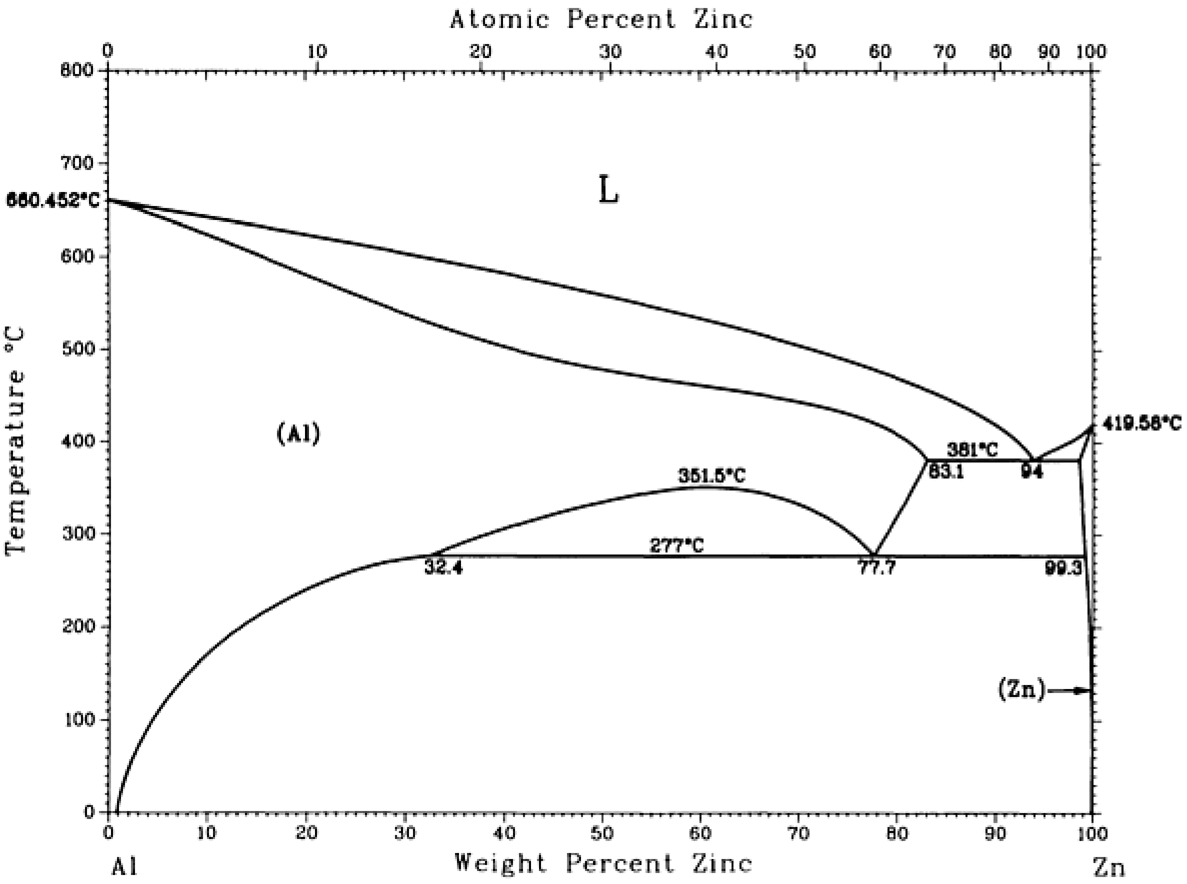

Fig. 13 Aluminum-zinc equilibrium phase diagram. Source: Ref 22

Commercially produced Zn-5Al alloy coatings have small additions of other elements. Galfan contains about 0.1% of mischmetal rare earths (cerium and lanthanum), which are added to increase the wettability of the bath and reduce the incidence of bare spots in the coating (Ref 25). Superzinc contains 0.1% Mg, which is added to counteract the adverse effects of lead and tin impurities on intergranular corrosion and paint adhesion (Ref 26).

The eutectic coatings generally have no added lead and no spangle. As a result, they are free of spangle cracking, and the coatings have better resistance to cracking during forming than does ordinary spangled galvanized.

The microstructure of a typical Zn-5Al alloy coating is characterized by a matrix of 5% Al eutectic and scattered regions of primary zinc (Fig. 14). No intermetallic layer is visible on steel sheet coated with the eutectic alloy because bath temperature is lower, and aluminum content is higher, than with ordinary galvanized.

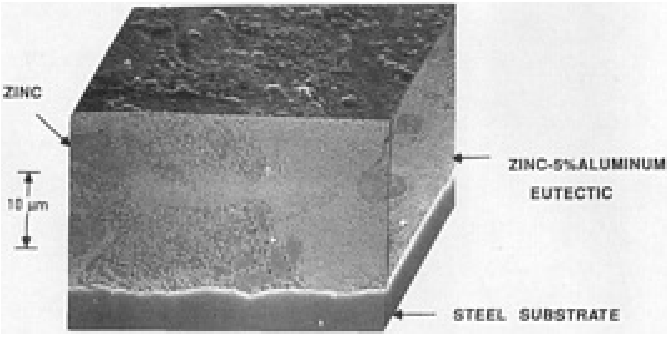

Fig. 14 Zn-5Al coating microstructure. Scanning electron microscope cross section

References cited in this section

22. H. Baker, Ed., *Alloy Phase Diagrams,* Vol 3, *ASM Handbook,* ASM International, 1992, p 2·56, 2·206
23. J.J. Friel and H.E. Townsend, Corrosion Resistance of Zinc and Zinc-Aluminum Alloy Coatings, *Sheet Metal Industries,* Vol 60 (No. 9), 1983, p 506-507
24. H.E. Townsend, Twenty-Five-Year Corrosion Tests of 55% Al-Zn Alloy Coated Steel Sheet, *Materials Performance,* Vol 32 (No. 4), 1993, p 68-71
25. J. Pelerin, B. Bramaud, J.F. Nouville, D. Coutsouradis, D.C. Herrschaft, and S.F. Radtke, Galfan: A New Zinc-Aluminum Coating, *Proceedings of the 13th International Galvanizing Conference,* Zinc Development Association, London, 1982, p 48/1-49/9
26. T. Kano and S. Higuchi, "Development and Properties of Zinc-Aluminum Alloy Coated Steel Sheet with High Corrosion Resistance (Superzinc)," Nippon Steel Technical Report 25, Nippon Steel Corp., April 1986, p 29-37

Zn-55Al Alloy Coatings

The purpose of Zn-55Al alloy coatings is to combine the excellent long-term atmospheric corrosion resistance of aluminum with the sacrificial characteristics of galvanized in a single coating (Ref 23, 24). Long-term studies showed that the 55% Al alloy was the optimum composition of the aluminum-zinc system. Steel sheet coated with this alloy was first produced commercially in 1972 in the United States under the trademark Galvalume. Coating thicknesses are usually in the range of 20 to 25 μm (0.8 to 1 mil).

About 80 vol% of the complex microstructure of the Zn-55Al alloy coating (Fig. 15) is composed of cored, aluminum-rich dendrites, representing the first solid to form during cooling. As predicted by the phase diagram (Ref 22) (Fig. 13), the final liquid to freeze in the interdendritic regions is enriched in zinc. A thin (1 to 2 μm) iron-aluminum-zinc intermetallic layer is evident at the steel surface.

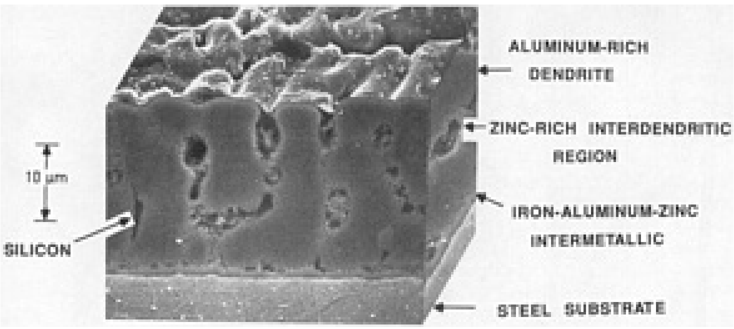

Fig. 15 Zn-55Al coating microstructure. Scanning electron microscope cross section

About 1.5% Si is added to the Zn-55Al bath for the purpose of minimizing alloy-layer growth during dipping. It is present in the form of scattered, needlelike particles, mostly in the interdendritic region. Some of the silicon is also concentrated in a thin layer at the overlay/alloy-layer interface, where it functions as a barrier to alloy-layer growth during the coating process.

Atmospheric corrosion resistance of the Zn-55Al alloy coating is generally at least two to four times that of an equal thickness of galvanized coating, as evident in Fig. 8 and Table 8. Most of the corrosion of the alloy coating takes place in the zinc-rich interdendritic regions. This enables the coating to exhibit the sacrificial characteristics of a galvanized coating. As the zinc-rich interdendritic regions of the coating corrode, zinc corrosion products are trapped in the interdendritic interstices and act as a barrier that slows further corrosion. As a result, the corrosion rate of the alloy coating decreases with time, as shown in Fig. 8.

Although the effective distance of the galvanic action provided by a Zn-55Al coating is roughly half that of galvanized, it is generally adequate to protect the cut edges of steel sheet with a thickness of one millimeter or less in most environments. Moreover, because of the greater durability of the 55% aluminum-zinc coating, it provides galvanic protection for a longer duration.

As shown in Fig. 8, the corrosion rate of the 55% Al alloy is greater than that of an aluminum coating. However, unlike an aluminum coating, the 55% Al alloy is able to prevent rust staining at cut edges and scratches, as well as resist crevice corrosion in marine environments.

As shown in Table 6, the spot welding tip life of the 55% Al coated sheet is less than that of galvanized. This reduction is attributed to the adverse effect of aluminum.

References cited in this section

22. H. Baker, Ed., *Alloy Phase Diagrams,* Vol 3, *ASM Handbook,* ASM International, 1992, p 2·56, 2·206
23. J.J. Friel and H.E. Townsend, Corrosion Resistance of Zinc and Zinc-Aluminum Alloy Coatings, *Sheet Metal Industries,* Vol 60 (No. 9), 1983, p 506-507
24. H.E. Townsend, Twenty-Five-Year Corrosion Tests of 55% Al-Zn Alloy Coated Steel Sheet, *Materials Performance,* Vol 32 (No. 4), 1993, p 68-71

Lead-Tin Alloy Coatings

Lead-tin alloy coatings are widely known as *terne* coatings, from the French word that describes their characteristically dull surface appearance. Generally, 3 to 15% Sn is added to the hot dip bath in order to facilitate wetting of the steel substrate. The solid solubility of tin in lead is very small, and it appears as patches in the lead overlay matrix (Fig. 16).

Fig. 16 Terne coating microstructure. Scanning electron microscope cross section

Terne-coated steel sheet has a long history of use in automotive fuel tanks and tubing because of its excellent weldability, solderability, and formability. Moreover, the low corrosion rate of terne allows it to function primarily as a barrier coating without the evolution of voluminous corrosion products that might otherwise clog fuel and hydraulic systems. Nickel terne is produced by applying the usual terne coating to steel sheet that has first been electroplated with a thin (1 g/m^2) nickel layer in order to improve the barrier properties.

Owing to concerns about the effects of lead in the environment, the future of terne is uncertain. Work is now under way to find suitable replacement materials. Zinc-alloy coatings (possibly hot dip zinc-iron or electroplated zinc-nickel) with an organic topcoat are among the most likely candidates.

Continuous Electrodeposited Coatings for Steel Strip

Stavros G. Fountoulakis, Bethlehem Steel Corporation

Introduction

CONTINUOUS ELECTRODEPOSITION involves electroplating a pure metal or alloy coating onto an endless steel strip. In practice, this is achieved by unwinding a coil of strip; welding it to the tail end of the preceding coil; passing it through the sequence of surface preparation, electroplating, and surface post-treatment; rewinding it; and then again cutting it from the preceding coil. The facilities used for this process are commonly called *continuous plating lines* and can handle strip of up to about 2080 mm (82 in.) in width. Strip is arbitrarily defined as having a rectangular cross section with a maximum thickness of 5 mm (0.2 in.) and width greater than 25 mm (1 in.) (Ref 1).

The greatest percentage of the steel processed in continuous steel strip plating lines is electrodeposited with one of five metallic coatings: zinc, tin, chromium, and alloys of zinc with either nickel or iron. Several other metallic coatings, such as copper, nickel, brass (Cu-Zn), and terne (Pb-Sn), are also applied by continuous steel strip plating but on a relatively smaller scale and production volume. Continuous strip plating of precious metals for electronics applications is also a related process. However, this too differs markedly from steel strip plating in both facility design and scale.

In 1991, the total capacity of continuous steel strip plating lines worldwide exceeded 34 million tons. It is very likely that more tonnage of steel and also more surface area is coated by this process than in all other batch-type plating processes combined (Tables 1, 2).

Table 1 Worldwide capacity for electrolytic tin- and chromium-coated steel for canstock by region, 1991

Region	Total capacity, tons/yr	ETLs	Number of continuous plating lines		
			ECPLs	Dual	Total
Western Europe	6,900,000	27	2	10	39
North America	6,665,000	16	6	7	29
Japan	3,288,000	13	9	. . .	22
Latin America	1,997,000	14	1	3	18
S.E Asia	1,220,000	9	. . .	1	10
Eastern Europe	1,510,000	5	1	. . .	4
South Korea	680,000	1	. . .	4	5
South Africa	550,000	1	1	1	3
Australia	500,000	2	. . .	. . .	2
Taiwan	250,000	3	. . .	. . .	3
China	160,000	2	. . .	. . .	2

Total	**22,720,000**	**90**	**19**	**25**	**134**

Source: Ref 4

(a) ETLs, electrotinning lines; ECPLs, electrolytic chromium plating lines,

Table 2 Worldwide capacity for electrolytic zinc and alloy (Zn-Ni, Zn-Fe) coated steel strip for primarily automotive body panels, 1991

The list does not include some medium and small strip plating lines that plate narrow steel strip for appliances, furniture, and other nonautomotive applications.

Region	**Total capacity, tons/yr**	**Number of plating lines**		
		Zn only	**Zn and Zn alloy**	**Total**
North America	3,500,000(a)	4	5	9
Japan	4,320,000(b)	1	10	11
Europe	2,480,000(c)	8	6	14
Korea	700,000	. . .	2	2
Taiwan	200,000	. . .	1	1
Latin America	250,000	1	1	1
Total	**11,450,000**	**13**	**25**	**38**

(a) See Table 4.

(b) See Table 6.

(c) See Table 5.

This article begins by describing some of the applications of continuous electroplated steel, to explain why there is a need for such a high production volume. For each category of applications, the type of coating needed and the key attributes of the coating are noted. The bulk of the article describes electrodeposition technology, including plating line components and process classification.

Acknowledgements

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References

1. L.W. Austin and J.L. Lindsay, "Continuous Steel Strip Electroplating," slide course, American Electroplaters and Surface Finishers Society, 1989
4. E. Mayo, World Tin Mill Production, *The Canmaker,* Dec 1992
7. G.W. Bush, Development in the Continuous Galvanizing of Steel, *Journal of Metals,* Aug 1989
8. B. Meuthen, Aspects of Zinc and Zinc Alloy-Coated Sheet Steel in Western Europe--with a Special View of the German Scene, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 91-100
9. S.G. Denner, An Overview of the Manufacture and Application of Zinc and Zinc Alloy Coated Sheet Steel in North America, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 101-110
10. T. Hada, Present and Future Trends of Coated Steel for Automotive Use, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 111-119

Applications

There are many applications for continuously electrodeposited steel strip (Table 3). Most of these fall within four of the largest markets in today's economy: food containers and other general packaging, automobiles, appliances, and furniture. The first two markets account for most of the total volume of production.

Table 3 Typical applications for continuous electrodeposited coatings for steel strip

Coating	**Applications**
Zinc	Auto body outer panels and some structural components
Zn-Ni (10-14 wt% Ni) alloy	Auto body outer and inner panels and some structural components
Zn-Fe (10-20 wt% Fe) alloy with or without a flash of Zn-Fe (>80% Fe)	Auto body outer panels and some inner panels
Zn-Ni with thin, weldable organic coating	Auto body outer and inner panels
Zn or Zn-Ni with various post-treatments (chromate, phosphate, organic)	Doors, housings, appliances
Tin (matte)	Two-piece drawn and ironed cans, automotive oil and air filters, baking trays
Tin (reflowed)	Three-piece welded cans with and without enameling, battery cases, lighting fixtures,

Chromium plus chromium oxide	Draw-redraw cans, can ends, crowns, signs, housings, parts in appliances, etc.

Packaging and containers include the main sector, food and beverage cans (Fig. 1), as well as general-purpose containers ranging from photographic film canisters to paint and solvent cans. The steel for these containers is electrodeposited with either tin or chromium, depending on the end use and the surface lubricity requirements of the manufacturing process (Ref 2, 3, 4, 5).

Fig. 1 Examples of containers made from continuous electrodeposited strip steel

Electrolytic tin-plated strip, commonly called *tinplate*, is used for applications requiring severe forming, with the tin coating serving as a lubricant. The tin coating also protects steel against corrosion and protects certain foods from discoloration. It can also prevent food oxidation, because tin is a strong reducing agent in certain environments (Ref 6).

Electrolytic chromium-coated steel, more commonly called *tin-free steel*, was developed in the late 1960s as a lower-cost alternative to tinplate. The extremely thin coating, composed of layers of metallic and nonmetallic chromium, is both a barrier coating against corrosion and an adherence enhancer for subsequent lacquering. However, it supplies no lubricity in forming operations or for food preservation. It is used mainly for draw-redraw containers and can ends, both of which are usually manufactured after a lacquer coating is applied.

Automobiles. Continuously electrodeposited steel strip is used in the manufacturing of automobiles (Ref 7, 8, 9, 10), almost exclusively for body panels but also for components such as oil filter shells and fuel tanks. Body panels are primarily made from zinc-plated strip, referred to as *electrogalvanized sheet*, but also from steel sheet plated with zinc alloys (Zn-Ni or Zn-Fe).

From 1986 to 1991, in the United States as well as throughout Europe and Asia, there was a tremendous increase in electroplating capacity and in the production of electrogalvanized sheet (Tables 4, 5, 6). This occurred because of the need to make outer body panels more resistant to corrosion in hot, humid, and marine environments and in regions where there is frequent use of deicing salt. Electrogalvanized steel was selected by most automakers for its superior surface quality vis-à-vis that of the hot-dipped galvanized products available at the time. The zinc coating generally follows the texture of steel and has no significant effect on surface roughness or paint appearance. Zinc was also chosen because of its galvanic or sacrificial protection of steel in areas where paint, which simply provides barrier protection for the steel, is scratched or otherwise damaged.

Table 4 Major U.S. electrogalvanizing lines and their capabilities

Plating line location	**Nominal capacity[(a)], tons/y**	**Plating cells**		**Total amperage kA**	**Coatings**	**Start-up**
		No.	**Type**			
Middletown, OH	250,000	16	Gravitel	736	Zn	1986
	280,000	21	Gravitel	1,056	Zn, Zn-Ni	1991
Dearborn, MI	700,000	42	CAROSEL	2,352	Zn, Zn-Fe	1986
Cleveland, OH	400,000	20	Vertical	1,320	Zn	1986
Columbus, OH	300,000	15	Vertical	990	Zn, Zn-Ni, Zn-Ni + organic	1991
Ecorse, MI	400,000	20	Vertical	1,000	Zn	1985
Gary, IN	400,000	18	CAROSEL	900	Zn	1977
Walbridge, OH	400,000	20	Gravitel	1,000	Zn, Zn-Ni, Zn-Ni + organic	1986
New Carlisle, IN	400,000	24	Gravitel	1,200	Zn, Zn-Ni	1991
Total	**3,530,000**					

Source: Updated from Ref 7

(a) Nominal capacity figures represent rough estimates made by the author from miscellaneous data.

Table 5 Major European electrogalvanizing lines started since 1980

Plating line location	**Nominal capacity, tons/yr**	**Plating cells**		**Total amperage, kA**	**Coatings**	**Width**		**Start-up**
		No.	**Type**			**mm**	**in.**	
Linz, Austria	200,000	12	Gravitel	360	Zn, Zn-Ni	1600	63	1985
Ste. Agathe, France	300,000	16	CAROSEL	928	Zn, Zn-Ni	1830	72	1983
Beautor, France	220,000	8	Radial	400	Zn, Zn-Ni	1520	60	1976
Mardyck, France	200,000	12	CAROSEL	600	Zn	1900	75	1991

Dormund, Germany	150,000	5	Vertical	300	Zn	1950	77	1986
Bochum, Germany	150,000	10	Horizontal	360	Zn	1600	63	1987
Neuwied, Germany	150,000	15	Vertical	320	Zn-Ni	1570	62	1985
Salzgitter, Germany	300,000	13	Gravitel	650	Zn	1850	73	1987
Duisburg, Germany	200,000	11	Horizontal	450	Zn	1900	75	1987
Torino, Italy	200,000	16	Radial	512	Zn	1600	63	1987
Genoa, Italy	80,000	10	Radial	320	Zn	1850	73	1991
Potenza, Italy	30,000	6	Horizontal	60	Zn	1800	71	1988
Varzi, Italy	50,000	4	Radial	100	Zn	1400	55	1986
Luxemburg	60,000	8	Vertical	150	Zn	1550	61	1983
Sagundo, Spain	60,000	4	Horizontal	160	Zn	1700	67	1986
Shotton Works, Deside, Wales	200,000	8	Vertical	528	Zn, Zn-Ni	1600	63	1972/1989
Genk, Belgium	300,000	10	Vertical	600	Zn, Zn-Ni	1080	43	1992

Source: Ref 8

Table 6 Major Asian electrogalvanizing lines started since 1976

Plating line location	**Nominal capacity, tons/yr**	**Plating cells**		**Total amperage, kA**	**Coatings**	**Width**		**Start-up**
		No.	**Type**			**mm**	**in.**	
Mizushima, Japan	360,000	19	Radial	662	Zn, Zn alloy	1830	72	1987
	300,000	. . .	Horizontal	. . .	Zn, Zn-Ni	1830	72	1991
Chiba, Japan	300,000	7	Radial	310	Zn, Zn-Ni	1700	67	1982
Fukuyama, Japan	360,000	11	Horizontal	550	Zn, Zn-Fe	1880	74	1983

	300,000	12	Horizontal	500	Zn, Zn-Ni	1830	72	1987
	240,000	7	Horizontal	350	Zn	1830	72	1992
Nagoya, Japan	360,000	17	Horizontal	640	Zn, Zn-Fe	1830	72	1983
Kimitsu, Japan	300,000	6	Horizontal	320	Zn, Zn-Ni, Zn-Ni + organic	2080	82	1985
Kashima, Japan	360,000	14	Vertical	672	Zn, Zn-Ni	1600	63	1984
	180,000	8	Vertical	384	Zn, Zn-Ni, Zn-Ni + organic	1600	63	1988
Wakayama, Japan	260,000	10	Horizontal	196	Zn, Zn alloy	1880	74	1968/1986
Kakogawa, Japan	360,000	10	Horizontal	400	Zn, Zn alloy	1600	63	1986
	300,000	. . .	Horizontal	. . .	Zn, Zn-Ni	1830	72	1991
Sakai, Japan	200,000	12	Horizontal	. . .	Zn-Ni	1600	63	1986
Hanshin, Japan	140,000	3	Horizontal	120	Zn, Zn alloy	1830	72	1986
Kwangyang, Korea	400,000	20	Radial	1008	Zn, Zn-Fe	1860	73	1990
Pohang, Korea	300,000	12	Radial	448	Zn, Zn-Ni	1650	64	1986
Kaohsiang, Taiwan	200,000	6	Radial	336	Zn, Zn-Ni	1676	66	1992

Source: Ref 10

Furniture and appliances markets make use of zinc and zinc alloy continuously plated steel strip. Metal office furniture, for example, may be manufactured using electrogalvanized sheet, normally with only a "flash" (about 1 to 2 μm) of zinc coating. Appliances such as toasters, dishwashers, washing machines, dryers, and so on may also be manufactured in part from further treated and painted electrogalvanized steel for extra corrosion protection.

References cited in this section

2. P.K. Frame, "The Year 2001--Will There Be Enough Tin?," *Proceedings of the Fifth International Tinplate Conference*, International Tin Research Institute, 1992
3. T.P. Murphy, Some Economic and Environmental Aspects of the Corrosion Behaviour of Tin and Its Alloys, *Progress in the Understanding and Prevention of Corrosion,* Vol 1, The Institute of Materials, 1993, p 696-711
4. E. Mayo, World Tin Mill Production, *The Canmaker,* Dec 1992

5. "Tin Mill Products," The Iron and Steel Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, 1992
6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
7. G.W. Bush, Development in the Continuous Galvanizing of Steel, *Journal of Metals,* Aug 1989
8. B. Meuthen, Aspects of Zinc and Zinc Alloy-Coated Sheet Steel in Western Europe--with a Special View of the German Scene, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 91-100
9. S.G. Denner, An Overview of the Manufacture and Application of Zinc and Zinc Alloy Coated Sheet Steel in North America, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 101-110
10. T. Hada, Present and Future Trends of Coated Steel for Automotive Use, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 111-119

Key Coating Properties and Characteristics

Described below are the key properties and characteristics of the major coatings that are applied by continuous strip electrodeposition. These include zinc-base coatings, which are applied primarily on automotive sheet steel, and electrolytic coatings, which are applied on the tin mill products used in the container industry.

Pure Zinc (Electrogalvanized) Coatings. Electrogalvanized sheet has a pure zinc coating. It is currently the most widely used coated sheet in the United States for exposed body panels of automobiles because of its generally uniform coating thickness and excellent surface characteristics. Coating thicknesses range from 4 to 14 μm (30 to 100 g/m^2) per side, although the most common coating masses are 8 and 10 μm (60 and 70 g/m^2). For nonautomotive applications such as doors, furniture, and appliances, a thickness of as low as 1.5 μm (10 g/m^2) can be used.

Typically, the electrodeposited zinc coating microstructure (Fig. 2) is a single-phase pure zinc, featureless, in unetched cross section (Ref 11). On the other hand, the coating surface is characterized by crystallographic facets of the hexagonal zinc crystals. Surface morphology, coating texture, and grain size may vary, depending on the chemistry of the plating solution employed as well as the specific deposition conditions of current density, temperature, and level of trace contaminants or additives (Ref 12). The zinc coating does not significantly alter the surface roughness of the steel sheet, and thus it does not affect appearance after painting. In addition, zinc galvanically protects the steel if a corrosive environment penetrates the paint layer.

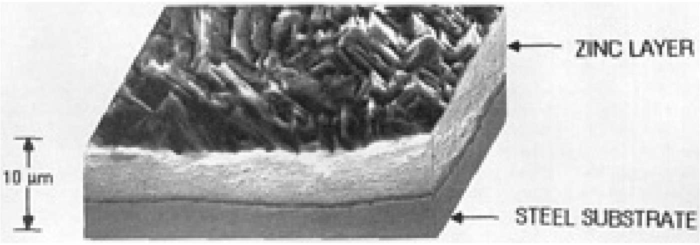


Fig. 2 Surface morphology and microstructure of electrogalvanized sheet. Scanning electron microscope section. Source: Ref 11

Zinc-nickel alloy coatings generally contain 10 to 14 wt% Ni. Coating thicknesses are typically 3 to 6 μm (20 to 40 g/m^2). Zn-Ni coated sheet steel is used for both exposed and unexposed automobile body panels. Although Zn-Ni electrodeposited strip has been available in the United States since the 1950s in narrow widths for automotive trim and nonautomotive applications, its production and use on wide sheet for body panels started in Japan in 1983-1984 (Ref 13). Currently, it is the most widely used electroplated automotive sheet steel in Japan, second only to Zn-Fe hot-dip coated sheet for auto bodies.

Zn-Ni coated automotive sheet is coated either with Zn-Ni only (Ref 14) or with Zn-Ni plus a thin organic coating. The latter product was initially developed in Japan (Ref 15) and is now available in the United States and Europe. The organic coating system normally consists of a proprietary chromate chemical pretreatment of the order of 20 to 100 mg/m^2 of chromium and a thin (about 1 μm) organic topcoat (epoxy or urethane-based) containing silicates. The organic coating was originally applied on one side of the sheet, protecting unexposed surfaces against inside-out perforation corrosion.

However, a two-side organic/Zn-Ni composite system, with chromate and organic layers applied on both sides of the sheet, is also now available and is used by at least one automaker.

In cross section, Zn-Ni coating microstructure is typically fine-grained, single-phase (gamma), Zn-Ni intermetallic. The surface is generally nodular and lacks the sharp crystallographic facets of electroplated zinc (Fig. 3). Reactivity of the Zn-Ni coating in wet salt environments, typically simulated by the salt spray test, is about three times lower than that of pure zinc. Its superior performance in salt spray and fog tests prompted its use as a thinner and more cost-effective alternative to pure zinc.

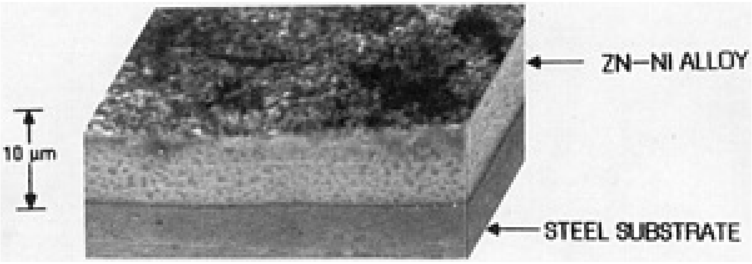


Fig. 3 Surface morphology and microstructure of zinc-nickel alloy coated sheet. Scanning electron microscope section. Source: Ref 11

Zinc-Iron Alloy Coatings. The electroplated Zn-Fe coating was developed mainly for automotive steel sheet for exposed panels, where the characteristics of the Zn-Fe hot-dip coating are desired but the uniformity and surface appearance of an electroplated coating are also required. However, recent advances in hot-dip coating technology have improved the quality of the hot-dip Zn-Fe coating or so-called *Galvanneal coating.* This has contributed to a decline in the production and use of the electroplated Zn-Fe coating, along with the fact that the Zn-Fe process is very difficult to operate at high speeds and volumes when insoluble anodes and sulfate-based electrolyte are used. The electrolyte, which should contain mainly ferrous iron, is easily oxidized to ferric iron, by both air and electrochemical oxidation at insoluble anodes. Therefore, such electroplating facilities must have added equipment or peripheral chemical processing plants for reducing or removing ferric iron and maintaining electrolyte stability. However, there are also chloride-based Zn-Fe processes used in the United States, Japan, and Korea that use soluble anodes to produce a uniform alloy composition over a fairly broad range of plating parameters, without the operational problems of the sulfate-based Zn-Fe electrolyte and insoluble anode process.

The electrodeposited Zn-Fe coating (Ref 16) normally contains 10 to 20 wt% Fe and is used in thicknesses up to 7 μm (50 g/m^2) per side. The coating microstructure for Zn-Fe may show fine layers corresponding to the number of plating cells in the line (Fig. 4). The surface morphology appears as nodular but becomes smoother with increasing iron content. At certain automakers, when this type of coating is used for exposed automotive panels, the Zn-Fe sheet is further electroplated with a second but much thinner top layer of iron-rich Zn-Fe coating, 3 to 5 g/m^2 of Zn-Fe containing at least 80 wt% Fe (Ref 17). The iron-rich top layer was developed to improve the paintability and formability of the primary zinc-rich alloy coating.

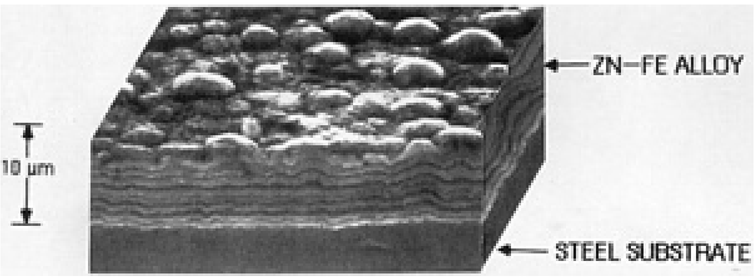


Fig. 4 Surface morphology and microstructure of zinc-iron alloy coated sheet. Scanning electron microscope section. Source: Ref 11

Electrolytic Tin Coatings. The continuous electrodeposition of tin on wide strip was introduced in 1940 (Ref 6), and wartime conditions stimulated its development. The electrodeposition process offers three main advantages over the hot-dip process: (a) higher-speed continuous strip processing; (b) better control and uniformity of coating thickness, allowing the use of thinner tin coatings; and (c) ability to plate different coating thicknesses on each surface of the strip, producing differential tinplate that can more cost-effectively meet the different corrosion resistance requirements of the inside and outside of containers.

Tin coatings are of the order of 0.4 μm thick, although they are usually expressed in terms of coating mass. Present values range from about 0.5 to 11 g/m^2 on each surface. In the United States, tin coatings have numbers (Table 7) that designate the total weight of tin (i.e., the weight of the tin on the two sides per base box, a measure of surface area equal to 31,360 in.^{2}, originally defined as 112 sheets, 14 by 20 in.). Presently there is a tendency, for economical and technological reasons, to apply lower-tin coatings, most commonly No. 20 or 25 (2.2 or 2.8 g/m^2).

Table 7 Electrolytic tin coating weight and mass designations

Designation No.	Nominal tin coating weight each surface, lb/base box[a]	Minimum average coating weight each surface test value, lb/base box[a][b]
Coating weights per ASTM A 624		
10	0.05/0.05	0.04/0.04
20	0.10/0.10	0.08/0.08
25	0.125/0.125	0.11/0.11
35	0.175/0.175	0.16/0.16
50	0.25/0.25	0.23/0.23
75	0.375/0.375	0.35/0.35
100	0.50/0.50	0.45/0.45
D50/25[c]	0.25/0.125	0.23/0.11
D75/25[c]	0.375/0.125	0.35/0.11
D100/25[c]	0.50/0.125	0.45/0.11
D100/50[c]	0.50/0.25	0.45/0.23
D135/25[c]	0.675/0.125	0.62/0.11

Nominal tin coating mass each surface, g/m^2	**Minimum average coating mass each surface test value, g/m$^{2(d)}$**
Coating masses per ASTM A 624M	
1.1/1.1	0.9/0.9
2.2/2.2	1.8/1.8
2.8/2.8	2.5/2.5
3.9/3.9	3.6/3.6
5.6/5.6	5.2/5.2
8.4/8.4	7.8/7.8
11.2/11.2	10.1/10.1
D5.6/2.8$^{(c)}$	5.2/2.5
D8.4/2.8$^{(c)}$	7.8/2.5
D11.2/2.8$^{(c)}$	10.1/2.5
D11.2/5.6$^{(c)}$	10.1/5.2
D15.2/2.8$^{(c)}$	14.0/2.5

Note: Listed above are the commonly produced coating weights and masses. Upon agreement between the producer and the purchaser, other combinations of coatings may be specified and the appropriate minimum average test values will apply.

Source: Ref 5

(a) Base box is a measure of surface area equal to 31,360 in.^{2}.

(b) The minimum value shall be not less than 80% of the minimum average tin coating weight.

(c) The letter D on differentially coated tin plate indicates the coated surface to be marked. For example, the examples indicate that the heavy-coated side is marked.

(d) The minimum spot value shall be not less than 80% of the minimum average tin coating mass.

Electrolytic tinplate is produced in two primary finishes. The first type is the so-called *matte-finish tinplate*, which is used simply with the as-deposited tin coating with its nonreflective microcrystalline surface morphology (Fig. 5). Matte-finish tinplate is used primarily for drawn and ironed two-piece containers for beverages and, more recently, for foods, with the body of the container being a single piece and the end being the second piece. The second and more common type is bright tinplate, which results when strip is heated above the melting point of tin and is quenched with water to form a bright, reflective surface. The high reflectivity and smoothness of this type of tinplate facilitates lithography, and it provides a good appearance for the end product, which is usually three-piece containers. Several variations of decorative effects and surface finishes can be obtained by varying the surface of the work rolls in the final temper-rolling or cold-rolling pass.

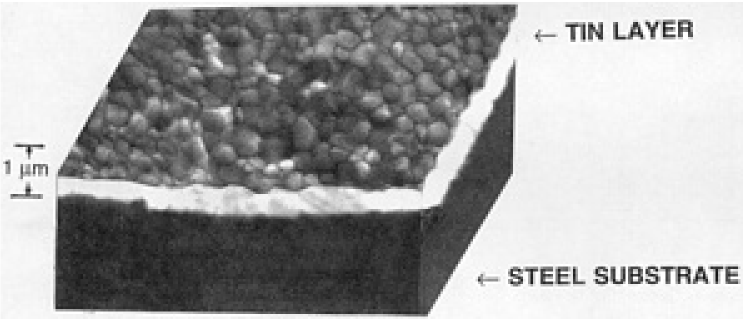


Fig. 5 Surface morphology and microstructure of tinplate. Scanning electron microscope section

Chromium Coatings. The chromium coating that is most widely applied to steel strip by continuous electrodeposition is an extremely thin coating consisting of layers of both metallic chromium and hydrated trivalent chromium oxides. The coating is specified by the coating weight range of the metallic chromium, 30 to 140 mg/m^2 Cr, and by the amount of chromium present as the oxide, 8 to 27 mg/m^2 (Ref 5). Electrolytic chromium-coated steel is further coated with a lubricating film and is used principally for can ends, closures as well as drawn bodies. However, it requires the application of an organic coating or plastic film to minimize abrasion, corrosion, and external rusting.

References cited in this section

5. "Tin Mill Products," The Iron and Steel Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, 1992
6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
11. H.E. Townsend, Coated Steel Sheets for Corrosion-Resistant Automobiles, *Materials Performance,* Oct 1991, p 60-65
12. T.R. Roberts, F.H. Guzzetta, and R.Y. Lin, The Effect of Processing Temperature on the Microroughness of Electroplated Zinc Coatings on Steel, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
13. S.A. Watson, "Zinc-Nickel Alloy Electroplated Steel Coil and Other Precoated Coil for Use by the Automotive Industry: A Review of Literature Published 1983 to 1987," Nickel Development Institute, 1988
14. R.N. Steinbicker and S.G. Fountoulakis, Production of Zinc-Nickel Electroplated Coatings, *Iron and Steel Engineer,* July 1989, p 28-31
15. T. Watanabe, Y. Shindou, T. Shiota, and S. Nomura, Development of Organic Composite Coated Steel Sheet with Bake Hardenability and High Corrosion Resistance, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan

16. T. Adaniya, T. Hara, et al., "Corrosion Resistance of Zn-Fe Alloy Electroplated Steel," Metals/Materials Technology Series 8512-022, American Society for Metals, 1985
17. M. Toda, H. Kojima, et al., "Development of Two-Layered Zn-Fe Alloy Electroplated Steel Sheet," Paper 840212, Society of Automotive Engineers, 1984

Components of Continuous Steel Strip Plating Lines

Figures 6, 7, 8, and 9 show schematic diagrams of continuous steel electroplating lines for tin, chromium, and zinc coatings. Figure 9 may be consulted in the following discussion of the general features of these lines. The line in Fig. 9 is also designed for painting over the metallic coated strip, which for economic reasons may become the trend, particularly for zinc and zinc alloy coating lines whose lower speeds can allow roll coating of the organic films.

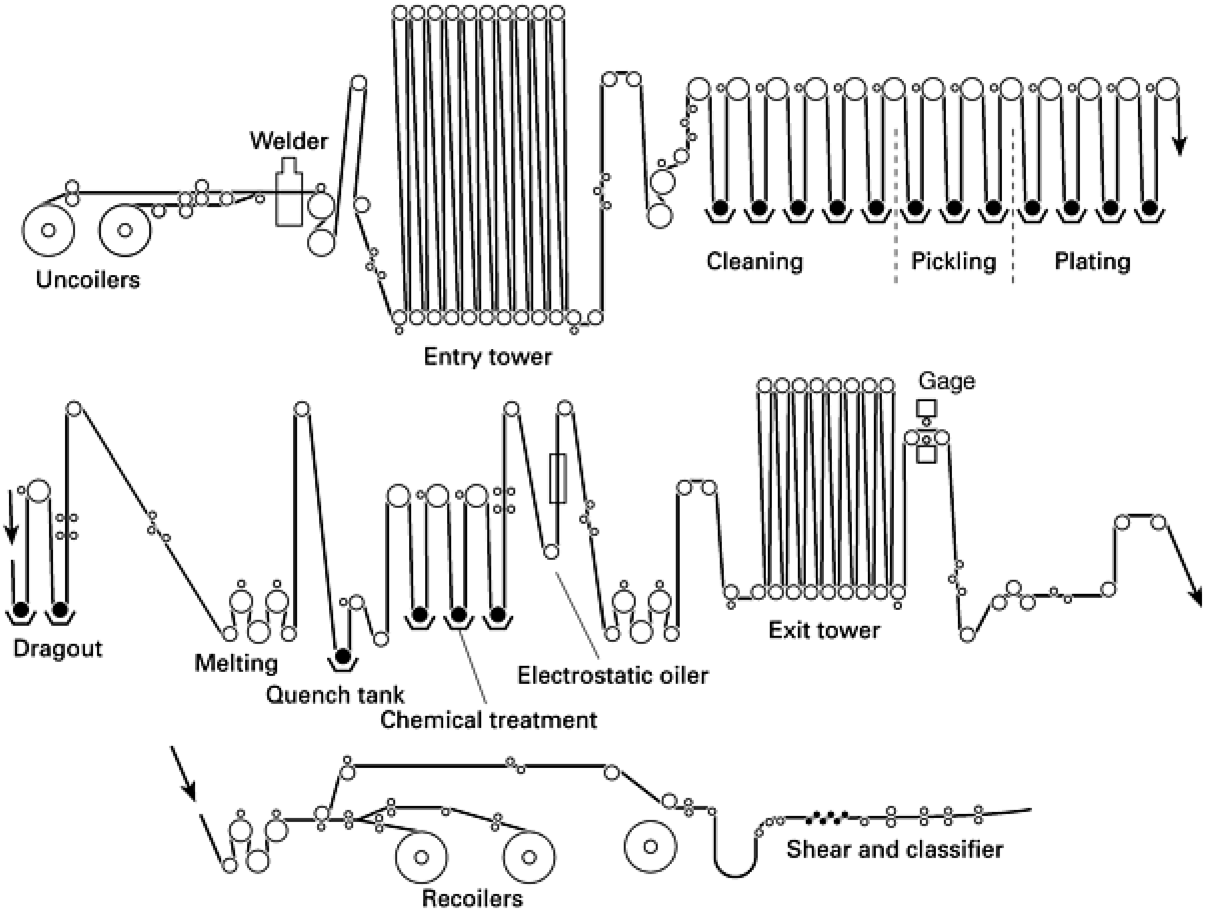


Fig. 6 Schematic diagram of a typical electrotinning line, using vertical plating cells. Source: Ref 1

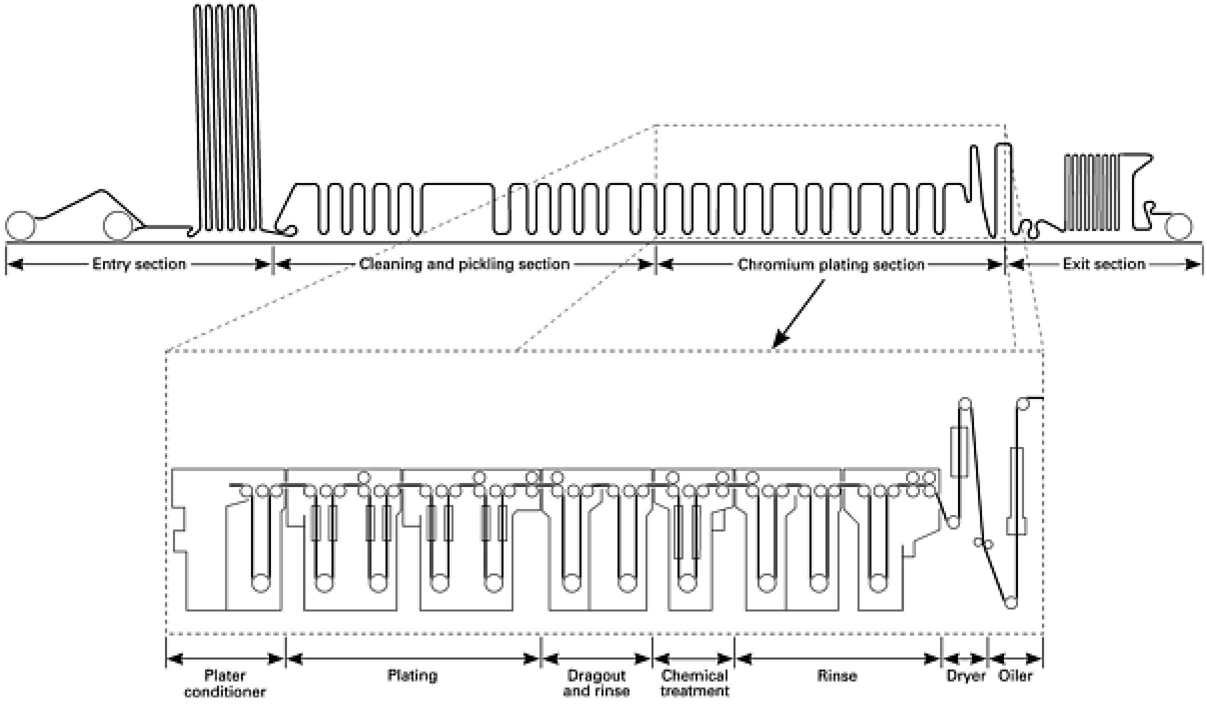


Fig. 7 Schematic diagram of a typical two-step chromium plating line, also called a tin-free steel line. Source: Ref 1

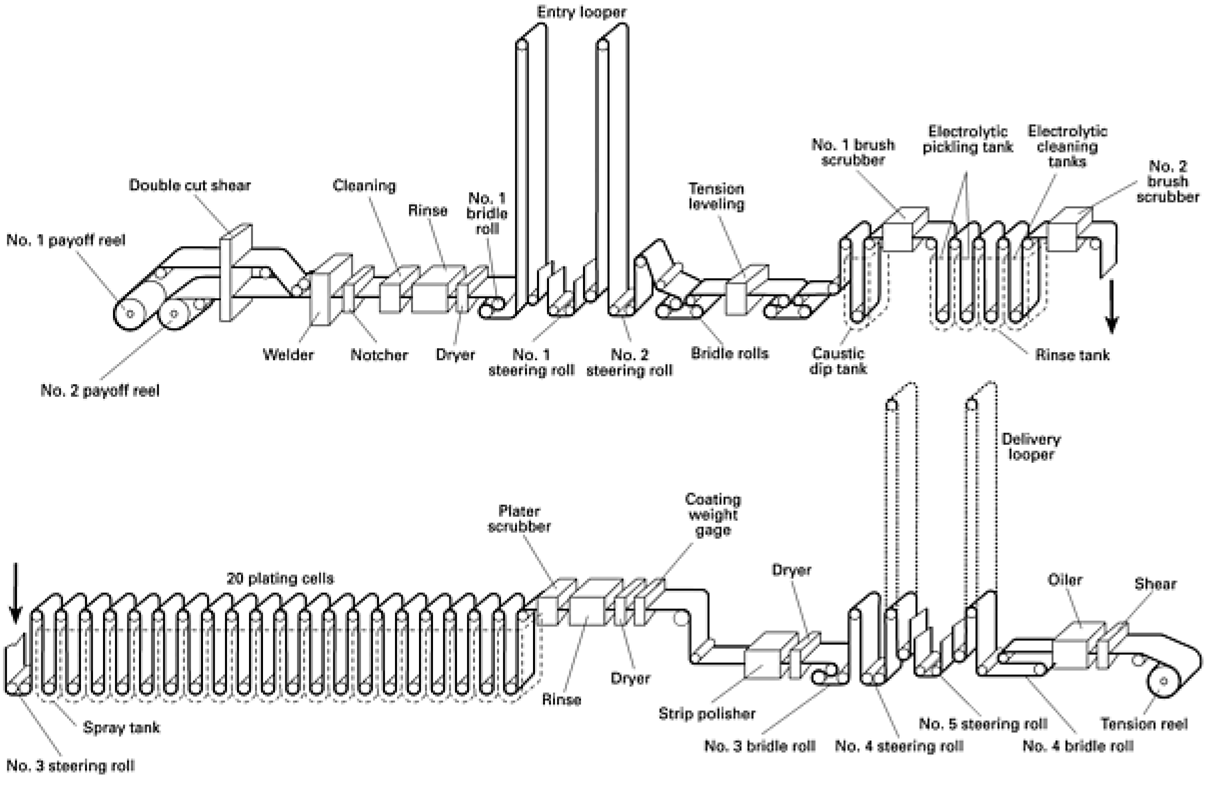


Fig. 8 Schematic diagram of a typical electrogalvanizing line with vertical plating cells. Source: Ref 1

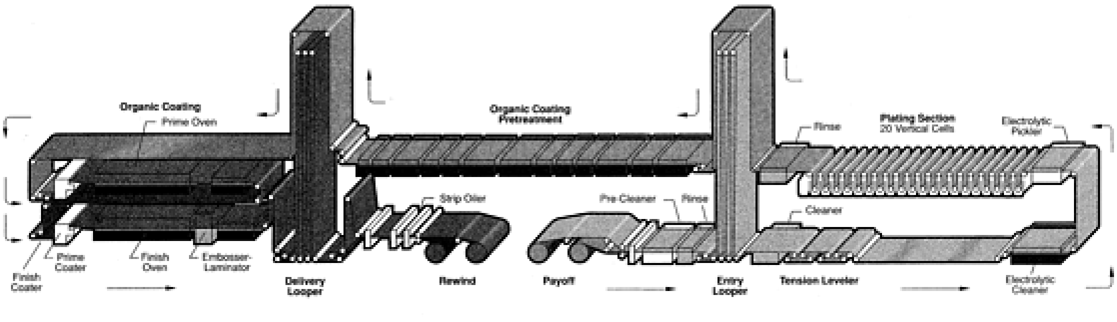


Fig. 9 Schematic diagram of an 1830 mm (72 in.) combination electrogalvanizing and coil coating line. Source: Ref 18

A typical continuous plating line has five main sections: payoff, pretreatment, plating, post-treatment, and delivery. The functions and key pieces of equipment of each of these sections are described below.

The payoff section feeds the strip into the line. It may consist of payoff reels, a shear, a strip welder, an edge-notcher, a burr masher, a degreasing section, and an accumulator tower. Coils of cold-rolled, fully annealed steel are loaded onto the entry reels and are fed into the continuous line. The head end of a new coil is welded to the tail end of the previous coil. The edges of the weld are notched or cut out to eliminate loose flaps when two different widths are welded together, and any steel edge burr is mashed. The strip passes through a precleaning and rinse station where the bulk of the rolling and protective oils are removed, then moves into the entry strip accumulator or looper. The looper, which can be either vertical or horizontal, accumulates extra strip ahead of the plating section and provides it to that section when the entry end is stopped to load a new coil.

The pretreatment section is where residual oil, surface carbon, and any light surface oxide are removed prior to plating. It normally consists of one or more alkaline cleaning and electrocleaning stations, brushing or scrubbing stations, pickling or electropickling stations, and rinsing stations. Many modern, high-speed lines have a tension leveler within the pretreatment section to flatten the strip. This guarantees the uniform anode-to-strip spacing needed to produce a highly uniform coating. The leveler location is such that strip coming into the unit is fairly clean, but additional cleaning follows the leveling process.

The plating section, the heart of the process, always consists of multiple plating cells located in a row (Fig. 10). At the beginning of the plating section, there is frequently a conditioning or preplating cell. A conditioning cell may simply contain the process electrolyte, to wet the strip surface prior to the application of current, but a preplating cell may also contain a slightly different or completely different electrolyte to deposit a thin initial layer. This layer can be used either to enhance the adherence of the main coating (e.g., in the case of alloys of zinc with nickel or iron) or to control a postplating process (e.g., a thin nickel layer may be deposited to limit tin-iron alloy growth during reflowing or subsequent processing of tinplate).

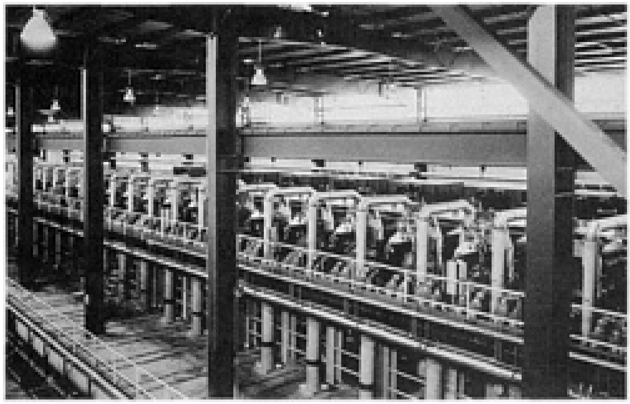


Fig. 10 Twenty vertical plating cells in a continuous plating line that applies zinc and zinc-nickel alloy coatings on sheet steel, primarily for the automotive market

The full thickness of the main coating is built up gradually as the strip moves from cell to cell. Associated with the cells are electrolyte distribution tanks, pumps, filters and heat exchangers, and electrolyte chemical replenishment reactors and systems. Upon exiting the last cell, the coated sheet is immediately rinsed and dried to prevent streaking or staining of the coated surface. Following the dryer, there is normally a coating thickness gage (x-ray fluorescence) that continuously monitors and records the edge-to-edge distribution of the coating on both sides of the strip.

The post-treatment section is present on most, although not all, strip plating lines. There are three basic types of post-treatments:

- *Surface-stabilizing post-treatments*: Examples are the etching solutions used to clean and stabilize the uncoated side of one-side electrogalvanized sheet (Ref 19, 20, 21)
- *Property-enhancing post-treatments* chemically convert the surface to accept further coatings, such as paint. In addition, post-treatments can impart certain surface properties, such as lower friction or change in ohmic surface resistance (which are important properties for forming and welding) or changes in surface brightness or appearance. Examples are the chromium-containing chemical conversion coatings that slow down surface oxide growth on tin (Ref 5, 6), zinc coatings that serve as pretreatments for the adhesion of paints for zinc and Zn-Ni (Ref 15), and enamels for tinplate (Ref 6).
- *Proprietary rinses, phosphates, and dry film lubricants* may be used to aid in the final manufacturing of parts (Ref 22).

Melting and reflowing of the tin coatings can also be characterized as a post-treatment. It is almost always followed by a chromate conversion or electrolytic post-treatment.

The delivery section starts with a delivery accumulator, which allows the processing sections to continue running while the delivery reels are stopped to remove coils. Several additional stations and pieces of equipment are included in the delivery section, such as for edge trimming, inspecting, marking, oiling, and sampling the final strip before it is coiled again onto the rewind reels (Fig. 11).

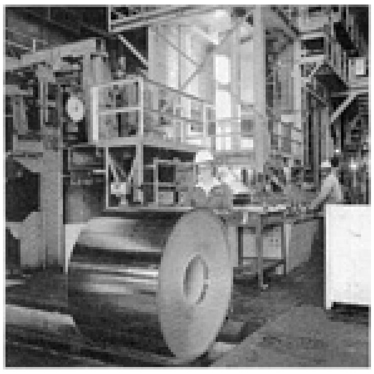


Fig. 11 Delivery section of a continuous tinning line

References cited in this section

1. L.W. Austin and J.L. Lindsay, "Continuous Steel Strip Electroplating," slide course, American Electroplaters and Surface Finishers Society, 1989
5. "Tin Mill Products," The Iron and Steel Society of the American Institute of Mining, Metallurgical, and

Petroleum Engineers, 1992

6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
15. T. Watanabe, Y. Shindou, T. Shiota, and S. Nomura, Development of Organic Composite Coated Steel Sheet with Bake Hardenability and High Corrosion Resistance, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan
18. W.A. Carter, R.L. Price, and R.N. Steinbicker, Electrogalvanizing at Walbridge Coatings, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
19. S.G. Fountoulakis, R.N. Steinbicker, and D.E. Hruskoci, Chemical Post-Treatment Process for One-Side Electrogalvanized Steel Strip, U.S. Patent 4,708,779, 1987
20. H. Bersch, K.-H. Kilian, and H.U. Weigel, "Method for Electroplating a Steel Strip with a Coating Metal, in Particular Zinc or Zinc-Containing Alloy," U.S. Patent 4,855,021, 1989
21. G.E. Jones, The Application of Tin Coatings in the Manufacture of Tinplate, *The Production of Wide Steel Strip,* Special Report 67151, Iron and Steel Institute, 1960
22. K.S. Raghavan, J.G. Speer, and T.J. Garrett, "Sheet Steel Surface Treatments for Enhanced Formability," Paper 94095, Society of Automotive Engineers, 1994

Classification of Continuous Electrodeposition Processes

Strip plating processes are generally classified by three process characteristics (Table 8): anode type, electrolyte chemistry, and plating cell geometry.

Table 8 Classification of continuous processes for the main electrodeposited coatings for steel strip, and key features of each category

Coating	**Cell geometry**	**Anode**	**Bath chemistry**
Zinc, Zn-Ni, Zn-Fe	Vertical	Insoluble (Pb alloys, Ir/IrOx coated Ti)	Zinc sulfate (plus nickel or ferrous sulfate), sodium and/or magnesium sulfate for conductivity, pH ≈2
		Soluble (Zn, plus Fe or Ni)	Zinc (plus nickel or ferrous) sulfate, and alkali sulfate conductive salts, pH ≈ 4
	Gravitel	Insoluble (Ir/IrOx coated Ti)	Zinc sulfate, pH ≈ 2
	Radial	Soluble	Zinc chloride, pH ≈ 4
		Insoluble (Pb alloys, Ir/IrOx coated Ti)	Zinc sulfate, pH ≈ 2
	Horizontal	Soluble	Zinc sulfate or chloride, pH ≈ 3-5
		Insoluble	Zinc sulfate, pH ≈ 2
Tin	Vertical	Soluble	Tin phenolsulfonate, pH ≈ 1

	Horizontal	Soluble	Tin fluoride and chloride (Halogen process), pH ≈ 3
	Radial	Insoluble	Methanesulfonate, pH ≈ 1
Chromium	Vertical, horizontal	Insoluble (Pb-Ag)	Chromic acid, catalyzed with sulfate and fluorosilicate ions

Anode type is either soluble or insoluble. Soluble anodes are consumable, dissolving anodically to replenish the metal or metals, which eventually deposit onto the steel strip as the coating. Insoluble anodes generally oxidize water and have oxygen evolution as the anodic reaction within each plating cell. More information about anode selection is given in the following paragraphs.

Electrolyte chemistry is generally characterized by the primary anionic species, such as sulfate or chloride. The key factor is obviously the capability of the particular chemistry to produce a high-quality, smooth, and compact coating. However, there are many other factors, including availability and cost of the starting metal salts; the ability of the resulting electrolyte to sustain electrodeposition at high current density, so as to maintain high line speed and productivity; and compatibility with the anode material.

Zinc and zinc alloy electrodeposition of steel strip, done at up to 213 m/min (700 ft/min), takes place from either a sulfate- or chloride-based electrolyte, although a mixed chemistry is used in some of the smaller and older plating lines. These electrolytes are aqueous solutions of zinc ions and ions of the alloying nickel or iron metal with sulfate or chloride ions, acidified with sulfuric or hydrochloric acid, respectively. Alkali or ammonium salts may also be used to increase the conductivity of these solutions.

As shown in Table 8, chloride electrolytes are used exclusively with soluble anodes, because insoluble anodes would oxidize the chloride into chlorine gas, which cannot be handled economically because of it corrosivity and hazardous nature. The most significant advantage of the chloride process is that the conductivity of the bath is many times higher than that of the sulfate bath, and so less electric power is consumed to deposit the same amount of coating as in the sulfate process. On the other hand, one must invest in corrosion-resistant materials for construction of equipment and have extra equipment or labor to replenish the consumable anodes. In addition, the chloride process may require some type of organic additive as a grain-refining agent in order to produce coatings with improved galling resistance. The world's largest steel electroplating line, in Dearborn, MI, uses this chemistry for depositing zinc and/or Zn-Fe coatings on over 700,000 tons of sheet steel per year (Ref 23, 24).

The most widely used zinc and zinc alloy steel plating process is the sulfate type. The main attribute of sulfate electrolytes is that they are compatible with insoluble anodes. Selecting the anode type, therefore, is truly the first step in deciding on the plating process to use. Sulfate-based processes are also simple in chemistry, as shown in Table 8. The main advantages of sulfate electrolytes are that they deposit finer-grain coatings without organic additives and operate over a wide range of current densities, temperatures, and acidity.

Tin electrodeposition of steel strip is normally done at 549 m/min (1800 ft/min) or higher line speeds. The two most widely used processes today are the Ferrostan and Halogen processes (Ref 25). Only one major tinplate producer, in Andernach, Germany, operates a third process, based on a fluoroborate electrolyte, and the original 1940s alkaline stannate electrolyte (Ref 6) is now employed in only one or two of the older remaining lines. A new process based on a solution of tin in methanosulfonic acid has been invented and evaluated (Ref 26), and it was recently put into commercial use in at least two electrolytic tin lines.

The electrolyte for the Ferrostan process is a solution of stannous tin in phenolsulfonic acid, with various addition agents to mitigate oxidation of stannous tin, promote the deposition of a compact and smooth coating, and improve wetting characteristics. This process was invented in 1942 (Ref 27), but it has since undergone some changes, primarily in terms of the addition agents used. The original additive package, dihydroxydiphenylsulfone and monobutylphenylphenol sodium monosulfonate (Ref 28) has been replaced with ethoxylated alpha-naphthol sulfonic acid. Ferrostan lines always employ vertical cells and generally employ soluble tin anodes.

The Halogen process, also known as the horizontal acid process, was developed in 1943 (Ref 29). It employs an aqueous solution of stannous and alkali (e.g., sodium) fluorides and chlorides. The basic composition has been modified over the years by various companies to suit their needs (Ref 30). To obtain smooth, compact deposits having the right wetting characteristics, addition agents are also required. Naphtholsulphonic acids or polyalkylene oxides are normally used, although others have also been found to be effective over the years.

Chromium and chromium oxide electrodeposition of steel strip employs two processes, both of which use similar electrolytes. In fact, the electrolyte is simply an aqueous solution of chromic acid (CrO_3), catalyzed with very small amounts of sulfate ions and fluorosilicate ions (Ref 31, 32). The two processes differ only in the number of steps used in depositing the metallic and nonmetallic components of the coating. The older process (Ref 31) uses two steps with two banks of plating cells or passes. In the first series of passes, the metallic chromium is normally deposited at higher current density and from a more concentrated chromic acid solution, and then the chromium oxides are deposited in the last plating passes, using low current density and dilute chromic acid solution as the electrolyte. The more recent process employs an electrolyte of intermediate chromic acid concentration, but still high current density, to deposit a mixture of metallic and nonmetallic chromium in one step (Ref 32). The two-step process is normally operated with vertical plating cells, whereas the single-step process uses vertical cells for conventional current density operation and horizontal cells for high-current-density operation. Both processes use insoluble lead alloy anodes.

Plating Cell Geometry. There are many different plating cells, with varying sophistication in coating capability, productivity, automation, specialized components, and so on. However, these can be classified into three main groups based on cell geometry: vertical, horizontal, and radial. Both the vertical and horizontal cells have been used for many decades in the production of tinplate for the container industry. In the 1970s, when the automotive industry started to downgage and thus required increased corrosion resistance, particularly for inside-out rust-through, radial cell geometry was developed to produce electrogalvanized sheet plated on only one side for use as the inner surfaces of auto body panels. Today, most electrogalvanized sheet is coated on two sides, but with the use of edge shielding, vertical and horizontal cells can also produce good-quality one-side plated product.

All three cell types can be used with either soluble or insoluble anodes. Each type must provide adequate current transfer to the steel strip and good electrolyte flow in the anode-to-strip gap. Both of these factors increase the speed of electrodeposition and thus the material throughput of the cell. Over the years, there have been many innovations in the basic cell designs, and the key innovations are discussed below within the description of each basic design.

Vertical Cell Design. Figure 12 shows four major variations of vertical cell design. The simple flooded cell is used with soluble anodes and phenolsulfonic acid electrolyte for tin plating, or with lead alloy anodes for the deposition of chromium and chromium oxide from chromic acid solutions. However, for electrogalvanizing, which is done at about a third of the speed used for tin and chromium, the vertical cell is normally modified to become a forced-flow or counter-current-flow cell in order to operate at higher current densities (Ref 33). The forced flow is provided by pumping electrolyte through nozzles, as shown in Fig. 12(a). Generally, these electrogalvanizing cells are used with insoluble anodes, lead alloy or noble-metal-coated titanium. However, they have also been used with soluble (zinc) anodes, with the anodes in the form of solid bars suspended from busbars (Fig. 12b) or pellets contained in a special anode basket (Fig. 12c).

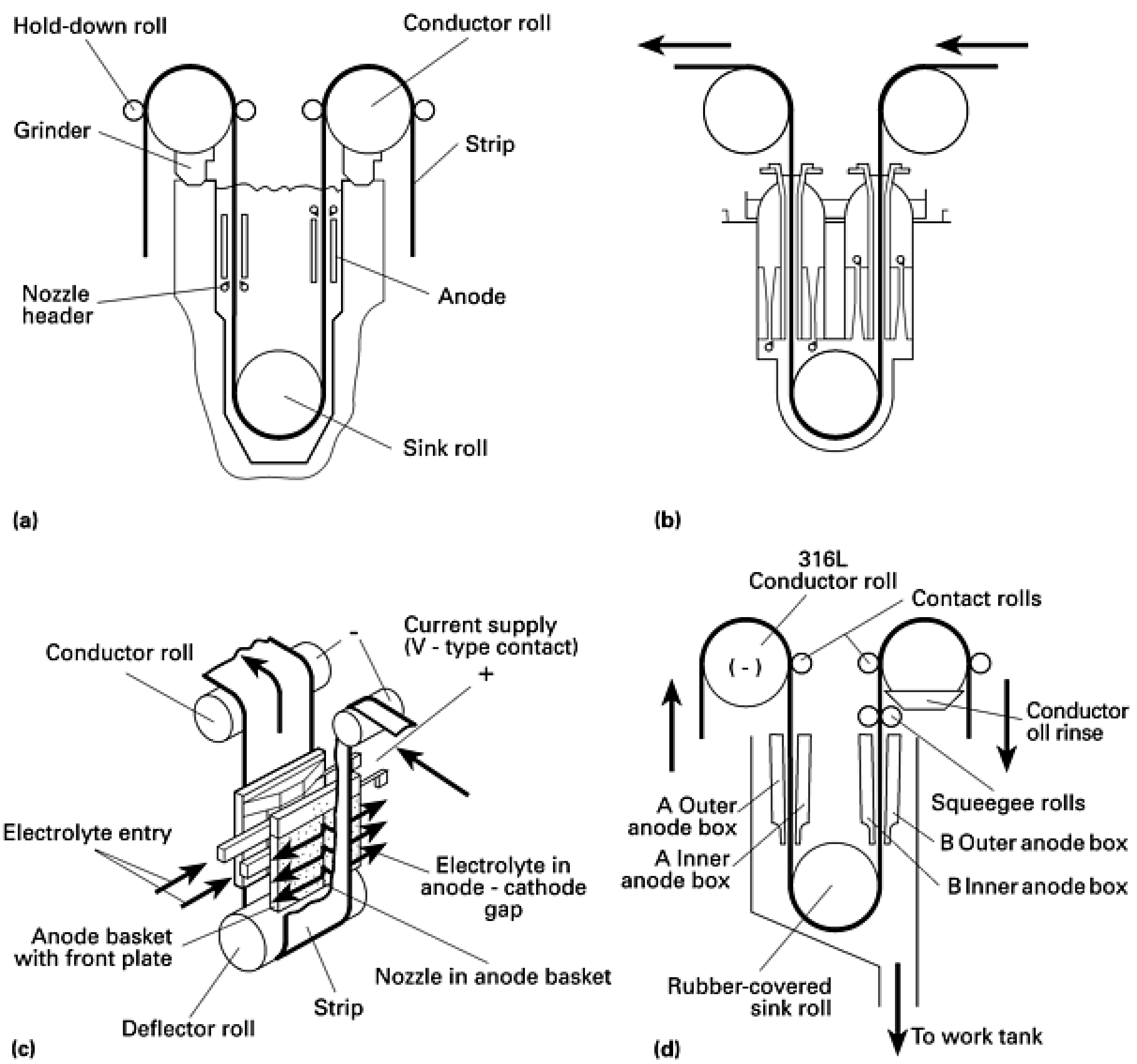


Fig. 12 Four major variations of vertical plating cell design. (a) Flooded and counter-current-flow plating cell with insoluble anodes. Source: Ref 33. (b) Flooded and counter-current-flow cell with soluble anode bars. Source: Ref 34. (c) Flooded cell with anode baskets containing metal granules. Source: Ref 35. (d) Gravitel plating cell with insoluble anodes. Source: Ref 36

A new type of insoluble anode vertical cell called Gravitel (Fig. 12d) was commercialized in 1985 (Ref 36). In this cell design, only the anode-to-strip gap is filled with electrolyte, and although the cell is housed in a similar tank, that tank is not filled with solution but simply contains the splashing of the solution, sending it down under the cell and into a large recirculation tank. Solution is pumped inside each hollow anode box, overflows the top of the box through a special V-shaped weir, falls into the gap between the anode and the strip, fills the gap, falls out the bottom of the gap, and returns by gravity to the recirculation tank. Because gravity increases the speed of the electrolyte along the height of the cell, the gap is tapered, being wider at the top (9 mm) and narrower at the bottom (7 mm). To plate both sides, opposing pairs of anode boxes are operated simultaneously. To plate one side of the strip, the anode boxes facing the unplated side are moved away, and electrolyte flow and plating current are maintained only on the side being plated.

Radial Cell Design. Figure 13 shows four major variations of radial cell design. The first radial cell (Ref 23, 24) evolved into the CAROSEL (Consumable-Anode Radial One-Side ELectroplating) technology. The distinguishing characteristics of this cell are a single but very-large-diameter conductor roll (about 2.4 m, or 8 ft, in diameter) in the center of the cell and large cylindrical consumable anode sections under this roll. Like all radial cells, this cell plates only one of the surfaces of the steel strip. However, by arranging multiple cells within a line into two tiers or elevations, and by inverting the strip as it goes from one tier to the next, the second surface can also be plated.

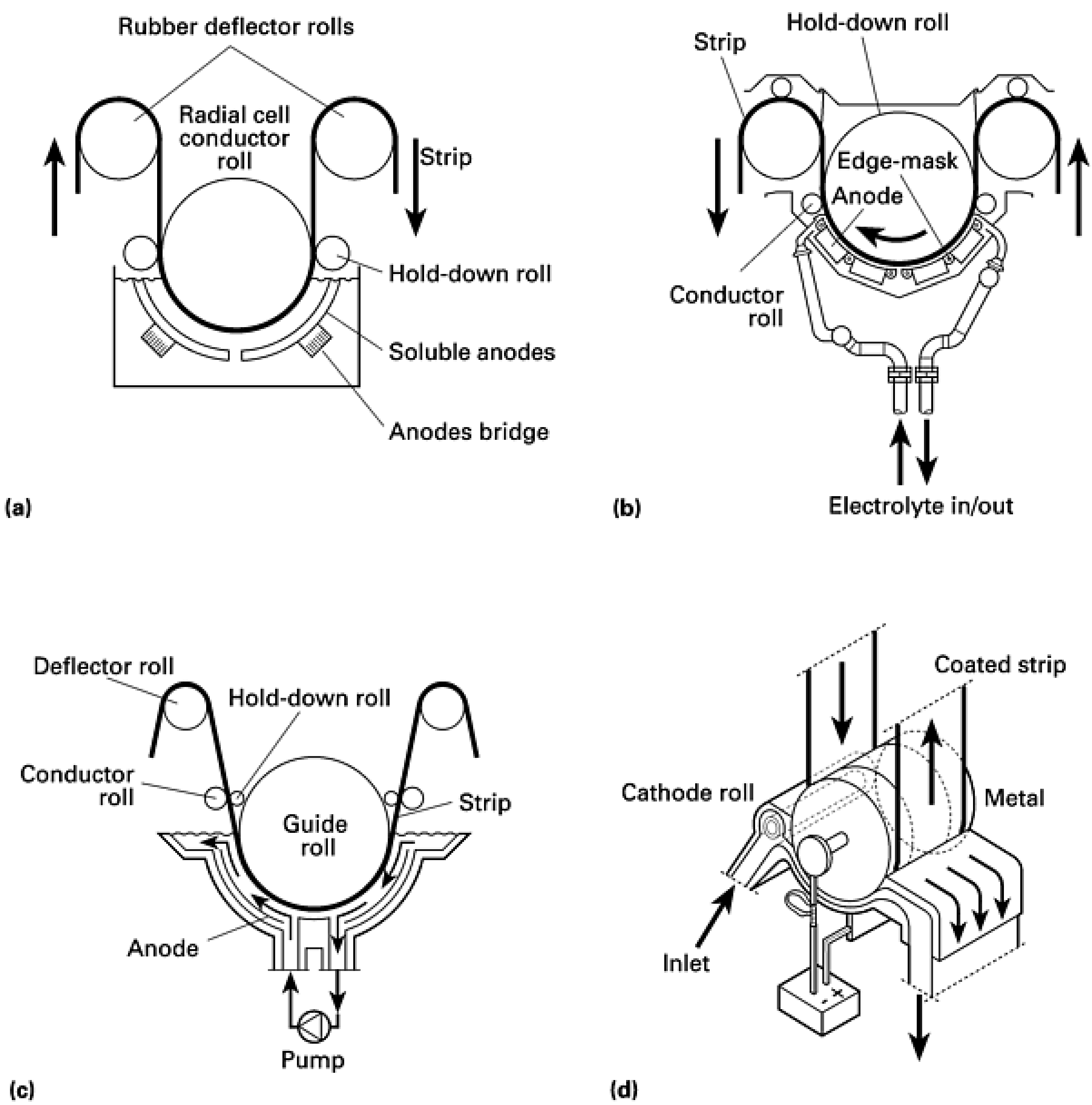


Fig. 13 Four major variations of radial plating cell design. (a) CAROSEL radial cell with soluble anodes (Ref 23), a large 8 ft diameter conductor roll, and the more recent addition of hold-down rolls. Source: Ref 24. (b) Soluble-anode radial cell with modifications made in the way new anodes are inserted into the cell. Source: Ref 37. (c) A radial cell with insoluble anodes and small-diameter conductor rolls in either side of the guide roll. Source: Ref 38. (d) Radial Jet Cell developed primarily for tin plating, not yet in commercial use. Source: Ref 39

Horizontal cell design was first employed for the Halogen tin process (Fig. 14a), which plates one surface of the strip at a time. However, horizontal cells with top and bottom anodes (initially soluble anodes) were later developed for electrogalvanizing (Fig. 14b). Then, in the 1980s, high-current-density (high-productivity) horizontal cells with insoluble anodes were introduced (Fig. 14c, d) to meet the high productivity requirements for electrogalvanized sheet production.

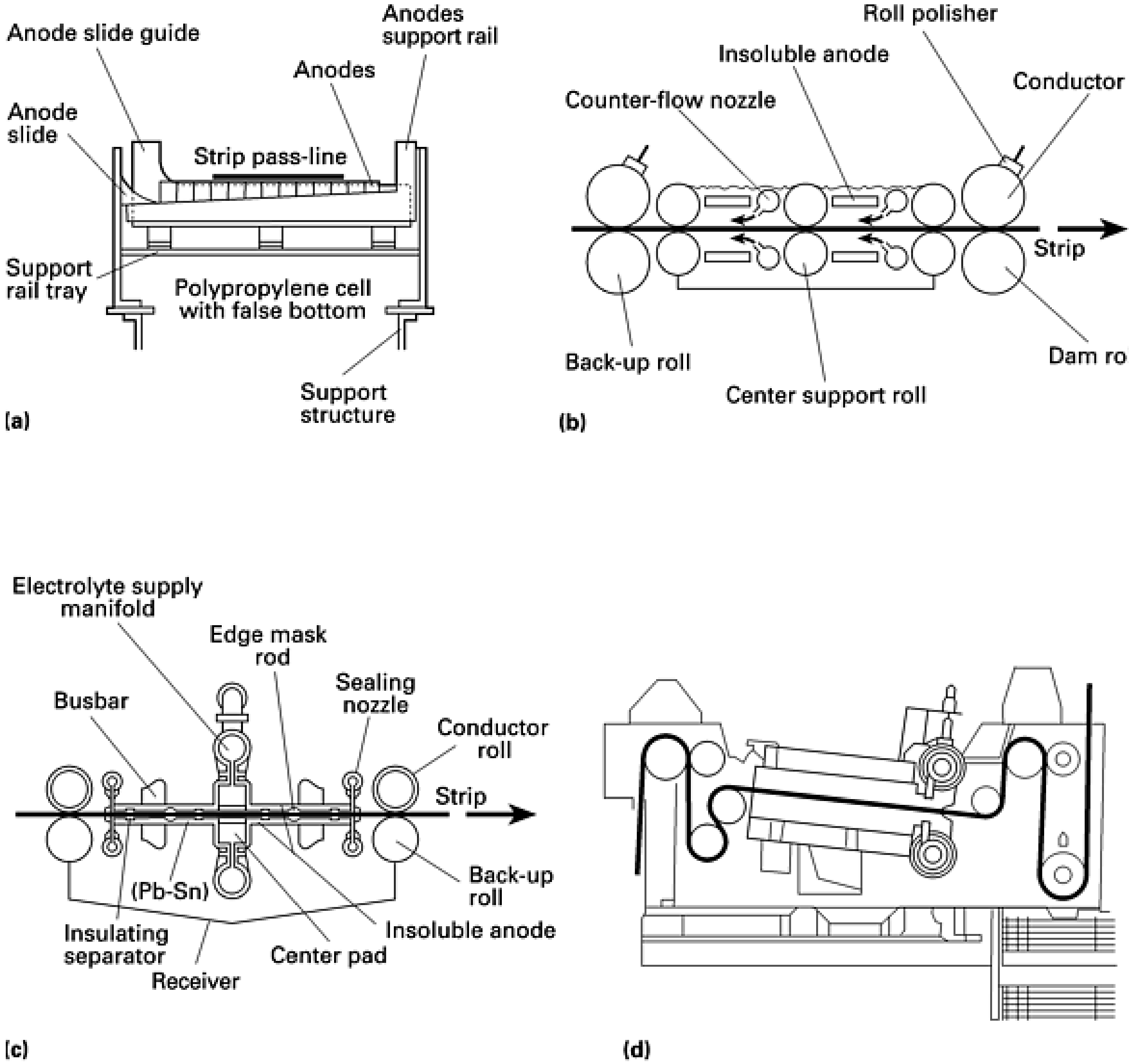


Fig. 14 Four examples of horizontal plating cells for continuous steel strip plating. (a) Front view of horizontal plating cell with soluble anodes, used in the Halogen tinning process. Source: Ref 30. (b) Conventional horizontal cell with insoluble anodes. Source: Ref 40. (c) LCC-H, a liquid-cushioned horizontal cell. Source: Ref 41. (d) Horizontal cell for high-current-density tin-free steel plating. Source: Ref 42

References cited in this section

6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
23. R.F. Higgs and W.R. Johnson, Coated Sheet Steel from Double Eagle Steel Coating Company, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
24. W.R. Johnson, C.J. Wu, T.A. Modrowski, and J.O. Stoddart, Improved Current Transfer and Productivity on the U.S. Steel CAROSEL Process through the Use of Hold Down Rolls, *Proceedings of Galvatech 1992* (Amsterdam, The Netherlands), Verlag Stahleisen, Dusseldorf, Germany
25. "Electrotinning of Continuous Steel Strip," slide course, American Electroplaters and Surface Finishers Society, 1992
26. G. Federman et al., U.S. Patents 4,871,429 and 4,880,507
27. T.W. Lippert, Food in Cans, *Iron Age,* Vol 149, 1942, p 29
28. E.F. Harris and Carnegie-Illinois Steel Co., Electrodeposition of Tin, U.S. Patent 2,450,794, 1948

29. A.H. DuRose, "Some Contributions from U.S. Supply Houses to Plating Science and Technology," *Plating,* Aug 1970
30. R.N. Steinbicker, Some Effects of Plating Bath Variables on the Quality Performance of a Halogen Tinning Line, *Proceedings of the Seventh Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1993
31. "Tin Free Steel (TFS) Product and Plating Process," slide course, American Electroplaters and Surface Finishers Society, 1992
32. G.A. Claytor, R.F. Higgs, et al., Chromium Plating by High Current Density, *Proceedings of the Fourth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1984
33. H. N. Hahn, D. R. Vernon, and K. Watanabe, The New L-S Electrogalvanizing Line, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
34. B. Meuthen, J.H. Meyer, and D. Wolfhard, A New Lease on Life for Electrolytic Zinc-Coated Sheet Steel: The German Scene, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
35. K.H. Kilian, K. Taffner, F. Weber, and H.-U. Weigel, Zinc-Nickel Coated Sheet Steel, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
36. W. Karner and G. Maresch, Electrogalvanizing of Strip Steel by the Gravitel Process, *Iron and Steel Engineer,* Nov 1989
37. A. Komoda, A. Kibata, et al., Development of Kawasaki Steel's Cassette Loading Cell for Electrogalvanizing, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 170-177
38. R. Ulivieri, High Speed Electrodeposition of Mono- and Multi-layer Electrogalvanized Steel Strip, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
39. G.C. van Haastrecht and B.K. Paramanathan, Economic Aspects of Reactor Design for Strip Plating Cells, *Proceedings of the Seventh Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1993, p 163-174
40. T. Nonaka, H. Oishi, et al., High Performance Continuous Strip Plating Process with Insoluble Anode, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
41. K. Sakia, M. Kamada, et al., Development of the Liquid Cushion Electroplating Cell,*Proceedings of the Fourth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1984
42. M. Develay, C. Kharouf, et al., Latest Developments in the Area of High V-Current Density Tin-Free Steel Process, *Proceedings of the Seventh Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1993, p 163-174

Batch Hot Dip Galvanized Coatings

Revised by Donald Wetzel, American Galvanizers Association

Introduction

HOT DIP GALVANIZING is a process in which an adherent, protective coating of zinc and zinc/iron compounds is developed on the surfaces of iron and steel products by immersing them in a bath of molten zinc. The protective coating usually consists of several layers (Fig. 1). Those closest to the basis metal are composed of iron-zinc compounds; these, in turn, may be covered by an outer layer consisting almost entirely of zinc.

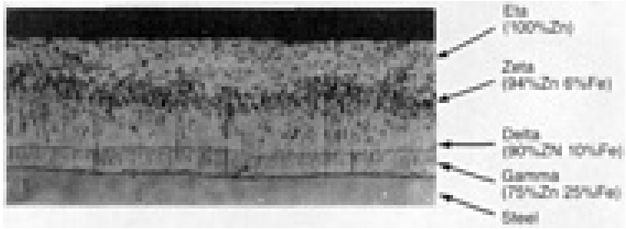


Fig. 1 Photomicrograph of typical hot dip galvanized coating. The molten zinc is interlocked into the steel by the alloy reaction, which forms zinc-iron layers and creates a metallurgical bond. See Table 3 for properties of alloy layers. 250×

The complex structure of layers that comprise a galvanized coating varies greatly in chemical composition and physical and mechanical properties, being affected by chemical activity, diffusion, and subsequent cooling. Small differences in coating composition, bath temperature, time of immersion, and rate of cooling or subsequent reheating can result in significant changes in the appearance and properties of the coating.

Hot dip galvanized coatings are produced on a variety of steel mill products, using fully mechanized, mass production methods. This article, however, is concerned primarily with the hot dip galvanizing of fabricated articles in manual or semiautomatic batch operations. For information about continuous coatings, see the article "Continuous Hot Dip Coatings" in this Volume.

ASTM and other standards related to galvanized coatings are given in Table 1.

Table 1 Standards relating to hot dip galvanized materials

ASTM	
A 123	Standard Specification for Zinc (Hot Dip Galvanized) Coatings on Iron and Steel Products
A 143	Standard Practice for Safeguarding Against Embrittlement of Hot Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement
A 153	Standard Specification for Zinc Coating (Hot Dip) on Iron and Steel Hardware
A 384	Standard Recommended Practice for Safeguarding Against Warpage and Distortion During Hot Dip Galvanizing of Steel Assemblies
A 385	Standard Practice for Providing High Quality Zinc Coatings (Hot Dip)
A 767	Standard Specifications for Zinc Coated (Galvanized) Steel Bars for Concrete Reinforcement
A 780	Standard Practice for Repair of Damaged Hot Dip Galvanized Coatings
E 376	Standard Practice for Measuring Coating Thickness by Magnetic-Field or Eddy Current (Electromagnetic) Test Methods
AASHTO	

M111	Standard Specification for Zinc (Hot Dip Galvanized) Coatings on Iron and Steel Products
M232	Standard Specification for Zinc Coating (Hot Dip) on Iron and Steel Hardware
CSA	
G164-M	Hot Dip Galvanizing of Irregularly Shaped Articles

Source: Ref 1

Reference

1. *Galvanizing for Corrosion Protection: A Specifier's Guide to Bridge and Highway Applications,* American Galvanizers Association, 1992

Applications

Galvanized coatings are applied to iron and steel primarily to provide protection against corrosion of the base metal. Some major applications of hot dip galvanized coatings include:

- Structural steel for power generating plants, petrochemical facilities, heat exchangers, cooling coils, and electrical transmission towers and poles
- Bridge structural members, culverts, corrugated steel pipe, and arches
- Reinforcing steel for cooling towers, architectural precast concrete, and bridge decks exposed to chlorides
- Pole line hardware and railroad electrification structures
- Highway guard rails, high-rise lighting standards, and sign bridge structures
- Marine pilings and rails
- Grates, ladders, and safety cages
- Architectural applications of structural steel, lintels, beams, columns, and related building materials
- Galvanized and painted structural steel for aesthetic, color-coded or extended-life applications, including communication towers, pipe and sign bridges, railings, fencing, and agricultural equipment
- Wastewater treatment facilities, composting buildings, catwalks, gratings, railings, support steel, and related nonimmersion applications

Hot dip galvanized tower and high-strength bolts are produced and used in large quantities for service conditions where long-term integrity of bolted joints is required. In short, wherever steel is exposed to atmospheric, soil, or water corrosion, hot dip galvanized zinc coatings are a standard, effective, and economical method of protection.

The usefulness of hot dip galvanized coatings depends on:

- The relatively slow rate of corrosion of zinc as compared with that of iron (Table 2)
- The electrolytic protection provided to the basis steel when the coating is damaged
- The durability and wear resistance of the zinc coating and the intermetallic iron-zinc alloy layers (Table 3)
- The relative ease and low cost of painting the zinc coating either initially or later, when it is necessary to further extend the life of the structure; such painting is usually done after 25 to 40 years of maintenance-free service in rural and light industrial atmospheres

Table 2 Comparative rankings of 37 locations based on steel and zinc losses

Note the relatively slow rate of corrosion for zinc as compared to steel.

Ranking of location by least amount of material lost		**Location**	**Material lost after 2-year exposure, g**		**Steel:zinc loss ratio**
Zinc	**Steel**		**Zinc**	**Steel**	
1	1	Norman Wells, N.W.T., Canada	0.07	0.73	10.3
2	2	Phoenix, Ariz.	0.13	2.23	17.0
3	3	Saskatoon, Sask., Canada	0.13	2.77	21.0
4	4	Esquimalt, Vancouver Island, Canada	0.21	6.50	31.0
5	6	Fort Amidor Pier, Panama, C.Z.	0.28	7.10	25.2
6	8	Ottawa, Ontario, Canada	0.49	9.60	19.5
7	22	Miraflores, Panama, C.Z.	0.50	20.90	41.8
8	28	Cape Kennedy, $\frac{1}{2}$ mile from ocean	0.50	42.00	84.0
9	11	State College, Pa.	0.51	11.17	22.0
10	7	Morenci, Mich.	0.53	7.03	18.0
11	15	Middletown, Ohio	0.54	14.00	26.0
12	9	Potter County, Pa.	0.55	10.00	18.3
13	20	Bethlehem, Pa.	0.57	18.30	32.4
14	5	Detroit, Mich.	0.58	7.03	12.2
15	36	Point Reyes, Calif.	0.67	244.00	364.0
16	19	Trail, B.C., Canada	0.70	16.90	24.2
17	14	Durham, N.H.	0.70	13.30	19.0

18	13	Halifax (York Redoubt) N.S., Canada	0.70	12.97	18.5
19	18	South Bend, Pa.	0.78	16.20	20.8
20	27	East Chicago, Ind.	0.79	41.10	52.1
21	29	Brazos River, Texas	0.81	45.40	56.0
22	23	Monroeville, Pa.	0.84	23.80	28.4
23	34	Dayton Beach, Fla.	0.88	144.00	164.0
24	32	Kure Beach, N.C. (800 ft lot)	0.89	71.00	80.0
25	17	Columbus, Ohio	0.95	16.00	16.8
26	12	Montreal, Quebec, Canada	1.05	11.44	10.9
27	16	Pittsburgh, Pa.	1.14	14.90	13.1
28	10	Waterbury, Conn.	1.12	11.00	9.8
29	25	Limon Bay, Panama, C.Z.	1.17	30.30	25.9
30	21	Cleveland, Ohio	1.21	19.00	15.7
31	24	Newark, N.J.	1.63	24.70	15.1
32	33	Cape Kennedy (180 ft from ocean, 30 ft elevation)	1.77	80.20	45.5
33	35	Cape Kennedy (180 ft from ocean, ground level)	1.83	215.00	117.0
34	31	Cape Kennedy (180 ft from ocean, 60 ft elevation)	1.94	64.00	33.0
35	26	Bayonne, N.J.	2.11	37.70	17.9
36	37	Kure Beach, N.C. (80 ft lot)	2.80	260.00	93.0
37	30	Halifax (Federal Building) N.S., Canada	3.27	55.30	17.0

Source: Ref 1

Table 3 Properties of alloy layers of a hot dip galvanizing coating

Layer[(a)]	**Composition**	**Hardness, DPN**	**Iron, %**	**Melting Temperature**	
				°C	**°F**
Eta	Zn	70	0	454	850
Zeta	$FeZn_{13}$	179	6	530	986
Delta	$FeZn_7$	244	7-12	530-670	986-1238
Gamma	Fe_8Zn_{10}	. . .	21-28	670-780	1238-1436

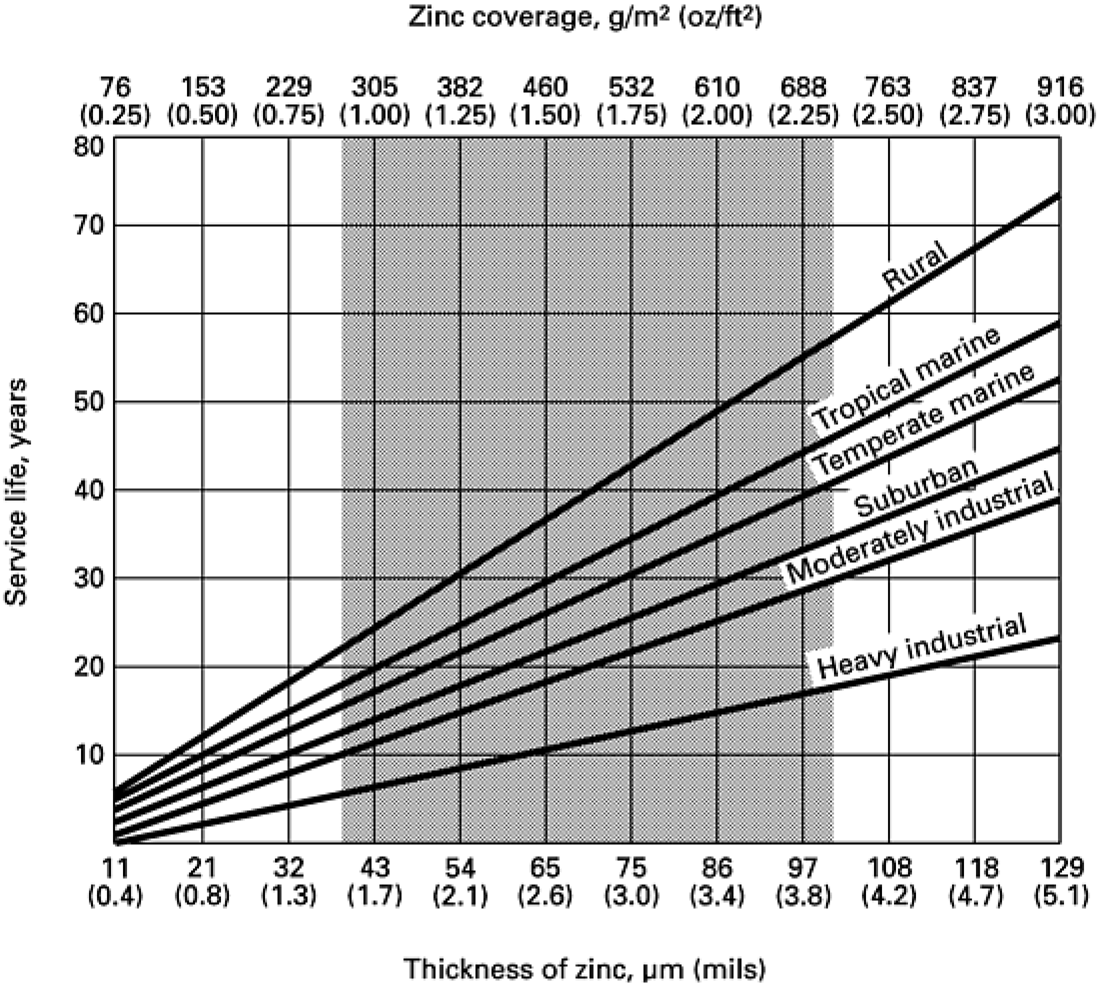
(a) See Fig. 1.

Hot dip galvanized zinc coatings have their longest life expectancy in rural areas where sulfur dioxide and other industrial pollutant concentrations are low (Fig. 2). These coatings also give satisfactory service in most marine environments (Table 4). Although the life expectancy of hot dip galvanized coatings in more severe industrial environments is not as long as for less aggressive environments, the coatings are still used extensively in those exposures, because in general, no more effective and economical method of protection is available. In cases involving particularly severe exposure conditions, coatings slightly heavier than the standard 710 g/m^2 (2.3 oz/ft^2) minimum in ASTM standard specifications A 123-89 or paint over galvanized coatings (known as duplex coatings) are often selected as the preferred protective system.

Table 4 Corrosion of zinc in different types of water

Water type	**Attacking substances**	**Passivating substances**	**Corrosion products**		**Relative corrosion rate**
			Solubility	**Adhesion**	
Hard water	O_2+CO_2	Ca+Mg	Very low	Very good	Very low
Sea water	O_2+CO_2+Cl	Mg+Ca	Low	Very good	Moderate
Soft water, with free air supply	O_2+CO_2	. . .	High	Good	High
Soft or distilled, with poor air supply	O_2	. . .	Very high	Very poor	Very high

Note: The different compositions of the corrosion products have not been included here because they are complex and depend on different compounds, salts, etc., that are present in all natural waters.



Atmosphere	**Description**
Heavy industrial atmospheres	These contain general industrial emissions such as sulfurous gases, corrosive mists, and fumes released from chemical plants and refineries. The most aggressive conditions are often found in places of intense industrial activity where the coating is frequently wetted by rain, snow, and other forms of condensation. In these areas, sulfur compounds can combine with atmospheric moisture to convert the normally adherent and insoluble zinc carbonates into zinc sulfite and zinc sulfate. These sulfur compounds are water soluble and adhere poorly to the zinc surface. They are removed by rain with relative ease, exposing a fresh zinc surface to additional corrosion. In general, zinc dissipates more when exposed to this type of environment than any other atmospheric environment. Still, the steel corrodes far more slowly in this type of environment when protected by zinc than when just bare steel is used.
Moderately industrial atmospheres	These environments are similar to those of heavy industrial atmospheric environments but, from the standpoint of corrosion, are not quite as aggressive. The amount of emissions in the air may be somewhat lower than that of heavy industrial environments, and/or the type of emissions may be less aggressive. Most city or urban area atmospheres are classified as moderately industrial.
Suburban atmospheres	These atmospheres are generally less corrosive than moderately industrial areas and, as the term suggests, are found in the largely residential, perimeter communities of urban or city areas.
Temperate marine	The length of service life of the galvanized coating in marine environments is influenced by proximity to the coastline and prevailing wind direction and intensity. In marine air, chlorides from sea spray can react with the

atmospheres	normally protective, initial corrosion products to form soluble zinc chlorides. When these chlorides are washed away, fresh zinc is exposed to corrosion. Nevertheless, temperate marine atmospheres are usually less corrosive than suburban atmospheres.
Tropical marine atmospheres	These environments are similar to temperate marine atmospheres except they are found in warmer climates. Possibly because many tropical areas are found relatively far removed from heavy industrial or even moderately industrial areas, tropical marine climates tend to be somewhat less corrosive than temperate marine climates.
Rural atmospheres	These are usually the least aggressive of the six atmospheric types. This is primarily due to the relatively low level of sulfur and other emissions found in such environments.

Fig. 2 Service life (time to 5% rusting of steel surface) versus thickness of zinc for selected atmospheres. Shaded area is thickness range based on minimum thicknesses for all grades, classes, etc., encompassed by ASTM A 123 and A 153. Source: Ref 2

When hot dip galvanized after-fabrication coatings are painted for protective or decorative reasons, a variety of surface preparation systems may be employed to prepare the galvanized surface for the top coat system. Table 5 shows the adhesion of paints to variously prepared galvanized surfaces. A wide range of proprietary top coat systems are available for use with materials hot dip galvanized after fabrication.

Table 5 Adhesion of air-drying paints applied to selected hot dip galvanized steel surfaces

Adhesion as determined by cross-hatch or V-cut test: E, excellent; G, good; F, fair; P, poor. See Table 9 for other characteristics of these paints.

Type of paint (vehicle base)	**Adhesion on indicated surface**			
	Freshly galvanized[(a)]	**Weathered galvanized**[(b)]	**Cold or hot phosphated**	**Sweep-blasted and galvanized**
1. Alkyd-tung oil-phenolic resin combinations[(c)]	F	G	E	E
2. DCO-alkyd-calcium plumbate[(d)]	E	E	E	E
3. Alkyd-acrylic combinations	G	G	E	E
4. Chlorinated rubber	F-G	F-G	G	E
5. Chlorinated rubber-acrylic combinations	G	G	E	E
6. Acrylate dispersions[(e)]	F-G	F-G	G	G
7. Acrylic-styrene dispersions[(e)]	G	G	G	E
8. Acrylic/diisocyanate (2 compositions)	G	F	G	E
9. Vinyl copolymers	F-G	F-G	G	G

10. PVC/acrylic combinations	G	G	E	E
11. PVC-dispersions(e)	F	F-G	G	F-G
12. Epoxy resin (2 compositions)(f)	G	G	G	E
13. Epoxy ester(g)	P	F	G	G
14. Epoxy/tar (2 compositions)	P	F	F	G
15. Polyurethane (2 compositions)(h)	P	F	F-G	G

Note: Variations in film properties may occur with variations in formulation.

Source: Ref 3

(a) Up to about 4 h after galvanizing.

(b) Weathered in an unpolluted or mildly polluted climate, for 1 to 3 months only.

(c) Precooked tung oil/alkylphenolic resin combinations, chilled with drying-oil-modified alkyd resins.

(d) Dehydrated castor oil (DCO)-modified alkyd resin, pigmented with calcium orthoplumbate (COP) as main pigment in the priming coat.

(e) Finely dispersed polymers in water.

(f) With polyamide hardener.

(g) Epoxy resin-dehydrated castor oil ester.

(h) With encapsulated diisocyanate hardener.

Galvanized steels perform well in contact with a wide variety of other materials (Table 6). Moisture conditions play an important role in the performance of galvanized steels in contact with other materials.

Table 6 Additional corrosion of zinc and galvanized steel resulting from contact with other metals

0, Either no additional corrosion, or at the most only very slight additional corrosion; usually tolerable in service. 1, Slight or moderate additional corrosion; may be tolerable in some circumstances. 2, Fairly severe additional corrosion; protective measures will usually be necessary. 3, Severe additional corrosion; contact should be avoided.

Metal in contact	**Environment**

	Atmospheric			**Immersed**	
	Rural	**Industrial/urban**	**Marine**	**Fresh water**	**Sea water**
Aluminum and aluminum alloys	0	0 to 1	0 to 1	1	1 to 2
Aluminum bronzes and silicon bronzes	0 to 1	1	1 to 2	1 to 2	2 to 3
Brasses, including high-tensile-strength brass (manganese bronze)	0 to 1	1	0 to 2	1 to 2	2 to 3
Cadmium	0	0	0	0	0
Cast irons	0 to 1	1	1 to 2	1 to 2	2 to 3
Cast iron (austenitic)	0 to 1	1	1 to 2	1 to 2	1 to 3
Chromium	0 to 1	1 to 2	1 to 2	1 to 2	2 to 3
Copper	0 to 1	1 to 2	1 to 2	1 to 2	2 to 3
Copper-nickels	0 to 1	0 to 1	1 to 2	1 to 2	2 to 3
Gold	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Gun metals, phosphor bronzes, and tin bronzes	0 to 1	1	1 to 2	1 to 2	2 to 3
Lead	0	0 to 1	0 to 1	0 to 2	(0 to 2)
Magnesium and magnesium alloys	0	0	0	0	0
Nickel	0 to 1	1	1 to 2	1 to 2	2 to 3
Nickel-copper alloys	0 to 1	1	1 to 2	1 to 2	2 to 3
Nickel-chromium-iron alloys	(0 to 1)	(1)	(1 to 2)	(1 to 2)	(1 to 3)
Nickel-chromium-molybdenum alloys	(0 to 1)	(1)	(1 to 2)	(1 to 2)	(1 to 3)

Nickel silvers	0 to 1	1	1 to 2	1 to 2	1 to 3
Platinum	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Rhodium	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Silver	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Solders, hard	0 to 1	1	1 to 2	1 to 2	2 to 3
Solders, soft	0	0	0	0	0
Stainless steel (austenitic and other grades containing approximately 18% Cr)	0 to 1	0 to 1	0 to 1	0 to 2	1 to 2
Stainless steel (martensitic grades containing approximately 13% Cr)	0 to 1	0 to 1	0 to 1	0 to 2	1 to 2
Steels (carbon and low-alloy)	0 to 1	1	1 to 2	1 to 2	1 to 2
Tin	0	0 to 1	1	1	1 to 2
Titanium and titanium alloys	(0 to 1)	(1)	(1 to 2)	(0 to 2)	(1 to 3)

Notes: Ratings in parentheses are based on very limited evidence and hence are less certain than other values shown. Values are in terms of additional corrosion, and the symbol 0 should not be taken to imply that the metals in contact need no protection under all conditions of exposure.

Source: Ref 2

Galvanized surfaces have a good tolerance to various chemicals within the range of 4 to 12.5 pH (Fig. 3). Some chemicals that have been successfully stored in galvanized containers are listed in Table 7.

Table 7 Selected chemicals that have been successfully stored in galvanized containers

Hydrocarbons Benzene (benzole) Toluene (toluole) Xylene (xylole) Cyclohexene Petroleum ethers Heavy naphtha

Solvent naphtha

Alcohols

Methyl parafynol (methyl pentynol)
Morpholinoisopropanol
Glycerol (glycerin)

Halides

Carbon tetrachloride
Amyl bromide
Butyl bromide
Butyl chloride
Cyclohexyl bromide
Ethyl bromide
Propyl bromide
Propyl chloride
Trimethylene bromide (1, 3-dibromopropane)
Bromobenzene
Chlorobenzene
Aroclors and pyroclors (chlorobiphenyls)

Nitriles (cyanides)

Diphenylacetonitrile
p-chlorobenzglycyanide

Esters

Allyl butyrate
Allyl caproate
Allyl formate
Allyl propionate
Ethyl butyrate
Ethyl isobutyrate
Ethyl caproate
Ethyl caprylate
Ethyl propionate
Ethyl succinate
Amyl butyrate
Amyl isobutyrate
Amyl caproate
Amyl caprylate
Methyl butyrate
Methyl caproate

Methyl propionate
Methyl succinate
Benzyl butyrate
Benzyl isobutyrate
Benzyl propionate
Benzyl succinate
Octyl butyrate
Octyl caproate
Butyl butyrate
Butyl isobutyrate
Butyl caproate
Butyl propionate
Butyl succinate
Butyl titanate(a)
Propyl butyrate
Propyl isobutyrate
Propyl caproate
Propyl formate
Propyl propionate
Isobutyl butyrate
Isobutyl caproate
Isopropyl benzoate
Isopropyl caproate
Isopropyl formate
Isopropyl propionate
Cyclohexyl butyrate

Phenols

Phenol
Cresols (methylphenols)
Xylenols (dimethylphenols)
Biphenol (dihydroxybiphenyl)
2,4-dichlorophenol
p-chloro-o-cresol
Chloroxylenols

Amines and Amine salts

Pyridine
Pyrrolidine
Methylpiperazine
Dicarbethoxypiperazine
1-benzhydryl-4-methylpiperazine
2,4-diamino-5-(4-chlorphenyl-6-)ethylpyrimidine
Hydroxyethylmorpholine (hydroxyethyldiethylenimide oxide)
p-aminobenzenesulphonyl-guanidine
Butylamine oleate
Piperazine hydrochloride monohydrate
Carbethoxypiperazine hydrochloride (dry)

Amides
Formamide Dimethylformamide

Miscellaneous
Glucose (liquid) Benzilideneacetone p-chlorbenzophenone Sodium azobenzenesulphonate Melamine resin solutions Crude cascara extract Creosote

Source: Ref 2

(a) And other unspecified titanates.

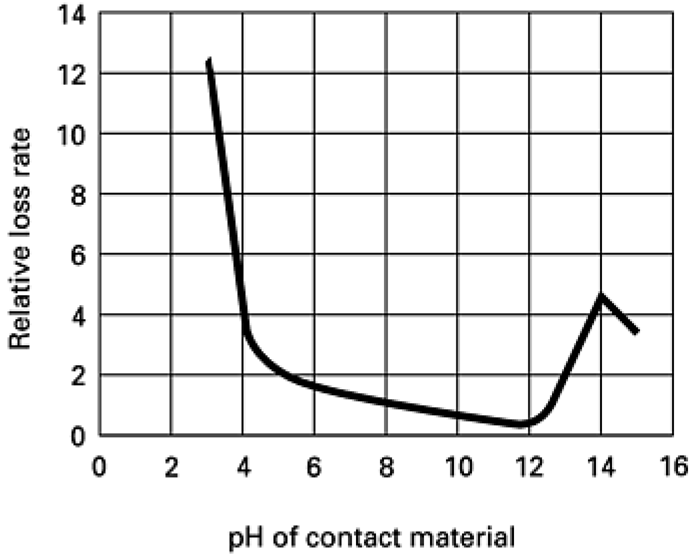


Fig. 3 Effect of pH on corrosion of zinc. Source: Ref 1

References cited in this section

1. *Galvanizing for Corrosion Protection: A Specifier's Guide to Bridge and Highway Applications,* American Galvanizers Association, 1992
2. *Hot Dip Galvanizing for Corrosion Protection of Steel Products,* American Galvanizers Association, 1989
3. Frank Porter, *Zinc Handbook: Properties, Processing, and Use in Design,* International Lead Zinc Research Organization, 1991

Metallurgical Characteristics of Galvanized Coatings

Iron and Steel Substrates. The chemical composition of irons and steels, and even the form in which certain elements such as carbon and silicon are present, determines the suitability of ferrous metals for hot dip galvanizing and may markedly influence the appearance and properties of the coating. Steels that contain less than 0.25% C, less than 0.05% P, less than 1.35% Mn, and less than 0.05% Si, individually or in combination, are generally suitable for galvanizing using conventional techniques. The results of a recent study suggest that a silicon level of 0.15% to 0.25% should also produce acceptable results. Another study suggests that optimum amounts of silicon and phosphorus can be defined by the formula $\%Si + 2.5(\%P) = 0.09$.

To avoid brittleness of the iron-zinc alloy layer in cast iron materials, substrate iron must be low in phosphorus and silicon; a preferred composition may contain about 0.01% P and about 0.15% Si.

Type of Zinc. Any grade of zinc in ASTM B 6-87(92) can be used in galvanizing. ASTM A 123-89 now stipulates that the zinc being used for galvanizing must contain 98% pure zinc. The remaining 2% may be such other elements as desired to produce an optimum coating. ASTM A 123 does not require prime western zinc, but some other galvanizing specifications do. Most galvanizers use either prime western (98.0% Zn) or high grade (99.90% Zn). Prime western has a lead alloy content of 0.5 to 1.4%, which is beneficial for hot dip galvanizing, and higher allowed levels of iron and other elements as impurities. When high grade zinc is used, lead is often added separately to the kettle. During galvanizing, there is a buildup of iron in the bath caused by dissolution of iron from the surface of steel work and the tank walls so that the equilibrium iron content of the bath is nearly equal regardless of the grade of zinc used. High purity special high grade (99.99% Zn) zinc coatings have the same metallurgical properties as those obtained with prime western zinc. High purity zinc has little metallurgical advantage for use on fabricated items.

Bath Alloying Elements. Cadmium and iron are usually present in zinc baths as contaminants, but are not intentionally added to the bath as alloying elements. An aluminum concentration up to 0.01% will improve drainage and increase the brightness of the galvanized coating. Small amounts of lead may be added to promote proper spangle and better drainage and to aid with drossing the bath. Other alloying elements have been tried with success. Nickel, vanadium, antimony, titanium, and rare earth metals are known to produce positive results under some circumstances.

An aluminum concentration less than 0.01% is generally maintained in the zinc bath when a preflux and/or a bath flux are used. The high chloride content of the fluxes reacts with the aluminum in the bath, producing a surface film of dross, oxide, and chloride on the bath surface.

Coating Thickness. In addition to base metal chemistry and surface profile, the thickness of coatings applied by hot dipping is primarily a function of:

- The duration of immersion, which controls the thickness of alloy layer (Fig. 4)
- The speed of withdrawal from the bath, which controls the amount of unalloyed zinc adhering (Fig. 5)
- The temperature of the bath, which affects both the alloy and the free zinc layers (Fig. 6)

Coating weight can be further affected by the amount of zinc removed by wiping, shaking, or centrifuging after the dipping process.

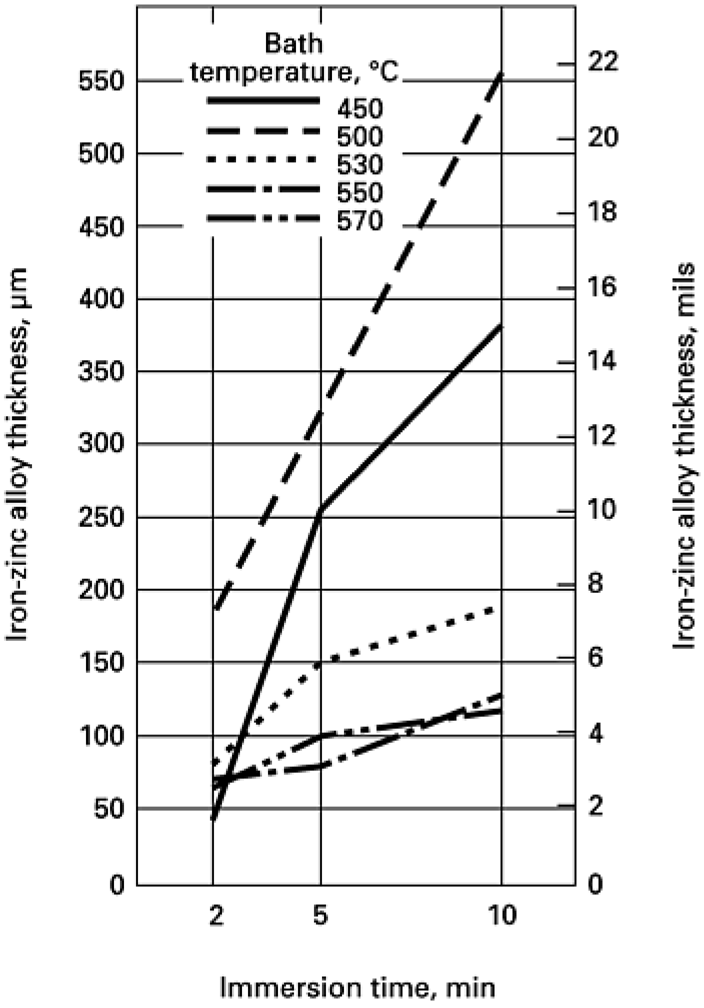


Fig. 4 Coating thickness versus immersion time for a typical silicon-killed steel galvanized at various temperatures. Source: Ref 4

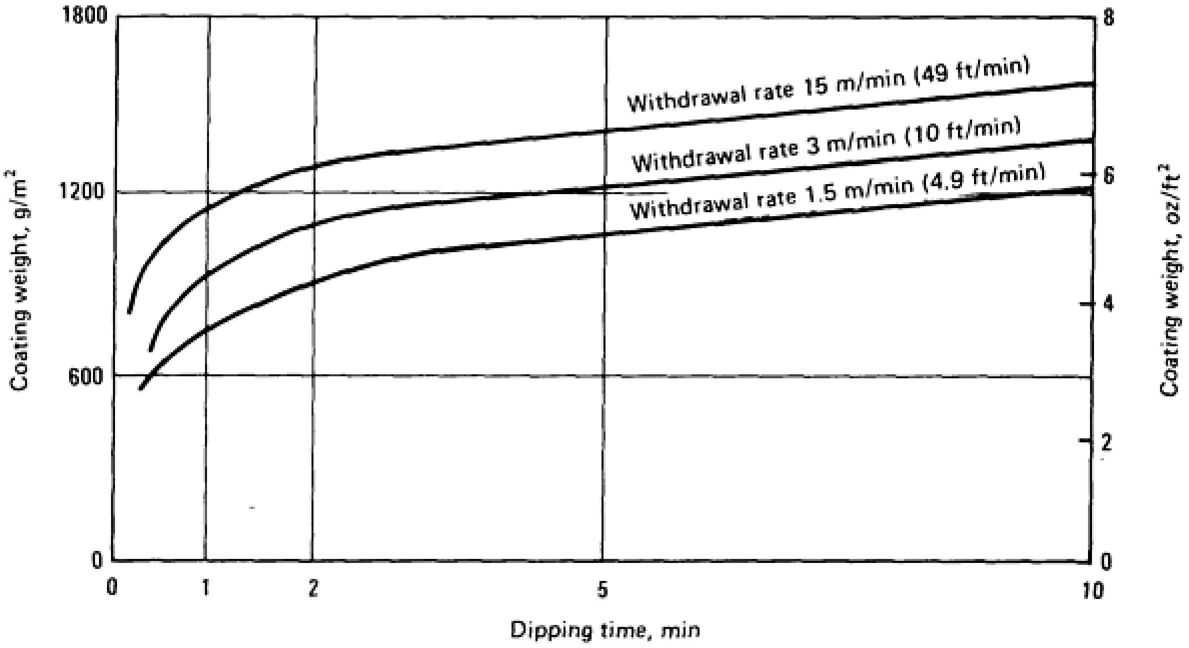


Fig. 5 Effect of withdrawal rate on weight of galvanized coatings. Bath temperature, 435 °C (815 °F)

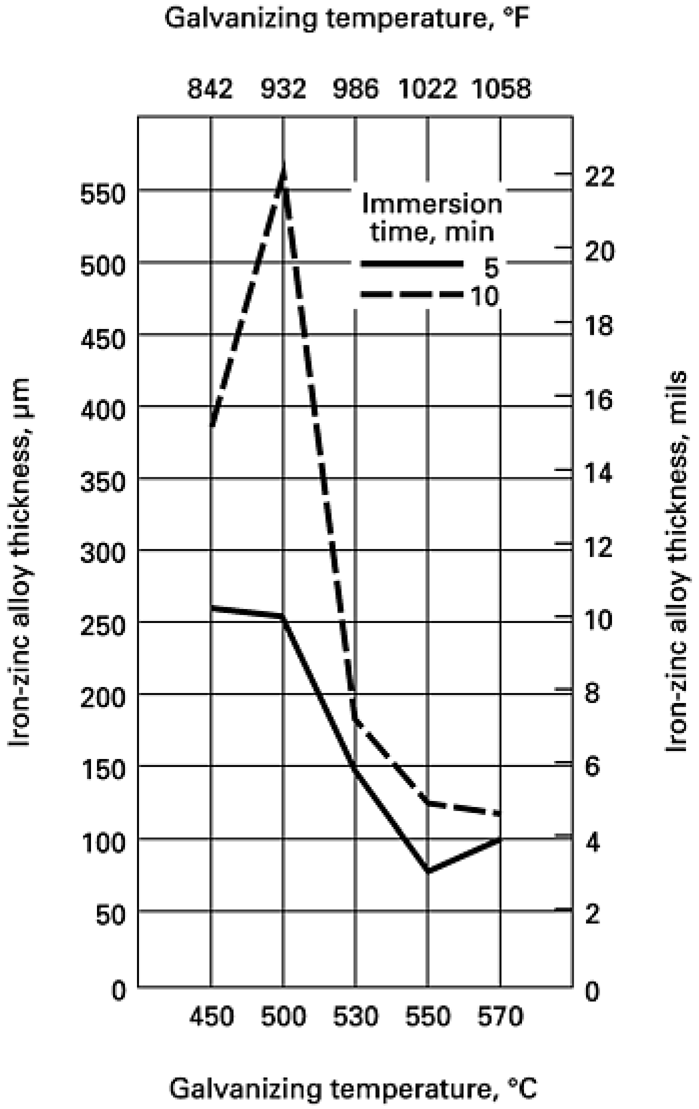


Fig. 6 Coating thickness versus galvanizing temperature for a typical silicon-killed steel at two different immersion times. Source: Ref 4

The protection against corrosion provided by zinc coatings is essentially determined by the thickness of the coating (Fig. 2). Many comprehensive studies have shown that all other factors, such as method of applying the zinc coating, purity of the zinc, and the extent to which it is alloyed with the iron, are minor in determining life, as compared with the thickness of the coating.

Zinc coatings applied by hot dipping after fabrication are measured in mils of zinc on the surface. However, the weight of galvanized coatings on sheet is stated in ounces per square foot (grams per square meter) of sheet. Since the sheet is coated on both sides, the coating weight per square foot (meter) of surface on each side is approximately one half the average weight of coating per square foot (grams per square meter) of sheet. ASTM A 123 and A 153 give coating weight requirements as a function of thickness and type of material to be coated.

Reference cited in this section

4. Richard Amistadi, *Very High Temperature Galvanizing,* St. Joe Minerals Corporation (now Zinc Corporation

of America), 1974

Effect of Galvanizing Process on Substrate Materials

Tensile Strength, Impact Toughness, and Formability. The tensile strength, yield strength, elongation at rupture, and reduction of area of hot rolled steels remain virtually unchanged after hot dip galvanizing. A study by BNF Technologies, Oxfordshire, England, indicates that, in welded structures, the weld stresses may be reduced by 50 to 60% as a result of hot dip galvanizing. Increased strength levels induced by cold working or heat treatment are generally reduced by hot dip galvanizing. The degree of strength reduction depends on such factors as the amount of working, the nature of heat treatment, and base steel chemistry. Impact toughness is slightly reduced, but not so much that the applicability of the steel is affected.

The formability of the steel is not affected. However, if the steel is sharply bent, the zinc coating may craze or crack on the tension side of the bend, depending on thickness of coating and bend radius.

Fatigue strength of various types of steels is affected differently as a result of the hot dip galvanizing process. Rimmed and aluminum-killed steels exhibit relatively little reduction of fatigue strength, whereas the fatigue strength of silicon-killed steels can be reduced considerably by hot dip galvanizing.

The reason for this difference in fatigue strength for silicon-killed steels is attributable to the different structure of the coating (Fig. 7). Under the influence of fatigue stresses, cracks may form in the iron-zinc layer and act as crack initiators in the steel surface.

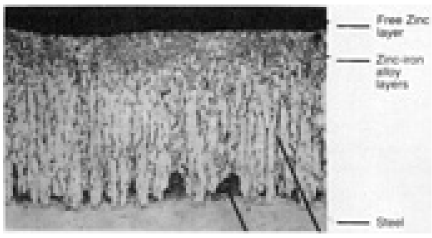


Fig. 7 Photomicrograph of a galvanized coating on a steel containing 0.40% Si. 250×

Fatigue strength is typically determined by laboratory tests where untreated new steels with mill scale are compared with hot dip galvanized material. If a steel structure is exposed outdoors in the untreated state, it is immediately attacked by rust. The corrosion pits that form result in a loss in fatigue strength. Thus, under in-service exposure conditions, the fatigue strength of ungalvanized steel declines rapidly as a result of the rust attack that occurs at the point of damage. For hot dip galvanized steels, however, the fatigue strength of the steel does not appreciably change during the exposure period as long as the zinc coating remains on the steel surface.

Hydrogen embrittlement does not result from the hot dip galvanizing of ordinary unalloyed and low-carbon mild steels. Any hydrogen absorbed during pickling is effectively eliminated on immersion in the zinc bath because of the relatively high temperature of about 460 °C (860 °F). Hardened steels can become brittle because of hydrogen diffusion into the steel. Such materials should always be tested for embrittlement after pickling before large lots are hot dip galvanized.

Intergranular cracking because of the penetration of zinc into the grain boundaries in steel can sometimes occur in connection with hot dip galvanizing, but only in cases where large stresses have been induced in the steel by welding or hardening. The risk of intergranular cracks and embrittlement failure because of zinc penetration is negligible in connection with hot dip galvanizing of ordinary low-carbon structural steels. However, hardened materials may be sensitive and should be tested for susceptibility to zinc penetration and cracking before hot dip galvanizing on large quantities of material is undertaken.

Cleaning Before Galvanizing

Iron and steel pieces to be hot dip galvanized after fabrication must be free of oil, grease, drawing lubricants, mill scale, and other surface contaminants before fluxing and immersion in molten zinc. Inadequate or improper surface preparation is the most frequent cause of defects and bare spots in galvanized coatings.

In batch hot dip galvanizing, the material to be galvanized is first degreased and then pickled in sulfuric or hydrochloric acid. Since any iron salts or particles left on the surface of the material form dross in the galvanizing kettle, each of the degreasing and pickling steps is followed by a water rinse.

Degreasing. Organic contaminants can be removed from the work by several methods. The most common of these in the after-fabrication hot dip galvanizing process is the use of heated alkaline cleaning baths. The alkaline cleaning process performs five basic functions.

- Dispersion by washing soil from the work
- Emulsification by breaking up the soil and suspending it in solution
- Film shrinkage by forming beads of oil to remove oil films
- Saponification by converting animal and vegetable oils to water-soluble soaps
- Aggregation by collecting soil particles away from the work where they can be more easily removed from the solution

The alkaline cleaning solutions should be heated to between 65 to 82 °C (150 to 180 °F).

Control of the strength of the heated alkaline solution is essential to an effective degreasing operation. These solutions lose strength because of chemical cleaning action effects and are diluted by make-up water added to replace dragout losses. Although experience can be a good indicator of cleaning solution activity, a better method is to test the alkaline solution periodically for strength and to make periodic additions to maintain the solution at the desired concentration. See the article "Alkaline Cleaning" in this Volume for additional information.

Acid Pickling. Aqueous solutions of sulfuric acid or hydrochloric acid are generally used to remove mill scale and rust from steel parts before galvanizing. These pickling solutions may either be sulfuric acid, 3 to 14 wt%, or hydrochloric acid, 5 to 15 wt%. To increase effectiveness, sulfuric acid solutions are always used hot at 60 to 79 °C (140 to 175 °F); hydrochloric acid solutions are usually used at about room temperature, 24 to 38 °C (75 to 100 °F), to avoid excessive fuming. To avoid overpickling, inhibitors are often used with both sulfuric and hydrochloric acid solutions.

Nitric acid pickling, although rarely used, may be employed for removing silicates from malleable and gray iron castings. Silicates are insoluble in hydrochloric or sulfuric acid.

Wetting and/or foaming agents may be added to the acid solutions to promote better drainage of acids and to minimize heat loss of hot solutions.

Abrasive Cleaning. Some assemblies are made up of both cast and wrought materials; these assemblies require additional surface preparation prior to fluxing and galvanizing. All assemblies of cast iron, cast steel, and malleable iron with wrought steel should be abrasively cleaned after assembly and before pickling. Many other parts may also be abrasively cleaned to minimize or eliminate pickling.

In general, cast materials require less pickling than hot-rolled steel products, unless scale is removed from steel by blast cleaning. Therefore, care must be exercised to avoid burning or damaging the castings in an assembly during the time required to pickle the hot rolled components.

General Batch Galvanizing Procedures

Wet and Dry Galvanizing. Two types of conventional batch galvanizing practices currently in use are the wet process and the dry process. Dry galvanizing was developed and refined in Europe. Recent surveys indicate that 40% of galvanizing operations in North America are wet and the remaining 60% dry. The dry process is generally considered to be less energy intensive than the wet process, but it is more sensitive to surface preparation deficiencies.

Wet galvanizing involves a kettle-top flux blanket; dry galvanizing uses a preflux, and no flux blanket on the kettle. Sulfuric or hydrochloric acid pickling can be used with either wet or dry galvanizing. The choice is primarily based on disposal and reprocessing costs for the acids.

In the dry galvanizing process, after the material is degreased and pickled, the workpieces are immersed in an aqueous flux solution, dried, and then immersed in the molten zinc bath. In the wet galvanizing process, the work is not usually prefluxed after cleaning and pickling but is placed in the molten zinc bath through a top flux blanket on the kettle. However, an aqueous preflux may be used in conjunction with a top flux on the zinc bath.

Workpieces are handled either mechanically, using overhead hoists, or with hand tools. Small items such as washers, fasteners, and nails are handled in baskets. The baskets are usually centrifuged as the work leaves the molten zinc bath to remove excess zinc and to distribute the coating evenly. In all cases, workpieces must be handled properly until the coating has completely solidified, which is accomplished by either quenching or air cooling.

Surface Conditioning Requirements. Although degreasing, pickling, water rinsing, and other cleaning procedures remove most of the surface contamination and scale from iron and steel, small amounts of impurities in the form of oxides, chlorides, sulfates, and sulfides are retained. Unless removed, these impurities will interfere with the iron-zinc reaction when the iron or steel part is immersed in molten zinc.

In the wet galvanizing process, a flux blanket on the surface of the molten zinc bath is used to remove these impurities and to keep that portion of the surface of the zinc bath through which the steel is immersed free from oxides. The flux blanket floats on the surface, and when workpieces are immersed in the bath, their surfaces are wetted by the molten flux. The flux must have sufficient chemical stability to maintain a chemically active foam at the galvanizing temperature and to perform its cleaning function at a high rate of speed.

Zinc ammonium chloride is generally used to provide a flux blanket on the molten zinc bath. There are several procedures for preparing the flux blanket. One generic method consists of mixing ammonium chloride (sal ammoniac) and zinc oxide to form the monoamine of zinc chloride. In the ensuing reaction, hydrogen and nitrogen are released, and the flux takes the form of a foam. Today, most commercial kettles are operated using premixed fluxes, which can be obtained from a variety of suppliers.

To be fully effective and to attain minimal fume galvanizing conditions, the flux should not contain an excess of ammonium chloride. To prevent abnormally rapid chemical breakdown of the flux, glycerin and other organic substances are added to the flux in small amounts of 1 to 2 vol%. These substances increase the foaming action, markedly reduce the loss of ammonia, and serve as insulators. Because the boiling point of a mixture of zinc chloride and ammonium chloride decreases as the ammonium chloride content increases (Fig. 8), no more than 2 to 3% ammonium chloride will remain in the molten salt solution at a kettle temperature of 455 °C (850 °F). However, to function effectively, a zinc chloride-ammonium chloride top flux must normally contain more than 5 to 10% dissolved ammonium chloride. To minimize fuming, it is necessary to reduce the top flux surface temperature, maintain an optimal level of dissolved ammonium chloride, and to disturb this equilibrium as little as possible.

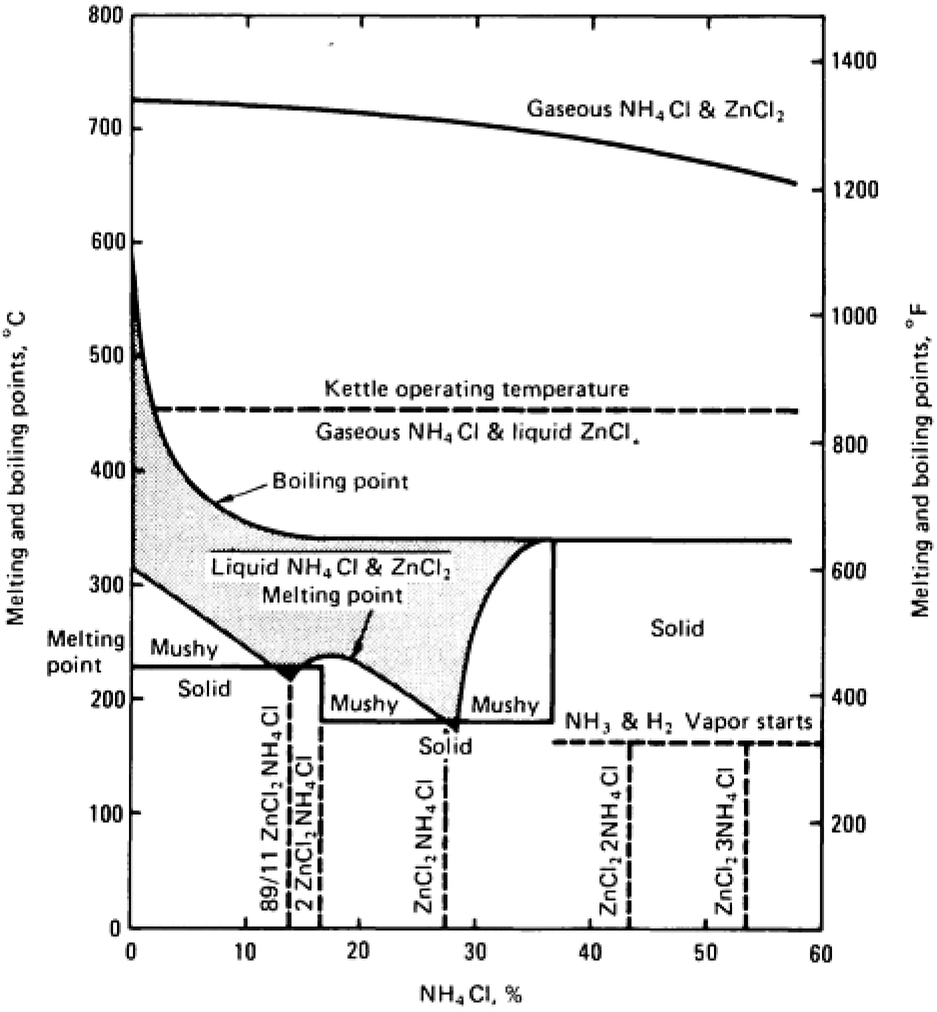


Fig. 8 Zinc chloride and ammonium chloride phase diagram

For dry galvanizing, it was once common practice to take the work directly from the hydrochloric acid pickle, dry it, and then put it in the molten zinc. However, the practice of going from the pickle tank to drying and then to the molten zinc produces more dross than the procedures of rinsing, prefluxing, and drying.

A preferred method, widely used today, is to pickle, rinse, flux in an aqueous zinc ammonium chloride, dry, and dip in the molten zinc bath. By using a preflux step, better control of the fluxing is possible, resulting in a more consistent finish. Also, the material may be held for about 1 h before dipping, which gives the galvanizer some flexibility in work flow on the galvanizing line.

Galvanizing Bath. The molten zinc bath is operated at temperatures usually in the range of 445 to 454 °C (830 to 850 °F). At 480 °C (900 °F) and above, the dissolution rate of iron and steel in zinc is extremely rapid, and the effects of these temperatures on both workpiece and galvanizing tank are generally harmful. Within the conventional galvanizing temperature range, an increase in temperature:

- Increases the fluidity of molten zinc
- Accelerates the formation of oxides on the bath surface
- Heats the part to a higher temperature, thus increasing the time required for the zinc to solidify when the part is withdrawn
- Reduces immersion time, thereby increasing the kettle utilization factor

Each of these considerations has a distinct effect and may be used to control the galvanizing process.

An increase in the fluidity of the bath improves drainage and is desirable provided the bath temperature does not exceed the normal operating range. An increase in bath temperature produces a much sharper temperature gradient from the surface to the center of the part, which depending on shape may result in an increase in distortion.

Unless the bath contains aluminum or unless its surface is well protected by a foam blanket of flux, an increase in bath temperature will accelerate the formation of an oxide film (or ash) on the surface of the bath. Some of this oxide film may cling to the workpiece when it is withdrawn from the bath, interfering with drainage and contributing to the formation of a coating with less desirable aesthetic properties. The effects of these oxides are most apparent on parts of thin cross section and large surface area.

Depending on the chemical composition of the iron or steel, the bath temperature may have significant metallurgical effects on the galvanized coating. The temperature at which the iron-zinc alloy layers are formed affects the relative amounts of each iron-zinc phase formed and the depth or total thickness of alloy layer (Fig. 4).

In the hot dip galvanizing of fabricated articles, the thickness of the coating is controlled by immersion time. Although timing is to some extent dependent on ease of handling and must be established by trial for each design of part being coated, the duration of immersion is usually in the range of 3 to 6 min. The speed of immersion influences the uniformity of the coating, particularly with long articles for which the difference in immersion time between the first and last areas to enter the bath may be considerable.

The reaction between clean low silicon steel and molten zinc proceeds rapidly for the first 1 or 2 min after the work has been immersed, producing an alloy layer that continues to grow at decreased rate the longer the article is left in the bath. However, for steels containing silicon in excess of 0.05%, the coating weight increases linearly with respect to the time of immersion producing, in general, heavier coatings (Fig. 9) Therefore, it is important to minimize immersion time for silicon-bearing steels to prevent excessive alloy growth and coating weight.

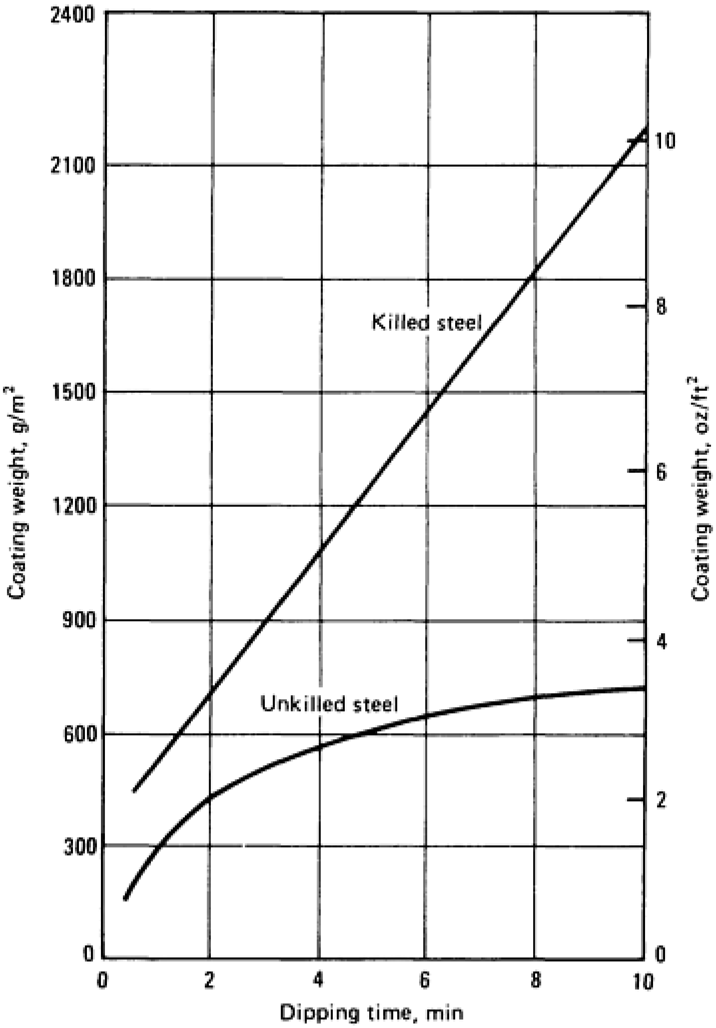


Fig. 9 Effect of immersion time on galvanized coating weight for killed and unkilled steels. Galvanizing temperature, 455 °C (850 °F). Killed steel: 0.35% C, 0.26% Si, 0.46% Mn. Unkilled steel: 0.13% C, trace Si, 0.40% Mn

To provide a uniform coating of minimum thickness, work that is not subsequently to be centrifuged is withdrawn from the bath slowly and at a controlled rate, thus permitting maximum drainage. Two-speed hoists are usually employed, permitting the work to be immersed rapidly and withdrawn slowly. The rate of withdrawal, which partially determines the thickness of the unalloyed zinc layer left on the work (Fig. 5), varies according to the type of process being operated. The optimum withdrawal rate for most articles is about 1.5 m/min (5 ft/min).

With long articles, for which the withdrawal occupies a large part of the total cycle time, higher speeds may be necessary to maintain a reasonable rate of production. If possible, however, it is better to overcome this difficulty by using special jigs and carriers for dipping and withdrawing the work in batches. Provided the work is not withdrawn faster than the rate at which the zinc drains freely from the surface, the unalloyed zinc layer of the coating is uniformly distributed. With faster rates of withdrawal, the surplus zinc carried clear of the bath runs down the surface until it solidifies, and the resultant coating may be lumpy and uneven.

When withdrawal from the bath at a slow controlled rate of speed is not feasible or economical, as it generally is not for small parts, the withdrawal rate may be greatly increased, and drainage is accomplished by spinning the parts in a basket. The excess zinc is drained from the parts by centrifugal force. Mechanically wiping the excess zinc from the parts with tools designed for this purpose is an alternative method of forced drainage.

Cooling. Because of retained heat, the iron-zinc reactions can continue to occur even after the surface layer of zinc has frozen. This type of post-immersion reaction may occur if cooling is hindered by the stacking of parts in close proximity and by the heat capacity of the part. Some or all of the pure zinc layer may be converted to iron-zinc alloy, thus darkening the surface and altering its properties. Very slow cooling or holding of the material at temperatures over 190 °C (375 °F) may cause small voids in the coating due to interdiffusion between the coating and the base metal. The problem, known as the Kirkendall effect, may result in peeling failure of the coating.

To avoid delayed cooling, parts should be spaced adequately after immersion to permit the free circulation of air. Parts with large cross-sectional areas or parts fabricated of silicon-bearing steel may require forced cooling with air or water.

Galvanizing of Silicon-Killed Steels. The difficulties encountered in galvanizing silicon-bearing steels have been noted under the preceding discussions on conventional galvanizing practice. Many techniques have been studied in an effort to find a better way to control the iron-zinc reaction kinetics in the presence of silicon, none of which has proven to be fully acceptable over the silicon content ranges commonly being encountered. At temperatures not exceeding 460 °C (860 °F), aluminum additions of 0.02 to 0.04% to the bath may be of advantage for steels containing up to 0.05% Si. The most common method has been to use conventional techniques at a temperature not exceeding 440 °C (825 °F) coupled with a short immersion time. For light structural shapes, this is possible without any additional measures. Heavy structural shapes require preheating to reduce the immersion time to an acceptable level.

However, three technologies developed during the 1970s permit better control to be maintained in the galvanizing at reactive temperatures of silicon-bearing steels. One is a patented process using the zinc alloy Polygalva for galvanizing. The second is by galvanizing at high temperatures, 550 °C (1020 °F), instead of the temperatures used for the conventional process, 450 °C (840 °F). The third uses small amounts of nickel in the bath. All three methods are used to some extent in Europe. Polygalva is not available in North America, but the other two methods have seen limited use. Several North American galvanizers use the nickel addition method, and at least one uses the high-temperature method.

Polygalva Process. Polygalva is essentially a zinc alloy containing controlled amounts of aluminum, magnesium, tin, and lead. The aluminum is used to retard the formation of the intermetallic layer, and the other elements help to ensure continuity of the galvanized coating. As with the conventional process, thorough surface preparation prior to galvanizing is essential for good results and must include the following steps unless otherwise indicated:

- Degrease in an alkaline bath heated to 80 to 90 °C (176 to 194 °F)
- Rinse in running water
- Pickle in 50% hydrochloric acid with inhibitor
- Rinse in running water
- Pickle in 70% hydrochloric acid without inhibitor (in most situations this step is optional)

Routine maintenance of pretreatment facilities is important.

Also, a weekly zinc bath chemical analysis is required to ensure that the alloy composition is being maintained within the working range. During galvanizing operations, two master alloys are added to the bath to compensate for losses of aluminum and magnesium. By doing this, proper alloy balance is reportedly readily maintained.

As shown in Fig. 10, Polygalva is most effective in galvanizing steels with silicon in the range of 0.05 to 0.20%. Comparative micrographs of a steel with 0.08% silicon galvanized using conventional and Polygalva techniques are shown in Fig. 11. Above 0.20% Si, the Polygalva alloy reportedly loses at least part of its effectiveness.

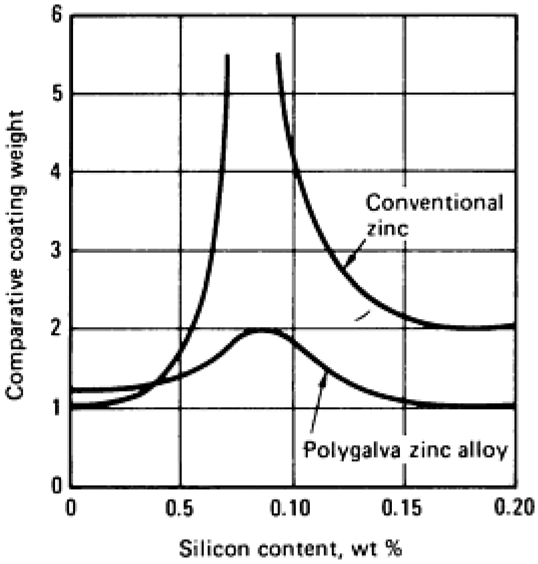


Fig. 10 Comparison of coating weight as a function of silicon content for conventional and Polygalva galvanizing processes

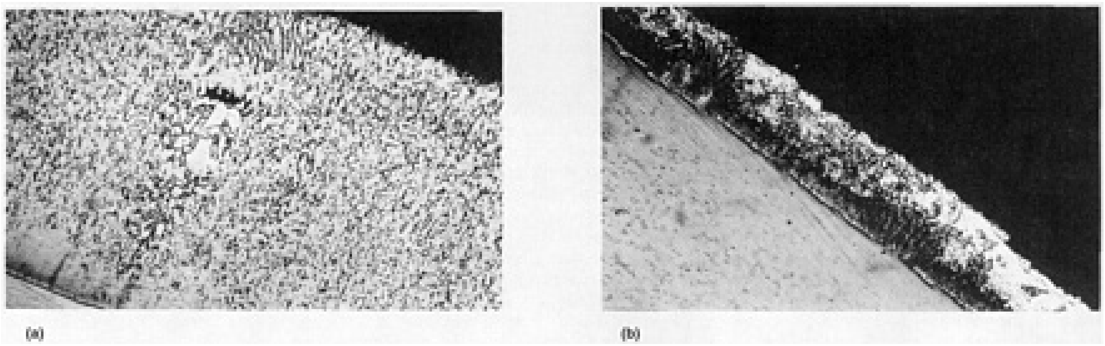


Fig. 11 Micrographs of a silicon-bearing steel (0.08% Si) galvanized (a) in a conventional bath and (b) in a Polygalva bath

High-Temperature Galvanizing. It has been found that when galvanizing is performed at a temperature of approximately 550 to 560 °C (1020 to 1040 °F), a coating weight to immersion time relationship is obtained for silicon-bearing steels which is much less sensitive than at conventional galvanizing temperatures (Fig. 6). The effect of immersion time at elevated galvanizing temperatures is shown in Fig. 12; the coating weight increases at a rate less than linear with time. Doubling the time of immersion from 4 to 8 min increases the coating weight by about 30%.

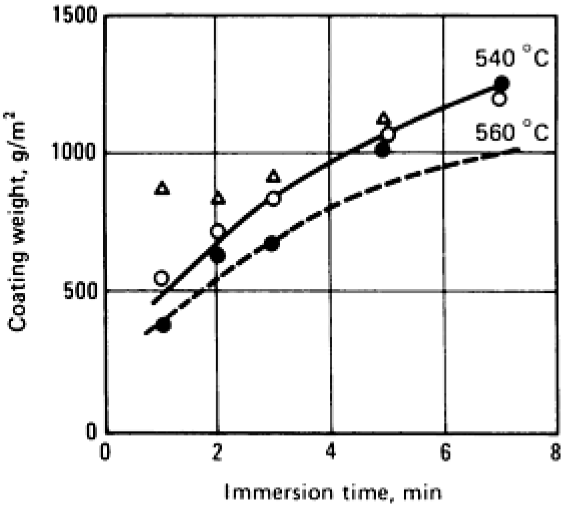


Fig. 12 Coating weight versus immersion time for three steels with varying silicon contents galvanized in a high-temperature bath containing 0.22% Fe. d , steel containing 0.02% Si; •, steel containing 0.22% Si; V , steel containing 0.42% Si

Because of the high reactivity between molten zinc and steel at these temperatures, a ceramic-lined steel kettle is used. While the available ceramic kettle technology is adequate for this application, the state of the art of ceramic kettle heating currently lacks the efficiency of flat flame burners used to heat steel kettles. The development of immersion heaters to heat the ceramic baths is proceeding and offers good promise of improved efficiencies. Pending development of an operationally suitable immersion heater system, ceramic galvanizing kettles are top heated. This technique is relatively inefficient and interferes with the handling of materials into and out of the kettle.

In the bath, the solubility of iron increases from 0.03% at 450 °C (840 °F) to 0.3% at 550 °C (1020 °F). By controlling the iron content, the coating weight can be controlled. As shown in Fig. 13, increasing the iron content from zero to 0.3%, the solubility limit at 550 °C (1020 °F) increases the coating thickness by a factor of 2. Controlling the iron content within the range 0.1 to 0.2% produces coating weights which meet specifications and are not excessively heavy.

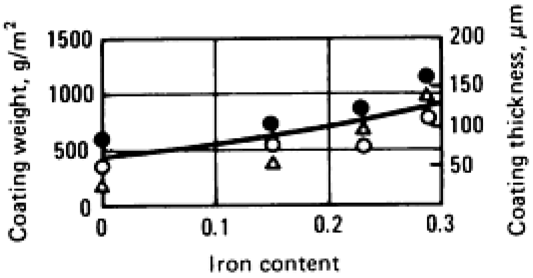


Fig. 13 Coating weight as a function of galvanizing bath iron content for three steels with varying silicon contents. Galvanizing time, 3 min at 550 °C (1020 °F). d , steel containing 0.02% Si; •, steel containing 0.22% Si; V , steel containing 0.42% Si

In a high-temperature galvanizing bath, aluminum up to 0.5% does not appear to have any systematic effect on coating weight. However, above 0.3%, it produces a floating dross which can mar the coating appearance. An aluminum addition of 0.03% is sufficient to brighten the coating if this is desired.

There have been reports of occasional adherence deficiencies of high-temperature galvanized coatings. At this time, it is believed that this is the result of a lead-deficient bath. As a result, the bath lead level should be maintained at 1%. Therefore, the following bath conditions are considered ideal:

- Temperature at 560 °C (1040 °F)
- Iron content between 0.1 and 0.2%
- Lead content about 1%
- Aluminum content of 0.05%

The coating has a light gray, uniform appearance that does not vary with silicon content of the basis steel. Brighter coatings can be obtained by the aluminum addition to the bath described above and by quenching instead of air cooling. Coating adhesion and ductility are equivalent to coatings galvanized at conventional temperatures. The metallographic structures of all high-temperature coatings are similar, the only variation being in the constituent proportions of some of the layers (Fig. 14).

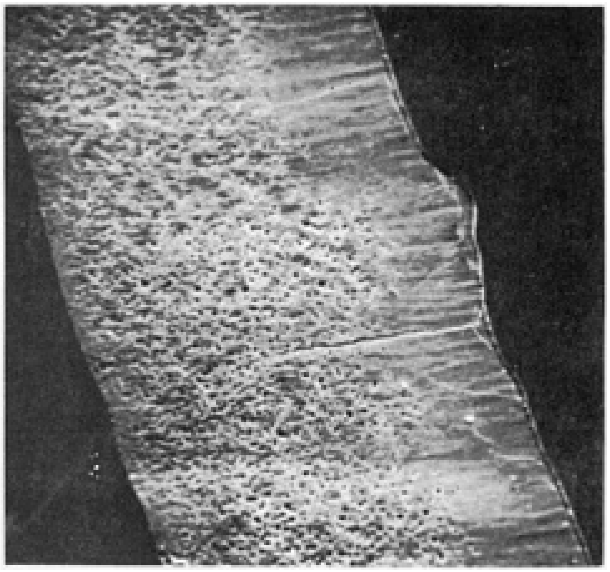


Fig. 14 Electron-scanning image of a high-temperature galvanized coating

Mechanical property tests of the basis steel subjected to high-temperature galvanizing reveal no significant differences from the results obtained using conventional galvanizing techniques. These tests include tensile properties on plain, punched, and welded specimens, reverse bend tests for strain age embrittlement, ductility bend tests, and pulsating tension fatigue tests.

Because of the recent development of high-temperature galvanized coatings, their performance is not as well documented as that of conventional coatings. Based on a limited body of longer term exposure data and accelerated weathering tests in marine, urban, and industrial environments, it appears that the performance of these coatings is at least equal to that of coatings produced by conventional techniques.

Nickel Addition to the Bath. It has been known since the 1960s that the addition of certain alloying elements to the bath will minimize the reactive effect of silicon-killed steels.

European galvanizers have been adding nickel to kettles since the 1970s. The process was brought to North America in the early 1980s and has been used in Canada with some success; it has also been in limited use in the United States since that time.

In this process, nickel is added to the bath as part of the zinc, as a special additive similar to brightener bars, or as a powder. The bath nickel concentration should be 0.05 to 0.09%; experience has shown that maximum effectiveness is achieved in this range. This technique has maximum effectiveness for steels with silicon levels below 0.25%. For steels with higher silicon contents, it provides only minimal coating improvements.

Nickel generally decreases the reaction between the zinc and steel for all steels. It is possible that nickel additions may produce low coating thicknesses on some steels. Care must be taken to ensure adequate zinc thicknesses. Figures 15 and 16 show the effects of nickel additions in the galvanizing bath.

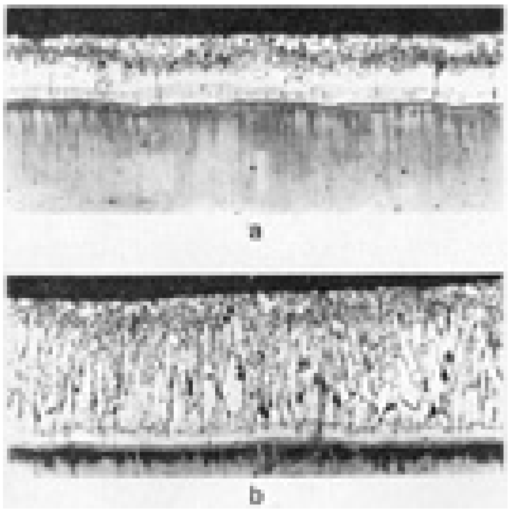


Fig. 15 Effect of nickel additions to the galvanizing bath. (a) Typical hot dip galvanized coating on mild steel. (b) Coating on silicon-killed steel, galvanized in bath containing nickel additions. Note the relatively thin delta layer and the thick, coarse zeta layer in (b). Both 250×. Source: Ref 6

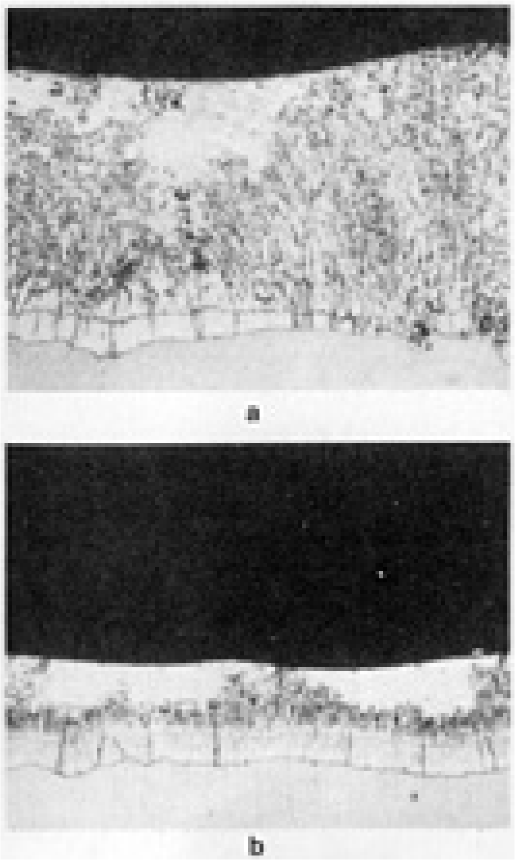


Fig. 16 Effect of nickel additions in the galvanizing bath for a steel containing 0.15% Si. (a) Galvanized in nickel-free bath. (b) Galvanized in bath containing 0.095% Ni. Source: Ref 6

Additions of vanadium, 5% Al, and rare earth metals have also shown positive effects on galvanizing of silicon-killed steels.

Reference cited in this section

6. Richard F. Lynch, Hot-Dip Galvanizing Alloys, *J. Met.*, Vol 39 (No. 8), Aug 1987, p 39-41

Batch Galvanizing Equipment

Because the galvanizing kettle is the most important piece of equipment used in galvanizing, its selection should be based on the careful evaluation of several major variables, such as size, shape, wall thickness, tank material, source of heat, and auxiliary equipment requirements.

Size and Shape. Although the size and shape of the galvanizing kettle are governed primarily by the parts to be galvanized in it, other factors must also be considered. The kettle must be large enough to contain an adequate thermal mass; that is, it must possess sufficient heat capacity in the molten zinc to compensate for the loss of heat encountered when cold workpieces are immersed in the tank. The minimum and maximum operating temperatures that must be maintained depend on production requirements; usually, the weight of zinc in the tank should be equivalent to 15 to 20 times the weight of parts that are to be galvanized in 1 h. In many production installations, the weight ratio of zinc to workpieces is more likely to approach 40 to 1.

Although the shape of the kettle must accommodate the workpieces that are to be immersed, it should also be designed to expose a minimum of bath surface. If the size of a kettle is to be increased to accommodate a particular part, the depth of the kettle rather than its length or width should be increased to minimize the exposed surface area of the bath. A minimum surface area conserves heat and produces less surface oxide than a larger area. Kettles of complicated shape should be avoided because they are susceptible to damage by severe thermal stresses. Simple, rectangular kettles are most widely used.

Wall Thickness. Theoretically, the selection of wall thickness of a galvanizing kettle should be governed by:

- The rate of corrosive attack by liquid zinc
- The hydrostatic load imposed against the kettle walls by the volume of the zinc bath
- The strength of the kettle wall material at the operating temperature of the bath
- The support afforded the kettle walls by the surrounding brickwork or by other reinforcing elements

Because the variables are so numerous and complex, accurate calculation of a required wall thickness is not practical, and selection is based entirely on empirical data. Depending on the size of the kettle and its reinforcing elements, wall thickness usually varies from 20 to 50 mm ($\frac{3}{4}$ to 2 in.).

Kettle Material. Aside from strength, the principal requirement of a galvanizing tank material is the ability to resist the corrosive attack of molten zinc. The most widely used material is boiler plate of firebox quality with low silicon. The chemical composition of this steel ensures a minimum rate of attack by molten zinc; also, the good welding and bending characteristics of this material are essential features in kettle fabrication. The chemical composition of the welding rods used in kettle fabrication should also be of low carbon and low silicon. Composition of the rod is very critical; obtaining the advice of welding experts is strongly recommended.

If a flux layer is to be maintained on the bath surface, a collar of firebrick or other suitable ceramic material should surround and abut the top 150 or 180 mm (6 or 7 in.) of the tank to retard heat transfer in this area and thus reduce attack by the flux on the steel kettle wall. A similar brick or insulated area of 150 to 205 mm (6 to 8 in.) should exist at the bottom of the kettle to reduce dross attack.

Source of Heat. Galvanizing kettles can be suitably heated by combustion of oil or gas, by electrical resistors, or by electromagnetic induction. The source of heat is of minor importance provided the heating installation satisfies the following requirements:

- High efficiency factor
- Good adjustability and control to maintain an even temperature
- Ability to maintain the minimum temperature required on the outside walls of the kettle
- Uniform heating along the outer walls, without hot or cold spots

Failure to satisfy all these requirements severely curtails the life of the kettle and may result in unexpected kettle failure. Due to energy costs, electric heat and induction heat are not widely used for job shop kettles.

Temperature Controls. When a new galvanizing tank is installed, a complete temperature survey should be made of the molten zinc bath. Based on this survey, control thermocouples may be located in the bath to maintain temperature uniformity and control.

Post Treatments

Wet Storage Film Inhibitors. A white film (sometimes called white rust or wet storage stain) may appear on zinc surfaces during storage or shipment. The film is found on material with newly galvanized, bright surfaces and especially in such areas as crevices between closely packed sheets and angle bars. Wet storage film can form if the surfaces come into contact with condensate or rainwater and the moisture does not dry quickly. Zinc surfaces that have developed a normal protective layer of corrosion products are seldom attacked.

When zinc coatings corrode openly in air, zinc oxide and zinc hydroxide are normally formed. In the presence of atmospheric carbon dioxide, these compounds are transformed to basic zinc carbonate. If the supply of air to the surface of the zinc coating is restricted, as in a narrow crevice, then sufficient carbon dioxide is not supplied for the formation of the normal layer of zinc carbonate.

The layer of zinc oxide and zinc hydroxide is voluminous and porous and adheres loosely to the zinc surface. Consequently, it does not protect the zinc surface against oxygen in the water. Corrosion can therefore proceed as long as there is moisture left on the surfaces. When wet storage film occurs, the objects should be arranged so their surfaces dry rapidly. The attack ceases, and with a free supply of air to the surfaces, the normal protective layer of corrosion products forms. The white corrosion products gradually wash off, and the surface of the coating takes on the normal appearance of a hot dip galvanized, exposed object.

Because the corrosion products are very voluminous (about 500 times that of the zinc that has been consumed), any attack may appear serious. Usually, however, such an attack of wet storage film is of little or no importance to the durability of the corrosion protection.

Wet storage film is best avoided by preventing newly galvanized surfaces from coming into contact with rain or condensate water during storage and transport. Materials stored outdoors should be arranged so that water can easily run off the surfaces and so that all surfaces are well ventilated (Fig. 17).

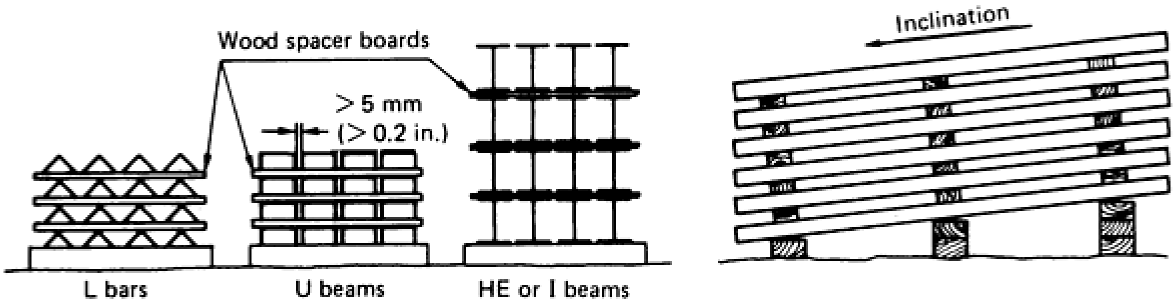


Fig. 17 Galvanized materials stacked with spacers and on an incline to prevent the formation of wet storage film

Temporary protection against wet storage film is obtained by chromating or phosphating. Painting after galvanizing also provides effective protection. Acrylic films containing corrosion inhibitors can also be applied to prevent the formation of wet storage film.

Where the surface staining is light and smooth without growth of the zinc oxide layer as judged by lightly rubbing fingertips across the surface, the staining will gradually disappear and blend in with the surrounding zinc surface as a result of normal weathering in service. When the affected area will not be fully exposed in service or when it will be subject to a humid environment, wet storage film must be removed, even if it is superficial, to allow formation of the basic zinc carbonate film which normally contributes to the corrosion resistance of galvanized coatings.

Medium to heavy buildup of white corrosion product must be removed, otherwise the essential protective film of basic zinc carbonates cannot form in affected areas. Light deposits can be removed by brushing with a 2% solution of sodium or potassium dichromate with the addition of 0.1 vol% of concentrated sulfuric acid. This is applied with a stiff brush and left for about 30 s before thoroughly rinsing and drying.

Paint Over Galvanizing. Hot dip galvanized steel may need to be painted for the following reasons:

- Additional corrosion protection for exposure to aggressive environments is needed, especially if future maintenance will be difficult or if the zinc coating is thin, such as on sheet metal.
- Another color of coating is desired for aesthetic reasons, for warning purposes, or for camouflage.
- Protection against galvanic corrosion is needed because the hot dip galvanized steel is to be in contact with another metal such as copper.

Hot dip galvanizing combined with painting offers good corrosion protection, even in very aggressive environments. The durability of such a duplex system is 1.5 to 2.7 times that of the durability of either the painted bare steel or the zinc coating alone.

The zinc coating can be painted immediately after hot dip galvanizing or after some time of exposure (Table 5). In most cases, painting immediately after hot dip galvanizing is preferable, since the surfaces are least contaminated.

Regardless of whether the paint is applied to a fresh, bright coating surface or to an exposed surface with corrosion products, the surfaces must be cleaned carefully prior to painting. The paint on zinc surfaces is more sensitive in this respect than many other materials, because even small quantities of impurities on the surfaces can affect the adhesion of the paint film.

However, the surfaces of zinc coatings are often much easier to clean than steel surfaces. It is important that an appropriate cleaning procedure be used for the particular impurities present on the surfaces.

Exposed Matte Surfaces. When zinc coatings are exposed, the surface corrodes and is covered with corrosion products. The basic zinc carbonate that forms in clean air can be painted. This is the reason for the traditional recommendation to wait from 6 months to 1 year before painting hot dip galvanized objects.

Today, however, the air is seldom clean. The layer of corrosion products contains such substances as sulfides, sulfites, sulfates, and chlorides. Many of these compounds are water soluble and some are even hygroscopic. To achieve good results when painting, all water-soluble impurities must be removed.

Cleaning and Surface Preparation. Heavily contaminated surfaces, both fresh and exposed, should be washed with a suitable organic solvent such as white mineral spirits, and then bristle brushed to remove solid particles and corrosion products. This washing should be followed with a thorough rinsing with water at high pressure, if possible.

Moderately contaminated surfaces, for example, fresh newly galvanized surfaces and surfaces that have been exposed for a longer period of time but have not been contaminated with oil and grease, can be washed with water to which 5 to 10% ammonia, caustic soda (NaOH), or acetic acid has been added. Afterwards, the surface should be buffed with a soft brush. This treatment must be followed by very thorough rinsing with water at high pressure, if possible.

Chromated surfaces, on continuously hot dip galvanized sheet, for example, can also be washed with ammonia, caustic soda, or acetic acid in water and buffed, followed by thorough rinsing. The alkaline or acid solution dissolves the chromate layer. In general, when galvanized after fabrication material is to be painted as a post-treatment, it should not be chromate treated.

Surfaces that have been exposed, moderately contaminated surfaces, or newly galvanized surfaces can also be brush blasted, that is, blasted with low pressure and a rapid motion of the nozzle, for example 0.3 MPa (0.04 ksi) at 6 mm (0.2 in.) nozzle diam and 250 to 300 mm (9.8 to 11.9 in.) nozzle distance. Abrasives consisting of silicates and slags of 0.2 to 0.5 mm (0.008 to 0.02 in.) are recommended. Glass beads and fine-grained aluminum oxide can also be used.

Sweep blasting effectively removes any corrosion products and provides an advantageous roughening of the surface of newly applied bright zinc coatings. However, brush blasting must be carried out carefully so that the zinc coating is not destroyed and large stresses are not built into the coating. These stresses may subsequently cause flaking of the paint coat.

General Surface Conditions After Galvanizing. Table 8 provides a general guide to the inspection of galvanized surfaces.

Table 8 Guide for visual inspection of galvanized surfaces

Condition	**Causes**	**Grounds for rejection?**
Bare spots	Paint, grease or oil residues	Yes, except where bare spots are small and suitable for patching
	Scale or rust residues	
	Residual welding slag	
	Rolling defects in basis steel	
	Embedded sand in castings	
	Overdrying of preflux	
	Excess aluminum in bath	
	Articles in contact during galvanizing	
General roughness	Analysis or original surface condition of steel	No, except by prior agreement
	Overpickling	
	Uneven cold working	
	High galvanizing temperature and/or long immersion time	

Dross protrusions	Entrapped dross particles	No, unless dross contamination is heavy
Blisters	Surface defects in steel	No
	Absorbed hydrogen	Not if due to steel composition
Lumpiness and runs	Withdrawal speed too high	Only on basis of prior agreement
	"Cold" galvanizing bath	
	Delayed run-off from seams,joints, bolt holes, etc.	
	Articles in contact during withdrawal	
Flux inclusions	Stale flux burnt on during dipping	Yes
	Surface residues on steel	Yes
	Flux picked up from top of bath	Yes, unless removed
Ash inclusions	Ash burnt on during dipping	Yes, if in gross lumps
	Ash picked up from top of bath	
Dull gray coating or mottled appearance	Steel composition (high silicon, phosphorus, or carbon) or severe cold work	Not if due to steel composition or condition, or limited to occasional areas
	Slow cooling after galvanizing	
Rust stains	"Weeping" of acid, etc., from seams and folds	No
	Storage on or near rusty material	No
Wet storage film ("white rust")	Confinement of close-packed articles under damp conditions	No, unless present prior to first shipment or unless severely pitted.
	Packing of articles while damp	Customer to exercise caution during transportation and storage

Choice of Paint. Paints suitable for direct application to properly cleaned hot dip galvanized steel are discussed below. As with most other paints, first apply a suitable primer to the zinc surface.

Paints consist of 10 to 20 different components and each different manufacturer has its own formula for a certain type of paint. Paints of the same type but from different manufacturers can have different properties. Detailed recommendations can be obtained from the manufacturer. Table 9 compares characteristics of some of the most common paints used with galvanized coatings.

Table 9 Comparative characteristics of paints and paint films used on hot dip galvanized steel

E, excellent; G, good; F, fair; P, poor. Other symbols used are defined in the table footnote.

Paint (film) characteristics	**Numbers of paints in Table 5**														
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Application method(a)	B	B	B	S	S	S/B	S/B	S	S	S	S/B	S	S	S	S
Drying time(b)	Lo	Lo	Mi	Sh	Sh	Mi	Mi	Mi	Sh	Sh	Mi	Mi	Mi	Mi	Mi
Hardening-through time(c)	Lo	Lo	Mi	Mi	Mi	Lo	Lo	Mi	Mi	Mi	Lo	Mi	Mi	Lo	Mi
Hardness	F	F	F	G	G	F	F/G	G/E	G	G	F	G	F/G	F	G/E
Flexibility	E	E	E	F/G	G	G	G	G	G	G	G	F/G	F/G	G	G
Impact resistance	E	E	E	G	E	G	G/E	E	G	E	G	G	G	G	E
Gloss retention(d)	G	E	E	P	F	F	F	E	P	F	F	P	F	P	E
Color retention(e)	P	F	G	P	F	E	E	E	P	F	F	F	F	. . .	E
Can stability(f)	G	G	E	E	E	G	G	P	E	E	G	P	G	P	P
Thermal resistance(g)	P	P	F	P	P	F	F	G	P	F	F	F	F	P	G
Weather resistance(h)															
Rural	E	E	E	E	E	E	E	E	E	E	E	E	E	P	E
Marine	G	G	G	E	E	F	E	E	E	E	G	E	G	G	E
Industrial	G	F	G	G	E	F	F	G	G	E	G	E	F	E	G
Resistance(i)															
Acid solutions	F	P	F	E	E	P	F	G	G	G	F	E	F	E	G

Alkaline solutions	P	P	P	E	E	P	P	F	G	G	P	G	P	E	E

Note: Paint and film characteristics may show differences because of variations in paint formulations; therefore, all indications are relative.

Source: Ref 3

(a) B, mainly by brush; S, mainly by spraying (air or airless).

(b) Drying time to tack-free: Sh, short (<1 h); Mi, intermediate (1 to 4 h); Lo, long (4 to 12 hours).

(c) Hardening-through time: Sh, short (3 h); Mi, intermediate (1 to 7 days); Lo, long (>7 days).

(d) Poor and fair ratings are mainly due to chalking.

(e) Poor and fair ratings are mainly due to yellowing.

(f) E, stable for more than 6 months; G, stable for approximately 6 months; F, stable for approximately 1 month; P, stable for less than 36 h (after adding hardeners).

(g) E, permanent resistance to temperatures between approximately 50 and 150 °C (120 and 300 °F); G, resistance to temperatures between approximately 50 and 75 °C (120 and 165 °F); F, resistance to temperatures between approximately 50 and 75 °C (120 and 165 °F) for short periods only; P, practically no thermal resistance above 50 °C (120 °F).

(h) Not counting changes in gloss and/or color.

(i) Indications depend on time of exposure and concentration and temperature of aqueous solutions.

In moderately corrosive atmospheres paints based on acrylate and PVAc-latex are suitable. However, it takes about 10 to 14 days for these paints to achieve maximum hardness and adhesion. If the objects are to be handled or transported within this time, special care must be observed to avoid damage.

Under severe chemical conditions, such as in industry, and in aggressive atmospheres, paints with better chemical resistance than latex paints are required. Such paints are based on PVC, vinyl copolymers, chlorinated rubber, polyurethane, and epoxy.

In water and soil, tar/bitumen paints are recommended, preferably in combination with epoxy. and polyurethane. Certain aluminum-pigmented asphalt solutions can also be used for structures in water, but they have relatively poor mechanical strength.

Additional information is available in the article "Painting" in this Volume.

Reference cited in this section

3. Frank Porter, *Zinc Handbook: Properties, Processing, and Use in Design,* International Lead Zinc Research Organization, 1991

Babbitting

William P. Bardet and Donald J. Wengler, Pioneer Motor Bearing Company

Introduction

BABBITTING is a process by which relatively soft metals are bonded chemically or mechanically to a stronger shell or stiffener, which supports the weight and torsion of a rotating, oscillating, or sliding shaft. The babbitt, being softer than the shaft and having excellent antifrictional qualities, prevents galling and/or scoring of the shaft over long periods of use. Compositions and selected properties of babbitts are summarized in Tables 1 and 2 and Fig. 1.

Table 1 Compositions and physical properties of tin-base babbitts

ASTM B 23 alloy No.	Specific gravity	Composition, %				Compressive yield point[a][b]				Ultimate compressive strength[a][c]				Hardness, HB[d]		Melting point		Complete liquefaction		Proper pouring temperature	
						At 19 °C (66 °F)		At 100 °C (212 °F)		At 19 °C (66 °F)		At 100 °C (212 °F)		At 20 °C (68 °F)	At 100 °C (212 °F)						
		Cu	Sn	Sb	Pb	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi			°C	°F	°C	°F	°C	°F
1	7.34	4.56	90.9	4.52	None	30.3	4.4	18.5	2.7	88.6	12.9	41.7	6.1	17.0	8.0	223	433	371	700	440	825
2	7.39	3.1	39.2	7.6	0.03	42.1	6.1	20.7	3.0	103	14.9	60.0	8.7	24.5	12.0	241	466	354	669	425	795
3	7.46	8.3	83.4	8.3	0.03	46.9	6.8	21.4	3.1	121	17.6	68.3	9.9	27.0	14.5	240	464	423	792	490	915

(a) The compression test specimens were cylinders 38 mm (1.5 in.) long, 13 mm (0.5 in.) in diameter, machined from chill castings 50 mm (2 in.) long, 19 mm (0.75 in.) in diameter.

(b) Values were taken from stress-strain curves at a deformation of 0.125% reduction of gage length.

(c) Values were taken as the unit load necessary to produce a deformation of 25% of the length of the specimen.

(d) Tests were made on the bottom face of parallel-machined specimens that had been cast at room temperature in a steel mold, 50 mm (2 in.) in diameter by 16 mm (0.625 in.) deep. Values listed are the averages of three impressions on each alloy, using a 10 mm (0.4 in.) ball and applying a 500 kg load for 30 s.

Table 2 Compositions and physical properties of lead-base babbitts

ASTM B 23 alloy No.	Specific gravity	Composition, %					Compressive yield point[a][b]				Ultimate compressive strength[a][c]				Hardness, HB[d]		Melting point		Complete liquefaction		Proper pouring temperature	
							At 19 °C (66 °F)		At 100 °C (212 °F)		At 19 °C (66 °F)		At 100 °C (212 °F)		At 20 °C (68 °F)	At 100 °C (212 °F)						
		Cu	Sn	Sb	Pb	As (max)	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi			°C	°F	°C	°F	°C	°F
7[e]	9.73	0.50	10	15	75	0.60	24.5	3.6	11.0	1.6	108	15.7	42.4	6.2	22.5	10.5	240	464	268	514	338	640
8	10.04	0.50	5	15	80	0.20	23.4	3.4	12.1	1.8	108	15.7	42.4	6.2	20.0	9.5	237	459	272	522	340	645
15[f]	10.05	0.5	1	15	82	1.40	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	21.0	13.0	249	469	281	538	350	662

Source: Sleeve Bearing Materials, *Metals Handbook*, 8th ed., Vol 1, ASM, 1961, ASTM B 23-83, and Ref 1

(a) The compression test specimens were cylinders 38 mm (1.5 in.) long, 13 mm (0.5 in.) in diameter, machined from chill castings 50 mm (2 in.) long, 19 mm (0.75 in.) in diameter.

(b) Values were taken from stress-strain curves at a deformation of 0.125% reduction of gage length.

(c) Values were taken as the unit load necessary to produce a deformation of 25% of the length of the specimen.

(d) Tests were made on the bottom face of parallel-machined specimens that had been cast at room temperature in a steel mold, 50 mm (2 in.) in diameter by 16 mm (0.625 in.) deep. Values listed are the averages of three impressions on each alloy, using a 10 mm (0.4 in.) ball and applying a 500 kg load for 30 s.

(e) 0.10% max Fe.

(f) Range of arsenic content 0.80 to 1.40% with 1.0% preferred.

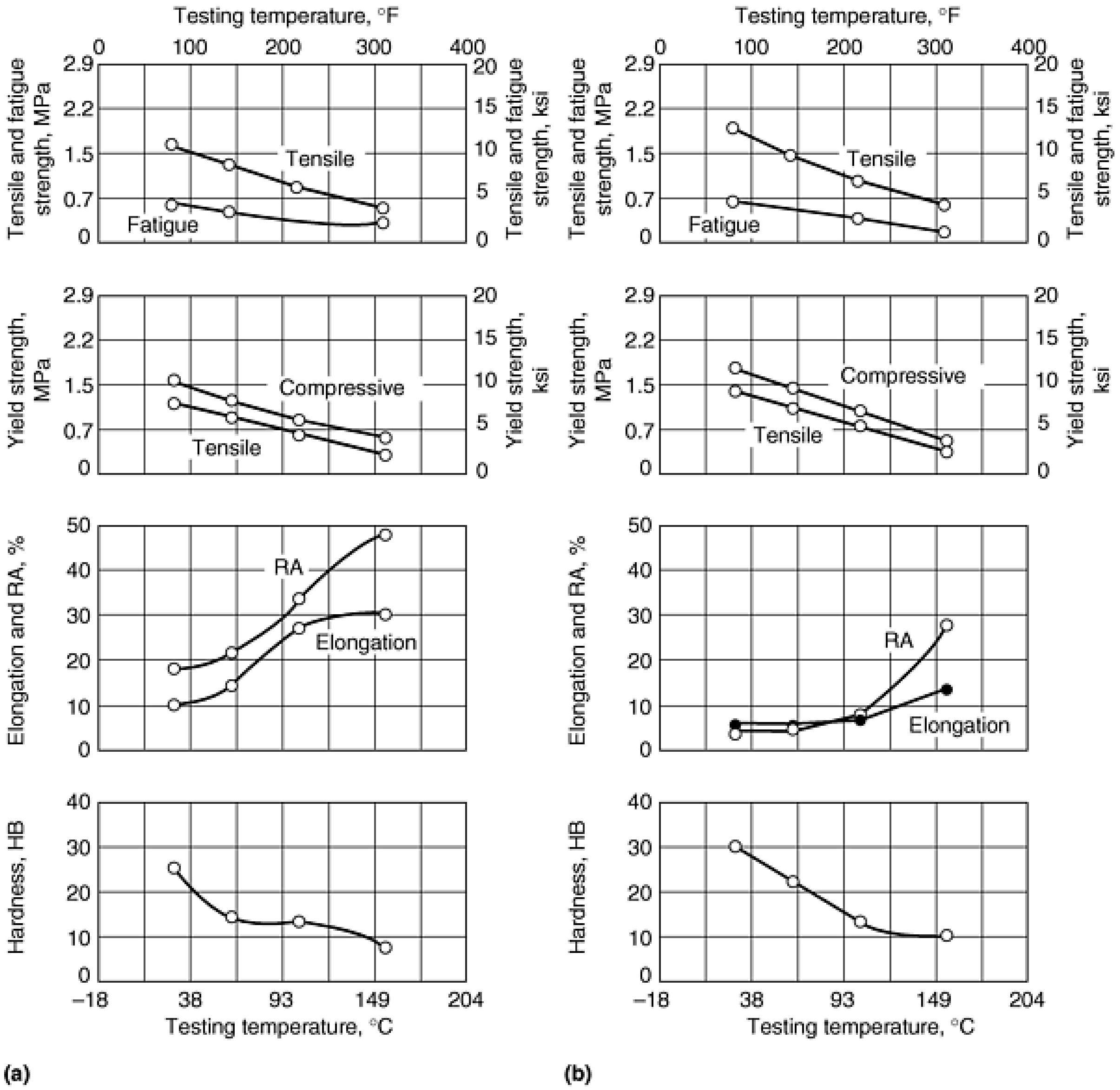


Fig. 1 Effect of testing temperature on mechanical properties of ASTM B 23 tin-base babbitt. (a) Grade 2 (75%

Sb, 3.5% Cu). (b) Grade 3 (8% Sb, 8% Cu). RA, reduction in area

Babbitting is named for Isaac Babbitt, who patented the process in the United States in 1863. Babbitt metals, which are more widely known as *white metals*, are comprised principally of tin alloys (hardened with copper and antimony) or lead alloys (hardened with tin and antimony and, in some cases, arsenic). In the babbitting process, the relatively soft bearing material (babbitt) is bonded to a stronger supporting base metal, typically mild steel, cast iron, or bronze. The base metal may be in the form of mild steel strip unwound from a coil, a half-round mild steel pressing or bushing, or a bronze or iron casting. The bonded bimetal material is shaped and machined to make plain, fluid film lubricated bearings for a wide variety of automotive, industrial, and marine applications.

Babbitt is used in small bearings for high-volume applications, such as electric motors and internal combustion engines, and for large rotating and reciprocating machinery with low to modest volume requirements, such as high-speed turbines and low-speed marine diesel engines. In addition, babbitt has been used for jewelry, shot, filler metals, and various other applications. Lead-base alloys enjoy a cost advantage, while tin alloys offer modest technical advantages, particularly in high-speed centrifugal equipment. It should be noted that government regulations now discourage the use of lead-base alloys for health and hazardous waste disposal reasons.

Babbitting of bearing shells can be accomplished by three methods:

- Static babbitting (hand casting)
- Centrifugal casting
- Metal spray babbitting

Centrifugal casting and static (gravity) casting are the two babbitting methods used in the manufacture and repair of large, low-volume journal (radial) and thrust bearings. Centrifugal casting of journal bearings offers both technical and economic advantages if special spinning equipment is available. Flat shapes (thrust bearings) are usually statically cast.

Repairing of industrial and marine babbitted bearings is routinely accomplished by melting off the old metal and rebabbitting the shells with new metal, following the same basic casting methods described below for producing new products. Emergency repair methods using proprietary tinning compounds, babbitt spray, or welding techniques can be employed. Suppliers of such repair equipment should be consulted for operating instructions.

Thin-wall babbitted half bearings, rolled bushings, and flat thrust washers are mass produced from bimetal strip stock. The strip stock is produced by continuously feeding coils of low-carbon steel in ribbon form first through appropriate cleaning and tinning baths and then through a stream of molten babbitt, which is gravity cast on the moving strip. The strip is immediately water-chilled from below. After excess babbitt is removed, the stock is recoiled and is ready for press blanking, forming, and finish machining operations. Details of mass production methods for making babbitted bearings are proprietary to the manufacturers involved, and beyond the scope of this article.

Regardless of the method used to produce the babbitt, bond quality is an important factor, particularly when heat transfer through the babbitt into the shell is expected to contribute to extending the life of the bearing. In all cases, a metallurgical (chemical) bond must be achieved to ensure good heat transfer and satisfactory babbitt fatigue life. Mechanical retention, through the use of design details such as dovetail grooves and tapped holes, does not meet this requirement, but is sometimes still used in large metallurgically bonded bearings as a form of backup insurance against bond failure. This approach (see the section "Mechanical Bonding" in this article) is more likely to be found in cast iron shells, which are more difficult to prepare for babbitting.

Acknowledgement

The sections "Cleaning by Degreasing or Pickling" , "Fluxing" , and "Single-Pot Tinning" were adapted from D.J. Maykuth, Hot Dip Tin Coating of Steel and Cast Iron, *Surface Cleaning, Finishing, and Coating*, Volume 5, 9th Edition, *Metals Handbook*, American Society for Metals, 1982, p 351-355

Reference

1. *Manual of Bearing Failures and Repair in Power Plant Rotating Equipment,* EPRI GS-7352, Electric Power Research Institute, July 1991

Preparation

Prior to casting by any method, the workpiece must be scrupulously prepared by various cleaning, fluxing, and tinning steps. The preferred methods for accomplishing these steps are described below.

After the single-pot immersion tinning step, the surface must visually demonstrate 100% wetting as evidence it is ready for babbitting by either centrifugal or static casting methods. If the surface is not 100% wetted, faulty bond areas are likely to result. Small "dry" spots can be eliminated while the tinning is still molten by application of flux scrubbed in with a stainless steel brush and retinning of the questionable areas with tin sticks. If the workpiece is still not satisfactory, it must be reprocessed by mechanically removing all tinning and starting over with basic cleaning steps described below.

The babbitting procedures described in the sections "Centrifugal Casting" and "Static Casting" in this article assume that a substrate material of low- or medium-carbon steel is being babbitted with ASTM B 23 alloy 2, the 89% Sn alloy widely used in industrial and marine machinery. Base metals other than mild steel (bronze, cast iron, etc.) are babbitted using the same procedures, although the preparatory cleaning, fluxing, and tinning steps may differ.

Typical tin bronze and leaded bronze alloys are readily tinned (Ref 2) using methods very similar to those for mild steels, but at reduced temperatures and tinning times to minimize dissolution of the bronze and growth of brittle copper-tin intermetallic compounds. As noted before, the final step before babbitting should be a visual in-process inspection of the tinned shell to confirm that it is 100% wetted by the tinning material. The tinning material is usually commercially pure tin or a tin-lead solder; pure tin produces somewhat stronger bonds, but is more expensive.

Cleaning by Degreasing or Pickling. Iron and steel parts must be free of surface contaminants such as oil, grease, drawing lubricants, and mill scale before fluxing and immersion in molten tin. Inadequate or improper surface preparation is a frequent cause of defects such as poor adhesion.

Degreasing. Oil, grease, soap, and other lubricants used in machining, drawing, and forming can be removed by one or more of several methods, including vapor degreasing, solvent cleaning, alkaline cleaning, and emulsion cleaning. Some details of various processes are given below.

The organic solvents generally used are trichloroethylene or, occasionally, perchloroethylene. Degreasing is effected by placing the articles in the hot liquid, or in the vapor, or in both in turn. In the liquid process, the solvent is continuously circulated and purified by distillation. In the vapor process, the cold articles are cleaned by the condensed vapor of the boiling solvent condensing on them. Commercial equipment for solvent degreasing is available.

Solvent procedures are ideal for removing mineral oils, greases, and many types of vegetable oils, but are less effective with certain types of drawing compounds and spinning soaps which leave behind solid constituents. In a liquor-vapor plant, a short cooling period should follow immersion in the boiling solvent to ensure that adequate condensation of solvent occurs on the articles which should be so racked or supported that the condensed solvent runs off them completely and does not collect in recesses.

Wet articles must not be loaded into a solvent degreaser, because corrosion of the units may cause decomposition of the solvent. Smoking and naked flames must be prohibited close to trichloroethylene degreasing plants to avoid the risk of phosgene poisoning.

Alkaline detergents act be penetrating the contaminant layer and removing it by emulsification, saponification, or flocculation. Appropriate commercial salts are available in powder or crystal form, which are dissolved in water at a concentration of from 1 to 10%, according to the instructions. Alkaline cleaning solutions may be made more effective by employing electrolysis at the same time, but this is not commonly practiced.

Alkaline cleaners usually contain sodium hydroxide with other constituents added to render the grease soluble. Proprietary cleaners are recommended because they are formulated to deal with specific types of contaminants and basis metal. The temperature of alkaline solutions should not be below 85 °C (185 °F).

A simple 5% sodium hydroxide solution at 80 to 90 °C (185 to 195 °F) often is adequate for the anodic electrolytic cleaning of steel, but a specifically formulated proprietary solution is preferred. The articles are suspended to form one electrode, and a plain steel tank containing the alkaline solution is the other electrode. A 6 to 12 V direct current is applied between busbar and tank to obtain a current density on the work of between 2 and 5 A/dm^2 (20 to 50 A/ft^2) of surface. Generally, the use of electrolysis allows more latitude in the temperature of the alkaline bath, but the hotter the solution, the more efficient the cleaning. Tenacious oil films causing slow pickling and tinning difficulty are sometimes best removed by an electrolytic cleaning treatment.

Articles should be rinsed immediately as they are removed from alkali to avoid deposition of salts or de-emulsification of the grease on the surface. The best procedure consists of a hot water rinse, followed by a final rinse in a cold water tank provided with running intake and overflow. The rinse water should not contain acids or salts likely to bring about the breakdown of emulsions adhering to articles removed for rinsing. For this reason, avoid using the same rinse tank for degreasing and pickling.

Ultrasonic cleaning involves the use of high frequency mechanical vibrations from a transducer device in a cleaning solution to achieve a higher degree of cleanliness and at a much faster rate than is possible by conventional methods. Frequencies of 20 to 40 kHz are frequently used. The scouring effect penetrates into crevices, holes, and complex contours that are inaccessible to mechanical action such as brushing.

The temperature of the cleaning liquid is important as it affects density and volatility. Aqueous solutions are used at about 50 °C (120 °F) instead of the more conventional 80 to 95 °C (175 to 205 °F), and emulsifying agents may be present which are effective at lower temperatures. Organic-solvent, ultrasonic, degreasing plants usually have a special compartment containing cool solvent in which the transducers are fitted. Articles are initially degreased in boiling solvent before passing to the ultrasonic treatment chamber. A final degreasing in vapor alone may be used.

The use of many degreasing solvents is being restricted due to environmental concerns. Additional information is provided in the article "Vapor Degreasing Alternatives" in this Volume.

Pickling of steel, usually done in aqueous solutions of hydrochloric or sulfuric acid, can be used to remove mill scale and rust before hot tinning. Hydrochloric acid pickles efficiently at room temperature, and in most applications, no provision is made for heating it. Dilutions range from one part acid in two parts water to three parts acid in one part water. Immersion times range from 10 to 60 min. When pickling for hot dip tinning, immersion in the pickling bath should be prolonged for a few minutes beyond the time required for the total removal of visible scale and rust. This gives the steel a light etch, which will promote wetting of the base metal during the tinning process.

Depending on the condition of the surface being treated, the composition of the aqueous sulfuric acid pickling solution varies from about 4 to 12% sulfuric acid. The recommended operating temperature range for these solutions is 80 to 85 °C (175 to 185 °F). Removing light scale or rust normally requires an immersion time of $\frac{1}{2}$ to 2 min; even heavy scale should not require an immersion time of more than 15 min. In sulfuric acid pickling baths, inhibitors are commonly added to concentrate the attack on the scale and reduce acid consumption, metal loss, spray, and risk of hydrogen absorption by the steel.

Difficult steels, such as those having surface layers formed by decomposing lubricants, often require oxidizing conditions and a hydrochloric or sulfuric acid immersion sufficient to remove surface oxides followed by 1 to 3 min in 10 to 25 vol% nitric acid to achieve a tinnable surface.

Cast iron should not be acid pickled for tinning, because a heavy carbon smut derived from graphite forms over the whole surface and prevents tinning.

Details of operating procedures and equipment required for pickling in hydrochloric and sulfuric acid, as well as the use of inhibitors to minimize acid attack, are given in the article "Pickling and Descaling" in this Volume.

Abrasive blast cleaning must be done on castings and all assemblies of cast iron, cast steel, and malleable iron with wrought steel prior to hot dip tinning. Iron castings to be tinned by the direct chloride method or by wiping should be blasted with fine (70-mesh) angular chilled iron grit. Blasting should be thorough with all surfaces to be tinned treated for 30 to 60 s. For a description of the equipment and techniques used in abrasive blasting, see the article "Mechanical Cleaning Systems" in this Volume.

Fluxing facilitates and speeds the reaction of molten tin with iron or steel, promoting the formation of a continuous thin layer of tin-iron or other intermetallic phases on which the liquid tin coating can spread in an even, smooth, continuous film. In hot dip tinning, fluxes may be used in three different ways:

- As aqueous solutions in which the work is briefly dipped before it is immersed in the molten tin
- As a molten fused layer or cover on the top of the molten tin bath
- As a solution, paste, or admixture to tin powder that is applied to the surface of the work prior to wipe tinning

The material compositions of two aqueous flux solutions are given in Table 3.

Table 3 Compositions of flux solutions used in hot dip tinning

Solution	Constituents									
	Zinc chloride		Ammonium chloride		Sodium chloride		Hydrochloric acid(a)		Water	
	kg	lb	kg	lb	kg	lb	cm^3	oz	L	gal
A	11	25	0.7	1.5	. . .	. . .	296-591	10-20	38	10

(a) Commercial grade, 28%

A cover of molten flux should be maintained on the surface of the first tin dipping bath. The flux cover, which must be molten at the operating temperature of the bath, is normally regenerated by absorbing aqueous flux solutions on the surface of the incoming work. The addition of water as a fine spray to the surface of the flux may still be necessary at intervals to rejuvenate it. Compositions of two effective flux covers are given in Table 4. The salt components of the various flux solutions given in Table 3 form suitable flux covers.

Table 4 Compositions of flux covers for hot dip tinning baths

Mixture	Melting point		Constituent	Content, wt%
	°C	°F		
A	260	500	Zinc chloride	78
			Sodium chloride	22
B	260	500	Zinc chloride	73
			Sodium chloride	18

			Ammonium chloride	9

After being pickled, rinsed, and dried of excess rinse water, the steel (or in the case of iron castings, the dry, shot-blasted workpiece) is immersed in an aqueous flux solution. Workpieces may require some movement in the flux bath to remove all air locks and to ensure that all surfaces are fully wetted by the flux. Work should be immersed in the flux only long enough to ensure complete coverage; nothing is gained by prolonged immersion. When the workpiece is withdrawn from the bath, the excess flux should be allowed to drain briefly. The workpiece is then ready for immediate immersion in the tin bath.

Single-pot tinning is used to provide a preliminary coating for bonding. The tinning operation does two things: It establishes a bond between the base material, and it raises the temperature of the backing to a level where it will maintain the tinning in a molten state ready to bond with molten babbit when casting commences.

The process involves a single immersion of fluxed workpieces in a molten tin bath heated to 280 to 325 °C (535 to 615 °F). The average operating temperature of the bath is maintained at about 300 °C (575 °F). When the workpiece is withdrawn from the bath, the surface of the work may have spots of flux, which must be removed by suitable washing.

Flux is placed on the surface of the molten tin bath in an amount sufficient to provide a molten flux layer that covers about two-thirds of the surface area. The use of partial rather than total flux coverage helps eliminate excessive pickup of flux when the work is withdrawn.

After being coated with aqueous flux, the workpieces are picked up by pretinning tongs, hooks, or perforated baskets and lowered gently into the molten tin, passing through the portion of the bath that is covered with flux. The optimum immersion rate normally ranges from 13 to 51 mm/s ($\frac{1}{2}$ to 2 in./s). Heavy sections are immersed at a slower rate than light sections. The work need only be immersed long enough to reach the temperature of the bath.

In order to minimize flux pickup and to shed any particles of iron-tin compound that have accumulated in the bath, workpieces are withdrawn from the bath with a clean, rapid movement through an area not covered with flux. Flux may be moved to one side with a paddle.

The operations that follow withdrawal from the tin bath vary considerably. The work may be shaken or swung by hand to remove excess tin. To remove tears or droplets of tin that collect at lower or outer edges of the workpiece, the teared edge can be allowed to touch barely the surface of the clean metal in the pot. This slight contact pulls the droplets away from the work by surface tension. Centrifuging or spinning of jigged work is also used to remove excess molten tin.

After the excess tin has been removed, the work is cooled in air, then flux residues are removed by rinsing in cold water acidified with about 1 vol% hydrochloric acid or 5 to 10 vol% citric acid. A water rinse follows. Quenching the work in water or kerosene is also possible.

Mechanical bonding of a babbitt to a shell is a simple fastening process. Mechanical methods used in babbitting shops include anchor groove dovetails and drilled and tapped holes into which molten babbitt flows, locking the babbitt in place. Copper or brass screws inserted into threaded holes also help hold the babbitt to the shell. In some instances, brass or copper bars are tinned and recessed into the bore and bolted or screwed into the bore of the casting. In most cases, these methods are used on cast iron when caustic treatment is not available. The heads of the screws must be recessed into the babbitt to prevent the screw head from becoming exposed when the babbitt is machined to a final bore size.

Reference cited in this section

2. C.J. Thwaites, "Practical Hot Tinning," Publication No. 575, International Tin Research Institute

Centrifugal Casting

Centrifugal casting is the preferred method for babbitting medium- and thick-wall, half-shell or full-round (nonsplit) journal bearings because it virtually eliminates porosity and allows close control of the cooling process to promote a strong bond. Disadvantages are the need for more extensive equipment and tooling than static casting requires and minor segregation of the intermetallics in the babbitt across its thickness. (It should be noted, however, that segregation along the axial length of a statically cast bearing can be more serious, and is more difficult to detect). The spinning axis is usually horizontal, but vertical orientation is sometimes employed for unusual sizes (e.g., large diameters or short lengths). The descriptions of equipment and procedures below apply only to horizontal casting.

Equipment. Centrifugal babbitting requires a machine expressly designed or modified for this purpose (Fig. 2). No mandrel is used in horizontal applications. A variable-speed centrifugal casting (spinning) machine is fitted with a safe means for supporting and rotating a reasonably well-balanced workpiece clamped between recessed sealing plates. With the shell rotating, molten babbitt is fed to the inside of the prepared bearing through a hole in the outboard spinning plate, then solidified by air and/or water sprayed on the outside diameter of the shell while it is spinning. A speed is selected that produces a centrifugal force high enough to eliminate porosity but low enough to minimize metal segregation. Too low a speed causes metal "tumbling," while too high a speed causes segregation. Table 5 shows a range of spinning speeds for various bearing sizes (inside shell diameter), based on minimum centrifugal forces of 20 g for tin-base alloys. The minimum for lead-base babbitts is 16 g. To promote directional solidification after the babbitt is poured, the tooling plates must be preheated to 200 °C (390 °F) minimum and faced with gaskets cut from sheets of environmentally approved insulating materials, such as Inswool, to seal and insulate both ends of the bearing when it is clamped between the support plates by hydraulic pressure. The centrifugal casting machine must be of fail-safe design in the event of a loss of power and/or clamping pressure.

Table 5 Centrifugal casting speeds for tin-base babbitt bearings

Optimum speed is slowest speed that will produce sound (porosity-free) castings with minimum segregation.

Inside diameter of bearing shell		Centrifugal casting speed, rev/min
mm	in.	
51	2	850-975
76	3	700-800
102	4	600-700
127	5	535-610
152	6	485-550
178	7	450-525
203	8	420-500
229	9	395-470
254	10	375-450
279	11	360-430
305	12	345-410

330	13	330-395
356	14	320-370
381	15	305-360
406	16	295-350
432	17	285-340
457	18	280-330
483	19	275-325
508	20	265-315
533	21	260-310
559	22	250-300
584	23	245-295
610	24	240-290
635	25	235-285
660	26	230-280
686	27	230-275
711	28	225-270
737	29	220-265
762	30	215-260
787	31	215-255
813	32	210-250
838	33	205-245

864	34	200-245
889	35	200-240
914	36	195-235
965	38	190-230

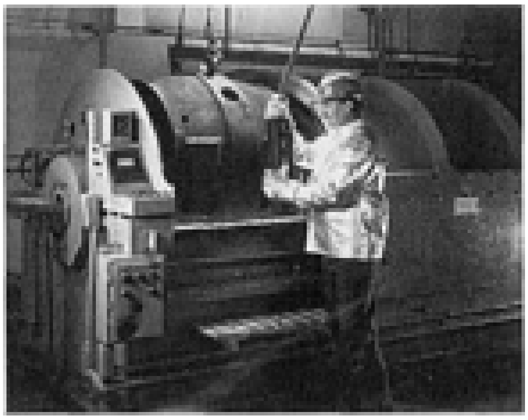


Fig. 2 Loading of a large steam turbine generator bearing into a centrifugal babbitting machine. Courtesy of Pioneer Motor Bearing Company

Procedure. After tinning, full-round (nonsplit) shells require no further preparation and can be immediately loaded into the casting machine. Split-type bearings (in halves) or segmented (tilting pad) style journal bearings require fixturing after the pretinning of each component to make up an assembly ready for spinning. The fixturing consists of laminated spacers for each parting face. These spacers must prevent both radial and axial leakage without unduly restricting the smooth flow of the molten rotating metal.

Spacers can be cut from steel sheet with a minimum thickness of 1.0 mm (0.04 in.) and faced on both sides with 3 mm (0.12 in.) gaskets that are cut to fit. Total spacer thickness should be at least 7 mm (0.28 in.) before assembly to allow for the later separation of the halves or segments by saw cutting through the babbitt without damage to the steel parting faces.

When the spacers are in place and the halves or segments are retained by bolting or other means of safe clamping, the assembly must be reheated in the tinning bath, if necessary, to ensure a minimum temperature of 300 °C (570 °F) before loading in the casting machine. Alternatively, the cold assembly can be mounted in the machine and slowly rotated while gas torches are applied along the outside of the bearing until it reaches tinning temperatures. This latter method, however, does not allow visual in-process inspection to ensure complete wetting (tinning) before casting commences. In any case, there must be little time lost after tinning temperatures are reached, and before babbitt metal is poured, to achieve a satisfactory bond; tinning must be molten when the babbitt is poured.

The babbitt alloy should be melted in a temperature-controlled cast iron pot that is held at its recommended pouring temperature (Tables 1 and 2) and stirred with a vertical motion to promote uniform metal temperature and to avoid metal segregation. Dross on the surface of the pot is skimmed aside while a preheated ladle, preferably of the bottom-pour style, is filled with a predetermined volume of metal. The volume of metal poured should be sufficient to provide a minimum of 4 mm (0.16 in.) machining stock per side after babbitting so that impurities, which float to the inside during centrifugal casting, can be removed.

With the bearing shell rotating at a preselected speed (Table 4), the metal is ladled in one continuous pour directly, or through a preheated trough, into the spinning shell. Water cooling should be started immediately after pouring is completed, and the bearing rotation should continue until the assembly temperature drops to around 150 °C (300 °F). At this point, the water should be shut off and the bearing allowed to air cool more slowly while spinning. This cooling regime minimizes the stress imposed on the bond by the difference in thermal coefficients between typical babbitts and backing materials. (The ratio is almost 2:1 between babbitt and steel, and 1.5:1 between babbitt and bronze.) A controlled flow of coolant along the length of the bearing ensures directional solidification. That is, the babbitt freezes (solidifies) uniformly along the bond line first, then progressively toward the inside of the casting. This ensures that molten metal under pressure is available to feed the shrinkage and to squeeze out trapped gases and dross. When a shell has a nonuniform cross section, the coolant flow should be adjusted to promote uniform solidification from end to end.

Nonsplit journal bearings follow the same basic procedures as above without the need for assembling half shells or tilting pad segments and reheating them before they are loaded into the casting machine.

Static Casting

The static casting method is used for babbitting of flat surfaces (thrust plates or pads, etc.) and journal bearings. The latter may not lend themselves to centrifugal casting because of odd shapes, equipment requirements, or tooling costs. Static babbitting requires a babbitting mandrel to form the babbitt in the bearing shell. Mandrels can be designed for use in a vertical or horizontal position. Plates are placed at each end when the mandrel is designed for use in a horizontal position. Vertical casting is preferred when possible.

Flat workpieces are cleaned and tinned and fitted with a preformed steel fence clamped around the perimeter of the part. The fence must be sufficiently high to provide a 6 mm (0.25 in.) riser for the mold. The assembly is supported on insulated blocks in an open pan. Once it has reached a minimum temperature of 300 °C (570 °F), the babbitt is poured in a steady stream to fill the mold. The pan is then flooded with tap water to just above the bottom of the workpiece; this must be done immediately to ensure directional solidification. Heat may be added by gas torch to the babbitt surface while the metal is gently agitated to promote the release of any trapped air or dross. Additional metal may be added to feed the shrinkage.

Split-type journal bearings can be statically cast by assembling both halves together with spacers around a vertical mandrel (core) on a level table. Alternatively, each half may be cast separately by clamping parting faces against flat wings projecting from each side of a vertical half-round core. A steel riser ring is placed over an appropriate gasket on top of the half shell or assembled pair of shells to provide a minimum 12 mm (0.5 in.) height of excess molten metal to feed the shrinkage during solidification. The inside diameter of the riser and gasket should be somewhat larger than the tinned inside diameter of the shell(s). The radius of the mandrel or core should be at least 5 mm (0.20 in.) smaller than half the finished bore diameter of the bearing to allow for later stock removal. Large bearings may require a greater allowance for machining stock because of inaccuracies in locating the core of the bearing shell when the babbitt is poured. The mandrel/core height should preferably be at least 50 mm (2 in.) higher than the riser to act as a backboard against which the babbitt can be ladled into the cavity with minimum turbulence.

The mandrel, riser ring, and casting table are preheated to 290 °C (550 °F) to promote directional solidification. The casting must solidify progressively from the bond line inward toward the core, and up from the bottom of the shell(s) to the top of the riser. If not, shrinkage cavities will occur at the interface and the bond will be weakened. The mandrel can be "smoked" with a reducing flame from an acetylene torch or coated with an appropriate stop-off material before heating to promote easy release of the bearing from the mandrel after solidification.

After tinning, the bearing assembly or half shell is immediately clamped against the half core or around the mandrel. If the shell is being rebabbitted, any openings (holes, slots, etc.) must be quickly and effectively plugged with a dry high-temperature packing material. The bottom of the bearing assembly or shell should be sitting on a sheet of gasketing material to insulate it and to prevent leakage; strips of gasket material can be used to seal the joint faces.

The bearing shell temperature should be a minimum of 260 °C (500 °F). Once the babbitt metal is heated to its recommended pouring temperature, it is stirred and skimmed and then the cavity is filled in one continuous pour to the top of the riser ring.

Castings can be cooled by air or by having water spray directed uniformly against the outside of the shell(s) from the bottom up while heat is added to the mandrel and/or riser with a gas torch. The molten metal can be gently agitated by continuous vertical stroking with a small-diameter stainless steel rod to promote the release of trapped gases while the cooling progresses upward and inward toward the core. Molten metal is added to feed the shrinkage. When the riser solidifies, the bearing can be separated from the core and air-cooled to room temperature.

Bond Quality

Bond integrity is arguably the most important manufacturing feature of any bimetal bearing. A bond failure can be very expensive to correct, particularly considering the cost of lost production while the bearing is repaired or replaced. The bond tensile strength of a metallurgically well-bonded steel-backed babbitted bearing should exceed 60 MPa (8700 psi); bronze-backed bearings should exhibit a minimum bond strength of 40 MPa (5800 psi). In other words, the bond strength should comfortably exceed the ultimate tensile strength of the babbitt.

Bond strength is determined by destructive tests for evaluating tensile strength and ductility (Ref 3). Nondestructive ultrasonic bond testing, when conducted and evaluated by an experienced and qualified operator, does not determine strength but does reveal the location and extent of any significant unbonded areas. An unblemished surface is a very good indication that proper preparation and casting techniques have been employed throughout the babbitting process and that at least minimum bond strengths can be reasonably expected.

Defective bonds can most often be traced to poor preparation (i.e., inadequate cleaning of the base metal). The second most prevalent cause is allowing the tinned shell to cool such that the tinning is not molten when the babbitt is centrifugally or statically cast. To correct either problem, the babbitt and tinning must be removed and the shell reprocessed, starting with the basic cleaning steps and following recommended temperature guidelines.

Reference cited in this section

3. Bond Testing, Babbitt-Lined Bearings, Military Standard DOD-STD-2183SH, 1985

Metal-Spray Babbitting

Babbitting by the metal-spray method requires special equipment consisting of an acetylene/oxygen flame spray gun that uses a high tin-base babbitt in wire form. The molten alloy is sprayed on a bond coating, which has been previously sprayed on the bearing shell. The buildup of the babbitt is relatively slow, and bond strengths are somewhat lower than with other methods; however, voids are eliminated and a high-quality product results. Spray babbitt thicknesses to 26 mm (1.02 in.) are possible, and spray control is sufficient to require only a small excess of deposit for subsequent machining. Overspray losses are minimal. Mechanical aids to hold the babbitt to the bearing shell are not necessary and are not recommended for this process, and skill levels for operators are not as high as those required for static babbitting.

Phosphate Coatings

Introduction

PHOSPHATE COATING is the treatment of iron, steel, galvanized steel, or aluminum with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid media, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. The weight and crystalline structure of the coating and the extent of penetration of the coating into the base metal can be controlled by:

- Method of cleaning before treatment
- Use of activating rinses containing titanium and other metals or compounds
- Method of applying the solution
- Temperature, concentration, and duration of treatment
- Modification of the chemical composition of phosphating solution

The method of applying phosphate coatings is usually determined by the size and shape of the article to be coated. Small items, such as nuts, bolts, screws, and stampings, are coated in tumbling barrels immersed in phosphating solution. Large fabricated articles, such as refrigerator cabinets, are spray coated with solution while on conveyors. Automobile bodies are sprayed with or immersed in phosphating solution. Steel sheet and strip can be passed continuously through the phosphating solution or can be sprayed.

Phosphate coatings range in thickness from less than 3 to 50 μm (0.1 to 2 mil). Coating weight (grams per square meter of coated area), rather than coating thickness, has been adopted as the basis for expressing the amount of coating deposited.

Phosphate Coatings

Three principal types of phosphate coatings are in general use: zinc, iron, and manganese. A fourth type, lead phosphate, more recently introduced, is operated at ambient temperatures.

Zinc phosphate coatings encompass a wide range of weights and crystal characteristics, ranging from heavy films with coarse crystals to ultrathin microcrystalline deposits. Zinc phosphate coatings vary from light to dark gray in color. Coatings are darker as the carbon content of the underlying steel increases, as the ferrous content of the coating increases, as heavy metal ions are incorporated into the phosphating solution, or as the substrate metal is acid pickled prior to phosphating. Zinc phosphating solutions containing active oxidizers usually produce lighter-colored coatings than do solutions using milder accelerators.

Zinc phosphate coatings can be applied by spray, immersion, or a combination of the two. Coatings can be used for any of the following applications of phosphating: base for paint or oil; aid to cold forming, tube drawing, and wire drawing; increasing wear resistance; or rustproofing. Spray coatings on steel surfaces range in weight from 1.08 to 10.8 g/m^2 (3.5×10^{-3} to 3.5×10^{-2} oz/ft^2); immersion coatings, from 1.61 to 43.0 g/m^2 (5.28×10^{-3} to 0.141 oz/ft^2).

Iron phosphate coatings were the first to be used commercially. Early iron phosphating solutions consisted of ferrous phosphate/phosphoric acid used at temperatures near boiling and produced dark gray coatings with coarse crystals. The term *iron phosphate coatings* refers to coatings resulting from alkali-metal phosphate solutions operated at pH in the range of 4.0 to 5.0, which produce exceedingly fine crystals. The solutions produce an amorphous coating consisting primarily of iron oxides and having an interference color range of iridescent blue to reddish-blue color.

A typical formulation for an iron phosphate bath is (Ref 1):

Component	Composition, %
Phosphate salts	12-15
Phosphoric acid	3-4
Molybdate accelerator	0.25-0.50
Detergents (anionic/nonionic)	8-10

Basically, then, iron phosphate formulations consist of primary phosphate salts and accelerators dissolved in a phosphoric acid solution. It is the acid that initiates the formation of a coating on a metal surface. When acid attacks the metal and begins to be consumed, solution pH at the metal surface rises slightly. This is what causes the primary phosphate salts to drop out of solution and react with the metal surface, forming a crystalline coating.

All iron phosphate conversion coatings are composed of partially neutralized phosphoric acid. But all iron phosphates are not created equal. Other ingredients, such as the specific accelerator used (Table 1), hold part of the key.

Table 1 Effect of accelerators on the weight of an iron phosphate coating

Accelerator	**Surface treated**	**Coating weight**	
		g/m^2	**oz/ft^2 × 10^{-3}**
. . .	Steel only	0.11-0.27	0.35-0.88
Metallic	Mixed metal loads, ferrous, zinc, and aluminum	0.22-0.38	0.71-1.24
Oxidizer	High-quality steel only	0.43-0.86	1.41-2.82

Source: Ref 2

Although iron phosphate coatings are applied to steel to provide a receptive surface for the bonding of fabric, wood, and other materials, their chief application is as a base for subsequent films of paint. Processes that produce iron phosphate coatings are also available for treatment of galvanized and aluminum surfaces. Iron phosphate coatings have excellent adherence and provide good resistance to flaking from impact or flexing when painted. Corrosion resistance, either through film or scribe undercut, is usually less than that attained with zinc phosphate. However, a good iron phosphate coating often outperforms a poor zinc phosphate coating.

Spray application of iron phosphate coatings is most frequently used, although immersion application also is practical. The accepted range of coating weights is 0.21 to 0.86 g/m^2 (6.9 × 10^{-4} to 0.26 oz/ft^2). Little benefit is derived from exceeding this range, and coatings of less than 0.21 g/m^2 (6.9 × 10^{-4} oz/ft^2) are likely to be nonuniform or discontinuous. Quality iron phosphate coatings are routinely deposited at temperatures from 25 to 65 °C (80 to 150 °F) by either spray or immersion methods.

Manganese phosphate coatings are applied to ferrous parts (bearings, gears, and internal combustion engine parts, for example) for break-in and to prevent galling. These coatings are usually dark gray. However, because almost all manganese phosphate coatings are used as an oil base and the oil intensifies the coloring, manganese phosphate coatings are usually black in appearance. In some instances, a calcium-modified zinc phosphate coating can be substituted for manganese phosphate to impart break-in and antigalling properties.

Manganese phosphate coatings are applied only by immersion, requiring times ranging from 5 to 30 min. Coating weights normally vary from 5.4 to 32.3 g/m^2 (1.8 × 10^{-2} to 9.83 oz/ft^2), but can be greater if required. The manganese phosphate coating usually preferred is tight and fine-grain, rather than loose and coarse-grain. However, desired crystal size varies with service requirements. In many instances, the crystal is refined as the result of some pretreatment (certain types of cleaners and/or conditioning agents based on manganese phosphate) of the metal surface.

Manganese-iron phosphate coatings are usually formed from high-temperature baths from 90 to 95 °C (190 to 200 °F).

References cited in this section

1. D. Phillips, Practical Application of the Principles Governing the Iron Phosphate Process, *Plat. Surf. Finish.*, March 1990, p 31-35
2. G.L. Tupper, "Finishing: Where Do You Start," paper presented at Fabtech International '89 (Rosemont, IL), 9-12 Oct 1989, Report No. FC89-572, Society of Manufacturing Engineers

Composition of Phosphate Coating

All phosphate coatings are produced by the same type of chemical reaction: the acid bath, containing the coating chemicals, reacts with the metal to be coated, and at the interface, a thin film of solution is neutralized because of its attack on the metal. In the neutralized solution, solubility of the metal phosphates is reduced, and they precipitate from the solution as crystals. Crystals are then attracted to the surface of the metal by the normal electrostatic potential within the metal, and they are deposited on the cathodic sites.

When an acid phosphate reacts with steel, two types of iron phosphate are produced: a primary phosphate, which enters the coating; and a secondary phosphate, which enters the solution as a soluble iron compound. If this secondary ferrous phosphate were oxidized to a ferric phosphate, it would no longer be soluble and would precipitate from the bath. Oxidizing agents are incorporated to remove the soluble secondary ferrous phosphate because the ferrous phosphate inhibits coating formation.

Although all phosphating baths are acid in nature and to some extent attack the metal being coated, hydrogen embrittlement seldom occurs as a result of phosphating. This is primarily because all phosphating baths contain depolarizers or oxidizers that react with the hydrogen as it is formed and render it harmless to the metal. In some instances, however, zinc-phosphate processes, intended for use with rust-inhibiting oils for corrosion resistance or manganese-phosphate treatments, can cause hydrogen embrittlement because they may contain a minimum amount of depolarizers and oxidizers. A dwell time before use or mild heating may be needed to relieve embrittlement.

The acidity of phosphating baths varies, depending on the type of phosphating compound and its method of application. Immersion zinc phosphating baths operate in a pH range of 1.4 to 2.4, whereas spray zinc phosphating solutions can operate at a pH as high as 3.4, depending on the bath temperature. Iron phosphating baths usually operate at a pH of 3.8 to 5. Manganese phosphating baths operate in a pH range comparable to that of the immersion zinc phosphating solutions. Lead-phosphate solutions are usually more acidic than any of the others.

Zinc, iron, and manganese phosphating baths usually contain an accelerator, which can range from a mild oxidant, such as nitrate, to one of the more vigorous nitrite, chlorate, peroxide, or organic sulfonic acids (Table 2). The purposes of these accelerators are to speed up the rate of coating, to oxidize ferrous iron, and to reduce crystal size. This is accomplished because of the ability of the accelerators to oxidize the hydrogen from the surface of the metal being coated. Phosphating solution can then contact the metal continuously, permitting completeness of reaction and uniformity of coverage. Accelerators have an oxidizing effect on the dissolved iron in the bath, thus extending the useful life of the solution. Some zinc and iron phosphating processes rely on oxygen from the air as the accelerator. Zinc phosphating baths for aluminum usually contain complex or free fluorides to accelerate coating formation and to block the coating-inhibiting effect of soluble aluminum.

Table 2 Accelerators used in phosphate coating processes

Type of accelerator	**Accelerator source**	**Effective concentration**			**Optimum operating conditions**				**Advantages**	**Limitations**
					Ratio	**Temperature**		**Addition**		
		%	**g/L**	**lb/gal × 10^{-3}**		**°C**	**°F**			
NO_3^-	$NaNO_3$, $Zn(NO_3)_2$, $Ni(NO_3)_2$	1-3	. . .	. . .	High $NO_3^- : PO_4^{3-}$	65-93	149-199	. . .	Lower sludge.	Reduction of $FePO_4$ increases the iron content of the coating.
NO_2^-	$NaNO_2$	. . .	0.1-0.2	0.8-1.7	NO_2:NO = 1:1	(a)	(a)	Continuous	Affords rapid processing even at low temperatures.	Corrosive fumes. Highly unstable at high bath temperatures. Frequent addition is required.

ClO_3^-	$Zn(ClO_3)_2$	0.5-1	. . .	. . .	. . .	(a)	(a)	Continuous	Stable in liquid concentrates. Can be used for bath makeup and replenishment. Overcomes the white staining problem.	Corrosive nature of chlorate and its reduction products. High concentrations poison the bath. Removal of gelatinous precipitate from the resultant phosphate coatings is difficult.
H_2O_2	H_2O_2	. . .	0.05	0.4	. . .	(a)	(a)	. . .	Low coating weight. No harmful products. Free from staining.	Bath control tends to be critical. Heavy sludge formation. Limited stability. Continuous addition is required.
Perborate	Sodium perborate	. . .	. . .	. . .	. . .	(a)	(a)	. . .	No separate neutralizer is required. Good corrosion resistance.	Continuous addition is required. Voluminous sludge.
Nitroguanidine	Nitroguanidine	. . .	. . .	. . .	. . .	55	130	. . .	Neither the accelerator nor its reduction products are corrosive.	Slightly soluble. Does not control the buildup of ferrous iron in the bath. Highly expensive.

Source: Ref 3

(a) Low temperature.

Reference cited in this section

3. T.S.N. Sankara Narayanan and M. Subbaiyan, Acceleration of the Phosphating Process: An Overview, *Prod. Finish.*, Sept 1992, p 6-7

Applications

On the basis of pounds of chemicals consumed or tons of steel treated, the greatest use of phosphate coatings is as a base for paint. Phosphate coatings are also used to provide:

- A base for oil or other rust-preventive material
- Lubricity and resistance to wear, galling, or scoring of parts moving in contact, with or without oil
- A surface that facilitates cold forming
- Temporary or short-time resistance to mild corrosion
- A base for adhesives in plastic-metal laminations or rubber-to-metal applications

Phosphate Coatings as a Base for Paint

The useful life of any painted metal article depends mainly on the durability of the organic coating itself and the adherence of the film to the surface on which it is applied. The primary function of any protective coating of paint is to prevent corrosion of the base metal in the environment in which it is used. To accomplish this purpose, the method of preparing the metal should reduce the activity of the metal surface, so that underfilm corrosion is prevented at the interface between paint and metal.

When used as a base for paint films, phosphate coatings promote good paint adhesion, increase the resistance of the films to humidity and water soaking, and substantially retard the spread of any corrosion that may occur. A phosphate coating retards the amount of corrosion creep, because the coating is a dielectric film that insulates the active anode and cathode centers existing over the entire surface of the base metal. By insulating these areas, corrosion of the surface is arrested or at least substantially retarded.

Zinc phosphate coatings of light to medium weight (1.6 to 2.1 g/m^2, or 5.2 × 10^{-3} to 6.9 × 10^{-3} oz/ft^2) and lightweight iron phosphate coatings (0.3 to 0.9 g/m^2, or 1 × $10^{-;3}$ to 3 × 10^{-3} oz/ft^2) are generally used for paint bases. Examples of products so treated are steel, galvanized and aluminum stampings for automobiles, household appliances, metal cabinets, and metal furniture (Table 3). Enamel that is baked at a temperature of 205 °C (400 °F) or higher can be successfully applied to phosphate-coated steel.

Table 3 Low-carbon sheet steel components spray phosphate coated for paint finishing

Part	**Area**		**Production, pieces/h**
	m^2	**ft^2**	
Zinc phosphate[(a)]			
Automobile body	74	800	50
Dryer shell	4.0	42.5	400
Cabinet back panel	1.18	12.7	700
Cabinet top	0.73	7.9	1400
Compressor housing	0.42	4.5	600
Motor access panel	0.15	1.6	4500
80 mm mortar shell	0.093	1.0	1000

Iron phosphate[b]			
Washing machine shell	4.91	52.9	330
Dryer top	1.18	12.7	660
Range side panel	0.90	9.7	660
Dishwasher door	0.78	8.4	660
Wiring channel	4.5	4.9	4950
Control housing	0.35	3.8	1980
Condenser cover	0.15	1.6	3330
Range gusset plate	0.078	0.84	4950
Conduit cover plate	0.029	0.31	8900

(a) 1.6 to 2.1 g/m^2 (5.2 × 10^{-3} to 6.9 × 10^{-2} oz/ft^2).

(b) 0.4 to 0.9 g/m^2 (1 × 10^{-3} to 3 × 10^{-3} oz/ft^2)

Phosphated surfaces to be painted should not be touched by bare hands or other parts of the body, to ensure good adherence of the paint film. Body salts can contaminate phosphate coatings. Contaminated areas can be reflected as surface imperfections of the paint film and can decrease corrosion and humidity resistance.

Metals Cleaned in Phosphoric Acid versus Those Coated with Phosphate. Phosphoric acid metal cleaners usually consist of phosphoric acid and a water-soluble solvent, with or without a wetting agent. In the preparation of metal with such solutions, the purpose is to complete the following steps in a single operation: remove oil, grease, and rust; and provide a slight etch of the metal to promote the adhesion of paint. The cleaning solution must contain enough acid (15 to 20% H_3PO_4) and solvent to remove rust, oil, and grease. This concentration of phosphoric acid prevents the formation of any substantial phosphate coating.

When metal surfaces are to be phosphate coated, articles are first freed of rust and grease by suitable cleaning methods. Articles are then treated with a balanced dilute acid phosphate salt with a slight excess of acid (0.6 to 1.0% H_3PO_4), so that reaction of the acid with the metal results in the conversion of the surface to a refined crystalline phosphate coating. Tests conducted on steel cleaned with phosphoric acid have revealed that the phosphate film remaining from the cleaning operation averages only 0.05 to 0.10 g/m^2 (1.6 × 10^{-4} to 3.3 × 10^{-4} oz/ft^2) of surface. In contrast, when steel is phosphated for painting by using standard zinc phosphating solutions, coating weights usually range from 1.08 to 4.3 g/m^2 (3.5 × 10^{-3} to 1.4 × 10^{-2} oz/ft^2), depending on the solution and method.

Corrosion Protection

Conversion of a metal surface to an insoluble phosphate coating provides a metal with a physical barrier against moisture. The degree of corrosion protection that phosphate coatings impart to surfaces of ferrous metals depends on uniformity of coating coverage, coating thickness, density, and crystal size, and the type of final seal employed. Coatings can be produced with a wide range of thicknesses, depending on the method of cleaning before treatment, composition of the phosphating solution, temperature, and duration of treatment. In phosphating, no electric current is used, and formation of the coating depends primarily on contact between the phosphating solution and the metal surface and on the temperature of the solution. Consequently, uniform coatings are produced on irregularly shaped articles, in recessed areas, and on threaded and flat surfaces, because of the chemical nature of the coating process.

The affinity of heavy phosphate coatings for oil or wax is used to increase the corrosion resistance of these coatings. Frequently, phosphate-coated articles are finished by a dip in nondrying or drying oils that contain corrosion inhibitors. The articles are then drained or centrifuged to remove the excess oil.

Medium to heavy zinc phosphate coatings, and occasionally, heavy manganese phosphate coatings are used for corrosion resistance when supplemented by an oil or wax coating. Zinc phosphate plus oil or wax is usually used to treat cast, forged, and hot-rolled steel nuts, bolts, screws, cartridge clips, and many similar items. Manganese phosphate plus oil or wax is also used on cast iron and steel parts.

Phosphate Coating as an Aid in Forming Steel

The contact pressure used in deep drawing operations sets up a great amount of friction between the steel surface and the die. The phosphate coating of steel as a metal-forming lubricant, before it is drawn:

- Reduces friction
- Increases speed of the drawing operations
- Reduces consumption of power
- Increases the life of tools and dies

When phosphate-coated steel is used in drawing seamless steel tubing, the resulting decrease in friction is so pronounced that greater reduction of tube size per pass is possible. This reduction may be as great as one-half.

Reduction in the number of draws and anneals in deep forming results in economy of operation. Conversion of a steel surface to a nonmetallic phosphate coating permits the distribution and retention of a uniform film of lubricant over the entire surface of the steel. This combination of lubricant and non metallic coating prevents welding and scratching of steel in the drawing operations and greatly decreases rejections.

Zinc phosphate coatings of light to medium weight are applied to steel to aid in drawing and forming operations. The phosphated surface is coated with a lubricant (such as soap, oil, drawing compound, or an emulsion of oil and fatty acid) before the forming operation. The zinc phosphate surface, which prevents metal-to-metal contact, makes it practical to cold form and extrude more difficult shapes than is possible without the coating. Table 4 lists and describes some products that are zinc phosphate dip or spray coated before being cold formed.

Table 4 Applications of zinc phosphate dip spray coating to facilitate cold forming

Part(a)	**Steel**	**Area**		**Coating weight**		**Production, pieces/h**	**Sequence of operations**
		m^2	**ft^2**	**g/m^2**	**$oz/ft^2 \times 10^{-2}$**		
Spark plug body	1110	0.0002	0.002	4.3-6.5	1.4-2.1	500	(b)
Universal-joint bearing cup	1010	0.005	0.05	4.3-6.5	1.4-2.1	2000	(b)

Truck wheel nut	1008	0.007	0.08	4.3-6.5	1.4-2.1	1000	[(b)]
Piston pin	5015	0.009-0.014	0.1-0.15	5.4-7.0	1.8-2.3	2600	[(b)]
Standard-transmission output shaft	4028	0.009-0.014	0.1-0.15	4.3-6.5	1.4-2.1	300	[(b)]
Rocket-nozzle plate (69.85 mm or 2.75 in.)	4130, 4140	0.05	0.5	4.3-6.5	1.4-2.1	150	[(c)]
Mortar shell (80 mm or 3.2 in.)	1010	0.07-0.11	0.8-1.2	4.3-6.5	1.4-2.1	4000	[(d)]
Cartridge cases (75 mm or 3 in.)	1030	0.08-0.28	0.9-8.0	4.3-6.5	1.4-2.1	1000	[(c)]

(a) Bath used for all applications listed is zinc phosphate bath accelerated with nitrous oxide.

(b) Alkaline wash, rinse, activating rinse, phosphate, rinse, neutralizing rinse, oil dip.

(c) Sulfuric acid pickle, rinse, rinse, phosphate, rinse, rinse, oil dip.

(d) Alkaline wash, rinse, sulfuric acid pickle, rinse, rinse, phosphate, rinse, oil dip

Wear Resistance

Phosphating is a widely used method of reducing wear on machine elements. The ability of phosphate coating to reduce wear depends on uniformity of the phosphate coating, penetration of the coating into metal, and affinity of the coating for oil. A phosphate coating permits new parts to be broken in rapidly by permitting retention of an adequate film of oil on surfaces at that critical time. In addition, the phosphate coating itself functions as a lubricant during the high stress of break-in.

Heavy manganese phosphate coatings (10.8 to 43.0 g/m^2, or 3.5×10^{-2} to 0.14 oz/ft^2), supplemented with proper lubrication, are used for wear-resistance applications. Parts that are manganese phosphate coated for wear resistance are listed in Table 5.

Table 5 Parts immersion coated with manganese phosphate for wear resistance

Part[(a)]	**Material**	**Coating time, min**	**Supplementary coatings**
Components for small arms, threaded fasteners[(b)]	Cast iron or steel; forged steel	15-30	Oils, waxes
Bearing races	High-alloy steel forgings or bar stock	7-15	Oils, colloidal graphite

Valve tappets, camshafts	Low-alloy steel forgings or bar stock	7-15	Oils, colloidal graphite
Piston rings	Forged steel, cast iron	15-30	Oils
Gears[(c)]	Forged steel, cast iron	15-30	Oils

(a) Coating weights range from 10.8 to 43.0 g/m^2 (3.5×10^{-2} to 0.14 oz/ft^2).

(b) Coating may be applied by barrel tumbling.

(c) Coating weights range from 5.4 to 43.0 g/m^2 (1.8×10^{-2} to 0.14 oz/ft^2).

When two parts, manganese phosphated to reduce friction by providing lubricity, are put into service in contact with each other, the manganese coating is smeared between the parts. The coating acts as a buffer to prevent galling or, on heavily loaded gears, welding. The phosphate coating need not stand up for an extended length of time, because it is in initial movements that parts can be damaged and require lubricity. For example, scoring of the mating surfaces of gears usually takes place in the first few revolutions. During this time, the phosphate coating prevents close contact of the faces. As the coating is broken down in operation, some of it is packed into pits or small cavities formed in gear surfaces by the etching action of the acid during phosphating.

Long after break-in, the material packed into the pits or coating that was originally formed in the pits prevents direct contact of mating surfaces of gear teeth. In addition, it acts as a minute reservoir for oil, providing continuing lubrication. As work hardening of the gear surfaces takes place, the coating and the etched area may disappear completely, but by this time scoring is unlikely to occur.

Phosphate-Coated Ferrous Alloys

In general, the stainless steels and certain alloy steels cannot be successfully phosphate coated. All other steels accept a coating, with difficulties experienced in the coating process varying with alloy content. Most cast irons are readily coated, and alloy content has little effect on their coatability.

Steels

Whether coatings are applied to steel by spray or immersion, a rule of thumb is that lightweight, amorphous phosphate coatings adhere better, while heavier, crystalline zinc phosphate coatings are more corrosion resistant (Ref 4).

Most phosphate-coated steel is low-carbon, flat-rolled material used for applications such as sheet metal parts for automobiles and household appliances, and phosphating processes have been designed for coating such material. Steels with carbon contents in the range specified for 1025 to 1060 inclusive are suitable for phosphating if the silicon content is held to normal limits. Steels with higher carbon contents, in the range from 1064 to 1095, may require the following modifications of phosphating processes to produce satisfactory results: increasing time; increasing temperature; or increasing solution strength. Copper content up to 0.3% in low-carbon steel, the normal limit for copper-bearing steel, is not a deterrent to phosphate coating. The addition of copper, by itself, at about 0.5% causes surface checking of steel during hot rolling. This acts as a restriction on the amount of copper that may be present to serve as a deterrent to phosphating.

Low-alloy, high-strength steel, provided nickel or chromium does not exceed 1%, can be successfully phosphated. Generally, with some modification, chromium content of up to 9% can be tolerated while still depositing a phosphate coating. Nickel-chromium and chromium stainless steels are not recommended for phosphate coating. For some applications, however, oxalate coating processes are used.

Because electrical steels used in motor laminations and electrical transformers have a silicon content in the range of 1.2 to 4.5%, they are not recommended for phosphate coating by normal phosphating processes. These require processes accelerated by the use of fluoride compounds or special dried-in place salts of phosphates.

Low-carbon steels annealed in a properly controlled atmosphere to provide a clean, oxide-free surface are readily phosphated. Temper-rolled, annealed, low-carbon steels are the most readily phosphated of all steels. Cold-reduced or cold-rolled, full-hard, low-carbon steels readily accept phosphate coatings.

Low-carbon, hot-rolled steel, and normalized and pickled steel, if thoroughly rinsed after pickling, phosphate well. Excessive amounts of residual pickling salts (sulfates) can interfere with normal phosphating. Pickling residue on cold-reduced or cold-rolled steels seldom presents problems, because of the extensive processing that follows the pickling operation. Cold reduction of 30 to 70% spreads the residue over large areas. Cleaning and scrubbing of a cold-reduced strip, followed by annealing and temper rolling, remove or dilute surface contaminants. Phosphating processes that provide for relatively long-time and high-temperature treatments are the least sensitive to small variations in alloy composition and surface conditions.

Stainless Steels (Ref 5). Although phosphate coating of stainless steel is difficult, it is sometimes attempted to protect against pitting in chloride atmospheres. Pretreatment is generally required if an organic coating will be applied.

One study achieved good zinc phosphate coatings using the following bath composition:

Component	Concentration	
	g/L	lb/gal × 10^{-2}
Zinc oxide	16-20	13.3-16.7
Phosphoric acid	13-16	10.8-13.3
Calcium chloride	9-12	7.5-10.0
Ferric chloride	0.5-1.0	0.4-0.8

The researchers tested temperatures from 40 to 80 °C (105 to 175 °F) and immersion times of 15 to 50 min. Various stainless steel pretreatments were tested for their effects on coating adhesion and quality: solvent degreasing, immersion in hydrochloric acid or sulfuric acid solution, and sand blasting.

The results showed that the most effective operating conditions were 60 to 70 °C (140 to 160 °F) with immersion times of 15 to 30 min. Sandblasting with 16-mesh sand proved to be the best pretreatment. The zinc phosphate coatings on stainless steel panels prepared under these conditions were uniform and well adherent. The corrosion resistance of the panels was tested by immersing them in 0.5% NaCl solution and exposing them to a salt-spray chamber, and no rust spots were observed within 15 days for either test. Paint adhered as well to phosphated stainless steel panels as to nonphosphated panels.

Galvanized Steel. Many parts produced from galvanized sheet steel, such as certain automotive stampings and some appliances, require a phosphate coating as a base for a subsequent paint film. Phosphating imparts superior resistance to corrosion and greater ability to retain paint to galvanized sheet and strip steel by converting the surface to an insoluble phosphate coating. Galvanized steel can be readily phosphated provided the surface of the plate has not been passivated by a chromate-based solution. The passivated surface of the chromate-treated material resists the action of a phosphating solution. Treatment of such passivated surfaces requires the use of an alkali-permanganate solution or, depending on the age and degree of passivation, removal with strong alkaline cleaners.

Cast Irons

Gray, ductile, or malleable iron castings are readily phosphated. The ability of a cast iron to accept a phosphate coating is not affected by alloy content, but hinges primarily on two requirements, a clean surface and a metal temperature approximately equal to that of the phosphating bath. Machined surfaces need no further cleaning; however, cast surfaces can be prepared by removing scale and sand by blasting or other cleaning.

Phosphating bath temperatures are not critical for cast iron. Acceptable coatings can be obtained in baths ranging from 70 to 95 °C (160 to 205 °F). Often, lower temperatures are viable. A problem usually exists in raising the temperature of a casting, particularly one with heavy sections, to approximate the temperature of the bath. Preheating heavy castings to the temperature of the bath minimizes or eliminates excessive pickling action in areas that require a long time to reach the temperature of the phosphating solution.

Manganese phosphate coatings, applied only by immersion, are easily deposited on cast iron surfaces. The normally coarse crystal breaks down readily to provide temporary lubrication during break-in. If this is not sufficient, castings may be given a supplemental oil dip. Interstices between the coarse crystals hold sufficient oil to provide adequate short-time lubrication.

Because manganese phosphate crystals on cast iron build up rapidly to thicknesses of as much as 25 μm (1 mil), machined dimensions carrying close tolerances may be altered significantly by coating. If this is not acceptable, the dimension can be reduced by removing some of the coating thickness. If a fine crystalline structure is necessary, the presence of an appropriate oil on the surface before phosphating, such as film remaining after emulsion cleaning, refines the normally coarse phosphate crystal. Preferably, special manganese phosphate activating chemicals are used in a water rinse preceding the manganese phosphate process.

References cited in this section

4. R. Bridger and P. Burden, Conversion Coating Is Becoming the Norm Prior to Powder Coating, *Prod. Finish.,* April 1988, p 6-8

5. J.A. Guirklis, Surface Finishing, *CAB Curr. Aware. Bull. (200),* April 2-3, 1990, 9012, p 3

Phosphate-Coated Nonferrous Materials

Aluminum. Zinc phosphate coatings, applied via spray, are easily deposited on aluminum surfaces provided fluoride ion is present in the bath. Sodium or potassium salts are also present to prevent the buildup of soluble aluminum in the bath, which inhibits coating formation. In the processing of a metal mix of aluminum, steel, and galvanized steel, separate fluoride additions to the bath may be required if the metal mix consists of greater than 10% aluminum. Coating weights range from 0.27 to 2.2 g/m^2 (8.8×10^{-4} to 7.2×10^{-3} oz/ft^2).

Zinc (Ref 6). For zinc castings, the phosphate coatings used commercially are amorphous phosphate/molybdate coatings and crystalline zinc phosphate coatings. The most widely used are zinc phosphate conversion coatings, which are used primarily as precoats for organic finishes. For example, under paint films, metal surfaces remain conductive, and corrosion will occur if the film is broken. Phosphate coatings give the zinc casting an insoluble nonconductive film that minimizes the spread of corrosion, improves mechanical adhesion, and reduces paint blistering (because the conversion coat is "micro-rough").

Reference cited in this section

6. D. Elliott, Finishing of Zinc Casting Alloys, *Die Cast. Manage.,* Feb 1992, p 28-31

Process Fundamentals

The application of a phosphate coating for paint-based application normally comprises five successive operations: cleaning, rinsing, phosphating, rinsing, and chromic acid rinsing. Some of these operations may be omitted or combined, such as cleaning and coating in one operation. Additional operations may be required, depending on the surface condition of parts to be phosphated or on the function of the phosphate coating. Parts exemplifying these exceptions are:

- Heavily scaled parts, which may require pickling before cleaning.
- Parts with extremely heavy coatings of oil or drawing compounds, which may require rough cleaning before the normal cleaning operation.
- Parts that are tempered in a controlled atmosphere before being phosphated, which may not require cleaning and rinsing before phosphating.
- Parts that are phosphated and later oiled for antifriction purposes, which may have the chromic acid rinse omitted, because corrosion resistance is not required. (Some rust-preventive oils negate the need for a chromic rinse while still providing excellent corrosion resistance.)
- Automotive parts when electrodeposition of a primer is involved. (A deionized water rinse is required after the chromic acid rinse.)

Hexavalent chromic acid for a passivating rinse is no longer used in some plants because of strict effluent controls imposed by the Environmental Protection Agency (EPA). Other, less restricted materials, such as phosphoric acid and various proprietary compounds, are being used.

Cleaning

Because the chemical reaction that results in the deposition of a phosphate coating depends entirely on the phosphating solution's making contact with the surface of the metal being treated, parts should always be sufficiently clean to permit the phosphating solution to wet the surface uniformly. Cleaning may involve chemical action, mechanical action, or both. Precautions must be taken to avoid carryover of cleaning materials into phosphating tanks. This is particularly true for alkaline cleaners, which can neutralize the acid phosphating solutions, rendering them useless. Other cleaning compounds can contaminate the bath, causing poor quality coatings, such as complex phosphates. A typical alkaline cleaner is formulated as follows (Ref 1):

Component	**Composition, %**
Caustic	8-10
Phosphate	4-5
Sequestering agents	0.5-1.0
Buffer (soda ash)	3-5
Detergents (anionic/nonionic)	8-10

Soil that is not removed can act as a mechanical barrier to the phosphating solution, retarding the rate of coating, interfering with the bonding of the crystals to the metal, or completely preventing solution contact. Some soils can be coated with phosphate crystals, but adherence of the coating will be poor and affect the ability of a subsequent paint film to remain continuous.

Ordinary mineral oil is usually easy to remove and presents no problem to the phosphating processes. However, with the use of more complex materials in forming metal, in rustproofing metal, in stripping paint, and in removing scale, cleaning has become a major consideration in any phosphating operation. Materials such as cutting oils, drawing compounds, coolants, and rust inhibitors can react with the base metal and form a deleterious film.

Several solutions to phosphating problems that arose because of improper or inadequate surface preparation have been used in actual production situations. In one plant, irregularities occurred in the thickness and crystal size of phosphate coatings on deep-drawn parts. These irregularities varied in severity, but were sometimes acute enough to cause roughness in the subsequently applied paint film. When fresh cleaning solutions were used, the problem was somewhat alleviated, but the irregularities recurred after cleaners had been in use for only a short time. Investigation revealed that a variety of drawing compounds were being used on the parts, and that each contributed in some degree to the contamination of the cleaner and the inability of the cleaner to remove soil. Some drawing compounds react with the steel surface, forming oxides not removable by regular cleaners. Other drawing compounds cause excessive, undesirable foaming when in contact with cleaners. Still other drawing compounds form into small globules in the cleaner and are redeposited on the metal and not completely removed in the subsequent rinse. The degree of cleanness of the parts was reflected in the degree of variation of the phosphate coating. The problem was solved by using a different cleaner with a different detergent system plus an increase in caustic content, and by selecting drawing compounds that, while still performing as required, would be effectively removed by this cleaner without contaminating it.

Another solution was used during an extended production run of 80 mm (3.2 in.) mortar shell cases. In this situation, dip phosphoric acid pickling was replaced by spray sulfuric acid pickling as the final cleaning operation before phosphating for a paint base. Pickling was followed by two rinses. Between pickling and phosphating, a 100% hydrostatic test was required for assurance that the pickling solution had not opened any pinholes through the soldered tail plugs of the shell cases. With sulfuric acid pickling, chromic acid was added to the second rinse as a rust inhibitor to protect parts during test and transfer. The phosphate coatings obtained after this changeover were of poor quality because little or no coating was deposited on the outsides of the shell cases, and inside surfaces rusted badly. All materials and processes were checked and found to be in order. Sample panels that were processed, but not pickled, accepted a satisfactory coating. The problem was traced to a passive film on the shell surfaces, left there by the chromic acid in the final rinse after pickling. Replacing the chromic acid rinse with an alkaline sodium nitrite rinse solved the problem.

In another plant, manganese phosphate coatings had been successfully applied to a variety of machined steel parts. One of these parts, produced in high volume, was a valve tappet of low-alloy steel, for which a surface finish of 0.1 to 0.3 μm (4 to 10 μin.) was required. For no apparent reason, difficulty was suddenly encountered in the form of mottled, noncrystalline coatings and occasional bare spots on the tappets. Other parts were satisfactorily coated. It was discovered that a change in polishing compound had been made to facilitate obtaining the required finish on the tappets. Carrier wax in the new compound contained a larger amount of unsaturated material than was in the wax in the previous polishing compound. These unsaturates are more readily oxidized to insoluble compounds by the heat generated in polishing than are fully saturated material. Reverting to the original polishing compound corrected the difficulty.

In another instance, an alkaline cleaner at a concentration of 7.5 g/L (6.3×10^{-3} lb/gal) was used in the cleaning stage in a zinc phosphating line for processing sheet steel stampings. Stampings were coated with mill oil and drawing oil, and cleaning was satisfactorily accomplished. On certain new parts, however, because of a difficult drawing operation, a pigmented drawing compound was required that consisted of emulsified palm oil and powdered French talc. The cleaner would not remove this drawing compound sufficiently to permit acceptable coatings to be deposited. It was found that the cleaner was removing the oil but leaving the talc on the parts. Increasing the concentration of the alkali in the cleaner to 15 g/L (0.13 lb/gal) resulted in no improvement. However, when the temperature of the cleaner was lowered to 70 °C (160 °F), both oil and talc were removed, permitting satisfactory phosphate coatings. This is counter to the concept that cleaning efficiency increases with the temperature of the cleaner.

Parts that have been tempered in air or a controlled atmosphere, as the last operation before phosphating, usually require no cleaning before being phosphated. The blue oxide film imparted by the normal tempering operation is not detrimental to phosphating. However, if tempering produces a scaly or sooty surface, or if scale or soot is produced in the heat-treating furnace and is not removed before tempering, the parts must be descaled by acid pickling, tumbling, or blasting. Incorporation of crystal refiners (titanation) into the alkaline cleaner promotes the deposition of a dense, finely crystalline zinc phosphate coating. Overheating (greater than 65 °C, or 150 °F) of the activated cleaner stage inhibits the crystal refinement effect.

Rinsing after Cleaning

In the past, water at 70 to 80 °C (160 to 180 °F) ordinarily was used for rinsing parts after cleaning and before phosphating. Hot water is in effect an additional cleaner, serving to remove cleaning compounds that adhere to part surfaces. Ambient temperature rinses are now often used. Parts may be rinsed by immersion or spray. A single rinse tank or spray stage is usually adequate for rinsing simple parts, and a minimum rinse time of 30 s is normally required. An additional spray rinse stage should be added for parts with blind holes or deep recesses.

Immersion Rinsing. Rinse tanks should be equipped to provide adequate agitation of rinse water to increase rinsing efficiency. Agitation may be accomplished using compressed air at low pressure, distributed through evenly spaced holes in pipes laid along the bottom of the tank. However, where compressed air is not available, pumping rinse water through similar pipes can provide suitable agitation. Fresh water may be continuously added to the tank through such pipes to provide agitation, but a siphon-breaker must be installed in the supply line to prevent siphoning contaminated rinse water into the water supply system. The supply of makeup water should be planned to provide adequate rinsing without wasting water. Relatively pure waters, containing less than 150 ppm total solids, require less replacement water than harder or impure waters containing 400 to 600 ppm total solids.

Use of solenoid valves, controlled by conductivity meters in water supply lines to rinse tanks, can maintain adequate rinse water purity at minimum waste. Another effective method of improving rinse water quality is to supply makeup water through spray nozzles. This process causes the fresh water to be the last water to hit the parts as they are being withdrawn from a dip rinse or carried from a spray rinse station. Rinse water makeup added to a water rinse tank other than by the methods discussed above should be supplied. to the end of the tank opposite the overflow trough. Water containing appreciable quantities of chlorides, fluorides, or sulfides may not provide good rinsing. The length of time parts are allowed to remain in the rinse tank depends on their complexity and on the material to be rinsed away.

Spray Rinsing. Vertical and horizontal spacing and size of the nozzles in a spray rinse tunnel are determined by the size and nature of parts being processed and the speed of the conveyor carrying parts through the tunnel. A pressure of 70 to 140 kPa (10 to 20 psi) at the nozzle is normally adequate. Minimum pump volume capacity is determined by multiplying the volume capacity of the nozzle at the desired pressure by the number of nozzles required and adding an allowance for losses required and adding an allowance for losses because of piping length and restrictions. A spray rinse tank should hold a minimum volume of $2\frac{1}{2}$ times the volume of solution piped through the nozzles per minute.

Rinse solutions should be piped from the pump or pumps through large main headers to vertical drop lines containing the nozzles. To assist in scale removal, drop lines should be fitted on the bottom with removable caps. Pressure that is too high may be relieved by drilling suitable holes in the center of bottom caps. This also enables excess rinse solution to flush out scale and sludge continuously. A hot water spray rinse station is shown schematically in Fig. 1. The rinse before phosphating should be maintained slightly alkaline (7.5 to 9.0 pH) to prevent rust-blushing of parts. A rinse containing crystal refiners is recommended just before the phosphate stage.

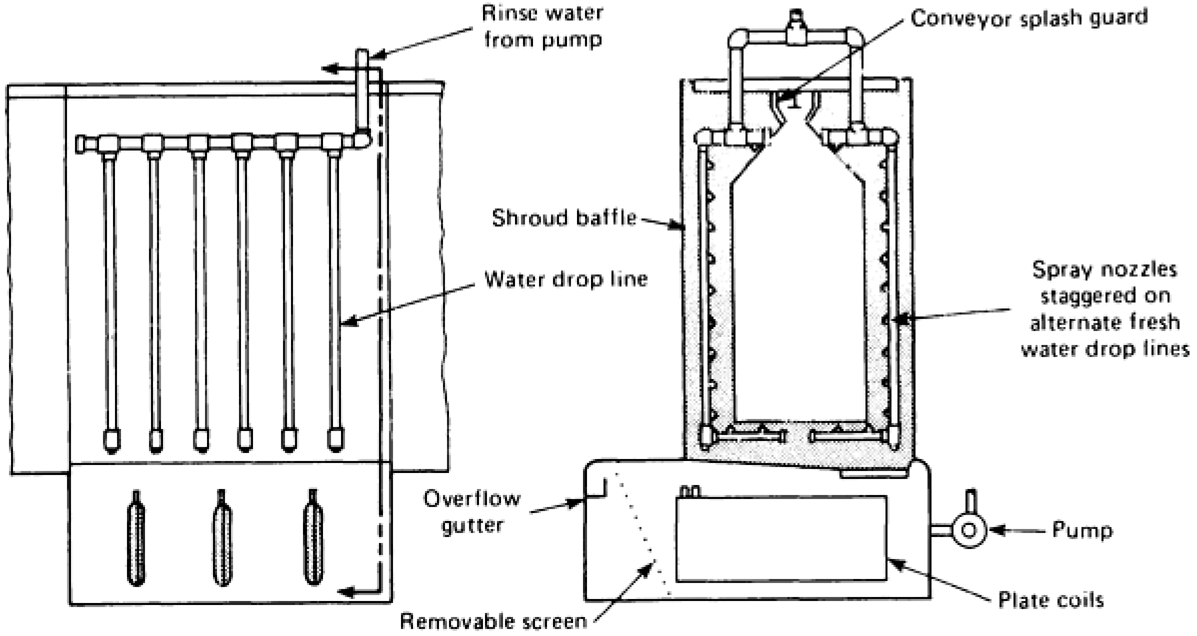


Fig. 1 Schematic of a hot water rinse station in a spray phosphating line

Phosphating Methods

Phosphate coatings may be applied to a surface by either immersion or spray, or a combination of immersion and spray. There has been a modern trend worldwide to the immersion treatment of automobile bodies using zinc-phosphate coating processes. This is usually a combination of spray and immersion. The work is sprayed as it enters the phosphate tank as well as when it exits. Occasionally, a surface may be coated by brushing or wiping, but these methods are seldom used.

Immersion. All three types of phosphate coatings, zinc, iron, and manganese, can be deposited by immersion. Immersion is applicable to racked parts, barrel coating of small parts, and continuous coating of strip. In general, smaller parts are more economically coated by immersion than by spraying. Small parts, such as springs, clips, washers, and screws that are produced in large volume, can be coated efficiently only in an immersion system. Such parts are loaded into drums that are rotated at approximately 4 rev/min after they are immersed in the phosphating solution. Small parts may be placed in a basket and immersed, without rotation, in the bath for coating. This method generally is not completely satisfactory, because no phosphate is deposited where parts contact each other or the basket. It is used as a stopgap method or when volume is too low to justify the use of rotating drums.

Low-volume larger parts are immersed manually in a tank. Certain large parts produced in large volume, but whose shape does not encourage complete coverage by spray phosphating, may be coated by immersion. Intricately shaped parts, such as hydraulic valves or pump bodies that have areas inaccessible to spray, are immersion coated. Either immersion or the spray method may be used to deposit heavy zinc phosphate coatings used as aids in cold extruding or drawing. However, the immersion system usually provides a heavier coating. Shell casings formed by cold extrusion are first coated by the immersion system to produce the heavy coating required for the cold extrusion of the metal. After finish machining, the shell casing can be either spray or immersion coated for a paint base. The immersion system usually is preferred, because of the necessity of coating internal areas.

Although a manually operated immersion system requires very little floor space, a conveyorized immersion system requires more floor space than a conveyorized spray system for comparable production quantities. When parts are of comparable size, the immersion system cannot equal the production output of a spray system. An advantage of an immersion system is that the heat required is much less than for a spray system because of the heat lost from the sprays. The use of an immersion system for automotive bodies provides phosphate coverage in areas not accessible by spraying, namely, box sections. In the immersion process, agitation of the solution accelerates coating formation.

Spray. Zinc and iron phosphate coatings are applied by the spray method, although manganese phosphate is not. The spray method is used to apply a phosphate coating to racked parts, such as panels for household appliances, or to a continuous strip. Occasionally, baskets of parts are passed through a spray system, but this is not a preferred method. Spray phosphating, because of the equipment required, is usually most applicable to high-volume coating of parts.

It is easier to control the coating solution for iron phosphating in a spray system, and the resulting coating is generally of better quality than the coating obtained from an immersion system. Zinc phosphate coatings produced by a spray system are usually lighter in weight than those produced by immersion. In addition, different zinc phosphate crystalline structures may result from spraying than those that result from immersion.

Phosphating Time. In general, the spray method produces a given coating weight at a faster rate than the immersion method. In spray zinc phosphating, a coating of 1.6 to 2.1 g/m^2 (0.52 to 0.68 oz/ft^2) normally can be obtained in 1 min or less, whereas obtaining a coating of this weight by the immersion method may require as much as 2 to 5 min. For galvanized steel treated in coil lines, zinc phosphate coatings are produced in times as short as 3 to 5 s; for iron phosphate coatings on cold rolled steel, 5 to 10 s. A 1 min spray application of one iron phosphating solution would result in a coating of approximately 0.3 to 0.4 g/m^2 (9.7×10^{-2} to 0.13 oz/ft^2). It is estimated that it would require 2 to 3 min to produce the same coating weight by immersion. Bath parameters are all interrelated, however. In some operations, coatings can be effectively deposited in 3 to 5 s.

The weight of manganese phosphate coatings on steel surfaces is a function of immersion time, as indicated by the curve in Fig. 2. The slope of this curve can vary. The time required to obtain a specific coating weight in a range of 5.4 to 32.3 g/m^2 (1.8×10^{-2} to 0.106 oz/ft^2) can vary from 2 to 40 min, depending on such factors as the type and hardness of the steel being coated and methods of precleaning and pretreatment. Exposure to the phosphating solution for a shorter time than recommended usually results in a coating that is incomplete, too thin, or both.

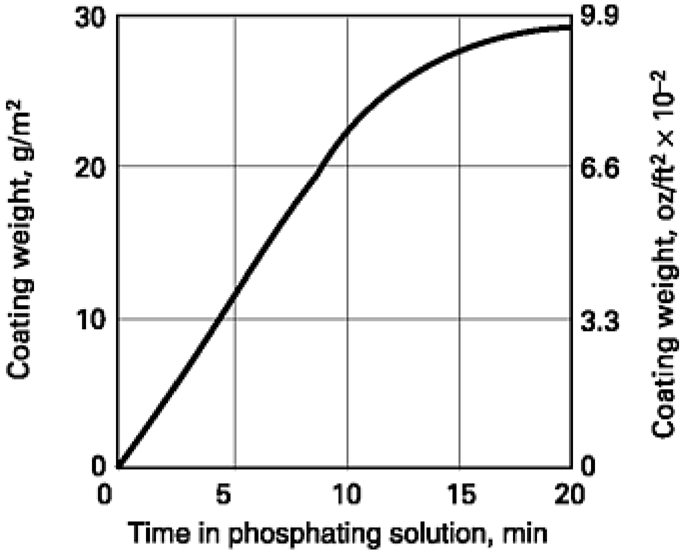


Fig. 2 Plot of manganese phosphate coating weight vs. time of exposure of steel surface to phosphating solution

Operating Temperature. Although operating temperatures of different phosphating solutions may range from 30 to 100 °C, or 90 to 210 °F (Table 6), individual solutions are compounded to operate at maximum efficiency within specific temperature limits. The trend in recent years has been to lower operating temperatures. A phosphating solution should be held within the specified operating temperature range. If the solution is permitted to operate below the minimum recommended temperature, the phosphate coating is thin or nonexistent. If the temperature of the solution exceeds the recommended maximum, the coating builds up excessively and has a nonadherent, powdery surface, and the bath solution may become unbalanced, resulting in excessive sludge and scale. Special low-temperature solutions are available for applying iron or zinc phosphate (see the section "Low-Temperature Coatings" in this article).

Table 6 Operating temperature ranges for phosphating solutions in phosphating applications

Phosphate coating method	**Metal treated**	**Reason for treatment**	**Operating temperature**	
			°C	**°F**
Medium iron, immersion	Steel	Paint bonding	60-82	140-180
Heavy zinc, immersion	Steel	Corrosion resistance	88-96	190-205
Medium zinc, immersion	Steel	Paint bonding	32-82	90-180
Medium zinc, immersion	Steel plated with zinc or cadmium	Paint bonding	60-82	140-180
Medium zinc, spray	Sheet steel	Paint bonding	38-60	100-140
Medium zinc, spray	Steel	Cold drawing	60-74	140-165
Medium zinc, spray	Galvanized steel	Paint bonding	49-60	120-140
Manganese, immersion	Steel	Wear resistance	93-99	200-210

Solution temperature influenced the results obtained in manganese phosphating small cast iron parts. Coatings deposited at the beginning of each day were thin and red-tinged. However, after the tank had been in operation for about $1\frac{1}{2}$ h, conventional coatings (heavy and dark gray) were obtained, and no further trouble was experienced for the rest of the day. Bath analysis revealed that the phosphating solution had an unusually high concentration of free acid at the start of each day's operation, but the concentration was normal at shutdown time. A review of past records indicated that this condition had not previously existed. Investigation revealed that the condition resulted from improper and excessive preheating of the bath before parts were processed. Only the steam bypass was being turned on, thus circumventing automatic temperature controls, which caused the solution to boil, upsetting composition and thereby affecting coating characteristics. A return to correct preheating procedures ended the problem.

Rinsing after Phosphating

Parts must be rinsed after being phosphated to remove active chemicals from the phosphating solution that remains on the surface of coated parts. Any chemicals not removed may cause corrosion of parts or blistering of a subsequent paint film. Any phosphating chemicals carried over into the chromic acid rinse may contaminate the solution used as a rinse. Rinsing after phosphating never should be hot. The temperature should range from 20 to 50 °C (70 to 120 °F), preferably maintained on the low side. A rinse that is too warm may set the residual chemicals and cause them to adhere to phosphate crystals, resulting in a rough coating, whitish appearance of coating, and lower corrosion resistance. Usually, only one rinse is required. If the water supply is so high in mineral content that a residue remains on the parts after rinsing, a rinse in deionized water may be required.

Chromic Acid Rinsing

Most phosphated parts that are used as a base for paint are given a treatment following the post-phosphating rinse. These post-treatments vary from simple chromic-acid solutions to complex proprietary formulas that may be free of chromium entirely. Because of difficulty experienced when these post-treatments are allowed to dry on a phosphated part, because of concentrations of the post-treatment at the lower edges and around openings such as holes or slots, the excess post-treatment should be removed with a deionized water rinse. Better proprietary post-treatments allow removal of the excess with deionized water without substantially decreasing the corrosion resistance of the painted system, while retaining good humidity and physical test results associated with conventional post-treatment. Environmental and health concerns have resulted in increasing interest in and the development of improved chromium-free post-treatments for paint-based applications. In the case of heavy zinc-phosphate coating used with oil for corrosion resistance, chromic acid post-treatment may or may not be used, depending on the quality and nature of the rust-preventing oil applied thereafter.

Zinc or manganese phosphate coatings applied to reduce friction usually do not receive a chromic acid rinse, because they are not applied for corrosion resistance. Rather, oil films are normally applied after phosphating to increase antifriction properties of coatings. On parts phosphated to assist in cold extrusion or drawing, application of drawing lubricants usually supplants the chromic acid rinse.

Reference cited in this section

1. D. Phillips, Practical Application of the Principles Governing the Iron Phosphate Process, *Plat. Surf. Finish.*, March 1990, p 31-35

Chemical Control of Phosphating Processes

An efficiently operated phosphating line includes close chemical control of all materials used. Even the mineral content of plain water rinses may need to be controlled to avoid leaving a residue on parts. To obtain satisfactory phosphate coatings on steel surfaces, phosphating solutions must be chemically controlled within limits. These limits vary, depending on the specific phosphating concentrate used. Solutions should be tested on a regular schedule. Frequency of tests is determined by the work load of the phosphating line.

Zinc Phosphating Solutions. When zinc phosphating solutions become unbalanced, the results are poor coatings, excessive sludge buildup, and insufficient coating weights. Several chemical tests are usually made on a zinc phosphating solution used for paint-based application, to determine its suitability for coating. These are tests of:

- Total acid value
- Accelerator content
- Free acid
- In the case of heavy zinc phosphate coatings for use with oil, the iron concentration (ferrous iron)
- Zinc concentration

Total Acid Value. Zinc phosphate solutions have a total acid value established that should be maintained for good performance. One regularly used solution is controlled at 25 to 27 points. To determine the total acid value, a 10 mL (3×10^{-3} gal) sample of the solution is titrated with 0.1 *N* sodium hydroxide (NaOH) (1 mL equals 1 point), 1 using phenolphthalein as an indicator. The end point is reached when the solution changes from colorless to pink.

Free-Acid Value. Zinc phosphate solutions have a free-acid value established that should be maintained for satisfactory performance. To determine the free-acid value, a 10 mL (3×10^{-3} gal) sample of solution is titrated with 0.1 *N* NaOH, using bromphenol blue or methyl orange indicator. The end point is reached when the solution changes from yellow to greenish-blue, for the former.

Accelerator Test. Sodium nitrite is used as an accelerator in some zinc phosphate solutions. It is usually controlled at 30 points. Before the test for sodium nitrite is made, phosphate solution should be tested for absence of iron. This is done by dipping a strip of iron-test paper in phosphate solution. If the paper does not change color, no iron is present in the solution. If the paper changes to pink, however, iron is present, and small additions of sodium nitrite are then made until an iron-test paper shows no change. The sodium nitrite test is made using a 25 mL (6.6×10^{-3} gal) sample of the phosphate solution. From 10 to 20 drops of 50% H_2SO_4 are added carefully to the solution and it is then titrated with 0.042 *N* potassium permanganate. The end point is reached when the solution turns from colorless to pink (1 mL equals 1 point).

The sodium nitrite test may also be performed using a gas evolution apparatus. After the apparatus is filled with the bath solution, sulfamic acid 4 g (0.14 oz) is added to the solution. Evolution of gas into the calibrated section of the apparatus provides the direct reading (in milliliters) of sodium nitrite in the bath. The milliliter of gas is equivalent to the milliliter reading obtained with the potassium permanganate ($KMnO_4$) titration procedure.

Iron Concentration. Because iron is constantly being dissolved from parts being zinc phosphated, the concentration of iron may build up until the efficiency of the solution is impaired. Some zinc phosphating solutions operate best when the iron concentration is maintained between 3 and 4 points. Production experience with a particular solution will indicate whether the iron content can be expanded without affecting the quality of the coating. To determine the iron content, a 10 mL (3×10^{-3} gal) sample of solution is first acidified with a sufficient amount of a 50% mixture of sulfuric and phosphoric acid to ensure a low pH while titrating (2 or 3 drops may be sufficient). The solution is then titrated with 0.2 *N* $KMnO_4$ until a permanent pink color is obtained (1 mL equals 1 point).

This titration is used for immersion zinc phosphating solution. Spray zinc phosphating usually does not involve a buildup of iron in the solution because of the oxidizers that are present. Immersion zinc phosphate solutions generate, in situ, sufficient nitrite to prevent iron buildup. Phosphate coatings formed with iron in the bath usually do not prevent galling during cold-heading processing as well as phosphate baths operated without iron in the bath (Toner side). Immersion zinc phosphating baths are usually controlled by a total and free-acid titration and acid ratio, total acid divided by free-acid values.

Iron Phosphating Solutions. If recommended chemical limits are not maintained in iron phosphating solutions, the results are low coating weights, powdery coatings, or incomplete coatings. To maintain required balance in iron phosphating solutions, titration checks are made to determine the total acid value and the acid-consumed value.

Total acid value is determined by titration of a 10 mL (3×10^{-3} gal) sample of phosphating solution with 0.1 *N* NaOH, using phenolphthalein as an indicator. The end point is reached when the solution changes from colorless to pink. The number of milliliters of the 0.1 *N* NaOH is the total acid value, in points, of the phosphating solution. A normal concentration would be 10.0 points.

Acid-consumed value is determined by titration of a 10 mL (3×10^{-3} gal) sample of phosphating solution with 0.1 *N* HCl, using bromocresol green indicator. The end point is reached when the solution changes from blue to green. A normal range for the acid-consumed value for a solution with a 10-point total acid value would be from 0.0 to 0.9 mL (0 to 2×10^{-4} gal) of 0.1 *N* HCl.

Manganese phosphating solutions used to produce wear-resistant and corrosion-protective coatings are maintained in balance by control of:

- Total acid value
- Free-acid value
- Acid ratio
- Iron concentration

Because the phosphate solutions are acid, these values are determined by titration methods using a standard basic solution. Frequency of control checks on manganese phosphating solutions depends on the amount of work being processed through the tank and on the volume of the solution. However, one to two checks per shift should be sufficient.

Total acid value is determined by titration of a 2 mL (5×10^{-4} gal) sample of phosphating solution with 0.1 *N* NaOH, using phenolphthalein as an indicator. The end point is reached when the solution changes from colorless to pink.

Free-acid value is determined by titration of a 2 mL (5×10^{-4} gal) sample of phosphating solution with 0.1 *N* NaOH, using bromophenol blue indicator. The end point is reached when the solution changes from yellow to blue/violet.

Acid Ratio. To obtain satisfactory coatings, the ratio of total acid to free acid contents of manganese phosphating solutions should be maintained within certain limits. For a solution with a 60- to 70-point total acid value, this ratio should be between 5.5 to 1 and 6.5 to 1. Low-ratio solutions produce incomplete coatings, poorly adherent coatings, or coatings with a reddish cast. High-ratio solutions also result in poor coatings.

Iron Concentration. Because iron is continually dissolved from parts going into the phosphating bath, the concentration of ferrous iron in the bath gradually builds up. Some manganese phosphate coating problems that can be traced to high iron concentrations are: light gray instead of dark gray to black coatings; powdery coatings; and incomplete coatings in a conventional time cycle.

Concentration limits of iron depend on the type, hardness, and surface condition of the steel being treated. A manganese phosphating bath operates satisfactorily with an iron concentration ranging from 0.2 to 0.4%. Production experience indicates whether iron concentration limits can be expanded without affecting the quality of the coating. To determine iron concentration, a 10 mL (3×10^{-3} gal) sample of phosphating solution is used. To this sample 1 mL (3×10^{-4} gal) of 50% H_2SO_4 is added. The solution is then titrated with 0.18 *N* $KMnO_4$. The end point is reached when the solution changes from colorless to pink. One milliliter of the 0.18 *N* $KMnO_4$ is equivalent to 0.1% Fe.

Iron Removal. If iron removal becomes necessary, the ferrous iron in the solution is oxidized with hydrogen peroxide, which causes iron to precipitate as ferric phosphate and also liberates free acid in the bath. Because free acid in the bath increases, lowering the acid ratio, the liberated free acid should be neutralized by adding manganese carbonate. The approximate amount of hydrogen peroxide needed to lower the concentration of iron by 0.1% is 125 mL/100 L (0.16 fl oz/gal) of solution. In this instance, about 450 g (1 lb) of manganese carbonate is needed to neutralize the liberated free acid. Iron removal may be unnecessary if the square footage of steel being processed and the volume of the phosphate bath limit the amount of iron buildup.

Chromic Acid or Other Post-Treatment Solutions. Control of chromic acid or other post-treatment solutions varies considerably because of the wide variety of chemicals and uses. The following procedures are often used with conventional nonreactive chromic-acid post-treatments.

Total acid value is determined by titrating a 25 mL (6.6 × 10^{-3} gal) sample of chromic acid solution with 0.1 *N* NaOH, using phenolphthalein indicator. The end point is reached when the solution changes from amber to a reddish shade that lasts at least 15 s. Each milliliter of 0.1 *N* NaOH required equals 1 point total acid.

Free-acid value is determined by titrating a 25 mL (6.6 × 10^{-3} gal) sample of chromic acid solution with 0.1 *N* NaOH, using bromocresol green indicator. The end point is reached when the solution changes from yellow to green. Each milliliter of 0.1 *N* NaOH required equals 1 point free acid. The concentration of free acid in chromic acid solutions is usually maintained between 0.2 to 0.8 mL (5 × 10^{-5} to 2 × 10^{-4} gal).

Chromate concentration may be determined by placing a 25 mL (6.6 × 10^{-3} gal) sample of solution into a 250 mL (6.6 × 10^{-2} gal) beaker, adding 25 mL (6.6 × 10^{-3} gal) of a 50% H_2SO_4 solution, 2 drops of orthophenan-throline ferrous complex indicator, and titrating with a 0.1 *N* $FeSO_4$ solution. Each milliliter of 0.1 *N* $FeSO_4$ solution of the amount required to change the solution from blue to reddish-brown is 1 point of chromate concentration. Chromate concentration ranges from 200 to 400 ppm (as chromium) and may also be determined with a test kit containing diphenylcarbazide.

In reactive chromate post-treatments, those that can be post-rinsed with deionized water, pH is often used as a means of determining whether the post-treatment solution is in proper balance.

Each supplier has its own particular means of checking the concentration in chromium-free post-treatments and, in some instances, the acidity of the solution.

Solution Maintenance Schedules

The frequency and extent of solution maintenance is dictated by the materials used and the work load of the line. In one plant, a schedule was established for solution testing, solution maintenance, and tank cleaning. The company revised solution-control procedures to correct problems experienced with zinc phosphate coatings produced in a large automatic line. Coatings periodically were coarse and nonuniform, making it necessary to interrupt production to change phosphating solution. A comprehensive program of testing and checking was inaugurated. Routines for solution maintenance and tank cleaning were established that eliminated defective coatings and downtime for changing phosphating solutions. It was determined that the phosphating bath maintained good coating ability for 9 to 10 weeks. However, tanks required cleaning every 4 to 5 weeks because of sludge buildup. The schedule established includes tank cleaning every 4 weeks and solution change every 8 weeks, coinciding with tank cleaning. Work is done on weekends so that production is not interrupted. The solution is allowed to cool and sit idle for 8 h.

For tank cleaning only, the entire contents of the tank are pumped to a reserve tank, the sludge is removed, and the solution is returned to the phosphating tank. When the solution requires changing, the procedure is as follows: top half of solution is pumped to a reserve tank; bottom half is discarded; and sludge is cleaned from the tank. Salvaged solution is then pumped back into the tank, and sufficient water and phosphating concentrate are added to bring the bath to correct concentration and operating level. Iron, in the form of steel wool, and soda ash are added to the solution to adjust it to proper operating condition, so satisfactory coatings can be produced when production is resumed.

Schedules for operating control and tank and solution maintenance were established by another company for a multistage phosphating process in which automobile bodies were phosphated. The surface area of the bodies approximated 70 to 80 m^2 (750 to 860 ft^2). The production rate could range as high as 75 car bodies an hour. The spray chamber of the phosphating line, including drain area, was 12 m (39 ft) in length. The phosphating solution tank, at operating level, holds 4.2 × 10^4 L (1.1 × 10^4 gal). A continuous desludging system is incorporated in the system (hydromation unit). Phosphating and accelerator solutions are replenished continuously and automatically via pH and redox measurements through variable-feed metering pumps. Corrective additions of caustic soda are made manually. Coating weights are maintained at 2.7 to 3.2 g/m^2 (8.8 × 10^{-3} to 1.0 × 10^{-2} oz/ft^2).

Operating Control

Table 7 gives a typical schedule of parameters that must be monitored on a daily basis to produce a quality phosphate coating.

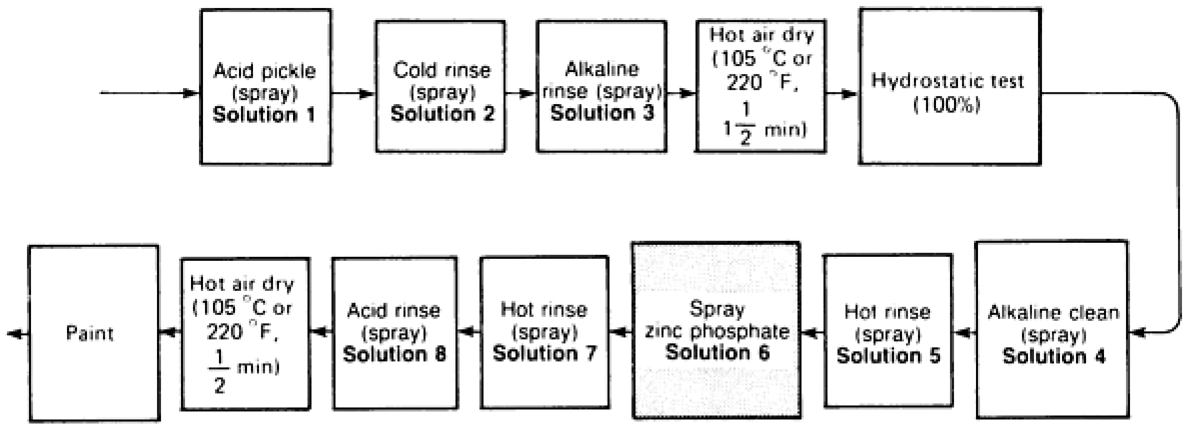
Table 7 Monitoring requirements for quality control of phosphate coating production

Hourly Phosphating solution titrations Total acid Free acid Visual coating appearance Chemical-supply pumps All stages Temperature Pressure Solution level Neutralizing rinse Add 30 mL (0.08 gal) activator, as indicated by visual check of coating continuity Check pH Check film thickness of soap lubricant
Twice per shift Alkaline cleaner stage titrations Alkalinity of water rinses before phosphating Acidity of water rinse after phosphating Activating rinse concentration
Once per shift Conductivity of recirculated deionized rinse, 100 μmho maximum

Tank and Solution Maintenance

The following maintenance schedule should be observed to ensure efficient phosphating operations for the setup described in the flowchart in Fig. 3.

- *Daily*: empty and clean stages corresponding to solutions 4 and 6.
- *Weekly*: empty and clean stages corresponding to solutions 7 and 8.
- *Twice monthly*: empty and clean stages corresponding to solutions 1 and 2.
- *Monthly*: empty and clean stage corresponding to solution 3.
- *Quarterly*: cleaner, water rinse, and phosphate stages should receive heated acidic cleanout. Blocked nozzles should be removed and cleaned or replaced. Heated acidic cleanout may involve inhibited hydrochloric acid.



Solution No.	Type	Composition	Operating temperature		Cycle time, min
			°C	°F	
1	Acid pickle	H_2SO_4, 25 wt%	71	160	2
2	Cold rinse	Water[(a)]	RT	RT	$1\frac{1}{4}$
3	Alkaline rinse	$NaNO_2$, 2.4 g/L (2.0×10^{-2} lb/gal)[(b)]	66	150	$1\frac{1}{4}$
4	Alkaline cleaner	Alkali, 0.7 g/L (5.8×10^{-3} lb/gal)	71	160	$\frac{1}{2}$
5	Hot rinse	Water	66	150	$\frac{1}{2}$
6	Zinc phosphate	NO_2, accelerated[(c)]	60	140	$1\frac{1}{2}$
7	Hot rinse	Water[(a)]	60	140	$\frac{1}{2}$
8	Acid rinse	Chromic and phosphoric acids[(d)]	71	160	$\frac{1}{2}$

(a) Purity maintained by overflow.

(b) Sodium hydroxide added to establish pH of 11.

(c) Total acid, 10 points; free acid, 0.7 to 1.1 points; acid checked using 10 mL (2.6×10^{-3} gal) sample. NO_2 accelerator, 1.5 to 2.0 points, determined using 25 mL (6.6×10^{-3} gal) sample.

(d) Free acid, 0.4 to 0.6 points; total acid, less than 5 points; checked using 25 mL (6.6×10^{-3} gal) sample

Fig. 3 Sequence of operations for spray zinc phosphating of 80 mm (3.2 in.) mortar shell casings before painting. Total area, inside and outside, of each shell was 0.1 m^2 (1 ft^2); coating weight ranged from 1.7 to 2.1 g/m^2 (5.6×10^{-3} to 6.9×10^{-3} oz/ft^2).

Phosphating Tank Maintenance. The phosphate tank should be desludged on a continuous, automatic basis. Depending on work appearance, nozzles and spray pressure at the nozzle may require checking on a monthly basis, rather than quarterly. Phosphate heat exchangers require a heated acidic cleanout to maintain heating efficiency. Acidic cleanout usually involves the following procedure:

1. Pump out solution to holding tank.
2. Flush tank and spray piping with water.
3. Fill to pumping level with water; add hydrochloric acid (1 *N* or 10% volume acid/volume water,V_a/V_w); add inhibitor.
4. Heat to 50 °C (120 °F); circulate spray system for 1 h.
5. Empty tank and flush with water.
6. Fill to pump level; add sodium hydroxide to pH of 10 to 12; circulate 5 to 10 min.
7. Empty tank; flush with water; and restore phosphate solution.

Break-in of Phosphating Solutions. Some zinc and manganese phosphating solutions, although mixed to recommended concentrations, must be broken in by the addition of ferrous salt, such as ferrous sulfate, before they can operate properly. Iron phosphating solutions require no break-in. After being mixed to proper concentration, iron phosphating solutions need only be raised to operating temperature to be ready for use. Most zinc phosphate processes used for paint base or for metal forming operate free of ferrous iron, and the break-in of these phosphating solutions is not a factor.

Zinc Phosphating Solutions. One method of breaking in a zinc phosphating solution is to tolerate a poor phosphate coating until some iron has gone into solution from the chemical reaction between the bath and the parts being coated. Some iron also may be present in sludge that has settled to the bottom of the tank or crusted on the sides from a previous bath. The coatings on first parts are of poorest quality; the coating quality gets progressively better as more iron goes into solution. A simple method is to suspend clean steel wool or scrap in the bath, or to introduce a small quantity of clean iron powder. Another method is to add 170 g (6 oz) of salt, such as ferrous sulfate, to each 380 L (100 gal) of solution. This is applicable to bath spray and immersion baths.

Manganese Phosphating Solutions. Careful attention should be given to breaking in a manganese phosphating bath because of its higher acid concentration in comparison to that of a zinc bath. For the best quality of manganese phosphate coatings, 0.2 to 0.4% Fe^{+2} in solution is the proper range. Usually, breaking in of a new bath is begun by the addition of 170 g (6 oz) of a ferrous salt, such as ferrous sulfate, powder to each 380 L (100 gal) of bath. This is followed by treatments using clean steel wool, powdered iron, or scrap iron to build up ferrous iron content. Manganese phosphating baths operate to best advantage when they have a steady, heavy work load. This permits considerable dissolution of iron, which usually maintains the ferrous iron content at a suitable level.

Equipment for Immersion Systems

An immersion phosphating system for all types of coatings (zinc, manganese, and iron) should include:

- Required number of tanks
- Temperature and solution-level controls
- Overflow and drainage systems
- Vapor-exhaust systems
- Material-handling devices

When drums are used to contain the parts, devices are required at each tank to rotate the drums at approximately 4 rev/min while the drums and the parts within are submerged.

Phosphating tanks are usually made from low-carbon steel plate about 6 mm ($\frac{1}{4}$ in.) thick. A tank and drum for immersion phosphating small parts are shown in Fig. 4. The normal life of a low-carbon steel tank for zinc phosphating solution under average operating conditions is about 1 year. However, some companies report 2 to 3 years of service. One company fabricates zinc phosphating tanks from 9.5 mm ($\frac{3}{8}$ in.) low-carbon steel plate. This tank lasts 4 to 5 years. Stainless steel may give longer life, but its greater cost generally is not justified for a zinc or iron phosphating line, unless acidic solutions contain high levels of chloride. Because of greater acid concentration in manganese phosphating solutions (6 to 10% V_a/V_w as compared with 1 to 3% V_a/V_w in zinc phosphating solutions) and higher operating temperatures used, low-carbon steel tanks for manganese phosphating solutions have a shorter life than those used with zinc or iron phosphating solutions. For this reason, stainless steel tanks may be economically practical for manganese phosphating solutions. Stainless steel should also be considered for the heating coils. Plastic, fiberglass, and rubber-lined tanks have also been used successfully.

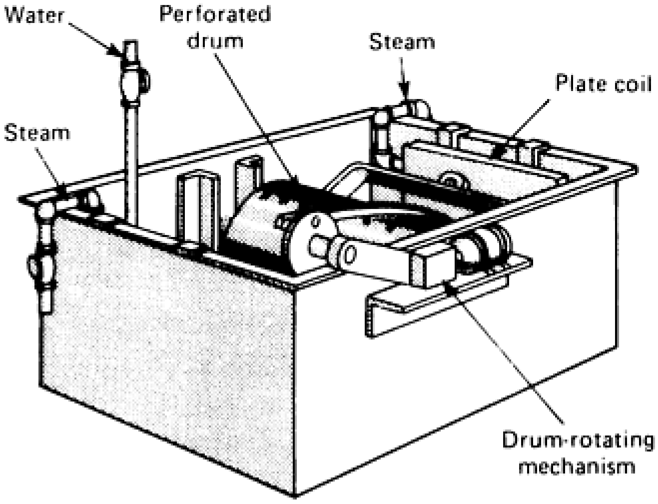


Fig. 4 Immersion phosphating tank for batch coating of small components. Drum into which parts are loaded is shown in immersion position.

Table 8, representing data from the experience of one company, shows a comparison of expected tank life, in years, for the three types of phosphating solutions using both low-carbon steel and type 316 stainless steel. These figures are approximately correct for all solutions. Some solutions permit extended tank life, and others shorten the tank life. One tank made of 6 mm ($\frac{1}{4}$ in.) mild steel has been in continuous operation for 15 years in an iron phosphating line.

Table 8 Expected service life of low-carbon steel vs. type 316 stainless steel phosphating tanks

Process	Service life, yr	
	Low-carbon steel	Type 316 stainless steel[(a)]
Iron phosphating	10[(b)]	20
Zinc phosphating	4-5[(c)]	10-20

(a) Any thickness that provides mechanical strength required. May be used as liner for low-carbon steel tank.

(b) 6.4 mm ($\frac{1}{4}$ in.) thick.

(c) 9.5 mm ($\frac{3}{8}$ in.) thick

Many phosphating tanks made of low-carbon steel are lined with glass fiber impregnated with polyester resins. Phosphating compounds have no effect on this material, and it will last indefinitely in normal service. It is, however, susceptible to damage from impact, and careless handling of equipment during loading or unloading of the tanks may cause fractures or cracks. Care must be exercised in the placement of heating coils when using polyester-impregnated glass fiber liners. The maximum temperature this material can withstand is about 105 °C (225 °F). Many polyester resins have little resistance to alkaline materials and should not be used where more than casual contact with strong alkaline cleaners is possible.

Tank accessories, including steam coils or other heating mediums, piping, screens, drum trunnions, and drum-rotating mechanisms, may be made of low-carbon steel or stainless steel. Electropolished stainless steel steam coils permit less sludge buildup on the coils.

Tank Design. Tanks should have sufficient capacity to stabilize solution temperature and solution concentration and to prevent rapid buildup of solution contamination. Tanks for the phosphating stage should have a sloping bottom, with at least 0.46 m (1.5 ft) of space below the lowest work level to accommodate sludge buildup.

Rinse Tanks. Water rinse tanks and associated equipment, including steam coils or other heating mediums, piping, and screens, may be constructed of low-carbon steel. Rinse tanks for certain parts sometimes require drum-rotating devices. Immersion rinse tanks should include a method for solution agitation to assist rinsing action. This can be accomplished by use of low-pressure air distributed through evenly spaced holes in pipes laid along the bottom of the tanks. Another method is to recirculate rinse water through a similar piping arrangement. For a clear water rinse, the pump housing, bearings, impeller, and any other part in contact with the water may be of normal material. Acidulated rinses containing chromium preclude the use of brass or bronze in any part of the pump or valving that is in contact with the solution.

Drying equipment for immersion phosphating systems can be of several types. For small parts, such as washers, a centrifuge may be used to spin off moisture. If parts are hot enough, no additional heated air is required. However, if parts are cold, heated air may be introduced into the centrifuge. When parts are centrifuged, the phosphate coating may be damaged on some parts, rendering them unacceptable. Such parts may be dried in a basket or on a rack, in the same manner that larger parts are dried. This is done in a final tank or enclosure in which the parts are held while heated air (at

120 to 175 °C, or 250 to 350 °F) is blown on them. Heat sources may be steam coils, gas burners, or electric heaters. Drying time usually ranges from 2 min for simple parts to 5 min for complex parts. If rinse solutions are retained in pockets or seams, drying requires additional time or temperature, a mechanical aid such as an air blast directed at the pocket or seam, or tilting of the part.

Drums for containing and rotating parts are usually made of low-carbon steel. To obtain longer life, stainless steels may be used; however, one company reports a life expectancy of approximately 10 years from similar drums made from low-carbon steel. This long life is attributed to a hard coating of phosphate that develops on surfaces of the drum. Drums should have a loading-and-unloading door with a positive latch to prevent accidental opening and loss of load during a processing cycle. A drum for containing small parts during batch phosphating is shown in Fig. 5.

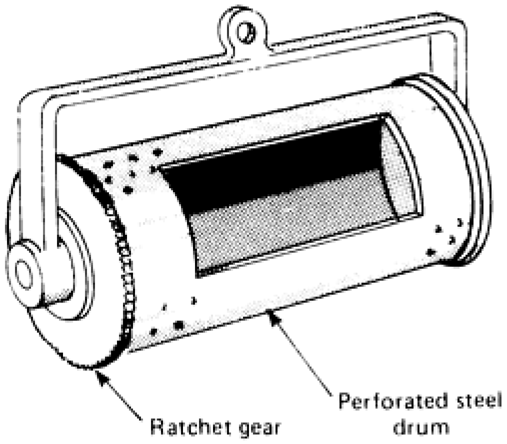


Fig. 5 Drum used in batch phosphate coating of small components

Baskets for handling parts too large for drums or too small or too heavy for racks can be made of either low-carbon or stainless steel. The choice is dictated by cost-life relationships.

Conveying equipment for the immersion process may be of any type that can transport work from the loading to the unloading stage. It must be capable of lowering work into and raising it out of various tanks in the proper sequence and at the proper time, either automatically or manually. Various types of conveying equipment are:

- *Overhead monorail conveyors* with manual or electric hoists. For very small production, the work can be moved manually from tank to tank.
- *Chain-driven conveyors* that lower and raise work into and out of each tank while it is continuously moving
- *Automatic equipment*, similar to automatic plating equipment but without equipment necessary for supplying electric current

Conveying equipment can be of varied design, but it must allow sufficient time for solution to drain from the work as it is raised from the tank. This solution should drain back to the original tank so it will not contaminate the next tank. Drainage and transfer time should not exceed 30 s, or the work may become discolored because of partial or complete drying between stages. The conveyor need not be made of acid-resistant material.

Work-supporting equipment, such as racks, hooks, and baskets, is similar in design and function to that used in electroplating, with the exception that it need not be electrically insulated. For phosphating, however, racks, hooks, and baskets should be resistant to alkaline cleaners, acid phosphating solutions, and other materials used in a phosphating line. Low-carbon steel is usually satisfactory. Stainless steel may be used where its additional life justifies the greater cost. Work-supporting equipment does not need to have tight contact with the work to be phosphated. Light contact with work-supporting equipment is more desirable, particularly on significant surfaces of the work, because coating may be thin or nonexistent at the point of contact, depending on the degree of insulation of the surface by hook, rack, or basket.

Equipment for Spray Systems

Spray systems usually are completely enclosed in a continuous, chambered tunnel or cabinet for better control of the process and cleanliness of the operation. Parts or panels to be processed are hung on racks or hooks, or placed in baskets, and are automatically carried through the various stages of the spray phosphating line (Fig. 6). Temperature and pressure gages and controls are required at all stations, as are pumps of adequate capacity. Time and space intervals between stages, and between the final rinse and the drying oven, must provide sufficient drain time to minimize carryover of solutions to succeeding stages. However, the time must also be as short as possible, because dried-on solutions cause blotchy coatings and can reduce final corrosion resistance or adhesion.

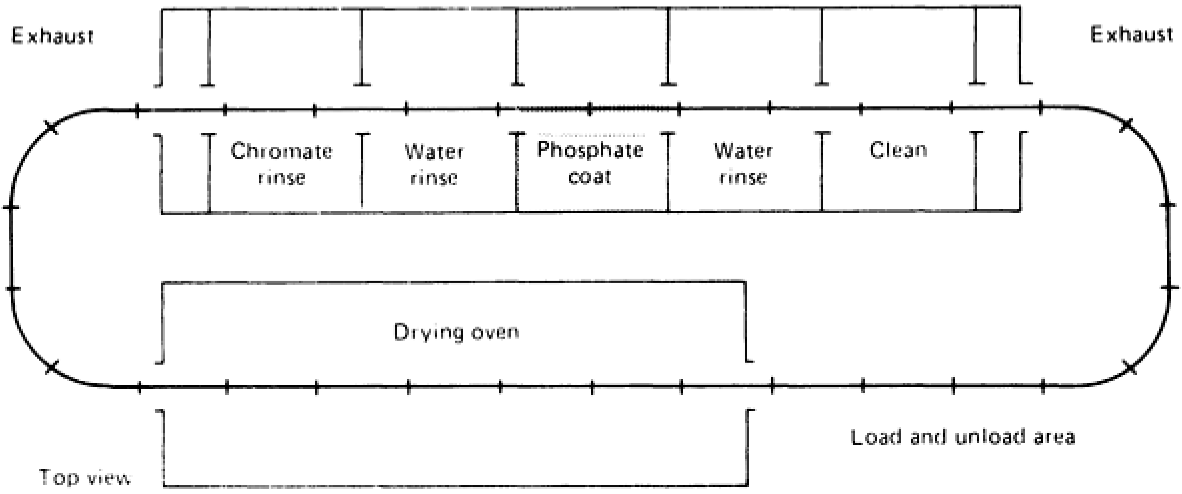


Fig. 6 Typical plant layout for a continuous conveyorized spray line for phosphating

Spray cabinets are usually made from low-carbon steel, as are the reservoirs from which the cleaners, phosphating solutions, and various rinses are pumped. Steam coils or other heating mediums, piping, screens, and valves also may be made of low-carbon steel. Spray nozzles may be made of low-carbon stainless steel, or polypropylene. Pumps may be of all-iron construction with stainless steel impellers. Valves may be all iron. As in immersion systems, because acidulated rinses usually contain chromium, no brass or bronze should be used in contact with these rinses. Also, no brass should be used in contact with alkaline cleaners or phosphate solutions. Potential suppliers of the chemicals should be consulted to ensure compatibility with the specific process to be used.

One large manufacturer doing extensive phosphate coating recommends that all parts and accessories in the phosphating stage of a spray zinc phosphating line be made of stainless steel except the storage tank. These tanks usually give satisfactory service when made from 9.5 mm ($\frac{3}{8}$ in.) thick low-carbon steel. Heating coils should be made from electropolished stainless steel to discourage a buildup of zinc phosphate sludge on the coils.

In a continuous spray phosphating line, baffle ridges on the floor and baffle doors or curtains are essential. Baffling between stages eliminates much of the mixing and contamination from carryover of the solutions. The storage tanks from which various solutions are pumped should have a minimum capacity of 2 to $2\frac{1}{2}$ times the volume pumped out per minute and provide phosphate solution tanks with a minimum capacity of $2\frac{1}{2}$ to $3\frac{1}{2}$ times the volume pumped out per minute, to provide room for sludge to collect.

Drying equipment for spray lines usually consists either of indirect-heated convection ovens, fired by gas or oil, or electric-fired or gas-fired infrared ovens capable of raising the temperature of parts to 150 to 205 °C (300 to 400 °F). If parts tend to hold rinse solutions in pockets or seams, it may be necessary to direct a blast of heated air at the pocket, or to tilt the part automatically to drain off the retained solution. Time required for drying varies from 2 min for simple, thin-gage parts to 6 min for complex parts. For phosphate coatings used ahead of electropaints, the dry-off oven is often omitted, and parts go into the electropaint tank either air-dried or wet.

Work-Supporting Equipment. The size and design of hooks, racks, and other work-supporting equipment used in spray phosphating depend on the size and contour of the parts being processed. These supports should be designed so that significant surfaces of parts receive the full impingement of phosphating solution as parts are conveyed through the unit. As in immersion phosphating, light or point contact is desirable so as not to mask off any surfaces of parts from the phosphating and rinsing solutions. Intricately contoured parts should be suspended in a manner that eliminates or minimizes the entrapment of solution, so that as little as possible is carried from one tank to another. Parts that, because of their shape, are impossible to suspend with mechanical racks or hooks can be suspended with magnetic hooks.

Work-supporting equipment usually is fabricated from low-carbon steel, although stainless steel can be used. Selection generally is predicated on economics, weighing the greater cost of stainless steel equipment against its longer life. Special care must be exercised in handling finished machined parts and other easily damaged parts in phosphating. Although such parts may be processed in special baskets, this often is unsatisfactory because coatings may be thin or completely absent at the numerous areas of contact. Racks usually are preferable.

Racks must be designed to hold parts in such a way that all significant surfaces are satisfactorily coated and parts are separated to prevent them from bumping and damaging each other during processing. On closely conforming racks, an accumulation of scale can hamper proper hanging or holding of parts or cause the rack to mask more than normal areas, causing imperfect coatings. These racks must be descaled frequently. Descaling can be done either by pickling in an inhibited solution of muriatic acid or by cracking the scale from the rack. Conveyor equipment carrying these racks must have a gentle motion to avoid knocking parts against each other. At the same time, conveyor speed must be rapid enough to prevent solutions from drying on parts as they are being moved between stations.

Conveying equipment used in spray phosphating may be of any type that can transport work through the various processing and draining stages. Continuously moving chain-driven conveyors, either overhead or floor-level, are usually used. Conveyor chains and part-carrying accessories can create problems by dragging out solutions and carrying them from one tank to another or from tank to part. The use of conveyor shielding can minimize some of these problems. In one application, such a problem occurred in a spray zinc phosphating line. Parts were hung on hooks suspended from a conveyor chain and remained on these hooks while being carried through the subsequent painting cycle. In the drying stage, phosphating solution (a proprietary solution containing sodium bifluoride) dripped from the conveyor chain and hooks onto the phosphated parts. Blisters in the paint film occurred in areas on which the solution had dripped. To correct this problem, a thorough system of rinsing, drying, and cleaning of the conveyor chain and hooks was initiated:

- A conveyor-chain washer was added; this consisted of several nozzles to spray fresh water on the conveyor chain between the phosphating stage and the subsequent rinse.
- Additional spray drop lines were added in the rinse stage, including a final drop line that sprayed fresh, rather than recirculated, water.
- Compressed-air nozzles for blowing off the conveyor chain and hooks were added immediately following the acidulated rinse stage.
- A final short rinse with unrecirculated demineralized water was added to remove any remaining contaminants from conveyor and parts.
- The frequency of removing accumulated paint from part hooks was increased to avoid entrapment of contaminants in built-up paint.

Process Selection: Immersion Coating versus Spray Coating

Equipment required for phosphate coating can vary from the simple to the elaborate. Some of the factors that influence equipment requirements include:

- Work load
- Size of products to be phosphated
- Material to be phosphated
- Processing method

Example 1: Manual Immersion Coating of Threaded Fasteners in a Zinc Phosphating Solution.

An example of equipment requirements and process cycles can be found in a company that produces threaded fasteners, zinc phosphates, and oil dips at an average of 3600 kg (8000 lb) of these parts each 8 h shift. One worker operates the entire immersion phosphating line. All parts are cleaned and pickled before being phosphated.

Production requirements for the manual immersion zinc phosphating of fasteners are listed below:

Requirement	Value
Weight of each piece, kg (lb)	0.013 (0.029)
Weight of each load, kg (lb)	193 (425)
Average weight processed per hour, kg (lb)	454 (1000)
Average number of pieces per hour	34,483

Equipment specifications required for manual immersion zinc phosphating are given in Table 9.

Table 9 Equipment specifications for typical manual immersion zinc phosphating coating of threaded fasteners

Component	Quantity	Unit capacity			
		Weight		Volume	
		kg	lb	L	gal
Work-handling equipment					
Workbasket for cleaning[(a)]	2	230	500	. . .	. . .
Perforated drums for phosphating[(b)]	3	230	500	. . .	. . .
Drum loading stand	1	230	500	. . .	. . .
Hoists	2	910	2000	. . .	. . .
Loading chute	1	230	500	. . .	. . .

Cleaning equipment					
Alkali soak tank	1	. . .	. . .	760	200
Acid tank (sulfuric acid)	1	. . .	. . .	760	200
Rinse tank	3	. . .	. . .	760	200
Phosphating equipment					
Phosphating tanks(c)(d)	3	. . .	. . .	760	200
Rinse tank	1	. . .	. . .	760	200
Chromic acid rinse tank(d)(e)	1	. . .	. . .	760	200
Centrifuge for drying(f)	1	. . .	. . .	. . .	. . .
Oil dip tank(g)	1	. . .	. . .	380	100

(a) Stainless steel.

(b) Motor-rotated.

(c) Heated by stainless steel steam plate coil.

(d) Automatic temperature control.

(e) Heated by steam plate coil.

(f) Equipped with hot-air blower driven by 2.2 kW (3 hp) motor.

(g) Corrosion resistant

Example 2: Automated Immersion Coating of Cast Iron Cylinder Heads in a Zinc Phosphating Solution.

The equipment requirements for zinc phosphate coating of cast iron cylinder heads include the use of an automatic indexing immersion phosphating machine. These parts, which weigh 121 kg (267 lb) each, are processed in baskets, three to a basket, and are loaded standing on their sides to facilitate drainage of solutions from inner passages. A coating weight of 3.8 g/m^2 (1.2 × 10^{-2} oz/ft^2) is obtained. The machine includes a phosphating tank that accommodates three workbaskets, thus allowing processing time equal to three times that of any other tank plus the time required to index the machine twice. Details of the equipment comprised by this automatic machine, together with production requirements and operating conditions for phosphating the cast iron cylinder heads, are given below:

Requirement	**Value**
Weight of coating, g/m^2 (oz/ft^2)	3.8 (1.2 × 10^{-2})
Size of each piece, mm (in.)	1143 × 406 × 152 (45 × 16 × 6)
Weight of each piece, kg (lb)	121 (267)
Pieces per load	3
Load weight, kg (lb)	363 (800)
Production per hour	20
Immersion time, min:	
Cleaning (each tank)	2
Cold water rinse	2
Hot water rinse (each tank)	2
Phosphating	8
Cold water rinse	2
Chromic acid rinse	2
Oil dip	2

Equipment specifications are given in Table 10.

Table 10 Equipment specifications for automated immersion zinc phosphate coating of cast iron cylinder heads

Component	**Size**[(a)]	**Material**	**Method of heating**	**Bath temperature range**	**Level control**

	mm	in.			°C	°F	Water	Liquid	Oil
Workbasket	1220 × 610 × 660	48 × 24 × 26	(b)	. . .	. . .	. . .	. . .	. . .	. . .
Cleaning tanks (2)	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	Steam plate coils	93-96(c)	200-205(c)	. . .	Automatic	. . .
Cold water rinse tank	1525 × 1065 × 1525	60 × 42 × 60	Low-carbon steel	. . .	. . .	. . .	Overflow	. . .	. . .
Hot water rinse tanks (2)	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	Steam plate coils	27-93(c)	80-200(c)	Overflow	. . .	. . .
Phosphating tank	1525 × 2720 × 1525	60 × 107 × 60	Stainless steel	Steam pipe coil	93-96(c)	200-205(c)	. . .	Automatic	. . .
Cold water rinse tank	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	. . .	. . .	. . .	Overflow	. . .	. . .
Chromic acid rinse tank	1525 × 1065 × 1525	60 × 42 × 60	Low-carbon steel	Steam plate coils	(d)	(d)	. . .	Automatic	. . .
Oil dip tank	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	. . .	. . .	. . .	. . .	. . .	(e)
Drip pan(f)	1525 × 890 × 1525	60 × 35 × 60	(b)	. . .	. . .	. . .	. . .	. . .	. . .
Phosphate sludge-settling tank(g)(h)	1525 × 2720 × 1525	60 × 107 × 60	Stainless steel	. . .	. . .	. . .	. . .	. . .	. . .

(a) Length, width, and depth, respectively.

(b) Not specified.

(c) Automatically maintained.

(d) As recommended by manufacturer of solution.

(e) Drain out carryover water and add oil as needed.

(f) Attached to oil dip tank.

(g) Method of transfer: centrifugal pump.

(h) Settling time 24 h

Automotive Applications. Automobile or truck fenders and hoods are zinc phosphate coated in an automatic, conveyorized spray phosphating line. Table 11 lists the sequence of processing stages and indicates operating conditions for each station. Although this example is based on a specific application, the data are applicable to the processing of similar parts.

Table 11 Sequence of operations in automatic spray application of zinc phosphate to automobile or truck small parts

Operation		Solution	Concentration	Temperature		Time, s	Pressure	
				°C	°F		kPa	psi
1	Clean	Alkaline titanated cleaner	4-6 mL(a)	60-65	140-150	60	100-140	15-20
2	Rinse	Water	1.0 mL max(b)	57-60	135-140	30	100-140	15-20
3	Clean	Alkaline titanated cleaner	4-6 mL(a)	60-65	140-150	60	100-140	15-20
4	Rinse	Water	1.0 mL max(b)	57-60	135-140	30	100-140	15-20
5	Phosphate	Accelerated zinc phosphate	20-25 mL(c)	52-55	125-130	60	55-83	8-12
6	Rinse	Water	1.0 mL max(c)	35-40	95-105	30	69-100	10-15
7	Acidulated rinse	Partially reduced chromic and/or phosphoric acids	150-250 ppm Cr^{6+}, pH 4.0-5.0	35-40	95-105	30	69-100	10-15
8	Demineralized rinse	Distilled water, deionized 100 μmho max						

(a) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the phenolphthalein end point using 0.1 *N* hydrochloric acid.

(b) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the bromocresol green end point using 0.1 *N* hydrochloric acid.

(c) Number of milliliters required to titrate a 10 mL (2.6 × 10^{-3} gal) sample to the phenolphthalein end point using 0.1 *N* sodium hydroxide.

(d) Or dry at 170 to 180 °C (340 to 355 °F) for 4 min

Consumer Product Applications. The sequence of operations involved in spray iron phosphating panels, brackets, and miscellaneous parts for household appliances is indicated in Table 12. Solutions, operating temperatures, and cycle times are also shown. The entire process is completed in $8\frac{1}{2}$ min. Coating weight ranges from 0.4 to 0.6 g/m^2 (1.3 × 10^{-3} to 2.0 × 10^{-3} oz/ft^2).

Table 12 Sequence of spraying operations in iron phosphating of panels, brackets, and other parts for household appliances

Operation		Solution	Concentration		Temperature		Time, s
			g/L	oz/gal	°C	°F	
1	Clean	Alkaline cleaner	5.6-9.40	0.75-1.25	66-74	150-165	60
2	Rinse	Water	. . .	. . .	66	150	30
3	Rinse	Water	. . .	. . .	66	150	30
4	Phosphate	Iron phosphate	50	6.7	68-74	155-165	60
5	Rinse	Water	. . .	. . .	(a)	(a)	30
6	Acidulated rinse	Chromic acid	0.29	0.04	54-86	130-150	30
7	Rinse(b)	Deionized water	(c)	(c)	(a)	(a)	30
8	Dry	. . .	. . .	. . .	150-230	300-450	240

(a) Ambient.

(b) Optional.

(c) 25 ppm (max) impurities

Military Equipment Applications. Manganese phosphate coatings are applied to military equipment to provide increased resistance to scuffing, galling, and corrosion. Table 13 lists the progressive stages of a phosphating indexing line, which is completely automatic, and indicates the operating conditions.

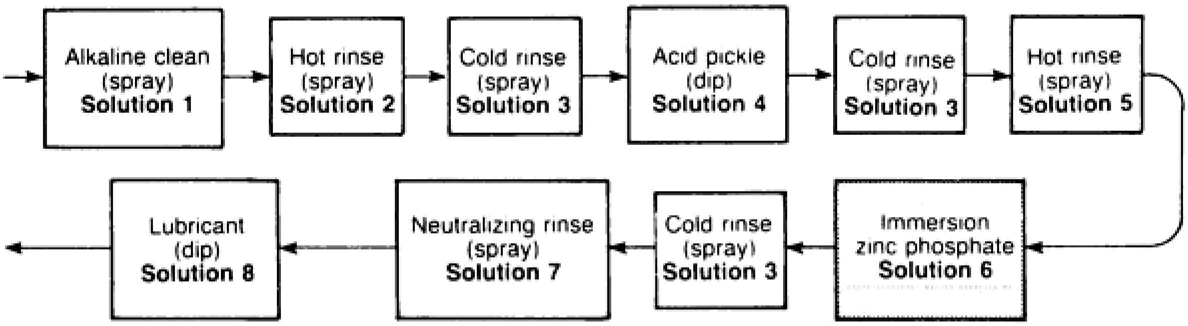
Table 13 Sequence and details of operations for an automatic manganese phosphating indexing line

Operation		Temperature		Time, min	Function	Concentration
		°C	°F			
1	Alkaline cleaner	50	125	5	Degrease, remove soils	6.0-8.0 mL(a)
2	Alkaline cleaner	70	160	5	Degrease, remove soils	4.0-6.0 mL(a)
3	Water rinse	70	160	0.5	Remove alkali from parts	. . .
4	Water rinse	90	195	0.5	Remove alkali from parts	. . .
5	Water rinse	90	195	0.5	Remove alkali from parts	. . .
6	Water rinse	35	95	0.5	Remove alkali from parts	. . .
7	Pickle	40	105	5	Remove scale or rust	Phosphoric acid, 20%
8	Water rinse	90	195	0.5	Remove acid from part	. . .
9	Activating rinse	35	95	3	Refine phosphate crystal	0.2-4% wt/vol
10	Phosphate	98	210	20	Manganese phosphate coating	FA 1.5-2.0 mL(b) TA 9.5-12.0 mL(b) Iron, 1.5-2.0 mL
11	Water rinse	35	95	0.5	Remove acidic phosphate solution	. . .
12	Acidulated rinse	35	95	0.75	Remove water salts, provide rust-proofing	. . .
13	Dryer	. . .	. . .	. . .	. . .	. . .

(a) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the phenolphthalein end point using 0.1 *N* hydrochloric acid.

(b) 2 mL (5.3×10^{-4} gal) sample size for free acid (FA) and total acid (TA) titrations. 10 mL (2.6×10^{-3} gal) sample size for iron titration

Mortar Shell Casings. Figure 7 shows a schematic layout of an automatic, conveyorized line for immersion zinc phosphating and lubricating of blanks from which casings for 80 mm (3.2 in.) mortar shells are cold formed. These blanks, made of 1010 steel, are coated at the rate of 4000 pieces/h. Each blank has an area of approximately 0.1 m^2 (1 ft^2). Conveyor speed is 2.0 m/min (6.6 ft/min). Details of operating conditions and solutions used are presented in the table accompanying Fig. 7.



Solution No.	Solution	Composition	Operating temperature		Cycle time, min
			°C	°F	
1	Alkaline cleaner	Alkali, 3.8 g/L (3.2×10^{-2} lb/gal)	82	180	1
2	Hot rinse	Water[(a)]	77	170	0.75
3	Cold rinse	Water[(b)]	RT	RT	1
4	Acid pickle	H_2SO_4, 15-18 wt%[(c)]	66	150	10
5	Hot rinse	Water	71	160	0.75
6	Zinc phosphate	Chlorate-accelerated[(d)]	82	180	6
7	Neutralizing rinse	$NaNO_2$, 1.1 g/L (9.2×10^{-3} lb/gal)	RT	RT	1
8	Lubricant	Soap, 10 wt%	66	150	6

(a) When lime is present in water, sequestering agent is added in concentration of 1.9 g/L (1.6 × 10^{-2} lb/gal).

(b) Purity maintained by overflow.

(c) Solution is discarded when iron content reaches 5%.

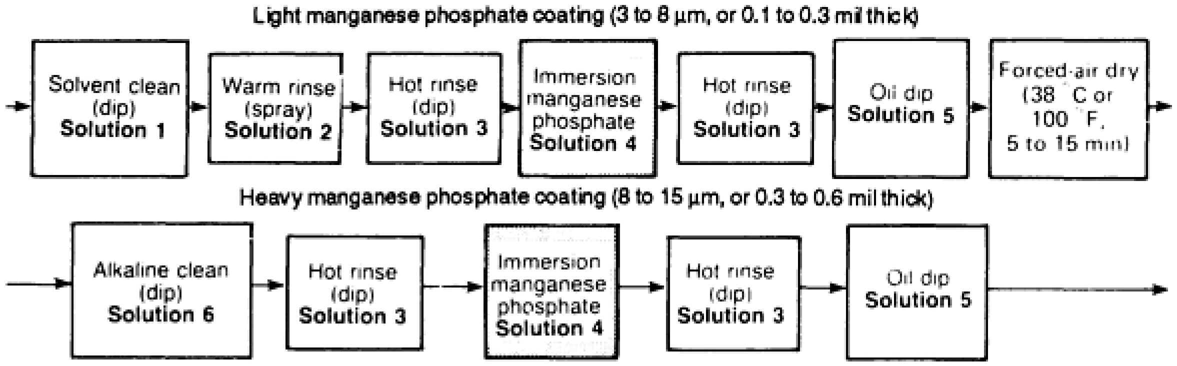
(d) Contains 36 points total acid, 7.5 points free acid, based on titration of 10 mL (2.6 × 10^{-3} gal) sample; concentration of accelerator, 3.5 g/L (2.9 × 10^{-2} lb/gal).

(e) (e)NaOH added to establish pH in range of 10 to 11

Fig. 7 Automatic, conveyorized cleaning, immersion zinc phosphating, and lubricating of 80 mm (3.2 in.) mortar shell blanks (1010 steel) before cold forming. Average area of shell blanks was 0.1 m^2 (1 ft^2); coating weight, 16 g/m^2 (5.2 × 10^{-2} oz/ft^2). Conveyor speed was 0.033 m/s (6.5 ft/min), and the production rate was 4000 pieces/h.

Control of Coating Weight

Figure 8 compares processing stages involved in manganese phosphating to two different ranges of coating thickness, 2.5 to 7.6 μm (0.1 to 0.3 mil) for light coatings and 7.6 to 15 μm (0.3 to 0.6 mil) for heavy, or conventional, coatings. The same phosphating compound is used in each line. Difference in coating weights depends on cleaner used and time in the phosphating solution. For conventional, heavy manganese phosphate coatings, parts are cleaned in an alkaline cleaning solution, providing a surface that permits good contact between metal and the phosphating bath. The resulting coating is heavy and coarse-grain, and it can readily absorb oil. For light coatings, a kerosene-based or similar solvent emulsion cleaner is used. A thin residue of oil left on the metal after two rinses acts as a buffering agent or grain-refiner, to produce a thinner, finer-grain coating. Usually, less lubricating oil is desired in conjunction with a fine-grain coating. Consequently, an additional step is involved for removing excess oil. The additional step is not usually necessary with a coarse-grain coating.


Light manganese phosphate coating (3 to 8 μm, or 0.1 to 0.3 mil thick)

Heavy manganese phosphate coating (8 to 15 μm, or 0.3 to 0.6 mil thick)

Solution No.	Type	Composition	Operating temperature		Cycle time, min
			°C	°F	

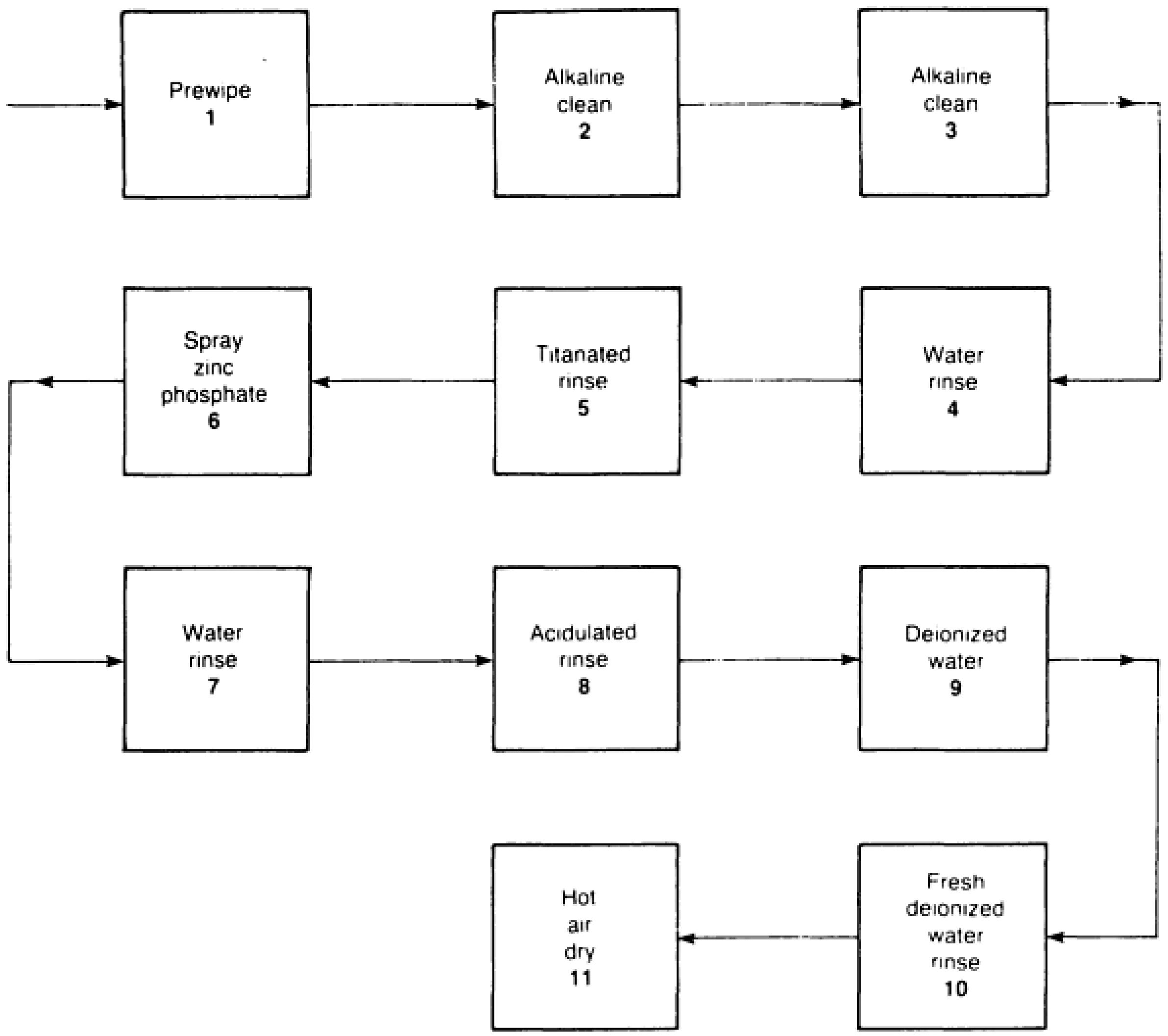
1	Solvent cleaner	. . .	. . .	. . .	3-10
2	Warm rinse	Water	38	100	1-3
3	Hot rinse	Water	82	180	1-3
4	Manganese phosphate	(a)	93	200	(b)
5	Oil	Soluble oil, 5%	60	140	1-3
6	Alkaline cleaner	. . .	93	200	3-10

(a) Contains 12 points total acid, as measured by titration of a 2 mL (5.3 × 10^{-4} gal) sample.

(b) For light coating, 8 to 12 min; for heavy coating, 10 to 20 min

Fig. 8 Sequence of operations for light vs. heavy applications of manganese phosphate coatings. Coating weight is function of specific cleaner used and immersion time in phosphating solution.

A phosphating line for spray zinc phosphating of automobile bodies is shown in Fig. 9. The bodies average 80 m^2 (860 ft^2) in area and the line speed ranges from 0.12 to 0.14 m/s (24 to 28 ft/min). Coating weights range from 1.6 to 2.4 g/m^2 (5.2 × 10^{-3} to 7.9 × 10^{-3} oz/ft^2). Production rate may reach 75 bodies per hour. The table accompanying Fig. 9 gives details of solutions used in this line and lists cycle times for various stages.



Stage	Type	Composition	Temperature		Time,s
			°C	°F	
1	Organic solvent	Mineral spirits	30	86	60
2	Alkaline cleaner	Titanated, alkali 6.0 g/L (5.0 × 10^{-2} lb/gal)	60-65	140-150	70
3	Alkaline cleaner	Titanated, alkali 6.0 g/L (5.0 × 10^{-2} lb/gal)	60-65	140-150	70
4	Hot rinse	Water	55-60	130-150	150
5	Activated water rinse	Titanated, 7.5-8.5 pH 0.5 g/L (4 × 10^{-3} lb/gal)	40-45	104-115	35
6	Zinc phosphate	ClO_3 accelerated[(a)]	50-55	122-130	70

7	Rinse	Water	35	95	15
8	Acidulated rinse	Partially reduced chromic acid (150 to 200 ppm Cr^{6+})	35	95	35
9	Rinse	Deionized water (100 μmho max)	35	95	70
10	Rinse	Deionized water (10 μmho)	35	95	15
11	Dryer	Hot air	. . .	. . .	. . .

(a) Total acid 20 mL (5.3×10^{-3} gal), free acid 0.9 mL (2.4×10^{-4} gal), nitrite accelerator 1.5 mL (4.0×10^{-4}gal); acid checked with 10 mL (2.6×10^{-3}gal) sample, accelerator checked with gas evolution apparatus

Fig. 9 Sequence of operations for spray zinc phosphating of automotive bodies

Tables 3, 4, and 5 present phosphate coating applications and weights. Table 3 deals only with spray application, but it covers both iron and zinc phosphate coatings as bases for paint films. By comparing the area of the parts and the production per hour controlled to obtain the uniform coating weights shown, it is easy to see the interrelation of size, production time, and coating weight. In all applications, the material being coated was low-carbon steel sheet. Table 5 lists applications for manganese phosphate coatings for wear resistance.

As indicated by the curve in Fig. 10, based on the experience of one processor of small threaded parts, the consumption of phosphating solution concentrate is directly proportional to the area and thickness of the coating applied. These parts were immersion zinc phosphated, processed in batches in a rotating drum, to a coating weight of approximately 10.8 g/m^2 (3.5×10^{-2} oz/ft^2). Figure 10 shows that the direct proportionality of area coated to concentrate consumed does not begin until an initial coat is deposited. At the time when parts are immersed, there is an immediate reaction in which an irregular coating is quickly deposited. Because the maximum area of bare steel is exposed to the bath at that time, maximum efficiency takes place. The remaining time in the bath serves to refine the coat by depositing crystals to fill gaps between existing crystals and to increase coating weight to uniform thickness by depositing crystals over previously deposited crystals.

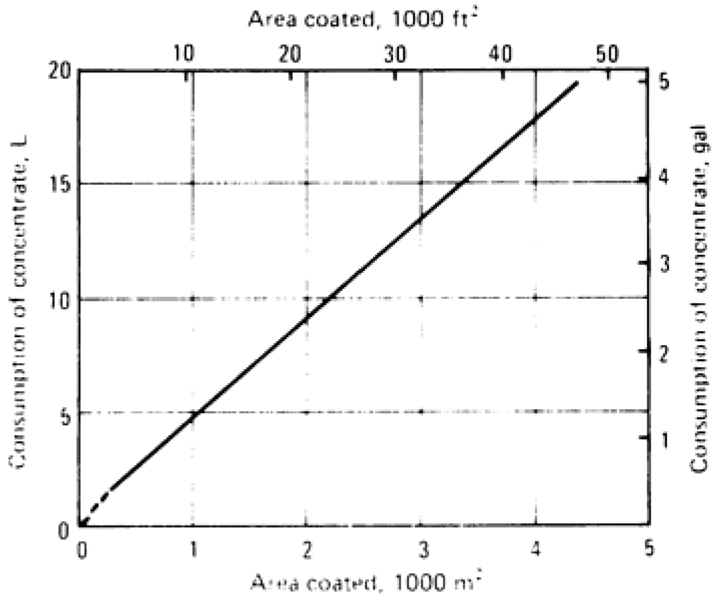


Fig. 10 Plot of zinc phosphating concentrate consumed vs. area covered for small threaded components coated to 10.8 g/m2 (3.5 × 10^{-2} oz/ft^2) with barrel phosphating

Control of Crystal Size

The crystalline structure of the chemically bonded phosphate coating (Fig. 11) provides a suitable base for subsequent paint or oil films. Crystals permit the paint to penetrate, providing the paint with exceptional adherence. When oil is the rust preventive, the interstices of the crystalline structure function efficiently as an oil-retaining reservoir. The adhesion of phosphate coating to the base metal, as determined by flexing of the metal, varies with the type and thickness of the coating. Generally, heavier coatings are composed of large crystals, which do not bond to each other or to the surface of the metal as well as do fine-grain, thinner coatings. Consequently, where adhesion and flexibility may be a problem because of the nature of the application, phosphating material is selected that produces a thin, fine-grain coating. However, this may not result in maximum corrosion resistance. Organic additives, special accelerators, and/or calcium added to a zinc phosphate process provides a microcrystalline structure that exhibits optimum paint adhesion and corrosion resistance.

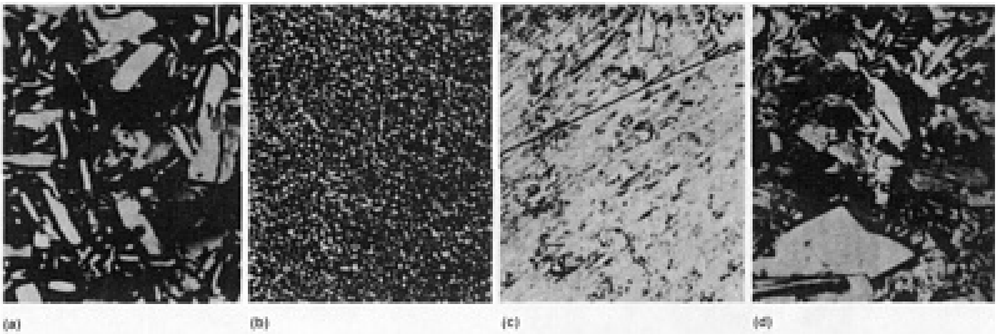


Fig. 11 Photomicrographs of microstructures for principal phosphate coatings. (a) Heavy zinc phosphate. (b) Microcrystalline zinc phosphate. (c) Iron phosphate (primarily iron oxide). (d) Manganese phosphate. 125×

Zinc phosphate coatings (Fig. 11a and b) are widely used as bases for paint or oil. A fine uniform crystal is necessary when gloss is desired for the paint film. Coarse crystals promote dullness and often require higher paint thickness to gain uniform and acceptable coverage. However, when coating is applied to provide lubricity, a coarse crystal may be preferable. With few exceptions, zinc phosphating concentrates are proprietary materials designed to produce, within a specified time and with available equipment, coatings that are within a specific range of weight and have a desired crystal size and texture.

Usually, strongly acid baths build coating at a slow rate but deposit large crystals. This is due to the longer time needed to develop neutralization at the coating interface. A bath that has been activated by an accelerator deposits coating more quickly and with a smaller crystal. Up to a point, as long as the part stays in the bath, solution continues depositing crystals by building up thinner sections of coating and filling interstices with more crystals. Because the coating gradually insulates metal from fresh solution, no crystals are deposited beyond a certain point. These characteristics are inherent in proprietary solutions, and little control can be exerted other than to maintain the bath as prescribed.

The surface condition of the parts being coated is a factor that influences the coating characteristics that can be controlled. Certain oils, residues from solvent cleaning or vapor degreasing, or solvent emulsions, when retained on the surface in very thin films, function as crystal refiners. An example is the film left on parts that are cleaned using a kerosene-based emulsion cleaner. Although this cleaning operation is usually followed by a hot water rinse, enough oil is retained on the surface to have a beneficial influence, if a fine crystal is desired. Conversely, if a strong alkaline cleaner is used and completely rinsed away, or if blast cleaning is used, a coarser crystal is obtained. Another method of refining or decreasing crystal size is the use of a proprietary titanium phosphating conditioner. These titanium phosphate salts can be used either in the water rinse that precedes phosphating or with certain alkaline-based cleaners.

Iron phosphate coatings (Fig. 11c) are generally of a very fine structure and are amorphous in appearance. Because these coatings are used primarily as bases for paint or to assist in bonding of metal to a nonmetallic surface, fine structure is desirable. With iron phosphate coatings, the problem is one of adherence and powdery coatings rather than crystal size or coating weight. Attention must be directed to surface cleanliness, maintenance of the bath within the prescribed limits, and proper processing.

Manganese phosphate coatings (Fig. 11d) are usually heavy and coarse. Because these coatings are generally used for their lubricating qualities and often incorporate a supplementary oil film, a continuous coating may not be mandatory. The length of time in bath may be varied, within limits, to vary the film thickness to meet the functional requirements of the coating. Crystal size and coating thickness are controlled by the condition of the surface to be coated. Oils, and residues from alkaline cleaning, solvent cleaning, vapor degreasing, and emulsion cleaners, serve as crystal refiners and reduce coating thickness. Proprietary crystal refiners are available and usually contain a heavy metal phosphate. They are used in the water rinse just before phosphating.

To meet severe requirements, manganese phosphate coatings may be produced to extremely heavy weights. It is difficult, however, to obtain uniformity in such coatings. Pretreatment, including cleaning, rinsing, and etching, as well as the equilibrium of the phosphating solution, is critical.

In one plant, carburized and hardened differential gears had been failing through localized surface seizure caused by extremely high unit loading. Extreme-pressure gear lubricants, zinc and manganese phosphate coatings of conventional weight, and various other surface treatments proved ineffective in preventing metal-to-metal contact. Manganese phosphate coatings that were extremely thick and heavy, 25 to 75 μm (1 to 3 mil) thick and 110 to 325 g/m^2 (0.36 to 1.07 oz/ft^2), prevented seizure under the most adverse conditions. The cycles for the application of a heavy manganese phosphate coating for lubrication of carburized and hardened differential gears are given in Table 14.

Table 14 Parameters for applying a heavy manganese phosphate coating that provides lubrication for carburized and hardened differential gears

Solution	Time, min	Temperature		Concentration	
		°C	°F	g/L	oz/gal
Alkaline immersion clean	15	99	210	30-45	4-6
Cold water rinses					
Sulfuric acid etch	5	(a)	(a)	(b)	(b)

(a) Ambient.

(b) 10 to 20% H_2SO_4.

(c) Total acid (total ions in solution), 55 to 85 points; free acid (hydrogen ions in solution), 8-17 points; ferrous iron concentration, 0.05-0.04 g/L (0.007-0.05 oz/gal). Points are the minimum milliliters of the titrating solution required to cause a reaction with a definite quantity of the solution being tested. Reaction is indicated by a color change of the solution.

Low-Temperature Coatings

Both iron and zinc phosphate coatings can be applied at much lower temperatures than have been traditional, thus reducing heat energy costs significantly. Manganese phosphate coatings still require solution temperatures around 95 °C (200 °F). Solutions are available to apply iron phosphate by either dip or spray at 24 °C (75 °F), producing coating weights from 0.44 to 0.66 g/m^2 (1.4 × 10^{-3} oz/ft^2). Zinc phosphate baths can be compounded to produce 3.3 to 5.5 g/m^2 (1.1 × 10^{-2} to 1.8 × 10^{-2} oz/ft^2) coatings at 40 °C (100 °F).

The energy demands of hot spray systems are determined primarily by their temperature and recirculation rate. In one plant, a paint preparation line using iron phosphate sprayed at 71 °C (160 °F) was found to be using 35.8 × 10^6 kJ/day (33.9 × 10^6 Btu/day). The iron phosphating stage is part of the pretreatment of an electrocoat prime paint line for castings and forgings. The energy requirements for the spray iron phosphate are:

Requirement	**Value**
Tank capacity, L (gal)	8.0 × 10^3 (2.1 × 10^3)
Pump rate, L/min (gal/min)	2.3 × 10^3 (6.0 × 10^2)
Temperature, °C (°F)	70 (160)
Operating time, h/day	16
Heat-up energy, kJ (Btu)	2.34 × 10^6 (2.22 × 10^6)
Temperature maintenance energy, kJ/h (Btu/h)	2.09 × 10^6 (1.98 × 10^6)
Total energy requirements per day,kJ (Btu)	35.8 × 10^6 (33.9 × 10^6)

Changing to a product operating at 24 °C (75 °F) allowed the system to operate with no heat required beyond the pump energy, which maintained the required 24 °C (75 °F). With no requirement for heating coils or heat exchangers, new installations saved those capital expenditures. Both systems produced coating weights of 0.44 to 0.55 g/m^2(1.44 × 10^{-3} to 1.80 × 10^{-3} oz/ft^2).

Although immersion baths have much lower heat losses than spray applications, worthwhile heat savings still can be realized. In general, heat losses rapidly increase at about 60 °C (140 °F).

A system producing fine-grain immersion zinc phosphate coatings on miscellaneous formed and machined parts was investigated, and the actual steam usage required to maintain temperature was measured at two operating temperatures (Table 15). Energy demands did not include heating the parts but can be calculated from their mass. Less energy was required to maintain the tank at temperature than to shut down for 8 h and reheat. The energy saved by operating the system at 55 °C (130 °F) instead of 88 °C (190 °F) amounted to 3.70 × 10^6 kJ/day (3.51 × 10^6 Btu/day) or 0.888 × 10^9 kJ/yr (0.842 × 10^9 Btu/yr).

Table 15 Energy demands of a system producing fine-grain immersion zinc phosphate coatings

Operating temperature	**Heat-up energy**	**Temperature maintenance energy**	**Total energy required per day**

°C	°F	kJ	Btu	kJ/h	Btu/h	kJ	Btu
88	190	1.28×10^6	1.21×10^6	0.17×10^6	0.16×10^6	3.98×10^6	3.77×10^6
55	130	9.3×10^4	8.8×10^4	1.2×10^4	1.1×10^4	0.27×10^6	0.26×10^6

Note: Tank capacity 4200 L (1100 gal). Tank surface area 2.8 m^2 (30 ft^2). Operating time 16 h/day

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Inspection Methods

The majority of phosphate coating quality control methods are based on visual inspections. For zinc and manganese phosphate, the coating must be continuous, adhere well to the surface, and be of uniform crystalline texture suitable for the intended use. Color should range from gray to black. Causes for rejection include loose smut or white powder (because of inclusion of ferric phosphate by-product into the phosphate coating or dried phosphate solution), blotchiness, excessive coarseness, and poor adhesion. Crystal size may be observed by using micrographs at magnifications of 10 to 500×, depending on the coating. Iron phosphate coatings have no apparent crystalline texture. Instead they appear to be amorphous. Their color varies from iridescent yellow to blue to brown. Loose or patchy coatings are cause for rejection.

Determination of coating weight on ferrous surfaces can be made by a stripping procedure, such as follows:

1. Phosphate a part of known surface area.
2. Thoroughly clean the part to remove all oil.
3. Weigh the part to the nearest tenth of a milligram.
4. Strip the phosphate-coated part in a $2\frac{1}{2}$% H_2CrO_4solution at 71 °C (160 °F), immersing for 10 min (zinc phosphate coating), 15 min (manganese phosphate coating), or 5 min (iron phosphate coating). Time and concentration of the chromic acid solution may require adjustment for specific coatings.
5. Rinse in clean water.
6. Dry.
7. Reweigh the stripped part to the nearest tenth of a milligram. The difference in weight from that in step 3 equals the total coating weight.
8. Calculate weight of coating per unit of area. Standard units are grams per square meter.

If the size or shape of items being coated preclude the performance of the above procedure, test specimens of identical material, heat treatment, and surface finish may be substituted. An accurate measurement of coating weight cannot be obtained by weighing the part, applying the phosphate coating, and then reweighing the part. Because the phosphating solution attacks steel, a measurable, but not always predictable, amount of steel is removed. This condition can vary with the acidity of the bath as well as with the type of metal being coated.

Coating voids or spots not covered may be checked by using a clean, dry phosphated specimen. Next, soak a piece of filter paper, 4.0×10^4 to 5.0×10^4 mm^2 (6.2 to 7.7 $in.^2$) in area, in a solution containing 7.5 g/L (1.0 oz/gal) $K_3Fe(CN)_6$ and 20 g/L (3 oz/gal) NaCl. Allow excess solution to drain off. Apply wet filter paper to the phosphated sample for 5 min. Remove and observe blue spots, which indicate noncoated areas. The method of rating may vary with different processes and requirements. One general method is as follows:

- *Excellent*: none to three fine spots up to 1 mm (0.04 in.)
- *Good*: not more than 10 fine spots
- *Satisfactory*: not more than 20 fine spots or up to 3 large spots

Repair of Phosphate Coatings

Small parts that do not accept a satisfactory phosphate coating can easily be stripped, cleaned, and rephosphated. Large parts with a faulty coating or with a coating that is damaged in processing are less easily handled, and repair of the phosphated surface may be preferable to stripping and rephosphating. The simplest method is to sand the phosphate film until all defective coating is removed and clean, bare metal is exposed. A proprietary phosphating solution compounded for this application is brushed or wiped on the area to be rephosphated and is allowed to remain for a prescribed length of time (usually measured in seconds). Surplus solution is then removed by thoroughly water rinsing and wiping dry with clean rags. These solutions range from simple systems (phosphoric acid, butyl cellosolve, and a suitable wetting agent, plus 50 to 70% water) to accelerated systems that produce a crystalline zinc phosphate coating. If the volume of repairs is considerable, a portable steam spray unit can be used. This will spray hot phosphating solution, water, and chromic acid rinsing solution through a hose and nozzle.

Limitations of Phosphating

Limitations Imposed by Shape. It is seldom impossible to phosphate a part because of its shape. However, shapes can restrict production or limit the choice of process. Parts with complex passages must be immersion coated, because spray phosphating cannot reach all areas of the passages. Cup-shape parts, phosphate coated by either method, present problems of handling to achieve complete drainage. Blind holes or cavities may entrap air, preventing phosphating solution in the immersion process from contacting all areas to be coated.

At one company, hydraulic pump components, such as gears, vanes, and valves, and hydraulic valve bodies were manganese phosphated to provide break-in lubrication. Many of these parts had blind tapped holes on several surfaces. Although all critical wearing surfaces of these components were adequately coated, investigation showed that many of the blind holes were only partially phosphated because of air entrapment. Similar parts, with holes or cavities that did require phosphate coating, would require special handling to ensure coating of these areas.

In another instance, large cylinder heads weighing approximately 120 kg (265 lb) as cast were coated with a microcrystalline zinc phosphate coating to prevent rusting during storage. These parts were placed in baskets in such a way that no air was entrapped. All internal surfaces were permitted to come in contact with the phosphating solution.

Tanks that require a phosphate coating on the inside after fabrication, and that have few drain holes or openings of any size, must be phosphated by immersion. However, if these tanks require phosphate coating on the outside only, spray coating is more appropriate.

Limitations Imposed by Size. The size of parts that can be phosphated is limited only by the size and type of equipment available. However, part size does generally determine the method of application. Very small parts, such as springs, clips, nuts, bolts, and washers, are almost always coated by immersion. Spray phosphating of these parts on a volume basis would be impractical. Conversely, for extremely large parts, such as transformer housings, that may be as much as 6 m (20 ft) high, spray phosphating is the only practical method for volume production. On extremely large parts produced in low volume, however, coatings are usually applied by brushing or wiping. Parts in between these extremes of sizes are coated by either spray or immersion, depending on the equipment available, quantity to be coated, and complexity of parts. Examples of parts satisfactorily coated by either method include automobile bodies, castings, panels, and machined parts.

Supplemental Oil Coatings

Unless they are to be painted, parts usually receive a supplemental coating of oil after being phosphated. This coating is applied to increase corrosion resistance, and it also neutralizes any residual acid that might remain on parts from the phosphating bath. The type of oil used depends on the degree of corrosion protection desired, subsequent operations to be performed on phosphated parts and the handling involved in these operations, appearance requirements, and compatibility of the oil with other lubricants in assemblies. Materials commonly used are water-soluble oils, nondrying oils, non-hard-drying greaselike materials, and oils that are dry to the touch.

Water-soluble oils provide both short-term and long-term protection against corrosion, depending on their composition. Water-soluble oils offer the advantage of allowing parts to go into water-soluble oil in a wet state. An additional advantage of the water-soluble oil is that it eliminates a fire hazard from the operation.

Figure 12 shows an immersion tank used in the coating of lightweight parts with soluble oil for applications in which subsequent handling or assembly requirements require a virtually dry part.

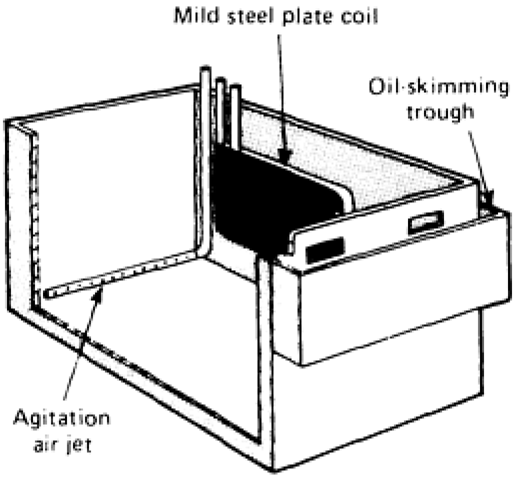

Fig. 12 Immersion tank for coating lightweight phosphated components with a soluble oil. Skimming trough removes floating globules of oil that might cling to parts.

Flash points of water-soluble oils are sometimes lower than those of petroleum-based oils or synthetic organic oils. However, after water-soluble oils are mixed with water to the 5 to 25% concentration range, little fire hazard attends their use.

Nondrying oils vary in type and viscosity and are selected on the basis of requirements of in-process handling or ultimate service. An advantage of this type of material is its ability to self-heal any scratches that may occur in bulk handling. Corrosion protection may be increased by adding a commercially available rust inhibitor that is compatible with the oil. Petroleum-based oils can be reduced with petroleum solvents to form a thinner film, if desired. If parts are not completely dry before the application of oil, water-displacing additives may be used.

Non-hard-drying materials are greaselike substances that have melting points above room temperature. These materials may be applied by dipping, spraying, or brushing. When necessary, these materials are readily removed by petroleum solvents. Figure 13 shows a tank for dip application of greaselike materials. The tank is provided with facilities for heating and cooling to maintain temperature control of the coating material.

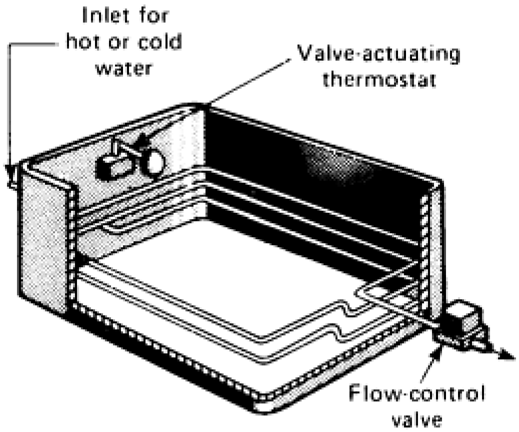

Fig. 13 Tank used for dip coating of phosphated parts with greaselike materials that require temperature monitoring

Decorative Stains (Ref 7)

Depending on the process and the substrate used, heavy phosphate coatings on steel vary from near-black to medium-gray. Manganese phosphate coatings are generally the darkest.

Many applications require a definitive, reproducible color, most often black, for decoration or identification purposes. This can be achieved by applying an alcohol-based stain, usually with a shellac or manila resin binder, and an original dye of the color desired. Because the stain has limited protective value, a light oil can subsequently be applied to help prevent corrosion and enhance appearance (see the section "Supplemental Oil Coatings" in this article). In heavy-duty applications, pigmented finishes can be used, but they produce thicker coatings that can cause problems with dimensional buildup on threaded components.

Figure 14 shows the corrosion resistance of black stain, corrosion-preventing oil, and black stain plus oil, relative to the type of phosphate coating applied.

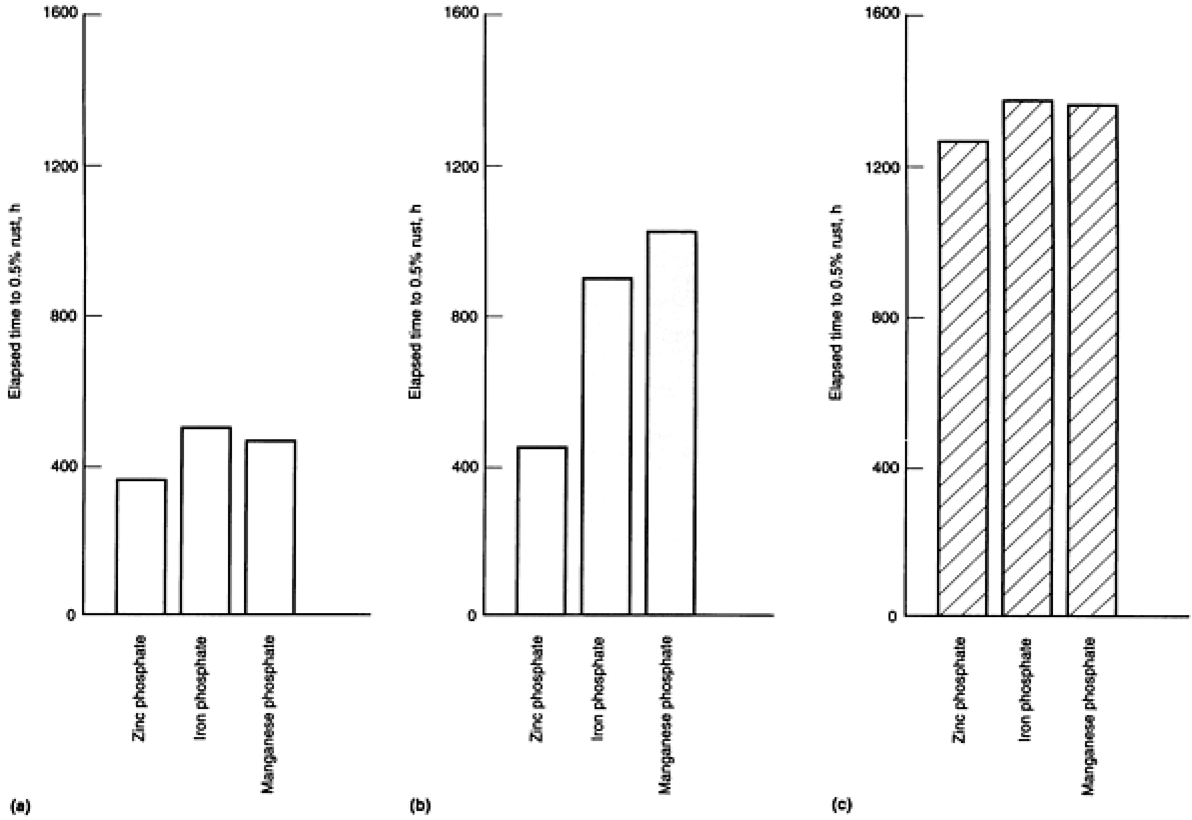

Fig. 14 Corrosion resistance of selected metal finishes relative to type of phosphate coating applied. (a) Black stain. (b) Corrosion-preventing oil. (c) Black stain and oil. Source: Ref 7

Reference cited in this section

7. D.B. Freeman, *Phosphating and Metal Pre-Treatment,* Industrial Press, Inc., 1986, p 76-77

Phosphate Coating Selection

Table 16 provides guidelines for choosing phosphate coatings based on application, coating weight requirements, and recommended process parameters.

Table 16 Process parameters for selected phosphate coatings

Coating type	Accelerator	Process type	Tank material	Coating weight		Operating conditions							
						Immersion				Spray			
						Time		Temperature		Time		Temperature	
				g/m^2	oz/ft^2 × 10^{-2}	s	min	°C	°F	s	min	°C	°F
Paint bonding applications													
Iron phosphate	Chlorate	Stripline alkaline phosphate	Mild steel	0.2-0.5	0.07-0.16	8-20	. . .	66-77	151-171	8-20	. . .	66-77	151-171
	Molybdate	Multimetal lightweight alkali metal phosphate	Mild steel	0.3-0.5	0.10-0.16	. . .	2-5	40-70	104-158	. . .	1-2	40-60	104-140
	Chlorate	Lightweight iron phosphate	Mild steel	0.3-1.0	0.10-0.33	. . .	. . .	. . .	. . .	. . .	1	70-75	158-167
	Nitrate (molybdate)	Combined cleaner/coater	Mild steel	0.2-0.5	0.07-0.16	. . .	. . .	. . .	. . .	. . .	1-2	35-70	95-158
	Molybdate	Low-temperature liquid cleaner/coater	Mild steel	0.2-0.5	0.07-0.16	. . .	. . .	. . .	. . .	. . .	1.5-3.0	25-35	77-95
	Molybdate	Multimetal lightweight alkali metal phosphate	Mild steel	0.2-0.5	0.07-0.16	. . .	2-5	40-60	104-140	. . .	. . .	. . .	. . .
						. . .	. . .	. . .	. . .	. . .	1-2	40-60	104-140

Zinc phosphate	Chlorate	Low-temperature immersion zinc phosphate	Mild steel	1.5-2.0	0.49-0.66	. . .	5-10	25-30	77-86	. . .	. . .	. . .	. . .
		Spray zinc phosphate	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	. . .	1-2	50-60	122-140
	Chlorate/metanitro-benzene sulphonate	Spray zinc phosphate	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	45-120	. . .	45-50	113-122
		Low-temperature spray zinc phosphate	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	80-180	. . .	25-35	77-95
	Hydrogen peroxide	Spray zinc phosphate for closed-loop operation	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	. . .	1-2	55-60	131-140
	Nitrite	Zinc phosphate	Mild steel	3-7	0.98-2.3	. . .	5-15	60-70	140-158	. . .	. . .	. . .	. . .
		Spray zinc phosphate	Mild steel	1.6-2.4	0.52-0.79	. . .	. . .	. . .	. . .	. . .	1-2	45-60	113-140
		Multimetal spray zinc phosphate	Mild steel(d)	2.0-3.5	0.66-1.1	. . .	. . .	. . .	. . .	. . .	1-3	55-70	131-158
		Multimetal zinc phosphate	Mild steel(d)	2-3	0.66-0.98	. . .	1-3	55-80	131-176	. . .	1-3	55-80	131-176
	Nitrite/chlorate	Spray zinc phosphate (low zinc)	Mild steel	1.6-2.0	0.52-0.66	. . .	. . .	. . .	. . .	. . .	1.5-2.0	50-55	122-131
	Nitrite	Calcium modified zinc phosphate	Mild steel	2.0-4.5	0.66-1.5	. . .	2-5	60-70	140-158	. . .	. . .	. . .	. . .

Zinc manganese phosphate	Nitrite	Low-temperature zinc phosphate	Mild steel	1.8-2.4	0.59-0.79	. . .	. . .	. . .	. . .	. . .	1-2	25-35	77-95
	Chlorate/metanitrobenzene sulphonate	Low-temperature spray/dip zinc phosphate(j)	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	1.5-3.0	25-30	77-86	15-30	. . .	25-30	77-86
Zinc iron phosphate	Nitrite	Immersion zinc phosphate (low zinc)	Mild steel(d)	2.8-3.4	0.92-1.1	. . .	2-4	55-60	131-140	. . .	. . .	. . .	. . .
	Chlorate/metanitrobenzene sulphonate	Spray/dip zinc phosphate(j)	Mild steel	2.0-2.5	0.66-0.82	. . .	2-4	50-53	122-127	20-30	. . .	50-53	122-127
Rustproofing applications													
Iron phosphate	. . .	Heavy iron phosphate	Mild steel(d)	7.5-15+	2.5-4.9+	. . .	15-30	96-99	205-210	. . .	. . .	. . .	. . .
Manganese iron phosphate	. . .	Manganese phosphate (unaccelerated)	Mild steel(d)	10-30	3.3-9.8	. . .	30-90	95-100	203-212	. . .	. . .	. . .	. . .
	Nitrate	Manganese phosphate	Stainless steel or rubber-lined	7.5-15+	2.5-4.9+	. . .	5-30	96-99	205-210	. . .	. . .	. . .	. . .
	Nitroguanidine	Manganese phosphate	Mild steel(d)	7.5-15	2.5-4.9	. . .	15-30	85-95	185-203	. . .	. . .	. . .	. . .
Zinc iron phosphate	Nitrate	Zinc phosphate	Mild steel(d)	7.5+	2.5+	. . .	10-30	80-90	176-194	. . .	. . .	. . .	. . .
Antifriction applications													

Manganese iron phosphate	Nitrate	Manganese phosphate	Mild steel$^{(d)}$	7.5	2.5	. . .	5-15	96-99	205-210	. . .	. . .	. . .	. . .	
Wire drawing applications														
Zinc phosphate	Nitrite	Zinc phosphate (in-line operation)	Mild steel$^{(d)}$	4-8	1.3-2.6	10-30	. . .	90-95	194-203	. . .	. . .	. . .	. . .	
Tube and wire drawing applications														
Zinc phosphate	Chlorate	Zinc phosphate	Mild steel	6-12	2.0-3.9	. . .	2-15	55-70	131-158	. . .	. . .	. . .	. . .	
	Nitrite	Zinc phosphate	Mild steel	10-20	3.3-6.6	. . .	$\leq$ 20	55-95	131-203	. . .	. . .	. . .	. . .	
	Nitrate	Low-temperature zinc phosphate	Mild steel	4-10	1.3-3.3	. . .	5-15	40-50	104-122	. . .	. . .	. . .	. . .	
	Zinc calcium phosphate	Chlorate	Zinc calcium phosphate (batch)	Mild steel$^{(d)}$	8-10	2.6-3.3	. . .	3-10	70-75	158-167	. . .	. . .	. . .	. . .
Zinc calcium phosphate (in-line)			Mild steel$^{(d)}$	8-10	2.6-3.3	20-30	. . .	75-80	158-176	. . .	. . .	. . .	. . .	
Nitrate		Zinc phosphate (low sludge)	Mild steel	6-10	2.0-3.3	. . .	4-10	65-75	149-167	. . .	. . .	. . .	. . .	
Tube drawing lubricant applications														
Iron	. . .	Combined phosphate	Stainless steel	2-5$^{(p)}$ 10-	0.66-1.6$^{(p)}$	. . .	5-15	65-	149-	. . .	. . .	. . .	. . .	

phosphate/lubricant		lubricant		15(q)	3.3-4.9(q)			80	176				
				Cold extrusion applications									
Zinc phosphate	Nitrite	Zinc phosphate	Mild steel(d)	10-20+	3.3-6.6+	. . .	2-10	55-95	131-203	. . .	. . .	. . .	. . .
Cold-forming aluminum applications													
Zinc phosphate	Nitrate	Zinc phosphate	Mild steel(d)	4-12	1.3-3.9	. . .	7-10	52-57	126-135	. . .	. . .	. . .	. . .
Galvanized steel applications													
Zinc phosphate	. . .	Stripline zinc phosphate	Mild steel(d)	1.6-2.0	0.52-0.66	5-15	. . .	62-69	143-156	5-15	. . .	62-69	143-156
Chromate/phosphate for aluminum applications													
Chromium phosphate	. . .	Chromate/phosphate	Stainless steel or PVC-lined mild steel	0.15-5.00	0.05-1.6	. . .	1-3	40	104	30-60	. . .	25	77

Coating type	**Control parameters**				**Other**	**Comments**	**Total acid**		**Free acid**	
	mL	**gal × 10^{-3}**	**mL**	**gal × 10^{-3}**						
	Paint bonding applications									

Iron phosphate	9-10	2.4-2.6	. . .	. . .	(a)	. . .							
	14-16	3.7-4.2	0.5-3.0	0.13-0.79	. . .	Requires precleaning. Superior performance to cleaner/coaters							
	9-10	2.4-2.6	. . .	. . .	(b)	Requires precleaning. Superior performance to cleaner/coaters							
	4.5-5.0	1.2-1.3	. . .	. . .	. . .	No precleaning necessary. Gives iridescent to gray coatings, blue when molybdate-accelerated							
	4.5-5.0	1.2-1.3	. . .	. . .	(c)	Single liquid chemical. Low operating temperature. Suitable for use with automatic control equipment							
	10-12	2.6-3.2	. . .	. . .	. . .	May be formulated as cleaner/coater for spray application	Zinc phosphate	28-30	7.4-7.9	1.3-1.5	0.34-0.40	. . .	Additions of neutralizer needed to control free acid
16-17	4.2-4.5	2.0-2.8	0.53-0.74	. . .	. . .								
10-12	2.6-3.2	0.8-1.0	0.21-0.26	. . .	. . .								
24-26	6.3-6.9	0.7-1.0	0.18-0.26	. . .	May contain fluoride and nickel for treatment of galvanized steel and limited quantities of aluminum								

14-16	3.7-4.2	0.7-1.2	0.18-0.32	. . .	Can be incorporated in closed-loop system to give total recycling of rinse water and no liquid effluent								
15-20	4.0-5.3	6-10	1.6-2.6	[e]	Tends to give coarse coatings after strong alkali cleaning or acid pickle without refining pre dip. Requires regular nitrite additions								
10-12	2.6-3.2	0.4-0.6	0.11-0.16	. . .	. . .								
15-20	4.0-5.3	. . .	. . .	[f]	Treats steel and galvanized steel in any proportion, together with maximum 15% aluminum								
14-16	3.7-4.2	0.5-2.5	0.13-0.66	. . .	Treats steel, galvanized steel and limited quantities of aluminum								
20-24	5.3-6.3	. . .	. . .	[g]	Control of zinc content may be necessary								
18-22	4.8-5.8	. . .	. . .	[h]	Refined coatings after alkali or acid cleaning without refining prerinse. Particularly suitable for one-coat finishes. Requires regular nitrite additions								
Zinc manganese phosphate	15-25	4.0-6.6	0.2-1.0	0.05-0.26	[i]	Low-temperature, low-stain. May have multimetal processing ability when fluoride-containing							
	24-26	6.3-6.9	0.7-1.0	0.18-0.26	. . .	May contain fluoride and nickel for treatment of galvanized steel and limited quantities of							

						aluminum							
Zinc iron phosphate	19-21	5.0-5.5	0.8-1.1	0.21-0.29	. . .	Submerged agitation and activating predip required							
	23-25	6.1-6.6	1.2-1.4	0.32-0.37	. . .	. . .							
Rustproofing applications													
Iron phosphate	28-32	7.4-8.4	. . .	. . .	. . .	"Working-in" of solution required. Will remove light rust. Minimum rinsing satisfactory. Not ideally suited for intermittent working							
Manganese iron phosphate	28-32	7.4-8.4	. . .	. . .	. . .	. . .							
	28-32	7.4-8.4	. . .	. . .	. . .	Coating weight and crystal structure dependent on cleaning method. Activating pre dip may be required for smooth coatings.							
	38-40	10.0-10.6	. . .	. . .	. . .	May be used without subsequent rinsing							
Zinc iron phosphate	38-42	10.0-11.1	. . .	. . .	(k)	Separate makeup and replenishment concentrates							
Antifriction applications													
Manganese iron phosphate	28-32(l)	7.4-8.4(l)	4.7-5.1(l)	1.2-1.3(l)	(k)	Coating weight and dimensional build-up dependent on pre-cleaning. Activating pre dip may							

						be required for smooth coatings.							
Wire drawing applications													
Zinc phosphate	60-70	15.8-18.5	. . .	. . .	(m)	Mild steel, stainless steel for longer life. Normally self-generating in nitrite							
Tube and wire drawing applications													
Zinc phosphate	18-22	4.8-5.8	. . .	. . .	. . .	Single chemical process. Has a higher consumption than more modern processes							
	18-22	4.8-5.8	. . .	. . .	(m)	Autogeneration of nitrite when used at 40+ points.							
	38-42	10.0-11.1	. . .	. . .	(m)	Total acid							
	40-50	10.6-13.2	. . .	. . .	(n)	Low sludge. Activating pre dip required							
Zinc calcium phosphate	18-22	4.8-5.8	. . .	. . .	. . .	Single chemical replenishment. Stable accelerator							
	65-75	17.2-19.8	. . .	. . .	. . .	Single chemical replenishment. Stable accelerator							
	20-24	5.3-6.3	. . .	. . .	(o)	. . .							
Tube drawing applications													

Iron phosphate/lubricant	. . .	. . .	. . .	. . .	(r)	No rinsing. Tubes drained at 5-15° slope for 30 min after treatment	**Cold extrusion applications**						
Zinc phosphate	18-22	. . .	. . .	. . .	(m)	Wide range of operating conditions to produce wide range of coating weights. Multichemical process							
Cold-forming aluminum applications													
Zinc phosphate	45-50	. . .	2-4	. . .	. . .	Regular fluoride additions required							
Galvanized steel applications													
Zinc phosphate	. . .	27-29	. . .	. . .	. . .	. . .							
Chromate/phosphate for aluminum applications													
Chromium phosphate	. . .	. . .	. . .	. . .	(s)	Coating weight controlled by fluoride level. Lighter coatings for paint bonding, heavier coatings for bare corrosion resistance							

Source: Ref 8

(a) 0.5-1.5 mL (1.3×10^{-4} to 4.0×10^{-4} gal) acid consumed.

(b) 1.5-3.5 mL (4.0×10^{-4} to 9.2×10^{-4} gal) acid consumed.

(c) 0.5-2.0 mL (1.3×10^{-4} to 5.3×10^{-4} gal) acid consumed.

(d) Stainless steel for longer life.

(e) 2-3 mL (5.3×10^{-4} to 7.9×10^{-4} gal) accelerator.

(f) 0.5-2.5 mL (1.3×10^{-4} to 6.6×10^{-4} gal) accelerator.

(g) Gas points (saccharometer, 0.5-2.0 mL (1.3×10^{-4} to 5.3×10^{-4} gal).

(h) 1.0-2.5 mL (2.6×10^{-4} to 6.6×10^{-4} gal) accelerator.

(i) 3-4 mL (7.9×10^{-4} to 1.1×10^{-4} gal) accelerator.

(j) Combinations of spray and dip.

(k) 0.2-0.4% Fe^{2+}.

(l) 0.2 M NaOH.

(m) Accelerator starch/iodide paper.

(n) 0.13% max Fe^{2+}.

(o) 0.2% max Fe^{2+}.

(p) Phosphate contribution.

(q) Lubricant contribution.

(r) H_2O content, 1.5-2.0%.

(s) Chromate pointage, 4-5 mL (1.1×10^{-3} to 1.3×10^{-3} gal).

Reference cited in this section

8. D.B. Freeman, *Phosphating and Metal Treatment,* Industrial Press, Inc., 1986, p 199-217

Product Standards for Phosphating (Ref 9)

In most industrialized countries, there exist published standards and specifications relating to phosphating. These standards describe various processes used in the phosphating (process standards) of iron and steel, zinc and its alloys (including both electrolytic and hot-dipped zinc) as well as cadmium and, to some extent, aluminum. Some of these standards relate specifically to the composition of the concentrates (chemical standards) used for making up the phosphating solutions. In addition, some countries provide standards for specific types of products, for which the phosphate coatings must possess certain properties.

Most standards and process specifications prescribe how the phosphate coatings should be prepared and how they enhance the properties of the substrate metal, with or without post-treatment. In several standards, a requirement exists for the presence of a phosphate coating on the base metal in question or for a qualitative test of its composition. Many standards relate to the coating weight required. In addition, these standards specify minimum coating weight or coating weight ranges for a given type of service. These specifications describe in detail the tests that can be used to determine the properties of phosphate coatings, both in their untreated state and also after post-treatment with corrosion-inhibiting oils, greases, or waxes, as well as paint and other coatings.

The extent to which standards and specifications are legally binding differs widely. Those carrying the greatest weight are issued by governmental bodies or military agencies, and regulatory bodies, both federal and military, exist not only in the United States but also in a number of European countries. An international standard relating to phosphating is in course of preparation (in collaboration with the International Standards Organization, or ISO) while in many countries, standards relating to phosphating have been published, in most cases after extensive collaboration with industry. Most of these standards provide a framework within which supplier and customer may draw up an agreement. In such national standards, care has been taken that the interests of both these parties are safe-guarded. However, it should be recognized that a number of firms and trade organizations impose their own modifications on national standards.

Phosphating standards and specifications for selected Western countries are listed in Table 17. Only rarely are phosphate coatings specified in terms of actual thickness. Most of these specifications detail methods used for analytical control and for testing of the phosphate coating itself.

Table 17 Industrial standards and process specifications for phosphating of metals in selected Western countries

Country	Standard	Section	Date of original adoption or last revision	Description
Federal Republic of Germany	DIN 50017 KK	. . .	. . .	Phosphate coating performance in condensed water at constant temperature
	DIN 50021 SS	. . .	. . .	Phosphate coating performance in salt spray
	DIN 50942	. . .	May 1987	Phosphating of metals: process fundamentals and test methods
Italy	UNI 4195	. . .	. . .	Magnetic method used to measure thickness of phosphate coatings

Country	Standard	Section	Date of original adoption or last revision	Description
	UNI 4236	4, 5	. . .	Qualitative testing for phosphate in coatings
		6, 7	. . .	Qualitative testing for zinc or manganese in phosphate coatings
	UNI 4239	. . .	. . .	Test for corrosion resistance of phosphate coating based on effect of acetic acid salt spray on coating porosity
	UNI 4527	. . .	. . .	Test for corrosion resistance of phosphate coating based on effect of aerated boiling water on coating porosity
	UNI 4528	. . .	June 1960	Surface treatment of metals; determination of phosphate coating weight
	UNI 4716	. . .	April 1961	Surface treatment of metals; properties of and tests for phosphate coatings to reduce seizing and to protect against wear
	UNI 4722	. . .	April 1961	Surface treatment of metals; testing efficacy of phosphate coatings to reduce fretting
	UNI 5343-64	. . .	Feb 1964	Chemical and electrochemical surface treatment; phosphate coatings for corrosion protection (types of coating, properties, testing)
Japan	JIS 3151	. . .	1987	Phosphate coatings as base for paint application
	JIS K 5400	. . .	. . .	General testing methods for coatings
		6.11	. . .	Impact test (uses 300 g, or 0.7 lb, weight dropped from 1000 mm, or 40 in., height)
		6.12	. . .	Flexibility test (bending over a 3 mm, or 0.12 in., diameter mandrel)
	JIS Z 0228	. . .	. . .	Wetting test method for rust-preventing oil
	JIS Z 2371	. . .	. . .	Corrosion testing with exposure to continuous salt spray (5% NaCl, with pH of 6.5 to 7.2, at temperature of 35 ± 2 °C, or 95 ± 4 °F)

Country	**Standard**	**Section**	**Date of original adoption or last revision**	**Description**
Sweden	FSD 6104	. . .	. . .	Corrosion resistance of phosphated surfaces exposed to salt spray for 240 h
	FSD 6238	. . .	10 Oct 1982	Phosphating and oiling of steel components
	FSD 6240	. . .	1 Jan 1985	Phosphating as an undercoat for painting of aluminum, zinc, and alloys of those metals
	FSD 7701	. . .	. . .	Immersion of workpiece components in corrosion-preventing oil
	K 242	. . .	. . .	Theoretical principles of surface treatment of metals
	K 3430	. . .	1968	Overview of surface treatment of metals
	K 3431	. . .	1968	Manganese phosphating of steel
	K 3432	. . .	1970	Zinc phosphating of steel
	K 3433	. . .	1970	Alkali phosphating of steel
	K 4531	. . .	1957	Bath control for surface treatment of metals
	YB 1303	. . .	. . .	Surface treatment guidelines for phosphating of zinc (or zinc-coated steel) with manganese or zinc phosphates prior to application of oils or paint coatings
	YB 5301	. . .	. . .	Nondrying oils for phosphate coatings
	YB 5302	. . .	. . .	Drying oils for phosphate coatings
	YB 7102	. . .	. . .	Testing corrosion resistance of phosphate coatings exposed to salt spray
United Kingdom	BS 1391	. . .	. . .	Salt-drop testing of phosphated and post-treated iron and steel components
	BS 3189	. . .	Sept 1973	Properties and applications of phosphate-coated irons and steels

Country	**Standard**	**Section**	**Date of original adoption or last revision**	**Description**
		Appendix B	. . .	Reduction of stress in the substrate of phosphate-coated components through the use of heat treatment
		Appendix D	. . .	Drop test to identify typical phosphate coatings
	BS 3900	. . .	. . .	Methods of testing paints
		Part 2	. . .	Resistance to humidity under condensation conditions
		Part 7	. . .	Determination of resistance to water
	BS AU148	. . .	. . .	Testing methods for motor vehicle paints
	DEF STAN 03-11/12	. . .	26 May 1986	Phosphating of iron and steel for corrosion protection and reduction of friction
United States	ASTM B 633	. . .	1985	Electrolytically coated zinc on iron and steel components
	ASTM D 2092	. . .	1986	Preparation of zinc-coated galvanized steel surfaces for painting
	DOD-P-16232 F	. . .	7 Nov 1978	Heavy-duty zinc or manganese phosphate coatings for steel
	Federal Test Method Standard 141, Method 6061	. . .	. . .	Corrosion resistance of coating exposed to 5% salt spray
	MIL-C-10578 D	. . .	28 Feb 1982	Phosphoric acid-based treatments for metal surfaces and for rust removal
	MIL-P-15328	. . .	. . .	Organic pretreatment coatings
	MIL-P-50002 B	. . .	5 Aug 1981	Phosphating chemicals for coating steels
	MIL-T-12879	. . .	21 Feb 1986	Chemical pretreatment of zinc surfaces for paint application and corrosion protection
	MIL-HDBK-205 A	. . .	15 July 1985	Phosphating and brown-colored coatings on ferrous metals

Country	Standard	Section	Date of original adoption or last revision	Description
	Federal specification TT-C-490 C	. . .	18 March 1985	Cleaning and pretreatment of steel surfaces (including cases where some surfaces are of zinc or aluminum) prior to the application of paint or other organic coatings

Source: Ref 9

Reference cited in this section

9. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 355-374

Safety Precautions

Safety precautions on a phosphating line must begin with the basic design of the equipment involved.

Immersion Phosphating. Proper ventilation of immersion tanks is necessary to eliminate concentration of vapors from the tanks in buildings or work areas. Local regulations in some areas, however, may prohibit exhausting directly to the outside, and special filtering equipment may be required. Tanks containing acid must be resistant to the acid they hold to eliminate the possibility of the acid corroding through the tanks and spilling on to the floor. Curbing should surround tanks to retain spilled or leaked solutions.

Spray Phosphating. Equipment used in spray phosphating must be properly vented for removing vapors. A heavy grating should surmount each of the various tanks for protecting the personnel cleaning and repairing tanks, risers, and spray nozzles. These gratings also prevent workpieces from falling into tanks from conveyors. Access doors in drain areas, which are used for checking carryover and condition of work, and for access during breakdown, should be easily opened from the inside.

Handling of Alkalis and Acids. All alkaline cleaners should be handled with care. Rubber gloves and face or eye shields should be worn when these materials are added to cleaning tanks. Should these materials contact the skin, it should be flushed with water as soon as possible. Repeated or prolonged contact can cause skin irritation.

These precautions apply also to handling the phosphoric acid and chromic acid used in phosphating. Although chromic acid is oxidizing, it does not burn the skin immediately, as do common mineral acids, but severe irritation results from prolonged exposure to the skin. Goggles or face shields should be worn at all times during handling of chromic acid, because contact with the eyes can cause serious damage. All contaminated clothing should be removed and washed before reuse.

To transfer liquid from a carboy, a carboy-tilter, commercial siphon, or bulb siphon should be used. Liquid should never be drawn from a carboy by using air pressure to force it out, even when using the so-called air pressure reducers. Danger is always present that the carboy will break, or even explode, and spray or splash acid on the operator. This also holds true for drums. All drums should be specified to be plugged with one-way breather plugs. If this is not possible, the solid plug must be removed carefully to avoid acid spray, and only enough to permit the compressed gases to escape slowly. Once the inside and outside pressures are equalized, the plug may be removed.

Cyanide (Ref 10, 11) is a highly toxic chemical that can kill almost instantly. Nevertheless, despite the constant and widespread use of cyanide, deaths and illnesses associated with its use are rare. There is little danger if certain guidelines are followed closely:

- All containers for cyanide, full or empty, should have airtight lids, be stored in a well-ventilated area, and be clearly labeled as containing poison. No unauthorized person should have access to them.
- Cyanide should be handled only with gloved hands or tongs, in a well-ventilated area.

- Keep work areas meticulously clean. Spills of acid and cyanide that combine on the shop floor, or in floor drains, can generate hydrogen cyanide gas. The gas is extremely lethal if inhaled; it is the primary cause of cyanide-related deaths.
- Be prepared to provide immediate first aid in case of contact with cyanide salts. Wash the affected area in water, then with dilute sodium hypochlorite or bleaching powder solution, when with water again.

References cited in this section

10. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold Company, 1984, p 342-343

11. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 409

Treatment of Effluents from Phosphating Plants

Because aqueous effluents from phosphating plants contain both organic and inorganic residues which can damage the environment, they must be treated before they can be discharged into a public drainage system or other watercourse. Legal requirements and local laws and regulations determine how extensively the by-products of the phosphating process must be treated for proper disposal.

U.S. Regulations (Ref 12)

In the United States, industrial waste discharges are regulated by the federal government under the Clean Water Act of 1977, revised by the Water Quality Act of 1987, and are subject to additional regulation by state and local governments. Federal environmental regulations are administered by the EPA and appear in the Code of Federal Regulations (CFR), Volume 40. Some overall requirements exist that are designed to protect U.S. waters from polluting contaminants and that establish prohibitions against pollution in a broad sense.

More specific requirements are found in what are referred to as categorical standards (for example, industry-specific regulations setting numerical limitations on specific effluent parameters). These regulations are managed under the National Pollutant Discharge Elimination System (NPDES) for direct discharge to surface waters and the Pretreatment Program for discharge to sewer systems. A permit is required to discharge wastewater to any surface water, and it sets forth conditions under which wastewaters must be managed, allowable contaminants in the discharge, and permitted effluent flows.

Federal regulations covering phosphating are primarily found under the electroplating (Volume 40, Part 413) and metal finishing categories (Volume 40, Part 433) in the CFR. Table 18 summarizes effluent limitations for these industry segments. Table 18 is an oversimplification of actual regulations; the specific categorical regulations are complicated by several qualifying statements and requirements. It does provide a good indication, however, of the prevailing limitations on effluents discharged from metal finishing and electroplating operations. Individual permit requirements may vary and will include limitations on pH, suspended solids, and oil and grease.

Table 18 Effluent limits for phosphate coating processes per U.S. Code of Federal Regulations

Component	Electroplating (40 CFR 413)				Metal finishing (40 CFR 433)			
	1-day max		4-day avg		1-day max		Monthly avg	
	mg/L	lb/gal × 10^{-5}	mg/L	lb/gal × 10^{-5}	mg/L	lb/gal × 10^{-5}	mg/L	lb/gal × 10^{-5}
Cadmium	1.2	1.0	0.7	0.6	0.69	0.58	0.26	0.22

Chromium	7.0	5.8	4.0	3.3	2.77	2.31	1.71	1.43
Copper	4.5	3.8	2.7	2.3	3.38	2.82	2.07	1.73
Cyanide (total)	1.9	1.6	1.0	0.8	1.2	1.0	0.65	0.54
Lead	0.6	0.5	0.4	0.3	0.69	0.58	0.43	0.35
Nickel	4.1	3.4	2.6	2.2	3.98	3.32	2.38	1.99
Silver	1.2	1.0	0.7	0.6	0.43	0.36	0.24	0.20
Zinc	4.2	3.5	2.6	2.2	2.61	2.18	1.48	1.24
Total toxic organics(a)	2.13	1.78	. . .	. . .	2.13	1.78	. . .	. . .

Source: Ref 12

(a) Summed concentration of a list of 110 specific organic compounds.

Groundwater protection is accomplished primarily through the Resource Conservation and Recovery Act (RCRA) of 1976, as revised by the Hazardous and Solid Waste Amendments of 1984, which regulate waste management. The significant effect of this legislation on the phosphating industry is through regulation of treatment, storage, transportation, and disposal practices for waste treatment sludges and spent baths. Requirements include a "cradle to grave" accountability for those wastes defined as "hazardous" by regulations, strict controls and permitting of waste management facilities, and prohibitions against land disposal without treatment by approved procedures or to meet specified standards.

Environmental impairment from past disposal practices and from accidental releases or spills is covered by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund due to the provision for government funding of cleanups when no responsible parties can be identified. Both RCRA and CERCLA regulations specifically prohibit contamination of groundwater. Enforcement occurs at both the state and federal levels, as for effluent discharge violations. Fines and criminal penalties are assessed for both corporations and individuals. The liability issues arising out of these regulations and the increasing cost of waste treatment and disposal have dramatically altered the approach to waste management and are driving industry toward recovery, recycling, and waste minimization.

State or local regulations may be more stringent than federal regulations, but they may not be less stringent. For example, the following limits were imposed on an ordnance manufacturer in Gadsden, Alabama, by the Alabama Water Improvement Commission (Ref 13):

Contaminant	Concentration limit (6.0 < pH <9.5), ppm
Cr	0.5

Cr^{6+}	0.1
PO^{3-}_4(as P)	1.0
Ni	0.5
Zn	0.8

Most states have applied for and obtained authority to implement the federal NPDES program, and many have additional regulations governing discharges. Enforcement is accomplished at the state and federal levels. Violations can carry both civil and criminal penalties.

Solid and Liquid Waste Disposal

The phosphating process generates both solid and liquid wastes that require proper disposal procedures to minimize any negative impact on the environment. Figure 15 shows typical techniques for collecting the sludge produced by the phosphating process. Typical sludge removal methods are described in Fig. 16.

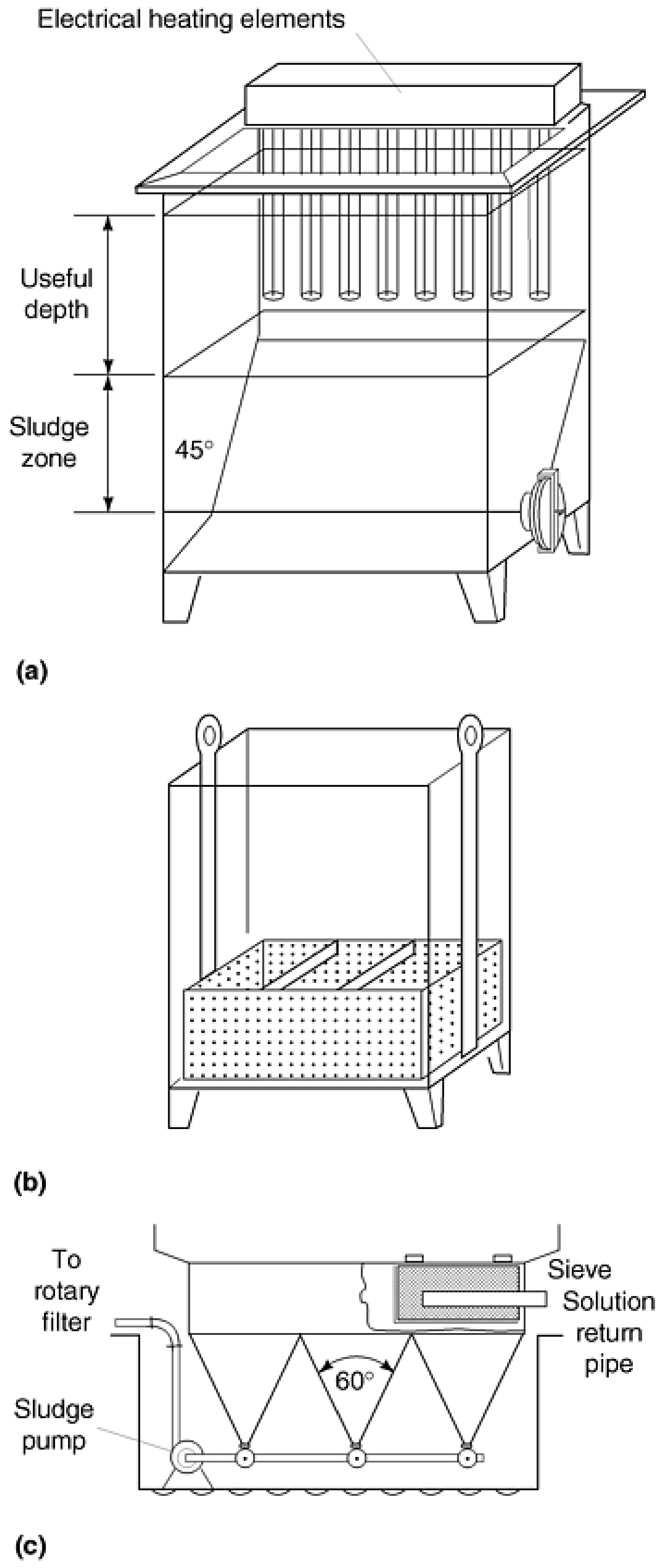

Fig. 15 Sludge-settling methods for immersion phosphate tanks. (a) Sloping bottom. (b) Removable settling box. (c) Conical-formed floor. Source: Ref 14

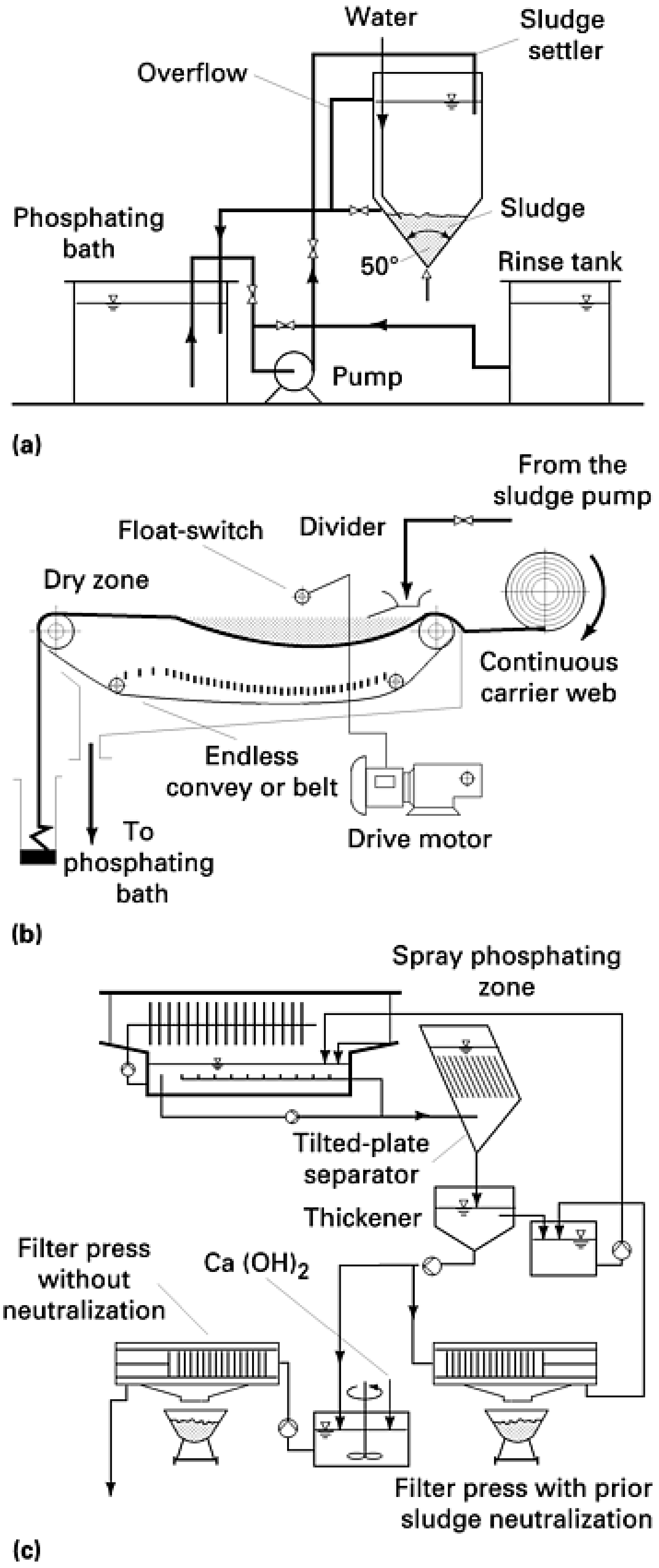

Fig. 16 Methods for removing sludge from a phosphating tank. (a) Settling tank. (b) Continuously operating cloth belt filter. (c) Tilting plate separator, thickener, and filter press. Source: Ref 15

Sludge Regulation (Ref 16). Under the RCRA, there are two types of hazardous waste: *categorical* (the waste comes from a certain industry or operation) and *characteristic* (the waste possesses certain hazardous characteristics: ignitability, toxicity, corrosivity, and/or reactivity). The EPA and the states are authorized to make these classifications. For example, according to the EPA, all wastewater treatment sludges from electroplating operations are categorically hazardous. The prepaint cleaner, phosphating and chromating sludges, spent baths, and rinsewaters used in electroplating operations are not considered categorically hazardous, but if they show hazardous characteristics upon testing, they would be subject to the RCRA.

Sludges in Prepaint Phosphating Lines (Ref 16). In the automotive industry, and other industries that use large zinc and iron phosphating lines, it has long been general practice to routinely filter sludge from phosphate baths. Today, the ever-higher cost of phosphating chemicals and the ever-tighter regulation of sludge disposal make it economically worthwhile for small operations to investigate filtering.

In the typical prepaint finishing line, there are several types of sludge: (*a*) sludge from the cleaner rinse and ultrafilter reject, which is not hazardous; (*b*) sludge from the phosphating rinse, which is hazardous if the nickel content is high; and (*c*) sludge from the chromating rinse, which is hazardous because of the presence of hexavalent chromium or because trivalent chromium wastes are mixed with other wastes that may oxidize the trivalent chromium to hexavalent. Although these sludges are initially separate, they usually become commingled because the wastewaters generating them are treated in a centralized system. Thus, the sludge is hazardous, from the chromium content alone if not from chromium plus nickel.

When zinc phosphating sludge is fed into a wastewater treatment system, a number of costs are incurred: the cost of process chemicals, the cost of lime (used to precipitate zinc and to neutralize residual phosphoric acid), and the cost of disposing large quantities of hazardous sludge. Moreover, precipitating the sludge by lime increases the volume of the sludge (Fig. 17). A filter press system can reduce this volume by dewatering phosphate sludges, changing them from 5% solids to 30% solids. It also saves phosphating chemicals.

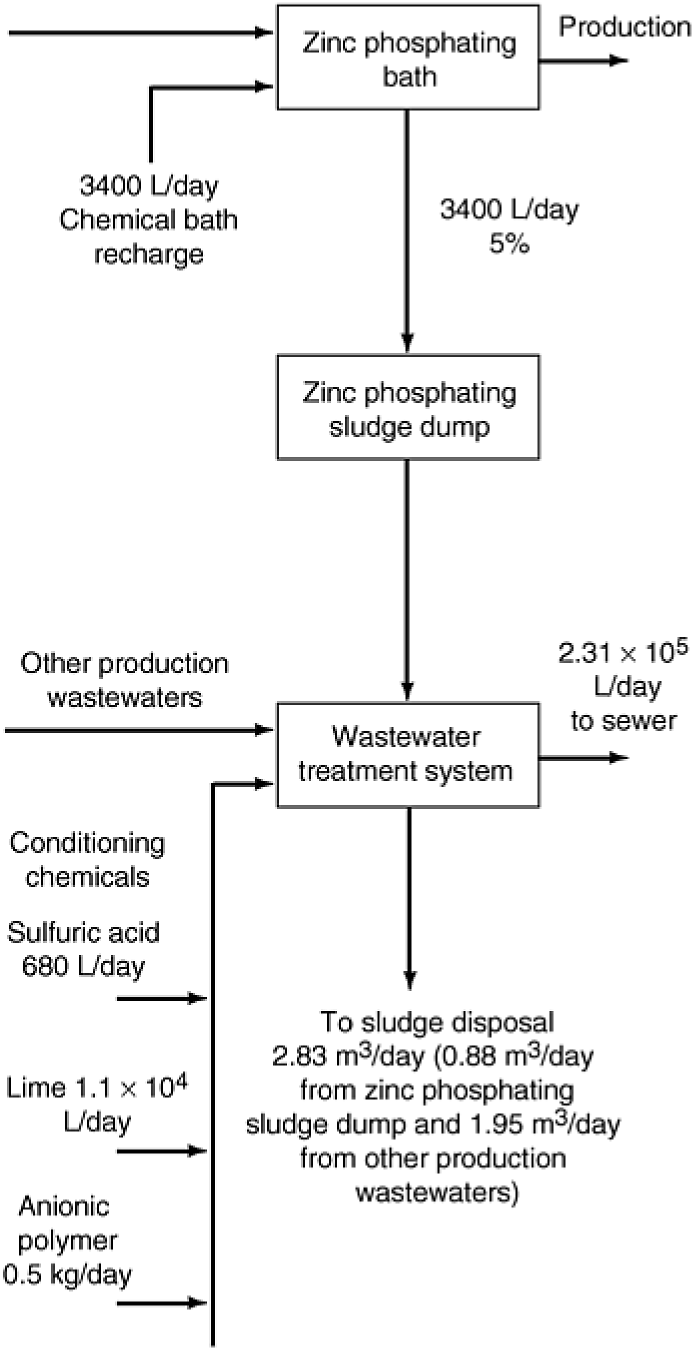

Fig. 17 Flowchart showing typical sludge output produced by zinc phosphate coil coating line. Source: Ref 17

If the flow of sludge to the wastewater treatment system is 190 L/min (50 gal/min), and the sludge consistency is 30% solids, the projected quantity of wet sludge, including zinc phosphating sludge, is 2.83 m^3/day (100 ft^3/day). The quantity produced by the wastewater treatment system after segregating the zinc phosphating sludge is 1.95 m^3/day (69 ft^3/day), but the projected quantity produced from the zinc phosphating bath after dewatering is 0.57 m^3/day (20 ft^3/day), resulting in a total net reduction of 0.31 m^3/day (11 ft^3/day).

Table 19 summarizes treatment options for sludges generated by prepaint phosphating lines.

Table 19 Treatment options for sludges generated by prepaint lines

Option	Treatment concept	Treatment technology

No.		
1	Dispose cleaner and phosphating rinsewater sludges and cleaner ultrafilter reject at Subtitle D facility. Segregate and treat separately the chromating wastewaters.	Batch tank for chromating wastewaters where hexavalent chromium is reduced to trivalent and precipitated. The sludge is sent to a Subtitle C facility (that is, a hazardous waste landfill).
2	Segregate the cleaner rinsewater and ultrafilter reject wastes. Treat and discharge separately.	Neutralization and oil recovery/destruction if effluent limits would be exceeded
3	Treat the phosphate rinsewaters in order to eliminate their hazardous contribution to the sludges, in combination with option 1.	Use reverse osmosis to recover the phosphating bath (that is, in the rinse plus technology listed above for option 1).
4	Leave sludges as they are and dewater as much as possible.	High-pressure filter press

Source: Ref 16

Equipment Selection and Operation (Ref 17). One plant chose as a dewatering device a filter press that is rated at 0.57 m^3/day (20 ft^3/day). A filter press system was chosen over continuous on-line filters and settling towers because these would have produced a liquid slurry that would have required drum disposal or further dewatering.

The components of the filter press system are a sludge holding tank, filter press feed pump, filter press, and filtrate return tank with transfer pump (Fig. 18). After the sludge in the zinc phosphating tank settles, it is pumped to the sludge holding tank for further compaction. Any solids-free bath is decanted back to the filtrate return tank. The filtered zinc phosphating bath solution is transferred to the process tank at the rate of 2860 L/day (750 gal/day), compared to the original 3430 L/day (900 gal/day), a makeup rate of 570 L/day (150 gal/day). This procedure is performed daily during the four hours of downtime for the zinc phosphating bath.

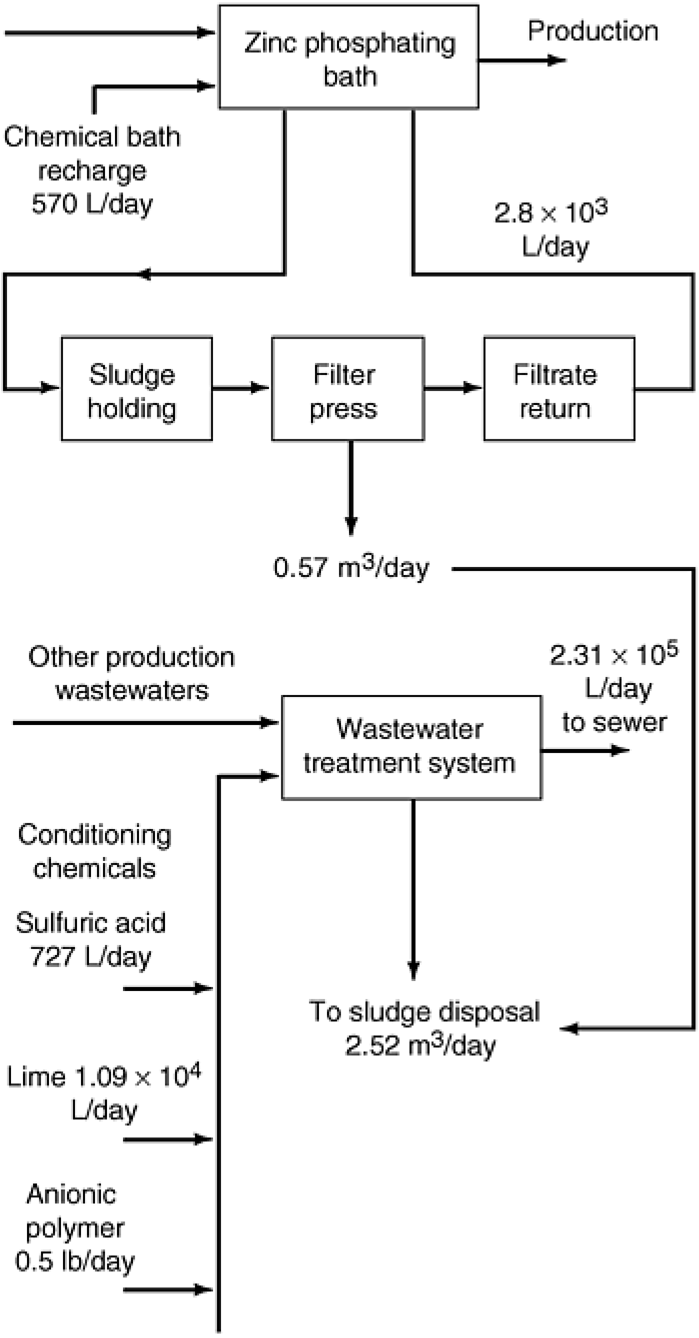

Fig. 18 Flowchart showing sludge output produced by zinc phosphate coil coating line retrofitted with a filter press. Source: Ref 17

Disposal of Solutions. Nearly all municipalities have maximum limitations on the acids, solids, chromium, zinc, nickel, iron, and oil that may be drained to a stream or sewer system. Because these limits vary widely, local governmental authorities should be consulted for specific restrictions on each toxic or nontoxic material in a phosphating system so that proper waste treatment plans can be made. The trend is toward stricter controls, and waste treatment programs should include a margin of safety to accommodate future changes. Limits and suggested treatments for the more serious contaminants from a phosphating system are indicated in Table 20. The waste treatment methods described are widely used, but other methods also are available.

Table 20 Limits and treatments of contaminants from a phosphating system

Containment	Direct discharge,	Publicly owned treatment

	ppm	**works, ppm[(a)]**
Chromium		
Hexavalent	0.05	0.05-5.0
Total	0.10-0.5	1.0-10.0
Zinc	0.1-0.5	1.0-5.0
Nickel	0.1-0.5	1.0-5.0
Oil	1.0-10.0	10.0-100

(a) Environmental protection laws are subject to change. Suppliers of the metal pretreatment should be contacted to determine needs in terms of treatments of these chemicals.

Two sets of limits need to be considered: direct discharge to streams, lakes, and rivers; and discharge to publicly owned treatment works. Table 20 lists the limits of contaminants.

Soda ash is not the best neutralizing agent. In order of preference, lime, caustic, and soda ash are suggested. Recommended neutralization pH values are:

Chemical	**pH range**
Zinc	7.0-9.0
Nickel	8.5-9.5
Chromium	8.0-9.0

Limits and Treatments of Contaminants. It is inevitable that contaminants such as metals, acids, and oils build up and must be removed from the phosphate bath when excess amounts interfere with the coating process.

Acidity is influenced by cleaning stage (alkaline), phosphating stage (acid), and final rinse (acid).

Chromium. Of all the materials used in metal pretreatment, those containing hexavalent chromium probably require the most stringent treatment, as the amount of hexavalent chromium allowed in discharges by most authorities varies from 0 to less than 1 ppm (Ref 18). Most of the chromium in final rinse stage is in the more toxic hexavalent form. However, it can be readily reduced to the less toxic trivalent form (reduction of Cr^{6+} to Cr^{3+} yields a product 100 times less toxic)(Ref 19) with sodium bisulfite or sodium metabisulfite in a pH range of 3.5 to 5.0. To remove the trivalent chromium, add an alkaline material such as soda ash, mixing thoroughly, to a pH of 8.5 to 10.0, allow to settle for 1 h, and draw off the liquid, leaving the chromium in the sludge. The drawn-off liquid is essentially water and may be discharged into a sewer or stream in the normal manner, in compliance with local regulations.

Zinc. Usually, it is economically desirable to avoid any loss of zinc phosphating solution, and therefore a problem exists only in disposal of the rinse solution (contaminated water) following the phosphating stage and disposal of the sludge periodically removed from the phosphating tank. The sludge should be hauled to a suitable dump, rather than discharged into a sewer or stream. If it is necessary to dispose of a zinc phosphating solution, or if the rinse water, following the phosphating stage, contains enough zinc phosphating solution from carryover to create a disposal problem, first precipitate the zinc by raising the pH to 8.5 to 10.0 with any available alkaline material, such as soda ash. Then, after thorough mixing, allow to settle for 1 h and draw off the liquid, leaving the zinc to be handled as a sludge. This drawn-off liquid also is essentially water and may be discharged into a sewer or stream in the normal manner, in compliance with local regulations.

Nickel. Some of the newer zinc phosphating compounds that coat both bare and galvanized steel contain appreciable quantities of nickel. This presents no in-plant problems of disposal because nickel is precipitated along with zinc when disposal of contaminated rinse water or phosphating solution is required. However, because nickel may be more harmful in a sewage disposal plant, some municipalities that have accepted small quantities of zinc in the drain water demand almost complete freedom from nickel. More complete processing of solutions is required in these situations.

Oil. Most phosphating systems do not present a serious problem in treatment of oil waste, but some manganese of zinc phosphating systems contain a final oil or soluble-oil dip. A few systems have sufficient oil removed from parts in the cleaning stage to require treatment. Most soluble-oil and water solutions can be broken with calcium chloride, often assisted by small additions of aluminum sulfate or flocculating agents. The separated oil layer is floated off for removal in a tank truck or in drums, and the water, if sufficiently clear, is metered to a sewer system. Oils must be physically removed for such nonharmful uses as dust-laying treatments of dirt or gravel roads or parking lots.

Cyanide (Ref 20). Users of cyanide incur perpetual liability as generators of hazardous sludge. For example, aluminum finishers remove cyanide from waste water by precipitation, and the sludge may contain a total cyanide concentration of 1 to 10% (10^4 to 10^5 ppm). The EPA has ruled that such a sludge cannot be landfilled, so aluminum finishers must either stop using cyanide or destroy it in the sludge. However, ferricyanide, the forum of cyanide in aluminum pretreatments, is extremely stable and cannot be destroyed by chlorination, the relatively simple process that destroys free cyanide. Commercial methods are under development for destroying ferricyanide, but they are complex and expensive.

U.K. Regulations (Ref 21)

Consent limits for discharge to public drains in the United Kingdom are set by the eight regional water companies. In general these limits are established on a case-by-case basis rather than by the imposition of overall national or local standards. In determining the limits in individual cases, consideration is given not only to the concentration of individual pollutants but also to factors such as location, total volume of discharge, and the capacity of, and methods used by, local treatment works.

Discharge to streams, rivers, and coastal waters is controlled by the National Rivers Authority.

It should be borne in mind that the transport and labeling of solid and liquid wastes is also regulated. Solid and semisolid waste arises from the neutralization and precipitation of effluent in in-house treatment facilities and also from the sludge generated as a by-product of heavy metal phosphating processes. This sludge is removed on a continuous or batch basis and is usually disposed of to landfill sites. However, before this is done, under the Control of Pollution Act of 1974, a disposal license must be obtained from the local disposal authority, which will require detailed data on the nature of the waste.

The conveyance and labeling of hazardous wastes is covered by:

- Dangerous Substances (Conveyed by Road in Tanks and Tank Containers) Regulations, 1981
- Road Traffic (Carriage of Dangerous Substances in Packages) Regulations, 1986
- Classification, Packaging, and Labeling of Dangerous Substances Regulations, 1984

Federal Republic of Germany Regulations (Ref 22)

Legislation covering water management (water management law WHG, amended as of 23 Sept 1984) relates to surface waters, coastal waters, and groundwater. It makes the use of water (for example, by its abstraction, as well as by introduction, into discharged water, of dissolved or suspended matter) a measure requiring official consent. In addition, it requires reservoirs or lagoons for the storage and/or settling of toxic substances (for example, acids, alkalis, and pickling salts) to be constructed and operated so that impurities cannot reach the water table. Consent for discharge will only be given where the burden of toxic materials is kept as low as possible, concentrations of specific species complying with legislative requirements (Table 21).

Table 21 Effluent levels for phosphate coating process discharges in the Federal Republic of Germany

Discharge type	**Temperature**$^{(a)}$		**pH value**	**Suspended solids**$^{(a)}$		**Chemical oxygen demand**$^{(a)}$		**Toxicity to finishes as a dilution factor (G_F)**$^{(a)}$	**Composition, mg/L(lb/gal × 10^{-5})**$^{(a)}$												
	°C	**°F**		**mL/L**	**mL/gal**	**mg/L**	**lb/gal × 10^{-3}**		**Saponifiable oils and fats**	**Hydrocarbons**	**Cd**	**Cr**$^{(b)}$	**Cr**$^{6+}$	**Fe**	**Cu**	**Ni**	**Zn**	**NH_4**	**F**	**NO_3**	**NO**
Discharge into watercourse$^{(c)}$																					
Electroplating	. . .	. . .	. . .	0.3	1.1	600	5.0	8	. . .	10 (8.3)	0.5 (0.4)	2 (1.7)	0.5 (0.4)	3 (2.5)	2 (1.7)	3 (2.5)	5 (4.2)	100 (80)	50 (42)	. . .	. . .
Organic coating	. . .	. . .	. . .	0.3	1.1	800	6.7	10	. . .	10 (8.3)	0.5 (0.4)	1 (0.8)	0.5 (0.4)	3 (2.5)	2 (1.7)	1 (0.8)	3 (2.5)	. . .	. . .	. . .	. . .
Discharge into main drainage systems																					
ATV A115 Jan 83	35		6.5-10	1	4	. . .	. . .	. . .	250 (210)	20 (17)	0.5 (0.4)	3 (2.5)	0.5 (0.4)	10 (8.3)	2 (1.7)	3 (2.5)	5 (4.2)	165 (138)	60 (50)	. . .	20 (17
State of Bad Wuerttemburg	35		6.0-9.5	1	4	. . .	. . .	. . .	. . .	20 (17)	1 (0.8)	2 (1.7)	0.5 (0.4)	. . .	2 (1.7)	3 (2.5)	5 (4.2)	50 (42)	50 (42)	. . .	10 (8.3
City of Mannheim	35		6.0-9.0	1	4	. . .	. . .	. . .	100 (84)	20 (17)	1 (0.8)	3 (2.5)	0.1 (0.08)	20 (17)	1 (0.8)	3 (2.5)	3 (2.5)	20 (17)	. . .	50 (42)	30 (25

Note: As specified by local, state, and federal government regulations.

Source: Ref 22

(a) Prescribed maximum values.

(b) Total chromium.

(c) Per standard. WHG 40, effluent VwV of 5 Sept 1984.

Discharge of effluent into main drains is governed by local authority legislation. These may specify the levels of toxic species discharged or the levels may be dealt with by consent at a case-by-case level. The basis, in all cases, will be guidelines as in Ruling ATVA 115, published by the Technical Effluent Group (ATV), which collaborates with the national association of urban environmental authorities (VKS)(Table 21).

According to effluent discharge legislation (AbwAG, most recent amendment 14 Dec 1984), those responsible for effluent discharge are liable to pay the local authority a sum based on the volume and nature of the effluent.

Under the terms of refuse legislation (AbfG, dated 11 Sept 1986), restrictions are imposed on the dumping of trade waste and other industrial materials that pose a potential threat to air or water quality. Such effluents can be handled, stored, processed, or shipped only at locations for which permission has been given. In the listing of types of noxious species published as an appendix to this legislation, the following categories of chemicals from the surface finishing industries are listed: acids, alkalis, oil emulsions, and residues from cleaning and degreasing baths.

References cited in this section

12. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 296-298
13. Treating Rinses from Zinc Phosphatizing, *Prod. Finish.,* Nov 1978, p 56-59
14. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 267-268
15. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 280
16. C.R. Marshall and T. Daily, Getting a Payback from Waste Treatment, Part III: Pretreatment Sludges, *Prod. Finish.,* 1990, p 75-80
17. T. Daily and T. Henley, Getting a Payback from Waste Treatment, Part II: Phosphating Chemicals, *Prod. Finish.,* Dec 1989, p 65-71
18. D.B. Freeman, *Phosphating and Metal Treatment,* Industrial Press, Inc., 1986, p 182
19. B.R.W. Hinton, Corrosion Prevention and Chromates, the End of an Era, *Met. Finish.,* Sept 1991, p 55-61
20. J.R. Favilla, No-Rinse Treatment for Aluminum, *Prod. Finish.,* Nov 1990, p 45-55
21. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 296
22. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 294-296

Chromate Conversion Coatings

Patrick L. Hagans, Naval Research Laboratory; Christina M. Haas, Henkel Corporation

Introduction

CHROMATE CONVERSION COATINGS are formed on metal surfaces as a result of the chemical attack that occurs when a metal is immersed in or sprayed with an aqueous solution of chromic acid, chromium salts such as sodium or potassium chromate or dichromate, hydrofluoric acid or hydrofluoric acid salts, phosphoric acid, or other mineral acids. The chemical attack facilitates the dissolution of some surface metal and the formation of a protective film containing complex chromium compounds.

A variety of metals and electrodeposited metal coatings, including zinc, cadmium, magnesium, and aluminum, can be chromate conversion coated. Several articles in this Volume contain details about the procedures used to apply chromate coatings to specific metals and metal coatings. The conversion coating of cadmium electrodeposits is discussed in the article "Cadmium Plating"; the articles "Surface Engineering of Aluminum and Aluminum Alloys" and "Surface Engineering of Magnesium Alloys" contain information relating to the application of chromate conversion coatings to these metals; and procedures for applying conversion coatings to electrodeposited zinc are described in the article "Zinc Plating." A comprehensive summary of literature sources related to chromate conversion coatings is available in a detailed review of surface treatments for aluminum alloys (Ref 1). In addition, processing and testing details for application of chromium conversion coatings to aluminum, magnesium, cadmium, copper, silver, and zinc are continuously updated and presented in concise form (Ref 2).

Chromate conversion coatings are generally used to increase the corrosion resistance of the metal to which they are applied. Most conversion coatings slowly dissolve in water and provide limited protection in this medium; however, they furnish excellent protection in marine atmospheres and in high-humidity environments. The protection provided by chromate coatings increases directly with thickness up to a certain point, after which the protective nature is sacrificed due to the formation of a porous, nonadherent film. Chromate conversion coatings are also used for a variety of decorative and functional applications. They can be produced in a variety of colors, ranging from the very bright coatings obtained on zinc and cadmium, which simulate the appearance of bright nickel and chromium, to the olive drab frequently applied to military equipment. Chromate coatings provide an excellent nonporous bonding surface for all paints that have good molecular adhesion. A summary of general uses for chromate conversion coatings is given in Table 1; more detailed information is provided in the section "Chromating Processes and Applications" in this article.

Table 1 Common uses of chromate conversion coatings

Metal	**General use**				**Remarks**
	Corrosion resistance	**Paint base**	**Chemical polish**	**Metal coloring**	
Aluminum	X	X	. . .	X	Economical replacement for anodizing if abrasion resistance is not required Used to "touch-up" damaged areas on anodized surfaces
Cadmium	X	X	X	X	. . .
Copper	X	X	X	X	Thin coatings prevent "spotting out" of brass and copper electrodeposits. No fumes generated during chemical polishing
Magnesium	X	X	. . .	. . .	. . .
Silver	X	. . .	. . .	. . .	. . .
Zinc	X	X	X	X	. . .

Source: Ref 2

Most of the formulations used in chromating today are of a proprietary nature, and many of the patents in this area expired long ago. Some specific formulations are given in Ref 1, but details about solution control are difficult to find. This is unfortunate, because understanding solution replenishment chemistry is key to extending the life of chromating solutions and enhancing their versatility. This article briefly describes the basic attributes of chromate conversion and the processes for applying them. It also provides information about the influence of substrate microstructure on the performance of coating deposits, the mechanism of substrate protection supplied by chromate coatings, and the development of new replacement technologies in response to the environmental constraints that have developed around the use of chromium-base compounds. (Information related to this last item is also available in the article "Chromium Elimination" in this Volume.) Most of the information provided in this article relates specifically to the chromating of aluminum and aluminum alloys, for these metals are by far the chief recipients of chromated films. However, most of the information is generally applicable to chromating of other metals as well.

References

1. S. Wernick, R. Pinner, and P.G. Sheasby, in *The Surface Treatment and Finishing of Aluminum and Its Alloys,* Vol 1, 5th ed., ASM International and Finishing Publications Ltd., 1987, Chap 5
2. F.W. Eppensteiner and M.R. Jenkins, Chromate Conversion Coatings, *Metal Finishing--Guidebook and Directory Issue '92,* Vol 90 (No. 1A), 1992, p 413-425

Characteristics of a Chromate Conversion Coating

Conversion coating does not simply involve the deposition of a thin layer of, for example, hydrated metal oxide that "converts" a surface to a corrosion resistant state (Ref 3). As illustrated in Fig. 1, an Auger electron spectroscopy (AES) depth profile for a typical chromated layer on aluminum alloy 2024-T3, the film contains not only chromium and oxygen, but also part of the substrate (in this case aluminum) and the principal alloying element (copper). The profile was taken on the solid solution matrix, off any of the intermetallic second-phase particulates that typically form in the aluminum-copper alloy system. In the case of chromate coatings, the amorphous hydrated oxide mixture that is formed on the surface must involve oxidation of the substrate, followed by precipitation of the dissolved metal ions. Precipitation arises from an increase in pH at the surface due to reaction with excess hydroxyl ions produced as a result of the cathodic (i.e., reduction) half reaction. Either reduction of dissolved oxygen or reduction of water itself will cause such an increase in pH at the surface. A similar mechanism is postulated for the formation of crystalline phosphate conversion coatings on steel, in which two principal crystalline phases have been identified: hopeite, $Zn_3(PO_4)_2{\cdot}4H_2O$, and phosphophillite, $Zn_2Fe(PO_4)_2{\cdot}4H_2O$ (Ref 5). The latter compound involves incorporation of the main element in the substrate (i.e., iron) through oxidation of the surface in the presence of acidic zinc phosphate.

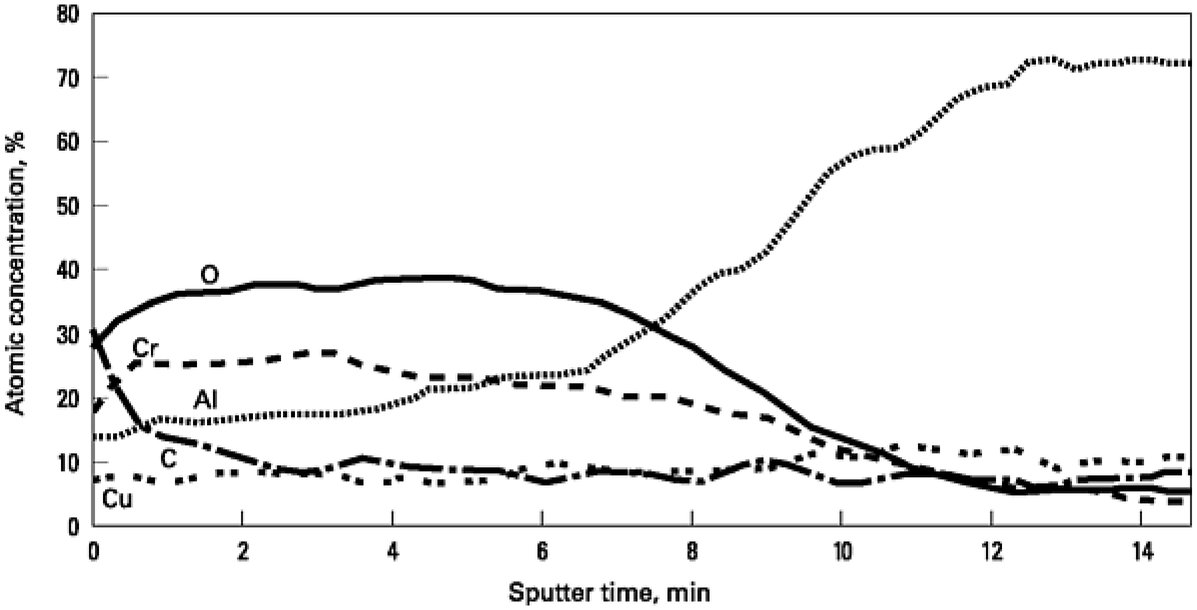

Fig. 1 Auger electron spectroscopy depth profile of polished aluminum alloy 2024-T3 solid solution matrix exposed to Alodine 1200S conversion coating solution for 5 min. Sputter rate approximately 300 Å/min (vs. SiO_2). Experiment details in Ref 7. Source: Ref 4

As evidenced by the above discussion, a conversion coating is simply a film that contains a mixture of the corrosion-resistant species and the major elements found in the substrate. The mixture promotes strong adhesion of the conversion coating to the substrate. This is unlike a film formed by physical vapor deposition, where there is a very clear interface between the film and the substrate and where essentially none of the substrate is distributed through the deposited film. Poor film adhesion can result at such an interface, and if water and/or oxygen reach the interface region, corrosion can readily occur and cause delamination of the film. Because no clear interface exists in conversion coating films, a certain amount of oxygen and water can be tolerated; the substrate concentration gradient is observed through the protective film.

References cited in this section

3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66

4. P.L. Hagans, Naval Research Laboratory, and C.M. Haas, Henkel Corp., unpublished data

5. S. Maeda, in *Progress in Organic Coatings,* Vol 11, 1983, p 1

7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.,* Vol 21, 1994, p 65

Chromate Conversion Coating Processes and Applications

Although the beginning of chromium-based conversion coatings can be traced back to 1915 (Ref 6), the advent of modern-day chromating treatments is dated from 1945 to the early 1950s, when tradenames such as Alodine (American Chemical Paint Co., later Amchem Products Co.), Alocrom (ICI Ltd.), Bonderite (Parker Rust Proof Co.), and Iridite (Allied Chemical Co.) were synonymous with the formation of highly corrosion-resistant conversion coatings. Unlike their predecessors, these coatings could be applied at or near room temperature for short times (a few seconds to several minutes, depending on the thickness and degree of corrosion resistance desired), and good results could be obtained on difficult-to-treat alloys such as aluminum-copper alloys and magnesium alloys. The use and solution control of surface activators (most notably fluoride ion) allowed chromating reactions to proceed at a very rapid rate. In addition, when maximum corrosion resistance was required, accelerators such as the ferricyanide ion were used, especially on difficult-to-treat alloys (Ref 3).

The importance of having fluoride present in the chromium-containing bath is illustrated in the AES depth profile of a conversion coating applied in the absence of fluoride (Fig. 2). Comparison of this profile with Fig. 1 indicates that, all other conditions being constant, the presence of fluoride increases film thickness by a factor of at least 30. With fluoride present (Fig. 1), the surface was found to contain 18 at.% Cr, whereas only 5 at.% Cr was observed without fluoride in solution (Fig. 2). Without fluoride present, very little chromium is deposited, and the enriched copper interface observed on the cleaned but untreated sample remains intact (data not shown; see Ref 7 for details).

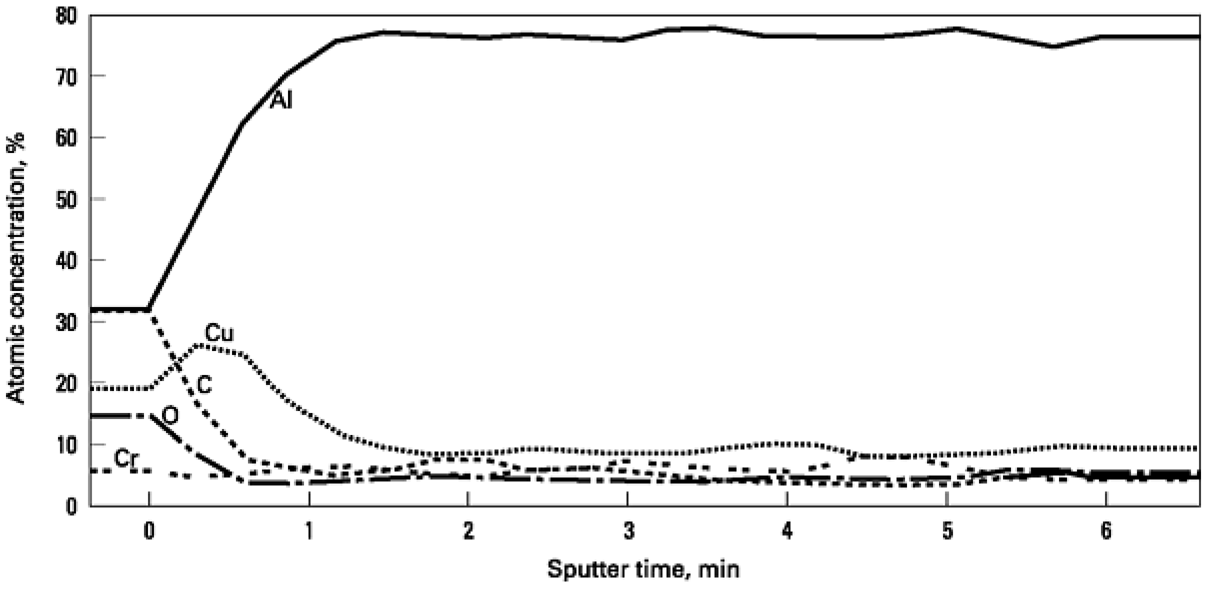

Fig. 2 Auger electron spectroscopy depth profile of polished aluminum alloy 2024-T3 solid solution matrix exposed for 5 min to the same solution as in Fig. 1 without fluoride ion present. Sputter rate approximately 300 Å/min (vs. SiO_2). Experiment details in Ref 7. Source: Ref 4

The fluoride-based treatments can be divided into two principal classes whose names reflect the predominant color of the conversion coating: "green" or amorphous phosphate treatment and "gold" or amorphous chromate treatment. The green treatments are obtained from solutions containing mixtures of chromic, phosphoric, and hydrofluoric acids; coatings ranging in weight from 5 to 10 mg/ft^2 (colorless) to 200 to 500 mg/ft^2 (deep green) can be produced. Monitoring of cation concentration in chromium phosphate baths is critical to maintaining bath life and coating performance since sludging can occur very easily due to precipitation of NaK_2AlF_6 and Na_3AlF_6. The gold treatments are obtained from solutions containing only chromic acid and a fluoride ion source; coating weights of 5 to 80 mg/ft^2 ranging in color from a light iridescence to a golden tan can easily be obtained.

In general, these treatments provide better unpainted corrosion resistance than the phosphate-based treatments and are much easier to control. The critical parameter for replenishment chemistry is control of the ratio of free-to-complexed fluoride ion. Many different fluoride ion sources have been used to affect this control. In addition to improving corrosion performance, these treatments serve as desirable substrates for promoting good paint adhesion and preventing underpaint corrosion. Corrosion performance can be enhanced by addition of accelerators such as the ferricyanide ion, which increases coating weight and also serves to complex copper in aluminum-copper alloys (see the section "Chromating Mechanism," below). Aluminum-copper alloys are some of the most difficult metals to protect against corrosion but are also some of the most often used aluminum-base alloys due to of their strength. Similar fluoride-ion-based treatments are used for magnesium and its alloys, with the Dow No. 7 treatment being the most often used where maximum corrosion protection is desired (Ref 8).

Chromate conversion coating treatments are used on five principal types of aluminum parts: aircraft and aerospace structural components, coil (for construction applications such as guttering and siding), extrusions (for window and door frames), heat exchanger parts, and containers (mainly beverage cans). A considerable amount of aluminum is also used in the automotive industry, but most receives a crystalline phosphate treatment because the aluminum is treated at the same time as the steel frame. As with chromating, fluoride ion is added to the phosphating bath to promote phosphate film growth on aluminum.

The major specifications that cover the performance of chromate conversion coatings are listed in Ref 2. The type of specifications used will depend on the end use of the fabricated part, which in turn will dictate the properties of the coating being sought. For example, in order to be used on military aircraft, aluminum alloy parts (such as those made from highly corrosive copper-containing aluminum alloy 2024-T3 or 7075-T6) must pass government specifications MIL-C-5541 and MIL-C-81706, which require that the unpainted chromated alloy must survive 336 h of salt fog testing (ASTM B 117). In addition, various tests are used to ascertain paint adhesion and underpaint corrosion under salt fog conditions. Aerospace companies use specifications similar to those used by the government. A boiling water test is often used in the container industry to detect the effectiveness of the chromate treatment in preventing discoloration caused by underpaint corrosion. Because the alloys used for manufacturing containers are not nearly as active, in a corrosive sense, as those used in aerospace, and because the specifications are not as severe, thin unaccelerated treatments are often used.

References cited in this section

2. F.W. Eppensteiner and M.R. Jenkins, Chromate Conversion Coatings, *Metal Finishing--Guidebook and Directory Issue '92,* Vol 90 (No. 1A), 1992, p 413-425
3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
4. P.L. Hagans, Naval Research Laboratory, and C.M. Haas, Henkel Corp., unpublished data
6. O. Bauer and O. Vogel, in *Mitt. a.d. Kgl. Materialsprufungsamts,* Vol 314, 1915, p 146; in *Internat. Z.f. Metallographie,* Vol 8, 1916, p 101; British Patent 226, 776, 1916
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.,* Vol 21, 1994, p 65
8. H.K. DeLong, in *Electroplating Engineering Handbook,* A. Kenneth, Ed., 3rd ed., Van Nostrand, 1971, p 465-474

Chromating Mechanism

Next to the alkali metals, the metals that chromate coatings must protect against corrosion (i.e., aluminum, magnesium, zinc, and cadmium) are the most active metals in the periodic table. In fact, from the large negative standard electrode reduction potentials for aluminum and magnesium dissolution, one would expect these metals to dissolve when immersed in water. This does not occur, of course; upon exposure to water or air, these metals immediately form a hydrated oxide film that is itself somewhat protective.

Chromate conversion treatments actually take advantage of this high surface activity. Through use of a strong oxidizing agent such as chromic acid, CrO_3, a redox reaction occurs at acidic pH (pH ≈ 2) where hexavalent chromium, either in the form of $CrO_{2}^{2-}{}_{7}$ or $HCrO_{4}^{-}$, is reduced to trivalent chromium while aluminum is oxidized to trivalent aluminum:

$$Al \rightarrow Al^{3+} + 3e^-$$
$$HCrO_4^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Probably due to of the presence of fluoride ion (see next paragraph), another reduction reaction besides that involving chromic acid can occur. This reaction involves the reduction of either water, hydronium ion, or dissolved oxygen to form hydroxyl ions at the metal surface. This surface-localized increase in pH results in the precipitation of an amorphous mixture of hydrated aluminum plus chromium oxides.

As described in the previous section, the presence of fluoride ion is important for building films of significant thickness; without its presence, film growth is extremely slow. Fluoride presumably serves two roles. First, it solubilizes the aluminum oxide initially present on the surface and allows the redox and deposition reactions to proceed. Second, it solubilizes a portion of the growing film, which allows penetration of the electrolyte to the surface and ion transport from the surface into the growing film. Fluoride has been characterized as a unique monodentate ligand that enhances the dissolution rate of aluminum oxide (Ref 9).

The high corrosion resistance offered by chromate films is attributed to the presence of both hexavalent and trivalent chromium in the coating. Analyses of coatings by wet chemical methods (Ref 10) and with surface-sensitive techniques (Ref 7, 11, 12) have shown that both Cr(VI) and Cr(III) are present in the films. The trivalent chromium is believed to be present as an insoluble hydrated oxide, whereas the hexavalent chromium imparts a "self-healing" character to the film during oxidative (corrosive) attack by species such as chloride ion. The hexavalent chromium is reduced during corrosion to form an insoluble trivalent chromium species that terminates the oxidative attack.

The enhanced corrosion resistance attributed to accelerated chromate conversion coatings has been ascribed to the increase in coating weight that is due to incorporation of the accelerator into the growing coating (Ref 3, 13, 14). Recent studies on ferricyanide-accelerated chromate coatings deposited on a high-copper-containing aluminum alloy indicate that ferricyanide is distributed throughout the film only on the high-copper-containing intermetallic phases such as $CuAl_2$ (Ref 7). Because these phases are known to accelerate greatly the corrosion rate of aluminum (Ref 15), the decrease in corrosion rate offered by the accelerator is believed to be due to the formation of copper ferricyanides on the intermetallic surface, which alters its activity with respect to the solid solution matrix. At adequate treatment times, corrosion resistance is also believed to be enhanced by the uniform surface composition of chromium and oxygen and the absence of aluminum and copper in the near-surface region.

References cited in this section

3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.,* Vol 21, 1994, p 65
9. W. Stumm, G. Furrer, E. Wieland, and B. Zinder, in *NATO ASI Series, Series C,* Vol 149, 1985, p 55
10. T. Drozda and E. Maleczki, in *J. Radioanal. Nucl. Chem. Lett.,* Vol 95, 1985, p 339
11. K. Asami, M. Oki, G.E. Thompson, G.C. Wood, and V. Ashworth, in *Electrochim. Acta,* Vol 32, 1987, p 337
12. M.W. Kendig, A.J. Davenport, and H.S. Isaacs, in *Corros. Sci.,* Vol 34, 1993, p 41
13. J.A. Treverton and N.C. Davies, in *Met. Technol. N.Y.,* Oct 1977, p 480
14. J.A. Treverton and N.C. Davies, in *Surf. Interface Anal.,* Vol 3, 1981, p 194
15. J.R. Scully and D.E. Peebles, Extended Abstract No. 35, *Proc. National Electrochemical Society Meeting,* Spring 1991, The Electrochemical Society, 1991

Effects of Substrate Microstructure

Because of specific physical property requirements, metal fabricators rely on a "mixed substrate," such as an alloy, rather than a pure metal. An alloy is typically of higher strength than a pure component because of the synergistic effect of the alloying element (e.g., a small amount of copper greatly strengthens aluminum for aerospace applications). The disadvantage of the alloy substrate from a conversion coating standpoint is twofold:

- The conversion coating must be tolerant of all the alloying elements. Formulating a conversion coating that can simultaneously treat all the elements present in an alloy can be difficult, depending on the elements' relative reactivity.
- The alloying elements may impart an accelerated corrosion rate to the metal. For example, when exposed to identical sodium-chloride-containing solutions, high-purity (99.999%) aluminum corrodes very slowly, whereas copper-containing aluminum alloys (e.g., the 2000-series alloys) corrode extremely rapidly (Ref 4). (On the other hand, alloying elements such as magnesium and zinc have very little effect on the corrosion rate of aluminum.) Aluminum used for alloying is typically of 99+% purity, and this aluminum will corrode at a faster rate than higher-purity material due to the presence of impurities, such as iron, that form intermetallic phases (e.g., $FeAl_3$). A few parts per million of iron, copper, or nickel in magnesium and magnesium alloys can also greatly accelerate the corrosion rate (Ref 16).

One of the principal difficulties in attempting to form a uniform conversion coating on an alloy surface is that alloys are seldom of homogeneous composition (i.e., they are not perfectly solid solutions). With the base metal and with themselves, the alloying elements often form second-phase particulates or "intermetallics" within the solid solution matrix (Ref 17). The intermetallics develop during the alloying process (as is found with precipitation hardening of a supersaturated alloy solution) and render the surface inhomogeneous. These intermetallics can form galvanic couples between themselves and the alloy solid solution matrix, and depending on their relative activity with respect to the matrix, they can either cause acceleration of the matrix or their own dissolution rate.

For example, the $CuAl_2$ that is found in aluminum-copper alloys is typically less active than (i.e., lies cathodic to) the solid solution matrix, which enhances the solid solution dissolution rate. In addition to enhancing the corrosion rate, this can have a profound effect on the uniformity achieved with a particular conversion coating process. As has been noted in a previous study (Ref 7), the activity difference between $CuAl_2$ intermetallics and the solid solution results in the application of a nonuniform (in thickness) conversion coating. A much thicker layer is found on the solid solution matrix because of its enhanced activity. The thinnest layers are found on the $(Fe,Mn)_3SiAl_{12}$ intermetallics, which appear to be less active than the $CuAl_2$ phases.

Alloy temper can also affect microstructure, which in turn can influence coating performance. For example, one study found that chromate treatments that were effective in protecting aluminum alloy 7075-T6 were not effective in treating the same alloy in the T73 (overaged) temper (Ref 18).

The pretreatment process, which usually includes cleaning and deoxidizing or desmutting steps, can have a strong effect on the surface microstructure and thus on the formation of a coherent conversion coating. In the case of the copper-aluminum alloys cited above, surface pretreatments involving either acid etching (Ref 4) or final polishing in a basic silicate electrolyte (Ref 7) produce a surface that contains a relatively uniform layer of copper, as detected by spatially resolved AES. The enriched copper found on the solid solution matrix results from either selective dissolution of the aluminum and/or redeposition of the copper that was dissolved from the intermetallics and/or solid solution. The chromate solution "sees" the homogeneous surface and readily forms a chromate conversion coating over the copper-rich interface, leaving the interface intact (Ref 7). As indicated by transmission electron microscopy studies of electropolished and acid-etched samples of high-purity aluminum that were subsequently chromated, the hydrated chromium oxide coating initially deposits on the metal ridges (the cathodic sites, produced by the pretreatment process) while the anodic sites, where the aluminum oxide was continuously attacked by fluoride ion, lie between the metal ridges (Ref 19). These studies illustrate the importance of the pretreatment steps in producing a homogeneous surface layer before application of the conversion coating.

References cited in this section

4. P.L. Hagans, Naval Research Laboratory, and C.M. Haas, Henkel Corp., unpublished data
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.*, Vol 21, 1994, p 65
16. J. Hillis, "The Effects of Heavy Metal Contaminants on Mg Corrosion Performance," Technical Paper 830523, presented at the Society of Automotive Engineers Annual Meeting, 1983

17. J.E. Hatch, *Aluminum: Properties and Physical Metallurgy,* ASM International, 1988, Chap 5
18. L.J. Bailin, P. Fitzpatrick, and M.J. Joyce, "Evaluation of Unpainted Alodine Chromate Conversion Coatings for Corrosion Resistance and Electrical Conductivity," Report F035575, Lockheed Missiles and Space Co., 1985
19. G.M. Brown, K. Shimizu, K. Kobayashi, G.E. Thompson, and G.C. Wood, in *Corros. Sci.,* Vol 33, 1992, p 1371

Environmental Concerns

The use and disposal of chromium and chromium compounds have received much regulatory attention because of the toxicity of chromium and indications that it is a cancer-causing agent. A summary of studies on the mutational effects of chromium compounds in bacteria, mammalian cells, and human cultures was published in 1986 (Ref 20). In 1993, a listing of hazardous chemicals stated that "Chromate salts are suspected human carcinogens producing tumors of the lungs, nasal cavity and paranasal sinus" (Ref 21). This list indicates that some type of mutational data was reported for all chromium compounds. Hexavalent chromium compounds appear to be the most severe; most are designated as "confirmed carcinogens." One trivalent chromium salt, Cr(III) acetate, is now also a confirmed carcinogen. Other Cr(III) salts are classified as "questionable human carcinogens."

To quote an earlier researcher in this field, "One of the biggest needs involving the future use of conversion coatings [for aluminum] in aerospace is to find non-toxic substitutes for those chemical processing solutions which are now labeled as pollutants" (Ref 3). Only aerospace was mentioned, because restrictions were expected to be first observed with aluminum fabricators due to the role played by the federal government in setting standards for aircraft manufacture. In the years that have elapsed since this statement was made, very few chromium-base treatments have been replaced by environmentally safer technology, and restrictions continue to be imposed on the levels of chromium in waste water effluent, solid waste, and the air to which workers are exposed.

In the United States, regulations regarding hazardous waste disposal and monitoring proliferated from the mid-1970s through the 1980s. Congress passed several laws empowering the Environmental Protection Agency (EPA) to set regulations for the control of hazardous waste (see Ref 22 for a review up to 1991). Much of this legislation espouses "cradle-to-grave " management of hazardous waste. Some of the principal legislation enacted by Congress includes the Resource Conservation and Recovery Act (RCRA) of 1976, the Safe Drinking Water Act (SDWA) of 1974, the Toxic Substances Control Act (TSCA) of 1976, the Hazardous and Solid Waste Act Amendments (HSWA) of 1984, and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) of 1980. Most of these laws have been amended (i.e., reauthorized) at least once since their initial passage. In a number of cases, considerable time passed after enactment of the law before the EPA was able to put the basic regulatory framework together (e.g., 4 years elapsed after passage of RCRA before the basic regulatory structure was in place). HSWA resulted from Congress's dissatisfaction with the EPA's progress with RCRA. All regulations are first published in the *Federal Register,* after which they become part of the Code of Federal Regulations under Title 40, which deals with protection of the environment.

As a result of these laws, chromium and its compounds became specific targets for regulatory control. In 1975 the National Institute for Occupational Safety and Health (NIOSH) recommended a standard for occupational exposure to Cr(VI) (Ref 23). The document described a number of studies that detailed medical problems observed by workers exposed to chromium. Included in this report was evidence indicating that certain Cr(VI) compounds were carcinogenic. The List of Suspect Carcinogens published by NIOSH now contains a number of chromium-containing compounds.

As a result of regulations enforcing RCRA, all facilities involved in electroplating were forced to comply by 1 July 1984 with the Electroplating Pretreatment Standards that appeared in the 28 January 1981 *Federal Register* (Ref 24, 25, 26, 27, 28). These standards were later broadened to include the anodizing and conversion coating industries; they were also made more stringent in the Metal Finishing Regulations that were printed in the 15 July 1983 *Federal Register* and enacted in 1986 (Ref 24, 25, 26, 29). Both sets of regulations were imposed by the EPA through local publicly owned treatment works. These regulations placed discharge limitations on various metals, such as chromium, and on other substances, such as those containing cyanide. Total chromium was limited to 2.77 mg/L/day, with a monthly average of 1.71 mg/L/day, and total cyanide was limited to 1.20 mg/L/day, with a monthly average of 0.65 mg/L/day.

In 1986, chromium and its compounds were put on the Community Right-to-Know List, which resulted from the Superfund Amendments and Reauthorization Act (SARA) of 1986 (Ref 21, 22). SARA established the Community Right-to-Know Program, which requires industry to provide information on the type of chemicals being used at their facility. This was only the beginning; many other regulations governing chromium compounds have been promulgated.

As of the time of this writing, the 1994 session of Congress is expected to pass a second reauthorization of the Clean Water Act (enacted in 1972 and first reauthorized in 1986) that will reflect the "polluter pays" philosophy (Ref 30). The intent of this reauthorization is to provide funding for public water pollution control projects through taxation on discharges. Five groups of taxable pollutants, with tax rates based on toxicity, have been compiled. Chromium falls in Group 4 and cyanide is found in Group 5; these two groups carry by far the highest tax rates. A few milligrams of these substances in the waste stream can warrant a large monetary fine over a year for a high-volume metal finisher.

Agencies such as the Department of Transportation are strengthening restrictions for shipment of treatment chemicals such as hydrofluoric acid, which is found in many chromate conversion coating formulations. Individual state EPAs may also enact their own restrictions, which could further restrict the use of harmful treatment chemicals. For example, on 24 July 1989, both Massachusetts and Oregon enacted sweeping toxic waste reduction bills (Ref 31). These bills require industries to prepare plans to reduce their use of toxic substances and to recover or reuse toxic materials from their effluents. The Massachusetts Toxics Use Reduction Act sets as a goal a 50% reduction of toxic waste in the state by 1997. Although no one can predict whether the use of chromium compounds and accelerators such as potassium ferricyanide will be completely banned, the trend in legislation is obviously making the search for viable alternatives to the current technology a top priority.

Furthermore, the Environmental Protection Agency (EPA) is scheduled to be elevated to the Cabinet level, with the head administrator assuming the post of Secretary of the EPA (Ref 30). This will attach an even greater significance to the role of the government in enacting and enforcing legislation directed at maintaining a safer environment.

References cited in this section

3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
20. G. Kazantzis and L.J. Lilly, in *Handbook on the Toxicology of Metals,* L. Friberg, G.F. Nordberg, and V.B. Vouk, Ed., Vol 1, Elsevier, 1986, Chap 14
21. R.J. Lewis, Sr., *Hazardous Chemicals Desk Reference,* 3rd ed., Van Nostrand, 1993; in *Sax's Dangerous Properties of Industrial Materials,* Vol 2, 8th ed., Van Nostrand, 1992
22. *Patty's Industrial Hygiene and Toxicology,* G.D. Clayton and F.E. Clayton, Ed., Vol 1, Part B, 4th ed., John Wiley & Sons, 1991, Chap 30 and 32
23. H.R. Garner, in *Plating and Surface Finishing,* Vol 1, 1981, p 36
24. D. Pierce, Jr. and R.S. Capaccio, in *Metal Finishing,* Vol 11, 1983, p 45
25. F. Altmayer, in *Plating and Surface Finishing,* No 1, 1984, p 44
26. R.F. Skach, in *Plating and Surface Finishing,* Vol 8, 1983, p 30
27. Current News, *Chemical Engineering,* 16 May 1983, p 22
28. P&SF Report, *Plating and Surface Finishing,* Vol 4, 1984, p 20
29. Staff of Mabbett, Capaccio & Associates, in *Metal Finishing,* Vol 11, 1986, p 13
30. R. Dhonau, in *Metal Finishing,* No. 11, 1993, p 35; No. 5, p 49
31. T.P. Driscoll, in *Metal Finishing,* No. 11, 1989, p 19

Alternative Technologies

Much research has focused on finding an alternative to chromium-base compounds for use in conversion coating formulations. In fact, the scientific and patent literature show that attempts have been made to incorporate most elements in the periodic chart (except for radioactive elements and the rare gases) into films. This article gives the rationale for various research paths, along with specific examples where appropriate. Three principal subjects are discussed: deposition of organic-based coatings from aqueous solution, deposition of multivalent metals from aqueous solution, and corrosion-resistant surface layers formed from the gas phase, with or without the use of high-energy light or particle beams (e.g., laser and ion beams).

Organic-Based Coatings. Given that a large number of water-soluble organic corrosion inhibitors are known to exist (Ref 32, 33), conversion coatings based on organic molecules are logical alternatives to chromium. For example, molecules containing the azole functional group (i.e., those having at least two ring nitrogens in a five-membered ring, such as benzotriazole) are known to be effective corrosion inhibitors for copper (Ref 34) and zinc (Ref 35) and are used commercially in cooling water applications to protect copper piping.

The difficulty in making organic-based conversion coatings of sufficient thickness is that organic species are normally poor oxidizing agents, such as chromic acid. This prevents film thickening because of aluminum oxidation and formation of insoluble oxide and hydroxide species. Typical inhibitor-formed films have thicknesses of only 100 Å or less, making their use in severely corrosive environments impractical. In addition, the time required to form such films can be hours or more (Ref 35) unless it is possible to accelerate their deposition through use of surface activators such as fluoride ion. Aqueous solubility can also be a limitation for some molecules.

Even though these films may be thin, they have application in areas such as the treatment of architectural aluminum (since this material is not usually continuously exposed to corrosive environments). In addition, organic-based conversion coatings have the potential of being excellent undercoats for organic (paint) finishes, for adhesion can be expected to be strong between similar types of molecules. Both sets of molecules contain various active functional groups that can interact (e.g., through hydrogen bonding or possibly formation of cross-linked or intertwined structures). It is likely that organic-based treatments will find some application in replacing chromium-base systems, but great difficulties exist in attempting to produce treatments that can pass the rigors of 168 and 336 h exposure to salt spray, as required by MIL-C-5541 and MIL-C-81706 on active aluminum alloys such as 7075-T6 and 2024-T3.

Multivalent Metals. The most logical method for obtaining a chromium replacement is to choose another transition, or even a rare earth metal, that has at least two stable oxidation states, is a good oxidizing agent, and has high corrosion resistance. To this end, patents and patent applications exist for using most of these metals in some type of formulation to yield a conversion coating. Not all metals are good oxidizing agents, but the ability of certain metals to oxidize can be enhanced through complexation with the appropriate species.

The fluoride-based formulations used in chromate conversion coatings cannot be used with most metals because of the insolubility of many metal fluorides. Other surface activators need to be chosen, and peroxide, nitrate, and chloride are common substitutes for fluoride (see examples below). The initial choices would be molybdenum-based and tungsten-based reagents, because these elements lie under chromium in the same group of the periodic table and both metals are well known for their corrosion resistance. These metals have been extensively researched, but formulations based on them have not been able to match, let alone surpass, the performance shown by chromate coatings (Ref 36). Molybdates and tungstates have found some application as accelerator replacements for the ferricyanides. Three multivalent metal-based systems that have recently received considerable attention in the open literature and/or have reached the trial stage in various aluminum industries are described below.

Rare Earth Metals. Treatments based on Ce(III) and other rare earth metals were examined first in Australia (Ref 37, 38, 39) and later in the United States (Ref 40, 41, 42). Coatings in excess of 1000 Å in thickness and rich in cerium + oxygen species were formed on aluminum alloy 7075 after a 20-day exposure to a 100 ppm $CeCl_3$ solution at pH 5.8 (Ref 43). X-ray photoelectron spectroscopy (XPS) indicated that the film contained both Ce(IV) and Ce(III) species, which likely existed as CeO_2, $Ce(OH)_4$, and $Ce(OH)_3$ (Ref 43). X-ray absorption near edge structure (XANES) studies likewise indicated the presence of a mixed cerium valence film (Ref 44). Coating process time was decreased to 10 min by adding hydrogen peroxide, lowering pH, and increasing the solution temperature (Ref 45). Immersion of the film in NaCl solution converted all of the Ce(III) to Ce(IV) (Ref 43). Measured corrosion rates of treated 7075 indicated that a 50% reduction in corrosion rate from that of an untreated substrate can be obtained (Ref 45). No mention of its effect on pitting corrosion was made, but excellent paint adhesion (comparable to that on chromated surfaces) was observed.

A cathodic mechanism has been proposed to account for cerium deposition: pH is increased at the cathodic sites, because of either oxygen reduction or hydrogen evolution, to form excess hydroxyl ions (Ref 37). The hydroxyl ions can attack the metal surface and react with metal ions in solution. The mixed metal oxide/hydroxide then precipitates onto the surface to form the corrosion-resistant film.

The development of "stainless aluminum" has also been claimed for cerium-treated pure aluminum and aluminum alloy 6061-T6 (less satisfactory behavior was obtained for aluminum alloy 2024-T3) (Ref 46). The treatment involves a 2 h exposure to three separate solutions: boiling 10 mM $Ce(NO_3)_3$, boiling 5 mM $CeCl_3$, and anodic polarization in the passive region in deaerated 0.1 M Na_2MoO_4. Excellent corrosion resistance was found upon immersion of treated samples in 0.5 N NaCl. Scratched surfaces also showed excellent resistance. No mention of salt spray testing of the cerium-based treatments was made, however.

Ce(III) molybdate has shown some promise as a corrosion inhibitor in an epoxy/polyamide primer but still does not match the performance of strontium chromate pigmented primers (Ref 47).

Manganese-based treatments for aluminum and aluminum alloys have recently been patented (Ref 48, 49, 50). One of the treatment steps involves exposure of the aluminum alloy surface to permanganate ion, which contains manganese in the +7 oxidation state. Like chromate, the permanganate ion is an excellent oxidizing agent, suggesting that the mechanism of film formation is similar to that of chromate. Although no information on film thickness or composition is given in the patents, one would expect that the manganese found in the film is in some reduced oxidation state (probably either +4 or, more likely, +2). This is a multistep treatment in which many of the steps require elevated temperatures. The last step, which involves a "seal" with alkali metal silicate, is probably necessary to block the pores created in the film during deposition. Good corrosion resistance, as evidenced from salt spray exposure, has been observed for high-copper-containing aluminum alloys.

Trivalent Cobalt. The final system is based on the use of basic solutions containing complexes of trivalent cobalt, for example, $Co(NH_4)_6^{3+}$ (Ref 51). $CoCl_2$ has shown some promise as an inhibitor for aluminum alloy corrosion (Ref 52). It is likely that Co(II) compounds have been examined in the presence of fluoride, for CoF_2 does possess appreciable solubility in water. This new system deposits a corrosion-resistant cobalt-containing film on aluminum alloys. Preliminary examination of this coating with electrochemical impedance spectroscopy (EIS) indicates that the coating has corrosion-resistant properties similar to those of a chromate treatment on aluminum alloy 2024-T3 (Ref 53). Good corrosion and paint adhesion properties are also claimed (Ref 51).

Gas Phase. Although gas-phase/high-vacuum techniques will probably not replace chromating of large parts or continuous chromating of high volumes (e.g., aluminum alloy coil stock for beverage cans) in the near future, these processes should not be ignored, for they offer the possibility of forming entirely new corrosion-resistant films. Experiments have already been undertaken in Japan to produce large surface areas of galvanized steel sheet through gas phase deposition of zinc (Ref 54). A partial selection of these techniques as they apply to the formation of corrosion-resistant films on aluminum and magnesium is briefly reviewed below.

Sputter deposition and ion implantation are nonequilibrium alloying techniques that allow solid solution alloys to be formed, which are unattainable by conventional alloying techniques. Corrosion-resistant aluminum-molybdenum and aluminum-chromium alloys have been formed by cosputter deposition of aluminum with each of the two metals (for details see Ref 55 and 56). Ion implantation of silicon, chromium, zirconium, niobium, and molybdenum into pure aluminum have been found to enhance pitting resistance of the aluminum, whereas implantation of magnesium and zinc had no effect on pitting resistance or lowered pitting resistance, respectively (Ref 57, 58). Beneficial results have been observed for iron and boron implantation into magnesium and magnesium alloys (Ref 59, 60). Ion implantation can easily form layers up to several thousand angstroms thick, depending on the mass of the species being implanted and the ion beam energy. Even thicker layers can be produced by ion beam mixing, which combines ion implantation with a vapor deposition process such as evaporation or sputtering.

Corrosion-resistant oxide mixtures can be formed on aluminum and magnesium by laser irradiation of a surface that contains a thin vapor-deposited metallic film such as chromium or molybdenum (Ref 61, 62, 63, 64). Laser irradiation is performed in an air or oxygen atmosphere to enhance the formation of oxides. The rapid heating and cooling rates provided by a laser can produce an amorphous, metastable surface composition that enhances the corrosion resistance of the substrate. Laser-irradiated chromium and molybdenum films on pure aluminum have been found to be very resistant to pitting by chloride ion (Ref 64).

Metal organic chemical vapor deposition (MOCVD) can also be used to deposit corrosion-resistant oxides onto low-melting metal substrates. MOCVD involves the deposition of thin oxide films by thermal decomposition of organometallic compounds. Metal alkoxides are the most commonly used precursors and have been used to deposit metal oxides such as SiO_2, TiO_2, Cr_2O_3, and Al_2O_3 (Ref 65, 66, 67, 68). The metal alkoxides generally have high vapor pressure and readily decompose at low temperatures (as low as 150 °C, or 300 °F). For example, Al_2O_3 films have been obtained by decomposition of the aluminum alkoxides: tri-tert-butoxide, tri-sec-butoxide, tri-n-butoxide, tri-isopropoxide, and acetyl-acetonate (Ref 69). Interestingly, the introduction of water vapor to aluminum acetyl-acetonate produces an extremely ligand-free, pure Al_2O_3 with a smooth surface morphology (Ref 70).

Additional information on alternatives to chromium is available in the article "Chromium Elimination" in this Volume.

References cited in this section

32. C.C. Nathan, Ed., *Corrosion Inhibitors,* National Association of Corrosion Engineers, 1973
33. S.N. Raicheva, B.V. Aleksiev, and E.I. Sokolova, in *Corros. Sci.,* Vol 34, 1993, p 343
34. M.M. Musiani, G. Mengoli, M. Fleischmann, and R.B. Lowry, in *J. Electroanal. Chem.,* Vol 217, 1987, p 187
35. W. Wippermann, J.W. Schultze, R. Kessel, and J. Penninger, in *Corros. Sci.,* Vol 32, 1991, p 205
36. B.R.W. Hinton, in *Metal Finishing,* No. 9, 1991, p 55
37. B.R.W. Hinton, D.R. Arnott, and N.E. Ryan, in *Metals Forum,* Vol 7, 1984, p 211
38. B.R.W. Hinton, D.R. Arnott, and N.E. Ryan, in *Materials Forum,* Vol 9, 1986, p 162
39. B.R.W. Hinton and D.R. Arnott, in *Microstructural Sci.,* Vol 17, 1989, p 311
40. F. Mansfeld, S. Lin, S. Kim, and H. Shih, in *Corrosion (NACE),* Vol 45, 1989, p 615
41. F. Mansfeld, S. Lin, S. Kim, and H. Shih, in *Electrochim. Acta,* Vol 34, 1989, p 1123
42. F. Mansfeld, S. Lin, S. Kim, and H. Shih, in *Mater. Sci. Forum,* Vol 44/45, 1989, p 83
43. D.R. Arnott, N.E. Ryan, B.R.W. Hinton, B.A. Sexton, and A.E. Hughes, in *Appl. Surf. Sci.,* Vol 22/23, 1985, p 236
44. A.J. Davenport, H.S. Isaacs, and M.W. Kendig, in *Corros. Sci.,* Vol 32, 1991, p 653
45. L. Wilson and B.R.W. Hinton, International Patent Application PCT/AU/88/00060, 3 March 1988
46. F. Mansfeld, V. Wang, and H. Shih, in *J. Electrochem. Soc.,* Vol 138, 1991, p L74
47. K.R. Baldwin, M.C. Gibson, P.L. Lane, and C.J.E. Smith, The Development of Alternatives to Chromate Inhibitors for the Protection of Aerospace Aluminum Alloys, *Proceedings of the Seventh European Symposium on Corrosion Inhibitors,* Supplement 9, 1990, p 771-785
48. J.W. Bibber, U.S. Patent 4,878,963, 1989
49. J.W. Bibber, U.S. Patent 4,755,224, 1988
50. J.W. Bibber, European Patent Application 89107533.5, 3 Jan 1990
51. M.P. Schriever, European Patent Application 91103498.1, 27 Nov 1991
52. D.R. Arnott, B.R.W. Hinton, and N.E. Ryan, in *Corrosion (NACE),* Vol 45, 1989, p 12
53. C.J. Johnson and K.Y. Blohowiak, Extended Abstract 180, *Proc. National Meeting of the Electrochemical Soc.,* Fall 1991, The Electrochemical Society, 1991
54. K. Shimogoori, H. Sato, M. Toyama, H. Nishimoto, T. Ikeda, and J. Kawafuku, Japanese Patents 01 42,571 (89 42,571) and 42,572 (89 42,572), 14 Feb 1989
55. W.C. Moshier, G.D. Davis, and G.O. Cote, in *J. Electrochem. Soc.,* Vol 136, 1989, p 356
56. G.D. Davis, B.A. Shaw, B.J. Rees, A. Iyengar, and E.L. Principe, Electrochemical Behavior and Surface Chemistry of Nonequilibrium Aluminum Alloys: Passivity Mechanism and Fabrication Methods, Final Report for ONR Contract N00014-C-93-0007, 17 Jan 1994
57. P.M. Natishan, G.T. Peace, and P.F. Slebodnick, in *Metallography,* Vol 23, 1989, p 21
58. P.M. Natishan, E. McCafferty, and G.K. Hubler, in *J. Electrochem. Soc.,* Vol 135, 1988, p 321
59. S. Akavipat, C.E. Habermann, P.L. Hagans, and E.B. Hale, in *Proceedings of the Symposium on Fundamental Aspects of Corrosion Protection by Surface Modification,* E. McCafferty, C.R. Clayton, and J. Oudar, Ed., The Electrochemical Society, 1984, p 52-61
60. S. Akavipat, E.B. Hale, C.E. Habermann, and P.L. Hagans, *Mater. Sci. Eng.,* Vol 69, 1985, p 311
61. P.L. Hagans, *Proceedings of the 41st World Magnesium Conference* (Dayton, OH), International Magnesium Association, 1984, p 30-38
62. P.L. Hagans and R.L. Yates, U.S. Patent 4,613,386, 1986

63. P.L. Hagans and R.L. Yates, U.S. Patent 4,767,678, 1988
64. P.L. Hagans and R.L. Yates, in *Proceedings of the Symposium on Environmental Degradation of Ion and Laser Beam Treated Surfaces,* K. Grabowski and G. Was, Ed., The Metallurgical Society, 1989, p 215-236
65. D.C. Bradley, R.C. Mehrotra, and D.P. Gauer, *Metal Alkoxides,* Academic Press, 1978
66. D.C. Bradley, in *Chem. Rev.,* Vol 89, 1989, p 1317
67. P. Kofstad, *High Temperature Corrosion,* Elsevier, 1988
68. K. Natesan, in *Corrosion (Houston),* Vol 41, 1985, p 646
69. V.A.C. Haanappel, H.D. van Corbach, T. Fransen, and P.J. Gellings, in *Thin Solid Films,* Vol 230, 1993, p 138
70. J.S. Kim, H.A. Marzouk, P.J. Reucroft, J.D. Robertson, and C.E. Hamrin, Jr., in *Thin Solid Films,* Vol 230, 1993, p 156

Rust-Preventive Compounds

Revised by Harry D. Ferrier, Jr., Quaker Chemical Corporation

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Introduction

RUST-PREVENTIVE COMPOUNDS are removable coatings that are used to protect the surfaces of iron, steel, coated or galvanized products, and other alloys. Some compounds also protect nonferrous metals, such as aluminum, brass, and copper. Coatings of these compounds should be considered temporary, because their function is to protect surfaces during storage, handling, shipping, and fabrication. An additional application may be necessary after parts are fabricated. In some instances, the coating may need to be removed before fabrication or assembly.

Rust-preventive compounds are a combination of basic materials, inhibitors, and specialty additives. They vary in physical characteristics, depending on the properties required and the amount of protection needed at corrosion sites. A corrosion cell is like a battery, which has a cathode (-), an anode (+), and an electrolyte (liquid in cells). By coating the corrosion sites (anodes and cathodes) on a surface, rust-preventive compounds prevent contact with electrolytes, such as oxygen and moisture-containing materials.

Constituent Materials

A rust-preventive compound can consist of only one or a combination of these four basic parts: a carrier, a film former, polar materials, and specialty additives. For example, the rust protection offered by film formers, such as grease, petrolatum, and low-melting-point waxes, can be enhanced by the addition of a polar material, which has an affinity for steel and attaches to steel surfaces like a magnet.

Carriers, which can be oil, water, or solvent, facilitate the application and handling of the required amount of protective film.

Oil is the most widely used material. Because it provides little protection itself, it is usually used with both polar and specialty additives to form a temporary rust-preventing film. Oil can function as both a carrier and a film former.

As a carrier, it is widely used in the steel, aluminum, and brass industries, and is used to some extent in the pipe and tube industry. Fogging oils are used on fabricated parts for the metal-working industries (for example, appliance, automotive, and metal furniture industries), where temporary storage is needed before assembly. These parts can be readily cleaned prior to the painting process.

Water is used as a carrier when short-term indoor protection is needed. It can be used with polarity-type products and other specialty additives. Water also is used as the carrier for certain drawing compounds, but the use of water-based products is predicated on the amount of time the parts need to be stored. A fogging oil over the water-based film is sometimes required if there is a need to exceed the recommended storage time period.

Solvent, which is used with both barrier and polar additives, is designed to evaporate and leave a continuous film that affords either barrier or polar protection, or a combination of both. This type of carrier is used to coat the edges and exposed outer wraps of coiled or stacked sheet metals. When its solids content is very low, a solvent leaves behind a barely perceptible film, and has therefore become known as vanishing oil. It provides effective but temporary rust prevention on hot-dip galvanized products and other alloys used in the construction industry.

Film formers include grease, petrolatum, low-melting-point waxes, and thixotropic materials.

Grease and petrolatum are considered to be barrier films, because their consistency effectively bars electrolytes from contacting the surfaces to which they are applied. These films are usually quite viscous and are essentially self-healing in that they reflow over an area that has been disturbed during shipping and handling. Although they can be applied by brush or wiped on at room temperature, they are usually applied at elevated temperatures, in either a dip tank operation or by spray, and then allowed to set until they return to room temperature. The warm dip or spray application makes it easier to control the amount of film being applied.

Waxes also provide a barrier film that can be applied in a solvent cutback, which allows control of the coating weight, based on the amount of solids present, and facilitates application. After the solvent evaporates, a barrier film of lesser quantity remains, but good corrosion protection is still provided. A wax film is not as self-healing as one of petrolatum because it is slightly harder after the solvent evaporates.

Thixotropic materials are thick and heavy, like the petrolatum-based materials, even though they are primarily dispersed in a solvent carrier. They are used with other forms of barrier protection. When agitated under shear conditions, thixotropic materials become thin, but under static conditions, they regain their original high viscosity. After the solvent evaporates, it leaves a continuous barrier against rust.

Polar additives are used as temporary rust-preventive compounds. The addition of polar material to barrier films, waxes, or thixotropic materials will increase their corrosion protection. The unique properties of polar materials include a slight electrochemical charge and a corresponding attraction to metal surfaces. As these materials attach themselves to metal, they lift water from the surface and allow it to evaporate. Even when these additives are diluted in oil, they are usually readily removable using solvent, milk alkaline cleaners, and emulsifiers.

Water-dispersed or water-soluble oil compounds containing polar additives are typically used for short-term indoor protection of the in-process type, where subsequent operations do not exceed the stipulated protection time. The polar emulsifiers that are usually in these compounds stay with the protective film, making it readily removable. Although the length of protection afforded by these compounds is considered moderate, they are widely used because they are easy to apply and to remove, and they are economical.

Specialty additives are used to enhance both corrosion protection and the adaptability of products to subsequent operations. They also can provide short-term inhibition to in-process materials. They help reduce stain on the metal surface, and they can retard the shellacking, or oxidizing, of the rust-preventive film.

Certain additives will adhere to and passivate metal surfaces, providing short-term protection. Other additives act as oxygen scavengers, preventing oxygen from reacting with a metal surface and causing corrosion. Wetting-agent additives help spread a film and act as emulsifiers, aiding in film removal. They also serve a water-displacement function. Lubricants such as esters, soaps, and extreme-pressure additives (which are effective under high pressures and temperatures) are often used.

There also are additives that facilitate fingerprint neutralization and removal. They neutralize acids, salts, and other residues that may be introduced during handling. Lubricants such as esters, soaps, and extreme-pressure additives (which are effective under high pressures and temperatures) are oftem used. In some instances, rust-preventive compounds are removed after they have performed the intended operation and prior to reapplication of a longer-term rust-preventive compound.

Types of Rust-Preventive Compounds

Many rust-preventive compounds are designed for dual purposes. For example, in the metal-forming operations of automotive, appliance, metal furniture, and bearing industries, products are used not only as rust preventives, but as lubricants. In the steel industry, a rust-preventive compound is put on the surface of steel that has been pickled after hot rolling. This compound, which is usually compatible with the cold-rolling oil, sometimes enhances lubrication of the rolling oil. It is referred to as a pickle oil.

In situations where steel is rolled prior to shipping, temper-mill lubricants are used. These lubricants must be compatible with the slushing oils that are designed to protect surfaces during shipping and handling. The use of polar additives in these slushing oils displaces the water diluent of the temper-mill lubricants.

Prelubes, or mill-applied lubricants, have more than dual functions. They function in tandem to other operations, offering corrosion protection, water-displacing properties that aid in removing water from the previous temper-mill operation, and lubrication that is sufficient for the parts fabrication process.

Generally, rust-preventive compounds are available as either dry films or water-based films. Products in both categories are described below.

Dry films can be categorized as those that will be removed from the metal and those that will not. The two types of products that are commonly used are hot-melt dry films and those that are diluted in either water or solvent. These products differ from the usual barrier type of protection in that they are dry to the touch and essentially stay in place. If they are disturbed in the course of handling, they cannot reflow and self-heal.

Hot-melt dry films, which are applied at elevated temperatures, are widely used as lubricants. They must be cooled prior to coiling or stacking to avoid nonadherence to the surface they must contact. Specialty additives are used in some of these films to facilitate removal when it is desired, as in the case of a prelube used in metal forming, which must be removed prior to any painting operation.

Solvent-cutback dry films, as well as hot melts, are used to control the amount of material being used. This solvent dilution allows the incorporation of specialty additives, such as those used for drying purposes or cosolvents used for fingerprint neutralization.

Hard, thin dry films are formed by the evaporation of the solvent, which leaves a product that is similar to a shellac or varnish. This product offers good protection, but is difficult to remove. Once set, the film resists abrasion during handling and cannot be removed by solvent wipes. This type of product is used in the pipe industry as a final protective film in situations that do not require its removal prior to the end use. Certain films are used as undercoats or primers in selected painting operations.

Water-based dry films use specialty additives to aid in drying, curing, or removability. Polar additives, small amounts of wax and resin (mostly acrylic), and other reactive-type additives are also used in these films. Some of these films are designed to be used without first being removed, whereas others do require removal. The films that provide the shellac-type finish are used when removal is not necessary.

Other water-based dry films are specifically designed as rust preventives and lubricants. They must be readily removable in alkaline cleaners prior to prepaint and painting operations. They also can be used in metal-forming operations, which necessitates film removal prior to painting.

Tables 1 and 2 list the characteristics, applications, and properties of rust-preventive compounds covered by military specifications. These tables indicate which of these compounds can also function as lubricants or drawing and forming compounds. For example, the MIL-L-6085 product acts as a lubricant for instruments and provides corrosion protection, whereas the MIL-H-6083 product is a hydraulic fluid that also must protect against corrosion.

Table 1 Characteristics and applications of rust-preventive materials covered by military specifications

Specification number	Specification title	Description	Intended use
MIL-C-450 (Types I, II, and III)	Coating compound, bituminous, solvent type, black	Black asphalt, dry coating; solvent cutback	Protect battery racks; coat interior of projectiles

Specification number	**Specification title**	**Description**	**Intended use**
MIL-C-4339	Corrosion-preventive soluble oil, for water-injection systems	Mineral oil with emulsifying agents and inhibitors	Protection against corrosion by water and alcohol
MIL-C-5545	Compound, corrosion preventive, aircraft engine heavy oil type	Thixotropic preservative oil; leaves soft, greasy film that becomes fluid when engine is started	Corrosion protection of internal parts and surfaces of engines and equipment
MIL-C-6529	Corrosion preventive, aircraft engine	Concentrate intended for 1-to-3 dilution with Navy symbol oil	Preservation of turbojet and reciprocating engines
MIL-C-8188	Corrosion-preventive oil, gas turbine engine, aircraft synthetic base	Synthetic oil plus corrosion inhibitors	Preservation of turbojet and turboprop engines
MIL-C-10382	Corrosion preventive, petrolatum, spraying application for food-handling machinery and equipment	Thin film, easily removable when dry; solvent cutback	Corrosion protection of food-handling equipment
MIL-C-11796			
Classes 1 and 1 A(a)	Corrosion-preventive compound, petrolatum, hot application	Thick, nondrying, dark, firm, grease-like film; leaves oil slick on salt water(a)	Unshielded outdoor storage of gun tubes; long-term protection of highly finished parts of simple design
Class 2	Corrosion-preventive compound, petrolatum, hot application	Thick, dark, medium-firm, greasy film	Unshielded outdoor storage in moderate climates, at below flow point of compound (64 °C or 145 °F); general packaging of automotive parts
Class 3	Corrosion-preventive compound, petrolatum, hot application	Fairly thin, soft, greaselike material	Protection of highly finished, cleanable parts of complex design; preservation of antifriction bearings
MIL-C-15074	Corrosion preventive, fingerprint remover	A mixture of organic solvents, petroleum solvents, and inhibitors	Removal of fresh fingerprint residues; temporary corrosion prevention
MIL-C-16173			
Grades 1 and 1A(b)	Corrosion-preventive compound, solvent cutback, cold application	Hard, dark film about 50 to 100 μm (2 to 4 mils) thick; solvent cutback; dries to touch in 4 h(b)	On metals under outdoor conditions; general-purpose preservation, indoor or outdoor, with or without cover; domestic or overseas shipment where a dry-to-touch film is required; not for intricate assemblies

Specification number	**Specification title**	**Description**	**Intended use**
Grade 2	Corrosion-preventive compound, solvent cutback, cold application	Amber-colored soft film about 25 µm (1 mil) thick; solvent cutback; drying time, 4 h; 200 µm (8 mils) maximum thickness	Extended undercover protection of interior or exterior surfaces of machinery, instruments, bearings, or materials with or without overwrap
Grade 3	Corrosion-preventive compound, solvent cutback, cold application	Nondrying film about 8 to 20 µm (0.3 to 0.8 mil) thick; solvent cutback	Where water or saline solution must be displaced; protection of materials under cover for limited periods; protection of critical bare or phosphated steel surfaces for extended periods when overwrap is used
Grade 4	Corrosion-preventive compound, solvent cutback, cold application	Transparent, nontacky film; 25 µm (1 mil) maximum thickness	Shed or indoor storage where dry transparent coating is needed; permits stacking
MIL-C-22235	Corrosion-preventive oil, nonstaining	Lubricating oil with added inhibitors; pour point, -12 °C (10 °F)	Rust preventive for hot- and cold-rolled steel in storage, in stacks
MIL-C-40084	Corrosion-preventive compound, water emulsifiable, oil type	Mineral oil with corrosion inhibitors in an emulsion; soft film; fire resistant	Low-cost corrosion preventive, fire resistant, thin film
MIL-G-10924	Grease, automotive and artillery	Preservative grease	Lubricant for automotive and artillery equipment, at -54 to 51 °C (-65 to 125 °F)
MIL-G-18458	Grease, wire rope, exposed gear	Petroleum oil and soaps plus inhibitors	Lubrication and corrosion protection for running ropes and exposed gear
MIL-H-6083	Hydraulic fluid, petroleum base, preservative	Light petroleum hydraulic fluid with inhibitors	As a preservative oil in aircraft hydraulic systems and shock-absorber struts
VV-L-800	Lubricating oil, general purpose, preservative (water-displacing, low temperature)	Lubricating oil with added inhibitors; pour point, -57 °C (-70 °F) max	Lubrication and corrosion-protection of small arms; general application wherever a multipurpose, low-temperature oil is required
MIL-L-3150	Lubricating-oil preservative, medium	Lubricating oil with added inhibitors; similar to SAE 30; pour point, -7 °C (20 °F)	Corrosion protection of highly finished internal and external surfaces; not for internal-combustion engines
MIL-L-6085	Lubricating oil, instrument, aircraft, low volatility	Light, low-volatility, synthetic lubricant containing rust preventive; pour point, -57 °C (-70 °F)	Protection of bearings in instruments, electronic equipment, or wherever a low-evaporation oil is required for both high and low temperatures
MIL-L-11734	Lubricating oil, synthetic (for mechanical time fuses)	Synthetic oil with inhibitors	Lubricate and protect mechanical time fuses at normal and below-freezing temperatures

Specification number	**Specification title**	**Description**	**Intended use**
MIL-L-14107	Lubricating oil, for aircraft weapons	Synthetic lubricating oil with inhibitors; pour point, -59 °C (-75 °F)	Lubrication of aircraft automatic weapons; for use below -18 °C (0 °F)
MIL-L-17331	Lubricating oil, steam turbine (noncorrosive)	Petroleum oil plus inhibitors	Lubrication of main turbine gears, auxiliary turbines, air compressors, hydraulic equipment
MIL-L-19224 (Grades A, B, and C)	Lubricating oil, mineral, preservative; pour point -34 °C (-30 °F)	Lubricating oil in three grades with inhibitors	Lubricant and preservative where uninhibited oils do not afford sufficient protection
MIL-L-21006	Rust-retarding compound, flotation type, ballast tank protection	Petroleum-base fluid compound with inhibitors; pour point, -7 °C (20 °F)	Rust-retarder in tanks used for salt-water ballast
MIL-L-21260			
Grade 1	Lubricating oil, internal-combustion engine, preservative	Engine-lubricating oil (SAE 10W) with corrosion inhibitors, including hydrobromic acid neutralizers; pour point, -29 °C (-20 °F)	Lubricant in spark-ignition and compression-ignition reciprocating internal-combustion engines
Grade 2	Lubricating oil, internal-combustion engine, preservative	Same makeup as Grade 1, but SAE 30W and pour point of -18 °C (0 °F)	Same as Grade 1
Grade 3	Lubricating oil, internal-combustion engine, preservative	Same makeup as Grade 1, but SAE 50 and pour point of -9 °C (15 °F)	Same as Grade 1
MIL-L-46000	Lubricating oil, semifluid, automatic weapons	Synthetic gel-like oil plus inhibitors	Operation of M61, M39, and related types of automatic weapons
MIL-L-46002			
Grade 1	Lubricating oil, contact and volatile corrosion inhibited	Lubricating oil with added contact and volatile corrosion inhibitors, SAE 5	Preservation of enclosed systems
Grade 2	Lubricating oil, contact and volatile corrosion inhibited	Same as Grade 1, but SAE 30	Preservation of enclosed systems
MIL-P-3420	Packaging materials volatile corrosion inhibitor, treated, opaque	Barrier material, impregnated with volatile corrosion inhibitors	Protection of ferrous metal parts

Specification number	Specification title	Description	Intended use
MIL-W-3688	Wax emulsion (rest inhibiting)	Dry, hard, nontacky, flexible surface emulsion of wax in water	Dry lubricant and rust-inhibiting coating for general weatherproofing

(a) Class 1A is similar in all respects to Class 1, except that it will not leave an oil slick on salt water.

(b) Grade 1A is similar in all respects to Grade 1, except that drying time is 72 h.

Table 2 Properties of rust-preventive materials covered by military specifications

Specification number	Minimum melting point (MP) or flash point (FP), °C (°F)	Method(a)	Application temperature, °C (°F)	Coverage(b)		Method of removal	Viscosity(c)	Penetration
				m^2/L	ft^2/gal			
MIL-C-450 (Types I, II, and III)	. . .	B, S	Ambient	15	750	Petroleum solvent	I: 15-28 s(d) II: 120-190 s(d)	III: 150-250 at 25 °C (77 °F)
MIL-C-4339	. . .	D, S	Ambient	. . .	. . .	Petroleum solvent	100-400 SUS at 38 °C (100 °F)	. . .
MIL-C-5545	FP: 260 (500)	F(e)	96	10	500	Not required(f)	115-150 SUS at 99 °C (210 °F)	. . .
MIL-C-6529	FP: 205 (401)	B, D, S, or fill	Ambient	30	1500	Not required(f)	. . .	. . .
MIL-C-8188	FP: 180 (356)	B, D, S	Ambient	40	2000	Petroleum solvent	3.0 cSt at 99 °C (210 °F) 11.0 cSt at 38 °C (100 °F) 18,000 cSt at -54 °C (-65 °F)	. . . .
MIL-C-10382	FP: 38 (100) MP: 66 (151)	B, D, S	Ambient	20	1000	Petroleum solvent	. . .	. . .
MIL-C-11796								
Classes 1 and 1A(g)	MP: 68 (154) FP: 180 (356)	D, S	79-93(h) (174-199) 93-105(i) (199-221)	. . .	15/lb	Petroleum solvent	. . .	30-80 at 25 °C (77 °F)

Specification number	**Minimum melting point (MP) or flash point (FP), °C (°F)**	**Method(a)**	**Application temperature, °C (°F)**	**Coverage(b)**		**Method of removal**	**Viscosity(c)**	**Penetration**
				m^2/L	**ft^2/gal**			
Class 2	FP: 180 (356) MP: 66 (151)	D, S	71-88(h) (160-190) 85-90(i) (185-194)	. . .	15/lb	Petroleum solvent	. . .	90-150 at 25 °C (77 °F)
Class 3	FP: 180 (356) MP: 57 (135)	B, D, S	16-49(j) (61-120) 66-82(h) (151-180) 78-85(i) (172-185)	. . .	15/lb	Petroleum solvent	. . .	200-325 at 25 °C (77 °F)
MIL-C-15074	FP: 38 (100)	B, D	Ambient	. . .	. . .	Petroleum solvent	30 cSt at 38 °C (100 °F)	. . .
MIL-C-16173								
Grades 1 and 1A(k)	FP: 38 (100) MP: 66071 (151-160)	B, D, S	7-35 (45-95)	9	450	Petroleum solvent	. . .	25(l) at 25 °C (77 °F)
Grade 2	FP: 38 (100)	B, D, S	4-35 (39-95)	20	1000	Petroleum solvent	. . .	200 at 25 °C (77 °F)
Grade 3	FP: 38 (100)	B, D, S	4-32 (39-90)	20	1000	Petroleum solvent	. . .	. . .
Grade 4	FP: 38 (100)	B, D, S	4-32 (39-90)	20	1000	Petroleum solvent	. . .	. . .
MIL-C-22235	FP: 140 (284)	B, D, S	Ambient	30	1500	Petroleum solvent	100-140 SUS at 38 °C (100 °F)	. . .
MIL-C-40084	FP: 96 (205)	B, D, S	25-82 (77-180)	30	1500	Petroleum solvent	. . .	. . .
MIL-G-10924	160(m) (320)	Gun	Ambient	. . .	. . .	(f)(n)	. . .	265-295 at 25 °C (77 °F)
MIL-G-18458	66(m) (151)	Gun	Ambient	. . .	. . .	(f)(n)	. . .	200-300 at 25 °C (77 °F)

Specification number	Minimum melting point (MP) or flash point (FP), °C (°F)	Method[a]	Application temperature, °C (°F)	Coverage[b]		Method of removal	Viscosity[c]	Penetration
				m^2/L	ft^2/gal			
MIL-H-6083	FP: 93 (199)	Fill	16-49	. . .	. . .	Not required[f]	10 cSt at 54 °C (129 °F) 800 cSt at -40 °C (-40 °F)	. . .
VV-L-800	FP: 135 (275)	B, D, S	16-49	50	2500	Not required[f]	12 cSt at 38 °C (100 °F) 60,000 cSt at -54 °C (-65 °F)	. . .
MIL-L-3150	FP: 150 (302)	B, D, S	16-49	30	1500	Not required[f]	185-255 SUS at 54 °C (129 °F)	. . .
MIL-L-6085	FP: 185 (365)	D, S	Ambient	50	2500	Not required[f]	8 cSt at 54 °C (129 °F) 2,000 cSt at -40 °C (-40 °F) 12,000 cSt at -54 °C (-65 °F)	. . .
MIL-L-11734	. . .	B, D, S	Ambient	40	2000	Not required[f]	12.5 cSt at -38 °C (-36 °F) 15,000 cSt at -57 °C (-71 °F)	. . .
MIL-L-14107	FP: 160 (320)	B, D, S	Ambient	50	2500	Not required[f]	5.8 cSt at 38 °C (100 °F) 900 cSt at -59 °C (-74 °F)	. . .
MIL-L-17331	FP: 180 (356)	B, D, S	Ambient	. . .	. . .	Not required[f]	8.2 cSt at 99 °C (210 °F) 82-110 cSt at 38 °C (100 °F)	. . .
MIL-L-19224 (Grades A, B, and C)	(A)FP: 160 (320) (B)FP: 200 (392) (C)FP: 210 (410)	B, D	-30 to 74	30	1500	Not required[f]	Grade A: 90-120 SUS at 54 °C (129 °F); Grade B: 45-55 SUS at 99 °C (210 °F); Grade C: 60-70 SUS at 99 °C (210 °F)	. . .
MIL-L-21006	FP: 160 (320)	. . .	Ambient	24	1200	Not required[f]	. . .	. . .
Grade 1	PF: 180 (356)	F, S[o]	Ambient	30	1500	Not required[f]	44-50 SUS at 99 °C (210 °F) 12,000 SUS at -18 °C (-0.4 °F)	. . .
Grade 2	PF: 200 (392)	F, S[o]	Ambient	30	1500	Not required[f]	58-70 SUS at 99 °C (210 °F) 200,000 SUS at -18 °C (-	. . .

Specification number	Minimum melting point (MP) or flash point (FP), °C (°F)	Method(a)	Application temperature, °C (°F)	Coverage(b)		Method of removal	Viscosity(c)	Penetration
				m^2/L	ft^2/gal			
							0.4 °F)	
Grade 3	PF: 205 (401)	F, S(o)	Ambient	30	1500	Not required(f)	85-110 SUS at 99 °C (210 °F)	. . .
MIL-L-46000	. . .	B, D	Ambient	15	750	Not required(f)	. . .	350-385 at 25 °C (77 °F)
MIL-L-46002								
Grade 1	FP: 115 (239)	B, D, S	Ambient	40	2000	Not required(f)	12 cSt at 38 °C (100 °F) 10,000 cSt at -40 °C (-40 °F)	. . .
Grade 2	FP: 120 (248)	B, D, S	Ambient	30	1500	Not required(f)	9.65-12.98 cSt at 99 °C (210 °F) 95-125 cSt at -38 °C (100 °F)	. . .
MIL-P-3420	. . .	. . .	Ambient	. . .	. . .	(p)	. . .	. . .
MIL-W-3688	74(m) (165)	D, S, or wipe	Room temperature	. . .	. . .	Petroleum solvent	. . .	. . .

(a) B, brush; D, dip; F, fog; S, spray.

(b) Average anticipated coverage; subject to wide variation.

(c) Viscosity conversions: 100 SUS (20.55 cSt); 115 SUS (23.85 cSt); 150 SUS (31.70 cSt); 400 SUS (86.2 cSt). According to ASTM D 217, penetration is recorded in tenths of a millimeter. Penetration values for greases are frequently reported without the units.

(d) No. 4 Ford cup reading.

(e) For cylinders. For crankcase, dilute 1-to-1 with grade 1100 Navy symbol oil, fill, run engine until hot, then drain.

(f) Removal, if desired, may be effected with petroleum solvent.

(g) Class 1A is similar in all respects to Class 1, except that it will not leave an oil slick on salt water.

(h) For dip application.

(i) For spray application.

(j) For brush application.

(k) Grade 1A is similar in all respects to Grade 1, except that drying time is 72 h.

(l) On solids; needle penetration.

(m) Dropping point, minimum.

(n) Flush with fresh grease.

(o) Into cylinders or crank case.

(p) Remove powderlike residues with methyl alcohol rinse.

In the metal-stamping and -forming industry, the properties that are usually specified include corrosion protection, ease of removability, compatibility with prepaint operations and paint systems, and lubrication when a mill-applied product is used (usually performed as an on-line forming test).

Methods of Application

Rust-preventive compounds are applied by:

- Spraying or fogging electrostatically
- Dipping
- Flowing or slushing
- Brushing or wiping

The type of rust preventive and the quantity, size, complexity, and surface finish of the articles to be coated will determine which method should be used. The equipment and methods of application are similar to those used in painting.

Petrolatum compounds can be applied either hot or cold. Generally, cold application is restricted to parts that are either too large and bulky for practical tank immersion or require only localized protection, such as the ways for a lathe bed. When these compounds are applied cold, their consistency requires the use of brushing or wiping. When brushing is used, the bristles of the brush should be stiff enough to permit brush-out of the material, but not so stiff as to leave deep brush marks in the preservative. With these materials, it is often advantageous to build up coatings to the desired final thickness by the successive application of thin layers.

When petrolatum rust-preventive compounds are applied hot, dipping is the most practical method. Parts that are too large to be dipped can be coated by brushing, wiping, or spraying. Small parts to be dipped are placed in baskets, whereas larger parts are individually dipped. Dipping can be manual, when the volume of parts is low; conveyors can be used when parts are produced in large quantities.

Most dipping tanks for petrolatum compounds are heated by steam coils, hot-water jackets, electrical immersion heaters, or plate coils using either hot water or steam. Although precise temperature control is not usually required, the compound in the dipping tank must not become overheated. Overheating can cause decomposition of the preservative, and the resulting products may act as corrosion agents. Some petrolatum products have been applied at elevated temperatures electrostatically, which can afford better control of the amount of coating being applied.

Oil compounds can be applied electrostatically or by dipping, spraying, flowing, brushing, or wiping. The thickness of the coating depends on the viscosity, fluid characteristics (whether the fluid is Newtonian or non-Newtonian), and surface tension of the oil compound. Oils of high viscosity usually are heated before being applied. Parts or assemblies coated by immersion in oil preservatives should be turned or agitated to permit all trapped air to escape. When the material is applied at room temperature, the parts will require immersion only long enough to ensure complete coverage.

For spray or electrostatic application, oil-based rust-preventive compounds usually do not require dilution and are applied as received. Moderate air pressure or an airless spray is used to avoid misting and overspraying of the material. A wetting spray is usually sufficient. It is more difficult to control coating weight and uniformity by spray application than by dipping or by electrostatic application in coil or sheet stock. To ensure an adequate coat, the material should be applied according to the specifications supplied by the end user. Oil-based compounds used on coil or sheet stock are applied by using the roll-coater spray and electrostatic methods, which allow some control of the coating weight. After a spray application, squeegee rolls are used. Changing the pressure on the squeegee can help control the amount of film on the surface.

Emulsion compounds are oil-in-water emulsions that contain from 8 to 12% solids. These compounds, which are available as concentrates, are diluted with water at ratios of 4 to 10 parts water to 1 part concentrate, as specified in MIL-C-40084.

These compounds, which are widely used for small parts, are applied by dipping or spraying. The effectiveness of the application can be increased by heating either the parts or the compound. For example, the unheated compound can be applied in the third stage of a power washer in which the parts retain residual heat produced during the first two stages. If dipping is used, then the compound can be heated to a gentle boil before immersion of the unheated parts.

Oil-in-water emulsions are fire resistant during application. However, after the water has been removed by drying, the residual film has flammability characteristics that are comparable to those of petroleum oils or waxes.

Solvent-cutback compounds are essentially waxes modified with high-melting-point polar additives, such as soaps. Compounds that use organic solvents as the diluent are applied at room temperature. Small parts usually are batch coated in wire baskets, which are immersed, withdrawn, and centrifuged to remove excess material. Commercial equipment is available for this method of application. The parts are then removed from the basket and are either spread out to dry or conveyed through an air-drying stage, which may be mildly heated.

Because some solvent-cutback compounds develop dry, hard films, parts may become bonded together by the film. Separating these parts often results in tears in the coating. Large parts can be spray or dip coated, but all solutions are not necessarily applied equally well by both methods. Parts that are too large for dipping can be coated by spraying or brushing.

When this type of product includes polar materials, it can be used on coil and sheet stock to protect edges and other exposed portions during shipping and handling. Spray, brush, or paint-roller-type applicators can be used. High-flash-point vanishing oils (solvent cutback) have also been applied electrostatically. However, extreme caution should be taken to ensure against arcing. The equipment manufacturer should be consulted prior to testing or use.

Water-displacing compounds are most effective when they are applied by dipping, although spraying also can be used. These materials actually remove films or droplets of water from metal surfaces by preferential wetting, that is, the attraction of the rust-preventive compound to the metal surface is greater than that of water and, thus, the preservative displaces the water. Complete immersion of the part makes the coverage more positive.

A suitable dip tank for automatic water removal from a water-displacing preservative system is shown in Fig. 1. Because the specific gravity of the preservative is less than that of water, the height of the column of water is somewhat less than the height of the column of preservative. Parts that are too large to coat by immersion and too impractical to spray can be coated by wiping. Wiping is also used when only certain areas of parts need to be coated. Coiled and sheet stock can be electrostatically coated.

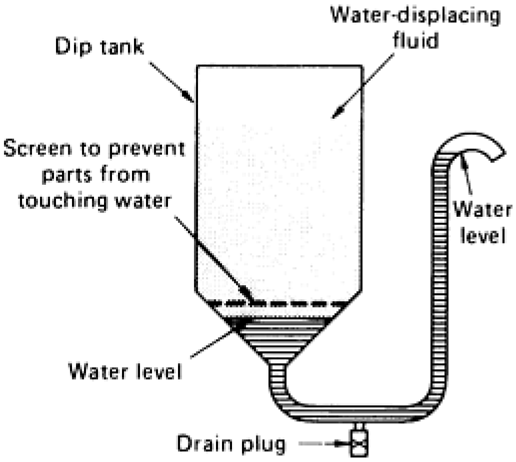


Fig. 1 Tank for dip application of water-displacing rust-preventive compounds

Fingerprint removers and neutralizers can be applied by spraying, dipping, or brushing, the latter of which is usually used only when a section of a part needs to be coated. These materials are applied at room temperature. Sufficient fluid should be present in the system to prevent gross contamination or preferential depletion of the active ingredients that dissolve or neutralize the corrosive materials.

Rust-Preventive Material Selection

The occurrence of rust on the surfaces of steel or other iron-base alloys is dependent on contact with moisture and oxygen. The extent of rusting is a function of the duration of this contact and of temperature. Temperature also affects the rate of rusting, which can be accelerated by the presence of chloride salts, oxides of sulfur, and other electrolytes that enter into or modify the chemical reactions involved.

The composition and metallurgical characteristics of the alloy also influence the extent and rate of rusting, and they frequently determine whether the rusting reaction affects the surface in a general and uniform way or by localized pitting. There are two important factors that determine the extent to which a surface must be protected from rusting. One is the degree of finish, that is, whether the surface is ground, rough machined, or as-forged. The other is the extent to which rust impairs function. The selection of rust-preventive compounds is primarily influenced by the:

- Environment, in terms of climatic conditions, geographic location, and type of storage facilities, as well as the anticipated amount of time a part must spend in storage
- Type of material to be protected and the need for removing the rust-preventive compound

These considerations are described below, whereas other selection parameters are described in the next section of this article.

Storage Environment and Duration. The severity of climatic, geographic, and storage environments varies considerably. Mild conditions are exemplified by a rural inland area with a daily temperature that ranges from -1 to 16 °C (30 to 60 °F) and a relative humidity that ranges from 25 to 70%. Severe conditions are exemplified by a southwestern seacoast or southeastern areas, where the temperature differential can exceed 33 °C (60 °F), and 100% relative humidity is reached once or twice each day. Moisture condensation results when these conditions cause the dew point to be reached. Therefore, the requirements for a successful rust-preventive compound appropriate for any specific surface stored for 6 months inside a completely enclosed building could range from a very light oil, in the rural area, to a heavy-film petrolatum, in the seacoast and southeast locations.

Because coiled stock is not fully exposed, it can be protected sufficiently for the short term by using a typical slushing oil that contains some barrier protection, along with the usual polar materials.

Outside storage in either location would require the use of a rust-preventive compound that has been designed to cope with the erosive effect of rainfall. In an industrial inland area, the corrosion-protection requirement must be extended to include resistance to the increased reactivity of the fumes present in an industrial atmosphere. For example, a very light oil might need to be replaced by a soft petrolatum. Careful determination of the environmental factors against which the rust-preventive compound must perform is of major importance in selecting the proper rust-preventive compound. Another important consideration is the duration of exposure to the environment.

The requirements of a rust-preventive compound can be affected significantly by the degree of auxiliary protection afforded by the type of enclosure used for storing coated articles. Maximum auxiliary protection is provided by storage in either a fully enclosed, humidity-controlled area in a permanent building or a container that is sealed against moisture and that holds desiccants to absorb any moisture originally present.

Types of Parts Requiring Protection. There are four general categories of parts or assemblies that require the application of rust-preventive compounds when they are being stored:

- Assembled machinery or equipment in standby storage
- Finished parts (in stock) or spare parts (for replacement)
- Tools, such as drills, taps, dies, and gages
- Mill products, such as sheet, strip, rod, and bar

Assembled machinery or equipment in standby storage requires two distinctly different types of protection. First, all exterior surfaces require protection from the atmospheric conditions to which they are exposed. The selected rust-preventive compound must be able to withstand normal handling conditions. Second, the interior surfaces of assembled machinery require the use of preservative oils that must act as temporary lubricants when the equipment is put into service. These oils must be completely compatible with the lubricating oils, hydraulic fluids, or greases that are to be used in service.

In an adequately heated, well-ventilated building, oil-film protection usually suffices for the external and internal surfaces of exposed machinery parts. In loosely constructed, inadequately heated buildings, where machinery may be subjected to extreme changes in humidity, petrolatum or solvent-cutback rust-preventive compounds are essential for all exposed surfaces. Interior surfaces must be protected with a good rust-preventive oil.

For outdoor storage or storage in open-sided or unheated sheds in a dry, clean atmosphere, petrolatum used as an outer coating and a rust-preventive oil used on interior surfaces should provide adequate protection. In marine atmospheres or environments where corrosive industrial fumes exist, hard-film corrosion preventives or heavy-duty petrolatum materials must be used on all exposed surfaces. Specially designed oil compounds are available for internal or physically shielded surfaces.

Machinery or equipment exposed to rough handling or mechanical abrasion that could damage or remove an oil or petrolatum film should be protected with a hard-film rust-preventive compound. This material should be of the type that can be removed when required.

One large manufacturer of machine tools, situated in an inland industrial location with a daily temperature differential of 11 °C (20 °F) and frequent occurrences of 100% humidity during spring and fall months, uses three basic types of rust-preventive products for in-plant preshipment protection of parts and assemblies. For in-process periods of 2 to 3 weeks, a very light fingerprint neutralizer suffices. For longer periods of in-plant storage, an oil-based compound with a viscosity of approximately 200 SUS (4.3×10^{-5} m^2/s, or 43 cST) at 38 °C (100 °F) is necessary. (SUS stands for *Saybolt Universal Seconds,* i.e., the time required for 60 cm^2 of a fluid to flow through the orifice of the Standard Saybolt Universal Viscometer at a given temperature under specified conditions.) When inventory needs to be stored for very long or indeterminate periods, or in covered storage outdoors, a solvent-cutback rust-preventive compound is used. For the shipment of assembled machine tools, products similar to those described in MIL-C-16173 (Tables 1 and 2) are used to protect exterior surfaces. Interior protection of lubricating systems and reservoirs is provided by preservative oils similar to grades 1 and 2 of MIL-L-21260 (Tables 1 and 2).

Finished machined parts and spare parts, such as gears, mill rolls, and mandrels, should be cleaned of coolants, machine oils, cutting oils, and other foreign matter before being coated with rust-preventive compounds. Highly sulfurized fatty or chlorinated cutting oils in prolonged contact with steel can cause staining. Covering these cutting oils and coolants with a rust-preventive compound does not prevent this corrosive action.

For short-term indoor protection, fingerprint-neutralizing compounds usually provide adequate protection for up to 2 weeks. Although test results for some products indicate protection for up to 6 weeks, the short-term recommendation should be followed. For long-term indoor storage, or for storage in corrosive atmospheres, fingerprint neutralizers are first applied to prevent corrosion or staining caused by body acids or salts that are deposited on the finished surfaces after finger contact. These neutralizers are then removed, and an appropriate long-term rust-preventive product is applied.

In an atmosphere that is not particularly corrosive, parts stored in a weatherproof building with no humidity control are protected with a light coating of an oil-based compound. In marine or industrial areas with corrosive atmospheres, appropriate petrolatum or solvent-cutback materials usually provide protection for 6 mo. Machined parts stored outdoors should be protected by a heavy coating of a petrolatum material.

Tools. Corrosion-protection measures may be necessary before drills, reamers, taps, cutter heads, tool holders, and other metal-cutting tools and accessories are placed in storage after use. Water-emulsion or soluble-oil cutting fluids should be completely removed before any tool is coated with a rust-preventive compound, in order to prevent moisture entrapment. One tool manufacturer suggests cleaning tools with 1,1,1,-trichloroethane before applying the protective film. Machine oils, used at the machine, may provide adequate protection for the short-term storage of tools and accessories. Surplus oil should be wiped off to minimize runoff in storage.

Although the oily, nondrying rust-preventive compounds will adequately protect tools stored in the normal crib, oil runoff or ruboff can be undesirable. Dry films circumvent this problem, and because the films are dry, normal shop dirt does not adhere to them. If the dry film is not thick, it may be unnecessary to remove it when the tools or accessories are again placed in service. If this protective material will not be removed, then it should be compatible with fluids used at the machines.

Tools such as drills, reamers, and milling cutters are sometimes protected from rust and abrasion after being coated with a strippable cellulose acetate compound. The coating is applied by dipping the tool in the compound at a temperature of approximately 120 °C (250 °F).

Hard film coatings are not recommended for use on adjustable chucks and other tool accessories, because the incomplete removal of a hard film could cause malfunction. Instead, thinner, oily films are usually recommended. If shop dirt is a problem, then a protective wrapping can be applied. In this case, it is necessary for the wrapping and the preservative to be compatible, so that accelerated corrosion of the metal is not initiated.

When a corrosive environment is not severe, molding, stamping, or forming dies may require only a light coating of rust-preventive oil, before being placed in storage. When the atmosphere is corrosive, these dies may require a petrolatum compound. It is often unnecessary to provide any additional rust-preventive coating once these dies have been used in production, because the oily film of the die lubricant that remains from the production run can provide sufficient protection. If residual die lubricants do not provide a complete film, then a thin oil is usually sprayed on the die. In extreme cases, a grease-like material is brushed on.

Dies for molding or extruding plastic parts, which are highly polished, are run in a dry condition. Consequently, a rust-preventive compound that is usually thin and oily is sprayed on the die or mold before storage. This material is then removed with a solvent before the die or mold is placed in production.

Mechanical gages require special consideration in the rust-preventive selection process. Although complete protection is required of a film, it must allow the gage to be used without the need to remove the film. Therefore, thin oil preservatives are applied in a light film. Periodic renewal of the film may be necessary.

During temporary storage, used gages often can be protected by being brushed with a soft petrolatum that can be removed easily by wiping. Specially treated papers for wrapping precision tools and gages for maximum protection are required during overseas shipment.

Mill products, as received from the mill, usually have light to medium oil coatings that protect against corrosion for short periods. It is often necessary to provide additional protection. For short-term outdoor storage, light oils usually provide adequate protection, although exposure to corrosive atmospheres may necessitate more protection. For an extended period of outdoor storage, heavy oils or petrolatums may be required.

The use of rust-preventive compounds on mill products must be considered in terms of the manufacturing operations that the products will undergo. For the protection of rod and bar stock, a rust-preventive compound must be compatible with the cutting fluids that will be used, so that there is no need to remove the compound. Sheet and strip that will go through a punch press can be coated with a compound that does not require removal and can also function as the lubricant to facilitate manufacturing. Other rust-preventive compounds, such as prelubes, are removed after the stamping process and prior to painting. Slushing oils applied to sheet and coiled stock utilize polar materials to retard corrosion. They are used primarily where they will eventually be removed, such as after drawing and forming operations. They also must be removed prior to plating operations.

Depending on either the severity of the expected storage conditions or the requirements of the user, finished tubing is usually protected by one of these products:

- Well-refined, neutral mineral oil (No. 1 or No. 2 color) with a viscosity of 100 SUS (2.05×10^{-5} m^2/s, or 20.55 cST) at 38 °C (100 °F), containing a suitable rust-preventive additive
- Rust-inhibited petrolatum of a soft, grease-like consistency, applied by dipping at 82 °C (180 °F). Its color should be amber to green; its melting point should range from 51 to 57 °C (125 to 135 °F); and its viscosity should be approximately 90 SUS (1.8×10^{-5} m^2/s, or 17.98 cST) at 100 °C (210 °F).
- Transparent, varnish-like rust-preventive compound in the form of a solvent-cutback hard-film product that is spray applied at room temperature. The coating should set in 25 min and be dry to the touch in 2 to 3 h.

Physical and Chemical Considerations. Some assemblies incorporate nonmetallic materials that can deteriorate upon contact with either hydrocarbon-based materials or preservatives containing acids and bases. Polymeric materials, for example, can swell, harden, crack, soften, or otherwise deteriorate and become unfit for service. Product storage and shipping requirements should be anticipated in the beginning stages of design, so that a proper preservative is selected to protect the metallic units of the assembly without attacking the nonmetallic components.

The physical form of a rust preventive, that is, whether it is an oil-based or petrolatum material or an aqueous emulsion, can either dictate or prevent its use for a specific application. For example, a petrolatum compound is unsuitable for the corrosion protection of internal components of high-speed business machines, because its heavy makeup could cause excessive sticking and eventual malfunction of the machine, even when the components are well protected from corrosion. The use of a solvent-cutback material also is undesirable, because minute traces of the solvent might vaporize after assembly of the components, and the resulting hard film could interfere with proper machine function. Solvent-diluted rust-preventive compounds should not be used in a confined system unless ventilation is provided to disperse the combustible solvent vapors and prevent internal degreasing. For this specific application, a rust-preventive compound based on a mineral oil of suitable viscosity should be selected.

The physical characteristics of the film left by a rust-preventive compound should be considered if the surface to which it is applied must receive additional coatings. The use of an oily material of any type is less desirable than the use of a material that forms a hard, dry film, if the surface is to be painted without an intermediate cleaning operation. Extremely viscous or semisolid rust-preventive compounds should not be used on intricate assemblies that may present a cleaning problem or on highly polished surfaces. For example, the polished surfaces of plastic molding dies must remain mirror bright. Rust-preventive compounds applied for storage or shipping purposes must be readily removed without any surface abrasion before the die can be used.

The protection of antifriction bearings with viscous or semisolid rust-preventive compounds is impractical because the removal of such materials is difficult. Antifriction bearings should be protected by a compound that does not require removal and is thin enough to permit satisfactory operation after the addition of lubricant. In one plant, antifriction bearings are coated with a rust-inhibited petrolatum that has a melting point of 40 to 43 °C (104 to 110 °F) and an application temperature of 115 °C (235 °F). The petrolatum coating produces a thin film that is compatible with any lubricant. Afterward, the bearings are wrapped with treated paper.

Chemical reactions that can occur between a rust-preventive compound and the surface to which it is applied must be considered in the selection process. Some aqueous-based rust preventives passivate the surface instead of forming a protective film. When these materials are based on alkaline solutions of organic chemicals in water, they should not be used in contact with magnesium, zinc, or other metals susceptible to alkaline attack. The corrosion inhibitor frequently used to regenerate automotive antifreeze solutions is one example of this material. Automotive radiators typically use dissimilar metals.

Rust-preventive compounds based on mineral oil, which are used on components of hydraulic systems, can be difficult to remove when preparing the system for operation, because many of the newer hydraulic fluids are incompatible with mineral oils. The U.S. Navy uses hydraulic fluids based on phosphate ester systems in various types of operating equipment. At the time of manufacture, such equipment needs to be protected by a rust-preventive compound based on a phosphate ester similar to that which will be used in operation. Because many government and industrial installations use water-glycol fluids in hydraulic equipment, any rust preventives used on this equipment should be compatible with the water-glycol fluid.

Other Selection Parameters

The film thickness of rust-preventive compounds must be controlled in order to maintain both uniform corrosion protection and a prescribed level of efficient application. Films that vary in thickness do not permit an accurate forecast of storage life or material cost.

The film thickness of oil compounds is controlled by viscosity and surface tension. However, gravitational pull causes oil to seek its own level. Thus, all oil films are reduced over time, so the viscosity effect is temporary at best. Rust-preventive compounds based on solvent cutbacks are formulated to provide a specific film thickness when the solvent evaporates. This thickness is controlled by the percentage of solids contained in the compound. For petrolatum compounds, thickness is controlled by the application technique and temperature.

Fluid types that are applied by any method will drain off to a thin film. Varying viscosity levels will initially allow varying coating weights, but both high and low levels will seek the same level of coating weight because of the pull of gravity. Roll coating and electrostatic application, as well as a spray application followed by wiping or squeegee rolls, will lay down a consistent film. Oil- and solvent-based films will migrate and puddle in low areas. On plated products, these puddled areas will appear shiny, in contrast to areas that appear dull. In the dulled area, however, oil is present at a lesser coating weight. Because coiled or sheet metals cannot be produced perfectly flat, puddling will occur over time. Usually, a sufficient amount of oil is present to provide corrosion protection.

When compounds are applied by hot dipping or hot spraying, the temperature of the coating and the temperature of the part both influence film thickness. Thick coatings will congeal on room-temperature parts that are dipped and withdrawn quickly, so that there is no appreciable increase in part temperature. However, if a part is immersed until its temperature approximates that of the heated rust-preventive compound, then a thinner coat results. In general, the greater the difference between the temperature of the compound and the temperature of the part at the time of withdrawal, the heavier the coating.

Figure 2 shows the influence of the temperature of a petrolatum rust-preventive compound and the temperature of dip-coated panels on the film thickness obtained when the panels are dipped and withdrawn rapidly (1 s for immersion, 1 s for withdrawal). The curve shown is for panels at 27 °C (80 °F). Comparisons of film thicknesses are presented for panels at temperatures of 21 and 32 °C (70 and 90 °F), dipped in rust-preventive compound with a temperature of 85 °C (185 °F).

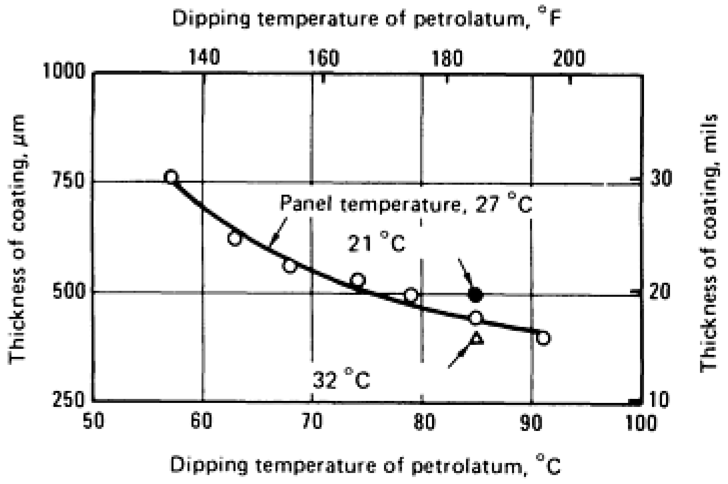


Fig. 2 Effects of panel and compound temperatures on thickness of petrolatum film applied by dipping

The specific gravity of the compound also influences coating thickness. For a specific weight of compound, the film thickness increases as the specific gravity of the compound decreases. The results of a test that determines the influence of specific gravity on film thickness are shown in Fig. 3. The panels used in this test were 75 mm (3 in.) long, 50 mm (2 in.) wide, and 3.2 mm ($\frac{1}{8}$ in.) thick. They were at an ambient temperature of approximately 24 °C (75 °F) when they were subjected to a 1 s dip into and a 1 s withdrawal from the petrolatum compound, which was heated to various temperatures to produce different film thicknesses. Five petrolatum preservatives were used, each of which had a different specific gravity.

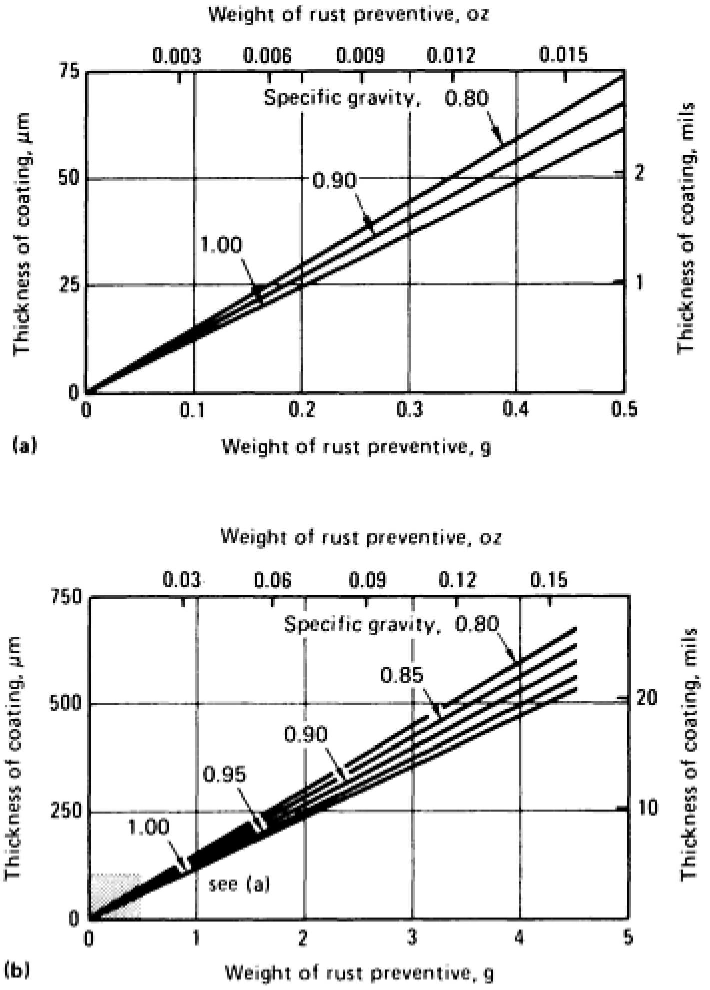


Fig. 3 Influence of specific gravity of petrolatum compound on film thickness for a specific weight of rust preventive applied to test panels. (a) Coating thicknesses up to 75 µm. (b) Coating thicknesses up to 750 µm

Tests also were conducted to determine the influence of four other variables on coating thickness obtained under laboratory conditions using a petrolatum rust-preventive compound. These variables were:

- Temperature of preservative
- Mass of metal specimen
- Duration of immersion
- Rate of withdrawal

Four conclusions were drawn from data obtained in these tests. First, as the temperature of the compound increased, its fluidity increased. Thus, progressively thinner coatings can be obtained with petrolatum rust preventives as temperature increases.

Second, the thickness of the panel (the mass of the metal specimen) influenced the thickness of the coating. With a greater metal mass, a temperature lag existed between the specimen panel and the heated preservative. The coating thickness was greatest with the greatest temperature differential. Thinner coatings developed as the temperature of the panel approached that of the compound.

Third, the duration of immersion had great influence on coating thickness. As immersion time increased, the coating first reached a maximum value, and then melted away uniformly as the panel temperature approached that of the compound.

Fourth, a slow rate of withdrawal left the surface of the coating smooth and regular, indicating uniform film thickness. Rapid withdrawal resulted in distorted, irregular surfaces with numerous small, shallow areas.

The curves in Fig. 4, which were obtained from these tests, show the influence of mass and withdrawal rate of the panel on film thickness for one petrolatum rust-preventive compound. For both curves, the immersion time was 10 s.

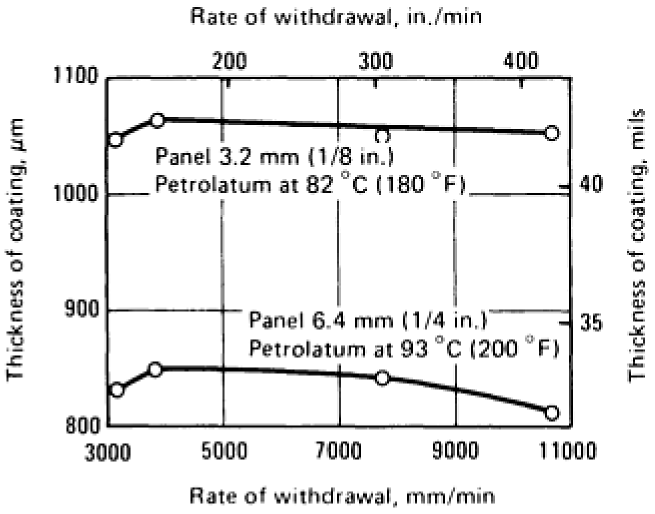


Fig. 4 Comparison of coating thicknesses obtained using the same withdrawal rate of panels from a petrolatum rust-preventive compound

The removability of rust-preventive compounds primarily depends on the thickness, hardness, and chemical characteristics of the protective film. Nondrying oil or grease compounds can be removed by simple petroleum solvents, preferably those with a flash point above 40 °C (105 °F). Vapor degreasing, hot power-spray washing with alkalies or strong detergents, and steam alkali or steam detergent blasting are also used to remove nondrying oil or grease compounds. Wiping can be used, as well, if the desired degree of removal will permit it. The solvent-cutback asphaltic or dry-film compounds usually require high-solvency organic solvents, vapor degreasing, or vigorous extended treatment with steam or hot spray cleaners.

Highly active rust-preventive compounds are difficult to remove. Therefore, when readily removable products are necessary, some corrosion protection usually must be sacrificed.

Scraping, blasting, or wire brushing may be required to remove hard-film preservatives that are completely or partially impervious to solvents, and damage to machined or polished surfaces can result. Compounds of hard film, viscous oil, or heavy grease, which are used to protect parts in either outdoor storage or highly corrosive atmospheres, will cause problems if they are not thoroughly removed, because their residues usually are incompatible with lubricating oils and greases. Examples of parts that can experience such problems are components of hydraulically actuated systems and precisionmachinetoolspindles. These rust-preventive compounds also can clog filters and screens in circulating-oil systems. Additionally, hard-wax rust preventives can cause serious problems in sliding bearing mechanisms if they are not completely removed.

Costs. Rust-preventive compounds are rarely selected on the basis of cost alone. Table 3 lists the typical duration of protection provided by four general types of compounds in three different storage conditions. In general, the cost per liter increases as the amount of protection increases.

Table 3 Duration of protection afforded by rust-preventive compounds

Type of compound	Duration of protection, method		
	Indoor	Shed	Outdoor

	storage	**storage**	**storage**
Petrolatum	Not used	12-24	6-18
Oil	2-12	1-6	1-2
Solvent	<1-3	<1	Not suitable
Solvent cutback	6-18	3-12	1-6
Emulsion	3-12	Under 3	Not suitable

The quality control of rust-preventive compounds is necessary for maintaining established levels of efficiency and performance. The extent and frequency of the quality-control program depends on the compound being used and the degree of control required. It is often advisable to start with frequent checks, in order to develop a system history, and then to adjust to safe intervals.

The checks should include the concentration level of the active ingredients; contaminant levels for dirt and water; and degree of oxidation, as determined by some means of pH and neutralization numbers. The nature of the processing operations prior to the application of the rust-preventive compound may make it necessary to run other special quality-control checks, such as those that determine viscosity, flash point, copper strip corrosion, and infrared spectra.

The viscosity and specific gravity, or both, of oil and solvent-cutback rust-preventive compounds are checked as received, at a specific temperature. Standard values, against which the result of checks are compared, either are obtained from the supplier or are established from material that has performed satisfactorily in controlled salt spray, humidity, or field tests. The viscosity is checked using effluent cups, or instruments that measure the resistance of the material to a moving circular spindle or a falling ball. Methods for testing viscosity are described in detail in the article "Painting" in this Volume.

Specific gravity, sometimes used to indicate solids content, is determined by the correct hydrometer. This measurement is usually taken at a specific temperature of the preservative. The viscosity of the compound should be checked when processing begins, and then rechecked at definite intervals in order to correct changes that result from usage conditions, such as the replacement of solvent lost by evaporation. However, because some materials have approximately the same viscosity as the material used to dilute it, periodic checking of specific gravity or other characteristics is necessary for maintaining the proper balance between solids and solvents.

The flow characteristics of petrolatum compounds can be determined empirically by methods described in ASTM D 937. The results obtained by this method are of maximum value when correlated with the flow characteristics of similar materials.

Film Characteristic. The efficiency of the film ordinarily is determined by exposing a precisely coated part to either a salt-spray test (ASTM B 117) or a humidity test (ASTM D 1748). However, the accurate projection of test results to give an expected service life requires experience. Because storage areas undergo varied and changing conditions, it is difficult to predetermine actual protection data. If the product is held under static or ideal conditions, then correlations between lab tests and storage conditions would be more reliable.

The preparation of surfaces to be protected has an important bearing on the effectiveness of a rust-preventive compound. Prior surface treatment ensures freedom from incompatible processing oils, waxes, hygroscopic or chemically reactive salts, or random dirt. These materials could either modify the adhesion or thickness of the film or counteract the inhibitors in the film.

Precleaning during routine parts processing should occur under effective process control, in order to minimize variance from acceptable limits of surface cleanliness. When a temporary setup is used, extra precautions against contamination are essential. Contamination of the compound itself from careless handling or storage procedures should be prevented.

Safety Precautions

Although rust-preventive compounds do not present abnormal or unusual hazards to personnel or equipment, their use and storage do require the observance of safety precautions. Of the oil-based, water-based, and solvent-cutback compounds, the latter type of material presents the most hazards.

Oil-based compounds generally present few health hazards and may have no more ill effects, physiologically, than household soaps. However, these materials usually owe their rust-preventing characteristics to surface-active agents, which can contain heavy metals, such as barium. If excessive quantities are allowed to remain on the skin for extended periods of time, then toxicity can result. This type of product should be kept from contacting the eyes. Some people also experience a sensitivity to oil when it contacts their skin for extended periods. Although oil-based compounds usually do not present fire or explosion hazards, they should not be exposed to intense heat.

Water-based compounds are rarely hazardous in terms of ignition or explosion. However, the additives they contain can cause dermatitis, depending on the degree of sensitivity of the individual exposed to them. These materials should be kept away from the face, especially the eyes.

Solvent-cutback compounds, if inhaled for a prolonged period, can either result in respiratory difficulties or produce the appearance of intoxication. These compounds include those materials that are diluted with low-boiling-point hydrocarbons; volatile solvents, such as the ketones and alcohols; and aromatic solvents, such as toluene and xylene. The aromatic solvents are probably the most hazardous, physiologically. When selecting a solvent, the regulations of the Occupational Safety and Health Administration should be consulted.

Solvent-cutback compounds also can present fire and explosion hazards. Solvent flash points can range from -12 to 40 °C (10 to 104 °F). Those solvents with flash points below 38 °C (100 °F) are considered hazardous, and some spraying shops do not use them. Whenever these materials are used, adequate ventilation is essential to reduce the solvent concentration below the lower explosion level and thereby eliminate explosion and fire hazards. Ventilation systems should be designed to maintain the vapor concentration at a level below explosive limits.

Painting

Revised by Jeffrey P. Gossner, PreFinish Metals Inc.; Kenneth B. Tator, KTA-Tator, Inc.

Introduction

PAINTING is a generic term for the application of a thin organic coating to the surface of a material for decorative, protective, or functional purposes. Painting offers the following advantages over other processes used for the protection or decoration of metal parts and assemblies:

- The equipment required for applying paint is usually less expensive to buy and install, is simpler to operate, and requires less control.
- Material and labor costs per unit area of surface coated often are much lower.
- Organic coatings are available in a wide range of pigments and vehicles and can meet practically any coating requirement for color, gloss, or surface texture.
- Paints have been developed that can withstand most corrosive conditions, and unlike many metallic protective coatings, organic films can simultaneously resist more than one corrosive condition, such as combinations of marine atmosphere and acid fumes.
- Conventional paint films have good dielectric properties, which enable them to inhibit galvanic action between dissimilar metals. Conversely, paints are available that contain special pigments to provide conductivity suitable for grounding induced or static electricity.
- Paints have been developed to meet newer environmental regulations.

Types of Paint

The general terms "paint" and "organic coating" are essentially interchangeable and are used to designate certain coatings having an organic base. Most organic coatings are based on a film former or binder that is dissolved or dispersed in a solvent or water. This film-forming liquid constitutes the vehicle in which pigments are dispersed to give color, opacity, and other properties to the dried film. Many other ingredients can be added to the vehicle to achieve specific film properties. These would include such things as driers to aid curing, plasticizers to impart flexibility and other properties, and stabilizers to lessen the deleterious effects of heat or sunlight. A wide variety of film-forming materials is available and includes oils, varnishes, synthetic resins and polymers such as cellulose, vinyl, epoxy, and polyester. In general, major performance characteristics depend on the binder used.

Enamels are topcoats characterized by their ability to form a smooth surface that is typically of high gloss, but may also include lower degrees of gloss such as flat enamels. Enamels may air dry or bake. Air-dry enamels are cured essentially by a combination of solvent evaporation and oxidation. Baking enamels incorporate catalysts and cross-linking agents that require heat for polymerization.

Lacquers are compositions based on natural or synthetic thermoplastic film-forming materials dissolved in organic solvent. These dry primarily by solvent evaporation. Lacquers are generally characterized by fast drying properties. Typical lacquers include those based on nitrocellulose, other cellulose derivatives, vinyl resins, and acrylic resins. A natural lacquer resin, based on secretions of the lac beetle, is called shellac.

Water-borne paints are dilutable with water. There are three principal types: solutions, colloidal dispersions, and emulsions. Solution coatings are based on water-soluble binders. Many conventional binders (alkyds, acrylics, and epoxies) can be made water soluble by chemically attracting polar groups such as carboxyl, hydroxyl, and amide, which are strongly hydrophilic. Some hydrocarbon solvents are usually necessary, up to 20% of the total, to improve solubility.

Colloidal dispersions are very small particles of binder, less than 0.1 μm in diameter, dispersed in water. Normally, these dispersions contain water-soluble polar groups to partially solubilize a portion of the resin. Emulsions, or latexes, are water dispersions that differ from colloidal dispersion by having much larger particle size on the order of 0.1 μm or larger. They are made by precipitation in water and therefore do not need to be dispersed.

Pigments must be compatible with water. Metallic particles are usually coated before being mixed into the paint to prevent chemical reaction with water, which would cause the mixture to generate gas. Water-reducible paints have a low volatile organic content (VOC) and comply with most environmental regulations. The advantages of water-borne paints include:

- Low flammability
- Reduced toxicity and odor
- Easy cleanup with water
- Good film continuity, with continuous film similar to conventional solvent systems
- Good mechanical stability; can be pumped in all types of equipment similar to conventional solvent paints
- Application by air spraying, dipping, flow coating, electrodeposition, and roller coating

The disadvantages of water-borne paints include:

- Application by electrostatic spraying requires complete electrical isolation because of the water conductivity.
- Coatings require a longer flash tunnel before curing.
- Temperature must be raised more slowly to evaporate water at a slow enough rate to prevent the coating from blistering.
- Coatings are more susceptible to dirt pickup.
- Proper temperature and humidity control are vital. If the humidity is too high or the temperature too low, coating can sag or run off the workpiece.

Electrophoretic paints are special water-reducible paints. Resin and pigment materials are shipped and stored as concentrates to be added to the production tank as needed. Electrophoretic films are always deposited from a dip tank. The operating bath consists of resin concentrate and pigment concentrate mixed with deionized water and small amounts of solubilizers and defoamers. The concentration of nonvolatile solids in the bath varies from about 10 to 20%, depending on type and composition. Paint films are deposited on the work by electrophoretic action. Immediately after the film has been deposited, the work is removed from the bath and rinsed with water to remove the excess paint bath, leaving a uniform, tightly adhering film of paint on the workpiece. The workpiece is then baked. Paints can be prepared to deposit films on either the anode or cathode. The resins used most frequently are epoxies and acrylics, including numerous modifications and hybrids. For more information on this process, see the section on electrocoating in this article.

Autophoretic paints are water-reducible paints deposited on metal surfaces by the catalytic action of the metal on the paint materials in the bath. Currently, only ferrous surfaces activate the autophoretic paints available commercially. Tubular automotive frames are coated with this method, because the entire length of the tubing can be coated inside and outside with equal ease.

High-solids paints contain 70% or more solids by volume. One method of obtaining high-solids paints is to use lower molecular weight polymers, which require less solvent to attain the desired application viscosity. Another method of reducing viscosity of high-solids paints is by heating the paint material to a temperature of about 32 to 52 °C (90 to 125 °F). Many two-component systems use a catalyst to increase the rate of the curing reaction. Fast-reacting two-component systems are usually applied with special spray guns that mix the two components at the spray nozzle. Single-component resins in high-solids paints include epoxy, acrylic, polyester, and alkyd; whereas two-component resins may be urethanes, acrylic-urethane, or epoxy-amine. The advantages and disadvantages of using high-solids paints are listed below:

Advantages

- Color control and color matching is no more difficult than with conventional solvent paints.
- These paints can be applied by higher speed (6000 to 30,000 rev/min) electrostatic bells and disks requiring minimum facility conversion from existing bell or disk systems.
- Performance properties are equivalent to those of conventional solvent paints.
- Applied cost per square foot is lower than that of conventional solvent paints.
- In many cases, these paints require less energy for curing than conventional solvent paints.
- VOC compliance is more readily attained because of reduced solvent use.

Disadvantages

- High-solids paints require specialized pumping and transport equipment.
- Cleanup of overspray is much more difficult than with conventional solvent paints.
- Toxicity of the isocyanates used with urethanes and amines used with epoxies can be a problem.
- Drying and/or curing times may be longer than those for conventional solvent paints unless the coatings are baked.

Powder paint consists of plastic resins, color pigments, and additives. In a mixing and grinding unit, the ingredients are combined in a homogeneous mixture that is heated to the melting point. The molten material is extruded into a thin sheet, which is cooled and crushed. The chips are pulverized to a fine powder of carefully controlled particle size, ensuring optimum fluidity and efficient flow through the finishing system. For more information on powder painting, see the section on methods of paint application in this article.

Selection of a Paint System

To select a paint system consistent with the production and economic requirements of the product being coated, a general knowledge of coatings is necessary, including favorable and unfavorable characteristics, available forms, relative costs, and application methods. Table 1 lists some of the major resins used and their general properties. Many of the resins listed are compatible with others, and when blended, undergo changes of properties which provide performance not available with the individual resins. From a performance standpoint, several equally good choices may be available. Many resins are supplied as both solvent- and water-borne types. These resins can be formulated for a wide variety of application methods, including conventional air atomized, airless, and electrostatic spray; roller coating; dip coating; and flow coating. Other resins have properties that make them suitable for special application techniques such as powder or electrophoretic coating. Although a wide variety of coatings is available, the ideal coating system, one with all desired performance properties, simple application, and low cost, is difficult to find. Factors such as regulations, service environment, substrate and service condition, basic function, application limitations, and cost usually must be compromised.

Table 1 Properties and applications of coating resins

Resin	**Forms available**	**Drying method**	**Favorable characteristics**	**Unfavorable characteristics**	**Cost**	**Uses**
Acrylic	Solvent, waterborne, powder	Air dry, bake	Water white, outdoor durability, chemical, heat resistance	Poor-fair adhesion, tendency to be brittle	Moderate, high	Automotive topcoats, appliances, coil coatings, aluminum siding, general industrial use
Alkyd	Solvent, waterborne	Air dry, bake	High gloss, flexibility, good durability, versatility	Poor alkali resistance, generally not hard, tendency to yellow, depending on resin	Low, moderate	Trade sales enamels, trim paints, exterior enamels, general metal finishing
Chlorinated rubber	Solvent	Air dry	Water, alkali, acid resistance	Abrasion resistance, hardness, gloss, sensitivity to solvents	Moderate	Maintenance coatings, ship bottom paints, swimming pool paints, chemical process equipment
Epoxy	Solvent, waterborne, powder	Air dry, bake	Excellent adhesion, chemical resistance, flexibility, abrasion resistance, hardness	Rapid chalking on exterior exposure, poor resistance to oxidizing acids, yellows in clears	Moderate, high	Maintenance paints, automotive primers, appliances, metal products
Fluorocarbon	Solvent, powder	Bake	Highest exterior durability, chemical resistance	Adhesion, recoatability, high baking temperatures	High	Coil coatings, siding
Nitrocellulose[(a)]	Solvent	Air dry, bake	Extremely fast drying, good hardness, abrasion resistance	Low solids content, fair to good exterior durability, low flash point solvents	Low, moderate	Furniture finishes, touch-up lacquers, general-purpose product finishes, aerosol lacquers
Phenolic	Solvent, waterborne	Air dry, bake	Hardness, adhesion, resistance to chemicals, corrosion	Darkens, can only be used in darkcolored coatings	High	Can linings, tank linings, maintenance paint on metals
Polyester	Solvent, waterborne, powder	Air dry, bake	High gloss, hardness, chemical resistance, high film build	Fair adhesion, may hydrolize under certain conditions	High	Wood finishes, coil coatings, specialty bake coats
Polyurethane	Solvent, waterborne,	Air dry,	Chemical resistance, abrasion resistance,	Some types yellow and chalk readily on	Moderate,	Aircraft finishes, maintenance paints,

	powder	bake	hardness, exterior durability	exterior exposure	high	metal and plastic coatings
Silicone	Solvent, waterborne	Air dry, bake	High heat resistance, exterior durability, gloss and color retention	Tendency toward brittleness. Unmodified types require high baking temperatures	High	Any finish for high heat resistance, exterior metal coatings
Vinyl	Solvent, powder	Air dry, bake	Chemical resistance, flexibility, fast air dry, formability, resistance to acid, alkali, abrasion	Generally low solids, low flash points	Moderate	Can and tank linings, maintenance paints, metal decorating paints

(a) Must be modified with other resins

Service Environment. When selecting a paint system, many factors concerning service environment must be considered. Needs are different for interior and exterior coatings. The specific properties needed, such as resistance to heat, cold, sunlight, and weathering must be determined. If the coating needs to be resistant to chemicals, the specific chemical, such as acid, alkali, solvent, or water immersion should be specified. Mechanical properties required, including hardness, flexibility, impact resistance, and abrasion resistance, should also be decided.

Substrate and Surface Condition. The type of substrate must be considered. A coating capable of giving excellent performance on one metal may fail badly on another. Smoothness, porosity, dimensional stability, and corrodibility affect the choice of a proper finishing system. Smooth, clean metal surfaces that cannot be phosphate coated lack sufficient "tooth" for good adhesion of some air-dried coatings. ("Tooth" is the coarse or abrasive quality of a substrate that facilitates the application and adhesion of a coating).

No special primer coats are required on surfaces containing small quantities of tightly adhering rust, if the finished parts are intended for indoor service in a mildly corrosive atmosphere. Attractive and durable finishes can be obtained over such surfaces with a single coat of a special paint that produces a textured finish, such as wrinkle finishes and pebble finishes. These paints are relatively inexpensive and hide surface irregularities with their own irregular appearance.

On parts intended for outdoor use where tightly adhering rust is present and not economically removable, a rust-inhibiting primer with good penetrating qualities must be used to prevent, or at least substantially retard, further rusting in service. Parts with heavy rust or mill scale should not be painted unless the loose rust and mill scale are removed.

The diverse requirements of substrate and environment often necessitate a dual or multiple coating system. In these systems, a primer with one composition is used to satisfy substrate adhesion and corrosion resistance, and a coating with a different composition is used as a topcoat to withstand environmental conditions, for example, a vinyl wash primer followed by an epoxy primer with an acrylic topcoat.

Basic Function. Coatings may be applied for appearance, to meet functional requirements, or to meet combined function and appearance needs. If the basic purpose is appearance, the gloss, color, and retention of these properties in service are emphasized. In some applications, functional requirements are of equal importance to appearance. On office furniture, for example, paint films must provide attractive appearance and resist marring and abrasion. On automobiles, paint films must be attractive in appearance, easily applied, and readily repaired, but be resistant to abrasion, marring, and impact as well as capable of protecting the underlying metal from corrosion. In other applications, such as corrosion protection of tanks or chemical equipment, the functional requirements of the paint film are of prime concern. Corrosion resistance is the most important of functional requirements.

Corrosion of steel and cast iron occurs in all common environments. The rate and extent of corrosion vary from mild attack in dry, clean environments to highly accelerated attack in marine or industrial areas where corrosive fumes are present in air. Table 2 lists paints selected for service in a wide range of corrosive conditions.

Table 2 Organic coatings selected for corrosion resistance in various environments

Coatings	**Applications**
Outdoor exposure	
Oil paints	Buildings, vehicles, bridges; maintenance
Alkyds	Trim paints, metal finishes, product finishes
Amino resin-modified alkyds	Automotive, metal awnings, aluminum siding
Nitrocellulose lacquers	Product finishes, aerosol lacquers
Acrylics	Automotive finishes
Marine atmosphere	
Alkyds, chlorinated rubber, phenolics, epoxies, vinyls, vinyl-alkyds	Superstructures and shore installations
Urethanes	Clear marine varnishes
Water immersion	
Phenolics	Ship bottoms
Vinyls	Ship bottoms, locks
Chlorinated rubber	Ship bottoms, swimming pools
Urethanes	Clear marine varnishes
Epoxies	Ship hulls, marine structures
Chemical fumes	
Epoxies, chlorinated rubber, vinyls, urethanes	Chemical-processing equipment
Extreme sunlight	
Vinyls	Metal awnings

Acrylics	Automotive finishes
Silicone alkyds	Petroleum-industry processing equipment
High humidity	
Amino resin-modified alkyds	Refrigerators, washing machines
Epoxies	Air conditioners
Catalyzed epoxies, chlorinated rubber, phenolics	Maintenance; chemical and paper plants
High temperature	
Epoxies	Motors, piping, 120 °C (250 °F) max
Modified silicones	Stove parts, roasters, 205 °C (400 °F) max
Silicones	Stove parts, roasters, 290 °C (550 °F) max; aluminum-pigmented paints 650 °C (1200 °F) max
Inorganic zinc-rich	Structural steel, chimneys to 370 °C (700 °F)

In service, paint films are frequently required to resist exposure to highly deleterious materials. For example, decorative finishes, such as those on home laundry equipment, must resist detergents, and paint films on equipment powered by gasoline engines must withstand attack from gasoline.

Paint films also may be required to resist acids and alkalis, solvents, staining, heat, impact, marring, and abrasion. Some coatings must be able to withstand flexing without cracking or flaking. Table 3 lists paints that have proven successful in withstanding mechanical and chemical action.

Table 3 Paints selected for resistance to mechanical or chemical action

Action	**Paint**
Abrasion	Vinyls; plastisols; polyurethanes
Impact	Epoxies; vinyls; polyurethanes
Marring	Thermosetting acrylics; vinyls
Flexing	Epoxies; vinyls

Acids	Chlorinated rubber; vinyls; epoxies
Solvents	Epoxies; phenolics
Detergents	Thermosetting acrylics; epoxies
Staining	Thermosetting acrylics
Gasoline	Alkyds; epoxies
Alkalis	Phenolics
Heat	Alkyd-amines; silicone resins

Application Limitations. In selecting a coating for a given purpose, application properties in relation to available facilities and conditions in which the coating is to be applied must be considered. The most suitable application, such as spraying, dipping, roller coating, or brushing, as well as drying speed, storage stability, flammability, and toxicity should all be determined. For example, toxic and flammable materials should not be used in areas without adequate ventilation and safety equipment. Heat-convertible coatings cannot be used unless adequate baking facilities are available. Two-component coatings, such as epoxies and some polyurethanes, have limited pot life after mixing and must be used within a determined period or discarded, unless two-component spray equipment is used.

Cost must be weighed against the performance required of the coating system. A low-cost coating that fails to perform its function is a wasted expense. With the effort involved in applying protective coatings, a short service life of a low-cost, inferior material makes ultimate coating and maintenance costs far higher than if a more expensive durable coating had been used originally. Other factors must also be considered in arriving at an overall cost estimate, including: spreading rate, the area adequately covered by a unit of volume of paint; probable application time and resulting labor costs; equipment required for application; and expected service life.

Examples of Selection. Paints are seldom selected to meet only one requirement. Most organic coatings must perform several functions. The considerations that governed the selection of paint in three different applications are described in the following production examples.

Example 1: Painting of Ballast Cases for Fluorescent Light Fixtures.

One plant annually produces over a million ballast cases for fluorescent lighting fixtures. Paint applied to these cases, which are rectangular steel boxes, must provide acceptable appearance, resist mildly corrosive exposure, and withstand a certain amount of handling and abuse during assembly. Processing and material costs must also be low. These requirements are met by a water-emulsion paint, applied by conveyorized dipping and subsequently baked. This paint is low in initial cost and because the solvent is water eliminates the usual cost of solvent replacement. It has good dipping qualities, provides adequate corrosion resistance, and stands up well in assembly. The paint has good tank stability and, unlike volatile-solvent paints, is nonflammable.

Example 2: Painting of Interior and Exterior Surfaces of Electric Motor Shells.

Electric motor shells, 75 mm (3 in.) long by 90 mm ($3\frac{1}{2}$ in.) in diameter, required a thin paint film for corrosion protection. Dip painting was desired, because both the inside and the outside of each shell were to be coated. To avoid the necessity of removing paint from the portion of the shell that mated with the motor end bells, the thickness of the paint film had to be closely controlled. The maximum permissible thickness was 50 μm (2 mils) to avoid misalignment of the bearings in the end bells and maintain a uniform air gap between stator and rotor in final assembly. No runs or beads could be tolerated.

A vinyl butyrate lacquer was selected for its good flow characteristics and hiding power. It provided the required corrosion protection and was compatible with cost limitations. By standing the parts vertically in coarse-mesh baskets and carefully controlling withdrawal from the dip tank, 36 parts at a time were successfully painted to coating thicknesses that met tolerances.

Example 3: Prime Coat and Top Coat Painting of Cold Rolled Steel Parts.

One company that had been painting cold rolled steel products with one coat of baking primer and one topcoat of baking enamel needed to expand production facilities. One method would have been to set up a duplicate finishing line. It was found, however, that an acceptable finish could be obtained by priming with an air drying, flash primer and finish painting with a topcoat of baking enamel. Rather than adding a complete painting line, only two prime booths for applying the primer and flash-off leg on the conveyor, to permit the primer to air dry, had to be added, saving a capital expenditure of several thousand dollars.

Numerous other examples could have been cited. Coating manufacturers and equipment suppliers can provide valuable assistance in the selection of an appropriate coating system for a desired product finish.

Surface Preparation

The importance of proper surface preparation to the durability of any coating system cannot be overemphasized. Without proper surface preparation, the finest paint, applied with the greatest of skill, will fall short of its maximum performance or may even fail miserably. A coating can perform its function only so long as it remains intact and firmly bonded to the substrate.

An adequately prepared surface not only provides a good anchor for the coating but also ensures a surface free of corrosion products and contaminants that might shorten the life of the film by spreading along the coating/substrate interface and destroying adhesion or by actually breaking through the coating.

Cleaning

Before being painted, metals usually are exposed to one or more fabricating processes, such as rolling, stamping, forming, forging, machining, and heat treating. In these processes, the metal surfaces pick up various contaminants that can either interfere with the adhesion of the paint film or allow corrosion to progress beneath the paint film and cause it to fail prematurely.

The principle surface contaminants that adversely affect the performance of paint films include oils, greases, dirt, rust, mill scale, water, and salts such as chlorides and sulfides. These contaminants must be removed from the surface before paint is applied.

Selection of cleaning process is governed by the soil or contaminant to be removed, the degree of cleanness required, the type of paint to be applied, and the size, shape, material and end use of the part. In addition, the speed with which the process runs will affect the cleaning characteristics.

Methods of cleaning metal surfaces can be classified as mechanical and chemical. To meet rigid requirements for surface cleanness, mechanical or chemical cleaning methods can be used in combination. For example, before structural steel intended for an application involving exposure to corrosive chemical environments is painted, oil, grease, rust, mill scale, and any other surface contaminants must be completely removed. Chemical paint strippers or solvent cleaners are often used prior to mechanical cleaning to remove oil, grease, or old paint.

Additional information is available in the article "Classification and Selection of Cleaning Processes" and in the other articles in the Section "Surface Cleaning" in this Volume.

Mechanical cleaning methods include power brushing, grinding, and abrasive blasting.

Power brushing is an abrasive cleaning operation utilizing a power-driven rotary brush. Different types of brushes, and various lengths and gages of wire or fiber provide a wide range of abrasive action. For heavy abrasion, steel wire brushes are used. Mild abrasion is obtained with fiber, horsehair, or other bristle-type brushes. Power brushing may be used to remove surface rust, dirt, and loose mill scale; it is unsuitable for removing embedded oxides or tight mill scale.

Grinding, using abrasive wheels of various shapes and grit sizes, is used for the removal of coarse irregularities, such as burrs or flash, and coarse mill scale and heavy rust. Selection of the proper grade of abrasive wheel is important: Too coarse a wheel may produce deep abrasions that are difficult to hide by paint; a wheel with grit that is too fine will clog easily and make the process inefficient.

Abrasive blast cleaning is accomplished by bombarding a surface with abrasive particles propelled at high velocity by air, water, or centrifugal force. The effects of blasting are influenced by the type, hardness, particle size, velocity, and angle of impact of the abrasive. Blasting is a rapid method of removing rust and mill scale. Virtually any degree of cleanness of the blasted surface is obtainable.

Chemical cleaning includes emulsion cleaning, solvent cleaning, vapor degreasing, alkaline cleaning, acid cleaning, pickling, and steam cleaning.

Emulsion cleaning, solvent cleaning, and vapor degreasing employ common organic solvents for the removal of oil, grease, loose metal chips, and other contaminants from metal surfaces. For a description of processing methods, see the articles "Emulsion Cleaning" and "Solvent Cold Cleaning and Vapor Degreasing" in this Volume.

Alkaline cleaning is an effective method for removing oils and greases, water-soluble residues, heat treating salts, acid deposits, and other inorganic dirt. Alkaline cleaners work by detergent action and saponification, and are usually used in soak tank, pressure spray, or electrolytic cleaning. Thorough rinsing or neutralizing of the cleaned surface is necessary after alkaline cleaning prior to painting. For a more detailed discussion of processes, see the article on "Alkaline Cleaning" in this Volume.

Acid cleaning is used for removal of light soil or rust. It is unsuitable for removing heavy coats of oil, grease, dirt, and mill scale. Acid cleaners used prior to painting usually are water solutions of phosphoric acid, organic solvents, acid-stable detergents, and wetting agents. These solutions are used either hot or cold, in soak tanks or spray cleaning systems. Cleaning is accomplished by emulsifying the oils that are on the surface and by dissolving or undercutting oxide films. For additional information on processing, see the article "Acid Cleaning" in this Volume.

Pickling also utilizes acid, for the removal of rust, mill scale, and some types of soil. Wide variations are possible in the type, strength, and temperature of the acid solutions. The acids most commonly used for pickling ferrous metals are sulfuric and hydrochloric. Inhibitors usually are added to pickling solutions to retard acid attack on the metal. Some parts are precleaned to remove films of oil, grease, or other contaminants that would prevent the pickling solution from contacting the metal surface. After pickling, thorough rinsing and neutralizing of the metal surface are necessary. For a more detailed discussion, see the article "Pickling and Descaling" in this Volume.

Steam cleaning may be used on parts too large or too heavy to be cleaned by conventional methods. In this process, a jet of live steam is directed against the metal surface. The cleaning power of the steam is enhanced by the addition of detergents or alkaline cleaners to the water being vaporized. When such additives are used, cleaning should be followed by thorough rinsing or neutralizing, and drying. Paint adhesion may be poor on steam-cleaned surfaces. If no further surface treatment is feasible, a paint such as one of the asphalt types is recommended. These paints adhere well to a wide variety of surfaces and usually have good adhesion on steam-cleaned metals.

The effectiveness of abrasive blast cleaning compared with wire brushing in removing mill scale is illustrated in the following example. A laboratory study was conducted to compare the effectiveness of abrasive blast cleaning and wire brushing in removing mill scale from hot-rolled carbon steel panels. Panel surfaces were cleaned by each method. Surfaces were then individually coated, under controlled conditions, with alkyd, vinyl, epoxy ester, or catalyzed epoxy-based paints. The panels were then exposed to an industrial atmosphere. Within 12 months, all coatings on the panels that had been wire brushed indicated failure in the form of either blistering of the paint or rusting of the steel surface. After 24 months, however, no signs of paint failure were evident on the panels that had been blast cleaned. The poor performance of the paint on the wire-brushed surfaces was the result of incomplete removal of mill scale by wire brushing.

A high degree of cleanness can be obtained by combining mechanical and chemical cleaning methods. Before being painted, steel surfaces of tank cars used to carry corrosive materials were alkaline or solvent cleaned and then abrasive blasted. This removed all contaminants. A corrosion-inhibiting primer was applied, followed by a chemical-resistant topcoat. This paint film, controlled to a minimum thickness of 75 μm (3 mils), has a life expectancy of 4 to 6 years.

Surface Smoothness

If a smooth, high-quality paint finish is desired, imperfections such as scratches, die marks, indentations, roughness, and localized porosity must be repaired before finish painting.

If the imperfections are deep (3.2 mm, or $\frac{1}{8}$ in., or more), they may be filled with wiping solders, which are lead-tin alloys prepared for this application. The metal surface is first degreased with a nonflammable solvent such as 1,1,1-trichloroethane. When dry, the surface is coated with a flux and heated using a torch. The solder is flowed into the indentation or depression and blended with the contour of the part. All traces of flux are removed with solvents or neutralizers. After the surface is dry, it is primed and sanded smooth and then given the prime and finish coats of paint.

Significant surface imperfections also can be primed and filled with a suitable putty. The putty used must be chemically compatible with both the prime coat and the finish coat and should adhere well to both. Putties are usually highly pigmented pastes, containing such materials as vinyls, epoxies, alkyds, or drying oils as binding or drying agents. Air drying or baking putties can be used, although air drying putty is most frequently used. Baking of thick putty films, either for curing the putty or for curing subsequent paint films, usually results in blisters or pinholes, because of the release of entrapped solvents during baking. Catalytically cured putties should be used when subsequent baking is required, because these putties cure with an exothermic reaction, driving the solvent from the film of putty before it is set and minimizing the formation of pits or blisters during subsequent baking of paint films.

Prepaint Treatments

In addition to cleaning and smoothing, the metal surface is often given a prepaint treatment to improve paint adhesion and reduce corrosion. Prepaint treatments include phosphate coatings and organic pretreatments known as wash primers or etch primers. The choice of a prepaint treatment depends largely on the substrate metal to be painted. Care should be taken to choose the appropriate pretreatment for the particular substrate being coated to ensure corrosion protection and paint adherence.

Phosphate coatings are formed by chemical reaction during immersion of the metal in the phosphate solution that deposits a nonmetallic and nonconducting coating. Both coating weight and crystal size can be varied to provide almost any surface condition required for the appearance or function of the paint. For a detailed discussion of coatings, equipment, and processing methods, see the article "Phosphate Coatings" in this Volume.

The advantages of a phosphate coating as a base for paint are indicated in Table 4, which outlines the results of comprehensive tests conducted on panels for a large manufacturer of home appliances. In these tests, three methods of surface preparation, including cleaning only, cleaning plus iron phosphating, and cleaning plus zinc phosphating, were evaluated by their effect on properties of subsequent paint films. Alkyd-melamine paints from various suppliers were used in the tests and prepared specifically for use following each of the prepainting surface-preparation methods. All panels were spray painted to the same film thickness and were baked and cured in the same manner to achieve polymerization.

Table 4 Effect of prepainting surface treatments on performance of paint films in tests

Alkyd-melamine paints were from various suppliers and specially prepared for each of the prepainting; after being applied, paints were baked for 30 min at 150 °C (300 °F) and cured for 72 h at 49 °C (120 °F); dry film thickness was 38 to 46μm (1.5 to 1.8 mils); gloss, as measured with 60° glossmeter was 82°.

Test	Results, for prepainting treatments		
	Cleaning only	Cleaning plus	
		Iron	Zinc

		phosphating	**phosphating**
Pencil hardness	HB[(a)]	HB-F	HB-F
Adhesion	Poor	Excellent	Excellent
Impact resistance (face and back)[(b)]	7.2 N · m (64 in. · lb)	7.2 N · m (64 in. · lb)	7.2 N · m (64 in. · lb)
Bend[(c)]	Fair to good	Excellent	Excellent
Crimp	100% failure	Excellent	Excellent
100% relative humidity at 43 °C (110 °F), h[(d)]	300 (max)	1000	1000
5% salt spray, h[(d)]	72 (max)	500(max)	750

(a) Pencil of this hardness cut through and removed paint cleanly; when cut, paint scratched cleanly with fingernail.

(b) Impacting surface 1.59 mm (0.0625 in.) in diameter tested with 0.9 kg (2 lb) weight.

(c) 180° bend over 6.4 mm ($\frac{1}{4}$ in.) mandrel.

(d) Hours to 65 mm (2.6 in.) creepage from scribe or to blistering, or both

It is important to note that phosphate coatings may not be suitable for all substrates.

Organic pretreatments, or wash primers, are materials that provide the properties of an inhibitive wash coat or metal conditioner in an organic film. The essential components of wash primers include polyvinylbutyral resin, chromate pigment, and phosphoric acid. Wash primers are described in Military Specifications DoD-P-15328 and MIL-P-8514. Organic pretreatments are formulated for spray application and should be used in the following situations: where phosphating equipment is not available, where size and shape of parts preclude use of the phosphating process, or where parts containing mixed metal components are assembled before painting.

Spraying

Spraying is adaptable to either large-volume or low-volume production. Applications may be limited because of solvent emissions, possible fire hazards, or potential damage from overspray. Spraying methods include conventional air spraying, in which the paint is atomized and propelled against the work by means of compressed air, hot spraying, hydraulic airless spraying, and air and airless electrostatic spraying.

Spraying is used for applications in which good appearance and uniformity of coating are desired, such as automobile bodies. Figure 1 shows large and medium-size metal housings that are examples of parts painted by conventional (air atomized) spraying to obtain a good appearance and uniform coating. In the application of metallic or polychromatic enamels, the spray process achieves the necessary dispersion of the particles. Also, very large objects such as bridges are usually spray painted.

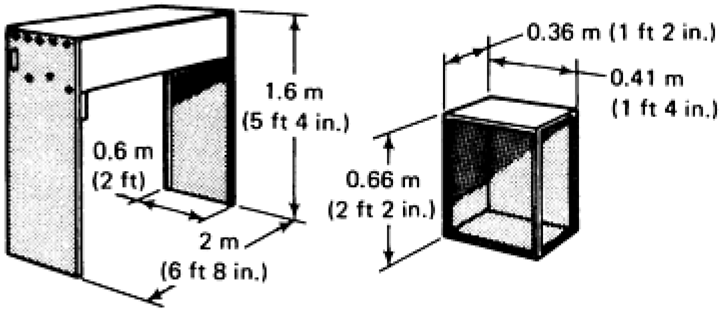


Fig. 1 Parts where conventional (air atomized) spray painting is used to meet requirements of good appearance and uniform coating

Spray painting generally consumes more paint than other painting processes, because of overspray losses. In air atomized spraying, only a small amount of the air at the nozzle is used for atomizing. The remainder of the air pushes the paint and controls the pattern and droplet size. The remainder of the air also causes overspray, as the atomized paint bounces off, or is driven past, the part being painted. The efficiency of the spray operation depends on part shape and size; operator ability; setup of spray guns; and type of equipment whether air atomized, electrostatic, or hydraulic airless spray systems are used.

Hot spraying is a method in which air atomized or airless spraying equipment is used in conjunction with a heat exchanger to heat the paint to a predetermined temperature. The temperature range for hot spraying is usually from 60 to 82 °C (140 to 180 °F). In air atomized spraying, viscosities suitable for application are obtained with the use of solvents. The hot spraying method uses heat to lower the viscosity to the optimum range for spraying, allowing the application of paint with higher solids content.

Heating units are available in two basic types, recirculating and nonrecirculating. Recirculating heating units circulate heated paint between the heater and spray gun, maintaining a constant temperature. Nonrecirculating units heat the paint only once. After the paint passes through the heater, it is subject to various degrees of cooling, depending on hose lengths and conditions of application.

When properly prepared paint materials are used, the hot spray method may have three distinct advantages over conventional spraying:

- Little or no solvent is used for thinning, reducing labor and solvent costs.
- Thicker films can be applied using fewer gun passes or fewer coats.
- Paint can be stored in unheated areas or at very low temperatures.

The principal disadvantages of hot spraying are:

- The purchase and operation of the heating unit add to the overall cost of painting.
- Spraying with paint containing a greater solids content can result in higher overspray losses if improper spraying techniques are used.

Airless spraying, with either heated or unheated paint, uses hydraulic (pumping) pressure to propel the paint through the hoses and atomizing nozzle. The main advantages of airless spray painting stem from the elimination of air as the force for atomizing and propelling the paint. Airless spraying requires the release of considerably less energy at the nozzle, and overspray is minimized. Heavier film thickness without runs or sags can be obtained when more viscous material is sprayed. As in air atomized spraying, however, airless spraying requires an increase in pressure as the paint increases in viscosity.

Elimination of air also permits the use of comparatively simple and inexpensive spray booth exhaust systems, permits full-coverage spraying into corners and recesses with a minimum of bounce-back, and reduces masking requirements. Airless systems use simpler, lighter weight guns, and fewer hoses than are required in air systems.

The chief disadvantage of airless spraying is that, unlike air spray guns, airless spray guns cannot be throttled. Because a full flow of paint comes constantly from the airless gun, greater operator skill is required for controlling coating application in difficult-to-reach areas.

Electrostatic Spraying. In electrostatic spray painting, electrically charged atomized particles of paint are attracted to the grounded part. Paint for electrostatic application can be atomized by conventional air, airless, or rotational techniques.

One of the chief advantages of electrostatic spraying is the small loss of paint from overspray. Whereas in conventional spray painting as much as 70% of the paint sprayed may be lost because of overspray, as little as 10% may be lost in electrostatic spraying. Another advantage is the ability of this method to produce a consistent paint film over a long production run.

The main disadvantage of electrostatic spraying is that the electrostatic attraction of the part for the paint draws the paint to the nearest edge or surface of the part, and it is difficult or impossible to get paint into deep recesses, corners, and shielded areas. Another disadvantage is that the necessity for grounding the surfaces to be coated makes it impossible to paint assemblies in which parts are insulated from other parts by a dielectric component.

Equipment for Air Atomized Spray Painting

Basic equipment for air atomized spray painting consists of a spray gun, a container for the paint, an air compressor, an air regulator or transformer, connecting pipes and hoses, a spray booth, and an air filter and moisture trap.

Spray guns are available commercially to fit virtually any requirement. An air cap at the front of the gun atomizes the paint and forms the desired spray pattern. Air caps may be interchanged to meet the requirements of different applications.

A fluid tip or nozzle, located directly behind the air cap, directs and meters the paint into the air stream. These tips vary in material and size according to the type and viscosity of the paint being applied and with the speed and volume requirements of the application. Larger orificed nozzles are required for heavy, coarse, or fibrous paints. Smaller orificed nozzles are used for thin paints. Because atomization of the paint improves as the nozzle size decreases, the smallest orifice that permits proper passage of the paint should be selected. Small nozzle sizes also permit more effective control of fluid pressures, a necessity when applying thin paints that have a tendency to sag. Abrasive or corrosive paints require tips made of materials with resistance to wear or corrosion.

Air compressors provide the force for air atomized spray painting. Air compressors may supply compressed air throughout the shop or only to the paint line. A fluctuating air pressure at the gun, usually caused by inadequate compressor capacity or an inadequate distribution system, can result in improper atomization of the paint and defective paint films.

Air regulators or transformers regulate air pressure as required. Air filters and the moisture trap remove oil, dirt, and moisture from the compressed air. Air regulators, filters, and the moisture trap are installed in the air-supply lines between the compressor and the paint container and between the compressor and the spray gun. The regulators and filters should be as close to the tanks and guns as possible.

Pipes and hoses that distribute the compressed air or paint must be of adequate size to handle peak loads without starving any station and must be able to withstand any abrasive or chemical effects of the paint.

Spray booths are fire-resistant enclosures that confine overspray and fumes and use ventilating systems to draw in fresh air and exhaust the contaminated air after filtering out the solids. A booth face air velocity of 0.559 to 0.635 m/s (110 to 125 ft/min) is required. Dry or water-wash filters may be used. In most installations, spray booth and exhaust stack are protected with automatic sprinklers.

In dry spray booths, fumes and overspray are forced through special filters that remove solids before exhausting the air and fumes. Dry spray booths with replaceable filters are usually less costly to install than water-wash booths, because no water or drain lines are required.

In water-wash spray booths, contaminated air is drawn through a series of water curtains and baffles to remove solids from overspray before air and fumes are exhausted. These booths also reduce fire hazards by collecting overspray in water. However, water-wash spray booths are usually more costly to install, operate, and maintain than dry booths. Some localities prohibit discharging spray booth water into sewers, and adequate recirculation systems and controls must be installed.

Spray booths exhaust large volumes of air, and to ensure a sufficient quantity of replacement air without creating drafts or heating problems in other areas of a plant, air replacement units must be installed. These units, which are placed next to the spray booths, draw in air from the outside, filter it, heat it, and deliver it to the spray booth. This permits proper functioning of spray booth exhaust systems and maintains the desired booth temperature for suitable spraying conditions. Few manufacturing operations are dust free, and air replacement units greatly reduce the possibility that airborne contaminants will be drawn into the paint area and deposited on wet paint surfaces.

Table 5 lists and describes the equipment required for air atomized spray painting of two production parts: a fire extinguisher shell 355 mm (14 in.) long by 75 mm (3 in.) in diameter, constructed from 1.0 mm (0.040 in.) thick steel; and an enclosure panel 915 mm (36 in.) long by 760 mm (30 in.) wide, produced from 0.268 mm (0.105 in.) thick sheet.

Table 5 Equipment requirements for conventional spray painting of two production parts

Procedure or equipment	**Shell for fire extinguisher**[(a)]	**Enclosure panel**[(b)]
Production requirements		
Surface preparation	Clean and phosphate[(c)]	Clean and phosphate[(c)]
Prime coating	Zinc chromate primer	Red oxide primer
Finish coating	Alkyd baking enamel	High-luster lacquer
Production per hour	500	40
Equipment requirements		
Overhead conveyor	305 mm (12 in.) hook spacing	610 mm (24 in.) hook spacing
Cleaning and phosphating[(c)]:		
Capacity and solution of rinse tanks	379 L (100 gal)	379 L (100 gal)
Solution and rinse temperature	66 °C (150 °F)	66 °C (150 °F)
Prime and finish coating:		

Spray booth[d]	2.4 × 2.1 × 1.5 m (8 × 7 × 5 ft)	3.7 × 2.4 × 1.8 m (12 × 8 × 6 ft)
Spray gun	Hand operated	Hand operated
Paint supply tank (with agitation)	95 L (25 gal), pressurized	95 L (25 gal), pressurized
Drying	Infrared oven[e]	Air dry[f]

(a) Shell, 75 mm (3 in.) in diameter and 355 mm (14 in.) long, of 1.0 mm (0.040 in.) steel.

(b) Panel 915 by 760 mm (36 by 30 in.), of 12-gage (2.657 mm, or 0.1046 in.) sheet steel.

(c) Proprietary phosphate cleaner coater used; 2-min immersion in solution and rinse tanks, followed by drying.

(d) Open-ended water-wash.

(e) Drying cycle, 10 min at 160 °C (325 °F).

(f) Drying of prime coat may be forced by brief infrared heating.

Equipment for Electrostatic Spray Painting

Basic equipment for electrostatic spray painting consists of a paint supply system, an atomizer (or gun), a source of electrical power, a spray booth with a ventilating system, a conveyor, and properly designed racks.

Paint supply systems deliver paint under pressure to one or more atomizers. In such systems, paint is prepared and stored in a central tank, from which it is distributed to the atomizers by air or variable-speed positive-displacement pumps.

Atomizers (guns) can be either air or airless. An air gun uses compressed air to atomize the paint delivered to it. In one air gun, the nozzle is insulated from the metal atomizer body by a plastic sleeve. The fluid tip and needle are charged to a high negative electrical potential that is imparted to the atomized paint particles as they leave the nozzle.

Another air electrostatic spray painting system uses ordinary air spray painting guns for atomization. Parts on the conveyor are surrounded by a grid of fine wires charged to a high negative potential. The paint is sprayed between the grid wires and the parts, where it picks up the negative charge and is repelled by the grid wires and attracted by the grounded parts on the conveyor.

Guns that are operated automatically may be mounted in a fixed, but adjustable position, or they may be attached to a mechanism that causes them to reciprocate vertically or horizontally as required by the size and shape of the part being painted.

Airless atomizers use a rotating component, either disk-shaped or bell-shaped, charged to a high negative electrical potential. Paint, forced up through the center of the rotating member, is charged with this same high negative potential. The centrifugal force of the spinning component moves the paint to the outer edge, where the combination of centrifugal and electrostatic forces atomizes the paint and disperses it. The paint is attracted electrostatically to the grounded parts on the conveyor.

Bell-shaped atomizers generally have the plane of the opening of the bell parallel to the surface being coated, and the work is carried past on a straight-line conveyor. The bell may be fixed or may reciprocate and can be used in any position. Hand-operated portable guns with bell-shaped atomizers are available.

Disk atomizers are operated as automatic or manual units. The disks operate in an essentially horizontal plane; however, in nonreciprocating installations, the disk may be positioned at up to a 35° angle to produce a greater vertical spray area. Because the paint is dispersed around the entire periphery of the disk, conveyors usually carry the part in a circular path around the atomizer. For long parts, the disk may be reciprocated up and down to facilitate coating the entire length of the parts as they are conveyed around the loop.

Power supply units must be capable of providing the high static potential required for each atomizer. These units can operate on 110, 220, or 440 V at 60 cycles. The power output is usually 90,000 to 120,000 V and 5 mA. One power supply unit can handle up to ten atomizers. Units produce a very small current to eliminate any serious hazard to the operator. Usually, an automatic cutoff control is incorporated for added safety.

Spray booths and ventilating systems are used to confine and collect the overspray and to exhaust the fumes from the vaporizing solvents. Minimum velocity of air through the booth is desired to avoid interference with deposition of paint on the part. However, velocity must be adequate to maintain the solvent concentration below its lower explosive level and toxic concentrations. Air velocities of 0.25 to 0.5 m/s (50 to 100 ft/min) are usually adequate for electrostatic spraying applications.

Racks and conveyors used in electrostatic spray painting, in addition to holding and moving the parts, must provide the electrical ground necessary to develop the electrostatic attraction. Parts should be mounted as close to one another as possible on the conveyor to minimize overspraying. Some parts require rotation as they pass the atomizer to ensure coating of all surfaces.

Dip Painting

Dip painting consists of submerging a part in paint contained in a tank, withdrawing the part, and permitting the part to drain. Parts with complex surfaces may be coated efficiently by dipping. Larger parts, produced in quantity, are racked or hung on conveyors, which carry the parts to the paint tank, automatically immerse and withdraw the parts, and carry them over drip troughs into which the excess paint runs off.

Dip painting is seldom used where uniformity of paint thickness is required. This procedure may be unsatisfactory for painting parts having machined holes or surfaces where masking is impractical. Usually, paint films applied by dipping are heavier at the bottom than at the top, because of paint runoff, and are thin at sharp edges. In addition, bubbles and bumps may be found at the bottom edges of painted pieces. Parts may be dip painted to obtain complete coverage and then spray painted to obtain a required surface appearance.

The blower wheel shown in Fig. 2(a) is an example of a part that requires coating of all surfaces, but for which a variation in the coating thickness is acceptable. Dip painting, followed by spinning to remove excess paint, is the preferred method for coating this part. If a part of this type were so large that dip painting would require a prohibitive volume of paint, flow coating could be substituted, although rotation of the part as it passes through the nozzles might be required. If the size were increased still further, spray painting might be used.

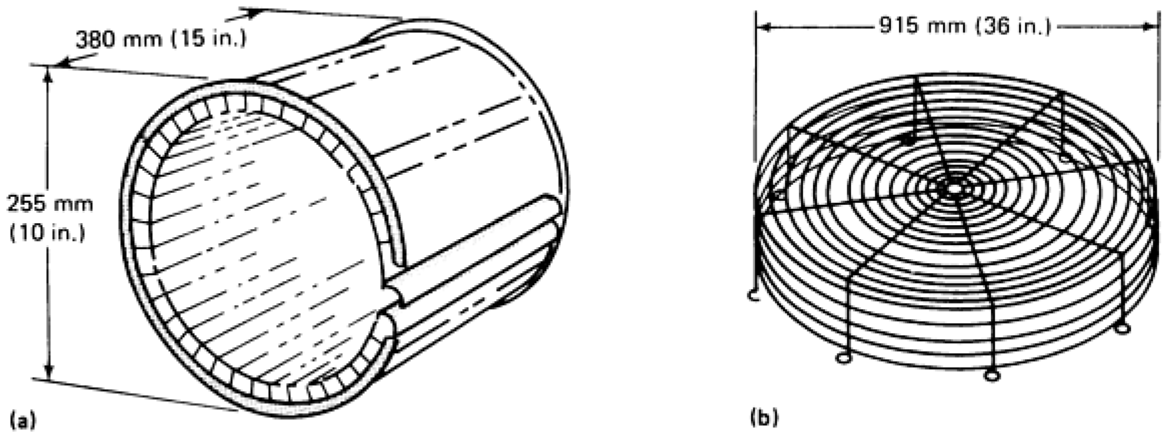


Fig. 2 Parts that can be efficiently coated by dip painting. If considerably larger, parts like these could be painted more efficiently by the flow coating process. (a) Blower wheel. (b) Wire fan guard

The wire fan guard shown in Fig. 2(b) is an example of a part that is difficult to cover efficiently by conventional spraying without considerable loss of paint by overspray, but can be efficiently coated by dipping. The part in Fig. 2(b) also could be painted by flow coating, electrostatic spraying, or electrodeposition. If the part were larger, flow coating might be preferred to dipping because of the smaller volume of paint required.

Equipment for Dip Painting

Basic equipment for dip painting consists of a tank to contain the paint, a device to agitate the paint and prevent settling or separation of ingredients, a device for lowering the parts into the paint and raising them out of it, a drip trough, and ventilators.

Dip tanks should be as small as possible, consistent with the maximum size of parts to be dipped. Smaller tanks require less paint to fill them, and the higher rate of turnover helps to maintain paint stability. Dip tanks should be designed to expose the smallest possible area of paint to prevent evaporation of paint thinner.

Dip tanks for conveyorized dipping should be designed with ends that slant according to the angle parts travel as they are conveyed into and out of the paint. This angle should be not less than 30°, measured from the horizontal, and should be 45° if possible. The sharper the angle of travel, the shorter the dip tank, and there is consequently less exposure of paint to air.

Introduction of fine air bubbles into the tank should be avoided, because these bubbles can cause pinholing in the final film. Pumps are used to dislodge trapped air bubbles from blind spots in parts. Mechanical devices, such as tipping bars that change the position of parts during immersion, are also used to dislodge bubbles.

Dip tanks should be designed with provision for paint agitation. The bottom of the tank should be just wide enough to accommodate the agitator.

Agitators in dip tanks prevent the paint from separating. Horizontal screw or horizontal paddle agitators may be used. Usually, agitators extend the full length of the tank and are no greater than 0.3 m (1 ft) in diameter. Tanks with a capacity of 7570 L (2000 gal) or more may require agitators of larger diameter.

Agitator speed is usually between 60 and 120 rev/min. Correct speed is usually determined by visual inspection of the tank surface. The entire surface of the tank should show agitation with no clear vehicle forming. Agitation should be of sufficient force to keep the paint well mixed and prevent the pigment from settling. Protective screening should be installed over the agitator to protect the blades from being damaged by parts that may fall into the tank.

A pump circulator added to an agitator system permits the use of strainers to remove lumps that may form or foreign material that may be introduced into the tank.

In tanks with a capacity of about 1135 L (300 gal) or less, complete recirculation of the paint every 20 min usually provides sufficient agitation for preventing settling or separation of ingredients. Paint should be withdrawn from the bottom of the tank and pumped back into the tank just under the minimum working level.

Ventilation. Dip tanks should have a means of ventilation to remove fumes from the tank. Hoods should not interfere with the conveyor system or the device for immersing parts.

Drip troughs catch the excess paint that drips from the parts after they have been removed from the tank. A conveyorized dip plating system usually includes a sloped drip trough to allow excess paint to flow back into the tank. Working areas around drip troughs and dip tanks must be equipped with adequate fire control equipment.

Table 6 lists equipment requirements for dip painting two production parts. One part is an angle bracket about 25 mm (1 in.) wide, produced from 3.2 mm ($\frac{1}{8}$ in.) thick stock and with each leg 75 mm (3 in.) long. The other, a spring hanger produced from 4.8 mm ($\frac{3}{16}$ in.) stock, is 100 mm (4 in.) wide with 150 mm (6 in.) and 100 mm (4 in.) legs.

Table 6 Equipment requirements for dip painting two steel production parts

Procedure or equipment	**Angle bracket**[(a)]	**Spring hanger**[(b)]
Production requirements		
Surface preparation	Clean and phosphate[(c)]	Clean and phosphate[(c)]
Prime coating	None	Red oxide primer
Finish coating	Lacquer; air dry	Lacquer; bake
Production per hour	1200	650
Equipment requirements		
Work handling	Manual; baskets[(d)]	Automatic; conveyor[(e)]
Cleaning and phosphating:		
Capacity of solution and rinse tanks	190 L (50 gal)	190 L (50 gal)
Solution and rinse temperature	66 °C (150 °F)	66 °C (150 °F)
Prime coating:		
Capacity of dip tank	. . .	190 L (50 gal)
Drying	. . .	12 m (40 ft) infrared oven[(f)]

Finish coating:		
Capacity of dip tank	190 L (50 gal)	190 L (50 gal)
Drying	Air dry	12 m (40 ft) infrared oven(f)

(a) 75 by 75 mm (3 by 3 in.) L-shaped bracket, 3.2 mm ($\frac{1}{8}$ in.) thick, 25 mm (1 in.) wide.

(b) L-shaped bracket, of 4.8 mm ($\frac{3}{16}$ in.) stock, 100 mm (4 in.) wide and with one 100 mm (4 in.) leg, one 150 mm (6 in.) leg.

(c) Proprietary phosphate cleaner coater used; 1-min immersion in solution and rinse tanks, followed by drying.

(d) 90 to 100 pieces per load.

(e) Hooks 305 mm (12 in.) apart.

(f) Parts conveyed through oven; drying cycle, 10 to 12 min at 160 °C (325 °F)

Flow Coating

In flow coating, paint is pumped from a storage tank through properly positioned nozzles, onto all surfaces of parts, as they are conveyed. Excess paint drains back to the storage tank for recirculation. Paint films applied by flow coating are wedge shaped, thinner at the top and thicker at the bottom of painted parts. In flow coating, utilization of paint approaches 95% as opposed to about 50% for atomized air spraying and 70 to 80% for dipping. Properly designed flow coat machines with vapor chamber flow-out reduce solvent losses and eliminate tears, sags, and curtains.

Flow coating is used extensively to paint panels for home appliances. Flow coating is also used to coat parts with recesses inaccessible to spraying, to coat parts (such as bedsprings) for which good appearance is desirable but is secondary to complete coverage and economical application, and to coat intricate parts that are too open in design to permit efficient spray painting and too large to be practical for dip painting.

Figure 3 shows a large assembly which, because of its size and construction, is an example of a part for which flow coating is the most efficient method of painting. Spraying would be inefficient because of overspray, and dip coating would require a large quantity of paint to fill the dip tank. However, flow coating would be impractical for a similar assembly twice as large, and spray painting would be preferred.

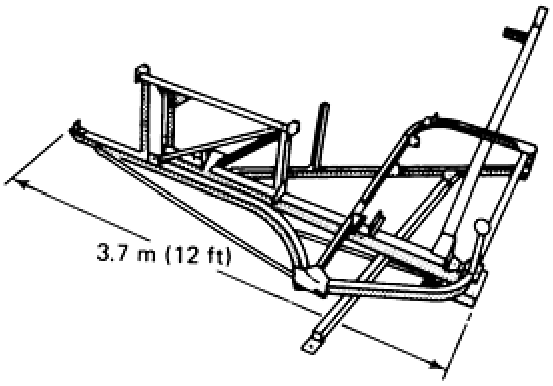


Fig. 3 Assembly for which flow coating is an efficient painting method

Equipment for Flow Coating

Basic equipment for flow coating consists of a chamber, a paint-storage tank, a pump, a drain-off section, and continuous conveyors. Because flow coating ordinarily is used only for high-volume production parts, equipment usually is set up as part of a continuous process, which may include cleaning, phosphating, drying, prime flow coating, finish flow coating, and baking. One conveyor may carry the parts through all operations. Process variables that require close control are nozzle pressure, viscosity and temperature of the paint, and hanger design and spacing of the parts.

Pressure control of paint in the circulating system is critical, particularly at the nozzle. Excessive pressure causes the paint to flow off the parts at too high a rate, resulting in high solvent losses and bubbles in the paint. Too low a pressure leaves areas on the work uncoated or improperly coated. Pressures vary from 0.02 to 0.2 MPa (3 to 30 psi). The higher pressures are used to coat difficult-to-reach or recessed areas. The lowest pressure that can be used in a particular operation is the most economical when solvent loss is considered.

Paint viscosity must be closely controlled. Viscosity that is too high causes poor flow-off of paint from the work. This results in sags, beads, blistering, and other defects associated with excessive paint thickness. Viscosity that is too low results in excessive solvent loss and inadequate film thickness. Viscosities are held within the range of 18 and 32 s (No. 2 Zahn cup), although paints with a No. 2 Zahn cup viscosity as high as 100 s have been used. Viscosity must be adjusted for each paint and each differently shaped part. Once the optimum viscosity has been determined, it should be maintained.

Temperature control of paint is essential. Too high a temperature results in excessive solvent loss and may cause instability of the paint. Too low a temperature requires increased use of solvents to maintain proper viscosity and can result in inadequate film thickness. Although temperatures as low as 16 °C (60 °F) and as high as 38 °C (100 °F) have been used, 21 to 32 °C (70 to 90 °F) is the recommended temperature range.

Drain-off chambers, enclosed tunnels immediately adjacent to the coating chamber, are incorporated in many installations. In drain-off chambers, a high concentration of solvent vapor is maintained to retard drying. This eliminates beads, bubbling, and other surface defects that result when flow-off of paint is incomplete. Some installations include an electrostatic detearing device to remove any beads or drops of paint still clinging to the edge of the part.

The equipment and production requirements for using flow coating to paint two steel production parts are discussed below. One part is a step hanger (an angle bracket) produced from 4.8 mm ($\frac{3}{16}$ in.) stock 50 mm (2 in.) wide, with two legs 355 and 125 mm (14 and 5 in.) long, respectively. The other, a bracket for holding a fire extinguisher, is produced from 1.5 mm (0.060 in.) stock and has legs 305 and 75 mm (12 and 3 in.) long; a metal clamp is attached to the 305 mm (12 in.) leg to retain the extinguisher. The production requirements are as follows:

Part A

- Step hanger, 4.8 mm ($\frac{3}{16}$ in.) thick; maximum dimensions 125 by 355 mm (5 by 14 in.)
- Production rate, 540 pieces per hour

Part B

- Bracket for holding fire extinguisher, 1.5 mm (0.060 in.) thick; maximum outside dimensions, 75 by 305 mm (3 by 12 in.)
- Production rate, 720 pieces per hour

Both parts

- Clean and phosphate, using proprietary phosphate cleaner coater with 2-min immersion in solution and rinse tanks before drying; color coat with alkyd baking enamel (no prime coat)

Equipment requirements for both parts are as follows:

Work handling	Overhead conveyor(a)
Cleaning and phosphating(b)	
Solution and rinse tanks	190 L (50 gal)
Solution and rinse temperature	66 °C (150 °F)
Flow coating	
Flow coater	Conventional; 2 nozzles
Nozzle pressure	275 kPa (40 psi)
Drying	Infrared; 7 to 8 min; 160 °C (325 °F)

(a) 305 mm (12 in.) hook spacing.

(b) Proprietary phosphate cleaner coater used; 2-min immersion in solution and rinse tanks, then drying

Roller Coating

Roller coating, or coil coating, is a high-speed machine painting process used for continuous coating of sheet and strip stock. The process consists of transferring an organic coating from a revolving applicator roller to the surface of sheet or strip as it is passed through the machine. The top, the bottom, or both surfaces may be coated in one pass. In addition, two and sometimes three coating layers can be applied in one pass. Paint can be rolled on with excellent control of film thickness.

Roller coating is one of the most economical and environmentally safe painting processes. Steel strip can be roller coated, baked, and coiled for later fabrication into parts, such as the slats used in the manufacture of Venetian blinds, building products, automotive parts, and a host of other items.

Because this process is similar to rotary printing, designs can be reproduced and repeated in any pattern necessary. Thus, bottle caps, food cans, toys, and similar painted parts can be produced economically. The designs are roller coated on the metal strip before it is stamped or formed to shape.

Equipment for Roller Coating

Equipment for roller coating, similar in function to a rotary printing press, may vary from a relatively simple machine to an elaborate complex installation several hundred feet long. The equipment transfers an organic coating from the revolving applicator roll to sheet or strip as it travels through the machine. The thickness of the film is regulated by a metering roll that controls the amount of paint transferred to the applicator roll.

Applicator rolls must be made of material that does not swell, soften, or dissolve from contact with paint. Usually, applicator rolls are made of, or faced with, a resilient material, such as neoprene or polyurethane. Resiliency permits rolls to conform to irregularities found in commercial stock.

Almost every organic coating material can be applied by roller coating. Usually, the paints use slow-evaporating solvents and are applied at higher viscosities than in other painting methods, which permits close control of paint flow and film thickness.

Curtain Coating

Curtain coating is a method of applying finishes at high speeds with little paint loss. In curtain coating, flat or shaped strip and sheet are moved by conveyor belt beneath a pump-fed reservoir with an adjustable slot opening at its lower edge. The slot opening provides a controlled continuous wet curtain of coating flowing onto the work. Some curtain coaters have heads that function by use of gravity overflow of material over one side of the reservoir.

The pressure-fed curtain coater applies a uniform wet film to flat or shaped surfaces of practically any material. Coatings can be applied between 13 and 2540 µm ($\frac{1}{2}$ and 100 mils) thick, depending on coating characteristics, conveyor speed, and parts being coated. Deposited films are smooth and uniform with no ridges, washboarding, or similar effects that can be found with roller coating. No sagging or uneven thickness occurs as with flow coating and dipping.

Equipment for Curtain Coating

Curtain coating equipment consists of a conveyor belt that moves the items to be coated under a special coating head. This coating head may be either pump fed or gravity overflow. In the former, the reservoir has an adjustable slot opening at its lower edge that provides a controlled continuous wet curtain of coating on the work as it moves past. In the latter, the material flows over one side of the reservoir. Viscosity must be closely controlled and flow properties adjusted to form a good curtain. A collection trough is located under the head and any of the coating that does not fall on the work is returned to the pump for reuse. Figure 4 shows examples of curtain coating equipment.

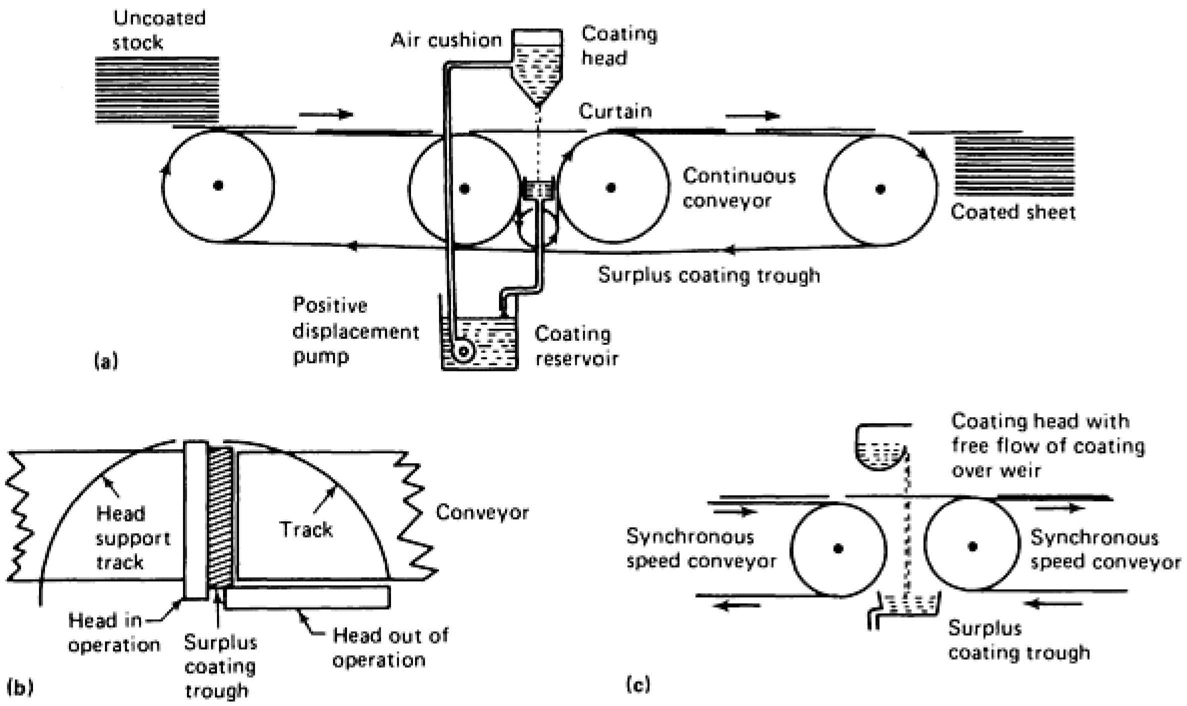


Fig. 4 Examples of curtain coating equipment. (a) Pressure head curtain coater. (b) Double head machine gives fast color changes, applies two component coatings. (c) Gravity flow coater with synchronized conveyors

Tumble Coating

Tumble or barrel coating is one of the most economical means of coating large numbers of small pieces. It is particularly useful for such articles as nails, screws, buttons, and other metal objects weighing less than 0.5 kg (1 lb). Tumble coating is also a good method for pretreating objects to be coated by other systems. In barrel coating, a predetermined weight of coating, adequate to produce a uniform finish over each item without causing drops to form, is poured over the items. The barrel is rotated to distribute the coating evenly over the parts. Drying air is then forced through the center axle and circulates through the continuously moving charge, finally escaping through the other end of the axle and removing solvent vapors. After sufficient air has passed through, parts are dry and ready for packing. In some cases, drying is not done in the barrel. Pigmented coatings are a good example, because the rubbing process during drying damages the appearance of the coatings. In this case, the parts are discharged wet onto a screen and allowed to dry by forced air or natural air circulation. The slight blemishes that occur at the points of contact are virtually invisible.

Electrocoating

Electrocoating is a process in which the object to be coated is dipped into a tank of water-borne paint, and a current is passed through to charge the paint particles electrically. The charged paint particles migrate to the object to be coated, which has an opposite charge. When the object is reached, the paint materials come out of solution and coat the surface. The article is then withdrawn from the tank, rinsed with water to remove any undeposited paint, and baked. This process is also known as electrodeposition, electrophoretic deposition, or electropainting.

Coating Thickness. Paint particles migrate to the part to be coated when a sufficient potential difference, usually between 80 and 180 V, is applied between the part and the tank or separate electrodes. Coating thickness depends on complexity of the part, time, temperature, voltage, solids content, throwing power of the paint, and its ability to penetrate recessed areas. Coating thicknesses up to 38 μm (1.5 mils) are obtainable. The applied coating has a solids content of about 95% and is essentially water insoluble. The relatively high electrical resistance of the coating drastically reduces the rate of deposition as thickness increases. The thickness on easily reached portions of a part builds up rapidly to a near-maximum value and then levels off, and the thinner coating at recessed portions continues to increase in thickness until a very uniform paint film is deposited on even the most complex parts.

Resins used for electrocoating include:

- Maleinized drying oils
- Styrenated and vinyl toluenated maleinized oil
- Phenolic modified maleinized oils
- Alkyds
- Epoxy esters
- Styrene-alkyl alcohol copolymer esters
- Acrylic copolymers
- Polyesters

Advantages and Limitations. Electrocoating offers several advantages over more conventional coating processes. These include:

- The process lends itself to total automation, reducing labor costs.
- Intermixed parts with different shapes and sizes can be coated.
- A more uniform coating thickness is obtained.
- Good edge and recess coverage without heavy buildup produces better corrosion resistance.
- Absence of runs and sags minimizes rework.
- Significant paint savings of as much as 30% are obtainable.
- Dangers of fire hazard are absent.

The disadvantages of the process should also be considered:

- Cost of equipment is high.
- Temperature, pH, and alkali content of the coating material must be controlled closely.
- Pretreatment and rinsing requirements are more stringent than with conventional coatings.
- Surface defects in the substrate are visible through the coatings.
- Only a single film can be applied.
- Changing colors is difficult and expensive.

Cathodic Systems. All early electrocoating systems were anodic. However, many have recently been converted to cathodic. The advantages of cathodic over anodic systems are as follows:

- In cathodic systems, unlike anodic, metal dissolution does not occur at the cathode. The absence of electrodissolved metal in the film results in better film properties, especially in the case of white electrodeposits over steel.
- Cathodic deposition tends to deposit over contaminants in the metal surface, and they do not appear in the film.
- Salt spray and humidity resistance is improved.
- Cathodic coatings have better color consistency over welded areas.

Equipment for Electrocoating

Electrocoating systems usually include a dip tank, power supply, heat exchanger, filters, plane replenishment tanks, and a baking oven. Dip tanks are equipped with stirrers and circulating pumps to keep the paint homogeneous. Tanks can range in size from several hundred to several thousand gallons. In an anodic system, parts may be made the anode or the cathode, and the tank the other electrode, or separate metal electrodes can be placed in an insulated tank. For cathodic systems, tanks must be insulated and kept at ground potential. A relatively large power supply is needed, with voltage ranging from 50 to 400 V and amperage from 50 to 4000 A. Heat exchangers are needed to keep the bath at optimum plating temperature, because the electrodeposition process generates heat. Ultrafilters are used for reclaiming dragout paint. Figure 5 illustrates an electrocoating system layout. Figure 6 depicts a basic layout of a cathodic electrodeposition system.

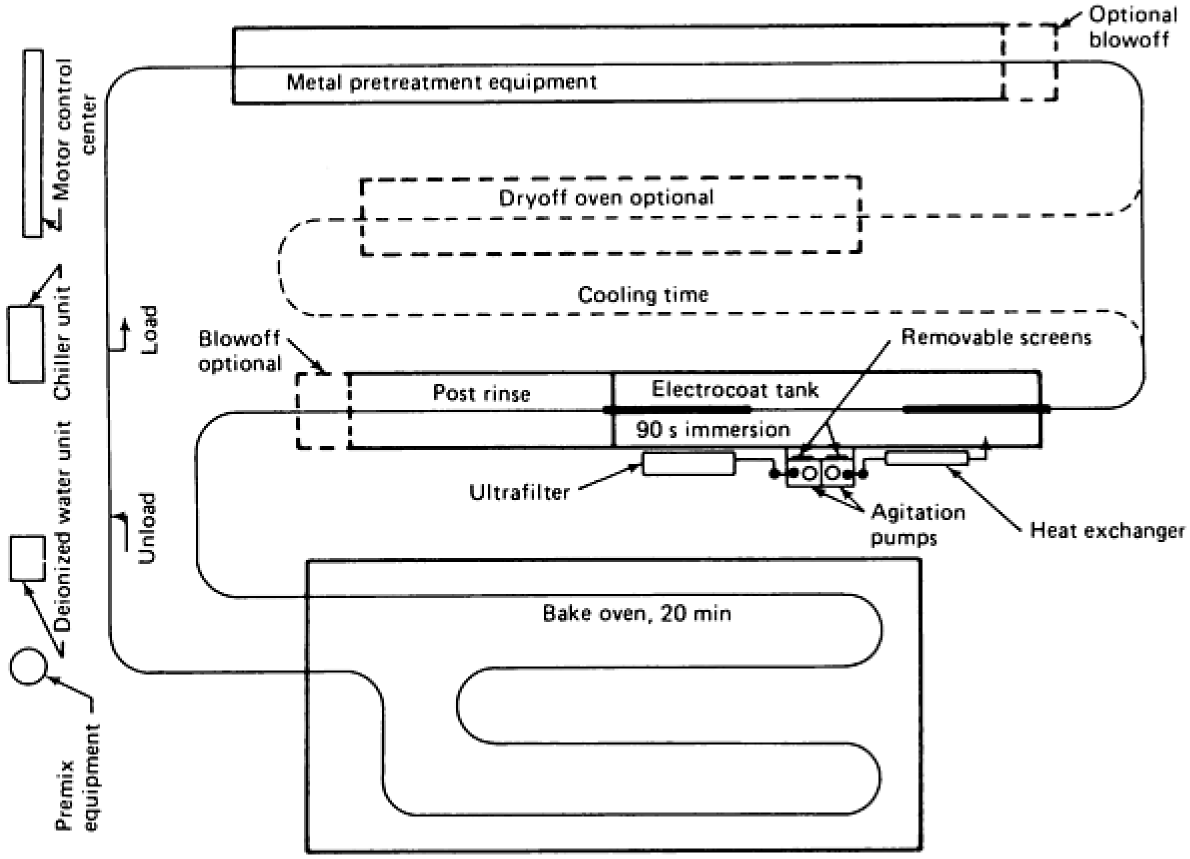


Fig. 5 Electrocoating finishing system

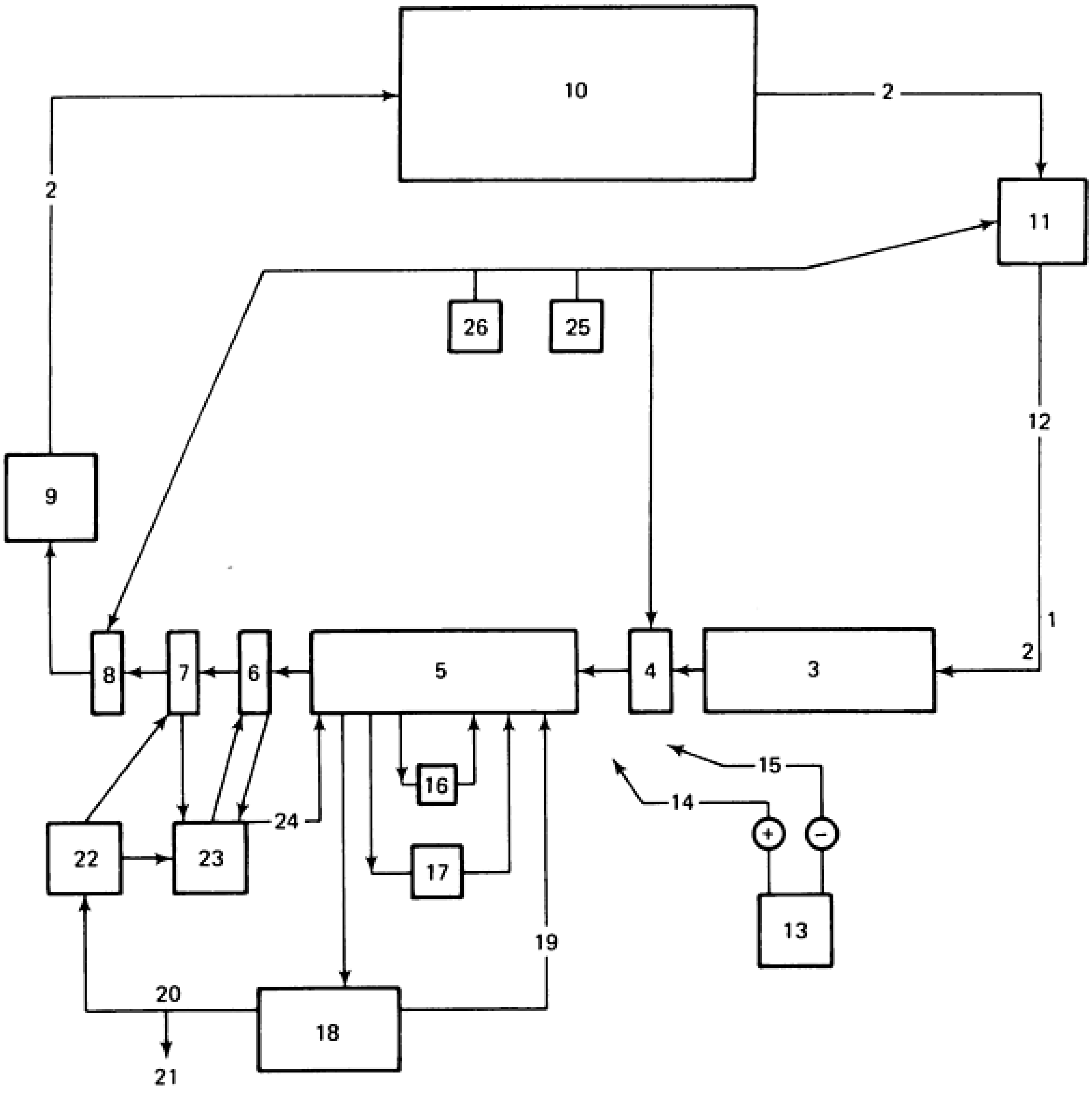


Fig. 6 Cathodic electrodeposition coating system. (1) Load area. (2) Conveyor. (3) Pretreatment. (4) Deionized water rinse. (5) Electrodeposition tank. (6) Recirculated permeate rinse. (7) Fresh permeate rinse. (8) Deionized water rinse. (9) Dryoff. (10) Curing oven. (11) Deionized quench for cooling. (12) Offload area. (13) Source for direct current. (14) To anodes in paint bath. (15) To work on conveyor. (16) Particle filter. (17) Cooler. (18) Ultrafilter. (19) Paint solids return. (20) Permeate. (21) Controlled flow to waste. (22) Permeate storage. (23) Recirculated permeate. (24) Overflow permeate. (25) Source of deionized water. (26) Deionized water storage

Powder Coating

Powder coatings are paint films that are applied to parts as a dry powder. The powders are basically the same type of polymers and resins (see Table 1) as used in liquid coatings except no solvent is used. Instead, the coating composition is ground to a fine powder. After application the film is formed by fusing the powder particles at temperatures above the melting point of the powder. Powder coatings are used on a wide range of products including metal furniture, wire goods such as baskets and racks, appliance housings, chemical and laboratory equipment, and aircraft and automotive components. The advantages and disadvantages of powder coating systems are given below:

Advantages

- The process meets all current EPA requirements for reduction in VOC emissions.

- Material use can approach 100% if powder can be collected and reused.
- Maintenance is less, because powder can be vacuumed from any unbaked surface.
- Exhaust air volume is greatly reduced from that used for solvent-borne systems.

Disadvantages

- Color change is difficult, because a separate booth is usually required for each color.
- Color matching is more difficult with powder coatings than with solvent coatings.
- Powder coating materials are discrete particles, each of which must be the same color. No tinting or blending by the user is possible.
- Applying films of 25 μm (1 mil) or less is extremely difficult, and at times, impossible.

Equipment for Powder Coating

The three primary methods of applying powder paints include: electrostatic spray, fluidized bed, and electrostatic fluidized bed. In addition, several variations can be applied to the basic electrostatic spray process. The best process for a particular application depends on such factors as: end-use of coating, coating thickness, size and shape of parts, rate of production, and material handling techniques.

Electrostatic spray is the most versatile and flexible application process. The electrostatic disk, cloud chamber, and Gourdine tunnel are variations of the basic electrostatic spray process.

The basic electrostatic spray process uses spray guns to apply powder to the parts (Fig. 7). These guns may be manual or automatic. Powder is delivered to the guns through flexible tubing from a supply hopper. At the guns, the powder is charged electrostatically. Coating parts are then carried to the oven, where the powder melts, flows, and fuses to the surface. Air exhausted from the booth serves three functions: maintains the powder-air concentration below the minimum explosive concentration (MEC), keeps powder from drifting outside the booth, and begins the powder recovery process. The dust collection equipment used may be a cyclone, a bag filter, or a cartridge filter. Air exhausted from the dust collector is returned to the plant. The moving filter belt is a modification of the basic powder recovery technique. An endless belt of porous fabric forms the floor of the spray booth. Booth exhaust air passes through the belt into a plenum beneath, and the powder is left on the belt. The belt carries the powder to the end of the booth beneath a vacuum pickup head.

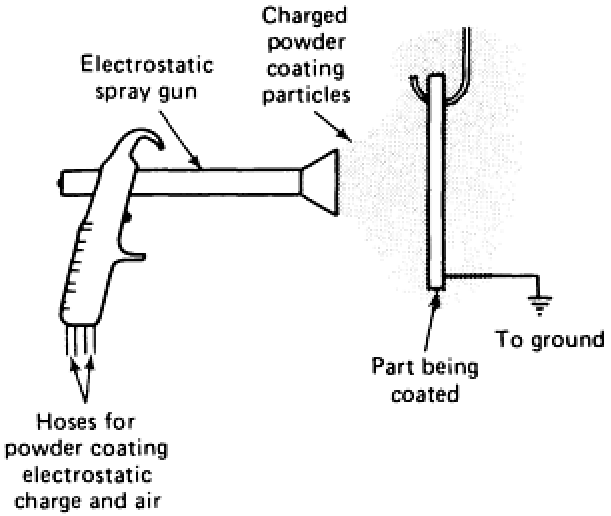


Fig. 7 Electrostatic spray system for application of powder coatings

The electrostatic disk is a variation of the electrostatic disk for liquid paint. The disk propels the charged particles outward by air force as it reciprocates. The workpiece passes around the disk in an omega booth.

In a cloud chamber, automatic electrostatic spray guns create a cloud of electrostatically charged powder in an almost totally enclosed booth. Powder not adhering to parts conveyed through the booth falls to a fluidized bed in the bottom of the booth. The powder is withdrawn from the fluidized bed and recycled to the guns. Only enough air is drawn into the booth to keep powder from drifting from the workpiece openings. Because there is the constant potential for exceeding the MEC, cloud chambers must be equipped with an explosion suppression system.

In the Gourdine tunnel, powder is sprayed in a nonconductive plastic tunnel. The tunnel is not grounded, and charged particles are not attracted to its surface. The parts themselves are grounded, and they move through the tunnel, first passing through the charging section where powder is sprayed from electrostatic guns on both sides of the workpiece. Parts then pass into a precipitation chamber, with interior walls lined with conductive plates charged at the same polarity as the powder particles. Air introduced into the tunnel carries particles not adhering to the part into the precipitation chamber. The particles are repelled by the charged plates and directed back toward the workpiece. The system is said to achieve 90% deposition efficiency, needing no recovery system. Like the cloud chamber, the Gourdine tunnel also needs explosion protection.

Conventional Fluidized Bed. In the fluidized bed process, dry air is forced through a porous plate or membrane into an open top tank that is about half filled with powder (Fig. 8). The air suspends the powder, increasing its volume, and makes the powder act like a fluid. The item to be coated is preheated above the fusion point of the powder and is dipped in the powder for a few seconds. The powder that comes in contact with the item fuses and forms a coating. The item is then removed, shaken or blown to remove any loose powder, and either recooled or reheated to obtain a more uniform film. Reheating is used if a thermoplastic powder is used or if a thermoset powder is used, and the film is to be cured. With the fluidized bed method, film thicknesses of 150 to 1525 μm (6 to 60 mils) can be obtained. Films of less than 150 μm (6 mils) are difficult to obtain with this method. This procedure does not coat recesses well and cannot coat one side of an object without the use of masking.

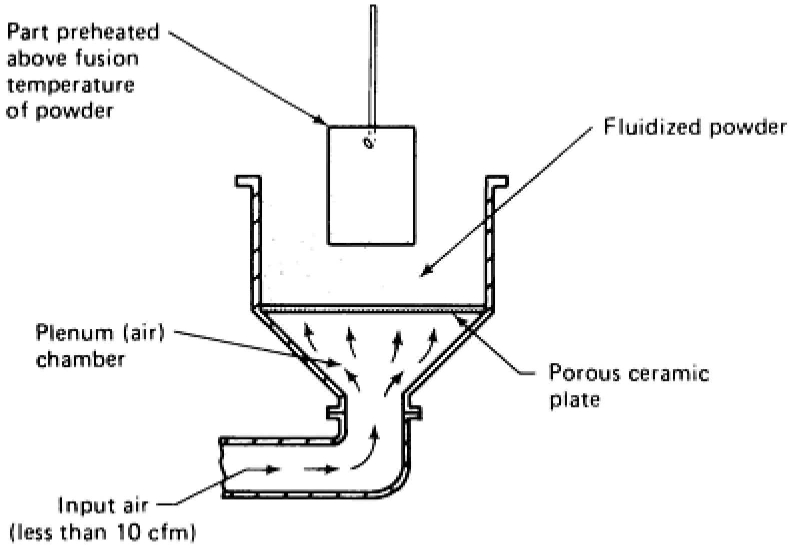


Fig. 8 Fluidized bed system for application of powder coatings

Electrostatic Fluidized Bed. In this system, an electrode is incorporated in the powder chamber (Fig. 9). The powder is fluidized as in the conventional procedure. However, high voltage is applied, and the particles receive a charge and rise in a fine cloud above the fluidized bed. When a grounded part is passed into or through the cloud, the charged particles are attracted to and adhere to the part. With this system, preheating is not necessary. A smaller amount of powder is necessary, and the less dense powder suspension permits better control of film thickness. This system also eliminates the need for dipping, because powder rises to the part. Because the part is not preheated, powder can be removed from areas that are to be left bare, eliminating the need for mechanical masking and the problems associated with it.

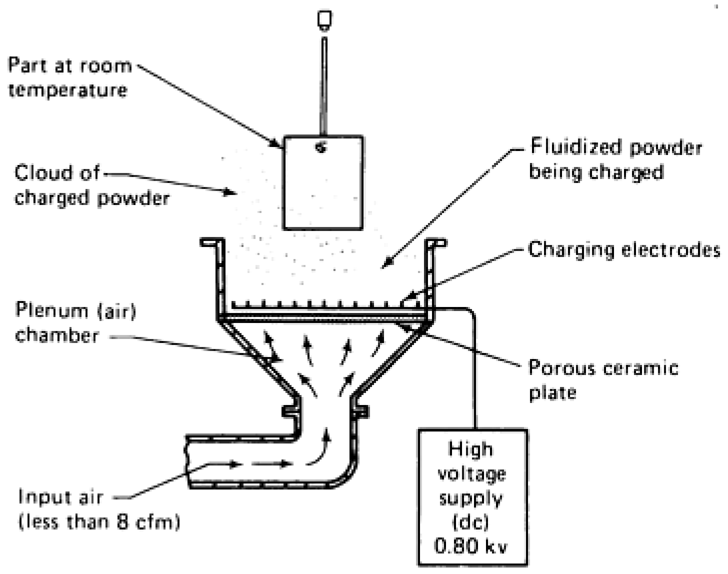


Fig. 9 Electrostatic fluidized bed for application of powder coatings

Curing of Paint Films

Curing is the process of converting an applied coating to a dry film. Baking or thermosetting coatings require heat to cure. Those coatings that dry by evaporating the solvent are air drying or thermoplastic. Ovens are used to supply the energy needed to cure the film and/or evaporate the solvent.

Heat is transferred by conduction, convection, or radiation. Convection and radiation are used in ovens for baking paint. Conduction takes place in shielded areas only incidentally. Convection baking ovens usually are heated by gas, although oil, electricity, or steam may also be used. Radiation ovens may be heated by gas or electricity, although electricity is used more frequently.

Batch ovens are used for baking paint films on parts produced intermittently, in limited quantities, or on parts not easily conveyorized. These ovens, which transfer heat by convection, consist of one or more insulated compartments equipped for heating, recirculating, and exhausting air. These compartments also regulate and control temperature.

Batch ovens range in size from small single-compartment units that accommodate only a few small pieces, to large units with single or multiple compartments for baking several bulky parts simultaneously. Multiple-compartment batch ovens may be used for simultaneous production of separate runs of parts that require different baking cycles. Batch ovens may be direct fired or indirect fired.

Direct-fired batch ovens (Fig. 10a) are used more often than indirect-fired ovens. In direct-fired ovens, fuel is burned directly in the circulated air. Direct-fired ovens are more economical to operate, because the heat does not have to be conducted through the walls of a heat exchanger. The disadvantage of direct-fired ovens is that the paint films are exposed to the products of combustion, which may harm some coatings.

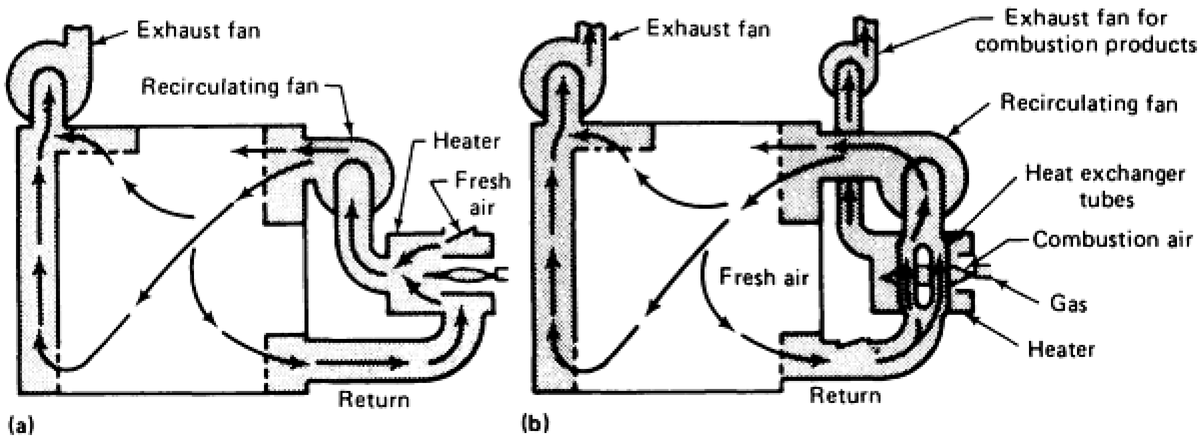


Fig. 10 Convection ovens for curing of paint coatings. (a) Direct fired. (b) Indirect fired

The solvent vapors extracted from the paint are burned when they are passed through the flame with the recirculated air. Proper circulation and introduction of a sufficient supply of fresh air are essential--particularly during the early minutes of the cycle, when the rate of solvent evaporation is greatest. The required dilution rate for safe operation depends on the total quantity of solvent present and on its lower explosive limit. Insurance and safety organizations have established minimum exhaust rates for safe operation of direct-fired baking ovens for most of the solvents used in paint films.

Most regulations require maintaining 25% or less of the lower explosive limit (LEL) of solvent in the oven. This is done by calculating solvent emission at full oven load and exhausting sufficient air to keep solvent level at or below 25% of LEL. New solvent level monitoring equipment allows automatic damper control of oven exhaust to maintain safe solvent levels, depending on actual load. This reduces energy requirements by reducing exhaust rates and provides richer solvent exhaust for more efficient use of incineration for VOC emission control.

Indirect-fired batch ovens (Fig. 10b) burn the fuel outside the oven walls, and the oven is heated by means of heat-exchange surfaces. Indirect-fired ovens are less efficient and consume more fuel than direct-fired ovens. The advantages of indirect-fired ovens are that the paint film is protected from the products of combustion, and solvent vapors are not exposed directly to the flame.

Continuous ovens are used in finishing parts produced in large quantities. Parts are conveyed through the ovens as a cycle in a continuous finishing process that may include cleaning, phosphating, drying, painting, and baking. Continuous ovens may use either convection or radiation.

Convection continuous ovens, direct fired or indirect fired, may use gas, oil, electricity, or steam as the source of heat, although steam usually limits oven temperature to 150 °C (300 °F). Figure 11 illustrates an indirect-fired continuous convection oven. Two 180° turns have been incorporated in the conveyor path to shorten the distance the heat must travel from the burner. Ductwork may be installed to direct and control the distribution of the heated air. A large volume of hot air can be directed to the area where the cold work enters and the volume of air can be limited to the area where the work has attained the desired temperature.

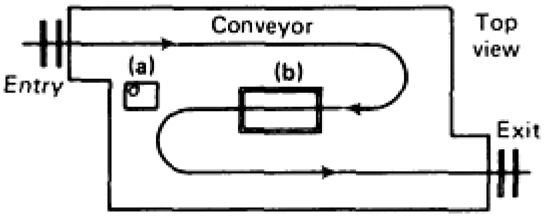


Fig. 11 Indirect-fired continuous convection oven for curing of paint coatings. (a) Exhaust system. (b) Burner

and recirculating fan

Heat retention is a problem in these ovens, because parts being conveyed must be permitted to enter and leave the oven in a continuous process without restriction. One method for heat retention is to slope entrance and exit chambers downward from the oven section, trapping rising heated air. For ovens into which the conveyor enters and exits at the same level as the hot zone, heat retention can be accomplished by high-velocity air seals (air curtains) across the entrance and exit of the oven.

Radiant continuous ovens are widely used. Using infrared radiation, radiant ovens require less insulation or heat sealing, as well as less complicated ventilation and exhaust systems. Many infrared continuous baking ovens have an enclosed tunnel construction to take advantage of the air heated by contact with the parts. A simple baking tunnel may consist only of racks of lamps on each side of the conveyor line. Heat is produced as required as parts are conveyed through the system, permitting a more flexible use of the baking facilities.

Infrared generators may be either electric or gas fired. Electric infrared generators are glass-lamp, ceramic-coated resistance wire, or quartz. Gas-fired infrared generators consist of ceramic grids heated by gas until the grids are radiant.

In infrared baking, electrical energy or heat energy from the burning gas is converted into radiant energy, which, when directed to the wet paint surface, is rapidly absorbed by both the paint film and the metal beneath it. The surface beneath the paint heats up as rapidly as the paint. This accomplishes solvent evaporation simultaneously throughout the thickness of the paint film, or in some cases, from the inside to the outside. Pits and blisters are thus minimized, and a uniform polymerization of the paint film is accomplished. This is a distinct advantage over convection baking, in which the outside paint surface is first to heat. Infrared baking decreases the tendency to form a skin or shell that traps the solvents under the surface, creating pressure and leading to the formation of pinholes or blisters when the vapors escape. Because it penetrates, infrared radiation also bakes faster than convection heat, provided that the entire painted surface is exposed to the radiant heat.

High-velocity ovens expose parts to very high temperatures for short times; 205 to 315 °C (400 to 600 °F) for 1 to 3 min is typical. If parts can tolerate high surface temperatures for a short time, high-velocity ovens may be an economical alternative to conventional ovens.

Heat Recovery. The combination of increased energy costs and stricter air pollution regulations in recent years makes the recovery of oven exhaust gases increasingly important. As much as 80% of the fuel energy may be exhausted from the oven. Considerable progress is being made in heat exchangers, afterburners, fume incinerators, and catalytic converters to recover some of the oven exhaust energy. This energy may be used to provide added heat source to preheat incoming prepared air for the oven, or to supplement the oven fuel supply. Oven manufacturers should be consulted for most recent developments in energy recovery.

Convection Baking Time and Temperature. Time and temperature of the baking cycle in convection ovens are dictated by the polymerization characteristics of the paint. Although baking temperatures often are expressed as oven temperatures, these may not be sufficient to ensure complete polymerization. Until the metal reaches baking temperature, it is conducting heat away from the paint at the interface. This may reduce the time at temperature of this part of the film enough to prevent complete polymerization. Thus, baking cycles are specified in terms of time, which makes allowance for the metal to attain the proper temperature.

The graph in Fig. 12 illustrates the importance of metal temperature in baking. Metal temperatures have been plotted against time for two panels of equal area but of different mass. Assuming that a baking temperature of 150 °C (300 °F) is desired, the 24-gage (0.607 mm, or 0.0239 in.) cold rolled steel panel can reach 150 °C (300 °F) approximately 10 min before the 13 mm ($\frac{1}{2}$ in.) thick casting.

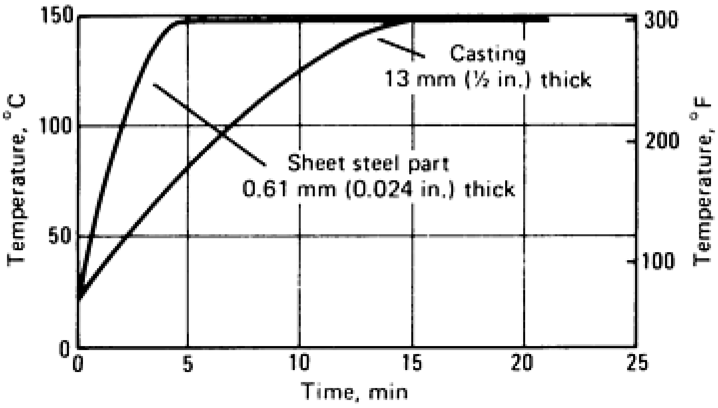


Fig. 12 Times required for interfaces of two steel parts of equal area but different mass to reach baking temperature of 150 °C (300 °F)

Adjusting the cycles so that the areas under the curves are approximately equal usually gives comparable baking results. This is not true, however, if the paint being baked has a critical curing temperature. Some urea-alkyds, for example, cannot polymerize at temperature below 120 °C (250 °F).

Prebake Solvent Evaporation. If paints are exposed to the heat of the oven too soon after being applied, particularly when infrared heat is used, the solvent materials vaporize too fast and disturb the continuity of the paint film. Vapors may also become entrapped because of incomplete ventilation in the oven. This results in a partial breakdown of the paint film and a chalky appearance. If vapor concentration is high enough, the paint film may break down completely.

To avoid these problems, sufficient time and ventilation should be allowed to permit some solvent evaporation and dispersion before baking. For batch baking, parts are allowed to stand in a well-ventilated area for a period of time before they are placed in the oven. In conveyorized painting and baking, the conveyor should pass through a well-ventilated area before carrying the parts into the oven. In this situation, forced circulation or clean air hastens the evaporation and dispersion of the solvent vapors, permitting a shorter interval of time and distance for conveyor travel.

Defects Attributable to Improper Baking. Table 7 lists some of the defects in paint films that may result from improper baking, the causes, and corrective measures that should be taken. Equipment and operating requirements for baking two specific parts are discussed in the following paragraphs.

Table 7 Causes and corrections of paint film defects associated with baking

Cause	**Correction**
Soft film	
Baking cycle inadequate	Increase time or temperature of baking
Metal not reaching curing temperature	Increase time or temperature of baking[(a)]
Pinholing or blistering	
Entrapment of solvent vapors because of quick drying at baking temperature	Extend air-drying time before baking to increase evaporation of solvent

Wrinkling	
Unequal curing, because of extreme temperature difference of film and metal	Extend air-drying time before baking, or change from convection to radiation
Hazing or poor gloss	
Temperature too high	Reduce temperature; decrease time
Combustion fumes in oven attacking paint	Increase input of fresh air and air circulation in oven
Venting of solvent vapors from oven not fast enough	Increase input of fresh air and air circulation in oven
Discoloration	
Temperature too high	Reduce oven temperature
Hot spots in oven	Control circulation of air in oven
Discontinuity of coating	
Solvent vapors collecting in oven to high concentration	Increase air input and circulation in oven; allow longer air-drying time
Entrapment of solvent vapors because of quick drying at baking temperature	Extend air-drying time before baking
Brittleness	
Overbaking (excessive time or temperature)	Careful control of time and temperature

(a) In convection ovens, adjust louvers to deliver greatest concentration of heated air to area in which parts have not attained baking temperature, or change to radiation heating.

Example 4: Baking of a Spray Painted Wing Bolt.

The upper half of a 64 mm ($2\frac{1}{2}$ in.) long shouldered wing bolt was spray painted to a wet film thickness of 30 μm (1.2 mils) with glossy bronze baking enamel, using toluene as the solvent. Before being painted, the parts were placed in aluminum racks incorporating 156 holes that accepted the wing bolts up to the shoulder on the body of the bolt, serving to mask the lower part from the paint. Parts were painted, air dried for 5 to 6 min, then baked at a production rate of 1500 pieces per hour. The operating conditions were the following:

Weight of each piece	0.032 kg (0.0702 lb)
Number of pieces per rack	156
Weight of rack plus load	5.089 kg (11.22 lb)
Pieces processed per hour	1500
Type of baking enamel	Glossy bronze
Solvent used	Toluene
Baking cycle	20 min at 150 °C (300 °F)

The requirements for the baking equipment included the following:

- *Racks:* aluminum sheet, 710 by 660 mm (28 by 26 in.) and 1.0 mm (0.040 in.) thick, with 13 rows of 12 equally spaced 9.5 mm ($\frac{3}{8}$ in.) diam holes (156 holes); weight 0.12 kg (0.27 lb)
- *Oven:* electrically heated single-compartment batch oven, 750 mm (30 in.) square and 622 mm (24.5 in.) high (inside dimensions), with shelves accommodating five racks of parts, which are placed in oven every 30 min
- *Heat input:* 13.3 kW/h, assuming that oven is at heat and that 15 min is required for load to reach oven temperature
- *Exhaust air:* 0.46 m^3/s (98 ft^3/min) at room temperature; 0.670 m^3/s (142 ft^3/min) at 150 °C (300 °F)
- *Air recirculation rate inside oven:* 3.8 m^3/s (800 ft^3/min) at 150 °C (300 °F)
- *Space for oven and controls:* width, 1625 mm (64 in.); depth 915 mm (36 in.); height, 2135 mm (84 in.)

Example 5: Baking of a Spray Painted Angular Welded Frame Assembly.

A welded frame assembly, angular in shape, 2 m (8 ft) long with each leg approximately 0.9 m (3 ft) long, was produced from 6.4 mm ($\frac{1}{4}$ in.) steel plate, and weighed approximately 410 kg (900 lb). The parts were spray painted to a wet film thickness of 30 μm (1.2 mils), using a glossy yellow baking enamel with xylene as the thinner. Before baking, the parts were air dried 10 to 20 min. The parts were supported during baking by special dollies designed to have minimum contact with the parts. Three parts were processed each hour. Operating conditions used in this process included:

Weight of each assembly	408 kg (900 lb)
Assemblies painted	3 per hour
Baking enamel	Glossy yellow

Solvent used	Xylene
Baking cycle	45 min at 135 °C (275 °F)

The requirements for the baking equipment included the following:

- *Dollies:* of steel construction, designed to support frame assemblies with minimum contact during finishing; 3 m (9 ft) long, 1 m (4 ft) wide, 380 mm (15 in.) high; weight 90 kg (200 lb). Nine required, three each in spray room, oven, and cooling area
- *Oven:* electrically heated walk-in batch oven with three compartments, each 1.5 m (5 ft) wide, 3.0 m (10 ft) deep, 2 m (6 ft) high
- *Heat input:* 95.6 kW/h, assuming that one dolly and part are replaced every 20 min and that 15 min is required for one dolly and part to reach oven temperature
- *Exhaust air:* 1.26 m^3/s (267 ft^3/min) at room temperature; 1.75 m^3/s (370 ft^3/min) at 135 °C (275 °F)
- *Air recirculation rate inside oven:* 30.68 m^3/s (6500 ft^3/min) at 135 °C (275 °F)
- *Space for oven and controls:* width, 6.1 m (20 ft); depth, 3.4 m (11 ft); height, 3.0 m (10 ft)

Radiation Cure Coatings

Radiation cure coatings are organic monomer or polymer resin binders of low viscosity that polymerize to a cured film when subjected to radiation. Two main types of radiation curing are used: electron beam (EB) and ultraviolet (UV). In both processes, the materials used are solvent free and 100% reactive, giving off little vapor, creating no pollution problems. Curing time ranges from a fraction of a second to minutes depending on the source of radiation. Curing is achieved at or slightly above room temperature, which allows heat sensitive materials, such as plastics, wood, and electronic components to be coated without harm. Because no baking ovens are needed, less floor space is required for finishing. The differences between EB and UV curing systems must be considered:

- Electron-beam radiation is much stronger than UV. Ultraviolet coatings usually require activators to initiate curing, potentially shortening storage life.
- Electron-beam coatings cure almost instantaneously, whereas UV coatings may require several seconds to several minutes.
- Ultraviolet coatings are generally limited to thin clear films (up to 75 μm, or 3 mils); EB can be clear or pigmented (up to 255 μm, or 10 mils).
- Ultraviolet lamps generate heat from 38 to 49 °C (100 to 120 °F); EB does not. Thermally sensitive substrates may cause problems if UV cured.
- Electron-beam curing has higher equipment cost than UV.
- Ultraviolet coatings are more readily available than EB coatings.

Quality Control

Once a coating has been chosen for production, it is necessary to ensure that future supplies of the coating are consistent from batch to batch, maintaining satisfactory application properties, appearance, stability, and performance characteristics. Only by so doing can production quality be maintained. Testing can be costly; consequently, quality control programs should be designed using the simplest test methods and the least number of tests necessary to ensure essential quality levels. Numerous tests and equipment for evaluating and monitoring of coatings are available, most of which are described in the following publications:

- *Annual Book of ASTM Standards,* Vol 06.01, Paint--Tests for Formulated Products and Applied Coatings; Vol 06.02, Paint--Pigments, Resins, and Polymers; Cellulose; Vol 06.03, Paint--Fatty Oils and Acids, Solvents, Miscellaneous; Aromatic Hydrocarbons
- Federal Test Method Standard No. 141a, "Paint, Varnish, Lacquer and Related Materials; Methods of Inspection, Sampling and Testing"

- *Paint Testing Manual, Physical and Chemical Examination of Paint, Varnishes, Lacquers, and Color*, STP 500, American Society for Testing and Materials
- Physical Testing for Paint Finishes, *NCCA Technical Manual,* National Coil Coaters Association

Table 8 lists a number of the most common tests for paint.

Table 8 Selected test methods for paint and painted surfaces

Test	**ASTM**	**Federal method 141**
Wet or liquid tests		
Nonvolatile (solids content)	D 2369	4041
Vehicle solids	D 2698	4052
Pigment content	D 2698	4022
Weight per gallon	D 1475	4184
Flash point	D 56, D 93, D 92	4291, 4293, 4294
Viscosity		
Ford cup	D 1200	4282
Brookfield	D 2196	4287
Stormer	D 562	4281
Zahn	D 3794	. . .
Gardner Holt tubes	D 1545	4271
Fineness of grind	D 1210	4411
Reducibility and dilution stability	. . .	4203
Drying time	. . .	4061
Dry film performance tests		

Hiding power	D 344, D 2805	. . .
Color (pigmented coatings)	D 1729	4250
Specular gloss	D 523	6101
Abrasion resistance		
Falling sand	D 968	6191
Taber abraser	D 1044	6192
Adhesion	D 2197	6303
Dry film thickness		
Magnetic gage	D 1186	6181
Mechanical gage	D 1005	6183
Hardness		
Pencil	D 3363	. . .
Sward Roeker	D 2143	. . .
Indentation	D 1474	6212
Humidity resistance	D 2247	6201
Salt spray resistance	B 117	6061

Viscosity. Controlling paint viscosity is necessary to maintain the desired properties of the coating and to ensure that the process operates at the maximum possible efficiency. Pigmented materials require close control of solids content to eliminate that influence on viscosity readings. Close control of the temperature is also necessary, because viscosity varies inversely with temperature.

Viscosity may be checked by:

- The efflux cup method
- The torsional method
- The bubble viscometer

Commercial equipment is available to assist in performing any of these tests for viscosity.

The efflux cup method uses containers closely controlled in size having a precise orifice in the bottom. After the cup is filled with paint to be checked, paint is permitted to drain through the orifice. The length of time, in seconds, to the first break in the flow stream of the paint is the viscosity. Several commercial cups are available, including the Zahn and Ford cups, designed to permit rapid testing of viscosity on the production line.

The torsional method measures the resistance of paint to rotation of a disk immersed in the paint. Several instruments for measuring the rotational resistance require that the paint be placed in a special container, and other instruments permit the viscosity to be measured in the shipping container.

With the bubble viscometer, the viscosity of the liquid is measured by the speed with which a bubble of air rises in the liquid. The material is confined in a glass tube, which is completely filled, except for a small bubble, and stoppered. The viscosity determination may be made in two ways:

- Comparing the rate of rise with that of a material of known viscosity contained in a tube of the same size
- Measuring the time required for the bubble to travel between two marks on the tube, which must have been calibrated with one or more liquids of known viscosity

Color of paint is most often controlled by visual comparison against a reference standard. One deficiency of this type of control, however, is the difficulty of retaining permanent color standards. Because of this difficulty, stabilized dry drift control panels have come into use. These panels can be either paper chips coated with paints designed to have a minimum of color change on aging, or porcelain or ceramic panels properly coated with the appropriate paint. Each control has its advantages; however, both are subject to soiling. All comparisons should be made under a standardized source of light to eliminate extraneous influences of various sources of light.

Visual comparisons do not permit the assignment of numerical values to differences and are subject to wide variations of opinion. It is possible, however, to analyze color on various instruments, assign numerical tolerances, and eliminate subjective judgment to some degree.

Colorimeters measure the three attributes of color: hue, saturation, and brightness. Colorimeters require the use of some reference standard, although not necessarily of exactly the same color as the paint being tested. Because the numerical values established with the colorimeter must still be related to a reference standard, they cannot be considered as absolute.

Spectrophotometers, which measure and analyze color throughout the entire visual spectrum of 400 to 700 nm, come nearest to being absolute measuring devices. Curves obtained on the spectrophotometer are used as a permanent, reproducible reference. Figure 13 shows spectrophotometric recordings of red, gray, and blue flat paints prepared by extending cadmium red, ivory black, and Prussian blue, respectively, with zinc white. These curves indicate the variation in the light reflectance of the three colors across the entire visible spectrum.

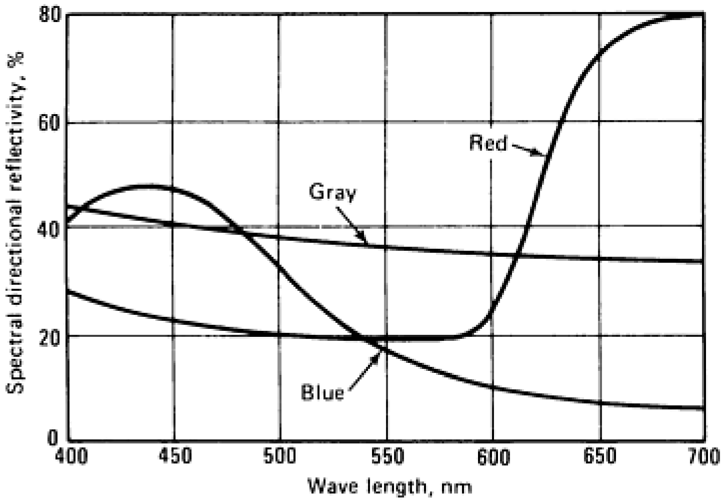


Fig. 13 Spectrophotometric curves of gray, red, and blue flat paints

Gloss. The procedure used for measuring gloss of a painted surface is by visual comparison with a known standard. By comparing the sharpness of an image reflected by a sample surface with the image reflected by a standard surface, even relatively small differences can be detected. However, because this procedure is based on human judgment and does not lend itself to the assignment of numerical values, instruments are often used for the measurement of gloss.

Photoelectric glossmeters measure gloss from various fixed angles. The viewing angle used most often is 60° from the vertical, but a viewing angle of 85° is more sensitive for low-gloss paints. The scale of glossmeters is calibrated from 0 to 100 with the higher numbers indicating higher gloss. Readings of 0 to 15 are generally considered flat, 15 to 80 are semigloss, and 80 to 100, high gloss. Instruments accurate to less than one unit are available. However, it is difficult to apply paint films to this degree of accuracy with any consistency, and a five-unit variation in gloss is acceptable.

Abrasion resistance of organic films may be determined by test methods using either falling sand or an abraser.

The falling-sand method uses a funnel-shaped hopper, which feeds sand to a vertical tube of 19 mm ($\frac{3}{4}$ in.) ID and 915 mm (36 in.) long. Sand is permitted to flow down the tube and impinge on the test panel, which is placed at a 45° angle beneath the tube. The test is complete when the sand abrades through the paint film, exposing a spot of bare metal 4 mm ($\frac{5}{32}$ in.) in diameter. The abrasion coefficient in liters per mil is found by dividing the volume (in liters) of sand used by thickness of the paint film (in mils).

The Taber Abraser method uses abrasive wheels of various grits, a method of applying loads of 250, 500, or 1000 g on the wheels, and a turntable to which the test panel can be clamped. This test can be used to obtain either the wear index (rate of wear) or the wear cycles (amount of wear) of the paint film.

Elongation properties of an applied organic film may be measured by bending a test panel over a tapered cone and measuring the length of the first continuous crack. The apparatus and test methods used are described in detail in ASTM D 522 ("Test Method for Elongation of Attached Organic Coatings with Conical Mandrel Apparatus").

Blistering. A water immersion test may be conducted to determine the resistance of organic films to failure when immersed in water in an accelerated manner. Distilled water is used to eliminate the influence of any chemicals contained in tap water. The test procedure is set forth in ASTM D 870 ("Practice for Testing Water Resistance of Coatings Using Water Immersion"). The method for evaluating degree of blistering is given in ASTM D 714 ("Method for Evaluating Degree of Blistering of Paints").

Environmental tests may be required to evaluate paint films in a particular service environment. For example, a detergent immersion test is used to determine the suitability of a particular paint for use on a home laundry machine. Tests for resistance to acids, alkalis, industrial fumes, and other corrosive media may be established, with the criterion for failure being predetermined by agreement.

Salt spray (fog) tests (ASTM B 117) are arbitrary performance tests useful in establishing and maintaining certain standards of quality for the organic finish, particularly when correlated with field tests. For example, if spring clips, phosphate coated and painted with two coats of phenolic-based zinc chromate primer, can withstand 100 h in salt spray before failure, they may be expected to last 5 years or more in applications such as license plate brackets, molding retainers, and wire retainers on automobiles.

The test consists of placing parts or panels to be tested in a chamber in which a 5 wt% solution of sodium chloride is atomized. The exposure zone of the salt spray chamber must be maintained at 33 to 36 °C (92 to 97 °F).

Exterior-exposure tests may be conducted in accordance with ASTM D 1014 ("Method for Conducting Exterior Exposure Tests of Paints on Steel") to determine the resistance of a paint film to exposure. These tests are usually conducted in specified areas to obtain information on the influence of various atmospheres, such as industrial fumes, arid but intensely sunny climates, or salt air.

Artificial weathering tests using apparatus for exposing specimens to water and carbon-arc light are detailed in ASTM G 23, "Practice for Operating Light- and Water-Exposure Apparatus (Carbon-Arc Type) for Exposure of Nonmetallic Materials." Fluorescent UV-condensation type tests are described in G 53, "Recommended Practice for Operating Light- and Water-Exposure Apparatus (UV-Condensation Type) for Exposure of Nonmetallic Materials." These test methods simulate conditions of atmospheric exposure that act in a highly accelerated manner on the test panels. ASTM D 822, "Recommended Practice for Operating Light- and Water-Exposure Apparatus (Carbon-Arc Type) for Testing Paint, Varnish, Lacquer, and Related Products," is concerned with the variations in test conditions and the evaluation of test results. This test predicts the results of more time-consuming exterior-exposure tests with some degree of reliability.

Dry film thickness bears a direct relation to product cost and product performance. Film must be measured accurately for control of cost and performance. Several types of equipment and methods may be used for measuring the thickness of dry paint films on ferrous and nonferrous metals. Among these are dial micrometers, eddy current and magnetic thickness gages, and penetration and microscopic methods.

Dial micrometers are accurate depth-measuring devices with a calibrated dial and a pressure foot with a maximum diameter of 3.2 mm ($\frac{1}{8}$ in). The test panel is clamped firmly to a base. The pressure foot of the dial comparator is brought into contact with the paint film, and a reading is taken. Without disturbing the panel, the paint film is carefully removed from the panel where the reading was taken. The pressure foot is then brought into contact with the panel at the point of the previous reading. The difference in gage readings is the thickness of the paint film. This procedure, set forth in ASTM D 1005 ("Test Methods for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers") is not adaptable to paint films thinner than 13 μm (0.5 mil) or unusually soft films.

Eddy current thickness gages work on the principle of induced current changes in a high-frequency alternating current coil in a probe held in close proximity to a metal surface. Thickness of nonconductive films may be measured on any metal substrate.

Magnetic thickness gages are available in several types, the most useful being the portable gage using permanent magnets. These instruments measure the reduction of magnetic forces by a nonmagnetic coat of paint between a permanent magnet and the magnetic base to which the paint is applied. This reduction in magnetic force is calibrated in terms of paint-film thickness. This method is suitable for films from 13 μm to 6.3 mm (0.5 to 250 mils) thick. The instrument accuracy is generally 5% of the thickness measured.

The penetration method is practical where the paint film is applied to a surface that conducts electricity. This method measures the depth of travel of a small drill. The drill and the painted metal are connected electrically to a signal light that lights when the drill tip touches the metal panel. The drill is set with the tip just touching the surface of the paint film. The drill is then rotated and advanced slowly into the paint film until the signal light indicates contact. The measured distance of travel of the drill is a direct measurement of the paint film thickness. The accuracy of this method is approximately 10% of the film thickness. A portable scratch thickness gage also is available for determining the thickness of a dry paint film by the penetration method.

The microscopic method of measuring dry film thickness is the most accurate of the methods described. A cross section of the painted panel or part is mounted and polished. Using a calibrated eyepiece or screen, the magnified image of the paint film is measured. This method has the disadvantages of being a destructive test as well as requiring more specimen preparation than other methods. The accuracy of the microscopic method is limited only by the optical equipment used and the care exercised in preparing the specimen.

A portable microscopic method uses a cutting tip of a precise angle to slice through the coating. The exposed cross section is then measured microscopically. This instrument is accurate for thicknesses ranging from 2.5 to 1250 μm (0.1 to 50 mils). However, it is not suitable for brittle or rubbery coatings unless a power-driven cutting tip is used.

Wet Film Thickness. Inspection gages may be used to measure the thickness of wet paint films. With these gages, it is possible to determine whether the wet film is of adequate thickness to develop the desired dry film thickness.

Hardness of a paint film may be approximately determined by scratching it with pencils of different hardness sharpened in a mechanical sharpener. This test does not reveal a specific hardness, but enables one paint film to be compared either to another paint film or to an acceptable standard film. The test is run to determine the softest lead that can penetrate the surface of the paint film. If only one manufacturer's pencils are used, more consistent comparisons are obtained. The disadvantage of this test is the possible variability of the force exerted by the operator. It is a useful test, however, when one skilled operator is making empirical comparisons of two panels side by side.

Coating hardness can also be measured by using a spring-loaded penetrating needle instrument. The depth of penetration, or pressure required for penetration, provides an indication of coating hardness. Instruments of this type are available for a range of coating types, from soft elastomeric coatings to hard metallic ones.

Adhesion of the paint film can be measured by a test described in ASTM D 3359, Method A or B. Method A involves cutting an X scribe through the coating to the substrate; Method B requires a cross-hatch cutting pattern. After the cut is made, a special tape is pressed over the cut area and then briskly removed. Adhesion is determined by the amount of delamination that occurs.

Adhesion testing can be simplified and standardized by using commercially available instruments, which have a solid cutting head that makes several parallel lines with one pass. Cutting guides are also available with various spacings to enable the user to cut a precise cross-hatch pattern with a sharp utility knife. The spacing of scribed lines is usually correlated to total film thickness, with thicker films requiring spacing of cuts to be wider.

Impact resistance may be determined by the use of an instrument that consists of a 25 mm (1 in.) diam impact rod that tapers to an impact nose with a 6.4 mm ($\frac{1}{4}$ in.) spherical radius, a tube 26 mm ($\frac{1}{32}$ in.) inside diameter (ID) that serves to guide the impact rod in its downward fall, a base plate with a 13 mm ($\frac{1}{2}$ in.) diam hole through it, and a bracket to support the tube and position the base plate. The tube is graduated in inch-pounds and is slotted, so that a pin, protruding from the impact rod, can be used to raise the rod to a specific inch-pound location. The base is positioned so that its 13 mm ($\frac{1}{2}$ in.) diam hole can engage the nose of the rod at the bottom of its fall.

To test the impact characteristics of a paint film, a test panel, or an actual part, if made of sheet metal, is placed over the base, and the impact rod is permitted to fall from a height that generates the desired force. Direct impact is obtained by facing the paint film toward the falling rod; reverse impact is obtained by facing the paint film away from the rod. The impact makes a 6.4 mm ($\frac{1}{4}$ in.) spherically radiused impression in the test panel. Results are measured by the force the paint film can withstand without cracking, chipping, or flaking.

The Gravelometer (Fig. 14) is another device that is used to compare impact resistance of organic films against an accepted standard. Using air at 70 kPa (10 psi), this device propels 14 kg (30 lb) of steel shot a distance of 685 mm (27 in.) against a painted area 125 by 150 mm (5 by 6 in.). The amount of paint that is retained on the panel is indicative of the impact resistance and the adhesion of the paint film. This is a more severe test than the rod impact tester, but the Gravelometer is more revealing, because of the greater area involved. The SAE J400 test uses graded gravel instead of steel shot and is gaining wide acceptance as a standard test.

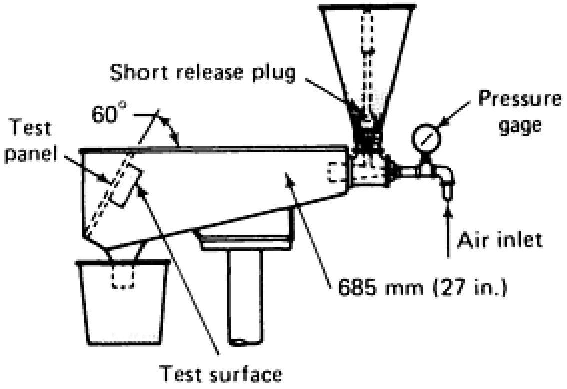


Fig. 14 Gravelometer. Used to measure impact resistance of paint films

Causes of Paint Film Defects

Defective paint films are usually the result of either improper preparation of the paint or substrate surface, or lack of control of processing variables. Paint film defects attributable to improper baking procedures are listed in Table 7; other paint film defects and frequent causes are listed in Table 9.

Table 9 Common causes of paint film defects

Defect	Cause	Susceptible application methods
Poor adhesion (peeling, flaking, poor bonding)	Paint applied over grease, oil, water, alkali residues, or other foreign materials on surface	Dip, flow, roller, spray
	Finish coat applied over incompletely dried undercoat	Dip, flow, roller, spray
	Paint applied to surface that is too hot (above 71 °C, or 160 °F) or too cold (below 16 °C, or 60 °F) or too cold (below 16 °C, or 60 °F)	Dip, flow, spray
	Film too thick	Dip, flow, roller, spray
Beading	Solvent vaporizes too rapidly	Dip, flow
	Parts drawn from paint too rapidly	Dip
Blistering (pimpling, bubbling, pinholing, pitting)	Moisture entrapped on surface of substrate	Dip, flow, roller, spray
	Air entrapment	. . .
	Improper solvents	Dip, flow, roller,

		spray
	Wide temperature differential between paint and work	Dip, flow, roller, spray
	Insufficient drying time between coats; solvent trapped in undercoat escapes through partially dried finish coat	Dip, flow, roller, spray
	Excessive air pressure and dry spraying of undercoat, causing porosity and air pockets under finish coat	Spray
	Water in air line	Spray
	Excess paint film, entrapping solvents	. . .
Brittleness	Improper composition of paint	Dip, flow, roller, spray
Checking (alligatoring, crazing, crowfooting, hairlining)	Application of finish coat over incompletely dried undercoat	Dip, flow, roller, spray
	Insufficient mixing of material to blend all pigment	Dip, flow, roller, spray
Color separation	Incomplete mixing of paint before application	Dip, flow, roller, spray
	Poor agitation during application	Dip, roller, spray
Cracking (shrinking, splitting)	Paint not thoroughly mixed before application	Dip, flow, roller, spray
	Surface not completely clean	Dip, flow, roller, spray
	Insufficient thinner	Dip, flow, roller, spray
	Undercoat too thick	Dip, flow, roller, spray
	Surfaces too hot or too cold	Dip, flow, spray
	Oil or water in air line	Spray
Cratering	Surface air bubbles	

	Silicone contamination	Dip, flow, spray
Slow drying	Application over grease, oil, or fingerprints	Dip, flow, roller, spray
	Application of too much paint	Dip, flow, roller, spray
	Poor ventilation, air drying only	Dip, flow, roller, spray
	Drying atmosphere too cold or too humid, air drying only	Dip, flow, roller, spray
	Oil in air line	Spray
	Solvent vaporizes too slowly	Dip, flow, roller, spray
Dusty or gritty appearance (dry spray)	Insufficient solvent	Spray
	Solvent vaporizes too rapidly	Spray
	Excessive air pressure	Spray
	Spray gun too far (over 305 mm, or 12 in.) from work	Spray
	Excess air movement in spray booth	Spray
	Spray pattern too wide,	. . .
	Airborne particles reach substrate	. . .
Edge pull-away	Solvent vaporizes too slowly	Dip, flow
	Too much solvent	Dip, flow
Poor flow-out	Viscosity of paint too high	Dip, flow, roller, spray
	Temperature of paint too low	Dip, flow, roller
	Solvent vaporizes too rapidly	Dip, flow, roller,

		spray
	Temperature of surface too low	Spray
Poor gloss	Paint film too thin	Dip, flow, roller, spray
	Application over incompletely dried undercoat	Dip, flow, roller, spray
	Drying atmosphere too cold or too humid, air drying only	Drip, flow, roller, spray
	Application over alkali residues	Dip, flow, roller, spray
	Too much solvent vapor in drying oven	Dip, flow, roller, spray
	Improper solvent	. . .
	Too much heat in cure cycle	Roller
Poor hiding	Pigment settling because of poor agitation	Dip, flow, roller, spray
	Solvent vaporizes too slowly	Dip, flow
	Too much solvent	Dip, flow, roller
	Withdrawal from paint too slow	Dip
	Vapor concentration too high	Dip, flow
Nonuniform film thickness (or uncoated areas)	Solvent vaporizes too slowly	Dip, flow
	Nonuniform roll pressure; roll out-of-round	Roller
	Improper hanging of panels	Dip, flow
	Paints not lapping properly when spraying	. . .
Orange peel	Excessive film thickness	Dip, flow, roller, spray

	Surface temperature too hot or too cold	Flow, dip, spray
	Improper adjustment of spray gun pattern	Spray
	Air pressure too high	Spray
	Solvent vaporizes too rapidly	Dip, flow, roller, spray
	Improper applicator/metering roll speeds	Roller
Undesirable pattern	Swelling of roll	Roller
	Roll improperly ground	Roller
	Foreign material on roll	Roller
	Poor spray gun technique	Spray
Runs (curtains, sags)	Too much solvent	Dip, flow, spray
	Paint surface or drying atmosphere too hot or too cold	Dip, flow, spray
	Solvent vaporizes too slowly	Dip, flow, spray
	Excessive paint applied	Dip, flow, spray
	Poor spray gun technique	Spray
	Distorted spray gun pattern	Spray
	Air pressure too low	Spray
	Withdrawal from paint too rapid	Dip
	Automatic equipment is jerky	Dip, flow
	Drafts	Dip
	Improper racking	Dip, flow, spray

Streaking	Metal too hot or too cold	Dip, flow, spray
	Poor spray technique; insufficient overlap between passes, should be 50%	Spray
	Distorted spray pattern	Spray
Water spotting	Rain or dew settling on finish	Dip, flow, roller, spray
	Washing before paint is completely dry	Dip, flow, roller, spray
	Uneven quenching of hot surface	Roller
Wrinkling	Excessive film thickness	Dip, flow, roller, spray
	Abnormally hot or humid drying environment, air drying only	Dip, flow, roller, spray

Calculating Coating Coverage and Costs

The cost of the applied coating is directly related to the cost per gallon of coating material, the application efficiency, the required thickness of film, and the spreading rate. To calculate the gallons needed and cost for coating an object the following information is needed.

- Volume of solids in coating
- Spreading rate of coating at application viscosity
- Dry film thickness required
- Area to be coated
- Application efficiency
- Cost per gallon

Volume solids content of the coating is the volume percentage of vehicle solids and pigments in a gallon of paint. The remaining volume percentage is the solvent that evaporates in the drying or curing process. The volume solids should not be given by the supplier and should not be confused with weight solids.

Spreading Rate. One U.S. gallon of any liquid is equivalent to 3785 cm^3 (231 $in.^3$). Thus, 100% volume solids liquid can cover 149 m^2 (1604 ft^2) at a thickness of 25 μm (1.0 mil). This figure is derived from the following formula:

$$\textit{Spreading}\ \text{rate}=\frac{\text{in}^3/\text{gal x vol solids}}{\text{in}^2.\text{ft}^2\ \text{x in}}$$

Using this formula, the spreading rate for any liquid coating can be determined. For example, if the volume solids of a product is 40% at application viscosity and a 38 μm (1.5 mil) dry film is required, the area covered by 1 gal of the paint is approximately 39.7 m^2 (427 ft^2) determined as follows:

$$\frac{231\ x\ 0{,}40}{144\ x\ 0.0015} = 427\ ft^2/gal(spreading\ \text{rate})$$

Table 10 is an approximation of spreading rates at various volume solids and dry film thicknesses. Because cost per gallon is determined at application viscosity, any solvent, thinner, or reducer added to the paint must be included in the final cost as well as the volume solids determined at application viscosity. The cost per gallon is equal to the cost per gallon of paint plus the cost per gallon of thinner divided by the total number of gallons.

Table 10 Theoretical spreading rate for coatings

Volume solids, %	**13 µm (0.5 mil)**		**25 µm (1.0 mil)**		**38 µm (1.5 mils)**		**51 µm (2.0 mils)**		**64 µm (2.5 mils)**		**76 µm (3.0 mils)**	
	m^2/L	**ft^2/gal**	**m^2/L**	**ft^2/gal**	**m^2/L**	**ft^2/gal**	**m^2/L**	**ft^2/gal**	**m^2/L**	**ft^2/gal**	**m^2/L**	**ft^2/gal**
10	6.4	320	3.2	160	2.14	107	1.6	80	1.3	64	1.1	54
20	12.8	640	6.4	320	4.26	213	3.2	160	2.56	128	2.14	107
30	19.2	962	9.62	481	6.4	320	4.8	240	3.94	197	3.2	160
40	25.68	1284	12.8	641	8.54	427	6.42	321	5.14	257	4.28	214
50	32.1	1605	16.0	802	10.7	535	8.02	401	6.42	321	5.34	267
60	38.52	1926	19.2	962	12.8	641	9.62	481	7.7	385	6.42	321
70	44.8	2240	22.4	1120	14.9	747	11.2	560	8.96	448	7.46	373
80	51.2	2560	25.6	1280	17.1	853	12.8	640	10.2	512	8.54	427
90	57.6	2880	28.8	1440	19.2	960	14.4	720	11.5	576	9.6	480

Application Efficiency. In addition to cost per gallon at application viscosity, the percent of the coating deposited on the substrate by the application method must also be considered. Table 11 lists the average efficiency of various types of application methods. The cost of paint for a part can be calculated using the following formula and the data in Tables 10 and 11.

$$Cost\ \text{per square foot}=\frac{\text{Cost per gal at application viscosity}}{\text{Spreading rate x application efficiency}}$$

Table 11 Average application efficiency of painting methods

Method	**Efficiency, %**

Conventional spray,	
Air atomized	50
Airless atomized	65
Electrostatic spray,	
Air atomized	70
Airless atomized	80
Centrifugally atomized	90
Dip, flow, curtain coat	80
Coil and roller coat	90
Electrodeposition	90
Powder coat	90

Safety and Environmental Precautions

The 1990 Amendments to the Clean Air Act (CAAA) and the promulgation of several Constructional Industry Standards by the Occupational Safety and Health Act administered through OSHA have had a major impact on the blasting and coating industries. Several of these regulatory initiatives are of special importance to industries that use paint and other organic coatings.

Volatile Organic Compounds (VOCs). Regulatory activity required under the 1990 CAAA continues to dominate the protective coatings industry. Many items are under negotiation with the Joint Industry, Government and Regulatory Negotiation Committee. Several items in the forefront of development and negotiation include

- A national volatile organic compounds rule on architectural and industrial maintenance (AIM) coating applied to stationary sources is being developed. Under a tentative agreement, industrial maintenance coating would be restricted to a maximum VOC level of 350 g/L as applied.
- Tentative VOC levels have also been established for around 50 other categories and subcategories of coating.
- The Regulatory Negotiation Committee has also tentatively agreed to reduce current average VOC emissions (CAVE), which are based on total corporate product line levels compared to 1990 levels. Reduction is scheduled for 25% by 1996, 35% by 2000, and 45% by 2003.
- The CAAA directs the EPA to develop control technique guidelines (CTGs) on shipbuilding and shipyard repair coating operations.
- Under the National Emission Standards for Hazardous Air Pollutants (NESHAP), the EPA under the CAAA must create a national standard regarding the control and emissions of 189 hazardous air pollutants.
- The CAAA mandates a review of the current ozone standard by the EPA.

- EPA has formally revised its Method 24 for measuring VOCs in coatings to make it applicable for use with multicomponent coatings. The method is now consistent with ASTM D 2369 and ASTM D 3960.

OSHA Cadmium Exposure Regulations. In September 1992, OSHA published a Cadmium Exposure in Construction Standard (29 CFR 1926.63) to address occupational exposure to cadmium during construction activities.

In 1993, OSHA published its final rule on permit-required confined space entry (29 CFR 1910.146). It established strict provisions for facility owner and contractors involved in confined space operations. This standard was printed in the Federal Register in January 1993 and became effective 15 April 1993.

OSHA Lead Exposure Regulations. OSHA published its Interim Final Rule on Lead Exposure in Construction (29 CFR 1926.62) in May 1993 for the protection of construction workers from overexposure of airborne lead. The Rule went into full effect in August 1993. The Rule lowers the permissible exposure limit (PEL) to 50 $\mu g/m^3$, incorporates many provisions of the General Industry Standard, and establishes "trigger tasks" to establish presumed exposure levels.

Published Standards. All aspects of the OSHA and EPA VOC requirements cannot be covered within this article. The following provide greater detail:

- Interim Final Rule on Lead Exposure in Construction (29 CFR 1926.62)
- Confined space entry (29 CFR 1910.146)
- Rule on Cadmium Exposure in Construction (29 CFR 1926.63)
- The Clean Air Act (42 USC 7401)
- The Clean Air Act Amendments of 1990

Individuals and organizations involved in industrial painting and coating should maintain contact with OSHA, EPA, and state and local regulatory agencies in order to keep abreast of current, revised, and pending regulations.

Painting of Structural Steel

Painting of structural steel is done to protect the environmental area affected by the structure being coated, to preserve manufacturing or plant functionality, and to provide aesthetic appeal. Painted structures may have to withstand high-operating temperatures, adverse weather conditions, and marine, industrial (urban) and rural exposure as well as chemical exposure. All these conditions dictate the frequency of coating application, selection of the method of surface preparation, and coating system selected.

As discussed previously in the section "Safety and Environmental Precautions" in this article, the introduction of restrictive regulations has had an impact on the use of painting coating systems. For example, the federal Environmental Protection Agency has limited the amount of volatile organic compounds that can be emitted from painting facilities. For the protection of the applicator, the use of active pigments in primers, such as lead compounds and chromates, has been listed by the Occupational Safety and Health Administration.

Composition and Characteristics of Organic Coatings for Structural Steel

Coatings have three components: the volatile vehicle (solvent or dispersant), the nonvolatile vehicle (resin), and the pigment. The volatile vehicle is the portion of the coating that allows the coating to be spread or applied. This component can be ketone, ester alcohol, petroleum solvent, water, or a combination of these materials. Water, for example, acts as the dispersant in water-reducible coating systems.

The pigment portion provides opacity and color, as well as viscosity control and reduced water permeability. Other pigments also provide corrosion resistance. Materials that are considered pigments include: driers, plasticizers, ultraviolet light absorbers, emulsifiers, and dispersing agents. These materials are added to modify coating properties as required.

A number of resins are used in the preparation of coatings. These include plant-derived oleoresins (linseed oil, safflower oil, and tung oil); fish oils (menhaden, sardine, and pilchard); lacquers (nitrocellulose, cellulose acetate, ethyl cellulose, and acrylic polymers); and synthetic resins (alkyds, aminoplast-alkyd blends, phenolic, epoxy, acrylic, vinyl, urethane, silicone, and chlorinated rubber). Table 12 provides information on some frequently used resins.

Table 12 Characteristics of the resins for coating structural steel

Resin	**Curing method**	**Solvents**	**Chemical and weather resistance**					**Remarks**
			Acid	**Alkali**	**Solvent**	**Water**	**Weather**	
Raw and boiled linseed oil	Air drying Oxidative polymerization	Aliphatic hydrocarbons	Fair	Poor	Poor	Fair	Fair	Vehicle for corrosion inhibitive primers for wire-brushed steel, slow drying
Oleoresinous varnishes	Air drying Condensation and/or oxidative polymerization	Aliphatic hydrocarbons and/or aromatic hydrocarbons	Fair	Poor	Poor	Good	Good	Pale-colored finishes that yellow on exposure
Alkyds	Air drying Oxidation Polymerization	Aliphatic hydrocarbons	Fair	Poor	Poor	Fair	Very good	Long oil alkyds are generally used, although these alkyds may be blended with medium oil alkyds
Modified alkyds	Air drying Oxidative polymerization	Dependent on modification A wide variety of solvents	Fair	Fair	Fair	Good	Very good	. . .
Epoxy, aliphatic amine or polyamide blends	Air dryingAddition polymerization	Blends rich in high ketones	Good	Very good	Very good	Very good	Good	Two-component compositions
Epoxy, fatty acid esters	Air drying Oxidative polymerization	Aliphatic and/or aromatic hydrocarbons	Fair	Fair	Poor	Fair to good	Fair	. . .
Polyester urethane	Addition polymerization	Blend rich in ketones and esters	Fair to good	Good	Very good	Fair to good	Very good	Two-component compositions
Vinyl resins	Air drying solvent evaporation	Blends usually rich in ketones	Very good	Very good	Poor	Very good	Good	Fire hazard, unless high solids compositions are used
Chlorinated rubber	Air drying solvent evaporation	Aromatic hydrocarbons	Good	Good	Poor	Very good	Good	Very poor heat resistance
Acrylic resins (water	Water evaporation and coalescing	Water dispersant	Fair	Fair	Very good	Fair	Good	Used as a maintenance coating system. Porosity of film results

emulsion)								in poor chemical and weather resistance

Linseed oil is the most important drying oil used in oil varnishes and in the preparation of alkyd resins because of its ready availability and relatively low cost. The main advantages of linseed oil are good surface wetting properties, easy preparation of surface, good application properties, and ease in coating preparation. Raw linseed has disadvantages as well, including very slow drying, lack of gloss when formulated into coatings, and poor leveling qualities.

Linseed oil is composed of a mixture of linoleic and linolenic triglycerides. Both of these acids contain a chain of 17 hydrocarbon members with an acid radical and 2 or 3 double-bonded positions. On drying (oxidizing) the double bonds cross link with other molecules to form a high molecular weight film.

Heat-treated oils fall into three categories: boiled oils, stand oils, and blown oils. Boiled oils are prepared by heating linseed oils in the presence of metal driers such as lead naphthenate and cobalt naphthenate. Boiled linseed oils have a higher viscosity and better drying properties because of higher molecular weight and more complex molecular structure. Boiled linseed oil is used in oil-based primers and in conjunction with oil varnishes and undercoats.

Stand oils have an even higher viscosity than boiled linseed oil. These oils are prepared by heat-polymerizing linseed oil alone or in a mixture with tung oil. Stand oils are mostly used in combination with oil varnishes and alkyd resins to improve application properties and increase total oil.

Blown oils are partially oxidized in addition to being polymerized. As the name implies, air is blown through the heated oil, which results in a poorly drying product. Generally, the blown oil is used as a plasticizer.

Oleoresinous varnishes are varnishes and paint media prepared from drying oils and natural or synthetic resins, such as rosins, gum congo, rosin-modified phenolics, and 100% oil-soluble phenolics. Oleoresinous varnishes are used to improve drying and film-forming properties.

The phenolic varnishes require surface preparations to provide at least a commercial blast-cleaned surface (SSPC-SP-6). (Table 13 lists Steel Structure Painting Council designations for surface preparations. Additional information is available in the section "Surface Preparation" in this article.) Tung-oil phenolic resin has very good water resistance and is mildly acid- and alkali-resistant.

Table 13 Steel Structures Painting Council (SSPC) designations of surface preparation methods for painted coatings

SSPC designation	Method of surface preparation	NACE designation	Equipment and materials	Remarks
SP1	Solvent cleaning	. . .	Mineral spirits, chlorinated solvents, coal tar solvents, using tack rags or dip tanks	For the removal of grease, oil, or other soluble materials before removing mill scale, rust, and coatings by other methods. Alkaline cleaners saponify oils and greases, but these cleaners must be neutralized with 0.1 wt% chromic acid, sodium dichromate, or potassium dichromate
SP2	Hand tool cleaning	. . .	Hand scrapers	Hand tool cleaning should be limited to removing loose material for materials for maintenance and normal atmospheric exposure; coatings with good wetting properties are brush applied
SP3	Power tool cleaning	. . .	Power wire brushes, grinders, sanders, impact tools, needle guns	For the removal of loose rust, loose mill scale, and loose paint by power tool chipping, descaling, sanding, wire brushing, and grinding without excessive roughing that causes ridges, burrs, or burnishing. Used when primer is to be brush applied

SP4	Flame cleaning	(a)	. . .	Removal of contaminants by high-velocity oxyacetylene flame burners. Usually followed by wire brushing
SP5	White metal blast	1	Abrasive blasting	Removal of 100% of oil, grease, dirt, rust, mill scale, and paint. Cleaning rate 9.3 m^2/h (100 ft^2/h), using 7.94 mm ($\frac{5}{16}$ in.) nozzle with 690 kPa (100 psig) at nozzle. Because of atmospheric contamination, maintaining this degree of cleanliness before primer application is difficult
SP6	Commercial blast	3	Abrasive blasting	Removal of 67% of oil, grease, dirt, rust, mill scale, and paint. Cleaning rate of 34 m^2/h (370 ft^2/h), using 7.94 mm ($\frac{5}{16}$ in.) nozzle with 690 kPa (100 psig) at nozzle. Used for general-purpose blast cleaning to remove all detrimental matter from the surface, but leaves staining from rust or mill scale
SP7	Brush-off blast cleaning	4	Abrasive blasting	All loose mill scale and rust are removed, with tight mill scale, paint and minor amounts of rust and other foreign matter remaining. The remaining rust is an integral part of the surface. This level of surface preparation is used for mild exposure and is suitable where a temperature change of less than 11 °C/h (20 °F/h) can be anticipated. Cleaning rate of 81 m^2/h (870 ft^2/h) using 7.94 mm ($\frac{5}{16}$ in.) nozzle
SP8	Pickling	. . .	Hydrochloric acid, sulfuric acid with inhibitors, or phosphoric acid with a final phosphate treatment	A shop method of surface preparation for removal of rust and mill scale from structural shapes, beams, and plates where there are few pockets or crevices to trap acid. Excess acid must be rinsed off with water, and painting is required as soon as possible to prevent recontamination of the surface
SP9	Weathering	(b)	. . .	Although mill scale is weathered away, this process is detrimental because surface contamination is more difficult to remove when weathered
SP10	Near-white blast	2	Abrasive blasting	Removal of 95% of oil, grease, dirt, rust, mill scale, and paint. A cost savings of 25% can be realized on average where this level of cleanliness can be tolerated. Shadows, streaks, or discolorations are distributed over the surface, but not concentrated in any area or particular spot. Cleaning rate 16 m^2/h (175 ft^2/h) using a 7.94 mm ($\frac{5}{16}$ in.) nozzle and 690 kPa (100 psig) at nozzle
	Water blasting	. . .	Inhibited water at pressures of 6900 to 69,000 kPa (1000 to 10,000 psig) used	Removal is slow and the degree of cleaning must be specified. High pressures may cause damage to substrate or structures
SP11	Power tool cleaning to bare metal	. . .	Same as SP3	Removal of all mill scale, rust, old paint, and oil, exposing bare metal. The resulting surface must be roughened as necessary to obtain a 25 µm (1 mil) surface profile

(a) Discontinued as of Jan 1982.

(b) Discontinued in 1971

Alkyd resins are produced by reacting a polyhydric alcohol with a monobasic and polybasic fatty acid to yield an ester. The more frequently used alcohols include ethylene glycol, glycerol, and pentaerythritol. Phthalic anhydride is the acid used most often because of the plentiful supply of the petrochemical orthoxylene from which it is made. Isophthalic acid is used in primers or where a harder, more weather-resistant coating is desired. Unsaturated dibasic acids, such as maleic anhydride, are used to provide higher molecular weight polymers.

For coating structural steel, air-drying alkyd resins are most frequently used. The films are formed by the oxidation of the drying oils these alkyds contain. The fatty acids are obtained from linseed, soya, sunflower, cottonseed, safflower, tung oil, and fish oils, in the form of a glycerol triester. These triesters, or the oils chemically separated, are used to prepare primers, intermediate coatings, and finishing coatings. The shorter (more reactive) the acid oil, the more brittle and less forgiving the primer. Short oil resins require more meticulous surface preparation, and they dry more quickly. Soya oil is used with other faster drying oils to produce non-yellowing white and pastel color compositions.

When additional hardness, chemical resistance, and durability may be required, alkyd resins are modified with vinyl, acrylic, silicone, and urethane and other adducts to the acid oil constituent. The resins resulting from these modifications are higher in molecular weight than the original alkyd and may require oxygenated solvents such as ketones.

Epoxy resins are long-chain polyhydric alcohols with epoxy end groups. The alcohol and epoxy groupings are available for reaction with the aliphatic polyamines, amine adducts, and polyamides to provide film formers with excellent chemical resistance at room temperature. The epoxy resins may be separated from their curing adducts such as polyamines and polyamides, as two-component coating systems. These components are mixed in the required proportions immediately before use. Epoxy coatings are used where chemical resistance is required. A surface preparation of SSPC-SP-6 or better is required.

Polyurethane resins are characterized by having isocyanate groupings at the end of the molecular chain, acting as the reactive groups that combine with moisture or a reactive polyol such as glycerol, glycol, phenols, alkyds, and many others. The latter resins are called two-component polyurethane coatings, and the former are classified as single-package for moisture-curing coatings. Two-pack urethane resins provide a chemical-resistant film of excellent quality and high gloss and are used to coat structural steel as a lining coating for petroleum storage tanks. Moisture-cured polyurethane coatings are aromatic urethanes that are less chemically resistant than the two-component systems.

Vinyl coatings, for most purposes, are prepared from polyvinyl formal, polyvinyl acetal, and polyvinyl butyral.

Vinyl resin paints are inert and are used for coatings applied to tanks, pipelines, petroleum equipment, offshore drilling rigs, railroad hopper cars, dairy and brewery equipment, and tanks that require acid and alkali resistance. Vinyl films are abrasion resistant, with low water permeability, high dielectric resistance, and high-speed drying capabilities. Vinyl paints require steel to be cleaned to an SSPC-SP10 or better, a near-white abrasive blast cleaning. Vinyl paints are ideal for immersion in fresh water and brackish water, but do not impart the same degree of protection in salt water, where coal tar or epoxy coatings would be preferred.

Chlorinated rubber resins are prepared by the chlorination of isoprene in solution to approximately 65 wt% chlorine. Natural rubber is used as the raw material, and when combined with chlorine, it results in a trichloro- and a tetrachloro-polymeric mixture. The resulting films provide excellent corrosion resistance for ferrous metals in marine environments, strong acids, and weak alkalis, but films chalk when exposed to sunlight. For a paint to be designated as a chlorinated rubber paint, it should contain not less than 60 wt% chlorinated rubber in the vehicle solids.

Acrylic resins are formed by the esterification of acrylic or methacrylic acids with alcohols. The major homopolymers are methyl, ethyl, butyl and isobutyl methacrylate, and methyl, ethyl and butyl acrylate. Lacquers and enamels, based on acrylic resins, have been developed for both ferrous and nonferrous metals. Latex emulsions are used in home painting.

Types of Paints for Structural Steel

Paints are generally described by their resin (binder) designation and sometimes their pigment composition, such as red lead alkyd or epoxy polyamide. Paints may be applied in single or multiple layers. When multiple layers are used, each layer has a special purpose.

The primer is the first layer to be applied. The main purpose of the primer is to wet the surface of the substrate and to provide adhesion and corrosion protection. Pigments such as red lead, zinc chromate, or zinc molybdate are active corrosion inhibitors. Titanium dioxide, chromium oxide, and ferric oxide pigments--while important pigments for color hiding, strength, and barrier reinforcement--are not corrosion inhibitors.

Intermediate coatings are sometimes applied to improve adhesion and impact strength between primer and topcoat and to provide a barrier layer between coats, as well as surfacers and sealers. Intermediate film also inhibits light penetration, reducing actinic degradation.

The final coating is described as the top or finish coat enamel, which provides environmental and chemical resistance. Also, the finish coat provides aesthetics of color and gloss, as well as film characteristics such as hardness and abrasion resistance. Table 14 shows the compatibility of paints applied as multiple layers.

Table 14 Paint compatibility

Primer or weathered paint	Topcoat												
	Solvent thinned				**Lacquer**			**Water thinned (latex)**		**Chemically reactive**			
	Oleoresinous	**Alkyd**	**Silicone alkyd**	**Phenolic oleoresinous**	**Vinyl**	**Chlorinated rubber**	**Styrene-butadiene/ styrene-acrylate**	**Acrylic**	**Polyvinyl acetate**	**Epoxy**	**Coal tar epoxy**	**Polyester**	**Urethane**
Solvent thinned													
Oleoresinous	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Alkyd	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Silicone alkyd	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Phenolic oleoresinous	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Lacquer													
Vinyl	CT	NR	NR	NR	CT	CT	CT	CT	CT	NR	NR	NR	NR
Chlorinated rubber	CT	NR	NR	NR	CT	CT	NR	CT	CT	NR	NR	NR	NR
Styrene-butadiene/styrene-	CT	CT	CT	NR	CT	NR	CT	CT	CT	NR	NR	NR	NR

Bituminous	NR	NR	NR	NR	CT	CT	CT	CT	NR	NR	NR	NR	NR
Water thinned (latex)													
Acrylic	C	C	C	NR	CT	CT	CT	CT	CT	NR	NR	NR	NR
Polyvinyl acetate	C	C	C	NR	CT	CT	CT	CT	CT	NR	NR	NR	NR
Chemically reactive													
Catalyzed epoxy	NR	NR	NR	NR	CT	CT	CT	CT	CT	CT	CT	CT	CT
Coal tar epoxy	NR	NR	NR	NR	NR	NR	NR	NR	NR	CT	CT	NR	NR
Zinc-rich epoxy	NR	NR	NR	NR	CT	CT	CT	C	NR	CT	CT	NR	NR
Polyester	NR	NR	NR	NR	CT	CT	CT	CT	CT	CT	CT	CT	CT
Inorganic zinc	NR	NR	NR	NR	CT	CT	CT	CT	NR	C	C	NR	CT
Cementitious	NR	NR	NR	NR	CT	CT	CT	CT	NR	C	C	CT	C
Urethane	NR	NR	NR	NR	NR	CT	CT	CT	CT	NR	CT	C	CT

Note: C: normally compatible. CT: compatible with special surface preparation and/or application. NR: not recommended because of known or suspected problems. Certain combinations

Enamels may be cured by air drying or oven baking. Air dry enamels are cured essentially by a combination of solvent evaporation and oxidation. Baking enamels incorporate catalysts and cross-linking agents that require heat for polymerization. Coatings may be classified according to curing method, as is shown in Table 15. Each generic type is discussed separately in the following sections.

Table 15 Classification of coatings according to methods of cure

Method of curing	**Generic type**	**Comments**
Air oxidation of drying oils (solvent thinned)	Oleoresinous	Good wetting, slow curing, soft film recommended in normal environments only
	Alkyd	Good wetting and appearance, poor in alkaline or solvent environments
	Silicone alkyd	Improved durability, gloss, and chemical resistance compared to alkyds, but still poor in alkaline or solvent environments
	Phenolic oleoresinous	Good resistance to abrasion and mild chemical environments; however, dark color of binder precludes use in white or light tints
Solvent evaporation (lacquers)	Vinyl (polyvinyl chloride-acetate)	Good water resistance, limited solvent resistance, poor adhesion unless surface has been properly prepared with abrasive blast cleaning
	Chlorinated rubber	Good water resistance, limited solvent resistance
	Styrene-butadiene, styrene-acrylate	Good water resistance, limited solvent resistance
	Coal tar	Soft, black only; of limited use, mostly on mechanically cleaned surfaces
	Polyvinyl-butyral	Exclusively used in pretreatment (wash) primers
Evaporation of water (latex, emulsion, water-thinned)	Acrylic	Recommended in normal environments only
Chemical reaction	Epoxy	Good water, chemical, abrasion, and solvent resistance, chalks freely on exterior exposure, difficult to topcoat
	Coal tar epoxy	Improved water resistance and lower raw material costs compared to epoxies, black only. Difficult to topcoat
	Polyester	Frequently used with glass fibers to give abrasion- and water-resistant coating. Only fair alkali resistance
	Zinc inorganic	Requires adequate surface preparation (SSPC No. 10, Near White Blast Cleaning); adequate curing time required; excellent corrosion protection; good abrasion, solvent, and high-temperature resistance; must be topcoated in aggressive environments; reacts with alkali-sensitive topcoats

	Cementitious	Inexpensive, requires adequate curing for best performance, and tends to chalk with aging, poor corrosion resistance
	Urethane	Good water, chemical, abrasion, and solvent resistance. Difficult to topcoat

Air-Oxidizing Coatings. Oleoresinous (oil-drying) coatings were among the earliest to be used to provide protection from environmental deterioration. These coatings contained natural vegetable or fish oils that cure to a solid by reacting with oxygen from the air. This usually slow reaction is accelerated by using driers in the coating formulation. Paints using these oils have excellent wetting properties and are used on poorly prepared surfaces such as SSPC-2 or 3.

Alkyd coatings are developed by reacting drying oils with phthalic anhydride or other polybasic acids that increase durability and hardness. Alkyd coatings are currently the most widely used coatings, because of their good wetting, flexibility, curing, and application properties. Alkyd coatings are among the most suitable for general atmospheric exposure.

Silicone alkyd coatings have a silicone resin reacted with the alkyd resin to form the resin binder. When compared to alkyd coatings, silicone alkyd coatings have superior chemical resistance, color retention, and gloss.

Phenolic coatings are prepared using resin binders that incorporate phenol-formaldehyde in dry oils. The use of phenol-formaldehyde improves water resistance, but lowers exterior durability.

Epoxy resins combined with drying oils improve the corrosion resistance of epoxy ester coatings. Epoxy ester coatings are single-component coatings and should not be confused with two-component chemically reacting epoxies.

Lacquers are coatings that dry by solvent evaporation. The major resins used are acrylics, cellulosics, and vinyl. Lacquer coatings contain dissolved solid resins that form a continuous hard film after the solvent evaporates from the coating. Because coatings are not chemically active during curing or weathering, they can be redissolved in the same solvent. This allows lacquers to be readily overcoated, resulting in excellent intercoat adhesion. Lacquer coatings have poor solvent resistance, but have excellent chemical and water resistance.

Acrylic resins are frequently used in lacquers, because of their fast drying properties and chemical and water resistance. Chlorinated rubber coatings are fast drying and are being used increasingly in this country. Chlorinated rubber coatings have excellent moisture resistance. Coal tar and asphaltic coatings are used on below-grade structural steel because of their moisture resistance and abrasion resistance. Polyvinyl-butyral coatings, such as those conforming to military specification DoD-P-15328D, are used as pretreatments for alkyd and vinyl coatings applied to steel and galvanized structures.

Two-Component Coatings. In general, coatings that cure by chemical reaction have the best combination of durability and water, solvent, and chemical resistance. Chemically cured coatings are packaged in two separate containers, and the chemical reaction is initiated after the two components are combined. Epoxy coatings have either an amine or polyamide curing agent although polyester and polyurethane constituents have been used. Amino-cured epoxies tend to have better chemical and solvent resistance. Polyamide-cured epoxies have better flexibility and water resistance. Because epoxy coatings cure to a hard, smooth, solvent-resistant finish, they are difficult to overcoat. To ensure good bonding, topcoats are applied to incompletely cured undercoats, allowing the topcoats to chemically react with the undercoats. If the solvent has not evaporated by the time the topcoat is applied the solvent can be entrapped, resulting in the blistering of the topcoat. If the undercoat is completely cured before the topcoat is applied, a fog or mist coat (thinned topcoat) is first applied to improve intercoat adhesion. Epoxy coatings chalk during weathering, although chalking occurs to a smaller extent with newer materials. When chalking occurs, it can be removed by sanding or brush-off abrasive blasting. Epoxies are exothermic when they cure; they cure slowly when applied below 8 °C (50 °F) and extremely rapidly above 32 °C (90 °F). Coal tar epoxies have coal tar pitch added to the epoxy resin. This combination increases the water resistance and makes the coating more tolerant to poor surface preparation. A coal tar epoxy cured with a low molecular weight amine is especially resistant to an alkaline environment, such as occurs on a cathodically protected structure. Some coal tar epoxy systems become brittle when exposed to the sun and must be protected. Coal tar epoxies are more difficult to overcoat than epoxies and come in colors ranging from tan to black.

Urethane coatings provide the tough, durable, smooth finish that is typical of chemically cured coatings. Aliphatic urethanes provide bright, chalk-resistant finishes with exceptional physical properties. Urethane coatings may be air dried or heat cured.

Polyester coatings are used most frequently with glass fibers or flakes for reinforcement. Polyester provides a thick coating that is tough and durable, with good resistance to abrasion.

Inorganic zinc coatings are available as primers or complete coating systems. Water-borne inorganic zinc-rich coatings are based on post- or self-curing alkali silicates (sodium, lithium, potassium), alone or in combination. Solvent-borne inorganic zinc coatings are based on an ethyl silicate vehicle. Finely divided zinc dust is added to the water- or solvent-borne binder just before application. An inorganic zinc coating applied to a well-prepared ferrous substrate can provide good protection without being topcoated at film thicknesses from 0.75 to 1.25 mm (0.03 to 0.05 in.). All topcoats applied to inorganic zinc must be alkaline resistant, or the topcoat can saponify and become water soluble. Zinc coatings should not be allowed to come in contact with gasoline, because the zinc is slightly soluble and will be leached from the film.

Organic zinc-rich coatings may be formulated with a number of resins, but the epoxy resins are most widely used. Zinc-rich coatings are not abrasion resistant and should be overcoated when required with a coating system containing a compatible binder similar to that used in the original coating. Zinc-rich organic coatings are more tolerant to poor surface preparation and are easier to topcoat.

Paint Application on Structural Steel

Basic application procedures must be followed to obtain optimum performance from a coating system regardless of the equipment selected for applying the coating. Cleaned, pretreated surfaces must first be coated within specific time limits established to prevent corrosion products, dirt, and moisture from accumulating and interfering with the coating process. Surface and ambient temperatures must generally be between 8 and 32 °C (50 and 90 °F) for water-borne coatings and 7 and 35 °C (45 and 95 °F) for solvent coatings. Some coatings that are catalyzed, such as epoxy and polyurethane coatings, dry within 4 h at 21 °C (70 °F), within 2 h at 27 °C (80 °F), and within 1 h at 32 °C (90 °F). These coatings in some circumstances may gel in the container or in the spray hoses unless two-component spray equipment is used. Paint should not be applied when temperature is expected to drop below freezing or when the relative humidity is higher than 80% and a temperature drop of more than 3 °C (5 °F) is expected. When successive coats of the same paint are used, each coat should be tinted differently to aid in determining proper application and to ensure complete coverage. Sufficient time must be allowed for each coat to dry thoroughly before overcoating. Allow the final coat to dry for as long as is practical before service is resumed.

Brush application procedures require brushes of first quality, maintained in perfect working condition. Brushes are identified by the type of bristle used, natural, synthetic, or mixed. Chinese hog bristles are the finest natural bristles, because of their length, durability, and resiliency. Hog bristles are unique; the bristle end forks out, resembling a tree branch. This flagging permits more paint to be carried on the brush and leaves finer brush marks on the applied coating that flow together more readily with the overall result of a smoother finish. Horsehair bristles are used in inexpensive brushes and are a very unsatisfactory substitute. Horsehairs do not flag, the bristles quickly become limp; they hold far less paint; and they do not spread the paint well. Badger hair brushes make good varnish brushes, and squirrel and sable bristle brushes are used in fine work in lining and lettering. Nylon brushes are used for water-thinned coatings, and these brushes are superior to horsehair. Nylon brushes cannot be used for lacquer materials, because the solvents may dissolve or soften the bristles.

Hand roller application (as opposed to roller coating, or coil coating, which was discussed previously in this article) involves the use of a roller, which consists of a cylindrical sleeve or cover that slips over a rotatable cage with attached handle. The sleeve, or cover, is generally 38 to 64 mm ($1\frac{1}{2}$ to $2\frac{1}{4}$ in.) in inside diameter and 75, 100, 175, or 230 mm (3, 4, 7, or 9 in.) in length. Special rollers are available in unusual shapes for corners and in lengths of 38 to 455 mm ($1\frac{1}{2}$ to 18 in.) for painting pipes, fences, and other hard-to-reach places. Pressure rolling equipment is available. The paint is fed to the roller under pressure, and the paint flow is controlled by a valve.

Fabrics used in covering the rollers include the following:

- *Lamb's wool (pelt):* This material is the most solvent resistant and is available in nap lengths of up to

31.8 mm ($1\frac{1}{4}$ in.). Lamb's wool is recommended for applying synthetic finishes on semismooth and rough surfaces. Lamb's wool mats badly in water and should not be used in water-thinned paints.

- *Mohair (angora):* Mohair is solvent resistant and may be used with water-thinned paints. Mohair is supplied in 4.8 and 6 mm ($\frac{3}{16}$ and $\frac{1}{4}$ in.) nap lengths.
- *Dynel (modified acrylic fiber):* Dynel has excellent water resistance and is somewhat tolerant to most solvents, except such strong solvents as ketones. Dynel is best for conventional water-thinned water paints and solvent systems, except ketone-containing lacquers. Dynel rollers are available in nap lengths from 6 to 31.8 mm ($\frac{1}{4}$ to $1\frac{1}{4}$ in.).
- *Dacron (polyester):* Dacron is a synthetic fiber softer than Dynel, suitable for exterior oil or water-thinned paints. It is available in nap lengths from 7.9 to 13 mm ($\frac{5}{16}$ to $\frac{1}{2}$ in.).
- *Rayon:* Rayon fabric should not be used because its use can lead to poor results. Rayon also mats badly in water.

Table 16 is a guide that can assist in the selection of a suitable roller.

Table 16 Roller selection guide

Product standards do not exist in the paint roller industry, and quality varies greatly among manufacturers; table is based on experience with first-line, high-quality products.

Paint	**Smooth metal**	**Surface blasted metal**	**Pitted and weathered metal**
Aluminum	C	A	A
Enamel or semigloss alkyd	A or B	A	. . .
Enamel undercoat	A or B	A	. . .
Epoxy coatings	B or D	D	D
Urethane coatings	B or D	D	D
Latex (water-thinned) paint	A	A	A
Metal primers	A	A or D	. . .
Varnishes, all types	A or B	. . .	. . .

Roller cover key	**Material**	**Nap length**					
		mm	**in.**	**mm**	**in.**	**mm**	**in.**

A	Dynel (modified acrylic)	6.4-9.5	$\frac{1}{4}$-$\frac{3}{8}$	9.5-19	$\frac{3}{8}$-$\frac{3}{4}$	25-32	1-1$\frac{1}{4}$
B	Mohair	4.8-6.4	$\frac{3}{16}$-$\frac{1}{4}$	. . .	. . .	. . .	. . .
C	Dacron (polyester)	6.4-9.5	$\frac{1}{4}$-$\frac{3}{8}$	13	$\frac{1}{2}$	. . .	. . .
D	Lamb's wool pelt	6.4-9.5	$\frac{1}{4}$-$\frac{3}{8}$	13-19	$\frac{1}{2}$-$\frac{3}{4}$	25-32	1-1$\frac{1}{4}$

Coating System Selection for Structural Steel

Selection of resin-type designations of coatings should be based on such factors as solvent limitations and chemical and weather resistance properties (as shown in Table 12), the category of the coating system based on surface preparation (see Table 17), and the estimated life of the paint (see Table 18).

Table 17 Minimum surface preparation requirements for steel with commonly used coatings

Listed coatings should not be used unless minimum surface preparation requirements can be met.

Coating	**Minimum surface preparation**
Drying oil	Hand or power tool cleaning (SSPC-SP2 or 3)(a)
Alkyd	Commercial blast (SSPC-SP6)
Oleoresinous phenolic	Commercial blast (SSPC-SP6)
Coal tar	Commercial blast (SSPC-SP6)
Asphaltic	Near white or commercial blast (SSPC-SP10 or 6)
Vinyl	Near white or commercial blast (SSPC-SP10 or 6)
Chlorinated rubber	Near white or commercial blast (SSPC-SP10 or 6)
Epoxy	Near white or commercial blast (SSPC-SP10 or 6)(b)
Coal tar epoxy	Near white or commercial (SSPC-SP10 or 6)
Urethane	Near white or commercial (SSPC-SP10 or 6)

Organic zinc	Near white or commercial (SSPC-SP10 or 6)
Inorganic zinc	White or near white (SSPC-SP5 or 10)

Note: No established criteria are available for the latex paints finding increasing use on steel.

(a) SSPC-SP: Steel Structures Painting Council Surface Preparation.

(b) Polyamide-cured epoxies require only a commercial blast.

Table 18 Estimated life of paint systems in years

Paint system	**Cleaning SSPC designation**	**Average dry film thickness**		**Climatic conditions**			**Immersion service**			**Splashes and spills**		
		μm	**mils**	**Mild**	**Moderate**	**Severe**	**Fresh water**	**Salt water**	**Petroleum products**	**Acid**	**Alkaline**	**Halogens**
Alkyd:												
3 coat	SP3	114	4.5	4	2	1.5	. . .	. . .	. . .	. . .	. . .	. . .
3 coat	SP6	114	4.5	6	4	2	. . .	. . .	. . .	. . .	. . .	. . .
Latex (acrylic):												
3 coat	SP3	127	5.0	6	3	1.5	. . .	. . .	. . .	. . .	. . .	. . .
3 coat	SP6	127	5.0	10	5	3	. . .	. . .	. . .	. . .	. . .	
Epoxy polyamide:												
2 coat	SP6	152	6.0	7	6	5	. . .	. . .	. . .	. . .	. . .	. . .
3 coat	SP6	254	10.0	10	8	5	5	. . .	. . .	5	6	5
Inorganic zinc:												
+3 coat	SP10	254	10.0	12	10	6	6	5	. . .	6	7	6

3 coat	SP10	305	12.0	14	10	7	6	. . .	12	5	6	5
Urethane-epoxy:												
Inorganic zinc + 2 coat epoxy + urethane	SP10	305	12.0	15	12	10	. . .	. . .	. . .	. . .	. . .	4
2 coat epoxy + urethane	SP10	254	10.0	15	10	8	. . .	. . .	20	7	7	5
Vinyl:												
Inorganic zinc + 3 coat	SP10	305	12.0	15	10	8	8	6	. . .	. . .	. . .	. . .
3 coat	SP10	254	10.0	12	8	6	6	4	. . .	3	5	4
Chlorinated rubber	SP6	305	10.0	10	9	8	5	5	. . .	9	6	9
Coal tar epoxy	SP6	406	16.0	8	7	6	8	6	. . .	4	. . .	4

Coating of Galvanized Steel. Special treatment must be provided for galvanized structural steel that normally has a nominal thickness of 0.13 mm (5 mils). Data indicate that in rural exposures rusting will not occur for 74 years, and in a marine environment, 33 years of rust-free service can be expected. For a marine-industrial exposure, 16 years of rust-free use can be expected. Normally, the galvanized structure must be degreased and acid phosphate etched using a vinyl butyral pretreatment similar to Mil-Spec DoD-P-15328. A primer, intermediate coat, and topcoat is then applied to the prepared surface. The primer coat must be selected to be compatible with the wash primer; the coatings manufacturer should be consulted at this point in the selection process. Careful control as to coating thickness of wash primer must be followed to provide a cohesive film. The wash primer must be between 0.006 and 0.013 mm (0.3 and 0.5 mil) thick followed by the appropriate thickness of the subsequent coating system.

Economic Factors. When painting steel structures, many economic factors need to be considered in preparing a job estimate, including:

- The area to be painted
- The surfaces to be coated, such as galvanized steel or ungalvanized steel or the combination of the two
- The complexity of the structure (e.g., the number and types of bolts, rivets, or welds)
- The type of structural member to be encountered
- The accessibility of surfaces with the tools required
- The downtime for the facility, including the time to erect scaffolds, place drop cloths, rope off the area, provide alternate parking and alternate storage if required
- The cost of scaffolding and drop cloths, which should include horticultural care such as plantings and grass
- Surface preparation and removal of debris

- Painting

Actual costs vary depending on the season and the location of the structure. Preparing some surfaces for specified paints may add to the cost. Steel that is pitted, gouged, or has discontinuous welds, requires filling with epoxy putty or similar filler material. Sometimes even rewelding and grinding are required for high value structures.

Surface Preparation

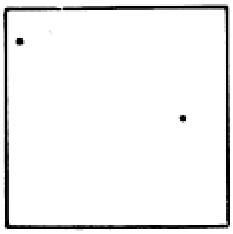
After the selection of a coating system, the most important factor to be considered is surface preparation. Surface preparation must be compatible with the primer and topcoating. Surface preparation is often the most costly phase of the corrosion prevention process for steel, averaging over half the cost of paint application exclusive of scaffolding.

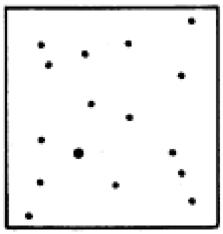
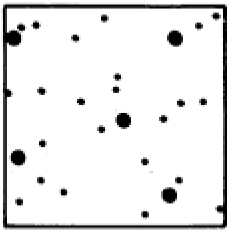
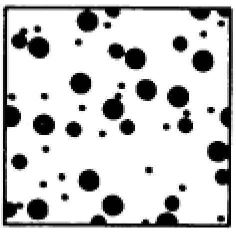
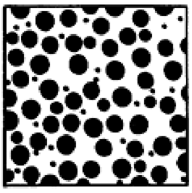
Surface preparation should remove mill scale, rust, oil, grease, atmospheric materials, weld spatter, and old coatings. Surface preparation also provides an anchor pattern to allow the primer and following coats of paint to key into the surface for a good bond. Table 17 shows minimum surface preparation requirements for steel with commonly used coatings. Table 13 summarizes various methods of surface preparation used before painting and provides the Steel Structures Painting Council (SSPC) designation for each method.

Inspection of Surface. Before proper surface preparation and painting method can be applied, the condition of the surface must be determined. For new or previously uncoated steel surfaces, the Steel Structures Painting Council visual standard (SSPC-VIS1) defines the four rust grades of structural steel and contains colored photographs presenting surface preparation standards. Shop primed coated steel would be expected to have no rusting except for small areas abraded during handling.

However, most of the steel structures encountered have been coated previously. The coating layers may be concealing as much rust as is showing on the surface. The surface condition of a previously coated steel substrate may be classified in accordance with ASTM 610/SSPC-VIS2 for the degree of rusting, as shown in Table 19 (SSPC-VIS2 for Pictorial Representation of Rust Classification). The chalking, blistering, flaking, erosion, checking, and cracking of the coating may be classified by the corresponding ASTM visual standards. Instrumentation is available for determining the presence of pinholes, the adhesion of the coating film to the substrate, and the film thickness.

Table 19 Steel Structures Painting Council standard SSPC-VIS2 for pictorial representation of rust classification for surfaces to be painted

Paint system condition	**Cleaning and painting recommended**	**Rust grades**	**Area of example, %**
Nondeteriorated, 0 to 0.1% rust			
Paint almost intact; some primer may show; rust covers less than 0.1% of the surface	Solvent clean (SSPC-SP1) entire repaint area, and spot prime, if necessary. If required to maintain film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	10-8	
Slightly to moderately deteriorated, 0.1 to 1% rust			

Finish coat somewhat weathered; primer may show slight staining or blistering; after stains are wiped off, less than 1% of area shows rust; blistering, loose mill scale, or loose paint film	Spot clean (minimum SSPC-SP2) entire repaint area, and spot prime. If required to maintain minimum film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	8-6	
Deteriorated, 1 to 10% rust			
Paint thoroughly weathered, blistered, or stained; up to 10% of surface is covered with rust, rust blisters, hard scale or loose paint film, very little pitting visible	Spot clean (minimum SSPC-SP2) entire repaint area, feather edges, and spot prime. If required to maintain film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	6-4	
Severely deteriorated, 10 to 50% rust			
Large portion of surface is covered with rust, pits, rust nodules, and non-adherent paint. Pitting is visible	Clean (minimum SSPC-SP6) entire repaint area, feather edges, and spot or full prime. If required to maintain film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	4-1	
Totally deteriorated, 50 to 100% rust			
	Clean (minimum SSPC-SP6) entire repaint area and apply primer, intermediate, and finish coats over entire repaint area	1-0	

Surface profile allows the coating to key into the metal substrate. Surface profile is determined by the abrasive material, including hardness, mass, and firmability, and the force with which the abrasive material impinges upon the surface. The selection of appropriate surface profile provides the bases for good primer adhesion. The coating formulator takes into account the viscosity of the primer, which allows the coating to fill the contact surface, the number of polar groups to come in contact with this surface, and the mechanical anchor or tooth that facilitates adhesion of the primer to the contact surface. Surface profile cannot expose the peaks of the metal once the primer is applied. Therefore, the abrasive blaster must use the correct angle of attack and distance from the work during the blasting operation. An abrasive-blasted surface profile of from 0.038 to 0.089 mm (1.5 to 3.5 mils), measured from the top of the highest peak to the bottom of the lowest valley, is used for most coating systems.

Surface inspection includes the determination of the condition of the surface before surface preparation and the results of the surface preparation. SSPC VIS1 provides a standard for surfaces before preparation and prepared surfaces. Surface comparison may also be made by using a surface-profile comparator and the NACE Standard TM-01-70, prepared by the National Association of Corrosion Engineers.

Structural design may limit access to the sections being prepared for painting. Access for abrasive blasting requires approximately 455 mm (18 in.) of clearance of the blast nozzle, although 150 mm (6 in.) can be sufficient if superficial cleaning can be tolerated. Sharp edges resulting from corrosion pits, deep gouges, or cut edges should be properly prepared. Pits and gouges over 3.18 mm ($\frac{1}{8}$ in.) deep should be filled with weld metal and ground flush to the surface or prepared for painting with an epoxy grout. Cut edges should be chamfered to a 3.18 mm ($\frac{1}{8}$ in.) radius by grinding. Bolts and rivets should be tight against the steel plates, not allowing crevices; areas surrounding bolts and rivets should be hand brushed with primer after the areas have been abrasive blasted. Discontinuous weldments or tack welds should be properly prepared. Continuous welds should be required, or an epoxy grout or caulk should be used to eliminate water accumulation. Where water may accumulate, in areas such as cross members joining channels and L sections that are directly exposed to the sky, weep holes are needed that are sufficiently large to allow water to drain and debris to be flushed through.

Quality Control

Paint materials should be purchased to meet the needs of the job at hand. Storage should be minimal to avoid material deterioration because of temperature variations. Coating materials, pretreatment primer, primer, intermediate coating, and topcoating, should be obtained from the same supplier and prepared by the same manufacturer to avoid incompatibility of materials and abrogation of the manufacturer's warranty. When using new and unfamiliar materials, the manufacturer's representative should be consulted and should supervise critical portions of the surface preparation and coating application.

Paint in freshly opened containers should not require straining. However, if skins, lumps, color flecks, or foreign materials are present, paints should be strained after mixing. First, remove any skins from the paint surface, thoroughly mix the paint, thin to application viscosity necessary, and strain through a fine sieve. Use straining as a standard procedure when paint is to be applied by spraying to avoid clogging the spray gun.

Paints should be ready for application by brush or roller when received. Unnecessary thinning or excessive thinning results in an inadequate film thickness and drastically reduces the longevity and protective qualities of the applied coating. In all instances, measure the viscosity of the material to determine that it is correct for the method of application established by the manufacturer. When thinning is necessary, it must be done by competent personnel using the compatible thinning agents recommended in label or specification instructions. Do not thin to improve brush or rolling of paint materials that are cold. Paint materials should be preconditioned to bring them to between 15 and 29 °C (65 and 85 °F) for application.

Sampling and testing of the coating material may be required before it is applied. This is done to confirm that the materials that have been supplied meet specifications. Tests should be performed by the supplier and if confirmation is required, additional testing should be performed by a qualified independent testing laboratory retained by the purchaser of the material.

Sending paints out to an independent testing laboratory requires accurate selection and labeling. Select samples from each lot of coating material supplied by the painting contractor, if more than 380 L (100 gal) of material of each kind is to be used on the job. A representative of the contractor should take these samples. The samples should be two full gallons if supplied in gallon containers or two 1-qt containers properly labeled. Inspect the containers to determine that full measure has been received. Record the following on each sample container: manufacturer's name and address, tradename and manufacturer's designation of the material, contractor's name and address and contract number when applicable, date and weather conditions when the sample was taken if put in a 1-qt container, batch or lot number, date of manufacture, and number of gallons represented by the sample. Forward the samples to the laboratory with a written request for the tests required, either full compliance or specific test desired. Include the above information in the request form.

Field and paint shop testing should be done if there is any doubt that materials meet specification requirements. When preparing the paint for use and during painting operations by contractors, limited testing should be done to determine if paints have been adulterated. However, limited field testing should not be considered as a substitute for standard laboratory techniques. Field testing is used to discover major flaws or adulteration in a coating material. Sampling on the job is done by the contractor in the presence of the inspector, unless other arrangements have been made.

Material storage should be at 24 °C (75 °F) plus or minus 6 °C (10 °F), because paint is a temperature sensitive product. Low temperatures cause paints to increase in viscosity and may require conditioning for 24 h before use. Freezing temperatures may ruin water-borne paints and cause container to bulge or burst. High temperatures result in lower viscosities, causing pigment to settle and thus producing poor flow characteristics. Coating materials may be extremely sensitive to heat. At temperatures over 38 °C (100 °F), gelation may occur, resulting in unusable material. At these high temperatures, pressure can build up within the containers enough to cause lids to blow off, creating a serious fire hazard. Application is seriously affected when coating materials are used after being stored at very high or low temperatures. Additional conditioning time and effort are required in these cases to ensure proper application and optimum surface protection.

Other factors to be considered are high humidity, which causes containers to corrode and labels to deteriorate, and poor ventilation, which allows the collection of excessive concentrations of solvent vapors that are both toxic and combustible. Pumps for drawing liquids from steel drums must be approved by fire underwriters. Gravity spigots, other than self-closing types, should not be used because of the possibility of accidental spillage. Stock should be stored so that all labels can be easily read and containers can be rotated to use older material first. Materials should be issued for each work shift in amounts that are consumed during that time without loss or spoilage.

Maintenance Program

The most economical approach to maintaining a coating system is the establishment of a periodic maintenance program. If the appropriate structural steel alloy is selected, uniform corrosion should be the only corrosion encountered without a protective coating system. Proper surface preparation and selection of a coating system suitable to the ambient conditions can provide a 10-year life cycle for the coating. An annual touch-up and the application of a full topcoat after 5 years of exposure can provide this 10-year life cycle.

A spotty appearance can result from periodic touch-ups, especially if the topcoat has chalked. In addition, catalyzed coating systems are difficult to topcoat, because only cohesive forces hold the freshly applied topcoat to the aged coating, and the aged coating must be roughened by brushoff blasting before applying a fresh coating. A maintenance coating must be compatible with existing coatings.

When programmed maintenance is instituted, all structural exteriors should be inspected annually to establish the following:

- Update the condition of the structure to determine the priority for painting
- Determine if washing is the only process needed to improve or maintain appearance
- Determine what portions of the structure require touch-up painting
- Determine if the structure requires a totally new coating system

Specifications and Industrial Guidance

Specifications and industrial guidance have been developed by the Steel Structures Painting Council committees. These specifications are used for industrial applications. A second source of standardization data and guidance is the Department of Defense publications. The standardization documents include military handbooks that reference federal and military specifications. All these federal and military documents are listed in the Department of Defense Index of Specifications and Standards (DoDISS). The American Society for Testing and Materials issues consensus standards on paint constituents and the testing of paints; however, these standards currently do not cover paints as supplied by industrial producers or vendors. Other specifications and guidance are available from the National Association of Corrosion Engineers and the American Society of Naval Architects. Most of the documents are available in various libraries throughout the United States.

Safety

Safety hazards are of two types--those resulting from the location of and access to the structural steel and hazards occurring as the result of exposure to paint as a possible toxic material. Hazards in the workplace are regulated by Department of Labor in the Occupational Safety and Health Administration (OSHA), which is responsible for establishing safety rules for workers and the materials they use. Hazards that are emitted to the environment are regulated by the Environmental Protection Agency.

Federal laws govern all works, and these laws established by congressional action are defined by OSHA rulings. These rulings are established by priority that is at the state and local level; therefore, the rulings can vary depending on where the work takes place and on the inspector who enforces the ruling. State safety requirements exert control in relevant areas whenever federal law or rulings do not cover projects. Municipal or township ordinances should be followed whenever specific rulings impose restrictions beyond the federal and state controls. It is at this level that safety requirement priorities are established and are moved up to the state, federal district, and national levels. Additional information is available in the section "Safety and Environmental Precautions" in this article.

Elastomeric Coatings for Automotive Plastics

Robert M. Piccirilli and John Burgman, PPG Industries

Introduction

THIS ARTICLE describes elastomeric coatings that are suitable for painting flexible plastic substrates. In particular, the coatings systems described are those that find utility in automotive exterior applications, where the requirements of appearance and durability are most severe. Wire coatings, for example, are not discussed even though they definitely have a demanding flexibility requirement. The article also focuses on substrates that have a high degree of flexibility, so it does not include coatings systems for more rigid plastics, such as fiberglass-reinforced polyester sheet molding composites or the more rigid nylon substrates, although some of the coatings systems described would certainly perform well in these applications.

More general information about the selection and application of organic coatings is available in the article "Painting" in this Volume.

Types of Elastomeric Coatings for Automotive Plastics

Flexible plastic substrates became popular for automotive use in the 1970s, when legislation mandated that automobiles should sustain little or no damage in low-speed collisions. As a result, the use of plastic bumpers and fascia capable of receiving these low-speed impacts without damage became widespread. These substrates are still widely used, including EPDM (ethylene-propylene-diene monomers), reaction injected molded polyurethane, glass-filled reaction injection molded polyurethane, and thermoplastic polyurethane. More recently, rubber-modified poly-propylene thermoplastic olefin has been used for many automotive exterior applications.

Paints that are used for these substrates must meet the automotive exterior requirements that the paint on the steel portion must meet. Among the most critical issues are durability, adhesion, appearance, and color match capability. In addition, flexibility of the painted substrate over a wide range of temperatures is a minimum requirement. Certainly the paint must be flexible enough that the part can be handled and attached to the car body in the assembly plant. However, many of the automotive specifications (e.g., Ref 1) require that the painted substrate be capable of being bent 180° over a 25 mm (1 in.) mandrel at temperatures below -18 °C (0 °F) with little or no cracking of the paint or substrate. In addition to performance requirements, elastomeric coatings must now comply with federal and local regulations that pertain to volatile organic compounds and hazardous air pollutants. All of these requirements have led to a wealth of research directed toward solving these challenges. Over the years elastomeric coatings have changed from low-solids enamels to high-solids basecoat clearcoat systems and, most recently, to water-based systems.

The types of chemistries that have been used for elastomeric coatings fall into two general categories:

- Modified polyester/polyurethane cross-linked with either melamine formaldehyde resin or polyisocyanate
- Modified acrylics cross-linked with either melamine formaldehyde resin or polyisocyanate

The details of these systems will be discussed as they pertain to structure, synthesis, and formulation.

Reference cited in this section

1. Specification ESBM 2J218A, Ford Motor Co.

Cross-linking Mechanisms

In the United States, the most popular mode of cross-linking for elastomeric coatings for exterior automotive fascia is via melamine formaldehyde chemistry. Coatings formulated in this fashion offer a number of advantages. First of all, they are single-component and therefore do not need any mixing or catalysis when applied. Melamine coatings have inherently good durability, and melamine formaldehyde resin is compatible with a wide array of resins, pigments, and solvents. One disadvantage of curing coatings with melamine formaldehyde is that somewhat elevated temperatures, approximately 120 °C (250 °F), are required to achieve adequate properties. Because many of the plastics that are used have a heat distortion temperature below 120 °C (250 °F), it is necessary to support the part during the painting and baking process. Another disadvantage of melamine cross-linked systems is susceptibility to environmental etching (i.e., spotting from acid rain), which has become a concern in recent years. It is not the purpose of this review to discuss the details of melamine formaldehyde chemistry; an excellent discussion is provided by Solomon (Ref 2).

Two-component isocyanate chemistry is finding increasing use in coating elastomeric parts. One advantage of this chemistry is its ability to cure at lower temperatures, which allows coating of unsupported plastic parts. Also, it appears that two-component isocyanate coatings offer enhanced resistance to environmental etching. These systems, however, require mixing just prior to application or at the gun because of limited pot life. Also, some care must be taken when handling the isocyanate portion because of its toxicity.

Either curing mechanism requires a polyol for cross-linking. In a given formulation, the type and amount of cross-linker required to achieve optimum performance may vary, but the basic properties of flexibility and durability are delivered by the polyol portion of the coating. Thus, this article focuses on that portion of the coating system. The types of polyols most commonly used fall into two major categories: modified acrylics and condensation polymers.

Reference cited in this section

2. D.H. Solomon, *Organic Chemistry of Film Formers,* Robert E. Krieger Publishing Co., 1982

Acrylic Polyols

Acrylic polyols that are not appropriately modified do not make good elastomeric coatings. A monomer composition with a low glass transition temperature (T_g) usually gives adequate flexibility, but the coatings are soft and do not possess good tensile strength. By raising the T_g of the acrylic polymer to improve hardness, the coating becomes too brittle to be useful over flexible substrates. Usually a modification is required that involves introducing some soft, low- T_g polymeric segment into the polymer backbone or pendant to the chain of a high-T_g acrylic polymer. This typically results in a good marriage of flexibility and hardness.

The use of polycaprolactone as a pendant group off the polymer chain is very common in the patent literature. Chang et al. (Ref 3) described the use of an adduct of hydroxyethyl acrylate and caprolactone to make useful elastomeric coatings from acrylics. Caprolactone reacts with alcohols to give adducts that contain flexible chain segments (Ref 4). If the alcohol is hydroxyethyl acrylate, an adduct is formed (Fig. 1). This adduct is further reacted with diisocyanate to form a long-chain polyester polyurethane with acrylate termination. This new low-T_g acrylate monomer can then be incorporated into a conventional acrylic by free radical polymerization. In this manner an acrylic polyol is prepared that has a polycaprolactone-based polyurethane pendant to the acrylic polymer chain.

$$CH_2 = CHCO_2CH_2CH_2OH + CO_2 - (CH_2)_5 \rightarrow CH_2 = CHCO_2CH_2CH_2O[CO(CH_2)_5O]_N - H$$

Fig. 1 Adduct of hydroxyethyl acrylate and caprolactone, used by Chang et al. (Ref 3) to make elastomeric coatings from acrylics

In another example in Ref 3, an isocyanate prepolymer was prepared by reacting methylene bis(cyclohexylisocyanate) with a polycaprolactone diol (prepared from caprolactone and diethylene glycol). This material was then reacted with hydroxyethyl acrylate to give a low-T_g acrylate functional polyurethane, which in turn was copolymerized with various other acrylate monomers to yield an acrylic polyol with urethane-modified polycaprolactone in the side chains. These polyols could be cured with N-butoxymethylacrylamide, melamine formaldehyde resin, or polyisocyanate to produce materials with good hardness and flexibility.

In the above examples, an acrylate monomer was prepared that contained a soft segment based on polycaprolactone. The acrylate monomer was then copolymerized with other acrylate monomers to yield a useful product. A second approach that yields similar products is to prepare an acrylic interpolymer that contains hydroxyethyl acrylate or some similar monomer, then react this material with a polycaprolactone-modified isocyanate prepolymer. Such materials are described in patents by Chang (Ref 5, 6). Although the examples are directed toward polycaprolactone-modified materials, these patents address the use of other low-T_g materials to modify the acrylic polymer, including poly(oxytetramethylene) glycols and other soft acrylic polyols with T_g < 10 °C, or 50 °F. Again, these materials could be cured with melamine formaldehyde resins to obtain useful coatings for elastomeric substrates.

The materials described above are high-molecular-weight polymers and thus are not suitable for use in high-solids coatings. In patents by Etzell et al. (Ref 7, 8, 9), acrylic polymers modified with caprolactone are described. The polymers are prepared in different ways, as described in the examples, but in each case the polycaprolactone moiety is attached to the polymer backbone through a hydroxyl-containing monomer, typically hydroxyethyl acrylate or hydroxypropyl acrylate. The caprolactone can be added while the acrylic polymerization is taking place, or a polycaprolactone-containing acrylate monomer can be used in the polymerization. In a typical example, caprolactone is mixed with solvent and a free radical catalyst. To this is added a mixture of monomers consisting of methyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate hydroxyethyl acrylate, and acrylic acid, and polymerization is conducted at elevated temperature. The polymers thus prepared are low in viscosity at reasonably high solids contents. The caprolactone-modified acrylics can be blended with melamine formaldehyde resin to produce coatings that have solids contents of 50% or greater and are generally quite useful over elastomeric substrates.

It should be noted that the coatings prepared from the caprolactone-modified acrylics of the Etzell patents (Ref 7, 8, 9) require the use of microgel to provide adequate sag resistance and metallic pattern control, whereas the low-solids materials described in Ref 5 and 6 provide the rheology control for good application. In fact, all high-solids coatings need some form of rheology control to maintain good application properties. The structure, synthesis, and function of pattern control agents are complex enough to be discussed in a separate review and will not be discussed here.

In general, acrylic polymers can be modified by caprolactone to make polyols suitable for cross-linking with melamine formaldehyde resin. In these cases, the working hypothesis is that one needs a relatively high-T_g acrylic backbone that can be modified with a relatively low-T_g side chain to achieve a good balance of hardness and flexibility. Polycaprolactone provides this soft side chain without any adverse effects on adhesion or durability. When the acrylic polyol is modified solely with caprolactone, high-solids coatings are possible. If the side chain is further modified with urethane linkages, lower-solids coatings are possible that do not require the use of rheology control agents for good application properties.

Soft side chains other than polycaprolactone can be incorporated into the acrylic polymer. Ryntz has shown a number of ways to incorporate a polyester into the backbone of an acrylic. In one invention, vinyl benzyl chloride is used to introduce copolymerizable vinyl groups onto a relatively soft polyester urethane (Ref 10). Thus, in a typical example, a polyester was prepared from 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, trimethylolpropane, and adipic acid. The polyester was reacted with diisocyanate and then further modified with vinyl benzyl chloride. This hydroxy functional carbon-carbon double bond bearing branched polyester was then copolymerized with butylmethacrylate, hydroxypropylmethacrylate, and methyl methacrylate to produce a graft copolymer of the invention. Finally, the graft copolymer was formulated into a high-solids coating composition with melamine formaldehyde resins, additives, and solvents to produce flexible, durable coatings.

Ryntz has described other methods of preparing polyester graft copolymers (Ref 11, 12). Instead of using vinylbenzylchloride to incorporate polymerizable moieties into a branched polyester, one can use a vinyl functional methoxy silane. Alkoxy silanes react with organic alcohols in a type of exchange reaction where the lower-molecular-weight alcohol is replaced by the higher-molecular-weight polymeric alcohol, in this case the polyester polyol, according to the equation

$$R\mathrm{Si}\,(\mathrm{O}R')_3 + R''\mathrm{OH} \rightarrow R\mathrm{Si}(\mathrm{O}R')_2(\mathrm{O}R'') + R'\mathrm{OH}$$

where R'' is a polyester polyol. In Ref 11 and 12, a polyester is prepared from 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate and Tone 301 (polycaprolactone triol). This material is then reacted with gmethacryloxypropyl trimethoxysilane to liberate methanol and to produce the polyester containing a polymerizable double bond. Copolymerization of the methacrylate-modified polyester with other durable acrylic monomers produces the grafted acrylic polymer described. Formulation of the grafted polymer with melamine formaldehyde resin produces coatings with good elongation and durability, as evidenced by gloss retention in cyclic ultraviolet accelerated weathering tests. It is believed that the use of the silicon compound in forming the vinyl functional polyester is responsible for the superior durability of these coatings.

An interesting approach to synthesizing polymers useful for elastomeric coatings is to attach a soft acrylic chain to a hard acrylic backbone. This can be accomplished through the use of mercaptoethanol. In patents by Simms (Ref 13, 14), a mercaptoisocyanate is prepared by reacting a diisocyanate with 2-mercaptoethanol. The mercaptoisocyanate thus formed is then reacted with a hydroxyethyl-methacrylate-containing acrylic to give an acrylic copolymer that has mercapto groups pendant to the polymer chain. (It should be noted that the T_g of this acrylic is too high to make a useful elastomeric coating.) The mercapto-modified acrylic copolymer is then grafted with a soft monomer composition (e.g., butyl acrylate) to yield a material with essentially two chains that are significantly different in T_g. These graft copolymers can be cured with polyisocyanate or melamine formaldehyde resin to give films with good elongation and excellent tensile strength.

Another approach to modifying acrylics to make good elastomeric coatings involves making a block copolymer of the A-B-A type (Ref 15). The B portion of the block copolymer is a urethane-modified polyester that contains terminal mercapto groups. The polyester is a linear, difunctional material that is reacted with diisocyanate to give a urethane-modified polyester with terminal isocyanate groups. Mercaptoethanol is added to the isocyanate-terminated polymer, resulting in the thiol-terminated B segment. A hard acrylic segment is grafted onto both ends of the B block through the thiol groups to provide the block copolymer of the invention. The block copolymer is formulated with another hard acrylic polymer, then cured with melamine formaldehyde resin or polyisocyanate to yield elastomeric coatings with excellent flexibility and durability.

Polysiloxane chains can also be grafted onto acrylic polymer backbones (Ref 16, 17). In a typical example, a hydroxy functional oligomeric polysiloxane reactant was prepared by reacting triethylene glycol with a commercially available methoxy functional polysiloxane, adipic acid, and trimethylol propane. The hydroxy-functional, polyester-containing polysiloxane unit was made acrylate functional by reacting with glycidyl methacrylate in such a way as to promote the epoxy hydroxyl reaction. This new carbon-carbon double bond bearing branched polysiloxane macromer was then copolymerized with styrene, butyl methacrylate, hydroxyethyl acrylate, and acrylic acid to produce an acrylic copolymer with polysiloxane grafted side chains. These materials have the advantage of having high solids at relatively low viscosity, which makes them suitable for high-solids coatings. Coatings prepared from these polymers are reported to have good durability, ability to adhere to a wide variety of substrates, and good flexibility. As with many of the polymers reported here, these materials need to be cured with melamine formaldehyde resin or polyisocyanate to produce useful coatings. Coatings of the high-solids type also need the appropriate rheology control agents to prevent sag and improve appearance.

In general, the types of acrylics useful for elastomeric coatings are those with a relatively hard polymer backbone, as defined by T_g, and a low-T_g or soft segment, usually pendant to the acrylic chain. The molecular weight of the two segments should be high enough that these materials exhibit the properties of both, in terms of phase transitions that are typical for multiphase systems. High-solids systems are possible with the appropriately modified acrylic, but to achieve good application properties, the proper rheology control additives are needed in the coating formulation.

References cited in this section

3. W.H. Chang, J.A. Erikson, and R.L. Scriven, U.S. Patent 4,034,017, July 1977
4. A. Schindler, *J. Coatings Technol.,* Vol 54, Oct 1982, p 693
5. W.H. Chang, J.A. Erikson, and S. Porter, U.S. Patent 4,208,494, June 1980
6. W.H. Chang, J.A. Erikson, and S. Porter, U.S. Patent 4,208,495, June 1980
7. R.A. Etzell, B.J. Miller, and D.J. Dziekan, U.S. Patent 4,546,046, Oct 1985
8. R.A. Etzell, B.J. Miller, and D.J. Dziekan, U.S. Patent 4,720,528, Oct 1985
9. R.A. Etzell, B.J. Miller, and D.J. Dziekan, Canadian Patent 1,246,769, Dec 1988
10. R.A. Ryntz, U.S. Patent 4,873,285, Oct 1989

11. R.A. Ryntz, U.S. Patent 4,870,140, Sept 1989
12. R.A. Ryntz, U.S. Patent 4,810,759, March 1989
13. J.A. Simms, U.S. Patent 4,243,573, Jan 1981
14. J.A. Simms, U.S. Patent 4,206,108, June 1980
15. J.A. Simms, U.S. Patent 4,346,201, Aug 1982
16. R.A. Ryntz and K.R. Kurple, U.S. Patent 4,673,718, June 1987
17. R.A. Ryntz and K.R. Kurple, U.S. Patent 4,754,014, June 1988

Condensation Polymers

Condensation polymers are polymers that are defined by condensation polymer kinetics, including polyesters, polyurethanes, or a combination of both. As will be shown below, these polymers are designed to be hydroxyl functional to enable cure with melamine formaldehyde resins or polyfunctional isocyanate. This class of polymers covers a large extent of the patent literature and can be divided into two major groups: high-molecular-weight, low-solids materials and low-molecular-weight, high-solids materials. Two factors are particularly important to good performance in this class of coatings: the branching or cross-link density of the condensation polymer employed, and the balance of low-T_g and high-T_g materials.

An early patent by Chang (Ref 18) described high-molecular-weight polyester polyurethanes that were useful for elastomeric coatings. In this patent, a polyester polyol that is subsequently modified with isocyanate is prepared from neopentyl glycol, trimethylolpropane, adipic acid, and isophthalic acid. The degree of branching of this polyester polyol is key to the performance of the resin in the coating. In this case the branching is defined as the number of moles of polyol or polyacid in 500 g of the polyhydric material, typically the polyester. The patent recommends that no more than one mole of material with a functionality of 3 or greater should be present per 500 g of material. Any amount higher than that results in poor flexibility of the coating.

A second key to good performance is the incorporation of urethane linkages through the use of polyisocyanate. The polyester polyol is reacted with diisocyanate to produce a polyurethane of sufficiently high molecular weight to provide good application properties and elasticity. The polyurethane polyols thus prepared are cured with melamine formaldehyde resin to give highly durable elastomeric coatings with excellent appearance. Elasticity can be further enhanced through the addition of a low-T_g polyol such as poly(oxytetramethylene)glycol to the coating formulation. Specifically, when one uses a soft, low-T_g polyol in the coating formulation it is best to employ a "harder," high-T_g polyol to achieve a balance of flexibility and hardness.

A variation on the aforementioned example was used to seal EPDM substrates, thereby preventing oil from the substrate from spewing out onto the coating (Ref 19). It was found that modification of the polyurethane polymer with a polyacid or anhydride in the later stages of the reaction gave good sealing properties. Thus, in a typical example, a polyurethane polyol was prepared from poly(hexanediol adipate), trimethylolpropane, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, triethylenediamine, and bis(isocyanatohexyl)-methane. To this polyurethane polyol was added maleic anhydride, and the reaction was carried out at a low enough temperature to allow only opening of the anhydride ring. The resin thus produced was cured with melamine formaldehyde resin to provide a good sealing primer for EPDM rubber. Even after accelerated weathering, EPDM rubber that was primed with the acid-modified polyurethane and then topcoated showed no yellowing or migration of plasticizing oils to the surface of the coating, whereas unprimed controls showed severe yellowing and loss of gloss.

In still another example of polyester polyols modified with isocyanate for melamine-cured elastomeric coatings, Guagliardo (Ref 20) recommends the incorporation of dimer fatty acid into the polyester portion of the polymer to improve the solvent and gasoline resistance of the coating.

A more classic example of elastomeric coatings is provided by Chang and Hartman (Ref 21). A polyurethane polyol is prepared from a high-molecular-weight, low-T_g polyol; a low-molecular-weight short-chain diol; and a diisocyanate. A typical experiment is described as follows: To a mixture of poly(oxytetramethylene)-glycol (molecular weight 1000), poly(neopentyl adipate), and 1,6-hexanediol in an appropriate solvent, methane bis(cyclohexyl-isocyanate) is added, followed by diethylenetriamine in cyclohexanone. The mixture is heated until all the isocyanate has reacted. The above polymer was formulated with melamine formaldehyde resin to give a coating with good low-temperature impact resistance and tensile strength. The key elements for good performance are a low-T_g polyol ($T_g < 25$ °C, or 77 °F), a short-chain diol or diamine, minimal branching in the polymer, and a polyisocyanate. The low-T_g polyol, which was poly(oxytetramethylene)-glycol in the above example, provides a soft, flexible matrix in which are embedded hard segments formed by the diisocyanate and short-chain diols and diamines. The molecular weight of the soft segment should be high enough to provide some phase separation of the smaller urethane segments. The diamine or polyamine delivers additional hard segments as well as sights for minimal branching.

A patent by Porter et al. (Ref 22) describes the use of polymeric polyol with a low T_g in combination with an excess of melamine formaldehyde resin. The low-T_g polyol is also low in hydroxyl content, and if it were cured with a stoichiometric amount of melamine resin a rather soft coating would result. However, when one uses a melamine formaldehyde resin that can homopolymerize in combination with the low-T_g polyol, coatings with excellent low-temperature flexibility result. Melamine formaldehyde resins that can homopolymerize are those that contain a high number of methylol groups, and these are well known.

In the above examples, it has been shown that urethane linkages are required for good elastomeric properties. They not only provide crystalline domains in the softer low-T_g matrix, but they also build viscosity by increasing molecular weight and hydrogen bonding. The higher molecular weight is a key factor in the durability and appearance of the coatings. However, Piccirilli et al. (Ref 23) have shown that polyesters alone can be made suitable for elastomeric coatings. The polyesters described are hydroxyl functional and are intended to be cured with melamine formaldehyde resin. Much like the polyurethanes, one of their keys to good performance is the minimal branching described above: 1 gram mole of polyol per 500 g of polyester. However, the major element required for good elastomeric performance is to keep the average molecular weight of these materials greater than 80,000, as measured by gel permeation chromatography. Examples described in Ref 23 show coatings having typical elongations of 80 to 150%. In addition, coatings made from the polyesters showed durability superior to that of some polyurethane coatings. These results indicate that molecular weight of the polyol is a factor in producing useful elastomeric coatings.

The above discussion of condensation polymers is intended to show the characteristics necessary to achieve elastomeric properties. These include polyurethane linkages, a mixture of low-T_g and high-T_g polymeric materials, a minimum of branching (as defined by the content of compounds having functionality of 3 or greater), and relatively high molecular weight. With respect to the last characteristic, it would appear that high-solids elastomeric coatings cannot be formulated, because they would require the use of low-viscosity, low-molecular-weight material. However, high-solids elastomeric coatings based on condensation polymers are described in a number of patents (Ref 24, 25, 26). Hard polyester polyols of low molecular weight are combined with soft polyurethane polyols of a defined molecular weight and an aminoplast or polyisocyanate curing agent.

The hard polyester polyol is characterized by its molecular weight, content of cyclic moieties, and hydroxyl functionality. The molecular weight of the polyester polyol is greater than 300, but usually less than 1000, to achieve the highest possible solids contents in the coating formulation. The hydroxyl equivalent weight is inversely proportional to the molecular weight and is generally kept low, approximately 200, to ensure adequate hardness characteristics from the hard polyester in the cured film. The hydroxyl functionality is typically 2, although it can be raised somewhat for special applications. The most important feature of the hard polyester polyol is the content of cyclic moieties present. These cyclic moieties can be either aliphatic or aromatic, although the aliphatic are preferred to achieve maximum flexibility. The cyclic moieties help to provide adequate hardness from the polyester polyol. Thus, in a typical example, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate is reacted with hexahydrophthalic anhydride to give a polyester polyol with a molecular weight of 544, a hydroxyl equivalent weight of 267, and a cyclic content of 27 wt%. The soft polyurethane polyol is prepared from a low-T_g polyol such as polycaprolactone or poly(oxytetramethylene)-glycol and a diisocyanate. The molecular weight of this material can be as low as 2000 or as high as 20,000, depending on the degree of flexibility required. The higher the molecular weight, the more flexible the coating becomes. These materials can be cured with melamine formaldehyde resin or polyisocyanate to obtain high-solids coatings with good durability and flexibility.

Alexander et al. (Ref 27, 28) describe the use of linear polyurethanes in combination with a hydroxyl-containing, urethane-modified polyester. In the specific examples given, a low-molecular-weight urethane diol is prepared and is subsequently reacted with other diacids, glycols, and polyols to give a relatively high-hydroxyl-containing material. The advantage of this procedure for preparing hydroxyl-containing urethanes is that it allows one to incorporate a high level of urethane linkages while avoiding gellation. It is proposed that the increased number of urethane linkages leads to a greater degree of flexibility. The hydroxyl-containing, urethane-modified polyester is relatively low in molecular weight, making it suitable for high-solids coatings, and the linear polyurethane is high enough in molecular weight to provide adequate flexibility. These materials are curable with melamine formaldehyde resin or polyisocyanate to give coatings with excellent elongation and weathering resistance.

Chang et al. (Ref 29) have described high-solids coating compositions that do not need higher-molecular-weight polyurethanes to achieve adequate flexibility. The polyol of this invention is characterized as above, by its content of cyclic moieties necessary for good hardness and durability, its hydroxyl content, and its urethane content. A representative composition involved the preparation of a polyester from neopentyl glycol, 1,6-hexanediol, and hexahydrophthalic anhydride. The polyester was subsequently modified with trimethylhexamethylene diisocyanate, resulting in a urethane-modified polyester. The resin was formulated into a coating composition with melamine formaldehyde resin that produced a paint with good hardness and moderate flexibility.

Elastomeric coatings cured with melamine formaldehyde are generally susceptible to environmental etching. A patent by Stephenson (Ref 30) describes compositions that have improved resistance to environmental etching. The coating compositions comprise a polyester, a silane-containing acrylic, a silsesquioxane (Fig. 2), and a melamine formaldehyde curing agent. The polyester portion of the formulation is very similar to the types of polyesters described above for the lower-solids elastomeric coatings. The silane-containing acrylic is a copolymer of standard acrylic monomers and an acrylatosilane such as g-acryloxypropyltrimethoxy silane. These are generally known in the art, and although the function of this polymer is not stated in the patent, it is presumed that it is necessary for some interaction with the silsesquioxane. The silsesquioxane is the key ingredient; coatings prepared with this additive show significantly improved acid etch resistance compared to controls that contain no silsesquioxane additive, without any compromise of other elastomeric coating properties except recoat adhesion. This drawback would be significant in a commercial application.

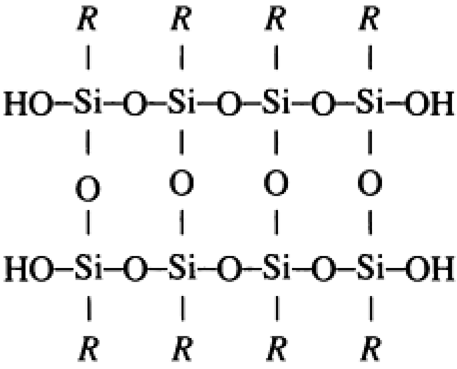


Fig. 2 Silsesquioxane used by Stephenson (Ref 30) to improve resistance to environmental etching

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References cited in this section

18. W.H. Chang and M.E. Hartman, U.S. Patent 3,954,899, May 1976
19. W.H. Chang, R.L. Scriven, and P.J. Prucnal, U.S. Patent 3,962,369, June 1976
20. M. Guagliardo, U.S. Patent 4,423,179, Dec 1983
21. W.H. Chang and M.E. Hartman, U.S. Patent 3,912,790, Oct 1975
22. S. Porter, Jr., R.L. Scriven, W.H. Chang, and J.B. O'Dwyer, U.S. Patent 4,154,891, May 1979
23. R.M. Piccirilli, W.H. Chang, D.T. McKeough, and S. Porter, U.S. Patent 4,205,115, May 1980
24. S. Porter, Jr., R.M. Piccirilli, W.H. Chang, J.B. O'Dwyer, and K.W. Lee, U.S. Patent 4,410,667, Oct 1983
25. R.M. Piccirilli, W.H. Chang, S. Porter, Jr., J.B. O'Dwyer, and K.W. Lee, U.S. Patent 4,410,668, Oct 1983
26. R.M. Piccirilli, W.H. Chang, S. Porter, Jr., J.B. O'Dwyer, and K.W. Lee, U.S. Patent 4,419,407, Dec 1983
27. D.J. Alexander, K.R. Kurple, and P.I. Kordomenos, U.S. Patent 4,524,192, June 1985
28. P.I. Kordomenos, K.R. Kurple, and D.J. Alexander, U.S. Patent 4,588,787, May 1986
29. W.H. Chang, R.R. Ambrose, D.T. McKeough, S. Porter, Jr., and D.R. Eslinger, U.S. Patent 4,540,766, Sept 1985
30. M.A.S. Stephenson, U.S. Patent 5,182,174, Jan 1993

Vapor Curing Systems

The above discussion has centered on polyols suitable for use with melamine formaldehyde resin or polyisocyanates. These two means of curing elastomeric coatings are the overwhelming choice for painting of fascia, bumpers, and other flexible automotive components. One other means of curing paint for elastomeric substrates that has not received much attention is vapor permeation curing, which offers the advantage of much lower baking temperatures, even as low as room temperature. Its disadvantage is the requirement of vaporous tertiary amine catalyst, which may be difficult to control in a production situation. Nevertheless, this coating technology can provide some very useful elastomeric coatings.

A good example is described in a patent by Blegen (Ref 31). In this case, a polyester is blended with a polyisocyanate, and the coating composition is applied to a suitable substrate. The film is then cured by exposure to tertiary amine vapor in an appropriate curing chamber. Cure times are as low as 20 to 60 s at room temperature. The polyester is unique in that it uses phenolic end groups, which apparently enhance the cure. A useful material for introducing the phenolic end groups is phydroxyphenylacetic acid, which is added at the very end of the polyesterification process. The coatings in the patent are reported to have good solvent resistance and excellent flexibility, as indicated by reverse impact testing.

In another example of amine vapor catalysis, Nahas et al. (Ref 32) made use of an amine functional acrylic in combination with polyisocyanate. An acrylic polymer was prepared from 4-vinyl pyridine, styrene, ethyl methacrylate, lauryl methacrylate, and hydroxyethyl acrylate. This polymer was blended with a polyisocyanate and cured for 4 min in the presence of vaporous dimethylaminoethanol. The resultant film was tough and flexible, whereas a film prepared from a similar acrylic polymer without the 4-vinyl pyridine did not cure at all. Obviously the extremely short cure times associated with amine vapor cure seem quite advantageous, but that has not offset difficulties associated with working with vaporous amines.

References cited in this section

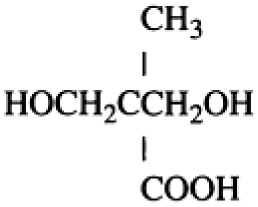
31. J.R. Blegen, U.S. Patent 4,374,181, Feb 1983

32. R.C. Nahas and C.H. Strolle, U.S. Patent 4,713,265, Dec 1987

Water-Based Systems

Water-based coatings for elastomeric substrates have only recently begun to see commercial use, in particular as basecoats for use with solvent-based clearcoats. However, the literature is abundant with references to water-based polymers, particularly polyurethanes, that have excellent elastomeric properties. To cover all of these references adequately would require a review article in itself. However, discussion of one patent can describe the general theme.

Scriven et al. (Ref 33) describe water-based polyurethanes that are useful as elastomeric coatings. In this case the now fairly classical polyurethane is prepared from a soft, low-T_g, long-chain diol; a low-molecular-weight, short-chain diol; a short-chain, carboxylic-acid-containing diol; a diisocyanate; and a chain extender, which is usually some sort of diamine. Specifically, an isocyanate-terminated prepolymer is prepared in a water-miscible solvent, and then this solution is added to water that contains a neutralizing amine and a chain-extending amine. The isocyanate prepolymer contains the long- and short-chain polyols as well as the acid-containing diol. Particularly useful as the acid-containing diol is dimethylolpropionic acid (Fig. 3), which provides carboxyl groups for neutralization with amine to render the material water-dispersible.



$$HOCH_2C(CH_3)(COOH)CH_2OH$$

Fig. 3 Dimethylolpropionic acid, used to make polyurethane water-dispersible

The carboxylic acid group in this material is sufficiently unreactive toward isocyanate that it can be introduced into the polymer backbone while the prepolymer is being formed. The prepolymer is relatively low in molecular weight, but after chain extension in water it becomes very high in molecular weight. The chain extension in water takes place almost exclusively with amine, because amine is about 10,000 times more reactive with isocyanate than water. Water-based polyurethanes prepared in this fashion are fairly common now, and because of their high molecular weight, they can be used as lacquers or cured with melamine formaldehyde resin.

At present, other water-based systems are being developed for use in elastomeric coatings, but they are still proprietary and will not be discussed here. However, the reader is referred to the review by Piccirilli (Ref 34) for a discussion of the idiosyncrasies in application of water-based coatings.

References cited in this section

33. R.L. Scriven and W.H. Chang, U.S. Patent 4,066,591, Jan 1978
34. R.M. Piccirilli and R. Pelo, "Waterbase Coatings for Plastics," paper presented at Finishing Automotive Plastics Conference, SME, Dec 1993

Coatings for Thermoplastic Olefins

The use of thermoplastic polyolefin (TPO) for exterior automotive parts has grown dramatically in recent years due to its low cost, low density, wide range of moduli, excellent appearance, and recyclability. However, due to its low surface energy, a pretreatment is required for good paint adhesion. Most TPOs have a total surface tension of about 30 dynes/cm, with a polar contribution of less than 3 dynes/cm. Although plasma or flame treatment of TPO can increase surface tension (Ref 35) and result in good adhesion, adhesion-promoting organic coatings are the pretreatments most often used in North America. Adhesion promoters are typically low-solids (5 to 10%), solvent-based coatings that contain chlorinated polypropylene. They are applied to power-washed or vapor-degreased substrates at low film thickness (5 to 10 μm) prior to priming and/or topcoating. Adhesion is provided by the chlorinated polypropylene. Other polymers have been reported to provide good adhesion to TPO, but they apparently have not found widespread use (Ref 36, 37, 38, 39, 40).

The chemistry and properties of chlorinated polypropylene have been described by Fujimoto (Ref 41). Chlorine content and crystallinity are key parameters that must be balanced to achieve sufficient solvent solubility and adhesive strength. The base polymer is isotactic poly-propylene. As the chlorine content of the polypropylene increases, the solvent solubility increases and the melting point and adhesive strength decrease due to lower crystallinity. A melting point minimum is reached at 20 to 30% Cl. Above this minimum, the softening point increases as the polymer becomes more amorphous. Although adhesive strength is higher at low chlorination levels, the polypropylene must contain enough chlorine to be soluble in organic solvents, which are used either to reduce the coating viscosity for spray application or to promote film formation following application. This balance is typically achieved with 20 to 30% chlorination.

Waddington and Briggs (Ref 42) suggest that chlorinated polypropylene promotes adhesion by diffusing into the substrate and forming a chain-entangled interface between the substrate and the adhesion promoter. These researchers used secondary ion mass spectroscopy and x-ray photoelectron spectroscopy to study the peeling failure between an adhesion promoter and two grades of TPO: one that exhibited strong adhesion and one that exhibited weak adhesion. Chlorine was detected on the surface of the TPO that exhibited strong adhesion, but not on the surface of the TPO that exhibited weak adhesion. In a separate experiment, the researchers coated the two grades of TPO with adhesion promoter and measured the amount of chlorine at the air interface of the adhesion promoter. Lower levels of chlorine were found over the TPO grade that exhibited better adhesion. This depletion of chlorine supports the theory that chlorinated polypropylene diffuses into the TPO. Also consistent with a diffusion mechanism is the improved adhesion, presumably due to increased mobility, that has been found when levels of rubber in TPO are increased (Ref 43).

Chlorinated polypropylenes are often modified for use in adhesion promoters. Each of the modifications described in the list below was intended to improve performance in some of the following key areas: adhesive strength, fuel resistance, humidity resistance, compatibility, and hardness. The first step is often to free radically graft acid or anhydride functionality onto the backbone. Maleic anhydride is commonly used at levels of less than 10 wt%. For example:

- Urata et al. (Ref 44) grafted maleic anhydride onto polypropylene using di-tert-butyl peroxide as an initiator. Following chlorination, the anhydride groups were partially reacted with a diepoxide such as Epon 828 to form a resin that could be blended with additional diepoxide to form a cross-linkable coating with good properties.

- Martz et al. (Ref 45) grafted maleic anhydride onto chlorinated polypropylene, then reacted the anhydride with a monohydric alcohol to form an esterified polymer with acid functionality. The polymer was then reacted with an excess of diepoxide to form an ungelled modified chlorinated polyolefin.
- Asato et al. (Ref 46) grafted maleic anhydride onto a chlorinated polypropylene, then esterified all of the carboxylic acid functionality. This polymer was blended with a polyurethane polyol to form a composition with good properties over nonpolar and polar substrates.
- Kinosada et al. (Ref 47) modified chlorinated polypropylene by reacting it with maleic anhydride and acryl- or methacryl-modified hydrogenated polybutadiene.
- Frey et al. (Ref 48) reacted a hydroxy amine with an anhydride functional chlorinated polypropylene to form an imidized polymer.
- Ashihara et al. (Ref 49, 50) did not graft maleic anhydride, but instead improved properties by copolymerizing acrylic oligomers, acrylic monomers, and polydienes with chlorinated polypropylenes.

Each of the above modifications led to some improvement in the performance of the adhesion promoter, but it must be realized that the key ingredient for adhesion is the chlorinated polyolefin. Water-based adhesion promoters for TPO are only now becoming available. As patents are issued and more publications become available, we will learn more about the vehicles that have been developed for water-based adhesion promoters for TPO.

References cited in this section

35. R.A. Ryntz, *J. Coatings Technol.,* Vol 63, 1991, p 63-68

36. J. Mayumi et al., European Patent Application EP 193126A1, 1985

37. T. Ito, M. Mogami, and K. Kobayashi, European Patent Application EP 226387A2, 1987

38. A.J. Kielbania, European Patent Application EP 18847 (1980)

39. C.H. Coney and J.R. Gossett, U.S. Patent 884,004, 1971

40. N. Miyazaki and T. Takayanagi, *Asahi Garasu Kenkyu Kokoku,* Vol 36 (No. 1), 1986, p 155-166

41. F. Fujimoto, *Paint & Resin,* Feb 1986, p 36-40

42. S. Waddington and D. Briggs, *Polymer Comm.,* Vol 32, 1991, p 506-508

43. E.J. West, *Polymers Paint Colour J.,* Vol 177, 1987, p 778-784

44. K. Urata and Y. Kurome, U.S. Patent 4,683,264, July 1987

45. J.T. Martz, J.B. O'Dwyer, and M.E. Hartman, U.S. Patent 4,997,882, March 1991

46. I. Asato, T. Nagatani, A. Inoue, and I. Fukuyama, U.S. Patent 5,030,681, July 1991

47. M. Kinosada, R. Orita, S. Tone, and T. Saito, U.S. Patent 5,135,984, Aug 1992

48. S.E. Frey, D.W. Magouyrk, A.J. Blankenship, P.J. Greene, and L.K. Johnson, U.S. Patent 4,954,573, Sept 1990

49. T. Ashihara, S. Tone, and R. Orita, U.S. Patent 5,130,373, July 1992

50. T. Ashihara, S. Tone, and R. Orita, U.S. Patent 5,143,976, Sept 1992

Porcelain Enameling

Technical Publications Committee of the Porcelain Enamel Institute, Inc.[*]

Introduction

PORCELAIN ENAMELS are glass coatings applied primarily to products or parts made of sheet steel, cast iron, or aluminum to improve appearance and to protect the metal surface. Porcelain enamels are distinguished from other ceramic coatings on metallic substrates by their predominantly vitreous nature and the types of applications for which they are used. These coatings are differentiated from paint by their inorganic composition and coating properties. They are fused to the metallic substrate at temperatures above 425 °C (800 °F) during the firing process.

The most common applications for porcelain enamels are major appliances, water heater tanks, sanitary ware, and cookware. In addition, porcelain enamels are used in a wide variety of coating applications, including chemical processing vessels, agricultural storage tanks, piping, pump components, and barbecue grills. They also are used for coatings on architectural panels, signage, specially executed murals, and substrates for microcircuitry. Porcelain enamels are selected for products or components where there is a need for one or more special service requirements that porcelain enamel can provide. These include chemical resistance, corrosion protection, weather resistance, abrasion resistance, specific mechanical or electrical properties, appearance or color needs, cleanability, heat resistance, or thermal shock capability.

Note

* John C. Oliver, Consultant to the Porcelain Enamel Institute, Inc. (Project Chairman); Douglas D. Giese, G.E. Appliances (Co-Chairman); Jeffrey F. Wright, Ferro Corp. (Co-Chairman); Ronald L. Allen, Ronalco, Inc.; Terry Conrad, Amana/Raytheon Corp.; John K. Cook, Chi-Vit Corp.; Ted Furr, Bethlehem Steel Corp.; Andrew Gordon, U.S. Steel, USX Corp.; Bernard L. Hall, Jr., JennAir/Maytag Co.; Michael Horton, Industrial Heating and Finishing Co.; William Huyser, Mapes & Sprowl Steel, Ltd.; Robert J. Long, American Porcelain Enamel Co.; Anthony R. Mazzuca, Miles, Inc.; Herbert Oliveira, Nordson Corp.; Arnold Preban, Inland Steel Co.; Charles R. Rarey, LTV Steel Co.; Donald R. Sauder, Porcelain Enamel Institute, Inc.; Narayan M. Sedalia, Whirlpool Corp.; Jeffrey Sellins, Magic Chef/Maytag Co.; Lester N. Smith, Porcelain Consultants, Inc.; Larry L. Steele, Armco Steel Corp.; Ted J. Wolowicz, G.E. Appliances

Types of Porcelain Enamels

Porcelain enamels for sheet steel and cast iron are classified as either ground-coat or cover-coat enamels. Ground-coat enamels contain metallic oxides, such as cobalt oxide and/or nickel oxide, that promote adherence of the glass/enamel to the metal substrate. Cover-coat enamels are applied over fired ground coats to improve the appearance and properties of the coating. Also, cover-coat enamels may be applied over unfired ground coats, with both coats being fired at the same time (i.e., two-coat/one-fire systems). Cover coats may also be applied directly to properly prepared decarburized steel substrates. The color of ground coats is limited to various shades of blue, black, brown, and gray. Cover coats, which may be clear, semiopaque, or opaque, may be pigmented to take on a great variety of colors. Colors may also be smelted into the basic coating material. Opaque cover coats are usually white.

Porcelain enamels for aluminum are normally one-coat systems. They are applied only by spraying. When two coats are desired, the first coat can be any color. Frits for porcelain enamels for aluminum are usually transparent and may be colored and opacified with inorganic pigments to produce the desired appearance.

Frits for Porcelain Enameling

The basic material of the porcelain enamel coating is called frit. Frits are smelted complex borosilicate glasses that are produced by quenching a molten glassy mixture. Frits generally are compounded from 5 to 20 or more components, which are thoroughly mixed together and melted into a glassy system. The molten glass is then quenched to a friable (easily broken up) condition by being either poured into water or rolled into a thin sheet between water-cooled rolls. When quenched in water, the frit is dried before use. When quenched in sheet form by water-cooled rolls, the sheet ordinarily is shattered into small flakes by mechanical means before use or shipment. Because porcelain enamels are usually designed for specific applications, the compositions of the frits from which they are made vary widely. A number of compositions of frits for enamels for sheet steel, cast iron, and aluminum are discussed below; however, many variations of these compositions are used commercially.

Enamel Frits for Sheet Steel. All the frits for which compositions are given in Table 1 are classified as alkali borosilicates and are used as ground coats on sheet steel. One of the functions of ground-coat enamels is to promote bond to the steel substrate. The addition of cobalt oxide and/or nickel oxide promotes adherence to the substrate. Compositions differ, depending on the end use application of the enameled product. For example, acid resistance is obtained by the addition of titanium dioxide and high levels of silicon dioxide with a corresponding decrease in the boron level. Resistance of the enamel to alkalis or to water can be improved by adding zirconium oxide or aluminum oxide (usually as zircon or alumina) to the frit while maintaining a high content of silicon dioxide. It is common practice to blend soft (low melting temperature), medium, and hard (high melting temperature) frits to obtain the maximum desired properties.

Table 1 Melted oxide compositions of frits for groundcoat enamels for sheet steel

Constituent	**Composition, wt%**			
	Regular blue-black enamel	**Alkali-resistant enamel**	**Acid-resistant enamel**	**Water-resistant enamel**
SiO_2	37.17	42.02	56.44	48.00
B_2O_3	22.21	18.41	14.90	12.82
Na_2O	18.44	15.05	16.59	18.48
K_2O	0.99	2.71	0.51	. . .
Li_2O	. . .	1.06	0.72	1.14
CaO	9.34	4.47	3.06	2.90
ZnO	. . .	. . .	. . .	. . .
Al_2O_3	4.53	4.38	0.27	. . .
ZrO_2	. . .	5.04	. . .	8.52
TiO_2	. . .	. . .	3.10	3.46
CuO	. . .	0.07	0.39	. . .
MnO_2	1.58	1.39	1.12	0.52
NiO	1.37	1.04	. . .	1.21
Co_3O_4	0.65	0.93	1.27	0.81
P_2O_5	1.15	0.68	. . .	0.20

Weather resistance has been shown to be a function of acid resistance. Porcelain enamels for use outdoors are made from various types of frits that produce the necessary acid resistance along with the specific color desired. Resistance to thermal shock and to high temperature is obtained by controlling the coefficient of expansion of the glass coating; this is accomplished by adjusting the frit composition and adding refractory materials, such as silicon dioxide, aluminum dioxide, and zirconium oxide, to the mill formula.

Cover coats for sheet steel are applied over ground coats or directly to properly prepared decarburized steel. Compositions of frits for cover-coat enamels are shown in Table 2. Electrostatic dry powder cover coats may be applied over an electrostatic dry powder base coat; then the entire two-coat/one-fire system is matured in a single firing. Electrostatic dry powder cover coats may also be applied over fired ground coats in a two-coat/two-fire process.

Table 2 Melted oxide compositions of frits for cover coat enamels for sheet steel

Constituent	Composition, wt%		
	Titania white enamel	Semiopaque enamel	Clear enamel
SiO_2	44.67	44.92	54.26
B_2O_3	14.28	16.40	12.38
Na_2O	8.27	8.67	6.55
K_2O	6.99	8.12	11.32
Li_2O	0.98	0.45	1.14
ZnO	. . .	0.74	. . .
ZrO_2	1.98	3.34	1.40
Al_2O_3	0.31	0.16	. . .
TiO_2	18.49	13.05	10.04
P_2O_5	1.32	0.88	. . .
MgO	0.5	. . .	. . .

Cover-coat enamels fall into three groups: clear, semiclear or semiopaque, and opaque. The clear frits do not contain high levels of titanium dioxide, and they remain clear when fired. The semiopaque frits are translucent and are used for light colors. The opaque frits, which contain high levels of titanium dioxide, become white upon firing.

Cover-coat enamels made from titanium-dioxide-opacified frits are generally quite acid resistant; even in amounts too small to provide any opacity, titania imparts acid resistance. For alkali resistance, zirconium oxide is a desirable constituent. Clear frits containing 8 to 11% titanium dioxide are used for strong to medium-strength colors. Semiopaque frits containing 12 to 15% titanium dioxide are used for medium-strength colors, and opaque frits containing 17 to 20% titanium dioxide are used for pastel colors.

Enamel Frits for Cast Iron. Compositions of frits for enamels for cast iron vary, depending on whether the frit is applied by the dry process or by the wet process (Table 3). Dry-process enamels are commonly used for large cast iron plumbing fixtures, such as bathtubs and sinks, where the enamel's brilliance and ability to cover small surface irregularities in the casting itself are useful characteristics. Acid resistance is imparted to these enamels by reducing the alumina content, increasing silica, and adding up to about 8% titanium dioxide. Ground coats are normally used to fill surface voids in castings. Ground coats for wet process enamels often are mixtures of frit, enamel reclaim, and refractory raw material used at very low application weight. Ground coats for the dry process method are applied by the wet process and are fused in thin, viscous coatings that protect the casting surface from excessive oxidation while it is heated to fusing temperature.

Table 3 Melted oxide compositions of frits for enamels for cast iron

Constituent	Composition, wt%				
	Groundcoats		Cover coats		
	Lead-bearing	Non-lead-bearing	Zirconium-opacified[(a)]	Titania-opacified[(a)]	Titania-opacified[(b)]
SiO_2	77.7	63.4	28.0	51.4	44.80
B_2O_3	6.8	10.9	8.8	9.6	13.14
Na_2O	4.3	7.1	10.0	10.1	6.48
K_2O	. . .	2.4	4.1	3.0	7.67
PbO	4.0	. . .	17.8	. . .	0.94
CaO	. . .	0.6	8.7	1.9	0.55
ZnO	. . .	. . .	6.1	0.9	. . .
Al_2O_3	7.2	15.1	4.5	2.1	. . .
Sb_2O_3	. . .	. . .	. . .	. . .	19.74
ZrO_2	. . .	. . .	6.1	. . .	1.64
TiO_2	. . .	. . .	. . .	18.4	. . .

F_2	. . .	0.5	5.9	2.6	5.04

(a) For dry process.

(b) For wet process

Enamel Frits for Aluminum. Enamel frits for aluminum are usually based on lead silicate or on cadmium silicate, but they may also be based on phosphate, vanadium, or barium. Table 4 gives the compositions of some frits for aluminum. Enamels for aluminum have a high gloss, good acid weather resistance, and good mechanical properties. They melt at relatively low temperatures.

Table 4 Melted oxide compositons of frits for enamels for aluminum

Constituent	Composition, wt%		
	Lead-base enamel	Non-lead-base enamel	Barium enamel
PbO	14-45	. . .	. . .
SiO_2	30-40	30-40	25
Na_2O	14-20	20-25	20
K_2O	7-12	7-11	25
Li_2O	2-4	3-5	. . .
B_2O_3	1-2	1-2	15
Al_2O_3	. . .	. . .	3
BaO	2-6	3-5	12
P_2O_5	2-4	2-4	. . .
F_2	. . .	. . .	. . .
TiO_2	15-20	15-20	. . .

Preparation of Enamel Frits

Frits for porcelain enameling are typically formulated and smelted by commercial frit manufacturers to meet the end use application requirements of their enamel shop customers.

Enamel shops using the wet application process normally receive their frit from their frit manufacturer in 100 lb bags. At the enamel plant, the frit is ground in a ball mill to prepare it for application to fabricated parts. The milling operations are described under the section "Grinding and Blending," which follows. Today most frit manufacturers are able to supply premilled, ready-to-use frit materials for wet application systems at plants not desiring to handle the milling operations at their facilities.

Porcelain enamel may also be applied to sheet steel components using the electrostatic dry spray application method. Frits for electrostatic dry application are ground without water by the frit manufacturer and are shipped to the porcelain enamel plant in a ready-to-use form. Small amounts of proprietary additives are included by the frit manufacturer during grinding to aid in electric charge retention during application and firing. Particle size is fitted to the appropriate level for each particular application. (See the section "Electrostatic Dry Powder Spray Process on Steel" in this article and Porcelain Enamel Institute Bulletin P-300, "Electrostatic Porcelain Enamel Powder Applications.")

Grinding and Blending. In the wet application method, porcelain enamel is applied as a suspension of finely milled frit in water. The frit is reduced to a fine particle size in the ball milling operation. For milling of the porcelain enamel material, the ball charge should occupy 50 to 55% of the volume of the mill. After loading the frit and mill additions such as clay, bentonite, electrolytes, and coloring oxides into the mill, the water is added. The mill is allowed to "grind" for a specific length of time in order to achieve the recommended fineness.

The recommended fineness of various types of porcelain enamels for sheet steel, cast iron, and aluminum is shown in Table 5. Typical end uses for porcelain enamels and the required service criteria are shown in Table 6.

Table 5 Fineness of various types of porcelain enamels for sheet steel, cast iron, and aluminum

Type of enamel	Milled fineness, % on 200-mesh screen[a]
Sheet steel	
Ground coat	4-9
Cover coat	
Non-acid resistant	4-8
Titania, acid resistant	0.5-3.0
Colored, non-acid resistant	0.5-5.0
Colored, acid resistant	0.5-3.0
Wet electrostatic	1-6[b]
Dry powder, electrostatic	0-6

Cast iron	
Ground coat	0.5-4.0
Wet process cover coat	3-6
Dry process	60-80(c)
Aluminum	
Ground and cover coats	0.2-1.5(b)

(a) Percentage of washed and dried wet-milled enamel sample remaining on 200-mesh screen.

(b) Percentage on 325-mesh screen, which replaces the 200-mesh screen in standard fineness test.

(c) Through a 200-mesh screen, dry test

Table 6 Typical end uses and required service criteria

Product	**Service criteria**
Wet process and dry powder, electrostatic	
Architectural panels	Acid and weather resistant
Chemicalware	Very acid resistant
Cookware	Acid and thermal shock resistant
Heaters and heat exchangers	Thermal shock resistant
Laundry units	
Exteriors	Alkali resistant
Interiors	Alkali resistant
Oven liners	

Conventional	Acid resistant
Pyrolytic	Acid and thermal shock resistant
Ranges	
Exteriors	Acid resistant
Top	Acid and thermal shock resistant
Grates and burners	Acid and thermal shock resistant
Reflectors, electric light	High reflectance, white
Refrigerators	Acid resistant
Sanitary ware, sheet steel	Acid resistant
Signs	Acid and weather resistant
Water heater tanks	Water resistant
Dry process	
Sanitary ware, cast iron	Acid resistant
Chemicalware	Very acid resistant

The enamel slip is unloaded either by gravity flow or by applying air pressure. Centrifugal or vibratory screening and magnetic separation of the slip as it is transferred from the mill to the storage tank is a recommended practice. To minimize contamination, separate mills should be used for grinding frits for ground coats, white cover coats, and colors. More complete information on ball milling is provided in Porcelain Enamel Institute Bulletin P-305, "Ball Mill Wet Grinding of Slips for Porcelain Enameling."

Premilled ready-to-use frit materials are available from frit manufacturers. These prepared products, are mixed and blended (blunged) by the enameler into a suitable enamel slip, using a high-speed blunger operating at 900 to 2000 rev/min.

Mill Additions. For sheet steel enamels, clays and electrolytes are used with frit to control the properties of the prepared porcelain enamel (slip) that is applied by the wet process. Refractory materials and pigments may be added to impart desired properties to the fired enamel. Table 7 lists some of the common mill addition materials used with wet process frits; also shown is the amount commonly used, along with the effect of each mill addition.

Table 7 Mill additions for wet-process enamel frits for sheet steel and cast iron

Additional material	**Amount added, %**	**Effect of addition**
Clay	2-8	Suspends glass; increases set; hardens bisque
Bentonite	0-0.5	Suspends glass; increases set; hardens bisque
Borax	0-0.75	Stabilizes suspension
Gum tragacanth	0-0.06	Hardens bisque
Alginates	0-0.06	Hardens bisque
Urea(a)	0-1	Reduces tearing
Sodium nitrite(a)	0-0.75	Increases set; reduces tearing
Magnesium carbonate	0-0.25	Increases set; moderately softens bisque
Potassium carbonate(a)	0-0.5	Hardens bisque; retards poppers; reduces tearing
Sodium aluminate	0-0.5	Increases set; stabilizes suspension
Potassium chloride(a)(b)	0-0.5	Increases set
Potassium nitrite(a)	0-0.75	Strongly increases set; reduces tearing
Potassium nitrate	0-0.06	Slightly increases set
Tetrasodium pyrophosphate(a)	0-0.33	Strongly decreases set
Zinc oxide	0-2	Fluxes enamel for lower firing temperature
Formaldehyde(a)	0-0.1	Prevents bacterial growth
Titanium dioxide	0-3	Increases opacity
Silica	0-15	Lowers gloss; increases resistance to chemicals and heat; increases refractoriness
Pigments	0-4	Produces desired color in fired enamels

Opacifiers	0-4	Produces opacity in fired enamels

(a) May be added to the slip after milling.

(b) Never used in direct-to-steel enamel slips

The soluble electrolytes that are highly alkaline, such as potassium carbonate and sodium aluminate, are responsible for flocculation of the clays. Flocculation is necessary to permit proper suspending action by the clays. Minor adjustments in the flow properties of the slip are made by varying the content of the clay and the electrolytes.

Mill additions for wet-process enamel frits for aluminum include boric acid, potassium silicate, sodium silicate, and other additives. These materials are used to control the wet suspension of the frits and to contribute to the characteristics of the fired enamel. Also, titanium dioxide is added to produce opacity, and inorganic pigments are added for the desired color.

Steels for Porcelain Enameling

There are a number of flat-rolled carbon steel products available today for porcelain enameling. The general categories are:

- Low-carbon enameling steels (enameling iron replacements)
- Decarburized steels
- Interstitial free steels
- Titanium-stabilized steels
- Common cold-rolled steels
- Common hot-rolled steels

Within each of these categories are products differing in chemical composition and/or method of production.

Aluminum killing and the steel industry's movement from ingot casting to continuous casting have added new sheet steel products for the porcelain enamel industry. At the same time, these industry changes have resulted in the gradual withdrawal of some long-time enameling-grade products from the market.

Low-Carbon Enameling Steels (Enameling Iron Replacements). For many years, enameling iron, a rimmed-ingot poured product with a low metalloid content, was used extensively for porcelain enameling. The enameling characteristics were excellent, with the caveat that the product required a separate ground coat before applying a cover coat. Because enameling iron is a rimmed steel, it cannot be continuously cast. The steel industry's movement to continuous casting has resulted in the recent withdrawal of the product from the market.

A number of highly serviceable enameling iron replacement products are now available for porcelain enameling. These aluminum killed steels have low carbon (0.02 to 0.04 wt%) and low manganese (0.15 to 0.30 wt%), along with 0.015 wt% P max, 0.015 wt% S max, 0.015 wt% Si max, and 0.03 to 0.07 wt% Al. Some contain a boron addition (0.006 wt% max) to aid in grain size control and to help improve resistance to enamel fishscale. The yield strength is 172 to 221 MPa (25 to 32 ksi), the tensile strength is 303 to 338 MPa (44 to 49 ksi), and the elongation is 38 to 46%.

Unlike the old enameling iron, these products do not require normalizing; they are either box annealed or continuously annealed. These processing changes result in steels that are more formable than their predecessors. Experience to date indicates that the enameling characteristics are similar to those of enameling iron, and these steels are being used in the same applications. They perform well with both ground-coat and two-coat/two-fire systems.

Decarburized Steels. The manufacture of fully decarburized sheet for direct-on cover coat enameling became practical following the development of the open coil annealing process. Different melting and teeming practices may be used to produce decarburized sheets: ladle aluminum killed-ingot poured, and ladle aluminum killed-continuously cast. These aluminum killed products are not subject to the return of yield point elongation following temper rolling. As killed steels, the hot coiling off the hot strip mill eliminates the possibility of having deep drawability as measured by the *R* value (plastic strain ratio), but in stretch and plane strain conditions, the decarburized products are excellent performers.

Enameling characteristics for decarburized steels are excellent, and these steels are being used in all types of today's enamel systems. The low carbon content eliminates primary boiling and consequent defects such as black specks, pullthrough, and dimples caused by the evolution of carbon monoxide and carbon dioxide through the porcelain enamel coating during firing.

These steels have excellent resistance to warpage. They also exhibit good resistance to defects such as "fishscale" and ground-coat reboiling during firing of the cover coat, both of which are caused by the evolution of hydrogen gas. If overpickled using the acid etch/nickel deposition metal preparation method, ladle killed steels will tend to have a "gassy" enamel surface, and enamel adherence is likely to be substandard. Ladle killing with aluminum and continuously casting is becoming the predominant way to produce these steels. It is expected that all decarburized steels will soon be manufactured by this method.

Interstitial-free steels are products in which all of the carbon and nitrogen contained in them are combined with an alloying element. Titanium or niobium (columbium), or a combination of titanium and niobium additions, are used to fully stabilize the steel. Domestically produced interstitial-free steels contain from <0.008 to 0.020 wt% C, 0.15 to 0.25 wt% Mn, 0.06 to 0.15 wt% Ti, and 0 to 0.10 wt% Nb. Vacuum degassing is used to produce the very-low-carbon versions, whereas the higher-carbon version is controlled by the basic oxygen shop. The yield strength is 138 to 165 MPa (20 to 24 ksi), the tensile strength is 290 to 317 MPa (42 to 46 ksi), and the elongation is 41 to 45%.

These steels have superior formability, particularly deep drawability as measured by the *R* value, which is in the range of 1.8 to 2.0. This permits extremely deep draws to be made successfully.

These steels exhibit excellent strength retention after strain and firing, as well as good base metal sag properties. They do not exhibit stretcher strain and are nonaging and nonfluting. Because titanium can effect the development of ground-coat adherence, enamel systems should be optimized to ensure satisfactory adherence with these steels.

There are many specific applications in the appliance and plumbingware sector where these steels have proved to be valuable, especially where deep drawing is required. Also, these products can be produced by either ingot pouring or continuous casting, thereby ensuring their future availability.

Titanium-stabilized steels are a variation of interstitial free steels. These steels are popular for large panels where maximum flatness can be achieved because of the product's resistance to warpage. Not being vacuum degassed, these steels are somewhat higher in carbon content than interstitial free steels.

This carbon is stabilized as titanium carbide by the addition of titanium. Stabilization provides carbon boil resistance, a high after-fire strength, and excellent deep drawability as measured by the *R* value. The higher titanium carbide content increases yield strength and reduces overall ductility. These steels offer high-temperature strength and resulting warp resistance, and they are now being produced as continuous-cast products.

Common cold-rolled steels have been used for many years in the porcelain enamel industry. They have been typically rimmed-ingot poured steels, but they are now being produced as continuous-cast products. They typically contain 0.04 to 0.07 wt% C and 0.25 to 0.040 wt% Mn. For cold-rolled drawing-quality steels, yield strength is 193 to 220 MPa (28 to 32 ksi), tensile strength is 295 to 330 MPa (43 to 48 ksi), and elongation is 40 to 44%. Enameling of cold-rolled steels should be restricted to ground coats and to noncritical appearance components.

Cold-rolled steels may also be used for two-coat enameling, where appearance is less important than in such components as range tops and other exterior parts for major appliances. Because of the high tendency of cold-rolled steel to warp and to carbon boil during porcelain enameling, the use of this material is generally restricted to components for which appreciable distortion during firing can be tolerated, applications using a low enamel firing temperature, or parts where a greater metal thickness is provided to minimize warpage. Most authorities recommend that parts fabricated from cold-rolled steels be porcelain enameled on one side only to minimize fishscale defects.

Common Hot-Rolled Steels. Hot-rolled sheets have a high susceptibility to fishscaling when porcelain enameled, especially if both sides of the steel are coated. When the use of hot-rolled steels is necessitated by the thickness and/or strength requirements for a given application, such as for water heater tanks, porcelain enameling should be limited to only one side of the sheet. This permits hydrogen gas, which produces the fishscaling, to escape from the unenameled side of the sheet.

Steel plate, tubes, pipes, and rolled sections may be porcelain enameled for specific applications. Examples include low-alloy steel pipe and tubing that is fabricated and porcelain enameled (i.e., glass-lined) for chemical pressure vessels and for sewage treatment plant piping systems, and low-carbon hot-rolled steel sections that are enameled for use as architectural components. The sheet should be thick enough so that sagging is reduced to an acceptable level.

Factors in Selecting Steel

The most important factors in the selection of steel for porcelain enameling are enamelability, freedom from surface defects, formability, sag characteristics, strength, and weldability. The relative importance of each depends on the requirements of the finished product.

Enamelability. Oxidation of carbon in the steel during enamel firing is the source of the carbon monoxide that causes primary boiling of the enamel. A limited amount of such gas evolution can e tolerated in two-coat/two-fire porcelain enameling, because the ground-coat enamel has high fluidity and tends to heal over defects. Because primary boiling does not reoccur on subsequent firing, a defect-free cover coat can be obtained.

In direct-on cover-coat enameling, however, very little gas evolution can be tolerated. Therefore, it is important to select a steel that is relatively free of carbon or one that has the carbon stabilized by the addition of titanium or a combination of titanium and/or niobium. When the higher-carbon steels are being selected for porcelain enameling, surfaces must be free of large angular cementite (iron carbide) particles.

Surface Defects. It is imperative that the surface of the steel be free of defects such as deep scratches, pits, slivers, scale, and open laminations. These defects are particularly troublesome in steels that are used for direct-on cover-coat applications.

Jagged metal burrs along scratches can protrude through the ground-coat enamel. Oxidation of these burrs during firing can cause copperheads in the ground coat and blistering in the cover coat. Folded-over burrs, deep scratches, and surface laminations can entrap dirt, drawing compounds, or cleaning and pickling solutions, all of which promote the formation of blisters in the porcelain enamel during firing.

Formability. Sheet steels for porcelain enameling are available in conventional commercial-quality, drawing-quality, and drawing-quality special-killed grades for varying severity of draw. The steels are usually supplied with a light application of oil to minimize rusting. This is particularly important in systems where acid etching is not employed during metal preparation.

Sag Characteristics. Sag is the permanent deformation or creep of steel due to its own weight during enamel firing. The sag resistance of steel is related to its strength at elevated temperatures and to the temperature at which the steel starts to transform from ferrite to austenite on heating. In general, the higher the strength and the higher the transformation temperature, the better the sag resistance of the steel. Figure 1 is a plot of typical metal sag of different enameling steels as a function of temperature. Thickness of these steels was 0.89 mm (0.035 in.).

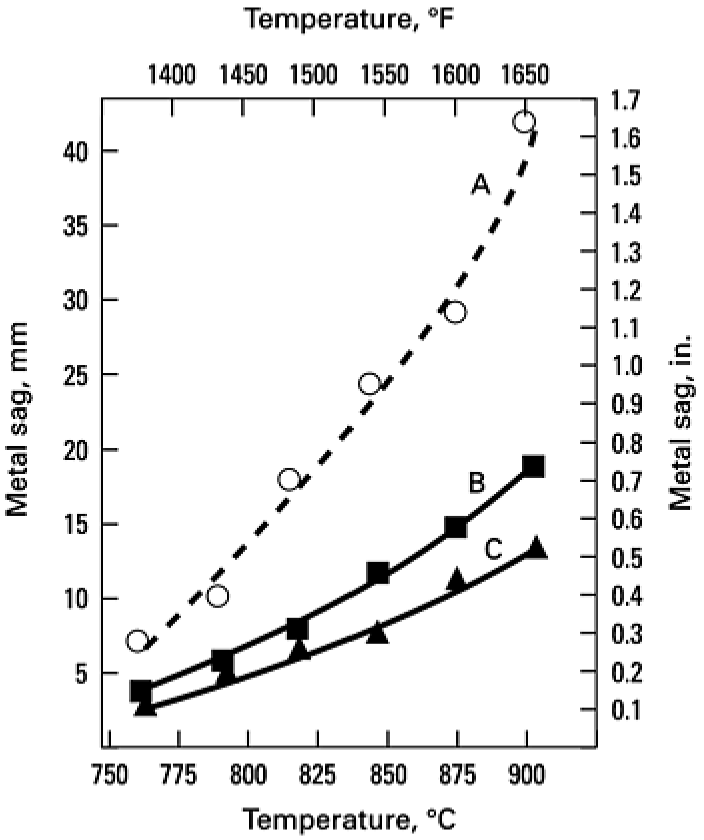


Fig. 1 Comparison of sag resistance of selected enameling steels. A, low-carbon enameling steels; B, decarburized steels; C, interstitial-free steels

Strength Retention. Some steels will exhibit critical grain growth and resulting loss of strength during the firing of the enamel coating 790 to 840 °C (1450 to 1550 °F) temperature range. Because the fired enamel coating is normally fractured when the base metal is strained beyond the elastic limit of 0.002 mm/mm (0.002 in./in.), the ability of a steel substrate to retain its strength after firing becomes an important factor when selecting steels for many service applications of the enameled component. In addition, the contour and thickness of the metal are other factors for consideration. Figure 2 shows the relative strength-after-firing characteristics of some commonly used enameling steels.

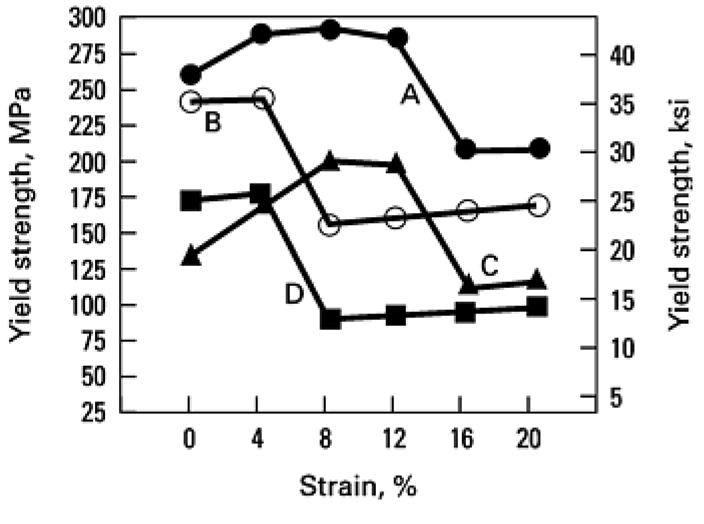


Fig. 2 Comparison of yield strength of four enameling steels after firing at 870 °C (1600 °F). A, low-carbon

enameling steels (drawing quality); B, low-carbon enameling steels; C, interstitial-free steels; D, decarburized

Weldability. Good welding characteristics are required for fabricated shapes. Welds must be free of inclusions, blowholes, and laminations.

Design of Metal Parts for Porcelain Enameling

The glasslike nature of porcelain enamel and the high firing temperatures used in its application impose limitations on the design of parts to be enameled. Proper design of each part is essential to ensure that finished work is within dimensional tolerances and has the durability for the intended service.

In general, the size of products or parts that can be porcelain enameled is limited only by the ability of fabricating and enameling facilities to accommodate their size. Table 8 indicates the maximum dimensions of workpieces that can be enameled in several types of conventional facilities.

Table 8 Maximum dimensions accommodated by enameling facilities

Type of enameling facility	Maximum dimensions of workpiece					
	Length		Width		Height	
	m	ft	m	ft	m	ft
Dial, small sign, or art	0.3	1	0.3	1	0.08	$\frac{1}{4}$
Range or laundry equipment	1.2	4	0.8	$2\frac{1}{2}$	1.2	4
Architectural; job shop	3.7	12	0.6	2	1.5	5
Special; chemical	18	60	4.6	15	4.6	15
Cast iron, dry process	1.8	6	0.9	3	0.8	$2\frac{1}{2}$

Steel Parts. The size relations for steel sheet given in Table 9 are recommended as a guide to ensure adequate flatness, rigidity, and sag resistance.

Table 9 Suggested sizes of steel sheet for adequate flatness, rigidity, and sag resistance

Sheet width	Maximum total area

mm	in.	m^2	ft^2
24-gage sheet			
150	6	0.05	$\frac{1}{2}$
305	12	0.3	3(a)
455	18	0.5	5(a)
22-gage sheet			
150	6	0.09	1
305	12	0.3	$3\frac{1}{2}$
455	18	0.5	6(a)
610	24	0.7	8(a)
20-gage sheet			
150	6	0.1	$1\frac{1}{2}$
305	12	0.5	5
455	18	0.7	8(a)(b)
610	24	0.9-1.4	10-15(a)(b)

(a) Should be embossed, flanged, or otherwise reinforced.

(b) All parts exceeding this area should be made from 18-gage 1.21 mm (0.0478 in.) or heavier thicknesses of steel sheet.

Distortion during firing is minimized by uniformity of stress and temperature during the cycle. Nonuniform thicknesses will heat at different rates and cause distortion and variations in enamel maturity. Specific aspects of design that should be considered are:

- Flatness requirements in a porcelain enameled part must be maintained at all processing stages. Wavy or buckled areas in the original sheet, as well as those introduced in forming and handling, will persist in the fired part.

- Bend and corner radii should be at least 4.7 mm ($\frac{3}{16}$ in.). In drawn parts, the use of symmetrical embossed ridges and panels increases resistance to distortion caused by uneven residual forming stresses.
- Flanges increase strength and flatness, but they can cause irregular stresses in firing. Flanges on one side only may require welded braces. Flanges meeting at a corner must be welded and should not vary in depth by a factor of more than three.
- Cutouts should have round corners; when cutouts are located on flange edges, at least 6.3 mm ($\frac{1}{4}$ in.) of flange should remain.
- Welded lugs and ears for attachment and assembly result in double metal thickness. They should be of the same or lighter gage as the main part and as small as possible.
- Spot and seam welds also result in double metal thickness. Spot welds are difficult to enamel because of metal movement during firing and possible entrapment of solutions used in preparing the metal part for enameling. Spot welds must be at least 0.32 mm (0.0125 in.) in diameter to minimize compression failure. Seam welds should be flattened to prevent burrs, rough projections, and protruding edges, all of which enamel poorly.
- Fusion welds must be free of crevices and oxide seams. Weld spatter must be removed to avoid coating defects.
- Sharp edges are subject to burnoff of enamel when the iron oxide formed during firing exceeds the amount of iron oxide that is soluble in the coating. The tight, matte-finish layer that results is protective, but it may not meet appearance or severe corrosion requirements.
- Holes must be designed up to 1.5 mm ($\frac{1}{16}$ in.) oversize to allow for enamel buildup. To avoid sharp areas on the appearance side of punched holes, the holes may be extruded inward, allowing maximum coverage on the face side but intensifying the burnoff on the reverse side.
- Fasteners should be provided with flexible washers or gaskets to distribute stresses and prevent crazing of the enamel.
- Processing requires some means of support for handling, usually by brackets or flanges. Holes, which may be required for drainage of metal preparation solutions and excess enamel slip, may also be used.

Figures 3, 4, 5, and 6 illustrate guidelines for proper design. For further reference, see Porcelain Enamel Institute Bulletin P-306, "Design and Fabrication of Sheet Steel Parts for Porcelain Enameling."

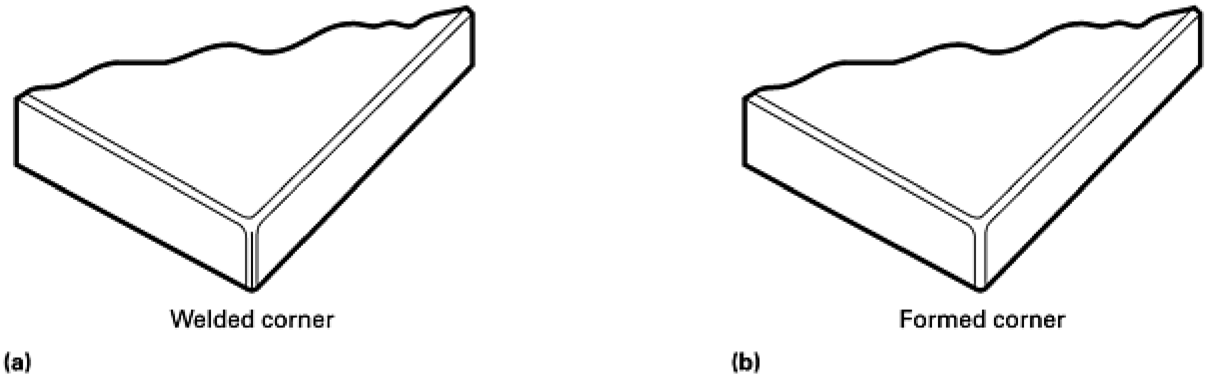


Fig. 3 Flange forming. (a) Flanges can be formed from blanks with notched corners, but they must be welded in the corner for strength, shape retention, and chip resistance. (b) Flanges can be formed with drawn shapes. Here, no welding is required.

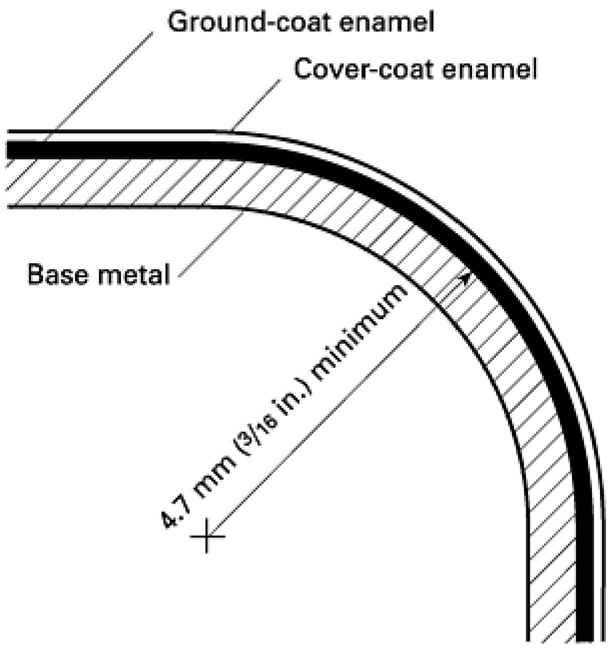


Fig. 4 Radius of curvature, two-coat enameling process. A minimum radius of 4.8 mm ($\frac{3}{16}$ in.) must be maintained at flanges, corners, and embossments to minimize assembly and field damage to parts coated by the two-coat enameling process.

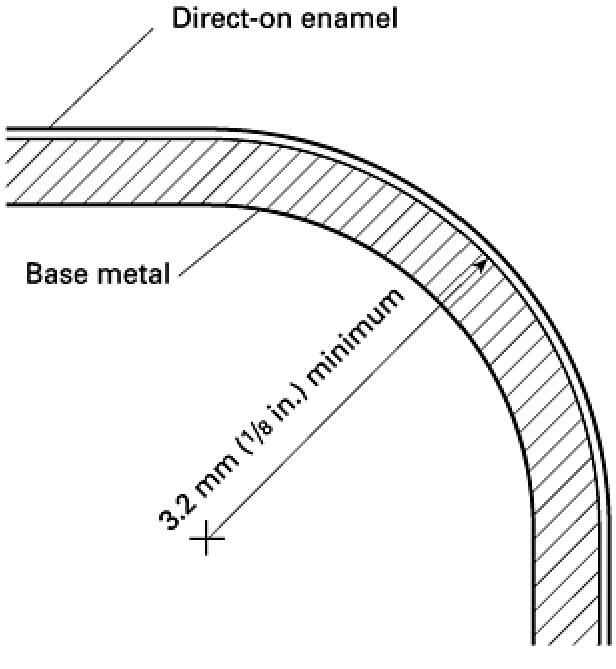
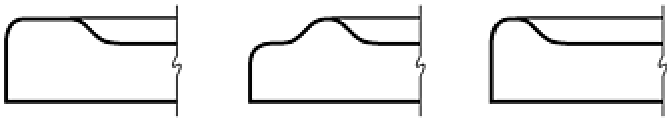
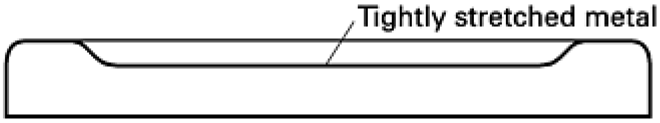


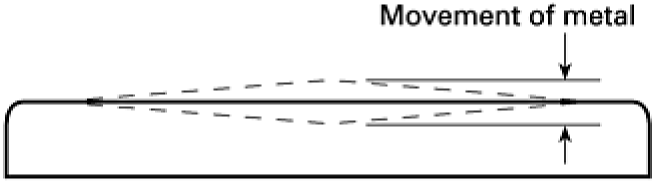
Fig. 5 Radius of curvature, one-coat enameling process. A minimum radius of 3.2 mm ($\frac{1}{8}$ in.) must be maintained at flanges, corners, and embossments to minimize assembly and field damage to parts coated by the one-coat enameling process.



Typical methods of embossing



Edged formed panel



"Oil can" effect

Fig. 6 Embossed panels. Panels may be embossed to increase strength of the part and to provide design relief for flat areas. Embossing also stretches the metal, thus reducing "oil canning." In embossing, an outside radius of 9.5 mm ($\frac{3}{8}$ in.) and an inside radius of 4.8 mm ($\frac{3}{16}$ in.) should be maintained for optimum enamelability and service life.

Cast Iron Parts. Uniformity of section, simplicity of design, and minimizing of lugs and braces are desirable characteristics for cast iron parts to be enameled. Radii of curved sections should be as generous as design limitations permit. The minimum radius may be 6.3 mm ($\frac{1}{4}$ in.) for decorative beading on a flat or slightly curved surface, or as large as 38 mm ($1\frac{1}{2}$ in.) for one of the components of a compound curve on a large casting.

Aluminum Parts. Because enamel ordinarily is applied to aluminum at only about half the thickness to which it is applied to steel, freedom from surface scratches, burrs, and irregularities is of double importance for the aluminum surface. Most shaping of aluminum is done before enameling, but the thin coating permits some bending, shearing, punching, and sawing of the part after it has been porcelain enameled.

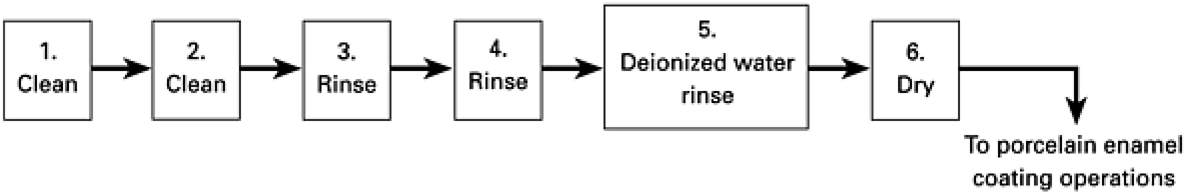
Surfaces to be enameled should have generous inside radii of not less than 4.8 mm ($\frac{3}{16}$ in.). Surfaces should have outside radii of not less than 1.6 mm ($\frac{1}{16}$ in.); 3.2 mm ($\frac{1}{8}$ in.) is preferred for both light and dark colors. Attachments should be welded to the unenameled backside of enameled heavy-gage aluminum sheet or extrusions. The visible metal surfaces must not be overheated; overheating causes the aluminum to blister and alters the color and gloss of the enamel. Welding can be done before enameling provided that the weld area is cleaned properly before coating.

Metal Preparation

The bond and appearance of porcelain enamel is heavily dependent on closely controlled cleaning of the metal surface. Complete removal of oil, drawing compounds, and other surface contaminants is essential. Steel may be prepared for porcelain enameling by the "clean only" method, and acid etch/nickel deposition process, or mechanical procedures.

Preparation of Steel for Porcelain Enameling

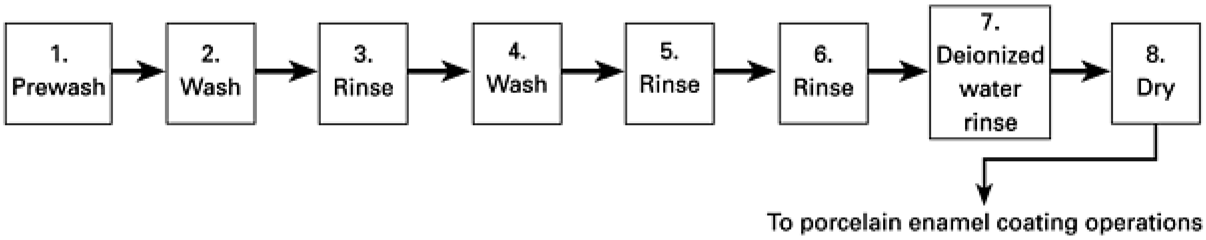
The "clean only " process has emerged in recent years as the dominant method for preparing steel components for porcelain enameling, especially for large-volume production using electrostatic dry powder application systems. Metal preparation using the "clean only" system requires at least the same amount of cleaning as is achieved using the acid etch/nickel deposition method, but no acid etching or nickel deposition is used. Benefits realized from using the "clean only" method include reduced operating costs, lower equipment costs, increased yield, reduced environmental problems, lower chemical usage, and reduced water consumption. Figures 7 and 8 illustrate the "clean only" cycle for both the spray process and the immersion process.



Stage	Solution composition	Temperature		Cycle time, min
		°C	°F	
1-Clean	Alkaline cleaner 30-60 g/L (4-8 oz/gal)	82-100	180-212	5-15
2-Clean	Alkaline cleaner 30-60 g/L (4-8 oz/gal)	82-100	180-212	5-15
3-Rinse	Tap water	49-71	120-60	1-2
4-Rinse	Tap water	Ambient	Ambient	1-2
5-Rinse[a]	Deionized water	Ambient	Ambient	$\frac{1}{2}$-1

(a) Deionized water rinse is required for two-coat/one-fire finish with excellent appearance

Fig. 7 "Clean only" metal preparation, immersion process

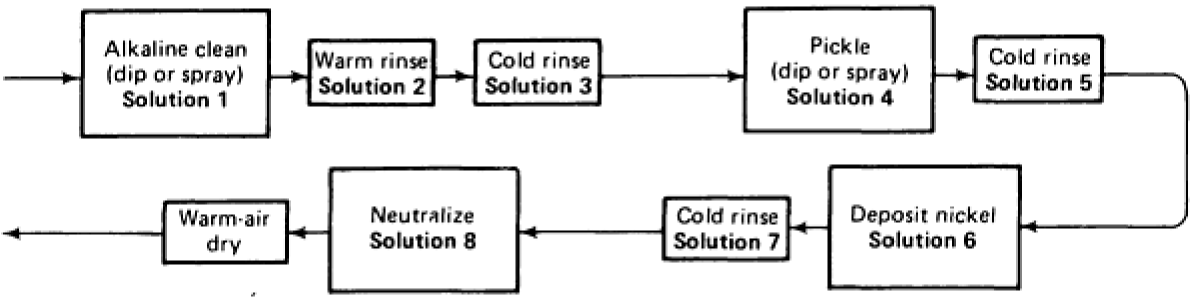


Stage	Solution composition	Temperature		Cycle time, seconds
		°C	°F	
1-Prewash	Tap water	Ambient to 71	Ambient to 160	30-60
2-Wash	Alkaline cleaner, 7.5-22.5 g/L (1-3 oz/gal)	60-71	140-160	60-90
3-Rinse	Tap water	60-71	140-160	30-60
4-Wash	Alkaline cleaner, 7.5-22.5 g/L (1-3 oz/gal)	60-71	140-160	60-90
5-Rinse	Tap water	Ambient to 71	Ambient to 160	30-60
6-Rinse	Tap water	Ambient	Ambient	30-60
7-Rinse(a)	Deionized water	Ambient	Ambient	10-30

(a) Deionized water rinse is required for a two-coat/one-fire finish with excellent appearance.

Fig. 8 "Clean only" metal preparation, spray process

In the acid etch/nickel deposition process, parts are placed on corrosion-resistant racks and dipped in or sprayed with a series of solutions. Mechanized equipment is required for high-production operations. The sequence of processing steps and the solutions used for the acid etch/nickel deposition method in production operations are indicated in Fig. 9. As is indicated in Stage 4, sulfuric acid is normally used to etch the metal. After drying at 93 to 150 °C (200 to 300 °F), the steel parts have a light straw color.



No.	Solution	Composition	Temperature		Cycle time, min	
			°C	°F	Dip	Spray
1	Alkaline cleaner(a)	Cleaner, 15-60 g/L (2-8 oz/gal)(b)	Ambient to 100(c)	Ambient to 212(c)	6-12	1-3
2	Warm rinse	Water	49-60	120-140	$\frac{1}{2}$-4	$\frac{1}{2}$-1
3	Cold rinse	Water	Ambient	Ambient	2-4	$\frac{1}{2}$-1
4	Pickle(d)	H_2SO_4, 6-8%	66-71	150-160	5-10	3-5
5	Cold rinse	Water, H_2SO_4(e)	Ambient	Ambient	$\frac{1}{2}$-4	$\frac{1}{2}$-1
6	Nickel-deposition(f)	$NiSO_4 6H_2O$, 5.6-7.5 g/L (0.75-1.0 oz/gal)(e)	60-82	140-180	5-10	4-6
7	Cold rinse	Water, H_2SO_4(e)	Ambient	Ambient	$\frac{1}{2}$-4	$\frac{1}{2}$-1
8	Neutralize	2/3 Na_2CO_3 and 1/3 borax, 0.60-2.10 g/L (0.008-0.28	49-71	120-160	1-6	1-2

(a) For spray cleaning, use a two-stage process.

(b) For spray cleaning, use 3.8 to 15 g/L (0.5 to 2.0 oz/gal).

(c) 60 to 82 °C (140 to 180 °F) for spray cleaner.

(d) Weight loss of metal is 3 to 5 g/m^2 (0.3 to 0.5 g/ft^2).

(e) Solution pH, 3 to 3.5, to prevent formation of ferric iron.

(f) Nickel deposit should be 0.2 to 0.6 g/m^2 (0.02 to 0.06 g/ft^2). Continuous filtration is commonly used to remove $Fe(OH)_3$.

Fig. 9 Ground-coat enameling, acid-etch/nickel-deposition process (dip or spray application)

When low-carbon decarburized steel is enameled in a direct-on cover-coat operation, parts must be etched to remove 11 to 22 g/m^2 (1 to 2 g/ft^2) of metal surface, and they must receive a nickel deposit of 0.9 to 1.3 g/m^2 (0.08 to 0.12 g/ft^2) of surface. Table 10 indicates modifications of the solutions and operating conditions for the acid pickling and nickel deposition cycles shown in Fig. 9 that have been used to provide increased metal removal and an increase in the amount of nickel deposited. Also, a ferric sulfate etching solution is sometimes used.

Table 10 Acid-etch and nickel-deposition solutions for preparing decarburized steels for direct-on cover coating

Solution[(a)]	**Composition of solution**	**Operating temperature**		**Cycle time, min**	
		°C	**°F**	**Dip**	**Spray**
Acid solutions[(b)]					
1	H_2SO_4, 6-8 wt%	71	160	15-30[(c)]	8-15[(c)]
2[(d)]	H_2PO_4, 17-20 wt%	60	140	4-8	2-5
3[(e)] First stage	Ferric sulfate[(f)], 5 wt%	65	150	2-4	$1\frac{1}{2}$-3
Second stage	H_2SO_4, 6-8 wt%	65	150	2-4	$1\frac{1}{2}$-3
4 Oxyacid	H_2SO_4, 6-9 wt%; $Fe_2(SO_4)_3$, 3-5 wt%; $FeSO_4$, 3-20 wt%	74	165	$1\frac{1}{2}$-4	$1\frac{1}{2}$-3
Nickel deposition solution[(g)]					

(a) Except for the use of these solutions, preparation entails processing as indicated in Fig. 9.

(b) Any of these solutions may be used in place of solution 4 in Fig. 9. Minimum metal removal required is 22 g/m^2 (2 g/ft^2) of metal.

(c) Cycle time may be reduced to that indicated in Fig. 9 for ground coats by oxidizing the metal 16 g/m^2 ($1\frac{1}{2}$ g of iron/ft^2) at 680 °C (1250 °F) in an air atmosphere, or by blasting with sand or steel grit to remove metal prior to pickling.

(d) Equipment containing lead or Monel cannot be used.

(e) Equipment containing lead cannot be used.

(f) Convert ferrous to ferric by adding hydrogen peroxide, sulfuric acid, and water.

(g) Nickel deposit should be 0.6 to 1 g/m^2 (0.06 to 0.10 g/ft^2).

(h) pH of solution, 3.2 to 3.5. Sulfuric acid or sodium hydroxide is used to adjust pH. The addition of 0.3 to 0.8 g/L (1 to 3 g/gal) of sodium hypophosphite to solution will increase the rate of nickel deposition and permit the use of the lower end of the temperature range without excessive cycle time.

A modification of the above-described system, identified as oxyacid, is also used. Oxyacid etchant solution is a mixture of sulfuric acid and ferric sulfate. The sulfuric acid and the ferric sulfate etch the metal, producing ferrous sulfate. The ferrous sulfate is then oxidized to ferric sulfate in the presence of sulfuric acid. In this system, all of the reactions take place in only one etching tank.

Mechanical preparation requires abrasive blasting using steel shot or steel grit. Grit or shot blasting is used on parts designed without pockets or crevices and with configuration and thickness that permit blasting without distortion. Parts with flat areas should be fabricated from sheet steel thicker than 16-gage, 1.52 mm (0.0598 in.) to avoid excessive distortion when cleaned by this method.

Abrasive blasting is often used for preparing hot-rolled steel and parts that are to be enameled on one side only, as for water heater tanks. The process is also used for preparing large parts and parts having enamels with poor bonding characteristics. Before blasting, oil and drawing compounds may be removed by alkaline cleaning or by heating at 425 to 455 °C (800 to 850 °F) to burn off the organic contaminants.

Preparation of Cast Iron and Aluminum for Porcelain Enameling

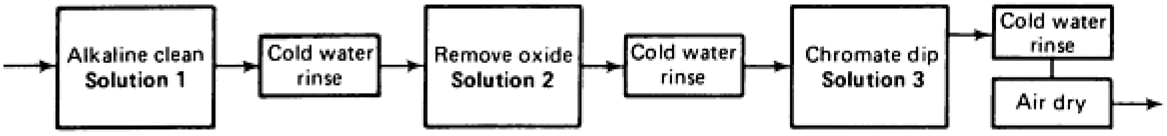
Cast iron is prepared by blasting to remove adhering mold sand and the thin surface layer from chilled iron. Because the surface contains more combined carbon than is present in the remainder of the casting, this carbon-heavy layer must be removed to prevent excessive evolution of gas during firing of the enamel.

Quartz sand of nearly spherical grains, propelled by compressed air, is commonly used for abrasive cleaning of cast iron; however, steel shot, steel grit, and chilled cast iron grit propelled centrifugally from rotating wheels are generally used for cleaning sanitary ware. Zircon sand and fused alumina grit are used for special purposes.

After blasting, the casting should be inspected for cracks, sand holes, slag holes, blowholes, fins, and washes. Cracks and larger holes need to be filled by welding, and the welds require spot grinding to blend the area with the surrounding surface. Also, fins and washes must be removed by grinding. The repaired casting is blasted a second time prior to enameling. Small holes need not be repaired by welding; usually they can be filled with a ceramic paste after final blasting.

Cast iron parts should be enameled within a few hours after cleaning, especially during periods of high humidity; even a very thin layer of rust will reduce the adherence of the enamel. Parts that have rusted excessively can be reconditioned by being heated to a red heat, cooled to room temperature, and cleaned abrasively.

Aluminum. The preparation of parts made of heat-treatable aluminum alloys for porcelain enameling involves the removal of soil and surface oxide and the application of a chromate coating. Figure 10 shows the sequence of these surface preparation treatments and gives operating conditions. Final drying removes all surface moisture; drying must be accomplished without contaminating the cleaned surface of the aluminum. Parts made of non-heat-treatable aluminum alloys or aluminum sheet require only the removal of soil, which can be done by alkaline cleaning or vapor degreasing.



No.	Type	Composition of solution		Operating temperature		Cycle time, min
		Constituent	wt%	°C	°F	
1	Alkaline cleaner[a]	[b]	[b]	60-82	140-180	2-5
2	Oxide removal	Chromic acid	3.5	82	180	3-10
		Sulfuric acid	18.0	. . .	. . .	. . .
3	Chromate dip	Chromic sulfate	0.2	Ambient	Ambient	1-6
		Potassium dichromate	14.4	. . .	. . .	. . .

(a) Vapor degreasing may be used instead of alkaline cleaning.

(b) Either inhibited or mildly etching (uninhibited) cleaners can be used.

Fig. 10 Process for preparing heat-treatable aluminum alloys for porcelain enameling

The Porcelain Enameling Process

Porcelain enamel may be applied to the base metal by either the wet process or the dry process. Wet process methods include manual spraying, electrostatic spraying, dipping, flowcoating, and electrodeposition (electrophoresis). Dry process methods are electrostatic dry powder spraying for application to sheet steel and, for application of the cover coat to cast iron, sprinkling the dry powder by means of a vibrating sieve onto the hot cast iron part.

The best method of application for a particular part is determined by quantity and quality requirements, the type of material being applied, units produced per hour, capital investment, labor cost, environmental considerations, and, ultimately, cost per part. Application techniques can be manual or mechanized. Manual application is necessary for parts having a variety of sizes and shapes that must go through the same enameling process system. Mechanization is essential for high-volume production of parts of the same or similar shape.

Wet-Process Porcelain Enameling of Steel

The prepared porcelain enamel (slip) may be applied to sheet steel using the wet process in a variety of ways.

Dipping is widely used as a method to apply the porcelain enamel, particularly when both sides of the parts require coverage. Dipping can be used for both ground-coat application and cover-coat application. It is performed by immersing the part in the prepared porcelain enamel slip, then withdrawing it and allowing the excess material to drain from the part. Sometimes it is necessary to rotate, tilt, spin, or shake complex shapes to ensure uniform coverage. In areas where excessive porcelain enamel slip is retained on the part after draining, the excess is removed with a siphon or a wiping device before the part is dried. In dipping, a wet coating thickness is applied to achieve a fired coating thickness of 50 to 125 μm (2 to 5 mils).

Automatic equipment is recommended when part configuration allows dipping and production volume warrants the investment. The rheology of the porcelain enamel slip can be better controlled if the dip tank is constructed with a double wall to allow the insertion of a heat exchanger to maintain the porcelain enamel slip at a uniform temperature. The dip tank walls should slope toward a central sump to facilitate recirculation and drainage from the tank.

Equipment to provide recirculation of the porcelain enamel slip consists of a diaphragm pump that continuously circulates the porcelain enamel slip through a magnetic separator and screens to remove iron particles and other foreign materials. The recirculation system helps maintain the consistency and uniformity of the porcelain enamel slip. AISI 300-series stainless steels are the preferred materials for the tank, piping, separators, and screens.

In flow coating, the prepared porcelain enamel slip is flowed onto the surface of the part. The process is especially applicable for high-volume continuous processing of parts requiring the same porcelain enamel coating. In automatic flow coating, the parts are placed on hangers at the proper angle for draining and carried by conveyor through the flow coating chamber. The porcelain enamel slip is pumped at a high volume, 570 L/min (150 gal/min), and low pressure, 70 to 105 kPa (10 to 15 psi) through a series of nozzles that are directed at various areas of the part to ensure complete coverage.

When flow coating a surface that must have a good appearance, such as the top of a kitchen range, it is necessary to incorporate a curtain of porcelain enamel slip near the exit of the flow coating chamber. This curtain, which is provided by flood plates, flows out the porcelain enamel slip into an even coating free of drain lines and splatter marks. On emerging from the flow coating chamber, flow-coated parts drain as they would in the dip method. Various devices can be added along the length of the conveyor to cause repositioning of the parts to provide a more even coating.

Another version of automatic flow coating involves the use of a constant-head tank to supply enamel slip at a constant velocity to headers and nozzles that flood parts with slip as they are conveyed through the flow-coat chamber. The advantage of this system is that the flow to the nozzles is constant and not subject to variations present in pumped systems.

Automatic flow coating is favored over hand dipping because it offers higher rates of production, improved coating quality, and reduced cost of the applied film. Control of the porcelain enamel slip and proper operation of the machine are important functions of flow coating. It is common practice to check the specific gravity and pickup of the porcelain enamel slip three or four times each hour. All parts of the flow-coating machine that come in contact with the porcelain enamel slip should be constructed of 300-series stainless steel.

Additional details on dipping and flow coating are available from Porcelain Enamel Institute Bulletin P-302, "Manual of Dipping and Flow Coating for Porcelain Enameling."

Spraying of the porcelain enamel slip is done primarily to achieve maximum appearance results and provide one-side coverage. It is also used for reinforcing enamel bisque and for making repairs on enameled surfaces. Spraying can be used for parts that are too large for hand or mechanical manipulation.

Figure 11 schematically illustrates equipment for the manual spray application of porcelain enamel slip. The prepared porcelain enamel slip is placed in the pressure feed tank and is constantly agitated to keep the material homogeneous. Regulated air pressure is applied to the pressure feed tank at 55 to 125 kPa (8 to 18 psi) to force the porcelain enamel slip through the fluid hose to the tip of the spray gun nozzle. Here, the slip is atomized by clean compressed air, regulated at 170 to 415 kPa (25 to 60 psi), and then directed to the part. The amount of air pressure required depends on the specific porcelain enamel slip and the shape of the part being sprayed.

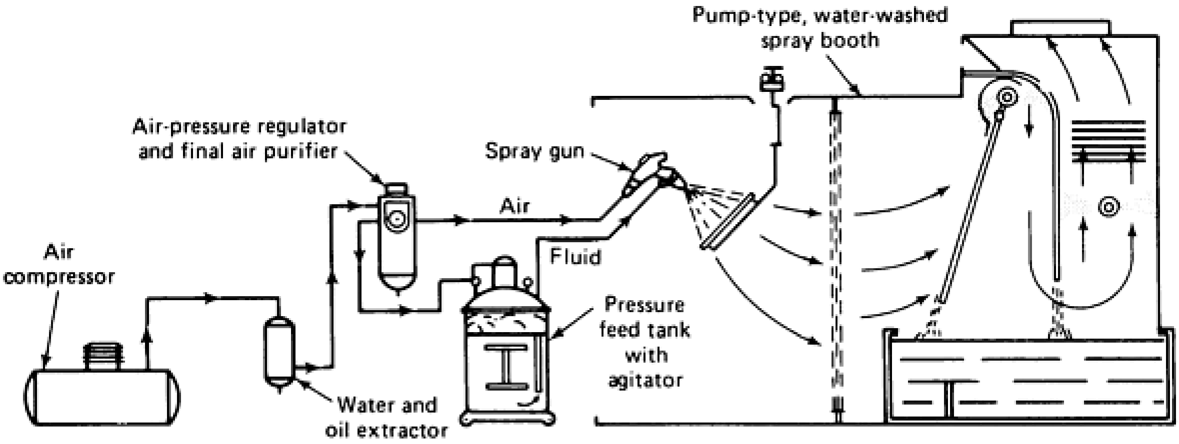


Fig. 11 Schematic of equipment for manual wet spray application

Wet electrostatic spraying is another method used to apply porcelain enamel. Here the porcelain enamel slip is charged during atomization to a potential of 100,000 to 120,000 V, and the electrostatically charged droplets are attracted to the grounded parts being sprayed. A major advantage is greater material utilization. A well-operated electrostatic unit can deposit up to 85% of the sprayed material on the part as compared to 30 to 50% in conventional spraying operations. Additional details on spraying are available from Porcelain Enamel Institute Bulletin P-301, "Manual of Spraying for Porcelain Enameling."

Electrodeposition, or electrophoresis, is another process used to apply porcelain enamel slip to steel. The process uses a series of tanks in which the parts are submerged, and enamel is deposited electrophoretically within 10 to 20 s, depending on the thickness requirements. This process is basically intended for direct-on enameling, but it can be considered for two-coat/one-fire applications. The advantages offered by electrodeposition include a very uniform coating, exceptionally thin enamel layers, and excellent edge coverage.

Drying of Porcelain Enamel Parts. Parts coated with porcelain enamel slip in any of the above wet-process methods are dried before firing to:

- Permit the application of additional porcelain enamel slip, when required, without disturbing the previously applied coating
- Permit brushing of the coated parts, if required
- Allow parts to be handled more easily for transfer to the holding fixture used during firing
- Reduce the amount of water vapor introduced into the firing furnace

Parts are normally placed in or conveyed through dryers using radiant heating or heated circulated air. Drying by radiant heating is at least 20% faster than by convection. For convection dryers, the air temperature is gradually increased to 120 °C (250 °F). A cycle time of 2 to 5 min is required to dry the coating completely in continuous dryers. Batch and intermittent dryers are also used; cycle time for these dryers ranges from 10 to 20 min, depending on the size of the load and the type of dryer used. Sufficient circulation of the air is needed to ensure uniform drying of the porcelain enamel slip. Moisture-laden air from both convection heating and radiant heating dryers must be exhausted from the dryers.

If drying temperature is too high, a hard film forms on the coating and traps moisture under the film. This condition results in tearing in the finished enamel. The rate of drying can be varied by controlling the temperature or the humidity (dew point). Humidity is generally controlled by regulating the amount of outside air entering the dryer.

The drying temperature can directly affect the strength of the dried porcelain enamel film (bisque), which in turn determines the relative ease with which the dried piece can be brushed or handled. In general, low dryer temperatures produce a film that is easily brushed, but that may be easily damaged when the piece is handled; on the other hand, high dryer temperatures produce a hard film that is easily handled but difficult to brush. Mill additions also affect the bisque strength and the brushability of the bisque.

The coating is absorbent during drying and collects gases that are present in the dryer. Most porcelain enamels do not tolerate the absorption of sulfur gases. Sulfur from any source causes a scum on the surface of the parts or pitting in the enamel surface. Therefore, dryers usually are indirect-fired to minimize the absorption of products of combustion of fuel gases.

During the initial stages of drying, the coating is still wet and is subject to contamination from dirt and other foreign particles that cannot be removed before firing. Therefore, drying must be accomplished in an atmosphere free of dirt, scale, and dust.

Auxiliary Coating Procedures. After drying and before firing, the coating may require reinforcing or brushing.

Reinforcing is the application of more porcelain enamel slip to areas where the coating is of insufficient thickness. It is usually performed on parts after the application of ground coat by dipping or flow coating when the coating thickness needs to be built up to prevent burnoff. Reinforcing is done by manual spraying, usually with a spray gun having a nozzle with a smaller opening than is used for full-coverage spraying.

Brushing is required to uncover an area of bare metal for electrical contact and to reduce the enamel thickness for areas with holes for screws or other attachments. Brushing removes the bisque; it can be done on both ground-coat and cover-coat bisques.

Electrostatic Dry Powder Spray Process for Steel

The electrostatic dry powder spray process is an excellent method to use for high-volume production of parts requiring the same porcelain enamel coating. Although parts need not be identical in shape or size, it is necessary that they all be of a configuration that can be evenly coated by this process. It is a highly efficient system, with up to 99% of the porcelain enamel powder material applied to the parts; at the same time, little or no direct labor is required for application of the coating. Further savings result from the elimination of mill room and related enamel preparation operations. Also, solid waste disposal problems and a host of environmental considerations are eliminated.

In this process, powder is delivered to the spray guns from a fluidized bed feed hopper, where it is diffused by clean compressed air into a fluidlike state. The fluidized powder is then siphoned from the feed hopper by the movement of high-velocity air flowing through a venturi-type pump. Here, it is mixed with air and propelled through flexible urethane feed tubes to the spray gun. The powder feed hopper, when equipped with an automatic level control, delivers a steady, controlled flow of powder to the guns. Independent control of powder and air volume ensures proper ratios to coat the part to the desired thickness.

The powder leaves the spray gun in the form of a diffused cloud that is propelled toward the workpiece. A high-voltage, low-amperage power unit supplies the voltage to the electrode in the spray gun. When the voltage is applied, charge builds up on the electrode. The concentration of a charge creates a very strong electric field that causes the air to ionize and a corona to form. The powder is transported through this field to the grounded part, picking up charge in the area where the field is strongest. Variable voltage allows the operator to make application adjustments and to change the various application parameters.

The powder recovery booth collects the unused powder material that did not remain on the parts being coated. The collected material moves through a closed-loop system with the use of primary and secondary/final filters, ensuring that none of the powder escapes into the environment.

The development of "clean only" metal preparation systems, along with the accompanying "for clean only" ground coats, has broadened the utility and increased the use of the porcelain enamel powder process. Using this process, coating materials are available for a variety of base-coat or full-ground-coat applications such as pyrolitic surfaces, reflectors, and oven liners, as well as a full range of cover coats.

The powder coating process is used for:

- *Direct-on ground-coat application over parts prepared by the "clean only" method:* Here, parts requiring only a ground coat may be enameled. Also, the ground coat may be applied and fired, providing the initial part of a two-coat/two-fire process when cover coats are later applied using the wet-process method.
- *Cover-coat application only:* Here, powder cover coats are applied over wet-system ground coats that have been fired earlier.
- *Two-coat/one-fire application:* Here, a thin base coat (1 mil) is applied over a "clean only" prepared metal surface. The cover coat powder is then applied directly to the base coat powder layer at a thickness of 5 mils, making a total thickness of 6 mils. Then both the base and cover coats are fired together.

For an electrostatic powder system of maximum efficiency, a well-designed and smooth-running conveyor system is essential to avoid loss of powder from the parts prior to firing. Also, the application of the powder to parts in process should be done in enclosures where temperature and humidity are fully controlled. Very low humidity limits the buildup of the powder layer, and very high humidity causes electrical charge loss that may result in falloff. Additional details on the electrostatic porcelain enamel dry powder process are available in Porcelain Enamel Institute Bulletin P-300, "Electrostatic Porcelain Enamel Powder Application."

Porcelain enameling of cast iron is done by either the dry process or by the same wet process used for enameling sheet steel.

In the dry process, a thin coat of ground-coat enamel slip is applied to the cold casting, generally by spraying, but sometimes by dipping or other methods. After the ground coat is dry, the casting is put in a furnace and heated to a bright red heat. It is then withdrawn from the furnace. While the casting is still hot the cover coat (in the form of dry powder) is sprinkled by means of a vibrating sieve over the surfaces to be coated. The enamel melts as it falls on the hot surface. The application of powdered enamel continues until the temperature of the casting drops to the point at which the enamel will not melt. Then the piece is returned to the furnace and heated until the enamel is properly fused. For some types of products, such as lavatories, one application of powdered enamel is sufficient; other products, such as bathtubs and combination sinks, require two or more applications.

In the wet process, the enamel is applied to the part when it is cold. Handling of the part is easier, and more uniform coats of enamel are applied than in the dry process. However, because of the composition of cast iron and because of casting irregularities, it is very difficult to satisfactorily enamel large articles (such as sanitary ware) by the wet process.

During heating, gas is evolved from surface reactions of carbon in the cast iron after the temperature reaches approximately 675 °C (1250 °F). Gases produce bubbles or blisters in enamel systems that mature at temperatures higher than the temperature at which the gas evolution begins. This varies with the composition and processing history of the cast iron. Flaws in the casting act as focal points for the evolution of the gas and produce large blisters at these areas than at areas where no flaws are present.

The dry process can be used for castings of almost any size or shape. The thin ground coat allows the gas to escape from the iron during the initial firing without forming large blisters. Many castings that can be enameled by the dry process without difficulty would encounter blistering in the wet process.

Thicker coats of enamel are applied by the dry process so that the normal roughness of iron castings can be hidden with one or two applications of cover-coat enamel. These thicker coats can be fired out to a finish that has more gloss and less waviness than is common when a wet-process slip is applied by spraying to a cast iron part.

Although cast iron enameled by the wet process represents only a small portion of the total tonnage of enameled cast iron products, the wet process is used in a great variety of products and parts. These include cookware, range grates, pump impellers, and piping. Ordinarily, a dark-colored enamel whose maturing temperature is below the temperature of gas evolution is used.

Porcelain Enameling of Aluminum. Porcelain enamel slips for aluminum usually are applied by spraying, using either manual or automatic equipment with agitated pressure tanks. Slips for aluminum are not self-leveling, and therefore they must be applied smoothly in an even thickness and without runs or ripples.

Many aluminum parts are coated satisfactorily by the one-coat/one-fire method. Although the heat-treatable alloys can be recoated one or more times, the opacity and color of the coating will change with the thickness of the porcelain coating and with repeated firing. The desirable minimum fired enameled thickness is 65 μm (2.5 mils) and the desirable maximum fired thickness is 90 μm (3.5 mils).

Enameling Furnaces

Fusing of the porcelain enamel coating to its metal substrate or to a ground coat can be done in a continuous, intermittent, or batch furnace. The furnace may be heated by oil, natural gas, propane gas, or electricity. With oil heating, a muffle furnace is required to prevent the products of combustion from contaminating the enamel coating. Gas-fired furnaces are either muffle or radiant-tube, with a limited number of luminous-wall, direct-fired furnaces being used.

Continuous furnaces are of either straight-through or U-type (Fig. 12) design; furnaces of both designs use air curtains to prevent heat losses through the end openings. A laydown wire-mesh-belt conveyor is used for small signs, dials, microcircuitry, and other small flat pieces. Most continuous furnaces, however, are equipped with overhead monorail conveyors located above the furnace roof. Alloy hook or drop rods extend down from the conveyor trolleys through a narrow slot in the furnace roof to transport the parts. Sealing of this slot is accomplished by the use of articulated steel or alloy seal plates carried by the conveyor. When over the furnace, these plates ride on a cast or fabricated alloy seal track that is incorporated into the furnace roof. Cycles for continuous-furnace firing of ground coats and cover coats on a number of different types of steel parts are given in Table 11.

Table 11 Cycles for firing ground-coated and cover-coated sheet steel parts in a continuous furnace

Type of part	Gage of steel	Operating temperature[(a)]		Firing time, min[(b)]
		°C	°F	
Architectural panels	16-22	805	1480	2-4
Home laundry equipment	18-22	805	1480	4-5
Water heater tanks	7-16	870	1600	8-12
Range equipment	18-24	805	1480	3-5
Sanitary ware	14-18	815	1500	4-6

(a) Temperature varies with composition of frit.

(b) Time in hot zone of furnace

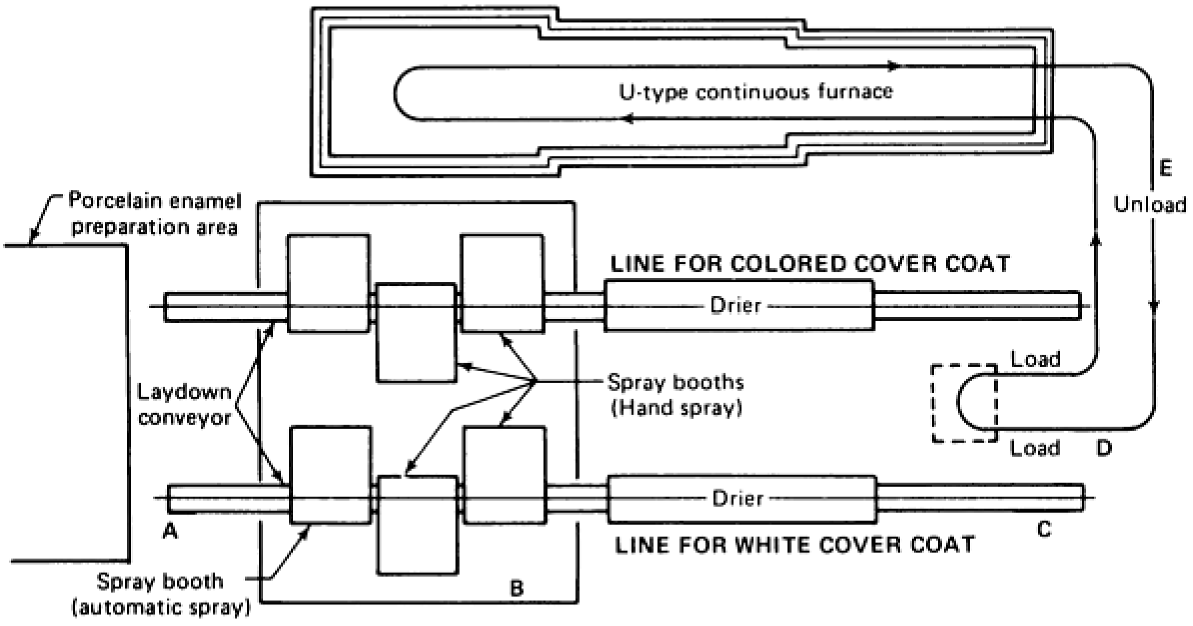


Fig. 12 Coating and firing installation using a U-type continuous furnace. Personnel stations: A, loader and stoner; B, spray operator; C, brusher; D, loader; E, unloader and inspector

Intermittent furnaces are equipped at both ends with split side-opening or articulating doors, air-cylinder operated, and have an overhead monorail conveyor similar to that of the continuous furnaces. With this type of furnace, however, the conveyor moves in increments, so that when one load is discharged, a new load enters the furnace where it remains until the firing cycle is completed. Doors and conveyor are electronically interlocked so that the firing cycle can be timer controlled. Figure 13 illustrates the small difference in temperature between the center and bottom of an intermittent 5 m (16 ft) radiant tube furnace set at 825 °C (1520 °F) for firing a load of sheet steel parts.

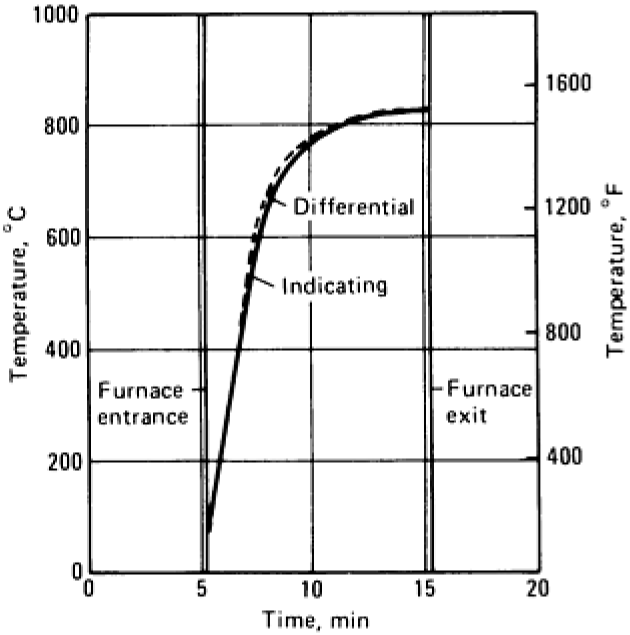


Fig. 13 Temperature and time data for an intermittent furnace. Difference in temperature between two sheet steel parts during a 10 min firing cycle at 825 °C (1520 °F) in a 4.9 m (16 ft) intermittent furnace with radiant-tube heating. Indicating thermocouple was 710 mm (28 in.) below the top of the conveyor and 580 mm (22.75 in.) above the differential thermocouple. Both thermocouples were attached to the parts.

Batch furnaces used for porcelain enameling are of two types. One type has a vertical-lift single door through which the load is charged and withdrawn by means of a charger fork. The second type has a slot in the roof and a manually operated overhead conveyor. The load for this furnace design is supported by alloy rods from overhead trolleys and is manually pushed into the furnace for firing.

Furnace construction for aluminum enameling generally requires the use of stainless steel inner liner sheets, low-density wall insulation, and plain carbon steel exterior shell. Current technology for either retrofitting existing furnaces or erecting new porcelain enameling furnaces, both continuous and batch units, uses a thin-wall lining; it is typically 150 to 205 mm (6 to 8 in.) of ceramic fiber in conjunction with radiant tubes in both the preheat and hot zones. This permits very short heat-up and cool-down periods with no resulting refractory damage. Consequently, these furnaces can be turned off during nonproduction hours, which achieves dramatic fuel savings.

Forced convection is the preferred method of heating furnaces for firing porcelain enamel on aluminum. The heat is provided by quartz-tube electric heaters, metal-sheath heaters, or electric package heaters; all are designed for operation at high ambient air temperature. Quartz-tube and metal-sheath heaters are adapted to the furnace so that radiant heat is available in the firing zone along with forced circulation. Package heaters are placed far from the firing zone to eliminate direct radiation and hot spots. Heat from the package heater requires adequate air circulation to maintain a temperature uniformity of ±1% of the normal operating temperature throughout the furnace.

Forced convection heating is also accomplished with gas-fired radiant tubes as the heat source. The tubes are baffled from the work or firing zone so that air circulation provides the same advantages as in electric-package forced convection heating.

Firing temperatures for enamel on aluminum range between 525 and 550 °C (980 and 1020 °F); cycles are shown in Table 12. To control the color and gloss of the enamel within acceptable limits, the temperature throughout the work must be held to $\pm 1\frac{1}{2}$ °C ($\pm\ 2\frac{1}{2}$ °F).

Table 12 Cycles for firing porcelain enamel on aluminum

Type of part	**Section thickness, 0.025 mm (001 in.)**	**Firing time, min**	**Firing temperature**	
			°C	**°F**
Any configuration	26-40	5-$6\frac{1}{2}$	540	1000
Any configuration	51-64	7-8	540	1000
Extrusions	125	10	550	1020

Role of Coating Thickness, Firing Time and Temperature, Metal Substrate, and Color

The properties and performance of the final porcelain enamel surface are markedly affected by the thickness of the applied coating, the firing time and temperature, and the selection and fabrication of the metal substrate. Color matching and control are often vital to the quality of the product or part.

Coating Thickness. The optimum thickness of porcelain enamel depends on the substrate metal and the service requirements of the part. In any application, however, the enamel coating should be applied at the minimum thickness to achieve the desired appearance and functionality.

On sheet steel, a wet ground coat 50 to 100 μm (2 to 4 mils) thick is applied to promote adhesion. To cover the ground coat, a very opaque white or pastel cover coat 100 to 150 μm (4 to 6 mils) thick is required. Thus, a two-coat wet system has a thickness ranging from 150 to 255 μm (6 to 10 mils). Brightly colored porcelain enamels are produced by applying less-opaque coats with more saturated colors over a white intermediate coating. For these, the total thickness of the coating system should range from 200 to 350 μm (8 to 10 mils). Some decorative finishes are textured; the thickest parts of these coatings may be up to 635 μm (25 mils). Coating thickness of 125 to 150 μm (5 to 6 mils) is required for cover-coat porcelain enamels applied directly to decarburized or to specially stabilized steels.

The thickness of wet porcelain enamel on a large steel part of simple configuration can be closely controlled when application is by a mechanical spraying system that is adapted to the part. For example, mechanically applied porcelain enamel on curved silo panels 2 by 3 m (5 by 9 ft) can be maintained within ±13 μm (±0.5 mil); however, when application is by hand spraying, the variation in enamel thickness may be as much as ±50 μm (±2 mils).

On aluminum, porcelain enamel is applied to produce a fired enamel thickness ranging from about 65 to 100 μm (2.5 to 4 mils). A tolerance of ±13 μm (± 0.5 mil) is required for a white enamel coating 65 μm (2.5 mils) thick, to achieve acceptable opacity.

Coatings for cast iron products are much thicker than those for sheet steel or aluminum. Dry process coatings on cast iron products, such as sanitary ware, range from 1020 to 1780 μm (40 to 70 mils) in thickness. Coatings applied to cast iron by the wet process range from 255 to 635 μm (10 to 25 mils) in thickness.

Firing Time and Temperature. Firing of porcelain enamel involves the flow and consolidation of a viscous liquid and the escape of gases through the coating during its formation. Within limits, time and temperature are varied in a compensating manner. For example, similar properties and appearance may result when a coated steel part is fired at either 805 °C (1480 °F) for $3\frac{1}{2}$ min or at 790 °C (1450 °F) for 4 min. Of course, there is a minimum practical temperature for the attainment of complete fusion, acceptable adherence, and desired appearance. Most wet ground-coat enamels for high-production steel parts exhibit acceptable properties over a firing range of 55 °C (100 °F) at an optimum firing time. However, control within 11 °C (20 °F) is ordinarily maintained to produce uniform appearance and to allow interchangeability of parts. The combined effects of increased firing time and temperature result in more thorough firing, and, up to a maximum, the following conditions occur:

- Colors shift dramatically, particularly reds and yellows. In general, white and colors shift toward yellow.
- Gloss of the enamel coating changes.
- Chemical resistance of the enamel coating increases.
- Gas bubbles are eliminated.
- Enamel coating becomes more dense and brittle and less resistant to chipping.
- Maximum adherence is attained in the optimum portion of the firing range.

Avoiding Metal Distortion. Sag and distortion of sheet metal parts result from low metal strength at the firing temperature, thermal stresses due to nonuniform heating and cooling, and transformation to austenite. Changes in design of the parts and firing practice alleviate the first two causes, and the use of extra-low-carbon content or of special stabilized steels minimizes transformation from ferrite to austenite.

Ground-coat enamels do not contribute significantly to any distortion of parts because their coefficients of thermal expansion approach that of steel. When ground coat is applied to both sides of the metal, there is a counterbalancing of expansion and contraction stresses.

The effect of cover-coat enamels on the flatness of porcelain enameled parts can be pronounced because of their lower coefficients of expansion and their one-side application. The likelihood of distortion is greatly increased when multiple or thicker coats of cover-coat enamels are necessary on one surface. Sometimes cover coats must be applied to the back side of parts to equalize the stresses.

Adjustments in the firing cycle can sometimes help minimize distortion. A cycle with relatively slow heating and cooling rates is preferable to rapid heating and cooling.

Variations in the method of supporting the work during firing can often reduce the sagging characteristics. Furnace supports and fixtures can be designed to distribute the load and equalize heating and cooling rates. Porcelain Enamel Institute Bulletin P-306, "Design and Fabrication of Sheet Steel Parts for Porcelain Enameling," has more information.

Color Matching and Control. In color matching, primary coloring oxides are normally used. In most instances, two or three oxides are sufficient to match any specific color. A minimum number of oxides should be used; for example, a stable green oxide is preferred to a blend of blue and yellow oxides. Usually, the proper color intensity is obtained first; then adjustment is made for the desired color shade.

Color stability can be adversely affected by improper mill additions. However, a color with only fair stability may be improved by the proper mill additions, and minor color adjustments.

Finer grinding reduces the intensity of the color. It is imperative that the fineness of the milled color be controlled within specified limits. The thickness of the fired enamel coating affects many colors. In general, thick coatings produce lighter colors and thin coatings result in darker colors.

The set and specific gravity of a colored enamel slip are important to the finished results. Color corrections of electrostatic dry powder cannot be made by the enameler.

Process Control

Proper workability during application of wet-process porcelain enamels depends on control of the prepared porcelain enamel slip, particularly with respect to stability of suspension; weight of enamel slip deposited and retained per unit area; specific gravity, consistency, and particle size of the enamel slip; and stability while aging at ambient temperature.

Stability of suspension, or the ability of the various mill additions to keep the milled frit in suspension, is determined by both slip measurements and visual observation of any separation that occurs. The enameler should note the accumulation of clear liquid on top of the enamel or of a heavier sludge on the bottom. Stability of the suspension is a function of many factors, but it is usually controlled by the quantity of colloid, in the form of clay or bentonite, and electrolytes used to flocculate the clay.

Pickup weight of enamel deposited and retained per unit area is measured by draining the enamel on a flat or cylindrical shape of known weight and area, then actually weighing the pickup of enamel in wet or dry form. This is a most useful test, particularly for dipping enamels, and one that closely simulates actual production operations. During the test, the operator can observe any tendency toward sliding, excessively long or short drain time, and variations in setting time. The pickup of an enamel is a function of specific gravity, colloid content, total salts content and type, and consistency. These are controlled by varying water content, addition of salts, and fineness of grind.

Specific gravity of enamel slips is measured by comparing the weight of a known volume with the weight of an equivalent volume of water or by using a hydrometer. Control of specific gravity is almost entirely a function of the ratio of water to solids. To ensure uniformity, testing for specific gravity is required for the preparation of all porcelain enamel slips.

Consistency of a porcelain enamel slip for spraying is commonly determined by the slump test. A fixed volume of the porcelain enamel slip is allowed to flow out suddenly in a circular pattern on a calibrated plate, and the diameter of the resulting pool is measured immediately. This is a simple and useful test for porcelain enamels that are to be sprayed because it indicates uniformity of slip conditions between various millings.

Other tests for consistency involve the use of viscosimeters of various types, including those that use the rotational, flow, and falling piston methods. However, enamel slips do not behave like ordinary liquids and do not follow the laws of viscous flow. With enamel slips, a certain amount of force is required to start the flow. This force is the yield value, and the rate of flow is referred to as the mobility. These can be determined by using a consistometer; however, in plant practice, careful control of specific gravity and slump should be adequate. A study of the flow properties of porcelain enamel slips indicates that they are non-Newtonian liquids and consequently show variable rates of shear with varying stresses.

For porcelain enamel slips applied by dipping, a measure of drain time is a useful test. Drain time is the total elapsed interval between the time a standard-size sample plate is removed from a container of well-stirred porcelain enamel slip and the time at which the draining motion of the slurry on the sample stops.

Particle size of the frit for porcelain enamel slips is commonly determined by standard screen analysis. Reproducible measurements are easily obtained when a standardized shaking device is used. The particle size of the frit is important to the suspension characteristics of the porcelain enamel slip, and slight solubility of the frit shows a major change with variation in the size of the particles.

Stability while aging is measured by exposing a tested sample of the porcelain enamel to whatever temperatures are expected in normal service. Exposure is for many hours and days, and retests of the critical properties are made at intervals during testing. Aging usually has an effect on the stability of the suspension, pickup, setting time, and consistency of the porcelain enamel slip. Aging can cause poor surface quality of the fired enamel.

Leaching of soluble elements, such as sodium or boron, from the frit is a cause of aging. This problem is encountered more with frits that are less water-resistant. The leaching effect is greater at higher temperatures.

In-Process Quality Actions

Ground Coat. Parts rejected at the ground-coat stage are repaired and refired, if necessary, before the cover coat is applied. It is good practice to confine repair techniques to the defective areas. It is important to remove dirt particles, scale, and similar contaminants with a sharp-pointed instrument. The disturbed area around the site should be lightly stoned. The dust generated should be blown off. Ground-coat enamel is spotted-in at the repair area, and the entire piece is lightly dust coated. The piece is then dried and fired.

Lumps, handling defects, chips, and similar flaws in the ground coat are normally lightly stoned, and if this proves satisfactory, the parts are ready for cover coating. Otherwise they are treated as described above.

Defects that cover more extensive areas or are located at or near the steel enamel interface, such as burnoff, blisters, "copperheads," embedded grit particles, and dents, require different repair techniques; it is often necessary to grind down to bare steel. Grinding may be accomplished with a power grinder, using an 80-grit silicon carbide disk. A damp sponge placed under the work area prevents overheating. After firing, the repaired ground coat area should be hand stoned to blend it into the surrounding area of the surface.

Cover Coat. Defects that are missed during inspection of the ground coat usually become visible in the cover coat. Specks, blisters, copperheads, and dents are typical of such transmitted defects; they need to be removed by grinding into the ground coat. The ground coat is then repaired as described above, before another coat is applied. Cover-coat defects such as lumps, handling defects, chips, and thin coating areas are repaired by stoning, respraying lightly, and refiring the piece.

Direct-on cover-coat applications are repaired in much the same manner as ground coats. If the defect area is small, a light grinding or stoning is all that is required. This is followed by a localized application of cover coat and then a full dust coat, drying, and firing. If the repair requires grinding into the steel, then a ground coat patch in that area is required for adherence. A half coat of cover-coat enamel over the fired ground-coat patch is required, followed by a dust coat over the entire piece.

Properties of Porcelain Enamels

Porcelain enamels possess an unusually wide array of properties that can be specially designed and formulated for a variety of demanding environments. Some of the special properties are summarized below. (See the Porcelain Enamel Institute "Properties Data Sheets," P-401, P-402, P-403, P-404, and P-405, for more detailed information).

Chemical Resistance. Porcelain enamel is widely used because of its resistance to household chemicals and foods. Mild alkaline or acid environments are generally involved in household applications. Table 13 presents examples of corrosive environments for which porcelain enamels are widely used for long periods of service. Special enamel compositions are available to resist most acids, except for hydrofluoric or concentrated phosphorics, to temperatures of 230 °C (450 °F). These compositions also resist alkali concentration to pH 12 at 93 °C (200 °F).

Table 13 Applications in which porcelain enamels are used for resistance to corrosive environments

Application	Corrosive environment			
	Temperature		pH	Corrosive medium
	°C	°F		
Bathtubs	≤ 49	≤ 120	5-9	Water; cleansers
Chemical ware	≤ 100	≤ 212	12	Alkaline solutions
	≤ 100	≤ 212	1-2	All acids except hydrofluoric
	175-230	350-450	1-2	Concentrated sulfuric acid, nitric acid, and hydrochloric acid
Home laundry equipment	≤ 71	≤ 160	11	Water; detergents; bleach
Range exteriors	21-66	70-150	2-10	Food acids; cleansers
Range oven lines, conventional	66-315	70-600	2-10	Food acids; cleansers
Range burner grates	66-590	70-1100	2-10	Food acids; cleansers
Kitchen sinks	≤ 71	≤ 160	2-10	Food acids; water; cleansers

Weather Resistance. Factors that determine the weather resistance of porcelain enamels are chemical durability, color stability, cleanability, and continuity of coating. Gloss and enamel texture do not necessarily affect weather resistance.

Appearance for Indoor Exposure. Where corrosive attack is unlikely and appearance is the principal requirement, enamel selection and processing are directed toward providing reproducible color matching and optimum gloss and smoothness. Often, different enamels are used on different parts of the same product to ensure the best balance of properties and cost, particularly if high volume is involved. For example, somewhat different enamel compositions are used for range tops and dishwasher liners because of differing property and appearance requirements, even though these parts may be processed in the same plant. Appearance standards, in particular, are established to respond to end use requirements. Small surface defects may be tolerated in areas not heavily used or readily seen in the finished part, provided that they do not affect basic serviceability.

Surface Temperatures. Softening of the glassy matrix limits the temperature to which porcelain enamels can be exposed. Softening releases gases remaining from reactions between the enamel and the metal substrate, producing random defects known as reboil. Service-temperature limits for porcelain enamels are shown in Table 14.

Table 14 Service-temperature limits for porcelain enamels

Service temperature		Limiting conditions
°C	°F	
425	800	Usual limit for enamels maturing at about 815 °C (1500 °F)
540	1000	Maximum for enamels maturing at about 815 °C (1500 °F), without reboil
760	1400	Operating limit for special high-temperature enamels
1095	2000	Refractory enamels useful for short periods for protection of stainless steels and special alloys

Thermal shock intensifies the effect of elevated temperature, as does operation under severe temperature gradients. Enamels are formulated so that expansion characteristics place the enamel in compression under service conditions. If combinations of mechanical stress and elevated temperatures place the enamel in tension, crazing forms a pattern of fine cracks perpendicular to the tensile stress. The relation between enamel and metal expansion patterns on heating and cooling is shown in Fig. 14.

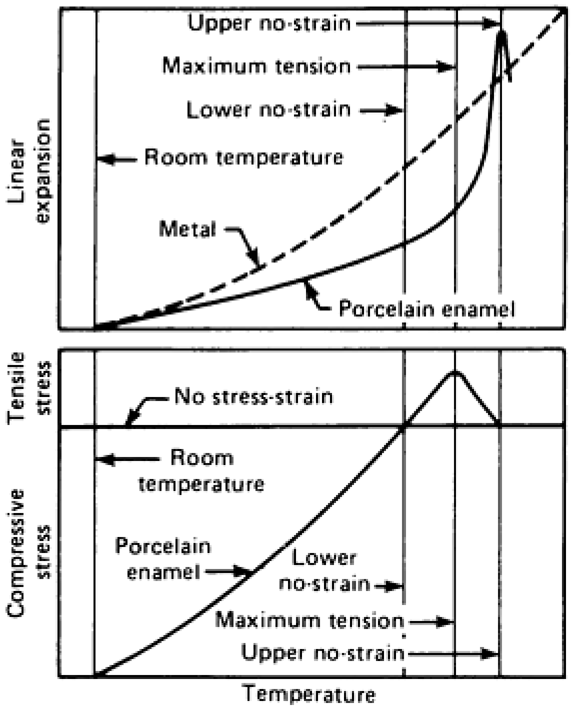


Fig. 14 Enamel/metal expansion and stress patterns. Linear expansion and stress in a composite of acid-

resistant cover-coat porcelain enamel and low-carbon steel

Mechanical Properties. The hardness of porcelain enamels ranges from 3.5 to 6.0 on the Mohs scale. Porcelain enamels show a high degree of abrasion resistance. Under abrasive test conditions where plate glass retains 50% specular gloss, porcelain enamel compositions retain from 35 to 85% specular gloss. Subsurface abrasion resistance varies with processing variables that affect the bubble structure of the enamel, that is, gas bubbles frozen in during cooling of the enamel. A decrease in abrasion resistance occurs with an increase in the number or size of gas bubbles. Enamel compositions are available that contain crystalline particles (from mill additions or devitrification heat treatment) that increase abrasion resistance as much as 50%.

The porcelain enamel coating contributes to the strength of sheet metal parts. Table 15 indicates the increased resistance to torsion provided by porcelain enamel on metal angles made of three different materials. Metal failure occurs at the point of maximum stress, which is followed by buckling of the angle.

Table 15 Effect if porcelain enamels on torsion resistance of metal angles

Material	Increase of stress, %(a)		
	Ground coat	One coat	Two coats
Cold-rolled steel	27	18	33
Electric steel	22	13	32
Enameling iron	22	16	42

(a) Increase of stress for metal failure, as provided by porcelain enamel, over stress for failure of annealed unenameled material

Electrical Properties. Porcelain enamels are electrical insulators. The electrical resistance per unit area is a function of thickness and enamel composition. In addition to resistance, usually expressed as resistivity, other electrical properties of interest are dielectric constant, dissipation factor, and dielectric strength. As with many glassy materials, these properties vary with temperature. In general, as the temperature increases, the resistivity and dielectric strength decrease, while the dielectric constant and dissipation factor increase. The dielectric constant and the dissipation factor also vary with frequency.

When porcelain enamel is used for its electrical properties, the selection of the enamel composition and the enameling process requires careful attention. For electronic applications, such as porcelain enameled substrates for hybrid circuits, special electronic-grade enamels are used. These compositions have considerably higher resistivities and dielectric strengths and are less sensitive to temperature changes than conventional porcelain enamels. Such specialty porcelain coatings are being used increasingly often in sophisticated electronic circuitry.

Evaluation of Porcelain Enameled Surfaces

Specifications and quality control for porcelain enamel coatings require the evaluation of a range of properties for the intended service of the porcelain enameled product. Although material and process variables can be brought into approximate control using small test panels, process control is maintained by the evaluation of finished parts, even though some of the mechanical and chemical tests are destructive. Standard test procedures are available for many porcelain enamel properties. Specific test methods for various properties are listed in Table 16. Some of these tests are discussed below.

Table 16 ASTM test methods for porcelain enamels (under jurisdiction of ASTM Porcelain Enamel Subcommittee B.08.12)

Designation	Title
C 282	"Acid Resistance of Porcelain Enamels (Citric Acid Spot Test)"
C 283	"Resistance of Porcelain Enameled Utensils to Boiling Acid"
C 285	"Standard Test Methods for Sieve Analysis of Wet Milled and Dry Milled Porcelain Enamel"
C 286	"Definitions of Terms Relating to Porcelain Enamel and Ceramic Metal Systems"
C 313	"Standard Test Method for Adherence of Porcelain Enamel and Ceramic Coatings to Sheet Metal"
C 346(a)	"Standard Test Method for 45° Specular Gloss of Ceramic Materials"
C 347	"Standard Test Method for Reflectance, Reflectivity and Coefficient of Scatter of White Porcelain Enamels"
C 374	"Standard Test Method for Fusion Flow of Porcelain Enamel Frits by the Flow Button Methods"
C 375	"Classification of Water Used in Milling in Porcelain Enamel"
C 385	"Standard Test Method for Thermal Shock Resistance of Porcelain-Enameled Utensils"
C 409(a)	"Torsion Resistance of Laboratory Specimens of Porcelain Enameled Iron and Steel"
C 448	"Standard Test Methods for Abrasion Resistance of Porcelain Enamels"
C 536	"Standard Test Method for Continuity of Coatings in Glassed Steel Equipment by Electrical Testing"
C 537	"Standard Test Method for Reliability of Glass Coatings on Glassed Steel Reaction Equipment by High Voltage"
C 538	"Standard Test Method for Color Retention of Red, Orange and Yellow Porcelain Enamels"
C 539	"Standard Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method"
C 540(a)	"Standard Test Method for Image Gloss of Porcelain Enamel Surfaces"
C 614	"Standard Test Method for Alkali Resistance of Porcelain Enamels"

C 632	"Standard Test Method for Reboiling Tendency of Sheet Steel for Porcelain Enameling"
C 633	"Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings"
C 660	"Practices for Production and Preparation of Gray Iron Castings for Porcelain Enameling"
C 664	"Standard Test Method for Thickness of Diffusion Coating"
C 694	"Standard Test Method for Weight Loss (Mass Loss) of Sheet Steel during Immersion in Sulfuric Acid Solution"
C 703	"Standard Test Methods for Spalling Resistance of Porcelain Enameled Aluminum"
C 715	"Standard Test Method for Nickel on Steel for Porcelain Enameling by Photometric Analysis"
C 743	"Standard Test Method for Continuity of Porcelain Enamel Coatings"
C 756	"Standard Test Method for Cleanability of Surface Finishes"
C 774	"Standard Test Method for Yield Strength of Enameling Steels after Straining and Firing"
C 810	"Standard Test Method for Nickel on Steel for Porcelain Enameling by X-Ray Emission Spectrometry"
C 839	"Standard Test Method for Compressive Stress of Porcelain Enamels by Loaded-Beam Method"
C 872	"Standard Test Method for Lead and Cadmium Release from Porcelain Enamel Surface"
C 988	"Standard Test Method for Image Gloss of Porcelain Enamel Surfaces"

(a) This test, while withdrawn from the latest ASTM list because of inability to obtain the required equipment, continues to be used by laboratories that possess the equipment.

Adherence refers to the degree of attachment of enamel to the metal substrate. A number of tests regularly used in the industry provide adherence criteria, but none gives the force per unit area required to detach the enamel by tensile force normal to the interface.

ASTM C 313 for porcelain enamel on steel deforms the metal and measures the area from which the porcelain enamel is removed. The indicator of adherence is the adherence index, which is the ratio of the porcelain enamel remaining in the deformed area to that in the same measured area prior to deformation.

Enamels for cast iron pose a special problem because of the relatively greater thickness of the coating, the rigidity of the metal substrate, and the brittleness of the iron. Here, simple nonstandard impact tests are used.

Resistance to spalling, a defect characterized by separation of porcelain enamel from the base metal without apparent external cause, is the indicator used to measure adherence of porcelain enamel on aluminum. Spalling can result from the use of improper alloys, improper enamel formulations, incorrect pretreatment of the base metal, faulty application, or unsatisfactory firing procedures. The most common test for spall resistance is ASTM C 703.

Thickness. A number of specifications for products and applications require a specific thickness for porcelain enamel coating. The procedure used to measure the thickness depends on the type of base metal used. For porcelain enamel products with a steel substrate, enamel thickness is measured according to ASTM D 1186. For porcelain enamel products with an aluminum substrate, enamel thickness is measured according to ASTM E 376. (Neither of these tests is listed in Table 16, because they are not under the jurisdiction of ASTM Porcelain Enamel Subcommittee B.08.12.) In some cases, such as laboratory investigations, enamel thickness is measured according to ASTM C 664.

Color and Gloss. Porcelain enamel finishes are produced in literally hundreds of colors and countless textures. The common method of specifying color is based on the capacity of the observed article to reflect light of different wavelengths and hence of different colors. A physical standard, such as a reference plaque of porcelain enameled steel, is provided as the color to be matched within stated limits. The difference in color between the control standard and the test specimen can be measured by a color difference meter, using the procedures specified in ASTM D 2244 (not under B.08.12 jurisdiction).

Gloss, which is defined in ASTM C 286 as "the shine or luster of porcelain enamel," is particularly desirable in some products, such as appliances, sanitary ware, and lighting reflectors. However, high gloss enamels capable of reflecting distinct images are not recommended for architectural porcelain enamel for exterior use. The most commonly used test to measure gloss of porcelain enamel is ASTM C 346. ASTM C 540 may also be used if the equipment is available.

Acid Resistance. Porcelain enamels can be formulated to exhibit high resistance to all acids except hydrofluoric or concentrated phosphoric. This resistance to food acids and certain chemical cleaners is of particular importance to manufacturers of ranges and other kitchen and household appliances, as well as plumbing fixtures and various industrial and chemical processing products.

The acid resistance of enamels under boiling conditions is important for certain uses, such as cookware. ASTM C 283 is used here. Similarly, acid resistance is a major consideration for predicting the weatherability of architectural porcelain enamel components. Extensive testing under controlled exposure conditions has shown a distinct correlation between acid resistance and weatherability. Here the test for determining acid resistance is ASTM C 282.

Alkali Resistance. Home laundry equipment, dishwashers, and similar applications normally exposed to an alkaline environment at elevated temperatures require an alkali-resistant coating. The standard test for alkali resistance is ASTM C 614.

Weather Resistance. Actual weathering performance of porcelain enamel panels has been documented in a series of onsite exposure tests carried out over periods up to 30 years in length by the National Bureau of Standards (now the National Institute of Standards and Technology) in cooperation with the Porcelain Enamel Institute. As mentioned above, acid resistance as measured by ASTM C 282 is important.

Weathering of porcelain enamel is evaluated in terms of the changes in gloss and color that occur during outside exposure. Multiyear weathering tests demonstrate that porcelain enamels have considerable inherent gloss and color stability. Tests that are used are ASTM C 346 and ASTM D 2244 (the latter is not under B.08.12 jurisdiction).

Spalling resistance of weathered porcelain enamel on aluminum is best ascertained through use of ASTM C 703.

Resistance to Organic Solvents. Porcelain enamels are inert to all common organic solvents; however, there is no standard procedure for determining this special performance characteristic.

Resistance to Chipping. Relatively thick layers of porcelain enamel are fractured when subjected to severe bending or other substrate deformation. However, thin coatings of 125 μm (5 mils) or less that are well bonded to a relatively thin metal substrate (for example, 26-gage 0.4546 mm, or 0.0179 in., or less) can withstand the bending of the substrate to radii of curvature within its elastic limit and return to the original shape with little or no apparent damage. Chipping of typical porcelain enamel on sheet iron occurs at about the strain required for permanent deformation of the metal base.

Torsion Resistance. In transit and during service, porcelain enameled products may be subjected to distortion through bending, twisting, or a combination of both. This can cause coating failures from fractures originating at the outer surface and normal to the tensional stress. ASTM C 409 evaluates the relative resistance to torsion-induced failure of laboratory test specimens for steel substrate thicknesses ranging from 24 to 12 gage.

Abrasion Resistance. The resistance of porcelain enamel to various types of abrasion is measured by ASTM C 448, which consists of three parts. The first determines the resistance to surface abrasion of porcelain enamels for which the unabraded 45° specular gloss is more than 30 gloss units. The second determines the resistance to surface abrasion of porcelain enamels for which the unabraded 45° specular gloss is 30 gloss units or less. The third measures the resistance of porcelain enamels to subsurface abrasion.

Thermal shock resistance of a porcelain enamel surface varies inversely with the thickness of the enamel. It is also affected by the compressive stress present in the enamel at room temperature. Most porcelain enamels can be quenched in ice water from a temperature of 205 °C (400 °F) without thermal shock failure. Some porcelain enamels specifically designed for resistance to thermal shock will not fail when quenched in ice water from 650 °C (1200 °F). ASTM C 385 is the standard for evaluating the durability of porcelain enameled utensils when subjected to thermal shock.

Continuity of Coatings. Ensuring continuity of coating after manufacture is important in porcelain enamel ("glassed steel") applications where a prime purpose of the coating is to protect the substrate against corrosion. Test methods used to determine either discontinuity of coverage or potential discontinuity through too-thin coverage are ASTM C 536 and ASTM C 743. Both tests essentially involve the use of electrical probes of relatively high voltage to discern either discontinuities in the coating or insufficient coverage for coating integrity in service use.

Resistance to Hot Water. Federal specification W-H-196J, "Heater Water, Electric and Gas Fired, Residential," specifies a solubility test to determine the resistance of porcelain enamels to hot water.

Ceramic Coatings and Linings

Revised by Woodrow W. Carpenter, The Ceramic Coating Company

Introduction

CERAMIC COATINGS include glasses, with or without additions of refractory compounds; high-temperature coatings based on oxides, carbides, silicides, borides, or nitrides; cermets; and other inorganic materials. Ceramic coatings are applied to metals to protect them against oxidation and corrosion at room temperature and at elevated temperatures. Special coatings have been developed for specific uses, including wear resistance, chemical resistance, high reflectivity, electrical resistance, and prevention of hydrogen diffusion. Ceramic-coated metals are used for furnace components, heat treating equipment, chemical processing equipment, heat exchangers, rocket motor nozzles, exhaust manifolds, jet engine parts, and nuclear power plant components.

Selection Factors

Several factors must be considered when selecting a ceramic coating:

- Service environment to be encountered by the coated metal
- Mechanisms by which the coatings provide protection at elevated temperatures
- Compatibility of the coating with the substrate metal
- Method of applying the coating
- Quality control of the coating
- Ability of coating to be repaired

Service environment may involve a wide range of conditions. The intended operating life of a coated part may range from a few seconds to several hundred hours. Conditions may involve exposure to atmospheric gases at various mass flows with velocities up to, or even beyond, Mach 10. Components made of the refractory alloys may be subjected to very high stresses, or they may be used as heat shields or furnace windings, for which the only load is the mass of the component. Heating and cooling rates may be gradual or rapid, and one or more thermal cycles may be involved. For any specific service environment, the coating selected must protect the metal from oxidation and the effects of hydrogen pickup by preventing or minimizing the diffusion of oxygen, nitrogen, and hydrogen from the atmosphere through the coating into the substrate.

Mechanisms of Protection. Ceramic coatings have two mechanisms to protect metals at elevated temperatures. One type of coating is applied as a layer of stable oxide on the surface of the metal, which prevents or delays contact between metal and atmosphere. The other type of ceramic coating is an intermetallic compound that forms a thin oxide film on its surface. The composition of the intermetallic is such that it provides the optimum combination of metallic elements for forming a stable and adherent protective oxide film on its surface and for healing the oxide film in the event the film is broken. Thus, this type of coating depends on the formation and preservation of the oxide film for protection of the substrate material.

Chemical and Mechanical Compatibility. Chemical compatibility of the ceramic coating with the substrate metal is important, especially when the coating is applied to refractory metals and nickel-base alloys for high-temperature service. The so-called stable oxide coatings, such as alumina, are not stable in the presence of some of the refractory metals, such as niobium (columbium) and tantalum, at temperatures above 1370 °C (2500 °F). Also, alumina reacts with metals such as titanium and zirconium, and the protective characteristics of the coating are soon exhausted.

The coating must also be mechanically compatible with the underlying metal, so that undesirable mechanical stresses are not induced in either material. Because most stable coatings are brittle at low temperatures, the coefficients of thermal expansion of the coating and substrate should not be greatly different; however, the coefficient of expansion of the coating should be somewhat less than that of the substrate, so that the coating will be in compression at low (room) temperature. The mismatch in expansion should be greater for parts subjected to thermal cycling. The system must be designed so the difference in the coefficients keeps the coating in compression at all temperatures below the softening point of the coating. if the coating is in tension at low temperature, it will crack. Conversely, if it is under too much compression, it will spall.

The effect of the coating on fatigue life and on the brittle transition temperature of the composite material should also be considered. In general, the coating is more brittle than the substrate metal, and cracks that form in the coating during service act as stress raisers on the substrate, thus reducing the low-temperature ductility and fatigue life.

Application Method. The method of applying the coating is restricted by the type of coating, the type of metal to be coated, and the size and configuration of the work. Many of the coating processes include heat treatment to promote bonding and sealing. The atmospheres used for spraying and heat treating must be closely controlled to prevent any deterioration in properties of the substrate metal.

Control of Coating Quality. It is important to ensure that the coating is capable of protecting the substrate. Thickness measurements and visual observations are two methods of determining coating quality. However, these methods are not satisfactory for coatings on complex shapes and internal passages that are difficult to see or reach. A preliminary oxidation test of a few minutes or hours in an oxidizing atmosphere at the operating temperature is also an acceptable method for determining quality of the coating.

Ability of coating to be repaired is an important consideration in coating selection. The ideal coating should be repairable if coverage is insufficient in the initial application or if the coating is damaged during handling or service. Repair procedures and their effectiveness differ for the various coatings, methods of application, substrate metals, and size and shape of work.

Coating Materials

The nonmetallic, inorganic materials used as ceramic coatings have several characteristics in common. Among these are relatively good chemical stability at elevated temperatures, hardness, brittle behavior under load, and mechanical continuity in thin cross section.

Silicate Glasses. Coatings prepared from glass powders, with or without additions of refractory compounds, have the greatest industrial usage of all ceramic coatings. Glass is typically manufactured by mixing specific proportions of minerals, heating the mixture to a molten or liquid state, and rapidly quenching. Quenching is normally accomplished by discharging the melt into cold water or by pouring it through water-cooled steel rolls. The former case results in small friable pieces of glass that can be ground into a powder with relative ease using a ball mill or other standard crushing equipment. These friable pieces are called *frit.* The word refers to the physical condition of the particle, not its composition or properties. Quenching through water-cooled steel rolls results in flake-like particles, somewhat less friable than those produced by water quenching but with less environmental nuisance.

Glass coatings are used for such long-duration elevated-temperature applications as aircraft combustion chambers, turbines and exhaust manifolds, and heat exchangers. Variations in composition of the glass are virtually unlimited. They range from alkali-alumina borosilicate glasses, which are relatively soft, low melting, and highly fluxed, to barium crown glasses.

Crystallized glass coatings have been developed. In these coatings, crystallization of the glass is controlled by formulation and heat treatment and by the presence of nucleating agents added to the glass during melting.

Several different refractory materials may be combined with glass to produce satisfactory coatings for elevated-temperature service. The addition of a refractory material depends on service requirements and on the compatibility of the refractory material with the glass, other mill-added materials, and the substrate metal. Raw batch compositions of glasses, their melted compositions, and slips (mixtures of frit and additives ground to a smooth consistency) for high-temperature service coatings are indicated in Tables 1, 2, and 3, respectively.

Table 1 Compositions of unmelted frit batches for high-temperature service silicate-based coatings

Constituent	**Parts by weight for specific frits**[(a)]						
	UI-32	**UI-285**	**UI-346**	**UI-418**	**NBS-11**	**NBS-331**	**NBS-332**
Quartz	29.3	21.2	18.3	31.2	18.0	38.0	37.5
Feldspar	42.0	30.2	47.4	. . .	31.0	. . .	. . .
Hydrated borax	28.9	21.0	17.9	. . .	37.1	. . .	. . .
Sodium carbonate	7.7	5.3	6.1	. . .	5.9	. . .	. . .
Sodium nitrate	5.0	4.0	4.4	. . .	3.8	. . .	. . .
Fluorspar	4.5	3.2	2.8	. . .	3.0	. . .	. . .
Tricobalt tetroxide	0.6	. . .	0.4	. . .	0.5	. . .	. . .
Nickel oxide	0.6	. . .	0.4	. . .	0.6	. . .	. . .
Manganese dioxide	1.8	. . .	1.1	. . .	1.1	. . .	. . .
Barium carbonate	. . .	. . .	. . .	26.3	. . .	56.6	56.6
Zinc oxide	. . .	. . .	. . .	4.2	. . .	5.0	5.0
Whiting	. . .	. . .	. . .	7.5	. . .	7.1	6.3

Vanadium pentoxide	. . .	. . .	1.3	. . .	. . .	. . .	. . .
Aluminum hydrate	. . .	15.1	. . .	. . .	. . .	. . .	1.5
Boric acid	. . .	. . .	. . .	12.0	. . .	11.5	11.5
Cerium oxide	. . .	. . .	. . .	4.2	. . .	. . .	. . .
Titania	. . .	. . .	. . .	4.2	. . .	. . .	. . .
Bismuth nitrate	. . .	. . .	. . .	4.2	. . .	. . .	. . .
Bismuth oxide	. . .	. . .	. . .	6.2	. . .	. . .	. . .
Beryllia	. . .	. . .	. . .	. . .	. . .	2.5	. . .
Zirconia	. . .	. . .	. . .	. . .	. . .	. . .	2.5

(a) UI numbers designate frit compositions developed at the University of Illinois; NBS numbers, frits developed at the National Bureau of Standards (now the National Institute of Standards and Technology, NIST)

Table 2 Compositions of melted silicate frits for high-temperature service ceramic coatings

Constituent	**Percentage for specific frits[a]**						
	UI-32	**UI-285**	**UI-346**	**UI-418**	**NBS-11**	**NBS-331**	**NBS-332**
Silicon dioxide (SiO_2)	56.5	51.1	57.0	37.0	42.0	38.5	37.5
Aluminum oxide (Al_2O_3)	8.4	19.8	10.7	. . .	5.6	. . .	1.0
Boron oxide (B_2O_3)	10.6	9.5	8.0	8.0	25.8	6.5	6.5
Sodium monoxide (Na_2O)	12.0	10.9	10.8	. . .	17.9	. . .	. . .
Potassium monoxide (K_2O)	5.1	4.6	6.7	. . .	3.4	. . .	. . .
Calcium fluoride (CaF_2)	4.5	4.1	3.4	. . .	3.0	. . .	. . .
Cobalt oxide (CoO)	0.5	. . .	0.45	. . .	0.5	. . .	. . .

Nickel monoxide (NiO)	0.6	. . .	0.45	. . .	0.6	. . .	. . .
Manganese dioxide (MnO_2)	1.8	. . .	1.3	. . .	1.2	. . .	. . .
Vanadium pentoxide (V_2O_5)	. . .	. . .	1.2	. . .	. . .	. . .	. . .
Bismuth dioxide(BiO_2)	. . .	. . .	. . .	10.0	. . .	. . .	. . .
Calcium oxide (CaO)	. . .	. . .	. . .	5.0	. . .	3.5	3.5
Barium oxide (BaO)	. . .	. . .	. . .	25.0	. . .	44.0	44.0
Zinc oxide (ZnO)	. . .	. . .	. . .	5.0	. . .	5.0	5.0
Cerium dioxide (CeO_2)	. . .	. . .	. . .	5.0	. . .	. . .	. . .
Titanium dioxide (TiO_2)	. . .	. . .	. . .	5.0	. . .	. . .	. . .
Beryllium oxide (BeO)	. . .	. . .	. . .	. . .	. . .	2.5	. . .
Zirconium oxide (ZrO_2)	. . .	. . .	. . .	. . .	. . .	. . .	2.5

(a) UI numbers designate frit compositions developed at the University of Illinois; NBS numbers, frits developed at the National Bureau of Standards (now the National Institute of Standards and Technology, NIST)

Table 3 Compositions of slips for high-temperature service silicate-based ceramic coatings

Constituent	**Parts by weight for specific coatings$^{(a)}$**										
	UI-32-22	**UI-32-53**	**UI-285-1**	**UI-346-2**	**UI-346-4**	**UI-418-1**	**UI-418-4**	**A-19H**	**A-418**	**A-417**	**A-520**
Frit$^{(b)}$	88$^{(c)}$	100$^{(c)}$	100$^{(d)}$	100$^{(e)}$	100$^{(e)}$	100$^{(f)}$	100$^{(f)}$	100$^{(g)}$	70$^{(h)}$	70$^{(i)}$	90$^{(i)}$
Diaspore	12	. . .	. . .	15	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Clay	7	10	7	7	10	7	6	10	5	5	6
Hydrated borax	0.75	0.5	0.75	0.75	0.5	0.75	. . .	. . .	. . .	. . .	. . .
Water	50	50	50	55	50	50	50	50	48	48	45

Sodium pyrophosphate	. . .	0.05	. . .	. . .	0.05	. . .	. . .	. . .	. . .	. . .	. . .
Calcined aluminum oxide	. . .	25	. . .	. . .	25	. . .	. . .	25	. . .	. . .	. . .
Tricobalt tetroxide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1	. . .	. . .	. . .
Citric acid	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.05	. . .	. . .	. . .
Chromic oxide	. . .	. . .	. . .	. . .	. . .	. . .	25	. . .	30	30	. . .
Copper oxide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	10
Sodium nitrite	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.025

(a) UI numbers designate coatings developed at the University of Illinois; A numbers, coatings developed at the National Bureau of Standards (now the National Institute of Standards and Technology).

(b) See Tables 1 and 2 for batch and melted compositions of frits.

(c) UI-32 frit.

(d) UI-285 frit.

(e) UI-346 frit.

(f) UI-418 frit.

(g) NBS-11 frit.

(h) NBS-332 frit.

(i) NBS-331 frit

Glass coatings can be applied by spraying or air brushing (for which the material is atomized and carried by compressed air), dipping and draining (which may be followed by spraying), slushing and draining, filling and draining, and flow coating. Under certain conditions, electrostatic spraying also can be used.

Spraying is the most commonly used method, except when the configuration of the part prevents complete coverage or when production requirements are great enough so that a saving in material costs would be realized by the use of dipping or slushing. Dipping and draining is the most economical procedure for coating small parts with simple shapes. For larger parts with restricted areas, filling and draining may be the best coating method. Rotation or shaking of parts is often necessary when dipping or filling is used to distribute the coating and obtain uniform draining.

Glass coatings are brittle, but when applied at the usual thickness of 25 to 50 μm (1 to 2 mils), they will withstand considerable abuse, even at edges and unavoidable sharp corners. Mechanical roughening of the metal surface before applying the coating provides a greater surface area, affects the rate of oxidation, and frequently improves adherence. After application, coatings are dried at slightly elevated temperatures and are subsequently fired at higher temperatures to provide them with the desired performance and appearance characteristics.

Another type of coating for high-temperature service is a combination of glass and metal called *cermet.* A high proportion of metal powder (e.g., aluminum) is added after the glass has been made into a slip (see above). These coatings can be exposed to temperatures above the original firing temperature. Small steel sheets coated with this type of coating can be quenched red hot in water without chipping or blistering of the surface. Appropriate applications are heat exchangers, exhaust systems for internal combustion engines, marine service, structural members and panels for vehicular tunnels, and fire boxes of central heating boilers. Additional information is available in the section "Cermets" in this article.

Oxides. Coatings based on oxide materials provide underlying metals, except refractory metals, with protection against oxidation at elevated temperatures and with a high degree of thermal insulation. Flame-sprayed oxide coatings do not provide refractory metals with the necessary protection against oxygen because of their inherent porosity. Oxide coatings can be readily applied in thicknesses up to 6.4 mm (0.25 in.), but their resistance to thermal shock decreases with increasing thickness.

Alumina (Al_2O_3) and zirconia (ZrO_2) are the oxides most commonly used as coatings. Alumina coatings are hard and have excellent resistance to abrasion and good resistance to corrosion. Zirconia is widely used as a thermal barrier because of its low thermal conductivity.

Table 4 lists the principal oxides used for coatings and gives their melting points. Basic oxide is the major constituent of an oxide coating, usually being present in excess of 95 wt%. Other materials, such as calcium oxide (CaO), chromium oxide (Cr_2O_3), and magnesium oxide (MgO), are added in small percentages for stabilization, increase of as-sprayed density, modification of surface-emittance characteristics, and improvement of resistance to thermal shock. Physical properties for alumina and zirconia coatings flame sprayed from rod are given in Table 5.

Table 4 Melting points of principal oxides used in ceramic coatings

Oxide	**Melting point**	
	°C	**°F**
Aluminum oxide (Al_2O_3)	2070±28	3760±50
Aluminum titanate ($Al_2O_3TiO_2$)	1860	3380
Beryllium oxide (BeO)	2570±84	4660±150
Calcium zircanate ($CaZrO_3$)	2345	4250
Cerium oxide (CeO_2)	Over 2600	Over 4710
Chromium oxide (Cr_2O_3)	2265±110	4110±200
Cobalt oxide (CoO)	1805±56	3280±100
Forsterite ($2MgO\cdot SiO_2$)	1885	3425

Hafnium oxide (HfO_2)	2900±110	5250±200
Magnesium oxide (MgO)	2850±28	5165±50
Mullite ($3Al_2O_3{\cdot}SiO_2$)	1810	3290
Nickel oxide (NiO)	1980±110	3600±200
Silicon dioxide (SiO_2)	1720±14	3130±25
Spinel ($MgO{\cdot}Al_2O_3$)	2135	3875
Thorium oxide (ThO_2)	3220±56	5830±100
Titanium oxide (TiO_2)	1870±28	3400±50
Uranium oxide (UO_2)	2875±56	5210±100
Yttrium oxide (Y_2O_3)	2455±56	4455±100
Zircon ($ZrO_2{\cdot}SiO_2$)	1775±11	3225±20(a)
Zirconium oxide (ZrO_2)	2710±110	4910±200

(a) Decomposes

Table 5 Physical properties of alumina and zirconia flame sprayed from rod

Coating	**Bulk density**		**Porosity, %**	**Color**	**Typical compressive strength**		**Thermal expansion**(a)		**Thermal conductivity**(b)	
	g/cm^3	**$lb/in.^3$**			**MPa**	**ksi**	**µm/m·K**	**µin./in.· °F**	**W/m·K**	**$Btu{\cdot}in./ft^2{\cdot}h{\cdot}°F$**
Alumina	3.3	0.12	8-12	White	255	37	7.4	4.1	33	19

(a) 20 to 1230 °C (70 to 2250 °F).

(b) 540 to 1095 °C (1000 to 2000 °F)

Oxide coatings are usually applied by the flame or plasma-arc spraying methods. Before spraying by either method, the substrate surface should be clean and rough; abrasive blasting provides a satisfactory surface condition. Sprayed coatings usually range in thickness from 25 to 2500 μm (1 to 100 mils).

Flame spraying, using either oxyhydrogen or oxyacetylene systems, can deposit any refractory oxide whose melting point is below 2760 °C (5000 °F). However, certain refractory oxides, particularly silicon dioxide, do not spray well even though their melting points are considerably below 2760 °C (5000 °F).

An oxidation-resistant nickel chromium alloy often is applied to the substrate before an oxide coating is deposited by flame spraying. Without such a base coat, the adhesion of the oxide may be inadequate. Coating rates during flame spraying are slow, usually in the range of 16 to 410 cm^3/h (1 to 25 $in.^3$/h).

All oxides that can be flame sprayed and those with higher melting points can be applied by plasma spraying. In general, plasma spraying produces coatings of greater density (porosity of sprayed oxide coatings ranges from 5 to 15%, depending on method of application), greater hardness, and smoother finish than those obtained by flame spraying. Also, the temperature of the substrate remains lower, because deposition is faster. Because of the inert gases used during plasma spraying, oxidation of the substrate is minimized.

In addition to spraying, any of the oxides may be applied by troweling. Troweled coatings usually are thicker than sprayed coatings and are designed to provide maximum thermal protection to the underlying metal. A bonding medium, such as sodium silicate, calcium aluminate, phosphoric acid, or glass, is used for coatings applied by troweling. In addition, the use of expanded-metal reinforcements greatly improves troweled coatings.

Carbides as ceramic coatings are principally used for wear and seal applications, in which the high hardness of carbides is an advantage. These applications include jet engine seals, rubber-skiving knives, paper machine knives, and plug gages. Carbide coatings for wear resistance are applied by flame spraying or detonation-gun techniques. Table 6 gives the melting points of ten carbides.

Table 6 Melting points of carbides

Carbide	Melting point	
	°C	°F
Boron carbide (B_4C)	2470	4480
Chromium carbide (Cr_3C_2)	1900	3440
Niobium carbide (NbC)	3480	6295
Hafnium carbide (HfC)	3890	7030
Molybdenum carbide (Mo_2C)	2410	4375
Silicon carbide (SiC)	2540	4605
Tantalum carbide (TaC)	3980	7200
Titanium carbide (TiC)	2940	5325

Tungsten carbide (WC)	2790	5050
Zirconium carbide (ZrC)	3400	6150

Silicides are the most important coating materials for protecting refractory metals against oxidation. Silicide-based coatings protect by means of a thin coating of silica that forms on the coating surface when heated in an oxygen-containing atmosphere. To improve the self-healing, emittance, chemical stability, or adherence of this thin silica coating, other elements, such as chromium, niobium, boron, or aluminum, are added to the coating formula.

Table 7 lists and describes several silicide coatings. These materials are usually applied to a substrate by some variation of the vapor-deposition process. Deposition, diffusion, and reaction of silicon (and any other elements added in small quantities) with the substrate metal at a high temperature produce the silicide-based coating.

Table 7 Silicide coatings for protection of refractory metals against oxidation

Constituents of as-applied coating		**Suitable substrate metal**	**Oxidation protection(a)**			**Application**		
			Temperature		**Life, h**	**Method**	**Thickness**	
Silicide	**Additives**		**°C**	**°F**			**µm**	**mils**
Molybdenum silicide ($MoSi_2$)	None	Mo-0.5 Ti	1480	2700	10	Fluidized bed	25-50	1-2
	Nb	Mo-0.5 Ti	1540	2800	12	Pack cementation	75	3
	Cr, Al	Mo-0.5 Ti	1540	2800	8	Pack cementation(b)	60	2
	Cr	Mo-0.5 Ti	1480	2700	36(c)	Pack cementation	60	2
	Cr, Al, B, Nb, Mn	Mo	1540	2800	19-45	Pack cementation	60-100	2-4
Niobium silicide ($NbSi_2$)	None	Nb-33 Ta-0.8 Zr	1480	2700	3	Fluidized bed	25-50	1-2
		Nb-10 Ti-10-10 Mo	1425	2600	15-25	Pack cementation	50	2
	Cr, Ti	Nb-10 Ti-10 Mo	1370	2500	Over 100	Vacuum pack(b)(d)	100	4
	Cr, B	Nb-10 Ti-10 Mo	1370	2500(e)	Over 15(e)	Pack cementation(b)	50	2
Niobium silicide ($NbSi_2$),	. . .	Nb	1370	2500	396	Pack cementation	Over	Over

($NbAl_3$)(f)							150	6
Tantalum silicide ($TaSi_2$), plus others(f)	. . .	Ta	1370	2500	275	Pack cementation	Over 150	Over 6

(a) Representative data only; can vary depending on test conditions.

(b) Multiple-cycle processing.

(c) 95% confidence.

(d) Variation of pack-cementation process; pack is elevated to remove residual air before heating.

(e) Life of coating system is at least 10 h at 1425 °C (2600 °F).

(f) Proprietary

Vapor-deposited and diffused silicide coatings are characterized by their superior adhesion to the substrate. Fairly precise control of coating thickness is obtained through this process. Uniform silicide coatings with a thickness of a few tenths of a mil to several mils are produced on both simple and complex shapes by either the pack-cementation or the fluidized-bed technique.

The slurry fusion process is the most commonly used method for the deposition of silicide coatings on refractory metals. A slurry of fine silicon powder with desired additives (iron, chromium, hafnium, or titanium) in an organic liquid is applied to the part by dipping, spraying, or brushing. The coated part is heated in a vacuum or inert atmosphere at 1300 to 1400 °C (2370 to 2550 °F) for 30 to 60 min. An excellent coating-to-substrate bond is developed.

Because they are more brittle than the substrate metals, silicide coatings are highly susceptible to crack formation, which can act as a stress raiser on the substrate. In general, silicide coatings have an adverse effect on all room-temperature mechanical properties of the substrate; the thicker the coating, the greater the effect. Silicide coatings generally embrittle the metals to which they are applied, but they do not necessarily impair the usefulness of the coated metals for structural applications.

Phosphate-Bonded Coatings. Phosphates for metal protective coating systems are formed by the chemical reaction of phosphoric acid and a metal oxide such as aluminum oxide, chromium oxide, hafnium oxide, zinc oxide, and zirconium oxide. The phosphate-bonded materials are used to protect metals against heat and to act as a binder in thin ceramic paint films. Thicker composites are troweled, rammed, or sprayed to the desired thickness. Phosphate-bonded coatings have low density, low thermal conductivity, and high refractoriness after curing in place at temperatures ranging from 21 to 425 °C (70 to 800 °F), and they can be applied in greater thicknesses than other ceramic coatings. Thus, a thick refractory composite can be used to protect lower-temperature-resistant metal systems. Phosphate-bonded composites, depending on composition, withstand temperatures up to 2425 °C (4400 °F) and have been applied in thicknesses up to 50 mm (2 in.).

Reinforcements, bonded or welded to the metal substrate, usually are used within phosphate-bonded coatings to facilitate bonding to the substrate and to provide resistance to vibration and impact. Reinforcements are corrugated metal screen, expanded metal, open metal strips, and metal and nonmetallic honeycomb.

When phosphate-bonded composites are prepared, one of the strongest bonds between the metal oxide particles is obtained with 85% orthophosphoric acid (H_3PO_4). However, composites bonded with orthophosphoric acid have lower maximum service temperatures than composites formed by the reaction of metal oxide and fluorophosphoric acid (H_2PO_3F). The use of fluorophosphoric acid also permits the use of lower curing temperatures.

After preparation, the composites are aged for 24 h or more to permit reaction between the acid and the metal oxide. The aged composite is troweled either directly onto the substrate or over another protective coating. The coating is then cured with close control of time and temperature. Oxides bonded with orthophosphoric acid are cured for 1 h at each of the following temperatures successively: 93, 120, 150, 215, 315, and 425 °C (200, 250, 300, 420, 600, and 800 °F). Oxides bonded with fluorophosphoric acid are cured for 3 h at room temperature and then for 1 h at 120, 150, and 205 °C (250, 300, and 400 °F). Table 8 identifies several common phosphate-bonded coatings and gives their densities and maximum service temperatures.

Table 8 Characteristics of phosphate-bonded ceramic coatings

Type of phosphate	Constituents	Density		Maximum service temperature	
		kg/m^3	lb/ft^3	°C	°F
Aluminum	85% H_3PO_4 + Al_2O_3	3040-3600	190-225	1925	3500
	H_2PO_3F + Al_2O_3	3040-3600	190-225	1980	3600
Hafnium	85% H_3PO_4 + HfO_2	4490-4810	280-300	1925	3500
	H_2PO_3F + HfO_2	4490-4810	280-300	2205	4000
Zinc	85% H_3PO_4 + ZnO	. . .	. . .	1650	3000
Zirconium	85% H_3PO_4 + ZrO_2	3200-4650	200-290	1925	3500

A reaction between the acidic coating and the substrate may cause bloating or blistering upon deposition or after initial curing as the result of the release of hydrogen from the acid. The volatilization of phosphorus pentoxide (P2O5), a decomposition product of the acid, also can cause blistering.

Various compounds, such as chromic oxide, ammonia compounds, or ferric phosphate, are added to the coating materials to prevent phosphorus pentoxide from corroding the substrate. These additives increase the pH of the coating without affecting the bonding action. Chromic acid may also be added to improve heat emission of the coating. Coatings are usually thixotropic and appear to have a greater viscosity than is actual because slight agitation causes the material to flow.

Coatings are formulated to possess optimum physical and thermal properties. Particle size and filler-to-binder ratio have a great influence on the final properties, including shrinkage, resistance to thermal shock, bond strength, porosity, and thermal conductivity. The common range of particle size for phosphate-bonded coatings is -14 to -325 mesh.

Phosphate-bonded coatings are used primarily to prevent deterioration of the substrate metal during high-temperature service. Applications include combustion-chamber linings, re-entry leading edges, hot gas ducts, and high-temperature insulation repairs.

Cermets. Table 9 lists the constituents of electrodeposited coatings based on cermets and indicates thicknesses, service life at elevated temperatures, and suitable substrates for these materials. Electrodeposited cermet coatings currently have only a few commercial applications.

Table 9 Cermet electrodeposited coatings for high-temperature oxidation protection

Constituents of coating as applied	Suitable substrate metal	Service temperature		Service life, min	Thickness	
		°C	°F		µm	mils
Cr + ZrB_2	Mo-0.5Ti	2130	3865	20	75-150	3-6
	Tantalum	2130	3865	20	75-150	3-6
	Tungsten	2205	4000	10	75	3
Pt-Rh + ZrB_2	Tungsten	2870	5200	1	510-760	20-30

Cermet coatings, consisting of a mixture of metal and ceramic oxides, protect metallic substrates against oxidation and erosion. The electrodeposition process used for applying these coatings is a combination of electroplating (for metals) and electrophoresis (for ceramics). The amount of ceramic that can be deposited depends on particle size, density, and composition. Ceramic particles ranging in size from less than 1 µm to 44 µm (40 to 1730 µin.) can be plated. These particles are suspended in any common electroplating bath by agitation. With ordinary procedures, coatings containing about 20 wt% ceramic can be obtained in a deposit; with special procedures, this can be increased to 50 to 60 wt%. Because most cermet coatings are for erosion-resistance applications such as rocket nozzles, coatings are relatively thick (>75 µm or >3 mils). Thinner coatings can be obtained, however, and thickness can be controlled to 25 µm (1 mil).

Cermets applied by plasma spraying or detonation gun processes are the basis for increasing the wear resistance of metals and superalloys. The most important cermets are metal-bonded carbides and borides, especially tungsten carbide with 8 to 15% Co. At the lower cobalt content, high hardness and wear resistance are produced. Increasing the cobalt content increases the toughness necessary for wear plus impact service. Tungsten carbides wear well to about 590 °C (1000 °F) in air. At higher temperatures, chromium carbide and certain nickel-chromium alloys are used because of self-lubricating qualities. Coatings based on aluminum oxide, refractory carbides, and an oxidation-resistant metallic binder are in use at temperatures above 870 °C (1600 °F).

Coating Methods

Ceramic coatings may be applied by brushing, spraying, dipping, flow coating, combustion flame spraying, plasma-arc flame spraying, detonation gun spraying, pack cementation, fluidized-bed deposition, vapor streaming, troweling, and electrophoresis. Most of these methods have been used for coating production parts.

Selection of coating method depends on the following factors:

- Substrate metal
- Coating material (some materials are restricted as to method of application)
- Size and shape of the part to be coated
- Cost
- Service conditions (coating method can modify the properties of the coating)

Spraying and Dipping

Spraying and dipping are two methods of applying ceramic coatings in a slip or slurry form. Spraying and dipping methods are used to apply silicates and other coatings onto engine exhaust ducts, space heaters, radiators, and other high-production parts.

Spraying can be used when the shape of the work permits direct access to all surface areas to be coated. This method is usually used for applying a closely controlled thickness of coating to exterior surfaces only.

Dipping can be used for almost all parts. This includes riveted or spot welded assemblies, except those in which faying surfaces would be inadequately covered by the slurry. For a uniform coating thickness, a handling cycle must be established for each part to produce drainage of each surface at the proper angle.

Surface Preparation. Parts must be thoroughly cleaned before spraying or dipping. Oily spots prevent adherence of the coating and cause blistering or spalling during firing. When sand blasting is used, the abrasive must be free of contaminants. Sharp workpiece edges should be rounded because they are difficult to coat. If sharp edges are coated without being rounded off, the coating will often spall after firing.

The principal cleaning processes used are chemical and abrasive. Chemical cleaning methods for metals of low-alloy content are similar to those used before porcelain enameling. (Additional information can be found in the article "Porcelain Enameling" in this Volume.) For high-alloy materials, such as stainless steels and heat-resisting alloys, heat scaling or trichloroethylene-vapor degreasing, followed by grit blasting, is the preferred cleaning method, except for parts made of thin-gage material or with inaccessible areas. For these parts, chemical cleaning is required. Table 10 shows the sequence of chemical cleaning solutions and immersion times used for stainless steels and heat-resisting alloys. The use of chemical cleaning with alkaline solutions is limited to parts that permit good drainage. All cleaning solutions must be removed from the work by water rinsing before the coating is applied.

Table 10 Descaling of stainless steels and heat-resisting alloys before ceramic coating

Alloy	Immersion time, min			
	Solution 1 Sodium hydroxide[(a)]	Solution 2 Sodium hydride[(b)]	Solution 3 Nitric-hydrofluoric acid[(c)]	Solution 4 Nitric acid[(d)]
410, 430	1-2	10-30	None	5-15
321, 347, 316; 19-9 DL	1-2	10-30	10-30	5-15
Inconel; Nimonic 75, 80A	1-2	10-30	5 max	5-15

(a) Molten sodium hydroxide at 400 to 425 °C (750 to 800 °F).

(b) Molten sodium hydroxide containing 0.1 to 2 wt% sodium hydride; bath at 370 to 400 °C (700 to 750 °F).

(c) Aqueous solution containing 1 to 4 vol% 70% hydrofluoric acid and 15 to 25% nitric acid (1.41 sp gr); temperature, 60 to 82 °C (140 to 180 °F). Solution may be used at ambient temperature by increasing immersion time.

(d) Aqueous solution containing 12 to 20 vol% nitric acid (1.41 sp gr); temperature, 60 to 82 °C (140 to 180 °F)

Abrasive blast cleaning should be used on parts that will not be distorted by the blasting action and whose surfaces are accessible to the blasting medium. Abrasive cleaning is particularly applicable when an extremely strong mechanical bond between the coating and substrate is required. Silica sand, the most commonly used blasting medium, has low initial cost. However, its high breakdown rate and its highly detrimental effect on blasting equipment results in high equipment maintenance costs. Use of materials with a higher initial cost, such as steel grit or shot, aluminum oxide, garnet, and glass shot, often results in lower overall cost. For additional information about materials, equipment, and techniques used in abrasive blast cleaning, see the article "Mechanical Cleaning Systems" in this Volume.

Processing. Ceramic coating materials may be purchased as slips, in which form only the specific gravity requires adjustment by either adding or pouring off water before application. Coatings may also be obtained as frits. Frits are milled in porcelain-lined mills with water to which refractory oxides or other inert materials, clay, and setup agents are added to produce the required analysis.

Changes from the recommended composition and specific gravity of a slip may produce undesirable results. A low specific gravity causes limited coverage or running of the applied coating. A high specific gravity results in thick coatings that spall on firing. To obtain satisfactory results, test pieces, 25 by 75 mm (1 by 3 in.) and of the same composition and gage as the work material, should be used to check the dry film weight of the slip and the characteristics of the coating as fired. The slip should be checked at the beginning of each working period and whenever an adjustment is made or when a new batch is prepared.

Application of the slip to the work is also critical because of the coating thickness. For stainless steels and heat-resisting alloys, coating thickness ranges from 13 to 75 μm (0.5 to 3 mils). No specific tolerances for coating thickness exist. If the coating is too thin, it oxidizes during firing and loses its protective value; if too thick, it spalls.

Dipping is the preferred method of coating for production operations, although spraying is also extensively used. In some instances, manual debeading is necessary to remove excess coating from points of buildup to prevent spalling. Complex shapes must be sprayed, because dipping builds up excessive beads or fillets in inaccessible areas.

After being applied, the slip is dried in forced circulating air at 60 to 120 °C (140 to 250 °F) for 10 to 15 min. If the drying temperature is too low, waterlines appear on the coating; if too high, the coating tears. All free water must be removed, or the coating will blister during firing.

Firing is accomplished in a gas or electrically heated furnace. Firing temperature and time depend on the thickness of both the coating and the substrate. The temperature and furnace atmosphere are controlled to produce the required as-fired appearance of the coating with maximum adherence. Overfiring causes excessive oxidation of the substrate, resulting in poor adhesion or a decrease in coating properties. Underfired coatings have poor adhesion and strength and do not develop maximum coating protection.

Equipment for spraying ceramic coatings is available commercially. The spray gun should have a nozzle with an orifice diameter of 1.30 to 2.80 mm (0.050 to 0.110 in.). Efficient nozzles have a spraying capacity of 260,000 to 330,000 mm^3 (16 to 20 $in.^3$) of coating material per minute using an air pressure of 345 kPa (50 psi) to propel the coating material to the work surface. The compressed air supply should be filtered to remove dirt, rust, oil, and moisture. A reliable air pressure regulator should be used to permit accurate adjustment of pressures, particularly in the range of 205 to 550 kPa (30 to 80 psi).

For most dipping applications, the equipment consists of a tank such as that shown in Fig. 1. The tank should be large enough to permit complete submersion of the part into the slip. An easel or rack is required for draining. Dipping equipment can be elaborated to include temperature-controlled dip tanks and recirculating systems with screens and separators in the line for removing contaminants. Automatic equipment incorporating positioners for proper drainage is often used.

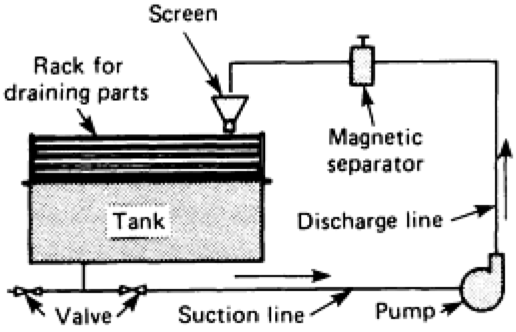


Fig. 1 Recirculating dip tank for the application of ceramic coatings

Flow coating is modified dipping and draining in which slip is flowed onto conveyorized parts. Slip flows from nozzles designed to flush all surfaces of the work, after which it drains into a catch basin and is recirculated.

Flame Spraying

Most ceramic coating materials used currently can be applied by flame spraying. Silicates, silicides, oxides, carbides, borides, and nitrides are among the principal materials deposited by this process. There are three methods of heating and propelling the particles in the plastic condition to the substrate surface: combustion flame spraying, plasma-arc flame spraying, and detonation gun spraying. The first two methods use coating materials in powder or rod form. Detonation gun spraying uses only powder materials.

Applicability. Flame-sprayed ceramic coatings can be applied to workpieces in a wide range of sizes and shapes. Practically all metals that can be adequately cleaned, textured by standard abrasive blasting equipment, and safely heated to 150 to 205 °C (300 to 400 °F) can be coated.

Spray equipment can be fitted with extensions having deflecting heads that can turn the spray direction up to 45°. Thus, any shape can be coated if the spray head can be placed within a few inches of the substrate and at an angle of ±45° to the surface.

From a practical standpoint, the maximum size limits for coating the outside and inside surfaces of workpieces depend only on the preparation and handling equipment. In general, the minimum size of the internal diameter is limited to 50 mm (2 in.), and the length should not exceed 3.7 m (12 ft) unless the diameter is large enough to accommodate the entire gun and the supply lines. The coating of curved passages is limited to sizes and shapes that permit approach of the gun at the angles and distances already prescribed. For example, satisfactory coatings have been applied to wires as small as 0.10 mm (0.004 in.) in diameter, to rocket nozzles with 6.4 mm (0.25 in.) throat diameter that were 13 mm (0.5 in.) in length, and to large ducting 2 m (6 ft) in diameter by 8.2 m (27 ft) long.

Combustion Flame Spraying

Processing variables of flame spraying that directly affect the serviceability of a coating are principally surface preparation, gun operation, spraying distance, temperature of the workpiece, and type of coating.

The serviceability of the coating depends on the surface preparation. If a surface is not absolutely clean or is not roughened sufficiently, bond strength may be reduced 50% or more.

Optimum adherence of the spray particles to each other (cohesion) depends on the fineness of the spray, uniformity of the spray pattern, correct adjustment of gas ratios and pressures, and proper material feed rate. These can be accomplished only by proper adjustment of the spray system.

The temperature and size of the spray particles must be closely controlled. If a rod gun periodically produces large spray particles, they are not sufficiently heated and are consequently less plastic, resulting in poor bonding to adjacent particles or to the substrate and creating a weak point or area in the coating.

Spray guns should be maintained at the prescribed distance from the substrate for the type of coating desired. If the gun is too close, the coating becomes crazed and has low thermal shock resistance. An excessive gun-to-work distance can result in soft, spongy deposits with low physical properties and decreased deposit efficiency.

Surface Preparation. Because flame-sprayed particles adhere to the substrate surface primarily by mechanical bonding, suitable methods of surface roughening are essential. These consist of undercutting, grooving, threading, knurling, abrasive blasting, and applying sprayed metal undercoats. Abrasive blasting and metal undercoats provide optimum surface conditions for ceramic coatings. When blasting is used, abrasives must be clean and sharp. Roughening should be uniform and should produce as many re-entrant angles and sharp peaks as possible.

Steel grit is one of the most satisfactory blasting abrasives. It disintegrates slowly and offers maximum life. The grit should be screened periodically to remove dirt and fines. Angular steel grit is available in many sizes. A G25 grit propelled by 275 kPa (40 psi) air pressure is used in many applications.

Fused-alumina grit may be used when surface contamination by a steel abrasive is objectionable. Optimum surface preparation is obtained with a No. 24 grit propelled at a pressure of 275 to 345 kPa (40 to 50 psi). This abrasive cuts faster than steel, but some breakdown of the grit occurs, and the fines should be removed before reuse. For light-gage materials, finer grit (No. 46) and lower blasting pressures are recommended to prevent distortion of the work. Silicon carbide also produces a satisfactory surface for ceramic coatings.

Sprayed metal coatings provide an anchoring base for flame-sprayed ceramics equal to that obtained by abrasive blasting. Sprayed molybdenum undercoatings are used as a bonding coat for subsequent application of ceramic coating to metal substrates that are too hard or too thin to receive adequate surface roughening through abrasive blasting.

Nickel-chromium or nickel-chromium-aluminum alloy sprayed undercoatings are used as an adherent base for flame-sprayed ceramic coatings that are repeatedly subjected to high temperatures. An undercoat in thicknesses of 50 to 330 μm (2 to 13 mils) develops an optimum bond for the ceramic coating. When the metal alloy is used, the substrate surface is first roughened by abrasive blasting. Areas that do not require coating can be protected with masking tape, rubber, or sheet metal, depending on the severity of the surface roughening operation.

Processing. After surface preparation, the spray gun is loaded with ceramic coating material of proper size, and the gun is ignited according to the procedure recommended by the manufacturer. Techniques used in flame spraying of ceramics are similar to those used in spraying paint. Successful application depends primarily on the skill of the operator.

Spraying distance and rate of gun traverse across the work should be held as nearly constant as possible. The distance and rate of traverse depend on the spraying equipment, composition of the coating material, substrate metal, and desired physical characteristics of the coating. Powder guns have a relatively long, bushy flame to heat the ceramic powder during its passage through the extensive heat zone. Consequently, powder guns may need to be placed 150 to 200 mm (6 to 8 in.) from the workpiece and traversed quite rapidly to minimize overheating. Rod guns using the same type of heating operate with a very short flame and heat zone, because heating of the ceramic always takes place at a fixed location at the end of the rod. For rod guns, the optimum spraying distance is about 75 mm (3 in.).

The gun should be moved continuously across a surface in such a manner that each pass slightly overlaps the preceding one. When the surface is completely coated, succeeding passes to increase thickness should be at right angles to those used for initial coverage.

When possible, the spraying angle should be 90° to the workpiece surface to produce the smoothest coating at the fastest rate. Spraying angles up to 45° from the preferred gun position can be tolerated if the slight reduction in physical characteristics of the coating is acceptable.

To obtain optimum coating properties, the workpiece temperature should be controlled. Adherence of the coating is greatly reduced if the substrate is heated over 260 °C (500 °F). Substrate temperatures can be measured on the reverse sides of panel specimens by applying temperature-sensitive paint or crayon that melts when a specific temperature is exceeded.

When a rod gun is used for coating flat surfaces, use the following practices to avoid overheating the substrate:

- Move the gun across the face of the work in a smooth motion and at a rate of about 0.3 m (1 ft) every 5 s.

- Maintain the proper distance between gun and work (about 75 mm or 3 in.) during spraying passes.
- If a workpiece is small, pause to the side of the work after a coating pass to permit the workpiece to cool slightly.

Overheating of substrates was overcome in one plant by fixturing the work and spraying for a limited time. The conditions of this operation are illustrated in Fig. 2. Combustion flame spray coating of the inside surface of the rocket combustion chamber shown in Fig. 2 caused melting or burning of the magnesium-alloy substrate when the zirconia coating was applied in a continuous operation. Destruction occurred before the required coating thickness of 890 to 1020 μm (35 to 40 mils) could be applied.

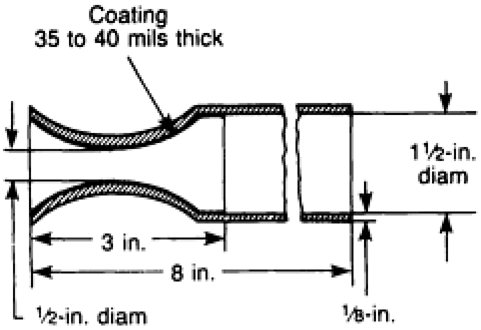


Fig. 2 Zirconia-coated magnesium-alloy rocket combustion chamber

This problem was solved by using a fixture comprised of three friction-loaded thin steel fingers that extended from a standard rotatable chuck. The fingers gripped the exterior of each combustion chamber with just enough force to hold the workpiece during rotation and to permit rapid interchange of the workpieces.

The coating operation consisted of rotating the workpiece at about 30 to 50 rev/min, spraying for not longer than 25 s, then removing the workpiece to permit cooling to room temperature, during which time uncoated or partly coated workpieces would be processed in the same manner. Each combustion chamber required eight or more cycles for producing a coating of the specified thickness.

Figure 3 illustrates a metal nozzle to which a coating of alumina and zirconia was applied 635 μm (25 mils) thick. The operating conditions were as follows: The total area coated on each nozzle was 7100 mm^2 (11 $in.^2$). The time required for preparation, sand blasting, coating, and handling is broken down as follows:

Conditions	**Coating material**	
	Alumina	**Zirconia**
Size of ceramic rod	4.8 by 610 mm ($\frac{3}{16}$ by 24 in.)	4.8 by 455 mm ($\frac{3}{16}$ by 18 in.)

Rods per nozzle coated	1	$1\frac{1}{2}$
Average feed rate	180 mm/min (7 in./min)	100 mm/min (4 in./min)

When large areas require coating, it may be more economical to use more than one spray gun. With the proper mechanical setup, one operator can operate four spray guns efficiently.

Process	**Cycle time, min**	
	Alumina	**Zirconia**
Fixturing	5	5
Masking	5	5
Sand blasting	1	1
Coating	3	6
Unpacking, repacking, transportation, paper work	6	6
Inspection, individual packaging	1	1

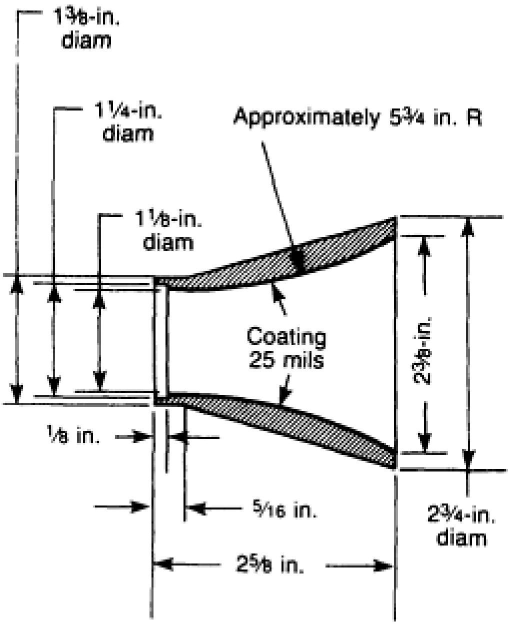


Fig. 3 Metal nozzle coated with alumina and zirconia

Equipment. Most parts require fixturing. For simple shapes that are hand coated, only a simple clamping device is needed for rigidly supporting the part within an exhaust hood during coating. Sheet metal is used for masking areas that do not require coating. A lathe is a suitable fixture for coating parts such as cylinders and nozzles. The chuck rotates the part, and the tool post carriage mechanically moves the spray gun. This setup requires a movable exhaust system for removal of the combustion products and excess spray material.

Gravity-feed or pressure-feed spray guns for powder, or electric-feed or air-motor-feed rod guns, are used in combustion flame spraying.

A typical gravity-feed powder spray installation consists of a fuel gas-control unit, including regulators, to provide a supply of oxygen and acetylene or hydrogen fuel gas; a meter for accurate measurement of aspirating gas flow; and a spray gun with a nozzle and a canister for containing powder. The principle of operation for this gun is illustrated in Fig. 4. Powder falls through a metering valve in the bottom of the canister into a stream of aspirating gas, which propels it to a stream of fuel gas that has been diverted through a valving system in the gun. The flow rate of the powder is controlled by the size of the metering valve and the amount of aspirating gas metered through the nozzle. This gun usually has a vibrator to maintain uniform powder flow.

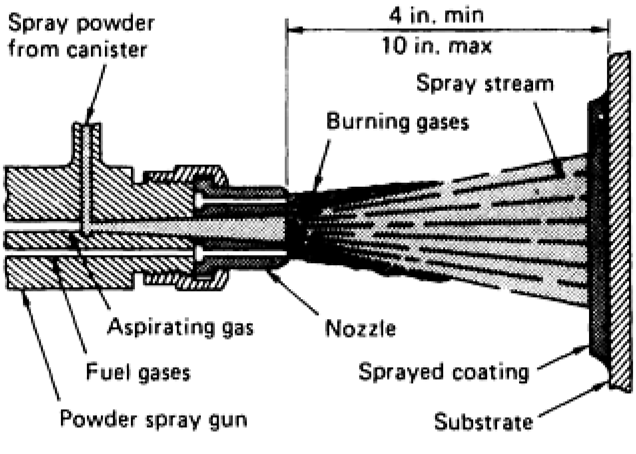


Fig. 4 Operational principle of a gravity-feed powder spray gun

In the pressure-feed system, the powder container is separated from the gun and connected by means of a hose through which powder and carrier gas flow. The carrier gas may be compressed air, fuel gas, or inert gas. Hydrogen is commonly used as both carrier and fuel gas.

Control of particle size is important in both gravity-feed and pressure-feed systems. However, the pressure-feed system requires less control of distribution of particle size because of the higher velocity of the carrier gas. Compared to rod spraying, powder spraying has lower initial equipment costs and greater flexibility of coating properties, as well as being adaptable to a wider variety of coating materials.

A typical rod spray installation is illustrated in Fig. 5. In addition to the auxiliary equipment required for the powder spray process, rod spraying requires a supply of compressed air, an air-control unit that includes a filter and a regulator, and an air flowmeter. A good grade of acetylene should be used, and at least two tanks should be manifolded so that withdrawal rates can be kept below a maximum of one-seventh of the volume of the tank capacity per hour to prevent acetone withdrawal. This is recommended because of the cooling effect that acetone vapor has on flame temperature.

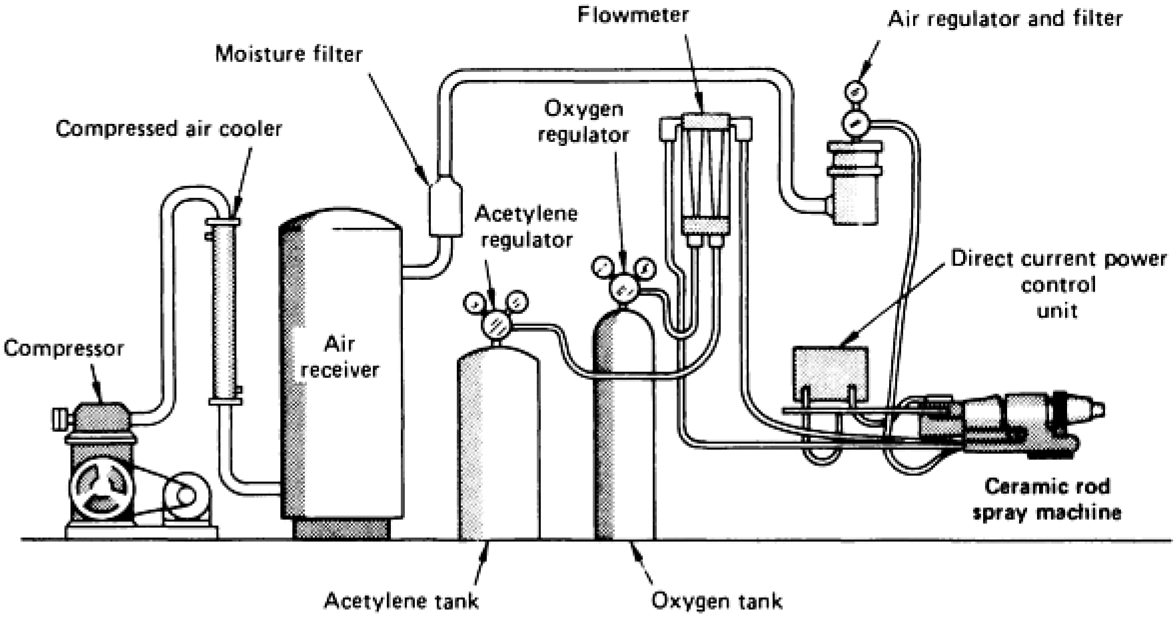


Fig. 5 Rod spray installation

The operation of a ceramic rod spray gun is shown in Fig. 6. The ceramic rod is fed through the center of the nozzle and atomized by the surrounding oxyacetylene flame and compressed air. Compressed air is used to cool the nozzle, increase the velocity of the sprayed material, and control the spray pattern. Control of the diameter and straightness of the rod is required to eliminate problems such as rod sticking and blowback. Control of rod speed is important for control of the density and surface characteristics of the coating. The rod and powder guns can be equipped with extensions and 45° angle air caps for coating inside diameters. The velocities of the sprayed particles from a rod gun and those from a powder gun are compared in Fig. 7.

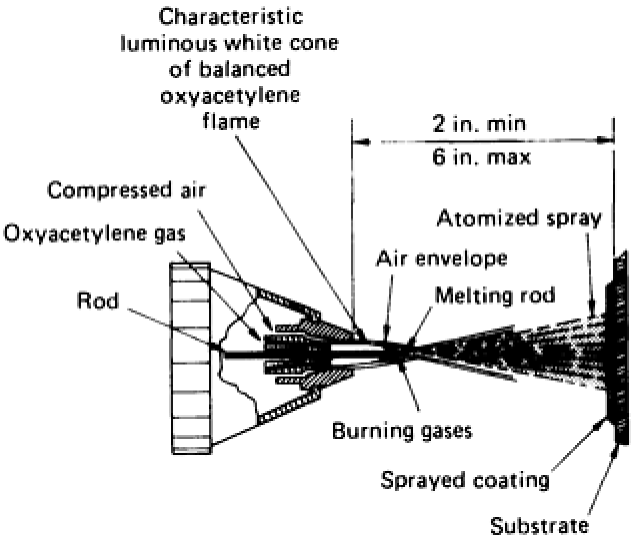


Fig. 6 Operational principle of rod gun

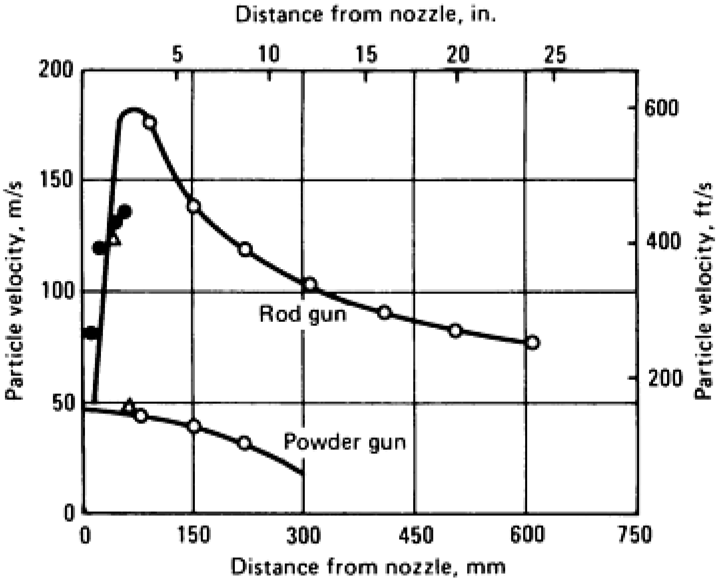


Fig. 7 Comparison of spray particle velocity from rod and powder guns. ○: Velocimeter; •: streak camera, fast particle; △: high-speed motion pictures

Rod spraying causes less heating of a workpiece than powder spraying, and it produces a coating with higher density and better bond between the coating and substrate.

Control of coating thickness is related directly to the method used for handling the workpiece and the spray gun. Hand-applied coatings can easily be held within a tolerance of ±50 μm (±2 mils). Mechanical systems for handling both workpiece and gun decrease this tolerance by 50% or more. The variation in coating thickness obtained by hand spraying alumina and zirconia on one side of steel test coupons (25 by 25 by 3.2 mm, or 1 by 1 by $\frac{1}{8}$ in.) with a rod gun is shown in Fig. 8.

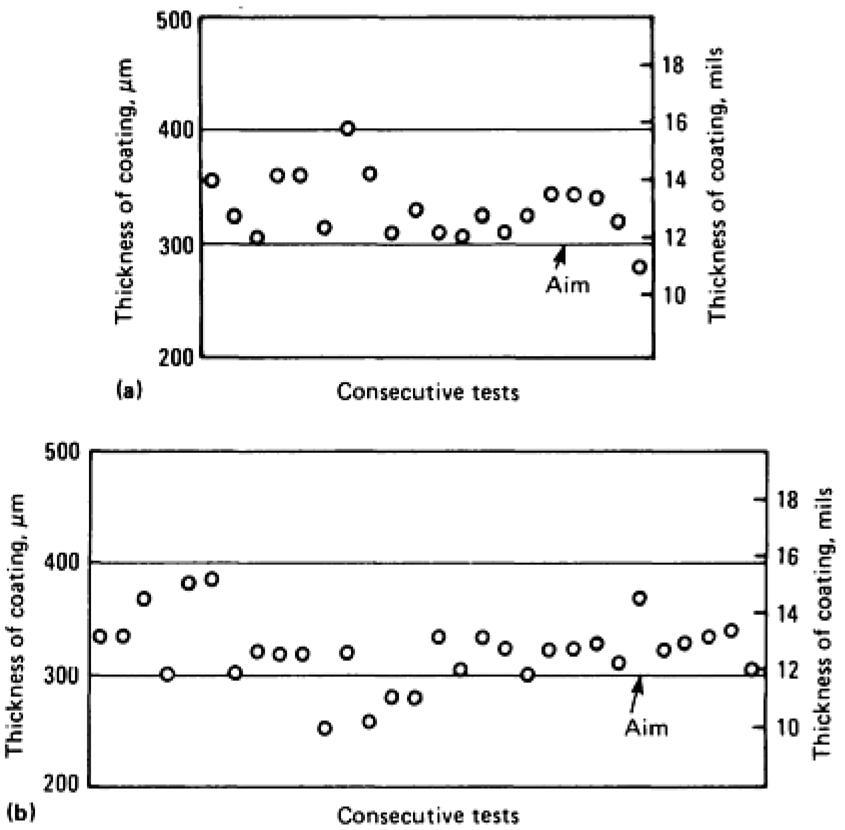


Fig. 8 Variation in thickness of hand-sprayed alumina and zirconia coatings on steel test coupons. Coatings flame sprayed from rod. (a) Alumina on steel, 20 tests. (b) Zirconia on steel, 30 tests

Flame-sprayed coatings are applied relatively slowly; therefore, after a uniform surface coverage system has been set up, control of the coating thickness depends on timing the duration of coating application with sufficient accuracy to achieve the desired tolerances. If closer tolerances or finer surface finishes are required, most flame-sprayed ceramic coatings can be ground by conventional grinding techniques.

Plasma-Arc Flame Spraying

In the plasma process, a gas or a mixture of gases, such as argon, hydrogen, or nitrogen, is fed into the arc chamber of the plasma generator and heated by an electric arc struck between an electrode and the nozzle. The gas is heated to temperatures as high as 8300 °C (15,000 °F) to form a plasma, or ionized gas, that is accelerated through the nozzle. The ceramic powder, carried by a gas stream, is injected into the plasma, where it is heated, melted, and propelled toward the workpiece.

The higher-temperature heat source of the plasma arc imparts an energy content to the ceramic particles that is different from that in the combustion flame process. This necessitates some modification of the gun position. When the plasma process is used, higher-melting ceramic materials, such as the refractory metal carbides, can be deposited with a greater deposition rate.

The processing operations for plasma-arc spraying are similar to those discussed in the section on combustion flame spraying in this article. For a more detailed discussion of plasma-arc spraying, see the article "Thermal Spray Coatings" in this Volume.

Thermal barrier coating is one current application using plasma-arc spraying. Applied to certain high-temperature components, such as the inside of combustion chambers or the first-stage vane or blade of a gas turbine engine, thermal barrier coatings act to insulate the metal substrate thermally. Coatings are designed to provide as much as a 110 °C (200 °F) drop in temperature at 980 to 1095 °C (1800 to 2000 °F), but they should be used in a temperature gradient, such as is provided by air cooling the substrate or metal side. A thermal barrier could be a 150 to 200 μm (6 to 8 mils) undercoat of a high-temperature nickel-cobalt-chromium-aluminum-yttrium alloy, followed by 255 to 305 μm (10 to 12 mils) of yttria-stabilized zirconia or magnesium zirconate ($MgO \cdot ZrO_2$). If greater thickness for greater insulation is desired, thermal stresses resulting from application should be carefully considered. In laboratory applications, a thermal cycling test is used followed by a bench engine evaluation to qualify the coating and estimate service life.

Detonation Gun Flame Spraying

Detonation gun flame spraying is markedly different from other flame spraying processes and was developed specifically for the deposition of hard, wear-resistant materials, such as tungsten carbide. Detonation gun spraying uses controlled detonations of acetylene and oxygen to melt and propel the particles onto the substrate.

Powder materials sprayed by this process are carbides containing a small amount of metal binder, and oxides or oxide mixtures. Coatings are usually less than 255 μm (10 mils) thick and are used primarily in applications requiring wear resistance under extreme service conditions. Applications include aircraft jet engine seals (for protection against high-temperature dry rubbing wear) and aircraft compressor and turbine blades (for protection against fretting corrosion at medium to high temperatures).

Coating particles emerge from the gun at supersonic speeds, and only those areas that permit the particles sufficient access are plated uniformly. This limitation prevents the coating of narrow holes, blind cavities, and deep V-grooves. Internal diameters over 9.7 mm (0.38 in.) and open at both ends can be coated to a depth of $1\frac{1}{2}$ times the diameter.

Cementation Processes

Pack cementation, the fluidized-bed process, and vapor streaming are three types of cementation processes used in ceramic coating. These processes are used to produce impervious, oxidation-protective coatings for refractory metals and nickel-base, cobalt-base, and vanadium-base alloys. The principal types of coating applied by the cementation processes are silicides, carbides, and borides, usually of the base metal although frequently of codeposited or alternately deposited other metals such as chromium, niobium, molybdenum, and titanium.

Pack Cementation

Preparation of the substrate surface for application of a ceramic coating by pack cementation consists of removing burrs, rounding edges (0.125 mm, or 0.005 in. minimum radius to half the edge thickness, for foil), and rounding corners (preferably to a minimum radius of 3.2 mm or 0.125 in.). Edges and corners must be rounded to prevent cracking of the coating (Fig. 9). This can be accomplished by manual sanding with fine-mesh cloth or with a small motor-driven fine-mesh conical grinding wheel. Mass (barrel) finishing can be used for removing burrs and rounding edges and corners of small articles such as rivets.

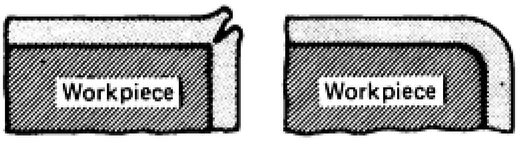


Fig. 9 Effect of sharp and round corners on the continuity of a ceramic coating

The next operation consists of cleaning the work by vapor degreasing followed by mechanical or chemical cleaning. Mechanical cleaning is usually preferable to chemical cleaning and may consist of wet blasting, abrasive blasting with 200-mesh alumina, or buffing. Parts that are buffed should be washed in acetone, and precautions should be taken to prevent adherence of the buffing compound. Chemical cleaning is used when the shape of the part is not suited to blasting or buffing. Parts must be rinsed and dried thoroughly after they are removed from chemical solutions, and precautions must be taken to avoid contamination of cleaned parts during subsequent handling.

Processing. After cleaning, parts are packed in a retort with the desired coating material. Parts should be placed about 25 mm (1 in.) from the retort walls; spacing may be from 3.2 to 13 mm ($\frac{1}{8}$ to $\frac{1}{2}$ in.) between parts, and from 6.4 to 25 mm ($\frac{1}{4}$ to 1 in.) between layers. Packing material must fill all cavities or areas that may entrap air. Sufficient packing material must be placed between the bottom of the retort and the first layer of parts, and over the top layer. The packed retort should not be handled roughly or be vibrated before or during the thermal process cycle.

An inert filler (aluminum oxide) is used to obtain the most efficient use of packing material when large assemblies or components are being coated. The filler should be no closer than 13 mm ($\frac{1}{2}$ in.) from the substrate surface. Figure 10 shows the use of a filler for filling space within the throat of a nozzle, the internal surfaces of which were being coated by the pack cementation process.

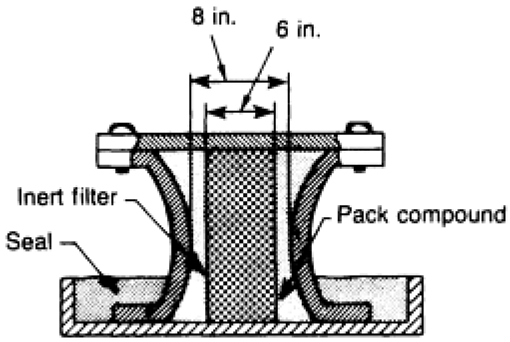


Fig. 10 Use of an inert filler during application of pack cementation coating to the internal surfaces of a nozzle

The packing material usually consists of coating materials (in elemental or combined form), a suitable activator or carrier-gas-producing compound, and inert filler material. A standard siliconizing packing material contains silicon powder (100- to 325-mesh), a halide salt (ammonium chloride, sodium fluoride, or potassium bromide), and an inert filler (aluminum oxide, 100- to 325-mesh). Occasionally, urea is incorporated in the pack material to purge entrapped air before the cementation reaction begins.

The processing temperatures used for pack cementation coating of refractory metals depend on the substrate metal and the desired coating characteristics. In general, temperature controls the rate of deposition, and time is varied to control the thickness of the coating. A low processing temperature results in a coarse, columnar structure and an uneven deposit. High processing temperatures result in deposits of uniform thickness and dense structure. The recrystallization temperature of molybdenum-base and tungsten-base substrates should not be exceeded because of resulting embrittlement. Table 11 gives time-temperature cycles adequate for applying oxidation-resistant coatings.

Table 11 Cycles for application of silicide and other oxidation-resistant ceramic coatings by pack cementation

Processing cycles suitable for depositing coatings of silicon, chromium, boron, aluminum, titanium, zirconium, vanadium, hafnium, and iron

Substrate metal	Processing cycle		
	Temperature[(a)]		Time, h[(b)]
	°C	°F	

Niobium alloys	1040-1260	1900-2300	4-16
Molybdenum alloys	1040-1150	1900-2100	4-16
Tantalum alloys	1040-1150	1900-2100	4-12
Tungsten alloys	1040-1370	1900-2500	3-16

(a) Tolerances: ±6 °C (±10 °F) at 1040 °C (1900 °F);±14 °C (±25 °F) at 1260 °C (2300 °F).

(b) Tolerance, ±10 min

After thermal treatment is completed, the retort may be cooled in the furnace or in air. The coated parts can be removed from the retort when they are cool enough to handle. Loose packing material is removed by washing the parts in warm water, bristle brushing, and spray rinsing. Water under pressure may be used to remove packing material from difficult-to-clean areas. If a second pack cementation operation is required for the addition of other coating elements, parts should be handled with clean gloves or plastic-tipped tongs. If contaminated, parts must be vapor degreased just before packing for the next coating cycle.

When a second coating cycle is not required, the coated parts may be subjected to a high temperature (about 1095 °C, or 2000 °F) to form a protective oxide surface. Normally, 15 to 30 min at this temperature is sufficient to form a protective film on refractory alloys.

Components of assemblies are coated individually, then assembled and packed for the second cycle to protect the joint areas. If assembling causes discontinuities or cracks in the coating, areas are wet blasted and dried or are lightly sand blasted before packing.

The optimum thickness of coating on refractory metals is from 25 to 100 μm (1 to 4 mils). In general, oxidation resistance increases with coating thickness; however, the sharp radii of foils do not permit a coating thickness of much over 25 μm (1 mil). The usual thickness of pack cementation coatings is 38 ± 13 μm (1.5 ± 0.5 mils) for machined components, formed parts, and sheet materials; for foils of 0.250 mm (0.010 in.) or less, the coating thickness is usually 25 ± 8 μm (1.0 ± 0.3 mils).

Equipment for pack cementation consists of a retort and a furnace of suitable size to accommodate the retort. Furnace atmosphere is not critical and may be air, endothermic, exothermic, or inert gas. When a specific atmosphere around the retort is essential, an atmosphere housing may be incorporated.

Retorts are either top-loaded or inverted and may be designed for shallow or deep sealing (Fig. 11). The type of material from which retorts are made depends on the operating temperature and furnace atmosphere. For operating temperatures between 980 to 1260 °C (1800 to 2300 °F), Inconel and types 310, 321, and 347 stainless steel provide satisfactory service. When the furnace atmosphere is oxidizing or carburizing, a stopoff slip ceramic coating on exposed areas of the retort prolongs its service life. Materials for sealing the retort may be sand, alumina, or garnet, with or without oxide scavengers such as silicon or titanium, or low-melting-point materials such as sodium orthosilicate.

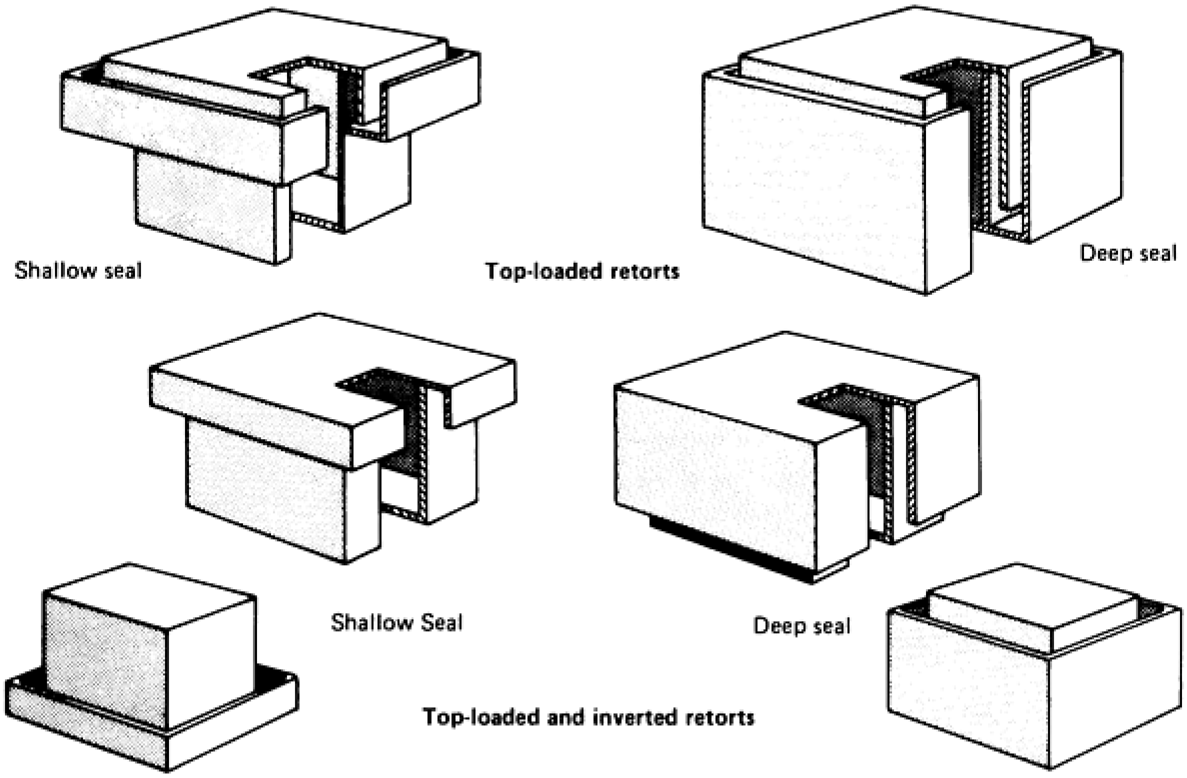


Fig. 11 Designs of retorts used in the pack cementation process

Fluidized-Bed Cementation Process

The fluidized-bed process for applying ceramic coatings involves:

- Thermal decomposition and displacement reactions of metal halides
- Presence of hydrogen to reduce the halides
- Diffusion of deposited materials into the substrate metal to produce an intermetallic compound, such as molybdenum disilicide

In this process, a bed of metal powder reactant and inert material is fluidized or floated at elevated temperature by an inert or reactive gas. The finely divided particles of reactant and inert material are constantly agitated by the fluidizing gas. Thus, the transfer of heat between the object to be coated, the coating material, and the gas is greatly increased by the diffusion of vapor and gas and by the relatively high flow rates. Vapors of coating material can be prepared within the fluidizing chamber by the reaction of particles in the bed with the gases, or they can be prepared and evaporated in a separate vessel. A schematic flow diagram of the fluidized-bed process is shown in Fig. 12.

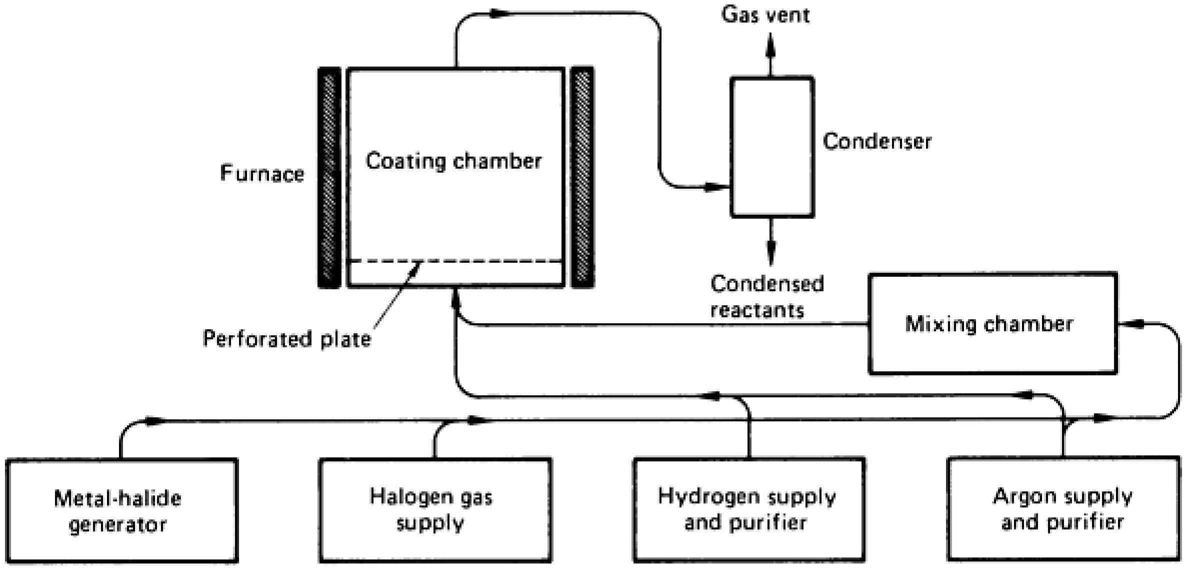


Fig. 12 Fluidized-bed cementation process

Processing. Preparation of the surface of the work consists of rounding the edges, buffing the surfaces and edges, and etching. The following etching procedure is used for molybdenum-base substrates:

- Dip in 80% nitric acid solution at room temperature for several seconds.
- Rinse in cold water (three rinses).
- Dip in 50% hydrochloric acid at room temperature for several seconds.
- Rinse in cold water (three rinses).
- Wash in acetone.

After etching, parts are placed into the fluidizing chamber and processed at 1065 °C (1950 °F) for 1 h. Coated parts are removed from the furnace when cool.

Effect of Process Variables on Coating Characteristics. The control of time, temperature, and carrier-compound concentration is important in the fluidized-bed process, because these variables control the thickness and uniformity of the coating, as well as the rates of deposition and diffusion. Temperature should be controlled to within ±14 °C (±25 °F).

Coating thickness as a result of time and temperature is shown in Fig. 13 for a silicide coating applied to Mo-0.5Ti alloy. The coating thickness represented by these data was calculated from the change in weight of the coated part, using the average density of molybdenum silicide ($MoSi_2$). Although data for operating temperatures below 925 °C (1700 °F) are included, coatings applied to refractory metals at these low temperatures have poor oxidation resistance.

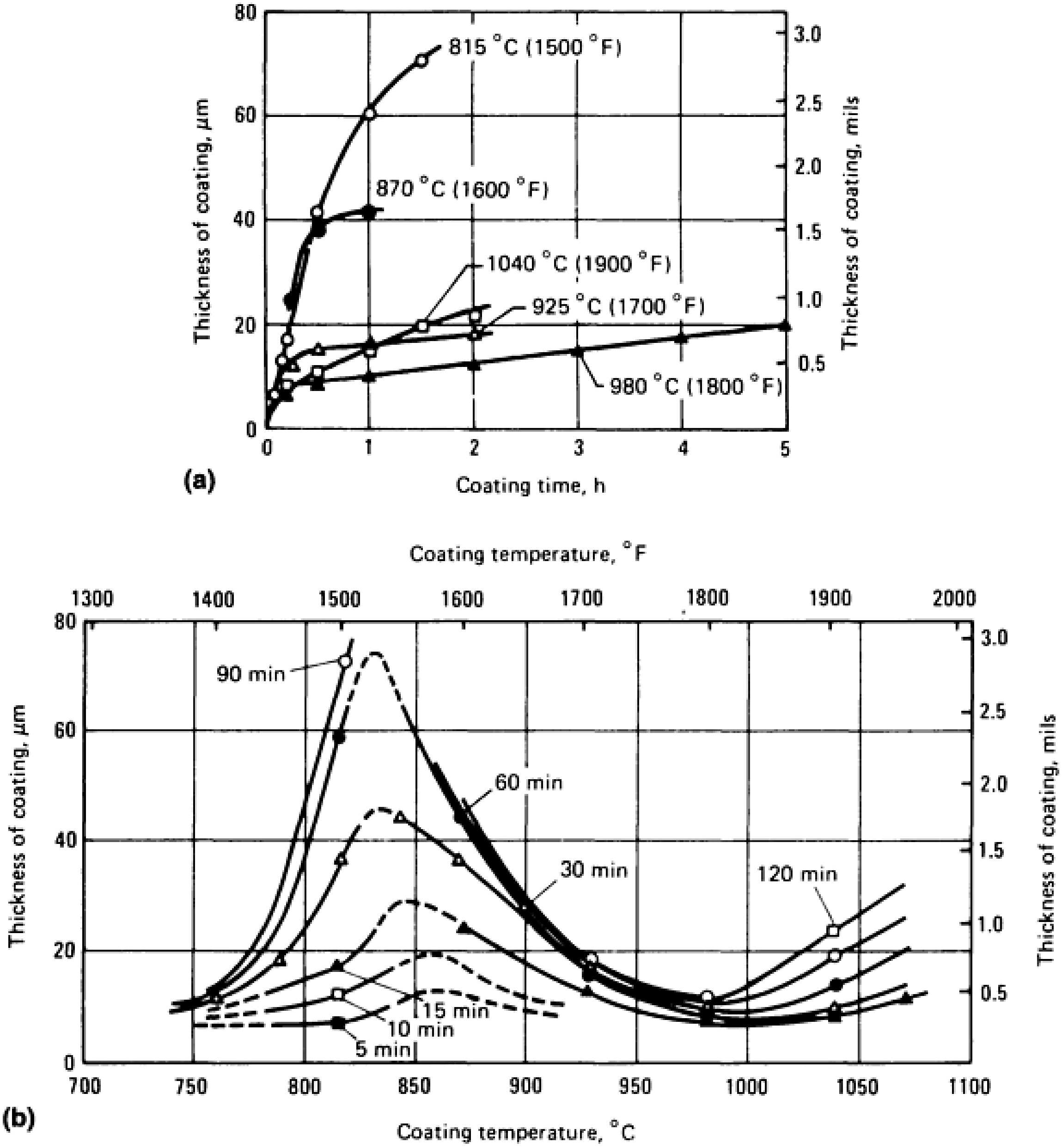


Fig. 13 Effects of (a) time and (b) temperature on the thickness of a silicide coating applied by the fluidized-bed process to Mo-0.5Ti alloy

Applicability. Complex shapes can be coated by the fluidized-bed process. With special techniques, inside surfaces of long small-diameter closed-end tubes can be coated. However, coatings will form only on edges with a radius of 0.125 mm (0.005 in.) or more.

Cracks around rivet heads and joints between sheets cannot be bridged by ceramic coating during elevated-temperature service. Therefore, double processing cycles are required, one before joining and one after assembly of the component parts.

Service life of a coating 50 to 75 μm (2 to 3 mils) thick on flat surfaces is about 1 to 2 h at 1650 °C (3000 °F). The effects of edges and corners combine to reduce this life, because coating thickness for satisfactory coverage is less at these locations.

Vapor-Streaming Cementation

Vapor streaming is a cementation process in which a vapor of the coating material is decomposed on the surface of a heated part. For example, silicide coatings are produced by passing silicon halide vapor in a hydrogen atmosphere over heated substrate. The silicon halide is reduced, and silicon deposits on the substrate and diffuses to form an intermetallic compound. Commercial application of this process has been insignificant.

Trowel Coating

Coatings applied by troweling are acid-bonded systems (phosphates and sulfates), hydraulic-setting cements (calcium aluminate and portland cement), soluble silicate-bonded systems (sodium, potassium, and lithium), and colloidal metal oxide-bonded ceramic oxides and carbides. Troweled coatings are used for furnace linings, hot gas ducts, and certain repair patches on other coatings for relatively short service exposure. The resistance to heat transfer of these coatings depends on the porosity, density, and thermal conductivity of the solid phase and on the thermal shorts caused by any reinforcement metal present. Coatings applied by troweling consist of filler, binder, carrier, and additives. Coating constituents are blended in a muller or other suitable mixer to a uniform consistency. Some materials, such as the acid-bonded coatings, require aging before application to permit reaction between constituents.

Surface Preparation. Surfaces to be coated must be free of contaminants such as oil and grease that may interfere with the wetting and bonding of these water-based coatings. Most coatings applied by troweling are chemically bonded or hydraulic-setting materials. Because these materials do not form a strong metallurgical bond with substrate metals, and because of the differences in coefficients of expansion, substrate surfaces must be roughened for maximum mechanical bonding and to minimize the effects of expansion, vibration, and impact during service. Surface roughening is accomplished by grit blasting or chemical cleaning, or by attaching mechanical reinforcements such as wire mesh, corrugated metal, angular clips, or honeycomb structures. Reinforcement is usually required for surfaces having a finish of less than 6.35 μm (250 μin.).

Processing. Application of coating material, in thicknesses ranging from 3 to 25 mm (0.1 in. to over 1 in.), is accomplished by standard troweling techniques. The material is worked under, around, and through the reinforcements. The smoothed thickness can be measured by a depth gage or with pre-fixed height gages. Vibration of the coating followed by retroweling produces a denser coating. Hydraulic-setting coatings must be applied immediately after mixing with water, because bonding occurs during dehydration.

After application, hydraulic-setting coatings may be cured at ambient temperature or by being heated at less than 100 °C (212 °F). If heat curing is used, the coated work should be raised to temperature at a slow rate to prevent the coating from blistering. The acid-bonded composites are cured at temperatures ranging from 20 to 425 °C (68 to 800 °F), depending on composition and thickness of the coating. Well-ventilated facilities must be used when working with acid-bonded coatings.

Soluble silicate materials are cured at temperatures from 21 to 425 °C (70 to 800 °F), depending on the system and special additives that produce air-drying properties. To remove entrapped moisture, chemical-setting materials are dried in air. Colloidal metal oxides require only the removal of excess water either by air drying or by heating to 100 °C (212 °F).

Electrophoresis

Electrophoresis is the migration of electrically charged particles suspended in a colloidal solution under the influence of an applied electric field. Deposition occurs at one of the electrodes where the charge on the particle is neutralized. The particles acquire a static charge during milling, or they can be charged artificially by absorption of certain additives or electrolytes. This coating process, now being used commercially with increasing frequency, is applicable to practically all substrates, including tool steels, stainless steels, superalloys, refractory metals, oxides, and graphite.

Coatings as applied are soft, and densification is sometimes required. Densification, if needed, may be accomplished by isostatic pressing, hot pressing, or a combination of these methods, depending on the substrate metal. The coating is sintered, usually in a controlled atmosphere.

During sintering, metal coatings are bonded to the substrate by diffusion; oxide coatings, by mechanical and electrochemical bonding. Coating thickness rarely exceeds 75 μm (3 mils), and the thermal expansivity of coating and substrate should be closely matched to prevent spalling. The electrophoresis coating process is simple and easily automated while providing better control of coating thickness and composition than is possible with the slurry and pack cementation processes.

Quality Control

No single nondestructive method is adequate for evaluating the quality of a ceramic coating. Although visual inspection or comparison is only of limited usefulness, many plants prepare samples of coating with surface defects that are known to be harmful to the protective value and service life of the coating and use these samples as visual comparators.

High-Temperature Test. The most reliable test procedure for determining coating continuity and oxidation resistance on complex structures made of refractory metals is to subject the structure to a high-temperature test environment under carefully controlled conditions. First, exposed surfaces are inspected visually under low-power magnification. The work is then heated to 1095 to 1205 °C (2000 to 2200 °F) in air. After a 15 min heating period, surfaces are examined while hot for evidence of evolution of an oxide gas (molybdenum trioxide when molybdenum is the substrate) or for the discoloration that accompanies oxidation of a niobium, tantalum, or tungsten substrate. If no evidence of oxidation is observed, the work is removed from the furnace, cooled, and examined under a magnification of 15 diameters; areas that may indicate oxidation of the substrate surface are examined at a magnification of 100 diameters. If no defects are observed, the work is reheated for an additional 45 min, cooled, and reexamined. Accessible defects observed after the 15 min heating period are repaired. Inaccessible defects, such as those on faying surfaces, may necessitate disassembly of the structure for reprocessing of the defective area.

Fluorescent-penetrant inspection is useful for detecting cracks, pits, and similar discontinuities in coating surfaces. The work is immersed in a penetrant, the excess penetrant is removed from the surfaces, and the surfaces are coated with a colloidal suspension known as a developer. Penetrant that has been entrapped by a defect seeps through the developer and reveals the outline of the defect when the surface is exposed to ultraviolet light. This is a sensitive test, and it frequently reveals very tight surface defects. When flexible-handle magnifying mirrors are used, this test method can be extended to the inspection of complex shapes and tubes.

Destructive tests can be performed on a workpiece or on specimens prepared and coated simultaneously with the workpieces. Standard test methods, such as for tensile strength, modulus of rupture, transverse bending, density, hardness, and metallographic and chemical analysis, can be used on specially prepared sections obtained from a thick section of the coating. An example is illustrated in Fig. 14(a). The tensile specimen of the coating is prepared as follows:

- Grind slots in coating with a cutoff wheel.
- Remove 13 mm ($\frac{1}{2}$ in.) wide sections of coating from the substrate and grind them flat to form 13 mm ($\frac{1}{2}$ in.) wide beam samples 0.125 mm (0.050 in.) in thickness. Beam samples may be tested in transverse rupture by a standard beam test. The coating can be removed by force when applied to a graphite substrate, because graphite has very low strength. A more widely used procedure is to use a substrate that can be chemically dissolved by a solvent that will not attack the coating.
- Grind samples to form a tensile specimen.

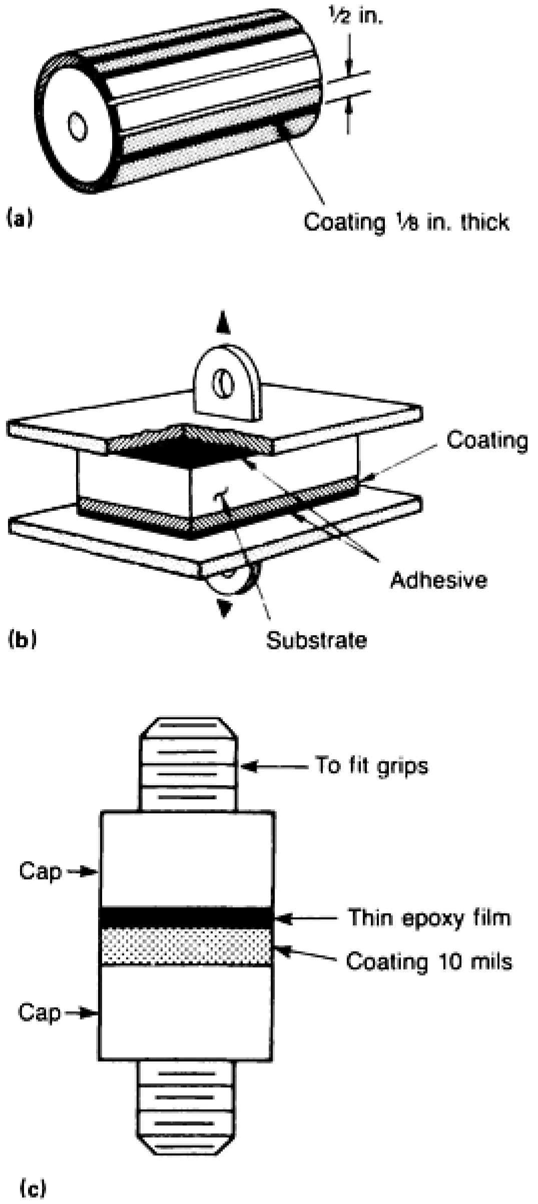


Fig. 14 Sectioning and testing of ceramic coatings. (a) Sectioning of 3 mm ($\frac{1}{8}$ in.) thick coating on a cylinder for preparation of specimens for determination of tensile strength, transverse bending, and other properties by standard test methods. (b) Testing the bond strength of coatings applied by plasma-arc or combustion flame spraying. (c) Testing bond strength of coatings applied by detonation gun process

Bond Strength. A simple test of the bond of a coating to a substrate is diagrammed in Fig. 14(b). This test, which makes use of an epoxy adhesive, is applicable to most coatings applied by plasma-arc or combustion flame spraying. A bond cap arrangement is illustrated in Fig. 14(c).

Impact Strength. Although conventional impact values can be obtained for a coating by an Izod or Charpy test on a specimen of the coating, a more useful impact test consists of projecting a pellet from an air gun with sufficient velocity to cause a measurable deformation of the substrate metal. The coating is then visually inspected for chipping and cracking. This test is best suited to coatings less than about 125 μm (5 mils) thick.

Wear Properties. In the dry-rubbing test, two specimens are mated and rubbed together with a load and relative surface speed selected on the basis of service severity. A similar setup can be used for determining wear properties at elevated temperatures, compatibility of the coating with lubricants or corrosives, and the effects of abrasives.

Structure and Hardness. The microscope is a useful tool for observing bond, binder, and metallic or oxide inclusions in a coating. Hardness testing provides a direct measurement of interparticle bond strength. For example, the true hardness of aluminum oxide usually ranges from 1800 to 2200 HV. Accepted Vickers hardness values of aluminum oxide deposited by various methods are 600 to 800 HV for flame-sprayed coatings, 700 to 1000 HV for plasma-sprayed coatings, and 1000 to 1200 HV for detonation gun-sprayed coatings. The maximum values represent the highest hardness obtained by these processes and thus the highest degree of interparticle bond. Accepted Vickers hardness values for three other ceramic coatings are indicated in Table 12. Hardness readings obtained with a Knoop indenter can be converted to Vickers for comparison.

Table 12 Hardness of three ceramic coatings deposited by three processes

Coating material	Hardness of coating, HV		
	Flame sprayed	Plasma sprayed	Detonation gun sprayed
Tungsten carbide + 8% cobalt	. . .	600-700	1200-1450
Tungsten carbide + 12% cobalt	. . .	600-700	1050-1200
Chromium oxide	900-1100	1200-1350	900-1150

Anodizing

Revised by Milton F. Stevenson, Jr., Anoplate Corporation

Introduction

IN GENERAL, anodizing refers to conversion coating of the surface of aluminum and its alloys to porous aluminum oxide. The process derives its name from the fact that the aluminum part to be coated becomes the anode in an electrolytic cell. This differentiates it from electroplating, in which the part is made the cathode. Whereas anodizing is typically associated with aluminum, similar processes are used for other base metals, including magnesium, titanium, and zinc; a brief discussion of anodizing of these materials is included at the end of this article. However, for the present, this discussion will be specific to aluminum and its alloys.

Anodizing aluminum can be accomplished in a wide variety of electrolytes, employing varying operating conditions including concentration and composition of the electrolyte, presence of any additives, temperature, voltage, and amperage. Several conventional anodizing processes and their resulting properties are shown in Table 1. As indicated in the table, depending on the process chosen, an anodizer can impart to the surface of the aluminum item specific properties as desired, depending on the end use. Some reasons for anodizing are outlined below:

- *Increase corrosion resistance:* Sealed anodic coatings of aluminum oxide are corrosion resistant and highly resistant to atmospheric and salt-water attack. The anodic coating protects the underlying metal by serving as a barrier to would-be corrosive agents. In order to achieve the optimum corrosion resistance, the amorphous aluminum oxide produced by anodizing is sealed by treating in slightly acidified hot water, boiling deionized water, a hot dichromate solution, or a nickel acetate solution. Sealing is discussed in a subsequent section of this article.
- *Improve decorative appearance:* All anodic coatings are lustrous and have relatively good abrasion resistance. Therefore, these coatings are used as the final finishing treatment when the natural appearance of the aluminum is desired or when a mechanically induced pattern is to be preserved. The degree of luster of anodic coatings depends on the condition of the base metal before anodizing. Dull etching decreases luster; bright etching, chemical or electrolytic brightening, and buffing increase luster, either diffuse or specular. Most of the aluminum used in architectural applications is anodized.
- *Increase abrasion resistance:* The hard anodizing processes produce coatings from 25 μm (1 mil) to more than

100 µm (4 mils) thick. These coatings, with the inherent hardness of aluminum oxide, are thick enough for use in applications involving rotating parts where abrasion resistance is required. Although all anodic films are harder than the substrate material, the coatings produced by chromic acid and some sulfuric acid baths are too thin or too soft to meet the requirements for abrasion resistance.

- *Increase paint adhesion:* The tightly adhering anodic coating offers a chemically active surface for most paint systems. Anodic films produced in sulfuric acid baths are colorless and offer a base for subsequent clear finishing systems. Aluminum-base materials that are painted for service in severe corrosive environments are anodized before being painted. A fully sealed anodize may result in interior adhesion.
- *Improve adhesive bonding:* A thin phosphoric acid or chromic acid anodize improves bond strength and durability. Such coatings are widely employed in the airframe structure of most modern aircraft.
- *Improve lubricity:* A combination of hand polishing and/or honing the hard anodizing to a smoother surface before applying a polytetrafluoroethylene coating is a perfect combination with the hard anodizing.
- *Provide unique, decorative colors:* Colored anodic coatings are produced by different methods. Organic dyes can be absorbed in the pores of the coatings to provide a whole spectrum of colored finishes. Certain mineral pigments can be precipitated within the pores to yield a limited range of stable colors. Integral color anodizing, depending on the alloy composition, is used to provide a range of stable earth-tone colors suitable for architectural applications. Electrolytic coloring is a two-step process involving conventional anodizing followed by electrodeposition of metallic pigments in the pores of the coating to achieve a range of stable colors useful in architecture. Coloring is discussed in a subsequent section of this article.
- *Provide electrical insulation:* Aluminum oxide is a dielectric. The breakdown voltage of the anodic film varies from a few volts to several thousand volts, depending on the alloy and on the nature and thickness of the film. The degree of seal also affects insulation properties.
- *Permit subsequent plating:* The inherent porosity of certain anodic films enhances electroplating. Usually, a phosphoric acid bath is used for anodizing prior to plating.
- *Detection of surface flaws:* A chromic acid anodizing solution can be used as an inspection medium for the detection of fine surface cracks. When a part containing a surface flaw is removed from the anodizing bath, then washed and dried quickly, chromic acid entrapped in the flaw seeps out and stains the anodized coating in the area adjacent to the flaw.
- *Increase emissivity:* Anodic films more than 0.8 µm (0.032 mil) thick increase the emissivity of the aluminum. When dyed black, the film has excellent heat absorption up to 230 °C (450 °F).
- *Permit application of photographic and lithographic emulsions:* The porosity of the anodic film offers a mechanical means of holding the emulsion.

Table 1 Conventional anodizing processes

Bath	**Amount, wt%**	**Temperature**		**Duration, min**	**Voltage, V**	**Current density**		**Film thickness**		**Appearance properties**	**Other properties**
		°C	**°F**			**A/dm^2**	**A/ft^2**	**µm**	**mils**		
Sulfuric acid bath											
Sulfuric acid	10	18	65	15-30	14-18	1-2	10-20	5-17	0.2-0.7	Colorless, transparent films	Hard, unsuitable for coloring, tensile strength design 250-370 Kgf/mm (2450-3630 N/mm)
Alumilite											
Sulfuric acid	15	21	70	10-60	12-16	1.3	13	4-23	0.1-0.9	Colorless, transparent films	Good protection against corrosion

Bath	Amount, wt%	Temperature		Duration, min	Voltage, V	Current density		Film thickness		Appearance properties	Other properties
		°C	°F			A/dm^2	A/ft^2	µm	mils		
Oxydal											
Sulfuric acid	20	18	65	30	12-16	1-2	10-20	15-20	0.6-0.8	Colorless, transparent films	Good protection against corrosion, suitable for variegated and golden coloring
Anodal and anoxal											
Sulfuric acid	20	18	65	50	12-16	1-2	10-20	20-30	0.8-1.5	Colorless, transparent films	For coloring to dark tones, bronze and black
Bengough-Stuart (original process)											
Chromic acid	3	40	105	60	0-50	0.3	3	5	0.2	Colorless to dark brown	Good chemical resistance, poor abrasion resistance; suitable for parts with narrow cavities, as residual electrolyte is not detrimental
Commercial chromic acid process											
Chromic acid	5-10	40	105	30-60	0 to increasing limit controlled by amperage	0.5-1.0	5-10	4-7	0.2-0.3	Gray to iridescent	God chemical resistance, poor abrasion resistance; suitable for parts with narrow cavities, as residual electrolyte is not detrimental
Eloxal GX											
Oxalic acid	2-10	20-80	68-175	30-80	20-80	0.5-30	5-300	5-60	0.2-2.4	Colorless to dark brown	Hard films, abrasion resistant, some self-coloring

Bath	**Amount, wt%**	**Temperature**		**Duration, min**	**Voltage, V**	**Current density**		**Film thickness**		**Appearance properties**	**Other properties**
		°C	**°F**			**A/dm^2**	**A/ft^2**	**µm**	**mils**		
											dependent on alloy, 450-480 Kgf/mm (4410-4710 N/mm) for tensile design
Oxal											
Oxalic acid	2-10	20-22	68-72	10-240	60	1.5	15	10-20 for 30 min 30-40 for 50 min	0.4-0.8 for 30 min 1.5-1.6 for 30 min	Colorless to dark brown	Hard films, abrasion resistant, some self-coloring dependent on alloy
Ematal											
Oxalic acid	1.2	50-70	120-160	30-40	120	3	30	12-17	0.5-0.7	Not transparent gray opaque enamel-like	Hard and dense type film possessing extreme abrasion resistance
Titanium salt $(TiOC_2O_4K_2 \cdot H_{20})$	40										
Citric acid	1 g (28 oz)										
Boric acid	8 g (224 oz)										
Water	4 L (1 gal)										

Anodizing Processes

The three principal types of anodizing processes are chromic processes, in which the electrolyte is chromic acid; sulfuric processes, in which the electrolyte is sulfuric acid; and hard anodic processes that use sulfuric acid alone or with additives. Other processes, used less frequently or for special purposes, use sulfuric acid with oxalic acid, phosphoric acid, oxalic acid, boric acid, sulfosalicylic acid, sulfophthalic acid, or tartaric acid. Except for thicker coatings produced by hard anodizing processes, most anodic coatings range in thickness from 5 to 18 μm (0.2 to 0.7 mil). Table 2 describes a few applications in which anodizing is used as a step in final finishing. The sequence of operations typically employed in anodizing from surface preparation through sealing is illustrated in Fig. 1.

Table 2 Typical products for which anodizing is used in final finishing

Product	**Size**		**Alloy**	**Finishing before anodizing**	**Anodizing process**	**Post-treatment**	**Service requirements or environments**
	mm	**in.**					
Auto head lamp	215 mm diam, 30	$8\frac{1}{2}$ in. diam, $1\frac{1}{4}$	5557-1125	Buff, chemical brighten	Sulfuric acid[(a)]	Seal	Atmospheric exposure
Canopy track	760 mm T-extrusion	30-in. T-extrusion	7075	Machine	Hard	None	Resist wear, sea air
Gelatin molds	150-205 mm overall	6-8 overall	1100-O	Chemical brighten as-drawn	Sulfuric acid	Dye, seal	Food
Landing gear	205 mm diam by 1.4 m	8 in. diam by $4\frac{1}{2}$ ft	7079-T6	[(b)]	Chromic acid	Paint	Corrosion resistance
Mullion	3.7 m by 180 mm by 100 mm[(c)]	12 ft by 7 by 4	6063-T6	[(d)]	Sulfuric acid[(e)]	Seal, lacquer[(f)]	Urban atmosphere
Name plates	Various sizes	Various sizes	3003-1114	[(g)]	Sulfuric acid	Dye, seal	Atmospheric exposure
Percolator shell	125 mm diam by 150	5 in. diam by 6	. . .	Buff, chemical brighten	Sulfuric acid	Seal	Coffee
Seaplane-hull skin	2850 by 1020	112 by 40	Clad 2014-T6	[(g)]	Chromic acid	None	Erosion; corrosion[(h)]
Seat-stanchion tube	50 mm diam by 610	2 in. diam by 24	7075-T6	Machine	Hard	None	Wear resistance
Signal-cartridge container	190 by 140 by 165	$7\frac{1}{2}$ by $5\frac{1}{2}$ by $6\frac{1}{2}$	3003-O	As drawn	Chromic acid	Prime, paint	Marine atmosphere

Tray, household	430 mm diam	17 in. diam	. . .	Butler	Sulfuric acid	Seal, buff	Food
Utensil covers	Up to 0.20 m^2 total area	Up to 2 ft^2 total area	1100	Buff, chemical brighten	Sulfuric acid(i)	Dye, seal	Steam, cooked foods(j)
Voice transmitter	50 mm diam	2 in. diam	5052-O	Burnish, alkaline etch	Sulfuric acid	Dye, seal(k)	Gas mask
Wheel pistons	Up to 5200 mm^2 area	Up to 8 $in.^2$ area	6151	Machine	Sulfuric acid(l)	Seal	Wear and corrosion(m)
Computer chip hat	160 by 160	6.2 by 6.2	6063-T6	Non-etch clean	Sulfuric acid	Deionized water seal	High dielectric, thermally conductive
Ice cream scoop	400 by 50	8 by 2	6061-T6	Light etch	Hard	Polytetrafluoroethylene seal	Food; good release

(a) Anodic coating 8 µm (0.3 mil) thick.

(b) Partially machine, clean with nonetching cleaner, and remove surface oxide.

(c) 5 mm (0.2 in.) thick.

(d) Lined finish (180-mesh grit) on 100-mm (4-in.) face; other surfaces alkaline etched.

(e) Anodized for 80 min; minimum coating thickness, 30 µm (1.2 mils).

(f) Sealed for 20 to 30 min. Methacrylate lacquer, 8 µm (0.3 mil) minimum.

(g) Clean with nonetching cleaner; remove surface oxide.

(h) Maximum resistance required.

(i) Anodic coating 5 µm (0.2 mil) thick.

(j) Must not discolor during service.

(k) Sealed in dichromate solution.

(l) Anodized in sulfuric acid solution (30% H_2SO_4) at 21 °C (70 °F) for 70 min at 2.5 A/dm^2 (25 A/ft^2).

(m) In presence of hydraulic brake fluids

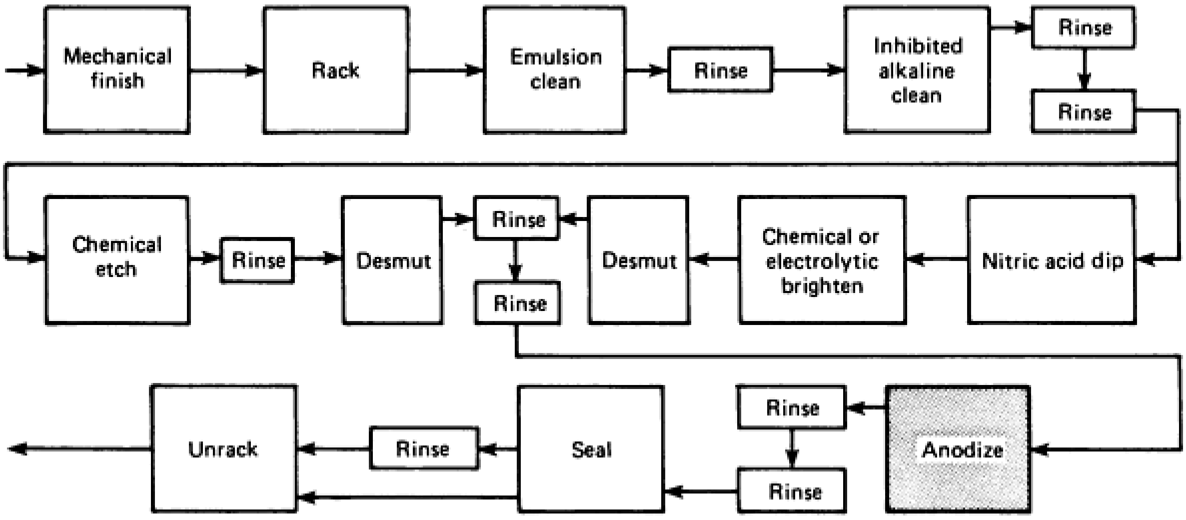


Fig. 1 Typical process sequence for anodizing operations

Surface Preparation. A chemically clean surface (free of all grease and oil, corrosion products, and the naturally occurring aluminum oxide found on even the cleanest-appearing aluminum) is a basic requirement for successful anodizing. The cleaning method is selected on the basis of the type of soils or contaminants that must be removed and the dimensional tolerance. Traditionally the first step employed was vapor degreasing; however, due to restrictions on ozone-depleting compounds, many of these degreasing solvents, such as trichloroethylene, are no longer in wide use. Alternatives to vapor degreasing, such as solvent wiping or alkaline soak cleaning, are now predominantly used for removing the major organic contaminants. The main function of this cleaning stage is to provide a chemically clean aluminum surface so that subsequent acid pickles or caustic etches can react uniformly over the entire surface.

After cleaning, the work is etched, pickled, or otherwise deoxidized to remove surface oxides. When specular surfaces are required, the work is treated in a brightening solution. After etching or brightening, desmutting usually is required for the removal of heavy metal deposits resulting from the preceding operations.

In order to treat precision-machined aluminum components, anodize pretreatment procedures that require neither etching nor pickling have been developed and are now widely employed.

Chromic Acid Process. The sequence of operations used in this process depends on the type of part, the alloy to be anodized, and the principal objective for anodizing. Due to the corrosive nature of sulfuric acid, chromic acid anodizing is the preferred process on components such as riveted or welded assemblies where it is difficult or impossible to remove all of the anodizing solution. This process yields a yellow to dark-olive finish, depending on the anodic film thickness. Color is gray on high-copper alloys. Table 3 gives a typical sequence of operations that meets the requirements of military specification MIL-A-8625.

Table 3 Sequence of operations for chromic acid anodizing

Operation	Solution	Solution temperature		Treatment time, min
		°C	°F	

Vapor degrease	Suitable solvent	. . .	. . .	. . .
Alkaline clean	Alkaline cleaner	(a)	(a)	(a)
Rinse(b)	Water	Ambient	Ambient	1
Desmut(c)	HNO_3, 10-25 vol%	Ambient	Ambient	As required
Rinse(b)	Water	Ambient	Ambient	1
Anodize	CrO_3, 46 g/L ($5\frac{1}{4}$ oz/gal)(d)	32-35	90-95	30(e)
Rinse(b)	Water	Ambient	Ambient	1
Seal(f)	Water(g)	90-100	190-210	10-15
Air dry	. . .	105 max(h)	225 max(h)	As required

(a) According to individual specifications.

(b) Running water or spray.

(c) Generally used in conjunction with alkaline-etch type of cleaning.

(d) pH 0.5.

(e) Approximate; time may be increased to produce maximum coating weight desired.

(f) Dependent on application.

(g) Water may be slightly acidulated with chromic acid, to a pH of 4 to 6.

(h) Drying at elevated temperature is optional.

Chromic acid anodizing solutions contain from 3 to 10 wt% CrO_3. A solution is made up by filling the tank about half full of water, dissolving the acid in water, and then adding water to adjust to the desired operating level.

A chromic acid anodizing solution should not be used unless:

- pH is between 0.5 and 1.0.

- The concentration of chlorides (as sodium chloride) is less than 0.02%.
- The concentration of sulfates (as sulfuric acid) is less than 0.05%.
- The total chromic acid content, as determined by pH and Baumé readings, is less than 10%. When this percentage is exceeded, part of the bath is withdrawn and is replaced with fresh solution.

Figure 2 shows the amount of chromic acid that is required for reducing the pH from the observed value to an operating value of 0.5.

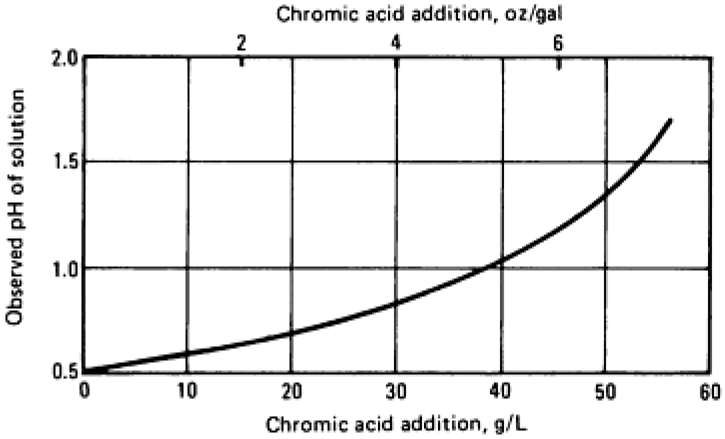


Fig. 2 Control of pH of chromic acid anodizing solutions. The graph shows the amount of chromic acid required to reduce pH to 0.5 from observed pH.

When anodizing is started, the voltage is controlled so that it will increase from 0 to 40 V within 5 to 8 min. The voltage is regulated to produce a current density of not less than 0.1 A/dm^2 (1.0 A/ft^2), and anodizing is continued for the required time, generally 30 to 40 min. Certain alloys, typically those in the 7*xxx* series, such as 7075, fail to develop a coating at 40 V, but running the process at 22 V produces acceptable results. Casting alloys should also be processed at 22 ± 2 V, as specified in military specification MIL-A-8625, type 18. Because of the porous structure of the casting alloys, processing them at higher voltages can cause excessive current densities that can be extremely damaging to the components. When the 22 V process is employed, times should be lengthened to 40 to 60 min. At the end of the cycle the current is gradually reduced to zero, and the parts are removed from the bath within 15 s, rinsed, and sealed.

According to MIL-A-8625, revision F, the coating weight should be checked prior to sealing, and depending on the type of alloy, the minimum coating weight should be 200 mg/ft^2. Measuring coating weight prior to sealing will allow the parts to be put back in the chromic anodizing tank so that anodizing can continue, if needed, and subsequent stripping can be avoided.

Sulfuric Acid Process. The basic operations for the sulfuric acid process are the same as for the chromic acid process. Parts or assemblies that contain joints or recesses that could entrap the electrolyte should not be anodized in the sulfuric acid bath. The concentration of sulfuric acid (1.84 sp gr) in the anodizing solution is 12 to 20 wt%. A solution containing 36 L (9.5 gal) of H_2SO_4 per 380 L (100 gal) of solution is capable of producing an anodic coating that when sealed meets the requirements of MIL-A-8625.

A sulfuric acid anodizing solution should not be used unless:

- The concentration of chlorides (as sodium chloride) is less than 0.02%.
- The aluminum concentration is less than 20 g/L (2.7 oz/gal), or less than 15 g/L (2 oz/gal) for dyed work.
- The sulfuric acid content is between 165 and 200 g/L (22 to 27 oz/gal).

At the start of the anodizing operation, the voltage is adjusted to produce a current density of 0.9 to 1.5 A/dm^2 (9 to 15 A/ft^2). Figure 3 shows the voltage required to anodize at two different temperatures with current density of 1.2 A/dm^2 (12 A/ft^2). The voltage will increase slightly as the aluminum content of the bath increases. The approximate voltages required for anodizing various wrought and cast aluminum alloys in a sulfuric acid bath at 1.2 A/dm^2 (12 A/ft^2) are:

Alloy	**Volts**
Wrought alloys	
1100	15.0
2011	20.0
2014	21.0
2017	21.0
2024	21.0
2117	16.5
3003	16.0
3004	15.0
5005	15.0
5050	15.0
5052	14.5
5056	16.0
5357	15.0
6053	15.5
6061	15.0
6063	15.0

6151	15.0
7075	16.0
Casting alloys	
413.0	26.0
443.0	18.0
242.0	13.0
295.0	21.0
514.0(a)	10.0
518.0(a)	10.0
319.0	23.0
355.0	17.0
356.0	19.0
380.0	23.0

(a) Current density, 0.9 A/dm^2 (9 A/ft^2)

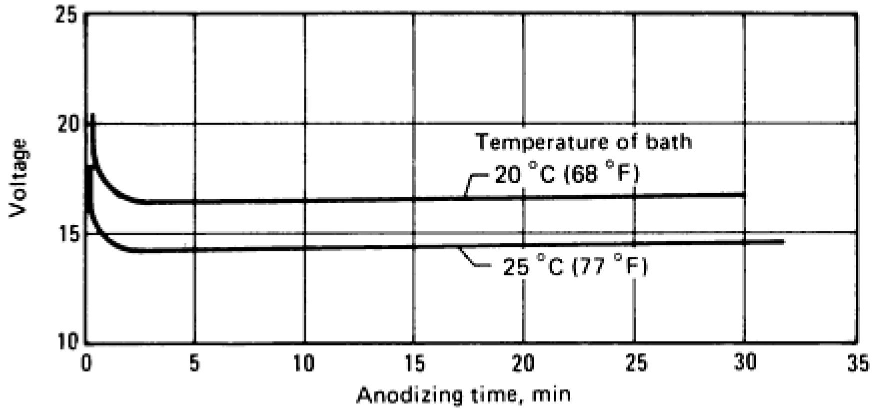


Fig. 3 Voltages required during sulfuric acid anodizing. To maintain a current density of 1.2 A/dm^2 (12 A/ft^2), a bath temperature of between 20 and 25 °C (68 and 77 °F) must be maintained.

When a current density of 1.2 A/dm^2 (12 A/ft^2) is attained, the anodizing process is continued until the specified weight of coating is produced, after which the flow of current is stopped and the parts are withdrawn immediately from the solution and rinsed. Figure 4 shows the effect of time on the weight of the coating developed on automotive trim anodized in 15% sulfuric acid solutions at 20 and 25 °C (68 and 77 °F), operated at a current density of 1.2 A/dm^2 (12 A/ft^2).

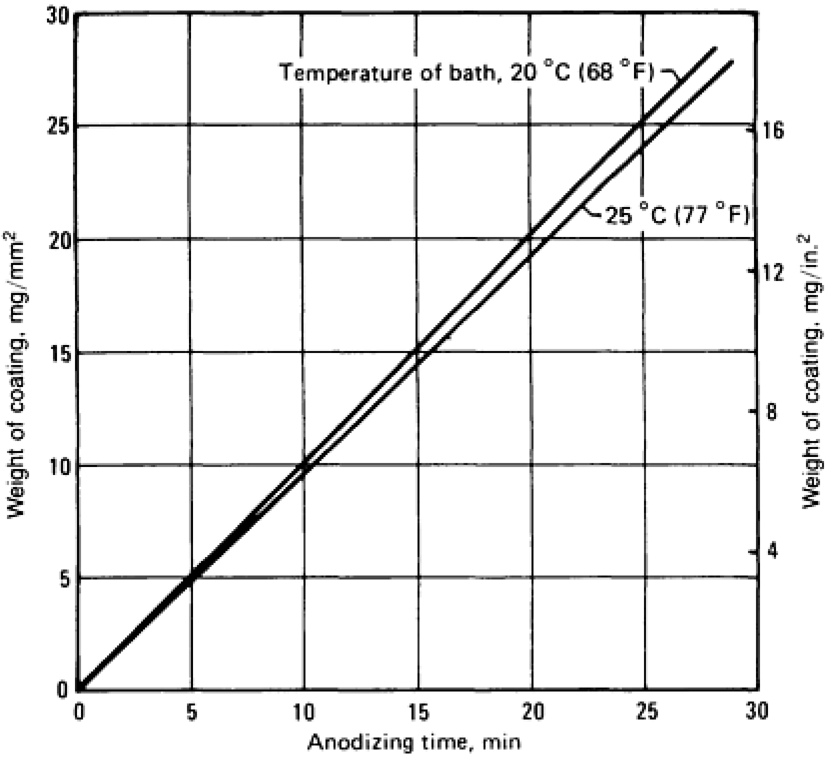
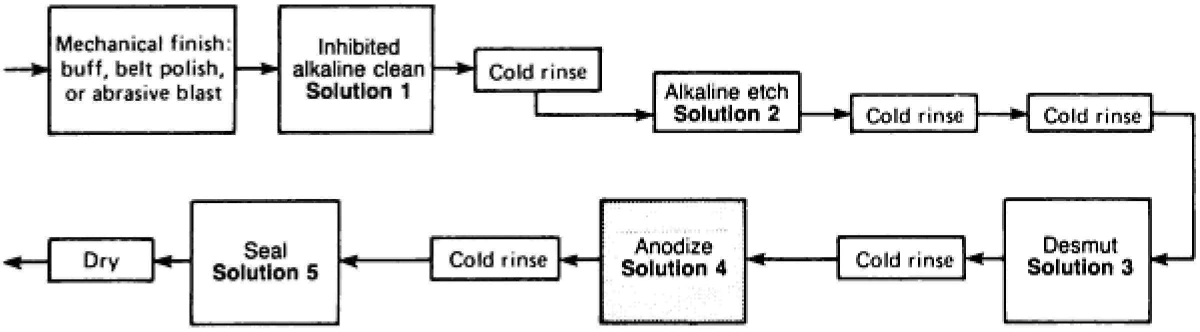


Fig. 4 Effect of anodizing time on weight of anodic coating. Data were derived from aluminum-alloy automotive trim anodized in 15% sulfuric acid solutions at 20 and 25 °C (68 and 77 °F) and at 1.2 A/dm^2 (12 A/ft^2).

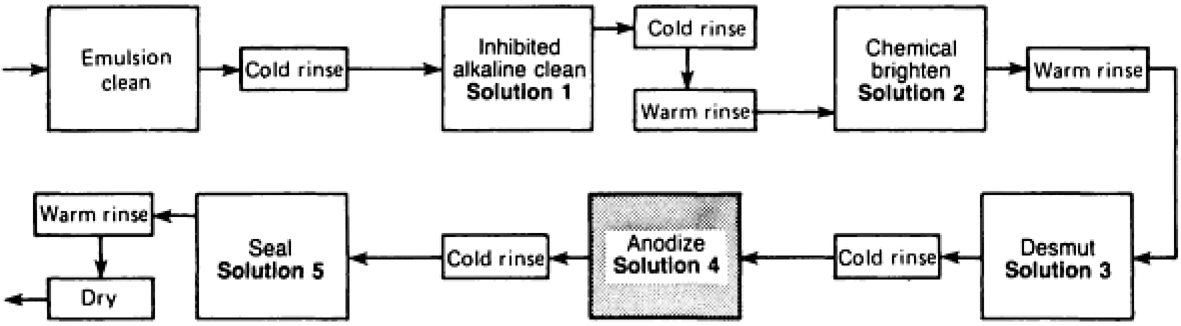
A flow chart and a table of operating conditions for operations typically used in anodizing architectural parts by the sulfuric acid process are presented in Fig. 5; similar information, for the anodizing of automotive bright trim, is given in Fig. 6.



Solution No.	Type of solution	Composition	Operating temperature	Cycle time, min

					min
			°C	°F	
1	Alkaline cleaning	Alkali, inhibited	60-71	140-160	2-4
2	Alkaline etching	NaOH, 5 wt%	50-71	120-160	2-20
3	Desmutting	HNO_3, 25-35 vol%	Room	Room	2
4	Anodizing	H_2SO_4, 15 wt%	21-25	70-75	5-60
5	Sealing	Water (pH 5.5-6.5)	100	212	5-20

Fig. 5 Operations sequence in sulfuric acid anodizing of architectural parts



Solution No.	Type of solution	Composition	Operating temperature		Cycle time, min
			°C	°F	
1	Alkaline cleaning	Alkali, inhibited	60-71	140-160	2-4
2	Chemical brightening	H_3PO_4 and HNO_3	88-110	190-230	$\frac{1}{2}$-5
3	Desmutting	HNO_3, 25-35 vol%	Room	Room	2
4	Anodizing	H_2SO_4, 15 wt%	21-25	70-75	5-60

Fig. 6 Operations sequence in sulfuric acid anodizing of automotive bright trim

Hard Anodizing. The primary differences between the sulfuric acid and hard anodizing processes are the operating temperature, the use of addition agents, and the voltage and current density at which anodizing is accomplished. Hard anodizing, also referred to as hardcoat or type III anodizing, produces a considerably heavier coating then conventional sulfuric acid anodizing in a given length of time. Coating weights obtained as a function of time are compared for the two processes in Fig. 7.

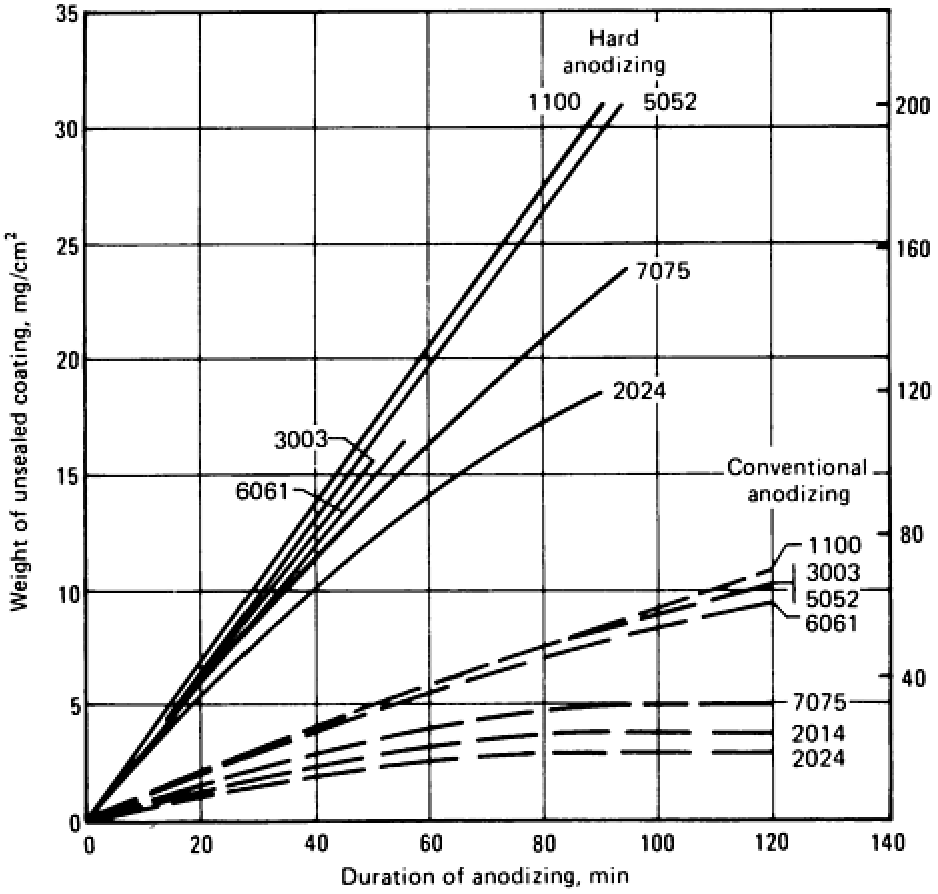


Fig. 7 Effect of anodizing time on weight of hard and conventional anodic coatings. The hard anodizing solution contained (by weight) 12% H_2SO_4 and 1% $H_2C_2O_4$ and was operated at 10 °C (50 °F) and 3.6 A/dm^2 (36 A/ft^2). The conventional anodizing solution contained 1% (by weight) H_2SO_4 and was operated at 20 °C (70 °F) and 1.2 A/dm^2 (12 A/ft^2).

The hard anodizing process uses a sulfuric acid bath containing 10 to 20 wt% acid, with or without additives. Typical operating temperatures of the bath range from 0 to 10 °C (32 to 50 °F), and current density ranges between 2 and 3.6 A/dm^2 (20 and 36 A/ft^2). With the use of particular additives and modified power, hard anodizing processes can operate at temperatures in excess of room temperature. However, some hard anodizing processes operated at high temperature may result in the formation of soft and more porous outer layers of the anodic coating. This change in coating characteristics reduces wear resistance significantly and tends to limit coating thickness. Without use of specific additives and/or modified power, such as superimposed alternating current over direct current or pulsed current, excessive operating temperatures result in dissolution of coating and can burn and damage the work.

Proprietary processes are commonly used. One of the more common of these processes uses a solution containing 120 to 160 g (16 to 21 oz) of sulfuric acid and 12 to 20 g (1.6 to 2.8 oz) of oxalic acid ($H_2C_2O_4$) per 3.8 L (1 gal) of water. This solution is operated at 10 ± 1 °C (50 ± 2 °F) and a current density of 2.5 to 3.6 A/dm^2 (25 to 36 A/ft^2) (voltage is increased gradually from zero to between 40 and 60 V); treatment time is 25 min/25 µm (1 mil) of coating thickness. Additional proprietary processes for hard anodizing are listed in Table 4.

Table 4 Process and conditions for hard anodizing

Process	**Bath**	**Temperature**		**Duration min**	**Voltage V**	**Current density**		**Film thickness**		**Appearance**	**Remarks**
		°C	**°F**			**A/dm^2**	**A/ft^2**	**µm**	**mils**		
Martin Hard Coat (MHC)	15 wt% sulfuric acid, 85 wt% water	-4 to 0	25-32	45(b)	20-75	2.7	29	50	2	Light to dark gray or bronze	Very hard, wear resistant
Alumilite 225 and 226	12 wt% sulfuric acid, 1 wt% oxalic acid, water	10	50	20,40	10-75	2.8(b)	30(b)	25,50	1,2	light to dark gray or bronze	Very hard, wear resistant, allows a higher operating temperature over MHC
Alcanodox	Oxalic acid in water	2-20	36-68	(a)	(a)	(a)	(a)	20-35	0.8-1.4	Golden to bronze	. . .
Hardas	6 wt% oxalic water, 94 wt% water	4	39	(a)	60 dc plus ac override	2.0	22	. . .	. . .	Light yellow to brown	. . .
Sanford	Sulfuric acid with organic additive	0-15	32-58	(a)	15-150 dc	1.2-1.5	13-16	. . .	. . .	Light to dark gray or bronze	. . .
Kalcolor	7-15 wt% sulfosalicylic acid, 0.3-4 wt% sulfuric acid, water	18-24	64-75	. . .	. . .	1.5-4	16-43	15-35	0.6-1.4	Light yellow to brown to black	A self-coloring process, colors are dependent on alloy chosen, the colors produced are light fast
Lasser	0.75 wt% oxalic acid, 99.25 wt% water	1-7	35-44	to 20	From 50-500 rising ramp	Voltage controlled	Voltage controlled	700	28	Colorless	Hard, thick coatings produced with special cooling

(a) Proprietary information available to licensees only. Also, the entire Toro process is proprietary information available to licensees only.

(b) Changes from 9th edition, *Metals Handbook*

A recent development in hard anodizing uses an intermittent pulse current that reduces tank time and makes it possible to use a 20 vol% sulfuric acid solution as the electrolyte.

Special Anodizing Processes. Table 5 gives the operating conditions for anodizing baths that are used to produce an anodic coating with a hardness and porosity suitable for electroplating, or to produce anodic coatings of hardness or thickness intermediate to those obtainable from chromic acid, sulfuric acid, and hard anodizing baths.

Table 5 Compositions and operating conditions of solutions for special anodizing processes

Type of solution	Composition	Current density		Temperature		Treatment, time, min	Use of solution
		A/dm^2	A/ft^2	°C	°F		
Sulfuric-oxalic	15-20 wt% H_2SO_4 and 5 wt% $H_2C_2O_4$	1.2	12	29-35	85-95	30	Thicker coating[(a)]
Phosphoric	20-60 vol% H_3PO_4	0.3-1.2[(b)]	3-12[(b)]	27-35	80-95	5-15	Preparation for plating
Phosphoric, Boeing process	10-12 wt%	0.5-0.8[(c)]	5-8[(c)]	21-24	70-75	20-25	Adhesive bonding preparation
Oxalic	3 wt% $H_2C_2O_4$	1.2	12	22-	72-	15-60[(d)]	Harder coating[(e)]

(a) Coating is intermediate in thickness between the coating produced by sulfuric acid anodizing and the coating produced by hard anodizing.

(b) Potential, 5 to 30 V.

(c) Potential, 10 to 15 V.

(d) Depends on coating thickness desired.

(e) Hardness greater than by other processes except hard anodizing

Process Limitations

Composition of the aluminum alloy, surface finish, prior processing, temper or heat treatment, and the use of inserts influence the quality of anodic coatings. The limitations imposed by each of these variables on the various anodizing processes are described below.

Alloy Composition. The chromic acid process should not be used to anodize aluminum casting alloys containing more than 5% Cu or more than 7.5% total alloying elements, because excessive pitting, commonly referred to as burning, may result. The sulfuric acid process can be used for any of the commercially available alloys, whereas the hard anodizing process is usually limited to alloys containing less than 5% Cu and 7% Si. Choice of alloys is important when maximum corrosion and/or abrasion resistance is required. Alloys such as 6061 are superior to the copper and copper-magnesium alloys in their ability to produce a hard, corrosion-resistant coating.

A recent development permitting hard anodizing of any aluminum alloy, including such newly released alloys as aluminum-lithium alloys, is ion vapor deposition of a thin layer of pure aluminum over the difficult alloy followed by subsequent anodizing. The newly deposited aluminum is entirely incorporated into the anodic layer without interference of troublesome alloying elements. This method is also useful in repairing expensive aluminum components undersized as a result of overcleaning or overetching.

Two or more different alloys can be anodizing at the same time in the same bath if the anodizing voltage requirements are identical. However, simultaneous anodizing of two different alloys is not normally recommended. This condition is more difficult for the sulfuric acid process than for the chromic acid process.

Surface Finish. Anodic films accentuate any irregularities present in the original surface. However, surface irregularities are emphasized more by the chromic acid bath than by the sulfuric acid bath. Additionally, the sulfuric acid anodizing process should be used instead of the chromic acid process where optimum corrosion- and/or abrasion-resistant surfaces are required. Clad sheet should be handled with care to prevent mechanical abrasion or exposure of the core material. Anodizing magnifies scratches, and if the core material is exposed, it will anodize with a color different from that of the cladding.

Anodizing grade must be specified for extruded products so that mill operations are controlled to minimize longitudinal die marks and other surface blemishes. Surface irregularities must be removed from forgings, and the surfaces of the forgings must be cleaned by a process that removes trapped and burned-in die lubricants. Special attention is required when polishing the flash line if this area is to appear similar to other areas of the forging after anodizing.

Castings can be anodized provided their composition is within the process limits described under alloy composition. From the standpoint of uniform appearance, however, anodizing usually is undesirable for castings because of their nonuniform surface composition and their porosity.

The cosmetic concerns surrounding anodizing of castings, especially dyed anodic processes, can be overcome by vacuum impregnation of the casting. Using this process, exposed casting porosity is filled with an impregnant such as a thermosetting epoxy polyester. In sealing this porosity, the corrosion resistance of the anodized casting is also improved. Improved results may also be obtained by soaking castings in boiling water after cleaning and before anodizing. This treatment, however, merely attempts to fill surface voids with water, so that voids do not entrap anodizing solution.

Usually, permanent mold castings have the best appearance after anodizing, then die castings, and finally sand castings. Permanent mold castings should be specified if an anodic coating of uniform appearance is required. Anodizing usually reveals the metal flow lines inherent in the die-casting process, and this condition is objectionable if uniform appearance is desired. In general, solution heat treatment prior to anodizing is beneficial for producing the most uniform and bright anodized finish obtainable on castings.

To facilitate better cleaning of a casting prior to anodizing, aggressive cleaning with fluorides (in the case of castings high in silicon) can be accomplished prior to final machining. Following aggressive cleaning, the part is returned to the customer for final machining and returned to the finisher for anodizing. However, if close machining tolerances are involved, removal of metal with aggressive cleaning may not be permissible.

Regardless of the product form, rough finishing should be avoided when maximum corrosion resistance or uniformity of appearance of the anodic coating is desired. Rough surfaces, such as those produced by sawing, sand blasting, and shearing, are difficult to anodize and should be strongly etched prior to anodizing to ensure even minimal results. The machined areas of castings or forgings may have an appearance different from that of the unmachined surfaces.

Prior Processing. Because of their effect on surface finish, welding, brazing, and soldering affect the appearance of the anodic coating, for the reasons discussed above. In addition, the compositions of solders usually are not suited to anodizing. Spot, ultrasonic pressure, or other types of welding processes where there is no introduction of foreign metal, fluxes, or other contaminants do not affect the appearance of the anodic coating. However, the sulfuric acid anodizing process should not be used for coating spot-welded assemblies or other parts that cannot be rinsed to remove the electrolyte from lap joints.

Temper or Heat Treatment. Identification of not only the alloy that is being used but also the temper to which the alloy has been heat treated is extremely important. For alloy 2024, for example, the voltage required to produce a given film thickness can vary by 25%, depending on whether the T-3 treatment or T-4 treatment was used. Failure to recognize the difference in heat treatment can be catastrophic, most notably in hard anodizing.

Differences in temper of non-heat-treatable alloys have no marked effect on the uniform appearance of the anodic coating. The microstructural location of the alloying elements in heat-treatable alloys affects the appearance of anodic coatings. Alloying elements in solution have little effect, but the effect is greater when the elements are precipitated from solid solution. The annealed condition should be avoided when maximum clarity of the anodic film is desired.

Inserts or attachments made of metals other than aluminum must be masked off, both electrically and chemically, to prevent burning and corrosion in surrounding areas. The masking must completely seal the faying surface between the insert and parent metal, to prevent adsorption of solution, which may result in corrosion and staining. Therefore, it is desirable to install inserts after anodizing.

Anodizing Equipment and Process Control

Chromic Acid Anodizing. Low-carbon steel tanks are satisfactory for chromic acid baths. It is common practice to line up to half of the tank with an insulating material, such as glass, to limit the cathode area with respect to the expected anode area (a 1-to-1 ratio is normal). The cathode area need only be 5% of the maximum anode area. In nonconducting tanks, suitable cathode area is provided by the immersion of individual lead cathodes; however, these require the installation of additional busbars to the tanks for suspension of individual cathodes. Provision must be made for heating the anodizing solution to 32 to 35 °C (90 to 95 °F); electric or steam immersion heaters are satisfactory for this purpose. Electric heaters are preferred, because they are easy to operate and do not contaminate the bath.

The anodizing process generates heat; therefore, agitation is required to prevent overheating of the bath and especially of the electrolyte immediately adjacent to the aluminum parts being anodized. Exhaust facilities must be adequate to trap the effluent fumes of chromic acid and steam.

Sulfuric Acid Anodizing. Tanks for sulfuric acid anodizing may be made of low-carbon steel lined throughout with plasticized polyvinyl chloride and coated on the outside with corrosion-resistant synthetic-rubber paint. Other suitable materials for tank linings are lead, rubber, and acid-proof brick. Tanks made of special sulfuric acid-resistant stainless steel containing copper and molybdenum, or made entirely of an organic material, may be used. As with chromic acid anodizing, individual lead cathodes or lead-lined tanks may be used for sulfuric acid anodizing. Alternatively, aluminum cathodes have been used, resulting in energy savings because they have higher conductivity than lead. The fact that lead effluent results from lead cathodes is another reason to prefer aluminum cathodes.

The tank should have controls for maintaining temperatures at between 20 to 30 °C (68 to 85 °F). Requirements for agitation and ventilation are the same as for chromic acid solutions. The surface of the floor under the tank should be acid resistant. The bottom of the tank should be about 150 mm (6 in.) above the floor on acid-resistant and moisture-repellent supports.

A separate heat exchanger and acid make-up tank should be provided for sulfuric acid anodizing installations. Tanks have been made of lead-lined steel. Lead may be preferred over plastic for the lining because lead withstands the heat generated when sulfuric acid is added. Polyvinyl chloride pipes are recommended for air agitation of the solution and for the acid-return lines between the two tanks. Cooling coils have also been made of chemical lead or antimonial lead pipe.

Hard Anodizing. Most of the hard anodizing formulations are variations of the sulfuric acid bath. The requirements for hard anodizing tanks are substantially the same as those for sulfuric acid anodizing tanks, except that cooling, rather than heating, maintains the operating temperature at 0 to 10 °C (32 to 50 °F).

Temperature-control equipment for all anodizing processes must regulate the overall operating temperature of the bath and maintain the proper temperature of the interface of the work surface and electrolyte. The operating temperature for most anodizing baths is controlled within ±1 °C (±2 °F). This degree of control makes it necessary for the temperature-sensing mechanism and heat lag of the heating units to be balanced.

When electric immersion heaters are used, it is common practice to have high and low heat selection so that the bath can be heated rapidly to the operating temperature and then controlled more accurately on the low heat setting. Standard thermistor thermostats are used for sensing the temperature within the bath and activating the heating elements.

In steam-heated systems, it is advantageous to have a throttling valve to prevent overheating. An intermediate heat exchanger is used in some installations to prevent contamination of the electrolyte and the steam system by a broken steam line within the anodizing bath.

Agitation may be accomplished by stirring with electrically driven impellers, by recirculation through externally located pumps, or by air. In some installations, the anode busbars are oscillated horizontally, thus imparting a stirring action to the work.

The two primary requirements of an agitation system are that it is adequate and that it does not introduce foreign materials into the solution. With air agitation, filters must be used in the line to keep oil and dirt out of the solution. In the case of hard anodizing, attention to proper agitation is critical to correct processing. Agitation that is not uniform or not adequate will be instrumental in burning.

Power requirements for the principal anodizing processes are as follows:

Process	Voltage	Current density	
		A/dm^2	A/ft^2
Chromic	42	0.1-0.3	1-3
Sulfuric	24	0.6-2.4	6-24

(a) Alloys prone to burning (i.e., high-copper alloys) may demand lower current density (down to 2 A/dm^2, or 20 A/ft^2) rather than the lower limit of 2.5 A/dm^2 (25 A/ft^2).

Direct current is required for all processes. Some hard anodizing procedures also require a superimposed alternating current or a pulsed current. At present, most power sources for anodizing use selenium or silicon rectifiers. Compared to motor generators, the selenium rectifiers have greater reliability, are lower in initial cost and maintenance cost, and have satisfactory service life.

Voltage drop between the rectifier and the work must be held to a minimum. This is accomplished by using adequate busbars or power-transmission cables. Automatic equipment to program the current during the entire cycle is preferred. Manual controls can be used, but they necessitate frequent adjustments of voltage. The presence of a recording voltmeter in the circuit ensures that the time-voltage program specified for the particular installation is being adhered to by operating personnel. Current-recording devices also are advantageous.

Masking. When selective anodizing is required, masking is necessary for areas to be kept free of the anodic coating. Masking during anodizing may also be required for postanodizing operations such as welding, for making an electrical connection to the base metal, or for producing multicolor effects with dye coloring techniques.

Masking materials are usually pressure-sensitive tapes, stop-off lacquers, or plastic or rubber plugs. Various tape materials, including polyvinyl chloride, Mylar, or Kapton, may be used. One type of tape may adhere better or be easier to remove after anodizing than another. For instance, while more expensive than other tapes, tapes with silicone adhesive hold up best during chromic acid anodizing, generally considered by anodizers to be the toughest anodize process to mask for. Metallic aluminum foil tape may also be used.

Stop-off lacquers provide satisfactory masking, but they are labor-intensive to apply and thus costly. Secondly, they are difficult to remove, often requiring the use of organic thinners or solvents. Rubber plugs, such as tapered laboratory stoppers, are effective for masking holes. They are widely available in various configurations and are known to anodizers by such names as "pull plugs," "dunce caps," and "mouse tails." In addition, where volumes and lead times are warranted, customized plugs may be molded from plastisol (unplasticized polyvinyl chloride) or another acid-resistant material.

Lastly, anodize itself may be used as a maskant. For example, on a precision-machined aluminum aerospace component requiring one small area to be abrasion resistant, the part might be chromic acid anodized all over, then machined in the area required to be abrasion resistant and subsequently hard anodized. The key to such an approach is to seal the initially applied chromic anodize. In such cases, nickel acetate sealing is highly preferable. Care must also be exercised by the machinist not to damage the chromic anodize layer in areas where hard anodize is undesirable.

Racks for Anodizing

Anodizing racks or fixtures should be designed for efficiency in loading and unloading of workpieces. Important features that must be included in every properly designed rack are:

- *Current-carrying capacity:* The rack must be large enough to carry the correct amount of current to each part attached to he rack. If the spline of the rack is too slender for the number of parts that are attached to the rack, the anodic coating will be of inadequate thickness, or it will be burned or soft as the result of overheating.
- *Positioning of parts:* The rack should enable proper positioning of the parts to permit good drainage, minimum gassing effects and air entrapment, and good current distribution.
- *Service life:* The rack must have adequate strength, and sufficient resistance to corrosion and heat, to withstand the environment of each phase of the anodizing cycle.

The use of bolt and screw contacts, rather than spring or tension contacts, is a feature of racks designed for anodizing with the integral color processes. These processes require high current densities and accurate positioning of workpieces in the tank. Bolted contacts are used also on racks for conventional hard anodizing. However, bolting requires more loading and unloading time than tension contacts.

Materials for Racks. Aluminum and commercially pure titanium are the materials most commonly used for anodizing racks. Aluminum alloys used for racks should contain not more than 5% Cu and 7% Si. Alloys such as 3003, 2024, and 6061 are satisfactory. Contacts must be of aluminum or titanium. Racks made of aluminum have the disadvantage of being anodized with the parts. The anodic coating must be removed from the rack, or at least from contacts, before the rack can be reused. A 5% solution of sodium hydroxide at 38 to 65 °C (100 to 150 °F), or an aqueous solution of chromic and phosphoric acids (40 g or $5\frac{1}{3}$ oz CrO_3 and 40 mL or $5\frac{1}{3}$ fluid oz of H_3PO_4 per liter or per gallon of water) at 77 to 88 °C (170 to 190 °F) can be used to strip the film from the rack. The chromic-phosphoric acid solution does not continue to attack the aluminum rack after the anodic film is removed.

Caustic etching prior to anodizing attacks aluminum spring or tension contacts, causing a gradual decrease in their strength for holding the parts securely. This condition, coupled with vibration in the anodizing tank, especially from agitation, results in movement and burning of workpieces.

On many racks, aluminum is used for splines, crosspieces, and other large members, and titanium is used for the contact tips. The tips may be replaceable or nonreplaceable. Although replaceable titanium tips offer versatility in racking, the aluminum portions of the rack must be protected with an insulating coating. However, if the anodizing electrolyte penetrates the coating, the aluminum portion of the rack may become anodized and thus become electrically insulated from the replaceable titanium contact. A more satisfactory rack design uses nonreplaceable titanium contacts on aluminum splines that are coated with a protective coating. Titanium contacts that are welded to replaceable titanium crossbars offer a solution to many racking problems created by the variety of parts to be anodized. These crossbar members can be rapidly connected to the spline.

Titanium should not be used in solutions containing hydrofluoric acid or any solution bearing any fluoride species. Titanium has the disadvantage that it has less than half the current-carrying capacity of aluminum, which can handle 650 A per square inch of cross-sectional area. However, recent rack designs employing cores of titanium-clad copper have offset this disadvantage.

Plastisol is used as a protective coating for anodizing racks. This material has good resistance to chemical attack by the solutions in the normal anodizing cycle; however, it should not be used continuously in a vapor degreasing operation or in chemical bright dip solutions. Furthermore, if the coating becomes loose and entraps processing solution, the solution may bleed out and drip on the workpieces, causing staining or spotting. Entrapment of bright dip solution containing phosphates can be a "silent killer" of sealing solutions. Phosphates in very small quantities that are subsequently released in the seal bath will prevent sealing from occurring.

Bulk Processing. Small parts that are difficult to rack are bulk anodized in perforated cylindrical containers made of fiber, plastic, or titanium. Each container has a stationary bottom, a threaded spindle centrally traversing its entire length, and a removable top that fits on the spindle to hold the parts in firm contact with each other. While bulk processing is more economical in that parts do not have to be individually racked, the drawbacks are that it results in random unanodized contact marks on the exterior of the part, and that it is usable only on parts without flat sections or blind holes. It is usually used on relatively small parts.

Anodizing Problems

Causes and the means adopted for correction of several specific problems in anodizing aluminum are detailed in the following examples.

Example 1:

Anodic coatings were dark and blotchy on 80 to 85% of a production run of construction workers' helmets made of alloy 2024. After drawing, these helmets had been heat treated in stacks, water quenched, artificially aged, alkaline etched with sodium hydroxide solution, anodized in sulfuric acid solution, sealed, and dried. The dark areas centered at the crowns of the helmets and radiated outward in an irregular pattern. Examination disclosed the presence of precipitated constituents and lower hardness in the dark areas. The condition proved to be the result of restricted circulation of the quench water when the helmets were stacked, which permitted precipitation of constituents because of a slower cooling rate in the affected areas. The problem was solved by separating the helmets with at least 75 mm (3 in.) of space during heating and quenching.

Example 2:

Pieces of interior trim made from alloy 5005 sheet varied in color from light to dark gray after anodizing. Rejection was excessive, because color matching was required. Investigation proved that the anodizing process itself was not at fault; the color variation occurred because the workpieces had been made of cutoffs from sheet stock obtained from two different sources. To prevent further difficulty, two recommendations were made:

- All sheet metal of a given alloy should be purchased from one primary producer, or each job should be made of material from one source. In the latter instance, all cutoffs should be kept segregated.
- More rigid specifications should be established for the desired quality of finish. Most producers can supply a clad material on certain alloys that gives better uniformity in finishing.

Example 3:

The problem was to improve the appearance of bright anodized automotive parts made of alloy 5357-H32. Deburring was the only treatment preceding anodizing. An acceptable finish was obtained by changing to an H25 temper. The H25 had a better grain structure for maintaining a mirror-bright finish during anodizing.

Example 4:

After alkaline etching, web-shape extrusions made of alloy 6063-T6 exhibited black spots that persisted through the anodizing cycle. These extrusions were 3 m (11 ft) long and had cross-sectional dimensions of 100 by 190 mm (4 by 7 $\frac{1}{2}$ in.) and a web thickness of 5 mm ($\frac{3}{16}$ in.). Cleaning had consisted of treatment for 1 to 4 min in 15% sulfuric acid at 85 °C (185 °F) and etching for 8 min in a sodium hydroxide solution (40 g/L or 5 oz/gal) at 60 °C (140 °F). The spots occurred only on the outer faces of the web. Affected areas showed subnormal hardness and electrical conductivity. Metallographic examination revealed precipitation of magnesium silicide there.

The defects were found to have occurred in areas where cooling from the extrusion temperature was retarded by the presence of insulating air pockets created by poor joints between the carbon blocks that lined the runout table. The extrusion had only to remain stationary on the runout table (end of extrusion cycle, flipped on side for sawing) for as little as 1 min for $MgSi_2$ to precipitate at locations where cooling was retarded. This type of defect is not limited to a particular shape; it can result from a critical combination of size and shape of the extrusion, or from extrusion conditions and cooling rate.

The solution to the problem was to provide uniform cooling of the extrusion on the runout table; this was accomplished by modifying the table and employing forced-air cooling.

Sealing of Anodic Coatings

When properly done, sealing in boiling deionized water for 15 to 30 min partially converts the as-anodized alumina of an anodic coating to an aluminum monohydroxide known as Boehmite. It is also common practice to seal in hot aqueous solution containing nickel acetate. Precipitation of nickel hydroxide helps in plugging the pores.

The corrosion resistance of anodized aluminum depends largely on the effectiveness of the sealing operation. Sealing will be ineffective, however, unless the anodic coating is continuous, smooth, adherent, uniform in appearance, and free of surface blemishes and powdery areas. After sealing, the stain resistance of the anodic coating also is improved. For this reason, it is desirable to seal parts subject to staining during service.

Tanks made of stainless steel or lined low-carbon steel and incorporating adequate agitation and suitable temperature controls are used for sealing solutions.

Chromic acid anodized parts are sealed in slightly acidified hot water. One specific sealing solution contains 1 g of chromic acid in 100 L of solution (0.1 oz in 100 gal). The sealing procedure consists of immersing the freshly anodized and rinsed part in the sealing solution at 79 ± 1 °C (175 ± 2 °F) for 5 min. The pH of this solution is maintained within a range of 4 to 6. The solution is discarded when there is a buildup of sediment in the tank or when contaminants float freely on the surface.

Sulfuric acid anodized parts may also be sealed in slightly acidified water (pH 5.5 to 6.5), at about 93 to 100 °C (200 to 212 °F). At temperatures below 88 °C (190 °F), the change in the crystalline form of the coating is not satisfactorily accomplished within a reasonable time.

Dual sealing treatments are often used, particularly for clear anodized trim parts. A typical process involves a short-time immersion in hot nickel acetate 0.5 g/L (0.06 oz/gal) solution followed by rinsing and immersion in a hot, dilute dichromate solution. Advantages of dual sealing are less sealing smudge formed, greater tolerance for contaminants in the baths, and improved corrosion resistance of the sealed parts in accelerated tests (e.g., the CASS test, ASTM B 368).

One specific sealing solution contains 5 to 10 wt% potassium dichromate and sufficient sodium hydroxide to maintain the pH at 5.0 to 6.0. This solution is prepared by adding potassium dichromate to the partly filled operating tank and stirring until the dichromate is completely dissolved. The tank is then filled with water to the operating level and heated to the operating temperature, after which the pH is adjusted by adding sodium hydroxide (which gives a yellow color to the bath).

For sealing, the freshly anodized and rinsed part is immersed in the solution at 100 ± 1 °C (210 ± 2 °F) for 10 to 15 min. After sealing, the part is air dried at a temperature no higher than 105 °C (225 °F). The dichromate seal imparts a yellow coloration to the anodic coating.

Control of this solution consists of maintaining the correct pH and operating temperature. The solution is discarded when excessive sediment builds up in the tank or when the surface is contaminated with foreign material. Sealing is not done on parts that have received any of the hard anodized coatings unless properties other than abrasion resistance are required. If the parts are to be used in a corrosive environment, sealing would be a requirement after hard anodizing. Another application where sealing would be a requirement would be to increase electrical resistance. Sealing will reduce abrasion resistance by 30%. Some other sealing processes are given in Table 6.

Table 6 Sealing processes for anodic coatings

Process	**Bath**	**Temperature**		**Duration, min**	**Appearance, properties**	**Remarks**
		°C	**°F**			
Nickel-cobalt	0.5 kg (1.1 lb) nickel acetate, 0.1 kg (0.2 lb) cobalt acetate, 0.8 kg (1.8 lb) boric acid, 100 L (380 gal) water	98-100	208-212	15-30	Colorless	Provides good corrosion resistance for a colorless seal after anodizing bath buffered to pH of 5.5 to 6.5 with small amounts of acetic acid sodium acetate
Dichromate	5 wt% sodium dichromate, 95 wt% water	98-100	208-212	30	Yellow color	Cannot be used for decorative and colored coatings where the yellow color is objectionable
Glauber salt	20 wt% sodium sulfate, 80 wt% water	98-100	208-212	30	Colorless	. . .
Lacquer seal	Lacquer and varnishes for interior and exterior exposure	. . .	. . .	. . .	Colorless to yellow or brown	Can provide good corrosion resistance provided that the correct formulation is selected. Formulations for exterior exposure use acrylic, epoxy, silicone-alkyds resins and for interior exposure the previously mentioned

Water for sealing solutions can significantly affect the quality of the results obtained from the sealing treatment, as evidenced in the following example.

Strips for automotive exterior trim that were press formed from 5457-H25 sheet were found to have poor corrosion resistance after anodizing, even though appearance was acceptable. The strips had been finished in a continuous automatic anodizing line incorporating the usual steps of cleaning, chemical brightening, desmutting, and anodizing in a 15% sulfuric acid electrolyte to a coating thickness of 8 μm (0.3 mil). They had been sealed in deionized water at a pH of 6.0 and then warm air dried. Rinses after each step had been adequate, and all processing conditions had appeared normal.

Investigation eliminated metallurgical factors as a possible cause but directed suspicion to the sealing operation, because test strips sealed in distilled water showed satisfactory corrosion resistance. Although the deionized water used in processing had better-than-average electrical resistance (1,000,000 Ω· cm or 10,000 Ω· m), analysis of the water showed that it contained a high concentration of oxidizable organic material. This was traced to residues resulting from the leaching of ion-exchange resins from the deionization column. The difficulty was remedied by the use of more stable resins in the deionization column.

When the resin is approaching full absorption rate, the silicons (silicates) are one of the first elements to come across as

Color Anodizing

Dyeing consists of impregnating the pores of the anodic coating, before sealing, with an organic or inorganic (e.g., ferric ammonium oxalate) coloring material. The depth of dye adsorption depends on the thickness and porosity of the anodic coating. The dyed coating is transparent, and its appearance is affected by the basic reflectivity characteristics of the aluminum. For this reason, the colors of dyed aluminum articles should not be expected to match paints, enamel, printed fabrics, or other opaque colors.

Shade matching of color anodized work is difficult to obtain. Single-source colors usually are more uniform than colors made by mixing two or more dye materials together. Maximum uniformity of dyeing is obtained by reducing all variables of the anodizing process to a minimum and then maintaining stringent control of the dye bath.

Mineral pigmentation involves precipitation of a pigment in the pores of the anodic coating before sealing. An example is precipitation of iron oxide from an aqueous solution of ferric ammonium oxalate to produce gold-colored coatings.

Integral color anodizing is a single-step process in which the color is produced during anodizing. Pigmentation is caused by the occlusion of microparticles in the coating, resulting from the anodic reaction of the electrolyte with the microconstituents and matrix of the aluminum alloy. Thus, alloy composition and temper strongly affect the color produced. For example, aluminum alloys containing copper and chromium will color to a yellow or green when anodized in sulfuric or oxalic acid baths, whereas manganese and silicon alloys will have a gray to black appearance. Anodizing conditions such as electrolyte composition, voltage, and temperature are important and must be controlled to obtain shade matching. One electrolyte frequently used consists of 90 g/L (10 oz/gal) sulfophthalic acid plus 5 g/L (0.6 oz/gal) sulfuric acid.

Another method for coloring anodic coatings is the two-step (electrolytic) coloring process. After conventional anodizing in sulfuric acid electrolyte, the parts are rinsed and transferred to an acidic electrolyte containing a dissolved metal salt. Using alternating current, a metallic pigment is electrodeposited in the pores of the anodic coating. There are various proprietary electrolytic coloring processes. Usually tin, nickel, or cobalt is deposited, and the colors are bronzes and black. The stable colors produced are useful in architectural applications.

Evaluation of Anodic Coatings

Coating Thickness. In the metallographic method, the evaluator measures coating thickness perpendicular to the surface of a perpendicular cross section of the anodized specimen, using a microscope with a calibrated eyepiece. This is the most accurate method for determining the thickness of coatings of at least 2.5 μm (0.1 mil). This method is used to calibrate standards for other methods and is the reference method in cases of dispute. Because of variations in the coating thickness, multiple measurements must be made and the results averaged.

In the micrometer method, the evaluator determines coating thickness of 2.5 μm (0.1 mil) or more by micrometrically measuring the thickness of a coated specimen, stripping the coating using the solution described in ASTM B 137, micrometrically measuring the thickness of the stripped specimen, and subtracting the second measurement from the first.

Effectiveness of Sealing. The sulfur dioxide method comprises exposure of the anodic coating for 24 h to attack by moist air (95 to 100% relative humidity) containing 0.5 to 2 vol% sulfur dioxide, in a special test cabinet. The method is very discriminative. Coatings that are incompletely or poorly sealed develop a white bloom.

Abrasion Resistance. In the Taber abrasion method, the evaluator determines abrasion resistance by an instrument that, by means of weighted abrasive wheels, abrades test specimens mounted on a revolving turntable. Abrasion resistance is measured in terms of either weight loss of the test specimen for a definite number of cycles or the number of cycles required for penetration of the coating. These procedures are covered by Method 6192 in Federal Test Method Standard 141. Weight (thickness) loss (see Method 6192-4.1.3 in Federal Test Methods Standard 141) is measured using eddy current as a check, because milligram weight loss in checking abrasion resistance is difficult to duplicate. Penetration testing can take more than 30 h. Although described in Method 6192, it is rarely used for hard anodizing.

Lightfastness. The fade-O-meter method is a modification of the artificial-weathering method, in that the cycle is conducted without the use of water. Staining and corrosion products thus cannot interfere with interpretation of results. A further modification entails the use of a high-intensity ultra-violet mercury-arc lamp and the reduction of exposure to a period of 24 to 48 h. Table 7 lists the various ASTM and ISO methods that can be used to evaluate the quality of anodic coatings.

Table 7 ASTM and ISO test methods for anodic coatings

Method	ASTM	ISO
Coating thickness		
Eddy current	B244	2360
Metallographic	B487	. . .
Light section microscope	B681	2128
Coating weight	B137	2106
Sealing		
Dye stain	B136(a)	2143
Acid dissolution	B680	3210
Impedance/admittance	B457	2931
Voltage breakdown	B110	2376
Corrosion resistance		
Salt spray	B117	. . .
Cooper-accelerated, acetic acid salt-spray	B368	. . .

(a) ASTM B 136 shows extremely poor sealing and is not considered a true sealing test. It is better classified as a test for staining by dyes.

Effects of Anodic Coatings on Surface and Mechanical Properties

As the thickness of an anodic coating increases, light reflectance, both total and specular, decreases. This decrease is only slight for pure aluminum surfaces, but it becomes more pronounced as the content of alloying elements other than magnesium, which has little effect, increases. The decrease in reflectance values is not strictly linear with increasing thickness of anodic coating; the decrease in total reflectance levels off when the thickness of the coating on super-purity and high-purity aluminum is greater than about 2.5 μm (0.1 mil).

Data comparing the reflectance values of chemically brightened and anodized aluminum materials with those of other decorative materials are given in "Anodic Oxidation of Aluminium and Its Alloys," Bulletin 14 of the Aluminium Development Association (now the Aluminium Federation), London, England, 1949.

Table 8 shows the effect of anodized coatings 2 to 20 μm (0.08 to 0.8 mil) thick on the reflectance values of electrobrightened aluminum of three degrees of purity. This table also includes specular reflectance values for surfaces after removal of the anodic coating. These data show that the degree of roughening by the anodizing treatment increases as the purity of the aluminum decreases. The reflectance values of the anodized surfaces are influenced by the inclusion of foreign constituents or their oxides in the anodic coating.

Table 8 Effect of anodizing on reflectance values of electrobrightened aluminum

Thickness of anodic coating		**Specular reflectance, %**			**Total reflectance after anodizing, %**
μm	**mil**	**Electro-brightened**	**Electro-brightened and anodized**	**After removal, of anodic coating(a)**	
Aluminum, 99.99%					
2	0.08	90	87	88	90
5	0.2	90	87	88	90
10	0.4	90	86	88	89
15	0.6	90	85	88	88
20	0.8	90	84	88	88
Aluminum, 99.8%					
2	0.08	88	68	83	89
5	0.2	88	63	85	88
10	0.4	88	58	85	87
15	0.6	88	53	85	86
20	0.8	88	57	85	84
Aluminum, 99.5%					
2	0.08	75	50	70	86
5	0.2	75	36	64	84

10	0.4	75	26	61	81
15	0.6	75	21	57	77
20	0.8	75	15	53	73

Source: Aluminum Development Council

(a) Anodic coating removed in chromic-phosphoric acid.

Metallurgical factors have a significant influence on the effect of anodizing on reflectance. For minimum reduction in reflectance, the conversion of metal to oxide must be uniform in depth and composition. Particles of different composition do not react uniformly. They produce a nonuniform anodic coating and roughen the interface between the metal and the oxide coating.

Anodizing Conditions. The composition and operating conditions of the anodizing electrolyte also influence the light reflectance and other properties of the polished surface. Figure 8 shows the effect of sulfuric acid concentration, temperature of bath, and current density on the specular reflectance of chemically brightened aluminum alloy 5457. These data show that a particular level of specular reflectance can be produced by varying operating conditions.

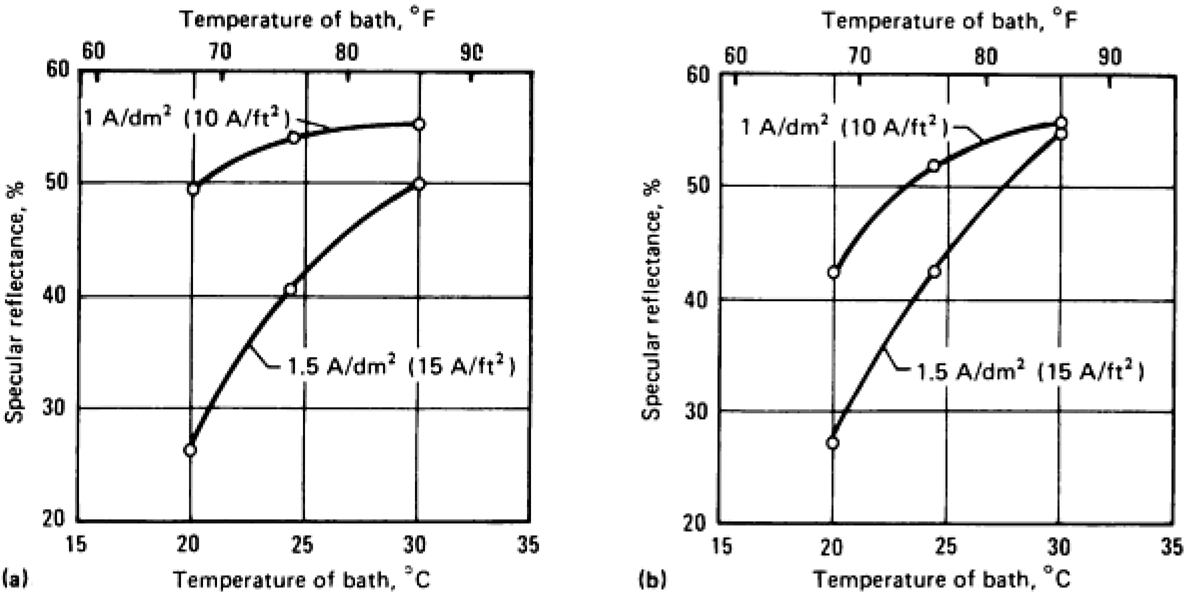


Fig. 8 Effect of anodizing conditions on specular reflectance of chemically brightened aluminum. Data are for a 5 μm (0.2 mil) anodic coating on 5457 alloy. (a) 17 wt% H_2SO_4. (b) 8.8 wt% H_2SO_4

Thermal Radiation. The reflectance of aluminum for infrared radiation also decreases with increasing thickness of the anodic coating, as shown in Fig. 9. These data indicate that the difference in purity of the aluminum is of minor significance. Figure 10 compares anodized aluminum surfaces and polished aluminum surfaces at 21 °C (70 °F) with respect to absorptance when exposed to blackbody radiation from sources of different temperatures. Although anodized aluminum is a better absorber of low-temperature radiation, as-polished aluminum is a more effective absorber of blackbody radiation from sources at temperatures exceeding 3300 °R (1850 K).

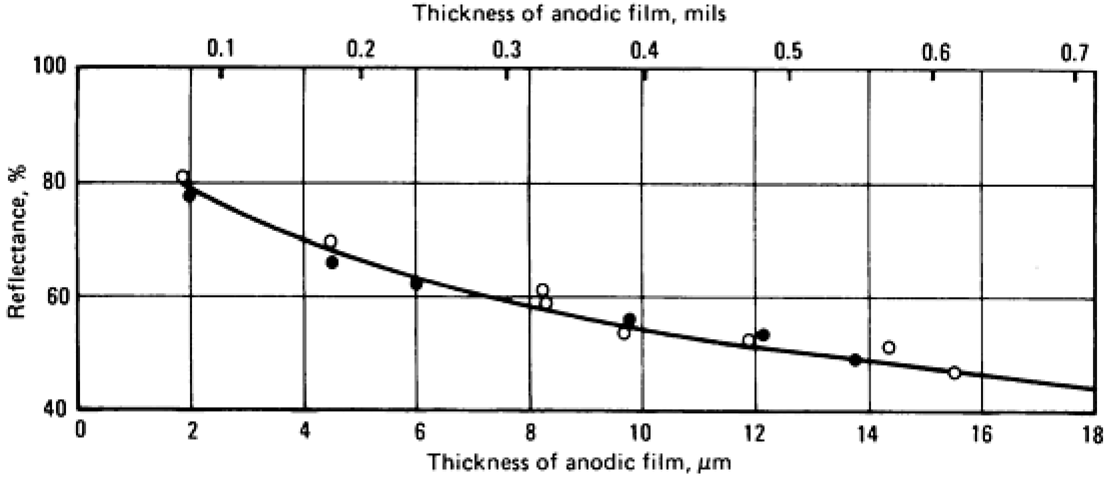


Fig. 9 Effect of anodic coating thickness on reflectance of infrared radiation. Temperature of infrared radiation source, 900 °C (1650 °F). ○: 99.99% Al. •: 99.50% Al. Courtesy of Aluminum Development Council

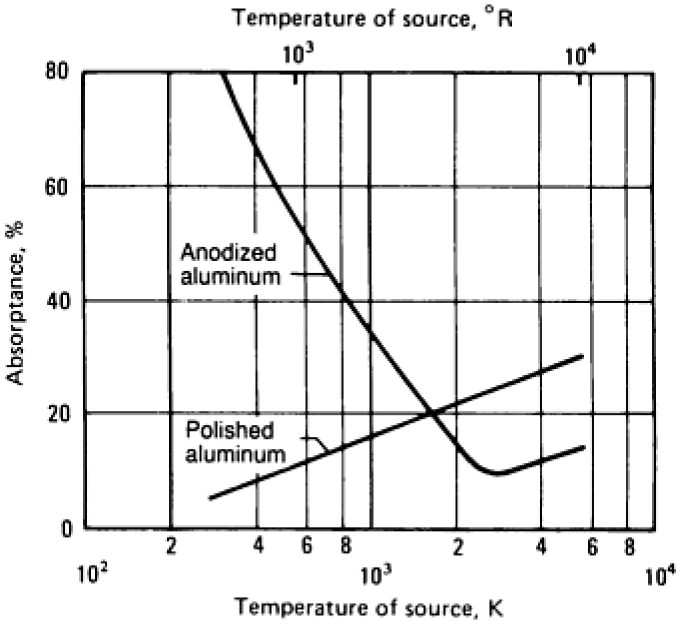


Fig. 10 Comparison of absorptance of blackbody radiation by anodized aluminum and polished aluminum. Temperature of aluminum surface. 530 °R (21 °C, or 70 °F)

Fatigue Strength. Anodic coatings are hard and brittle, and they will crack readily under mechanical deformation. This is true for thin as well as thick coatings, even though cracks in thin coatings may be less easily visible. Cracks that develop in the coating act as stress raisers and are potential sources of fatigue failure of the substrate metal. Typical fatigue-strength values for aluminum alloys before and after application of a hard anodic coating 50 to 100 μm (2 to 4 mils) thick are given in Table 9.

Table 9 Effect of anodizing on fatigue strength of aluminum alloys

Alloy	Fatigue strength at 1,000,000 cycles

	Not anodized		**Anodized**	
	MPa	**ksi**	**MPa**	**ksi**
Wrought alloys				
2024 (bare)	130	19	105	15
2024 (clad)	75	11	50	7.5
6061 (bare)	105	15	40	6
7075 (bare)	150	22	60	9
7075 (clad)	85	12	70	10
Casting alloys				
220	50	7.5	52	7.5
356	55	8	55	8

Note: Values are for sulfuric acid hard coatings 50 to 100 μm (2 to 4 mils) thick applied using 15% sulfuric acid solution at -4 to 0 °C (25 to 32 °F) and 10 to 75 V dc.

Source: F.J. Gillig, WADC Technical Report 53-151, P.B. 111320, 1953

Anodizing Non-Aluminum Substrates

Magnesium Anodizing. Three methods of anodizing magnesium are widely employed by industry. One uses only internal voltage generated as a result of a galvanic couple, and two use an external power source. The first method, often referred to as galvanic anodize or the Dow 9 process, uses a steel cathode electrically coupled to the magnesium component to be anodized. Dow 9 coatings have no appreciable thickness and impart little added corrosion resistance. However, the resulting coating is dark brown to black, which makes it useful for optical components and for heat sinks in electronic applications. This coating also serves as an excellent paint base.

The other anodizing processes, known as the HAE and Dow 17 processes, use an external power source. Both processes deposit an anodic layer about 50 μm (2 mils) thick, but they differ in that the solution used for Dow 17 coatings is acidic, a combination of ammonium bifluoride, sodium dichromate, and phosphoric acid, whereas the HAE process employs an alkaline bath. Details for both processes may be found by consulting military specification MIL-M-45202.

Titanium Anodizing. While extremely corrosion resistant in itself, titanium and its alloys are often anodized to impart properties other than corrosion resistance. For instance, in wear situations, titanium components are very prone to galling. In order to overcome its tendency to gall, titanium is often anodized in a caustic electrolyte. This application is detailed in the SAE specification AMS 2488.

Decorative colored coatings on titanium can be achieved by anodizing in slightly acidified solutions of phosphoric or sulfuric acid. By controlling the terminal voltage, vivid colors from magenta to cobalt blue can be obtained. Such decorative uses have been widely utilized by the jewelry industry for years, and these coatings are now finding functional use for medical implants and dental instruments.

Zinc Anodizing. Zinc can be anodically treated in a wide range of electrolytes using either alternating or direct current to form decorative, yet protective, coatings. Anodic coatings on zinc and zinc alloys are covered in military specification MIL-A-81801. The zinc to be anodized may be wrought or die cast zinc parts or zinc coatings obtained by electroplating, mechanical deposition, thermal spraying, or galvanizing.

Electrolytes are formulated from such materials as phosphates, silicates, or aluminates to which are added chromates, vanadates, molybdates, and/or tungstates. Solutions are typically heated to 65 °C (150 °F), and anodize times vary from 5 to 10 min. The resulting coatings are 30 to 40 μm (1.2 to 1.6 mils) thick and are either green, gray, or brown, depending on the electrolyte used. For optimum corrosion resistance, anodic zinc coatings should be sealed using a material such as sodium silicate or an organic lacquer or enamel.

Thermal Spray Coatings

Robert C. Tucker, Jr., Praxair Surface Technologies, Inc.

Introduction

THERMAL SPRAY is a generic term for a group of processes in which metallic, ceramic, cermet, and some polymeric materials in the form of powder, wire, or rod are fed to a torch or gun with which they are heated to near or somewhat above their melting point. The resulting molten or nearly molten droplets of material are accelerated in a gas stream and projected against the surface to be coated (i.e., the substrate). On impact, the droplets flow into thin lamellar particles adhering to the surface, overlapping and interlocking as they solidify. The total coating thickness is usually generated in multiple passes of the coating device.

The invention of the first thermal spray process is generally attributed to M.U. Schoop of Switzerland in 1911 and is now known as flame spraying. Other major thermal spray processes include wire spraying, detonation gun deposition (invented by R.M. Poorman, H.B. Sargent, and H. Lamprey and patented in 1955), plasma spray (invented by R.M. Gage, O.H. Nestor, and D.M. Yenni and patented in 1962), and high velocity oxyfuel (invented by G.H. Smith, J.F. Pelton, and R.C. Eschenbach and patented in 1958). A variant of plasma spraying uses a transferred arc to heat the surface being coated. It is considered by some to be a welding process akin to hard facing rather than a true thermal spray process, because the surface of the substrate becomes momentarily molten immediately beneath the torch.

A major advantage of the thermal spray processes is the extremely wide variety of materials that can be used to make a coating. Virtually any material that melts without decomposing can be used. A second major advantage is the ability of most of the thermal spray processes to apply a coating to a substrate without significantly heating it. Thus, materials with very high melting points can be applied to finally machined, fully heat-treated parts without changing the properties of the part and without thermal distortion of the part. A third advantage is the ability, in most cases, to strip and recoat worn or damaged coatings without changing the properties or dimensions of the part. A major disadvantage is the line-of-sight nature of these deposition processes. They can only coat what the torch or gun can "see." Of course, there are also size limitations prohibiting the coating of small, deep cavities into which a torch or gun will not fit.

Figure 1 shows an example of the variety of shapes taken by the molten droplets as they impact, flow, and solidify on the surface. The mechanism of bonding of the particles to the surface is not well understood but is thought to be largely due to mechanical interlocking of the solidifying and shrinking particles, with asperities on the surface being coated unless supplemental fusion or diffusion heat treatment is used. Indeed, most thermal spray coatings require a roughened substrate surface for adequate bonding. Some interdiffusion or localized fusion of as-deposited coatings with the substrate has been observed in a few instances with unique combinations of coatings and substrates. There is evidence of chemical bonding in some coating/substrate systems, not unreasonable when the high-velocity impact of particles might be expected to rupture any films on either the powder particles or the substrate. In addition, van der Waals forces may play a role if the substrate is extremely clean and no significant oxidation occurs during deposition.

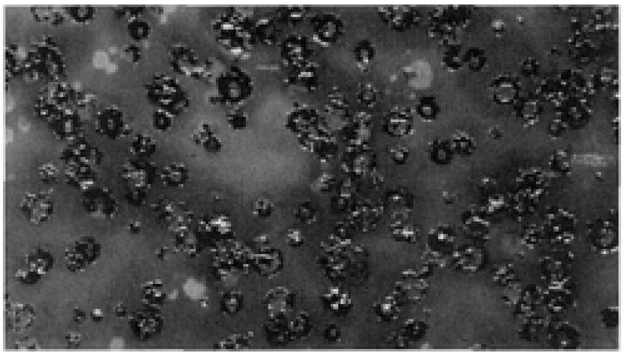


Fig. 1 Deformation of molten or semimolten particles resulting from spray impacting on a substrate

Thermal spray coatings are usually formed by multiple passes of a torch or gun over the surface. Typical cross sections of several examples of thermal spray coatings are shown in Fig. 2, illustrating the lamellar nature of the coatings. A coating can be made of virtually any material that can be melted without decomposing. Moreover, the deposition process itself can substantially alter the composition as well as the structure of the material. As a result, the microstructure and properties of the coatings can be extremely varied. Specification of a coating, therefore, must often involve more than simply stating the composition of the starting powder or wire and the general type of process to be used.

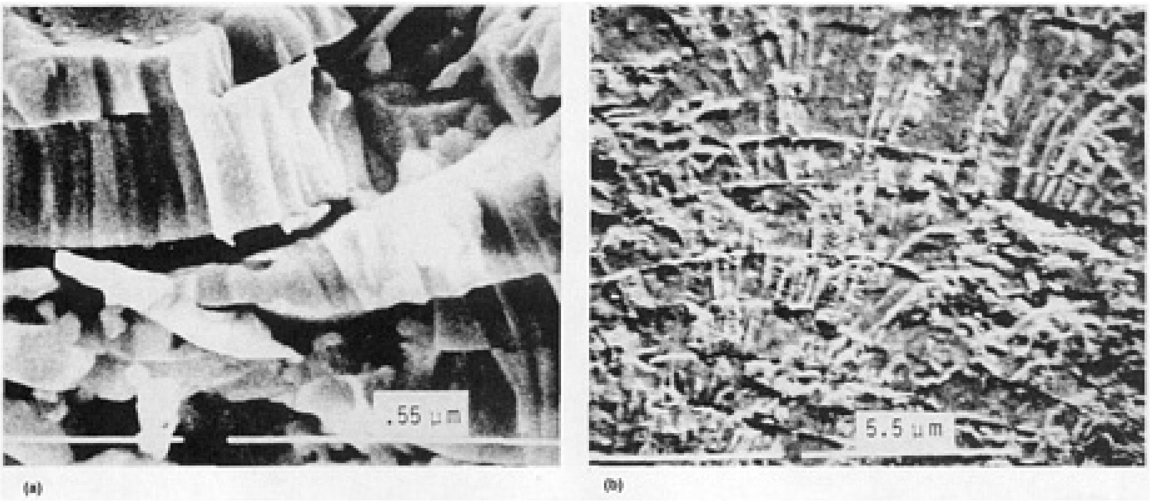


Fig. 2 Typical microstructure of a plasma-sprayed tungsten metal coating showing the splat structure and the fine crystalline structure within the splats. (a) Scanning electron micrograph of a fracture surface. (b) Light micrograph of the same coating. Courtesy of Praxair Surface Technologies, Inc.

The applications of thermal spray coatings are extremely varied, but the largest categories of use are to enhance the wear and/or corrosion resistance of a surface. Other applications include their use for dimensional restoration, as thermal barriers, as thermal conductors, as electrical conductors or resistors, for electromagnetic shielding, and to enhance or retard radiation. They are used in virtually every industry, including aerospace, agricultural implements, automotive, primary metals, mining, paper, oil and gas production, chemicals and plastics, and biomedical. Some specific examples are given in the section "Uses of Thermal Spray Coatings" in this article.

Acknowledgements

The author recognizes the contributions of James H. Clare and Daryl E. Crawmer, authors of the article "Thermal Spray Coatings" in *Metals Handbook,* 9th ed., Vol 5. In particular, the sections on flame spray, flame spray and fuse, and electric wire-arc spray, as well as several of the figures, were substantially adapted from the earlier edition.

Processes

Flame spray uses combustible gas as a heat source to melt the coating material (Fig. 3). Flame spray guns are available to spray materials in either rod, wire, or powder form. Most flame spray guns can be adapted to use several combinations of gases to balance operating cost and coating properties. Acetylene, propane, methyl-acetylene-propadiene (MAPP) gas, and hydrogen, along with oxygen, are commonly used flame spray gases. In general, changing the nozzle and/or air cap is all that is required to adapt the gun to different alloys, wire sizes, or gases. Figures 3(a) and 3(b) depict powder and wire flame spray guns. For all practical purposes, the rod and wire guns are similar.

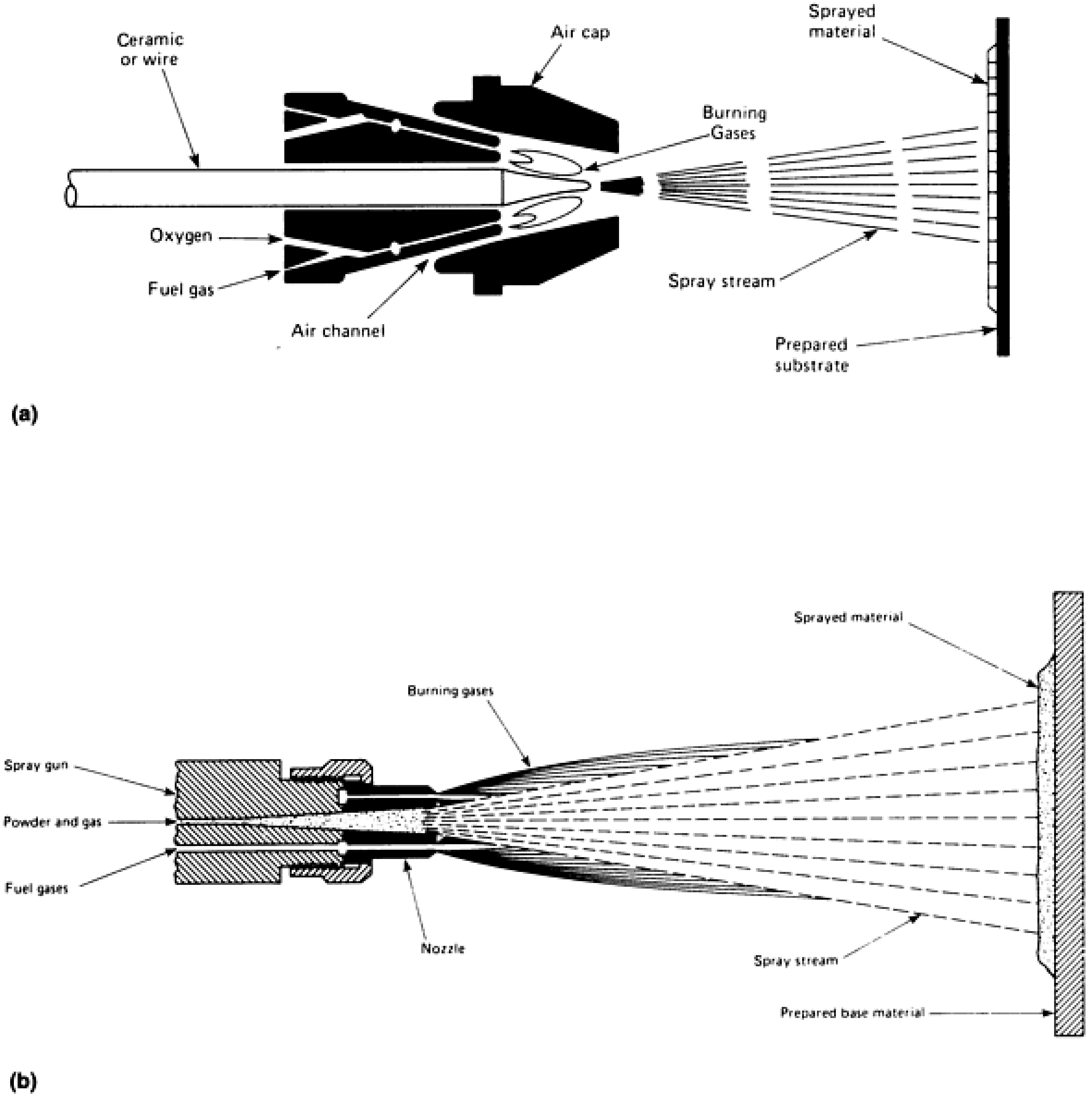


Fig. 3 Cross sections of typical flame spray guns. (a) Wire or rod. (b) Powder

Flame temperatures and characteristics depend on the oxygen-to-fuel gas ratio and pressure. The approximate temperatures for stoichiometric combustion at 1 atm for some oxyfuel combinations are shown in Table 1. The flame spray process is characterized by low capital investment, high deposition rates and efficiencies, and relative ease of operation and cost of equipment maintenance. In general, as-deposited (or cold spray) flame-sprayed coatings exhibit lower bond strengths, higher porosity, a narrower working temperature range, and higher heat transmittal to the substrate than most other thermal spray processes. The flame spray process is widely used for the reclamation of worn or out-of-tolerance parts, frequently using nickel-base alloys. Bronze alloys may be used for some bearings and seal areas. Blends of tungsten carbide and nickel-base alloys may be used for wear resistance. Zinc is commonly applied for corrosion resistance on bridges and other structures.

Table 1 Maximum temperature of heat sources

Heat source	Approximate temperature (stoichiometric combustion)

Propane-oxygen	2526 °C (4579 °F)
Natural gas-oxygen	2538 °C (4600 °F)
Hydrogen-oxygen	2660 °C (4820 °F)
Propylene-oxygen	2843 °C (5240 °F)
Methylacetylene/propadiene-oxygen	2927 °C (5301 °F)
Acetylene-oxygen	3087 °C (5589 °F)
Plasma arc	2200 to 28,000 °C (4000 to 50,000 °F)

Source: Adapted Publication 1G191, National Association of Corrosion Engineers

Flame spray and fuse is a modification of the cold spray method. The materials used for coating are self-fluxing (i.e., they contain elements that react with oxygen or oxides to form low-density oxides that float to the surface, thus improving density, bonding, etc. They have relatively low melting points and require postspray heat treatment. In general, these are nickel- or cobalt-base alloys that use boron, phosphorus, or silicon, either singly or in combination, as melting-point depressants and fluxing agents. In practice, parts are prepared and coated as in other thermal spray processes and then fused. There are two variants: Spray and fuse, and spray-fuse. In spray and fuse, the fusion is done after deposition using one of several techniques, such as flame or torch, induction, or vacuum, inert, or hydrogen furnaces. In spray-fuse, the deposition and fusion are done simultaneously.

The alloys used generally fuse between 1010 to 1175 °C (1850 to 2150 °F), depending on composition. Reducing atmosphere flames should be used to ensure a clean, well-bonded coating. In vacuum and hydrogen furnaces, the coating may have a tendency to wick or run onto adjacent areas. Several brushable stopoff materials are commercially available to confine the coating. It is recommended that test parts be coated and fused whenever the shape, coating alloy, or lot of material is changed, to establish the minimum and maximum fusing temperatures. Fusing temperature is known to vary slightly between lots of spray material. On vertical surfaces, coating material may sag or run off if the fusing temperature is exceeded by more than a few degrees. These coatings are fully dense and exhibit metallurgical bonds. Excessive porosity and nonuniform bonding are usually indicative of insufficient heating.

Spray-and-fuse coatings are widely used in applications where excessive wear combined with high stresses on the coating/substrate (shear or impact) is a problem. These alloys generally exhibit good resistance to wear and have been successfully used in the oil industry for sucker rods and in agriculture for plowshares. In many applications, these coatings make possible the use of less expensive substrate materials. Coating hardnesses can be as high as 65 HRC. Some powder manufacturers offer these alloys blended with tungsten carbide or chromium carbide particles to increase resistance to wear from abrasion, fretting, and erosion. Grinding is usually necessary for machining a fused coating because of the high hardness. Use of spray-and-fuse coatings is limited to substrate materials that can tolerate the 1010 to 1175 °C (1850 to 2150 °F) fusing temperatures. Fusing temperatures may alter the heat-treated properties of some alloys. However, the coating will usually withstand additional heat treatment of the substrate. Slower cooling rates may be required to reduce cracking where greater thicknesses are needed or where there is a substantial difference in the thermal expansion coefficients between the coatings and the substrate.

The electric-arc (wire-arc) spray process uses metal in wire form. This process differs from the other thermal spray processes in that there is no external heat source such as gas flame or electrically induced plasma. Heating and melting occur when two electrically opposed charged wires, comprising the spray material, are fed together in such a manner that a controlled arc occurs at the intersection. The molten metal on the wire tips is atomized and propelled onto a prepared substrate by a stream of compressed air or other gas (Fig. 4).

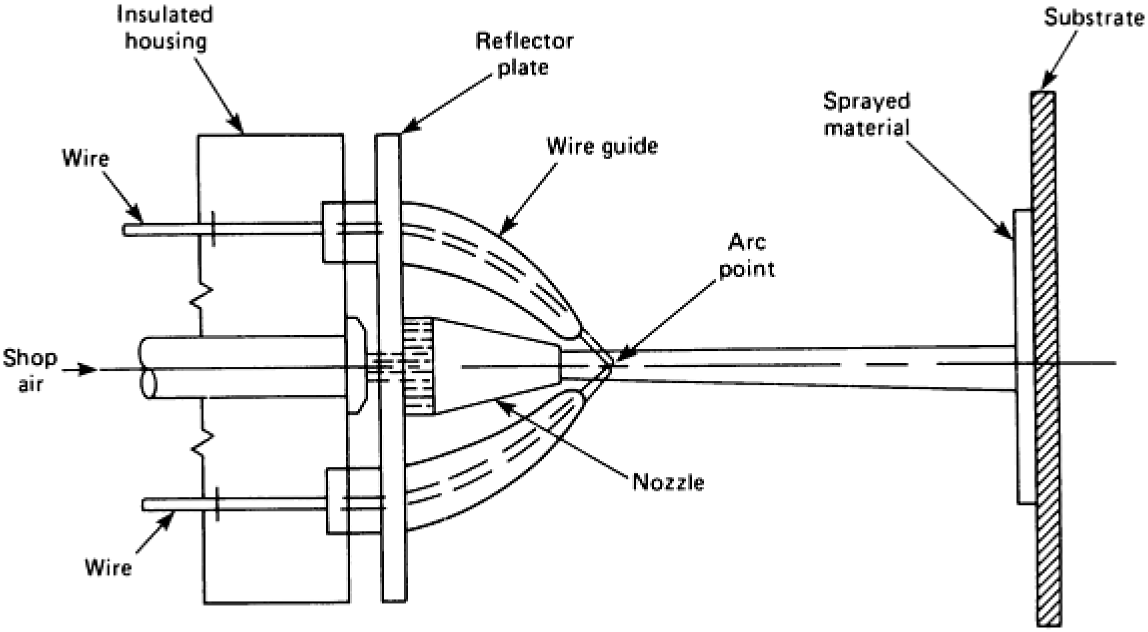


Fig. 4 Typical electric-arc spray device

Electric-arc spray offers advantages over flame spray processes. In general, it exhibits higher bond strengths, in excess of 69 MPa (10,000 psi) for some materials. Deposition rates of up to 55 kg/h (120 lb/h) have been achieved for some nickel-base alloys. Substrate heating is lower than in flame spray processes due primarily to the absence of a flame touching the substrate. The electric-arc process is in most instances less expensive to operate than the other processes. Electrical power requirements are low, and, with few exceptions, no expensive gas such as argon is necessary. The electric-arc process most commonly uses relatively ductile, electrically conductive wire about 1.5 mm (0.060 in.) in diameter. Electric-arc spray coatings of carbides, nitrides, and oxides are therefore not currently practical; however, the recent development of cored wires permits the deposition of some composite coatings containing carbides or oxides. By using dissimilar wires, it is possible to deposit pseudoalloys. A less expensive wear surface can be deposited using this technique. One wire, or 50% of the coating matrix, can be an inexpensive filler material.

Electric-arc coatings are widely used in high-volume, low-cost applications such as application of zinc corrosion-resistant coatings. In a more unusual application, metal-face molds can be made using a fine spray attachment available from some manufacturers. Molds made in this way can duplicate extremely fine detail, such as the relief lettering on a printed page.

Plasma Spray. A plasma spray torch is shown schematically in Fig. 5. A gas, usually argon, but occasionally including nitrogen, hydrogen, or helium, is allowed to flow between a tungsten cathode and a water-cooled copper anode. An electric arc is initiated between the two electrodes using a high-frequency discharge and then sustained using dc power. The arc ionizes the gas, creating a high-pressure gas plasma. The resulting increase in gas temperature, which may exceed 30,000 °C, in turn increases the volume of the gas and, hence, its pressure and velocity as it exits the nozzle. (Gas velocities, which may be supersonic, should not be confused with particle velocities.) Power levels in plasma spray torches are usually in the range of 30 to 80 kW, but they can be as high as 120 kW. Argon is usually chosen as the base gas because it is chemically inert and because of its ionization characteristics. The enthalpy of the gas can be increased by adding the diatomic gases, hydrogen or nitrogen.

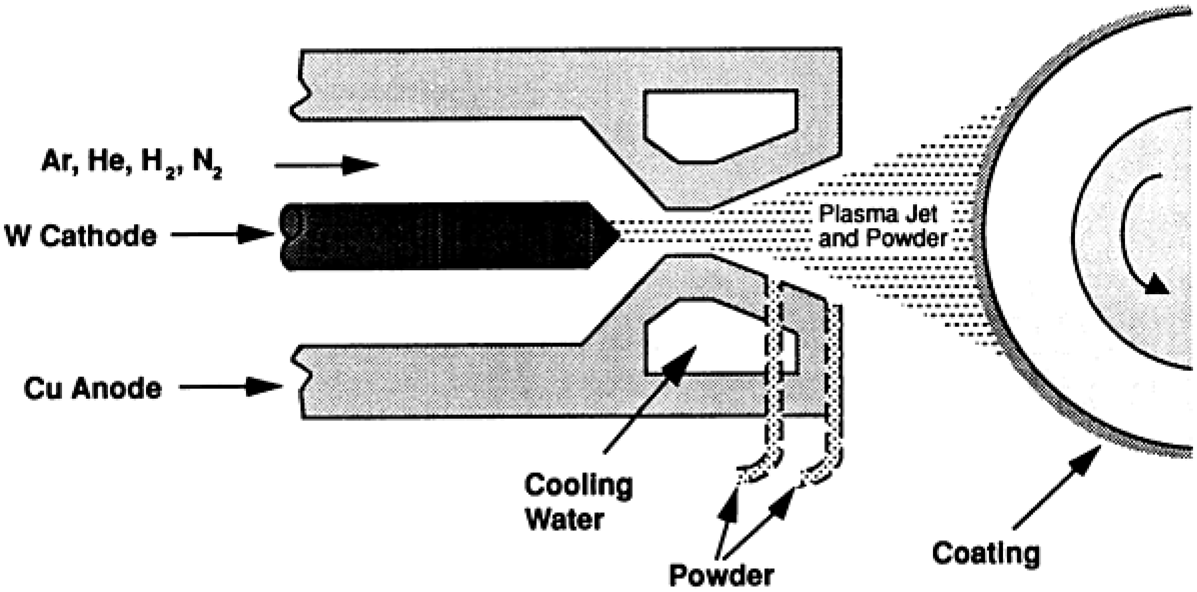


Fig. 5 Plasma spray process. Courtesy of Praxair Surface Technologies, Inc.

Powder is usually introduced into the gas stream either just outside the torch or in the diverging exit region of the nozzle (anode). It is both heated and accelerated by the high-temperature, high-velocity plasma gas stream. Torch design and operating parameters are critical in determining the temperature and velocity achieved by the powder particles. The operating parameters include not only the gas flows, power levels, powder feed rate, and carrier gas flow, but also the distance from the torch to from the substrate (standoff) and the angle of deposition. Standoff is of substantial importance because adequate distance must be provided for heating and accelerating the powder, but too great a distance will allow the powder to cool and lose velocity, because the gas stream is rapidly expanding, cooling, and slowing. The size and morphology of powder particles strongly influence their rate of heating and acceleration and, hence, the efficiency of deposition and quality of the coating. Frequently, a somewhat higher price paid for a powder with a tighter size distribution is more than compensated for by improved deposition efficiency.

The powder velocities usually achieved in plasma spray deposition range from about 300 to 550 m/s. Temperatures are usually at or slightly above the melting point. Generally, higher particle velocities and temperatures above the melting point, but without excessive superheating, yield coatings with the highest densities and bond strengths. The density of plasma spray coatings is usually much higher than that of flame spray coatings and is typically in the range of 80 to 95% of theoretical. Coating thickness usually ranges from about 0.05 to 0.50 mm (0.002 to 0.020 in.) but may be much thicker for some applications (e.g., dimensional restoration or thermal barriers). Bond strengths vary from less than 34 MPa (5000 psi) to greater than 69 MPa (10,000 psi).

In addition to powder temperature and velocity, a third very important factor is the extent of reaction of the powder particles with process gases or surrounding environmental gases (e.g., air) during the deposition process. With normal plasma spraying in air, the extent of oxidation of the powder particles is a function of the specific torch design, operating parameters, and standoff. Extensive oxidation of metallic and carbide powders can result in drastic reduction in coating density, cohesive strength, and bond strength with concomitant changes in performance. Such oxidation can be virtually eliminated by either effective gas shrouding of the effluent or spraying in a reduced-pressure, inert gas chamber.

Thermal spray done in an inert atmosphere and/or low-pressure chamber has become a widely accepted practice, particularly in the aircraft engine industry. Inert-atmosphere, low-pressure plasma spray systems have proven to be an effective means for applying complex, hot corrosion-resistant coatings of the Ni-Co-Cr-Al-Y type to high-temperature aircraft engine components without oxidation of the highly reactive constituents. Simple inert-atmosphere chamber spraying can also be used to confine hazardous materials. Hazardous materials are grouped into two categories: toxic and pyrophoric. Toxic materials include beryllium and its alloys. Pyrophoric materials include magnesium, titanium, lithium, sodium, and zirconium, which tend to burn readily when in a finely divided form or when purified by the plasma process.

A simple inert-atmosphere chamber spray system may include a jacketed, water-cooled chamber, an air lock, a plasma system, workpiece handling equipment, glove ports, a vacuum pumping system, and an inert gas backfill manifold. Usually, the chamber is pumped down to a pressure of 0.001 to 0.01 Pa (10^{-4} to 10^{-5} torr), then backfilled with high-purity dry argon. In any good inert-gas chamber, oxygen levels can be easily maintained below 30 ppm. Some metal powders tend to "clean up" when sprayed in an inert-gas chamber by the reduction of surface oxides. By the same mechanism, some oxide powders tend to be partially reduced when sprayed in an inert-gas chamber.

Inert-atmosphere spraying in a low-pressure chamber offers several unique advantages over conventional plasma spraying in an inert atmosphere at atmospheric pressure. Because of the lower pressure, the plasma gas stream temperature and velocity profiles are extended to greater distances, so the coating properties are less sensitive to standoff. In addition, the substrate can be preheated without oxidation. This allows better control of residual stress and better bond strengths. Deposition efficiency can be increased because of increased particle dwell time in the longer heating zone of the plasma and higher substrate temperature. The closed system also minimizes environmental problems such as dust and noise.

Figure 6 shows a typical inert-atmosphere and/or low-pressure plasma chamber. Normal operating procedures require that the spray chamber be pumped down to quite low pressures, as noted above, or be repeatedly cycled after pumping to approximately 55 Pa (0.4 torr) and then be backfilled with inert gas to about 40 kPa (300 torr). Once the system has been sufficiently purged to achieve an acceptable inert atmosphere, the plasma spray operation is activated and the chamber pressure is adjusted to the desired level for spraying. The entire spray operation is accomplished in a soft vacuum of approximately 6700 Pa (50 torr). The optimum spray condition exists when the plasma temperature at the substrate approximates the melting point of the powder particles; however, the optimum spraying conditions will vary with the chemistry and particle size of each spray material. These variables are similar to those of conventional plasma spraying. Because of the complexity of low-pressure spraying, the entire process is best controlled by computer to ensure complete reproducibility and uniformity throughout the coating. Productivity can be increased by using load/lock prepumping and venting chambers and robotics.

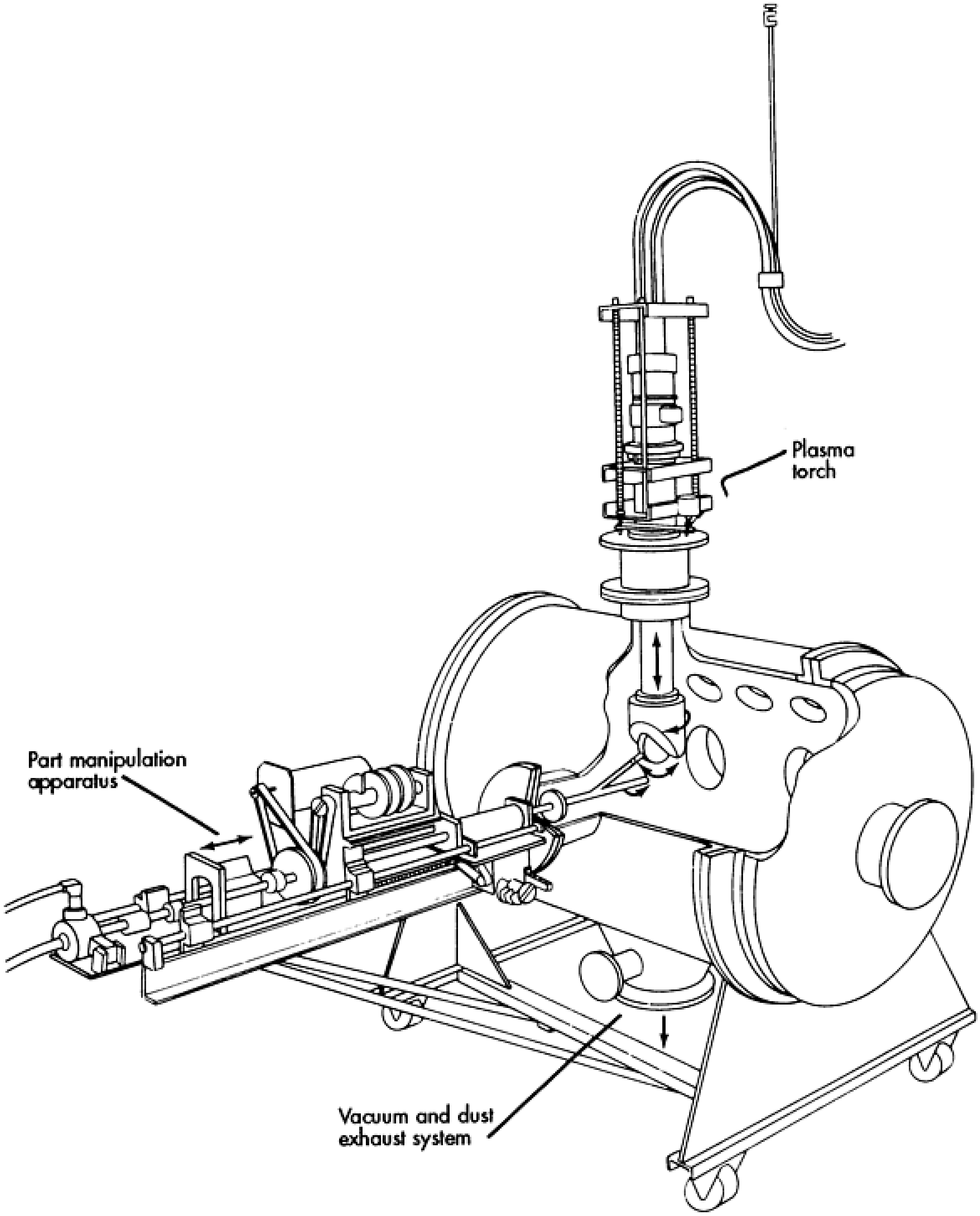


Fig. 6 Typical inert-atmosphere and/or low-pressure plasma chamber. Courtesy of Metco, Inc.

The complex low-pressure plasma spraying process is not required for all applications. Plasma spray using an inert-gas shroud around the plasma gas effluent can be just as effective in preventing oxidation during deposition as spraying in an inert-gas, low-pressure chamber. It has been used extensively to spray Ni-Co-Cr-Al-Y alloys on turbine blades, vanes, and outer air seals, and thermal barriers as an undercoat. Compared to chamber spraying, it has much lower capital costs but greater sensitivity to standoff. It is difficult to preheat the substrate to high temperatures without oxidizing the substrate, a technique used with low-pressure chamber spray to control the residual stress in some high-temperature, oxidation-resistant coatings. However, residual stress in these coatings can nonetheless be controlled when using inert-gas shrouding through control of deposition rates, auxiliary cooling, and so forth.

Plasma spray can be used to produce coatings of virtually any metallic, cermet, or ceramic material. The coatings are used for most of the types of applications described in a subsequent section.

The transferred plasma-arc process adds to plasma spray the capability of substrate surface heating and melting. Figure 7 is a schematic representation of the process. A secondary arc current is established through the plasma and substrate that controls surface melting and depth of penetration. Several advantages result from this direct heating: metallurgical bonding, high-density coatings, high deposition rates, and high thicknesses per pass. Coating thicknesses of 0.50 to 6.35 mm (0.020 to 0.250 in.) and widths up to 32 mm (1.25 in.) can be made in a single pass at powder feed rates of 9 kg/h (20 lb/h). In addition, less electrical power is required than with nontransferred arc processes. For example, for an 88% tungsten carbide, 12% Co material, plasma spray deposition 0.30 mm (0.012 in.) thick and 9.50 mm (0.375 in.) in width might require 24 passes at 40 to 60 kW to achieve maximum coating properties. This same material can be applied, using the transferred plasma-arc process, in one pass at approximately 2.5 kW.

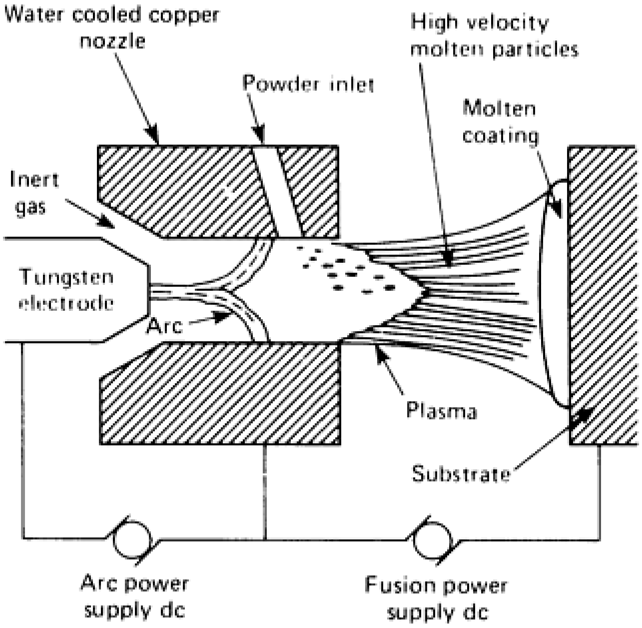


Fig. 7 Transferred plasma-arc spraying

The method of heating and heat transfer in the transferred plasma-arc process eliminates many of the problems related to using powders with wide particle size distributions or large particle sizes. Larger-particle-size powders, for example in the 50-mesh range, tend to be less expensive than closely classified 325-mesh powders.

Some limitations of the process should be considered for any potential application. Because substrate heating is a part of the process, some alteration of its microstructure is inevitable. Applications are also limited to substrates that are electrically conductive and can withstand some melting. The transferred plasma-arc process is used in hardfacing applications such as valve seats, plowshares, oil field components, and mining machinery.

High-Velocity Oxyfuel. A schematic of a high-velocity oxyfuel (HVOF) device is shown in Fig. 8. Fuel, usually propane, propylene, MAPP, or hydrogen, is mixed with oxygen and burned in a chamber. In other cases, liquid kerosene may be used as a fuel and air as the oxidizer. The products of the combustion are allowed to expand through a nozzle where the gas velocities may become supersonic. Powder is introduced, usually axially, in the nozzle and is heated and accelerated. The powder is usually fully or partially melted and achieves velocities of up to about 550 m/s. Because the powder is exposed to the products of combustion, they may be melted in either an oxidizing or reducing environment, and significant oxidation of metallics and carbides is possible.

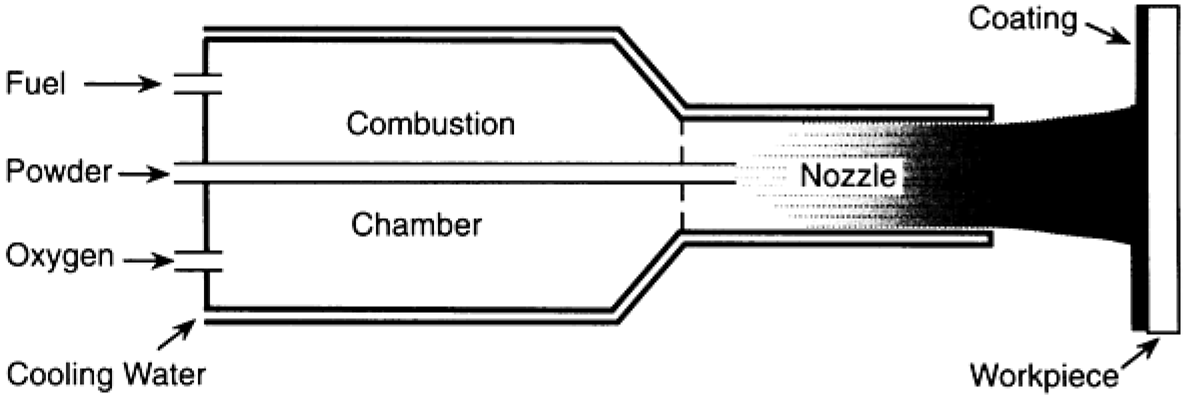


Fig. 8 High-velocity oxyfuel process. Courtesy of Praxair Surface Technologies, Inc.

With appropriate equipment, operating parameters, and choice of powder, coatings with high density and with bond strengths frequently exceeding 69 MPa (10,000 psi) can be achieved. Coating thicknesses are usually in the range of 0.05 to 0.50 mm (0.002 to 0.020 in.), but substantially thicker coatings can occasionally be used when necessary with some materials.

HVOF processes can produce coatings of virtually any metallic or cermet material and, for some HVOF processes, most ceramics. Those few HVOF systems that use acetylene as a fuel are necessary to apply the highest-melting-point ceramics such as zirconia or some carbides. HVOF coatings have primarily been used for wear resistance to date, but their field of applications is expanding.

Detonation Gun. In the detonation gun process, shown schematically in Fig. 9, a mixture of oxygen and acetylene, along with a pulse of powder, is introduced into a barrel and detonated using a spark. The high-temperature, high-pressure detonation wave moving down the barrel heats the powder particles to their melting points or above and accelerates them to a velocity of about 750 m/s. By changing the fuel gas and some other parameters, the Super D-Gun process achieves velocities of about 1000 m/s. This is a cyclic process, and after each detonation the barrel is purged with nitrogen and the process is repeated at up to about 10 times per second. Instead of a continuous swath of coating as in the other thermal spray processes, a circle of coating about 25 mm (1 in.) in diameter and a few micrometers thick is deposited with each detonation. A uniform coating thickness on the part is achieved by precisely overlapping the circles of coating in many layers. Typical coating thicknesses are in the range of 0.05 to 0.50 mm (0.002 to 0.02 in.), but thinner and much thicker coatings can be used.

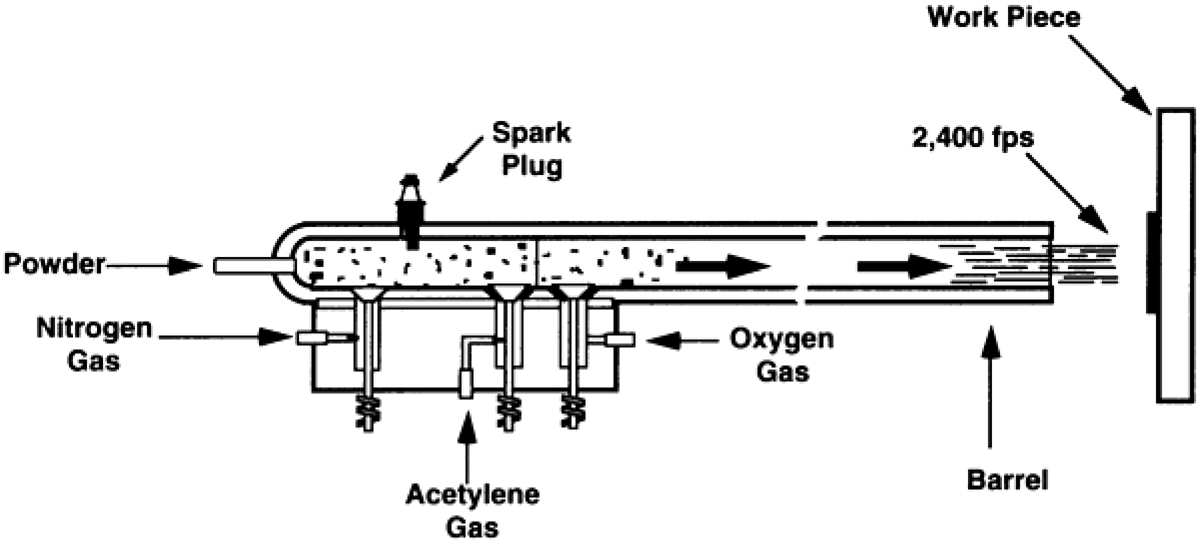


Fig. 9 Detonation gun process. Courtesy of Praxair Surface Technologies, Inc.

The detonation gun coatings have some of the highest bond strengths (usually exceeding the epoxy strength of the test, that is, 69 MPa) and lowest porosities (usually less than 2% when measured metallographically) of the thermal spray coatings. They have been the benchmark against which the other coatings have been measured for years. Careful control of the gases used generally results in little oxidation of metallics or carbides. The extremely high velocities and consequent kinetic energy of the particles in the Super D-Gun process allow most of the coatings to be deposited with residual compressive stress, rather than tensile stress as is typical of most of the other thermal spray coatings. This is particularly important relative to coating thickness limitations and the effect of the coating on the fatigue properties of the substrate.

Virtually all metallic, ceramic, and cermet materials can be deposited using detonation gun deposition. Detonation gun coatings are used extensively for wear and corrosion resistance as well as for many other types of applications. They are frequently specified for the most demanding applications, but often can be also the most economical choice because of their long life.

Process Comparison. A comparison of some of the characteristics of the major thermal spray processes is given in Table 2.

Table 2 Comparison of typical thermal spray processes

Process	Materials	Feed material	Surface preparation	Substrate temperature		Particle velocity	
				°C	°F	m/s	ft/s
Powder flame spray	Metallic, ceramic, and fusible coatings	Powder	Grit blasting or rough threading	105-160	225-325	65-130	200-400
Wire flame spray	Metallic coatings	Wire	Grit blasting or rough threading	95-135	200-275	230-295	700-900
Ceramic rod spray	Ceramic and cermet coatings	Rod	Grit blasting	95-135	200-275	260-360	800-1100
Two-wire electric-arc	Metallic coatings	Wire	Grit blasting or rough threading	50-120	125-250	240	800
Nontransferred arc plasma	Metallic, ceramic, plastics, and compounds	Powder	Grit blasting or rough threading	95-120	200-250	240-560	800-1850
High-velocity oxyfuel	Metallic, cermet, some ceramic	Powder	Grit blasting	95-150	225-300	100-550	325-1800
Detonation gun	Metallic, cermet, and ceramic	Powder	Grit blasting or as-machined	95-150	225-300	730-790	2400-2600
Super D-Gun	Metallic, cermet, and ceramic	Powder	Grit blasting or as-machined	95-150	225-300	850-1000	2800-3300

Transferred arc plasma	Metallic fusible coatings	Powder	Light grit blasting or chemical cleaning	Fuses base metal	Fuses base metal	490	1600

Ancillary Equipment. All thermal spray processes depend on the accurate control of gas flows, electric power, and powder, wire, or rod feedrates. A variety of equipment is available to do this, but it is essential for the best quality control of the coatings produced that all of this equipment be accurately calibrated, not only when it is initially installed, but also on a periodic basis thereafter. In addition, all of the plumbing for gases and water cooling, both internal to the torch or gun and external, must be checked to ensure that it is leak-tight.

Computer control of the more advanced thermal spray processes is being developed. On-line monitoring with closed-loop feedback control of electrical power, gas flows, cooling water flow and temperature, and powder feed rates are all possible. Although a variety of real-time coating thickness measurement techniques have been evaluated, most have been unsuccessful. The best technique currently seems to be that of accurate, reproducible deposition rate.

While some thermal spray devices are handheld, the only way to ensure uniform deposits is to automate the coating process to accurately control the rate of traverse of the gun or torch relative to the part being coated. This not only provides a uniform deposition of coating mass per unit area per unit of time, but also provides an accurate overlap between passes and uniform thermal input to the part. (Obviously this control is only meaningful if it is coupled with a uniform spray rate, which in turn requires uniform material flow and power to the torch or gun.) One of the simplest and most commonly used methods of automation for cylindrical parts is to rotate the part in a lathe-type machine and traverse the torch on what would correspond to the tool post. Small parts can be mounted on a circular plate and rotated on the lathe as an annular plate. Large, flat parts can be coated using a traversing two-axis machine. More complex shapes can be coated using robotics.

Surface Preparation

To ensure adequate bonding of thermal spray coatings, it is critical that a substrate be properly prepared. Surfaces must be clean, and usually substrates must be roughened after cleaning by grit blasting or some other means. Of course, the surface must remain uncontaminated by lubricants from handling equipment or body oils from hands and arms after it is prepared. It is recommended that the prepared surface be coated as soon as possible after preparation to prevent the possibility of contamination or surface oxidation.

Cleaning and Degreasing. Rust or other corrosion products; oils, grease, or other lubricants; paint; or other surface contaminants must be removed before coating deposition is begun. They can be removed by scraping, wire brushing, machining, grit blasting, or chemical action. Care should be taken not to embed scale and the like in the surface when trying to remove it, particularly when using grit blasting. Solvent degreasing has been the most common method for removal of lubricants and body oils, most conveniently with vapor degreasers. Large parts, and parts with attached hardware that may be damaged by vapor degreasing, should be degreased manually using the least hazardous material available. All solvents should be used only in well-ventilated areas, by properly protected personnel who are trained in their use and who follow local regulations for the use, care, and handling of solvents. More recently there has been a trend toward the use of aqueous detergents and alkaline cleaners, sometimes with ultrasonic agitation, to avoid the hazards and environmental concerns of organic solvents. Additional information is available in the Section "Surface Cleaning" in this Volume.

Surface Roughening. Three methods of surface roughening for thermal spray are widely used: rough threading, grit blasting, and a combination of rough threading followed by grit blasting. Rough threading is generally used for cylindrical surfaces and with thick flame sprayed coatings. The part to be prepared is mounted in a lathe and a single thread cut is taken. Tools for this purpose have a 60° to 70° point with a slight negative back rake. Screw feeds are approximately 0.80 to 1.25 mm (0.032 to 0.050 in.) or 0.78 to 1.26 threads/mm (20 to 32 threads/in.). The depth of the cut should vary with the screw feed and the required coating thickness. This technique is obviously limited to substrate sections thick enough to support the machining without significantly reducing its strength. It is most frequently used with flame sprayed coatings and is not recommended for thin coatings. Higher bond strengths are obtained when threading is followed by grit blasting. When the use of cutting fluid is necessary for threading, the part must be degreased before grit blasting or coating.

Grit blasting equipment used for thermal spray should not be used for other purposes, because dirt, paint, and lubricants contaminating the grit can be redeposited on the grit blasted surfaces. The grit should be continuously reclassified to remove fines. The air supply to the grit blast equipment must be clean and dry (including oil and particle filtration).

Aluminum oxide and chilled iron are the most widely used abrasive grits for thermal spray surface preparation. However, sand, crushed steel, and silicon carbide are also used in some situations. Sand is commonly used on large exterior structures such as bridges, towers, and piping where recovery of the grit is impractical. Crushed steel grit, obtained commercially in hardnesses to 65 HRC, is used in preparing some steels. Silicon carbide is used for some special applications (e.g., for very hard substrates or to minimize contamination), but it is relatively expensive, breaks down quickly, and tends to embed in softer substrates.

Consideration should be given to the substrate material in the selection of grit type. Traces of residual grit may adversely affect some coatings. Chemical compatibility in the finished coating system must be considered. Alumina, sand, and especially silicon carbide may embed in softer metals such as aluminum, copper, and their alloys. For these metals, lower air pressures are recommended to minimize embedding. Chilled iron or crushed steel should be used in preparing surfaces to be flame sprayed and fused. Alumina, silica, or silicon carbide may inhibit bonding of some of these coatings.

Practical grit size ranges are -10/+30 mesh, -14/+40 mesh, and -30/+80 mesh. Surface roughness is primarily the result of grit particle size, so the selection of the grit size is determined, in part, by the roughness required for adequate bonding and may be limited by coating thickness. Table 3 gives general recommendations for grit size selection. Surface roughness can also be varied slightly by air pressure. This factor should be considered on an individual basis for each combination of grit size, type, and substrate material. Grit blasting air pressure varies from 210 to 620 kPa (30 to 90 psi), with standoff or working distances of 50 to 150 mm (2 to 6 in.). Grit blast nozzle openings are generally 6 to 10 mm (0.25 to 0.375 in.) in diameter. The grit blasting angle to the substrate should be about 90°. Excessive grit blasting should be avoided to minimize grit inclusion in the surface.

Table 3 Recommended grit sizes for preparation of surfaces to be thermal spray coated

Roughness	**Grit size, mesh**	**Sieve openings**		**Applications**
		mm	**in.**	
Coarse	-10/+30	2.007/0.610	0.079/0.024	For coatings exceeding 0.25 mm (0.010 in.) and best adherence
Medium	-14/+40	1.422/0.432	0.056/0.017	For fair adherence and smoother finishes of coatings less than 0.25 mm (0.010 in.) thick
Fine	-30/+80	0.610/0.175	0.024/0.007	For smoothest finishes on coatings less than 0.25 mm (0.010 in.) thick to be used

The substrate should be cleaned following grit blasting to remove residual dust. Clean, dry air may be used. Again, it is very important that the surface remain uncontaminated by lubricants from handling equipment or body oils from hands and arms. It is recommended that the prepared surface be coated as soon as possible after preparation to prevent surface oxidation or contamination.

Finishing Treatment

Sealing. Thermal spray coatings usually have a structure with inherent porosity that ranges from less than 2 to more than 15 vol%, depending on the process by which the coating is deposited and the material sprayed. At least some of this porosity is interconnected. In many applications, coatings are exposed to corrosive fluids (liquids or gases) or hydraulic fluids that can infiltrate the pores, resulting in fluid leakage or corrosion throughout the coating or of the base material. These conditions can contribute to the premature failure of the coating. Many such applications, therefore, require the coating to be sealed before finishing. Sealing a coating may also help to reduce particle pullout from the surface during finishing for coatings with low cohesive strength.

To ensure as complete a sealing of the coating as possible, it is necessary to apply the sealant material as soon after coating as possible and prior to surface finishing. Sealant materials such as waxes, epoxies, phenolics, and inorganics are readily available and easily applied. The wax sealants are useful in preventing infiltration of liquids at low service temperatures. Resin-based sealants may be effective at temperatures up to about 260 °C (500 °F). Some silicone-based sealants have been reported to provide effective protection in salt spray tests conducted in accordance with military standards up to 480 °C (900 °F). Epoxy and phenolic sealants are usually more effective on coatings with higher porosity within their limits of stability (up to about 300 °C, or 570 °F).

One of the most effective methods of sealing coating porosity is vacuum impregnation. This method will usually fill all interconnected pores open to the exterior surface. To vacuum impregnate, the part is immersed in the sealant and placed in a vacuum chamber, and a soft vacuum is drawn. When the vacuum is released, air pressure forces the sealant into the pores. Most applications do not require this procedure, however. Low-viscosity anaerobic sealers may also be particularly penetrating. The depth of penetration of some sealants may exceed 1.8 mm (0.070 in.). Regardless of the method or type of sealant used, pores or interconnected channels that are not connected to the exterior surface cannot be sealed and machining or wear in service may open these with consequent loss of corrosion protection.

Coating Finishing. Although thermal spray coatings are used with their surfaces in the as-deposited condition for some applications, these surfaces are too rough for most service conditions. Therefore they are usually finished by methods such as grinding, lapping, polishing, machining, abrasive brushing, or vibratory finishing. Although the techniques are common to those used for finishing solid metallics and ceramics, great care must be taken not to damage the coatings, causing excessive surface porosity due to pullout of coating particles or cracking due to thermal stresses. The ultimate surface finish that can be achieved with a thermal spray coating is a function not only of its composition, but also of the deposition parameters used to produce it, because they are largely responsible for the amount and size of the true porosity in the coating and the cohesive strength or particle-to-particle bonding within the coating. The best finish that can be achieved may vary, therefore, from a matte surface with a roughness of about 1 μm (40 μin.) R_a and pits exceeding 0.05 mm (0.002 in.) in diameter for a flame-sprayed coating to a virtually pit-free mirror finish with a roughness of less than 0.025 μm (1 μin.) R_a for some very-high-velocity coatings.

If a coating is to be sealed, the sealing should be done before any finishing operation. It is extremely difficult to remove finishing fluids and debris from an unsealed surface, and these will interfere with the sealing. Sealing may also help to prevent the embedment of finishing debris in a surface, which would cause abrasive wear in service.

Some of the softer metallic coatings can be machined with single-point high-speed tool steels. Better surface finishes can be achieved with carbide or coated carbide tools. Table 4 includes typical parameters for machining some classes of metallic coatings. Usually, lower infeeds are used than with wrought materials. Figure 10 shows the configuration of typical carbide and steel tools. Burnishing is occasionally used with soft materials such as tin, zinc, and babbitt to produce a smooth, dense bearing surface.

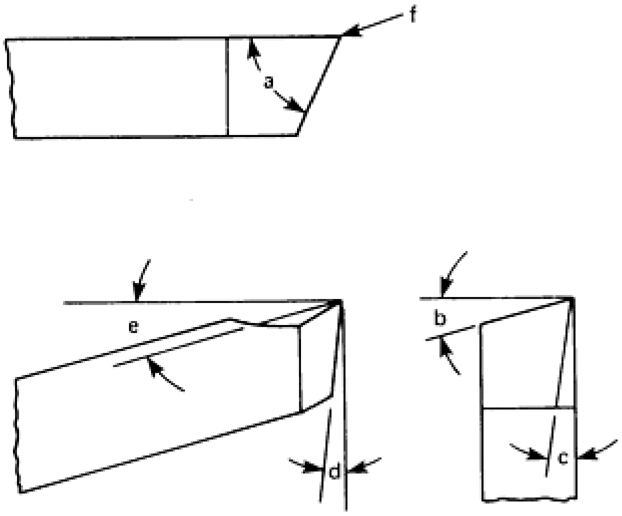
Table 4 Typical ranges of speeds and feeds used in machining thermal sprayed metal coatings

Coating metal	High-speed steel tool				Carbide tool[a]			
	Speed		Feed		Speed		Feed	
	m/s	sfm	mm/rev	in./rev	m/s	sfm	mm/rev	in./rev
Steels								
Low-carbon, medium-carbon, low-alloy	0.25-0.50	50-100	0.075-0.125	0.003-0.005	0.25-0.50	50-100	0.075-0.125	0.003-0.005
High-carbon, stainless	. . .	. . .	. . .	. . .	0.15-0.200	30-40	0.075-0.100	0.003-0.004

Nonferrous metals								
Brass, bronze, nickel, copper, Monel	0.50-0.75	100-150	0.075-0.125	0.003-0.005	1.25-1.80	250-350	0.050-0.150	0.002-0.006
Lead, tin, zinc, aluminum, babbitt	0.75-1.00	150-200	0.075-0.175	0.003-0.007	1.25-1.80(b)	250-350(b)	0.050-0.100	0.002-0.004(b)

(a) Composition: 6% Co, 94% WC.

(b) Aluminum only



Dimension	Carbide	High-speed metal
a	65-90°	80°
b	0°	0 to 15°
c	7°	10°
d	7° max	7° max
e	0-8° max	15° max
f	0.79375 mm	0762-1.016 mm

	(0.03125 in.)	(0.030-0.040 in.)

Fig. 10 Recommended shapes for carbide and high-speed steel cutting tools used in machining sprayed metal coatings

Cermet and ceramic coatings require grinding, and many metallic coatings can be more effectively ground than single-point machined. Some coatings can be ground with oxide or silicon carbide wheels, but cubic boron nitride or diamond wheels may be necessary for some of the hardest coatings, and they are frequently more cost-effective and produce better finishes for many other coatings. Specific grinding wheel selection is important and varies with the coating composition and type. It is probably best to consult with wheel manufacturers for specific coatings. Some guidelines for diamond grinding:

1. Check diamond wheel specifications. (a) Use only 100 concentration. (b) Use only resinoid bond.
2. Make sure your equipment is in good mechanical condition. (a) Machine spindle must run true. (b) Backup plate must be square to the spindle. (c) Gibs and ways must be tight and true.
3. Balance and true the diamond wheel on its own mount--0.005 mm (0.0002 in.) maximum runout.
4. Check peripheral wheel speed--25 to 33 m/s (5000 to 6500 sfm).
5. Use a flood coolant--water plus 1 to 2% water-soluble oil of neutral pH. (a) Direct coolant toward point of contact of the wheel and the workpiece. (b) Filter the coolant.
6. Before grinding each part, clean wheel with minimum use of a silicon carbide stick.
7. Maintain proper infeeds and crossfeeds. (a) Do not exceed 0.01 mm (0.0005 in.) infeed per pass. (b) Do not exceed 2.03 mm (0.080 in.) crossfeed per pass on revolution.
8. Never spark out--stop grinding after last pass.
9. Maintain a free-cutting wheel by frequent cleaning with a silicon carbide stick.
10. Clean parts after grinding. (a) Rinse in clean water, then dry. (b) Apply a neutral-pH rust inhibitor to prevent atmospheric corrosion.
11. Visually compare the part at 50× with a control sample of known quality.

Regardless of the type of grinding wheel used, the wheel should be dressed frequently enough, and operating parameters should be chosen, to ensure clean cutting of the coating. Sparkout passes (passes with low contact pressure run until virtually no contact is being made) should never be used. The smeared material created by such a procedure can be easily dislodged in service and cause abrasive wear and other problems.

If grinding does not produce a sufficiently smooth surface, it may be necessary to lap the coating after grinding. Again, it is advisable to consult the manufacturers of lapping materials for specific recommendations. Some guidelines:

1. Use a hard lap.
2. Use a serrated lap.
3. Use recommended diamond abrasives--Bureau of Standards No. 1, 3, 6, or 9.
4. Embed the diamond firmly into the lap.
5. Use a thin lubricant such as mineral spirits.
6. Maintain lapping pressures of 0.14 to 0.17 MPa (20 to 25 psi) when possible.
7. Maintain low lapping speeds of 0.5 to 1.5 m/s (100 to 300 sfm).
8. Recharge the lap only when lapping time increases 50% or more.
9. Clean parts after grinding and between changes to different-grade diamond laps--use ultrasonic cleaning if possible.
10. Visually compare the part at 50× with a control sample of known quality.

In addition to the traditional finishing techniques discussed above, a variety of other methods have been developed, particularly for nondimensional finishing. These include various abrasive brushes, belt grinding, "super" finishing, peening, and vibratory techniques. The use of nondimensional finishing is usually possible only when the dimensional specifications for the part are very loose, or when the part can be precisely and accurately preground and the deposition thickness and other characteristics such as waviness can be tightly controlled.

Coating Repair. The repair of thermal spray coatings by coating over service-worn or in-process damaged coatings is not generally recommended, even if the predeposited coating is reference ground, cleaned, and grit blasted. Adequate bond strength between the coating layers is seldom achieved, and there are no reliable nondestructive test techniques currently available to verify an adequately bonded interface. Therefore, the preferred procedure is to strip the existing coating and apply a completely new coating. Note that when applying a multilayered coating, it is best to apply each new layer over the as-deposited surface of the previous layer, not to grind and grit blast between layers.

Quality Assurance

There are few, if any, nondestructive evaluations that can be performed on a final coating, so the assurance of the quality of thermal spray coatings is more dependent on process control than on inspection of the final coating. This implies, of course, that the equipment used must be accurately and precisely produced and assembled, that all gages, flow meters, and the like must be calibrated, that the powders or other feed-stocks must be tightly controlled, and that standard procedures and operating parameters must be developed and followed for each coating. To ensure that the process is in control, it is common practice to coat a small sample using a standard set of parameters (standoff, traverse rate, angle of deposition, etc.) for metallographic examination of the coating before coating a part. The cross section of the coating sample is compared with standards to ensure that its microstructure, and usually its microhardness, are within acceptable ranges.

It should be kept in mind that the microstructure, hardness, and other properties of the coating on a small metallographic sample may not be the same as those of the coating on a part because of differences in standoff, angle of impingement, masking effects, cooling, and so on. Thus the evaluation of the coating on the metallographic sample only ensures that the process is in control. However, this, in turn, should ensure that the coating on the part will perform as it has in the past on the same part in the same environment, if the other deposition parameters, such as setup, traverse speed, and cooling, are unchanged.

Other features of a coating that must be controlled include finished surface characteristics and part dimensions. Standard techniques are adequate for these purposes. There is growing recognition that the average roughness of a surface may not be an adequate characterization of its fitness for service, and that other parameters, such as bearing area, peak-to-valley, skewness, and kurtosis, may need to be specified. Areas of coating coverage, including areas of optional overspray, must be specified and controlled in addition to dimensions such as diameters or thicknesses.

Metallography is usually done on cross sections of small samples coated under standard setup conditions of standoff, angle of deposition, traverse rate, and so on. These samples, if appropriately sized, may be mounted for examination directly, or, if too large, sectioned using abrasive cutoff saws. Some recommendations for cutting are found in Table 5. Standard mounting and polishing techniques may be used, but special precautions should be taken to ensure minimal damage to the coatings and as accurate and reproducible a representation of the structure as possible. It is fairly easy to induce cracking and pullout of the coating using overly aggressive cutting, grinding, and polishing techniques. It is also very important to minimize edge rounding of the coating, because the coating being examined is usually only about 0.25 mm (0.010 in.) thick. The major manufacturers of metallographic consumables and equipment have taken an interest in the metallography of thermal spray coatings in recent years and can provide useful recommendations for mounting and polishing. A substantial amount of training and skill is necessary to be able to grind and polish thermal spray coatings properly and reproducibly by hand. It is therefore recommended that automated polishing equipment be used following procedures established for each coating. A few guidelines are listed in Tables 6, 7, and 8.

Table 5 Guidelines for abrasive cutting of thermal spray coatings

Parameter	Notes
Wheel selection	

Abrasive	
Al_2O_3	To cut ferrous substrates
SiC	To cut nonferrous and ceramic
Diamond	Fine, precise cuts on small samples
Bond	
Rubber	General use, long life
Resin	Dry cutting
Combination	Wet cutting of hard materials
Grit size	
Coarse	Rough cuts, fast
Fine	Precise cuts, slow
Fixturing	
Direction of cut	Coating in compression
Clamps	Both sides of cut
Blocking	Wooden to protect coating
Coolant	Flood if possible
Cutting speed and pressure	Adjusted to prevent heating of part

Table 6 Typical metallographic preparation procedure for metallic and cermet thermal spray coatings using silicon carbide grinding paper

Number of specimens, 1-6; specimen size, 32 mm ($1\frac{1}{4}$ in.); cutting equipment, universal cutoff saw with an Al_2O_3 thin wheel; mounting equipment, vacuum impregnation unit; mounting resin, fast-curing epoxy cold mount; holder, 32 mm ($1\frac{1}{4}$ in.) plate; automated grinding-polishing machine

Process step	**Disk or cloth**	**Abrasive**	**Grit or grain size**	**Abrasive dosing**	**Speed, rpm**	**Load per specimen, N**	**Lubricant/ dosing**	**Time, s**
Grinding								
Planar grinding	Paper	SiC	220	. . .	150	25	Water	Until plane
Fine grinding								
Step 1	Paper	SiC	320	. . .	150	25	Water	30-45
Step 2	Paper	SiC	500	. . .	150	25	Water	30-45
Step 3	Paper	SiC	1200	. . .	150	25	Water	30-45
Polishing								
Diamond polishing	Hard polishing cloth	Spray diamond	3 µm	4	150	25	Low-viscosity alcohol-base lubricant/5	5-10 min
Final polishing	Soft, chemical-resistant cloth	Alumina polishing suspension	0.04 µm	10	150	10	. . .	30-60

Source: Struers

Table 7 Typical metallographic preparation procedure for metallic and cermet thermal spray coatings using an advanced diamond grinding format

Number of specimens, 1-6; specimen size, 32 mm ($1\frac{1}{4}$ in.); cutting equipment, universal cutoff saw with an Al_2O_3 thin wheel; mounting equipment, vacuum impregnation unit; mounting resin, fast-curing epoxy cold mount; holder, 32 mm ($1\frac{1}{4}$ in.) plate

Process step	**Disk or cloth**	**Abrasive**	**Grit or grain size**	**Abrasive dosing**	**Speed, rpm**	**Load per specimen, N**	**Lubricant/ dosing**	**Time, min**
Grinding								
Planar grinding	Paper	SiC	220	. . .	150	25	Water	Until plane

Fine grinding	Very hard polishing cloth	Spray diamond	9 µm	4	150	25	Alcohol-base lubricant/6	5
Polishing								
Diamond polishing	Hard polishing cloth	Spray diamond	3 µm	4	150	25	Low-viscosity alcohol-base lubricant/5	5-10
Final polishing	Soft, chemical-resistant cloth	Alumina polishing suspension	0.04 µm	10	150	10	. . .	$\frac{1}{2}$-1

Source: Struers

Table 8 Typical metallographic preparation procedure for tungsten carbide-cobalt thermal spray coatings

Specimens sectioned using a precision cutting saw with a diamond wafering blade and mounted using a pressure-cooled mounting press and edge-retention molding compound; specimen size 32 mm (1 $\frac{1}{4}$ in.); no etchant used after polishing

Process step	**Grinding/ polishing surface**	**Abrasive**	**Abrasive grain size, µm**	**Time min**	**Force per sample, lb**	**Speed, rpm**	**Relative rotation**	**Dispensing sequence**
Planar grinding	Very hard grinding platen	Diamond suspension	45	2 or until plane	5	240	Against	1 s spray on; 30 s spray off
Fine grinding								
Step 1	Medium-hard grinding platen	Diamond suspension	9	5	5	120	Same	1 s spray on; 30 s spray off
Step 2	Hard cloth	Diamond suspension	3	1.5	5	120	Same	1 s spray on; 30s spray off
Final polishing	Hard cloth	High-purity alumina-base mild attack polishing suspension	. . .	1.5	10	120	Against	. . .

Source: Buehler Ltd.

The microstructural features frequently examined include compositional phases, porosity, and oxide inclusions. These may be determined quantitatively by comparison with photographic standards or by standard metallographic techniques including point counting, line segment measurement, or optical electronic analysis techniques. Most of these analyses use light microscopes; however, scanning electron microscopes can be used if necessary.

Porosity is one of the more frequently specified parameters, but it is probably one of the most difficult to accurately determine metallographically. A distinction should always be made between absolute porosity and metallographically apparent porosity. Some porosity may be too small to be visible using light microscopy, or the amount of porosity on the surface may be more or less than the absolute bulk porosity because of pullout of coating or because polishing debris fills some real porosity. Thus, metallographic porosity standards or specifications can only have meaning if very reproducible grinding and polishing procedures are used.

The same considerations apply to other metallographic characterizations, although they may be somewhat less sensitive to preparation. The identification of the various phases present in a coating can be enhanced using standard etching techniques or optical enhancement, such as differential interference or polarized lighting. The use of advanced scanning electron microscopy techniques may minimize the need for these techniques.

Hardness Testing. Both surface and cross-sectional hardness measurements can be used for the quality control of coatings. If surface hardness measurements (e.g., Rockwell hardness measurements) are used, the thickness of the coating and the hardness of the substrate must be high enough to ensure that an accurate measurement is achieved. Microhardness measurements on cross sections are used more often than surface hardness measurements for the quality control of thermal spray coatings.

The guidelines of the ASTM recommended practices should be followed, regardless of the type of test used. The coating must be thick enough to support the indentation for the load chosen, and particular attention should be paid to the positioning of the indentations. Statistically valid procedures should be followed. These include calibration of the hardness tester, confirmation of the operator's skill using frequent measurement of standard test blocks, the proper placement of indentations, and an adequate number of indentations. All of these should be monitored using control charts and other statistical quality control tools. A greater number of measurements may be needed than with wrought materials because of the greater inhomogeneities in the microstructures of most thermal spray coatings.

Bond Strength Testing. A variety of tests have been developed to measure both the tensile and shear strength of thermal spray coatings. The most commonly used test is defined by ASTM C 633, "Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings," which measures the strength in tension perpendicular to the surface. In this test, a 25.4 mm (1 in.) diameter cylinder is coated on one end and then bonded to a mating cylinder, usually with epoxy. The couple is then pulled apart using a tensile testing machine. ASTM C 633 calls for a coating thickness of 0.45 mm (0.018 in.) to prevent penetration of the coating by the bonding agent. This may be necessary for some flame-sprayed coatings, but it is much thicker than necessary for the denser plasma, HVOF, or detonation gun coatings. A thickness of 0.25 mm (0.010 in.) is frequently used for the denser coatings, because it is closer to the thicknesses used in service and provides a more realistic measure of strength in light of the residual stresses that may be present in the coatings. The ASTM procedure should be referred to for dimensional and alignment requirements as well as specific preparation, coating, bonding, and testing procedures.

For the ASTM C 633 test to have practical meaning in a given application, the coated cylinder must be of the same or a very similar material and of the same hardness as the part, must be prepared in the same manner (e.g., grit blasted with the same grit at the same pressure and angle), and must be coated with the same deposition parameters (i.e., coated at the same angle, standoff, and traverse rate) as the part. This test is limited by the strength of the epoxy or other bonding agent used, currently a maximum of approximately 69 MPa (10 ksi). Most detonation gun coatings, many HVOF coatings, and a few plasma coatings exceed this, so the test is simply a proof test and not a measure of the actual bond or cohesive strength of the coating.

While a few lap shear and bend tests have been used to qualify coatings for specific applications, none is universally recognized. All of the known tests of this type have significant theoretical limitations, making interpretations of the results difficult. Because few applications place a coating in tension perpendicular to the surface, the value of the ASTM C 633 test is limited as well.

Health, Safety, and Environmental Concerns

There are some health, safety, and environmental concerns associated with thermal spray coating processes, as with most industrial processes. In general they are similar to those associated with welding processes. Obviously, all plant or laboratory, local, state, and federal government directives should be followed. None of the thermal spray processes should be attempted without proper training of all of the personnel involved and careful consideration of any hazards associated with the particular materials being used to prepare for or produce the coating. Proper care and maintenance of the equipment, including all gas and electric lines, will greatly reduce any hazards. In addition, design and procedure reviews for safety by qualified engineers are advisable. These should include the ancillary processes of surface preparation, part handling, and finishing as well as the coating process itself.

Dust and Fumes. All thermal spray processes produce dust and fumes, so operators must be protected and the dust and fumes collected. When possible, the coating process should be conducted in a cubicle equipped with ventilation and dust collection equipment and with the operators outside. Each thermal spray process has its own airflow requirement to provide adequate ventilation, and the equipment manufacturer should be able to provide guidelines. Nonetheless, dust monitors should be periodically used to ensure that the ventilation system is working properly. If the operators must be in the cubicle or the coating must be done in the open, the operators should wear respirators. It is no longer considered adequate to rely only on air flow away from the operator to provide adequate protection. The type of respirator used depends on the material being deposited. The effluent from the dust collection system should be periodically monitored to ensure compliance with all regulations.

Noise generated by thermal spray processes ranges from about 80 dB for some of the flame spray processes to over 120 dB for some of the HVOF processes, over 140 dB for some plasma spray processes, and to over 150 dB for the detonation gun processes. Individual ear protection is adequate for the former, but the latter must be operated in sound-reducing cubicles. Sound levels at the operator's position should be measured and compliance with all regulations ensured. In addition, all personnel in the vicinity of the spray operation should have their hearing checked periodically.

Light Radiation. The spectrum of light emitted by the thermal spray devices ranges from the far infrared to extreme ultraviolet. Adequate eye and skin protection must be used. Shade 5 lenses may be sufficient for some flame spray processes, but shade 12 is required for plasma spray and electric (wire) arc. Fire-retardant, closely woven fabrics should be worn to protect the skin from burns. Burns can be caused by heated particles bouncing from the substrate, hot gases, or light. Ultraviolet radiation will burn exposed skin and penetrate loosely woven fabrics, causing burns similar to a severe sunburn in minutes.

Coating Structures and Properties

Coating Microstructures. Thermal spray coatings consist of many layers of thin, overlapping, essentially lamellar particles, frequently called splats. Cross sections of several typical coatings are shown in Fig. 2, 11, 12, 13, and 14. Generally, the higher-particle-velocity coating processes produce the densest and better bonded coatings, both cohesively (splat-to-splat) and adhesively (coating-to-substrate). Metallographically estimated porosities for detonation gun coatings and some HVOF coatings are less than 2%, whereas most plasma sprayed coating porosities are in the range of 5 to 15%. The porosities of flame sprayed coatings may exceed 15%.

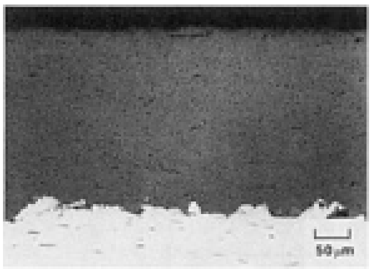


Fig. 11 Microstructure of plasma-sprayed chromium oxide. As-polished

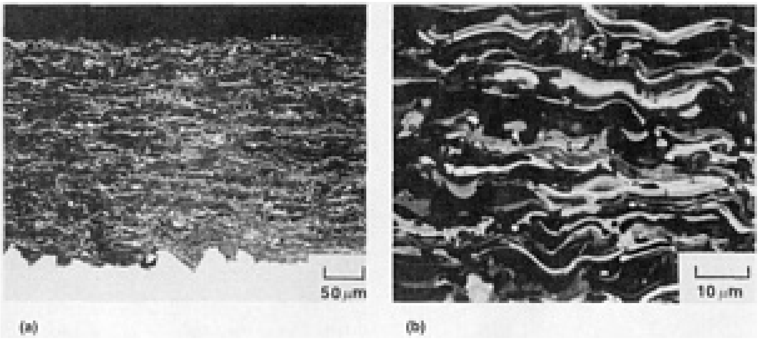


Fig. 12 Microstructure of detonation gun deposited alumina and titania. As-polished

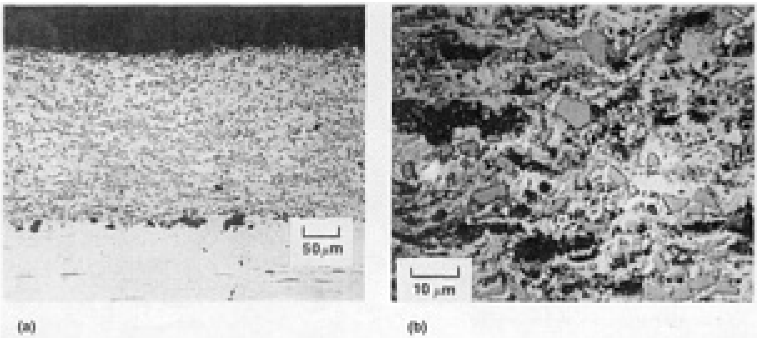


Fig. 13 Microstructure of a detonation gun deposited tungsten carbide/cobalt cermet coating. (a) As-polished. (b) Etched

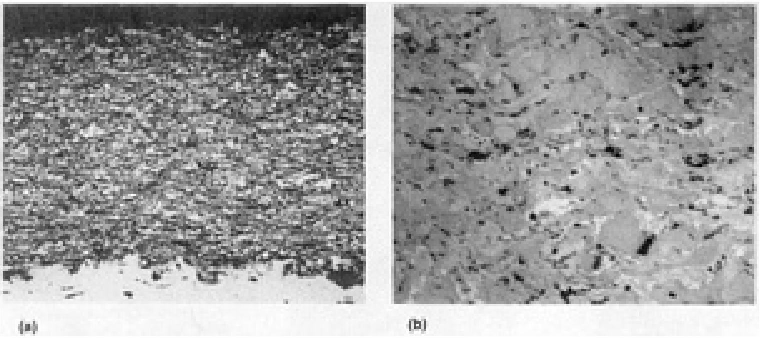


Fig. 14 Microstructure of a mechanically mixed chromium carbide/nickel chromium cermet coating. (a) As-polished.(b) Etched

The extent of oxidation that occurs during the deposition process is a function of the material being deposited, the method of deposition, and the specific deposition process. Oxidation may occur because of the oxidizing potential of the fuel-gas mixture in flame spraying, HVOF, or detonation gun deposition or because of air inspirated into the gas stream in plasma spraying or any of the other methods. Recall that the latter cause can be ameliorated by using inert-gas shrouds or low-pressure chambers with plasma spraying. Using carbon-rich gas mixtures with oxyfuel processes can cause carburization rather than oxidation with some metallic coatings. Metallic coatings are probably most susceptible to oxidation, but carbide coatings may suffer a substantial loss of carbon that is not particularly obvious in metallographic examination. Oxidation during deposition can lead to higher porosity and generally weaker coatings, and it is usually considered to be undesirable.

Most of the thermal spray processes lead to very rapid quenching of the particles on impact. Quench rates have been estimated to be 10^4 to 10^6 °C/s for ceramics and 10^6 to 10^8 °C/s for metallics. As a result, the materials deposited may be in thermodynamically metastable states, and the grains within the splats may be submicron-size or even amorphous. The metastable phases present may not have the expected characteristics, particularly corrosion characteristics, of the material, and this factor should be kept in mind in the selection of coating compositions.

The mechanical properties of thermal spray coatings are not well documented with the exception of their hardness and bond strength. These are discussed in the section "Quality Assurance" in this article. The sensitivity of the properties of the coatings to specific deposition parameters makes universal cataloging of properties by simple chemical composition and general process (e.g., WC-12Co by plasma spray) virtually meaningless. The situation is even more complex because the properties of coatings on test specimens may differ somewhat from those on parts because of differences in geometry and thermal conditions. Nonetheless, coatings made by competent suppliers using adequate quality control will be quite reproducible, and therefore the measurement of various mechanical properties of these standardized coatings may be very useful in the selection of coatings for specific applications. Properties that may be of value include the modulus of rupture, modulus of elasticity, and strain-to-fracture in addition to hardness. Examples of some of these are given in Table 9.

Table 9 Mechanical properties of representative plasma, detonation, and high-velocity combustion coatings

Parameter	**Type of coating Tungsten-carbide-cobalt**				**Alumina**	
Nominal composition, wt%	W-7Co-4C	W-9Co-5C	W-11Co-4C	W-14Co-4C	Al_2O_3	Al_2O_3
Thermal spray process	Detonation gun	High-velocity combustion	Plasma	Detonation gun	Detonation gun	Plasma
Rupture modulus, 10^3 psi[(a)]	72	. . .	30	120	22	17
Elastic modulus, 10^6 psi[(a)]	23	. . .	11	25	14	7.9
Hardness, kg/mm², HV_{300}	1300	1125	850	1075	>1000	>700
Bond strength, 10^3 psi[(c)]	>10,000[(b)]	>10,000[(b)]	>6500	>10,000	>10,000[(b)]	>6500

Source: Publication 1G191, National Association of Corrosion Engineers

(a) Compression of freestanding rings of coatings.

(b) Epoxy failure.

(c) ASTM C 633-89, "Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings," ASTM, 1989.

Any measurement or use of mechanical properties must take into account the anisotropic nature of the coating microstructure and hence its properties (i.e., the coating properties are different parallel to the surface than perpendicular to the surface because of the lamellar nature of the microstructure). Most mechanical properties are measured parallel to the surface, in part because it is easier to produce test specimens in this plane because the coatings are typically thin. Unfortunately, the major load in service is usually perpendicular to the surface. This does not, however, make measurements in the plane of the coating useless. It is frequently important to know, for example, how much strain can be imposed on a coating due to extension or deflection of the part without cracking the coating. Cracks in a coating may not only affect its performance, but also initiate cracks and fatigue failures in the part.

Uses of Thermal Spray Coatings

Wear Resistance. One of the most important uses of thermal spray coatings is for wear resistance. They are used to resist virtually all forms of wear, including abrasive, erosive, and adhesive, in virtually every type of industry. The materials used range from soft metals to hard metal alloys to carbide-based cermets to oxides. Generally, the wear resistance of the coatings increases with their density and cohesive strength, so the higher-velocity coatings such as HVOF and particularly detonation gun coatings provide the greatest wear resistance for a given composition.

A variety of laboratory tests have been developed to rank thermal spray coatings and compare them with other materials. Examples of abrasive and erosive wear data are shown in Tables 10 and 11. It should be kept in mind that laboratory tests can seldom duplicate service conditions. Therefore these tests should only be used to help select candidate coatings for evaluation in service. Only rarely, with good baseline data, can any precise prediction of wear life in service be made from laboratory data.

Table 10 Abrasive wear data for selected thermal spray coatings

Material	Type	Wear rate, mm^3/1000 rev
Carballoy 883	Sintered	1.2
WC-Co	Detonation gun	0.8
WC-Co	Plasma spray	16.0
WC-Co	Super D-Gun	0.7
WC-Co	High-velocity oxyfuel	0.9

ASTM G 65 dry sand/rubber wheel test, 50/70 mesh Ottawa silica, 200 rpm, 30 lb load, 3000-revolution test duration

Table 11 Erosive wear data for selected thermal spray coatings

Material	Type	Wear rate,μm/g
Carballoy 883	Sintered	0.04
WC-Co	Detonation gun	1.3
WC-Co	Plasma spray	4.6
AISI 1018 steel	Wrought	21

Silica-based erosion test; particle size, 15 μm; particle velocity, 139 m/s; particle flow, 5.5 g/min, ASTM Recommended Practice G 75

Friction Control. Thermal spray coatings are used in some applications to provide specific frictional characteristics to a surface, covering the full spectrum from low friction to high. Obviously, the surface topography is critical in these applications, and unique finishing techniques have been developed to provide the desired coefficient of friction without causing excessive wear or damage of the mating surface. The textile industry provides, as an example, applications covering the complete range of friction characteristics and surface topography to handle very abrasive synthetic fiber. Oxide coatings such as alumina are usually used with surfaces that vary from very smooth to nodular to quite rough, depending on the coefficient of friction required.

Corrosion Resistance. Flame sprayed aluminum and zinc coatings are frequently used for corrosion resistance on bridges, ships, and other structures. In this application, reliance is placed primarily on their anodic protection of the substrate. Other thermal spray coatings are used for their corrosion resistance, often coupled with their wear resistance, but the inherent porosity of the coatings must be taken into account and the coatings sealed, either by using an epoxy or other infiltrant or by sintering, as in the case of the M-Cr-Al-Y coatings. These aspects are discussed in the section "Processes" in this article.

Dimensional Restoration. Thermal spray coatings are often used to restore the dimensions of a worn part. On occasion, a coating with low residual stress and/or low cost is used to build up the worn area and then a thin, more wear-resistant coating is applied over it. In any use of thermal spray coatings for buildup, it should be kept in mind that the properties of the coating are probably far different than those of the substrate, and that the coating will not add any structural strength to the part. In fact, if care is not taken, the coating may degrade the fatigue strength of the part.

Thermal Applications. Plasma spray coatings, and to a more limited extent other thermal spray coatings, are used as thermal barriers. In particular, partially stabilized zirconia coatings are used on gas-turbine combustors, shrouds, and vanes and on internal combustion cylinders and valves to improve efficiency and reduce metal temperatures or cooling requirements. In other applications they may be used to dissipate heat as either surface conductors or thermal emitters. Because of their unique lamellar microstructure and porosity, the thermal conductivity of thermal spray coatings is usually anisotropic and significantly less than that of their wrought or sintered counterparts.

Electrical Applications. As with thermal properties, the electrical conductivity of thermal spray materials is anisotropic and is reduced compared to their wrought or sintered counterparts due to their lamellar microstructure and porosity. Metallic or conductive cermet coatings are, however, used as electrical conductors where wear resistance must be combined with electrical conductivity. Conversely, thermal spray oxide coatings are used as electrical insulators. In this application, it is usually important to seal the coating to prevent moisture, even from the air, from penetrating the coating and reducing its insulating capability. Thermal spray coatings have also been used to produce high-temperature thermocouples and strain gages. Electromagnetic or radio-frequency shielding can also be provided by flame or electric-arc sprayed layers of zinc, tin, or other metals.

Other Applications. A variety of other applications have been developed for thermal spray coatings, including coatings used as nuclear moderators, catalytic surfaces, and parting films for hot isostatic presses. Thermal spray materials can also be used to produce freestanding components such as rocket nozzles, crucibles, and molds.

Chemical Vapor Deposition of Nonsemiconductor Materials

Hugh O. Pierson, Consultant

Introduction

CHEMICAL VAPOR DEPOSITION (CVD) is a versatile process that can be used to deposit layers of nearly any metal, as well as nonmetallic elements, such as carbon and silicon (Ref 1). Compounds such as carbides, nitrides, oxides, intermetallics, and many others also can be deposited. This technology has become very important in these applications:

- Semiconductor and other electronic component manufacturing processes
- Coatings on tools, bearings, and other wear-resistant parts
- Optical, opto-electronic, and corrosion-resisting products
- Monolithic parts, ultrafine powders, and high-strength fibers

This article emphasizes the CVD of hard, tribological, and high-temperature coatings, as well as free-standing structures.

Reference

1. H.O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, 1992

Principles of Chemical Vapor Deposition

The CVD process can be defined as the deposition of a solid on a heated surface via a chemical reaction from the vapor or gas phase. It belongs to the class of vapor-transport processes that are atomistic in nature, that is, the deposition species are atoms or molecules, or a combination thereof. Other vapor-transport processes include the physical vapor deposition (PVD) techniques, such as vacuum, evaporation, sputtering, ion plating, ion-beam assist, arc, and ion implantation, which are described in other articles in this Section of the Volume, as well as in Ref 2. Unlike CVD processes, the PVD processes do not rely on a chemical reaction in the gas phase to form the product that will be deposited.

Although CVD competes directly with PVD, an important recent trend is the merging of these two techniques. For instance, CVD now makes extensive use of plasma (a physical phenomenon), whereas PVD is often carried out in a chemical environment (reactive evaporation and reactive sputtering). Likewise, CVD and PVD operations are often processed in the same integrated equipment in a sequential fashion without breaking the vacuum (thus minimizing contamination), and the distinction between the two basic processes becomes blurred (Ref 3).

CVD Reactions. The numerous chemical reactions used in CVD include thermal decomposition (pyrolysis), reduction, hydrolysis, disproportionation, oxidation, carburization, and nitridation. These reactions can take place either singly or in combination. Descriptions of certain reactions are provided in the section "Typical CVD Materials and Reactions" in this article.

A CVD reaction is controlled by these factors:

- Thermodynamic, mass transport, and kinetic considerations
- Chemistry of the reaction
- Processing parameters of temperature, pressure, and chemical activity

In most cases, a theoretical analysis of these factors is a recommended preliminary step. Such an analysis can predict the reaction mechanism (i.e., the path of the reaction as it forms the deposit), the resulting composition of the deposit (i.e., its stoichiometry), and the structure of the deposit (i.e., the geometric arrangement of its atoms). This analysis may then provide guidelines for choosing the appropriate CVD parameters, thereby avoiding a strictly empirical approach to the desired product. Computer programs are available to facilitate these studies (Ref 4, 5).

However, when a reaction is kinetically controlled, and when only one single condensed phase can form, the theoretical thermodynamic modeling of a CVD reaction has very limited applicability. It is becoming more evident that a useful modeling approach requires an examination of the chemical equilibrium aspects of the reaction, as well as the fluid dynamic aspects of the reactor system, to improve process efficiency. Many computational fluid-dynamic codes are now being used to design reactors that maximize the possible yields from a given reaction. These codes account for the reaction rate theory, thermodynamic equilibrium aspects, and the constraints imposed by the design of the deposition chamber. This means that one can design a complete CVD reactor on a computer workstation, change parameters to model fluid flow, velocity, and temperature profiles, and optimize deposition rates, *instead of* building the equipment and then using trial-and-error methods to optimize the process.

References cited in this section

2. K.K. Shuegraf, Ed., *Handbook of Thin Film Deposition Processes and Techniques,* Noyes Publications, 1988
3. M.E. Bader et al., Integrated Processing Equipment, *Solid State Technology,* May 1990, p 149-154
4. Outokumpu AT Computer Program, Outokumpu Research OY PO 60 SF 28101, Pori, Finland, 1992

5. T.M. Besmann, "SOLGASMIX-PV: A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems," TM-5775, Oak Ridge National Laboratory, 1977

CVD Processes and Equipment

Like all chemical reactions, CVD reactions require activation energy to proceed. This energy can be provided, in practice, by several methods. Thermal activation is the original process, and it is still the major method for the chemical vapor deposition of metals and ceramics.

In thermal CVD, the reaction is activated by high temperature, generally above 900 °C (1650 °F) (Ref 6). A typical thermal CVD apparatus consists of three interrelated components: the reactant-gas supply system; the deposition chamber, or reactor; and the exhaust system (Fig. 1). A fourth component that is often used is a closed-loop process-control monitor, which is now available in a PC-based design.

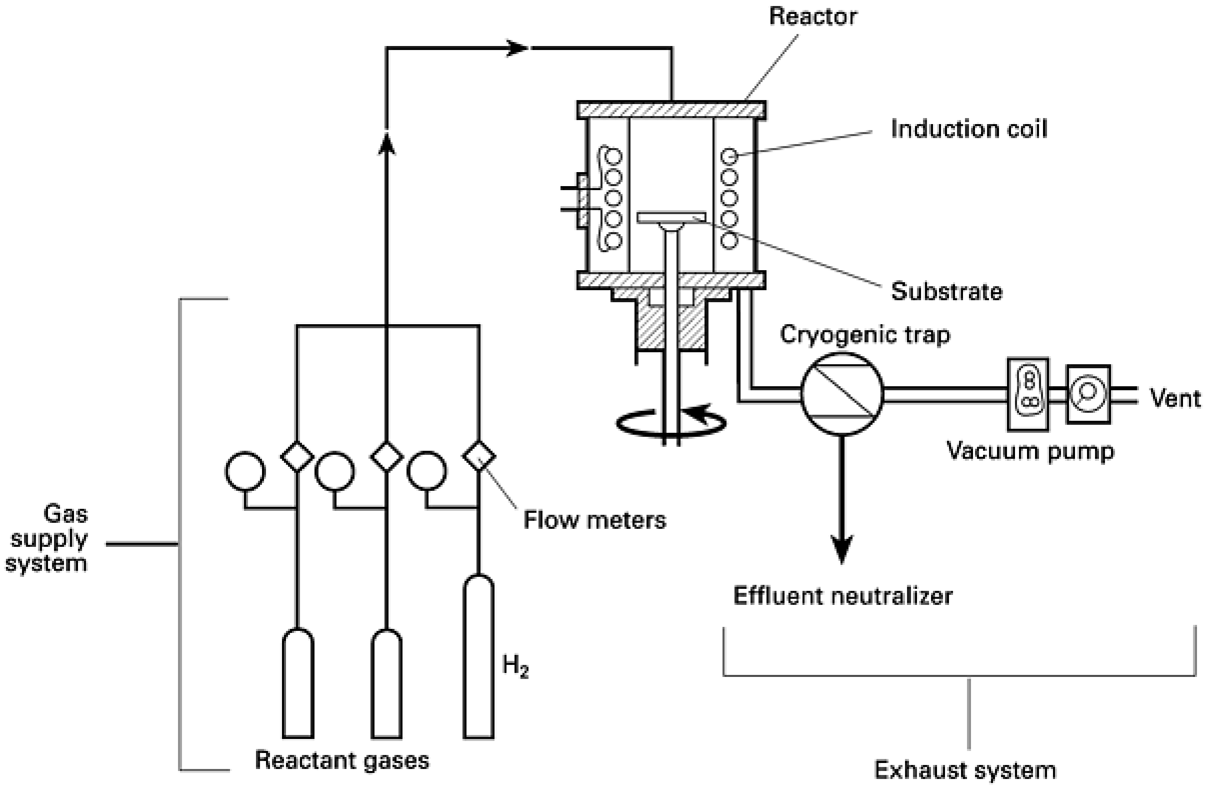


Fig. 1 Thermal CVD reactor

Plasma CVD is a method that operates at lower temperatures than thermal CVD. The reaction is activated by a plasma at temperatures between 300 and 700 °C (570 to 1290 °F). The process was developed because the high deposition temperature of thermal CVD precludes the use of many substrates, such as low-melting-point metals; materials that undergo solid-state phase transformation over the range of deposition temperatures; polymers; and others. In addition, large mismatches in the thermal expansion of a substrate and a coating will generate stresses that can lead to cracking and delamination or spalling during cooling (Ref 7, 8). In the plasma CVD process, the stress that is due to thermal-expansion mismatch is reduced, and temperature-sensitive substrates can be more readily coated. Table 1 compares the deposition temperatures for thermal and plasma CVD for several commercially important coatings.

Table 1 Typical deposition temperatures for thermal and plasma chemical vapor deposition

Material	Deposition temperature

	Thermal CVD		**Plasma CVD**	
	°C	**°F**	**°C**	**°F**
Silicon nitride	900	1650	300	570
Silicon dioxide	800-1100	1470-2010	300	570
Titanium carbide	900-1100	1650-2010	500	930
Titanium nitride	900-1100	1650-2010	500	930
Tungsten carbide	1000	1830	325-525	615-975

Plasma CVD was initially developed in the 1960s for use in the semiconductor industry, but applications have been expanding ever since and are now common in the nonsemiconductor applications discussed in this article. Most plasma CVD systems use radio frequency (RF) with operating frequencies of 450 KHz or 113.56 MHz. A typical RF reactor with parallel electrodes is shown in Fig. 2. Microwave glow discharge is also used at a standard frequency of 2.45 GHz.

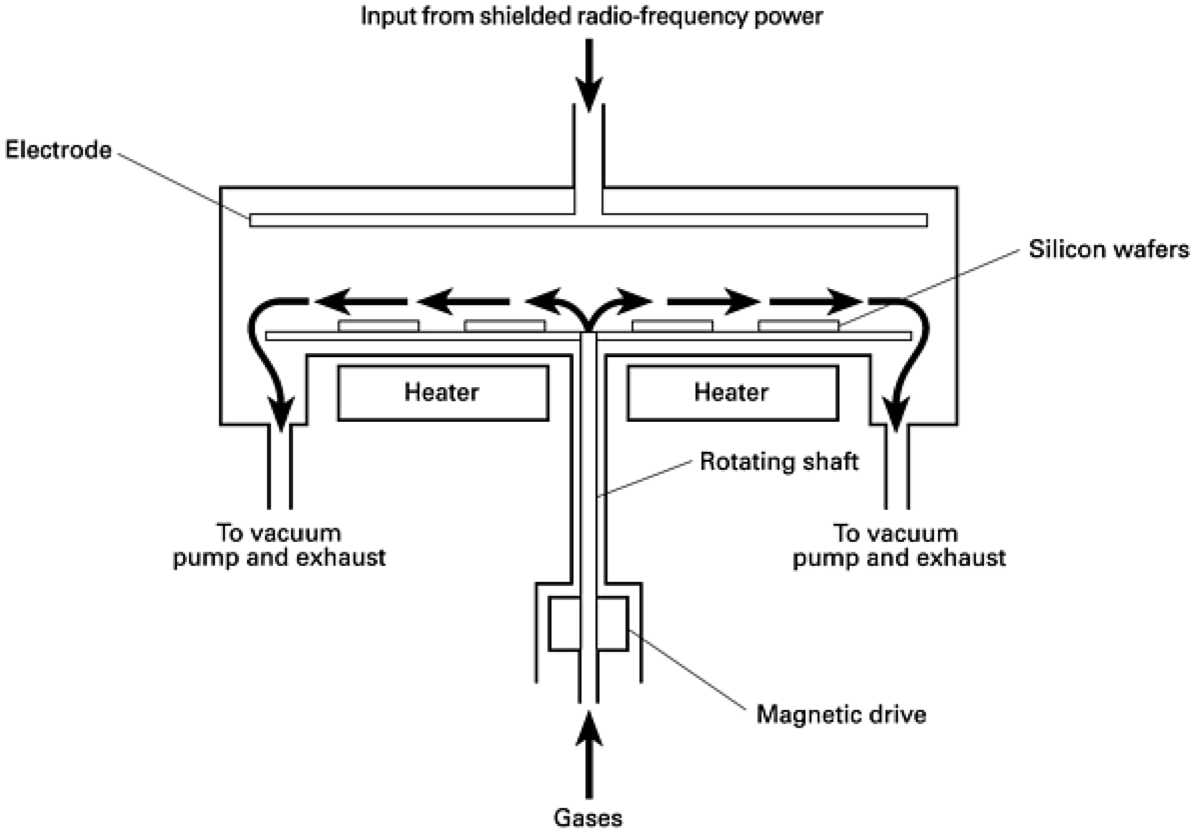


Fig. 2 Radio-frequency plasma CVD reactor configured for deposition on silicon wafers

A recent and promising development in the production of plasma is based on electron cyclotron resonance (ECR) and the proper combination of an electric field and a magnetic field (Ref 9). Cyclotron resonance is achieved when the frequency of the alternating electric field matches the natural frequency of the electrons orbiting the lines of force of the magnetic field. An ECR plasma reactor is shown schematically in Fig. 3. ECR and other plasma techniques are used extensively in semiconductor production but so far have remained mostly experimental in other areas of application (Ref 10).

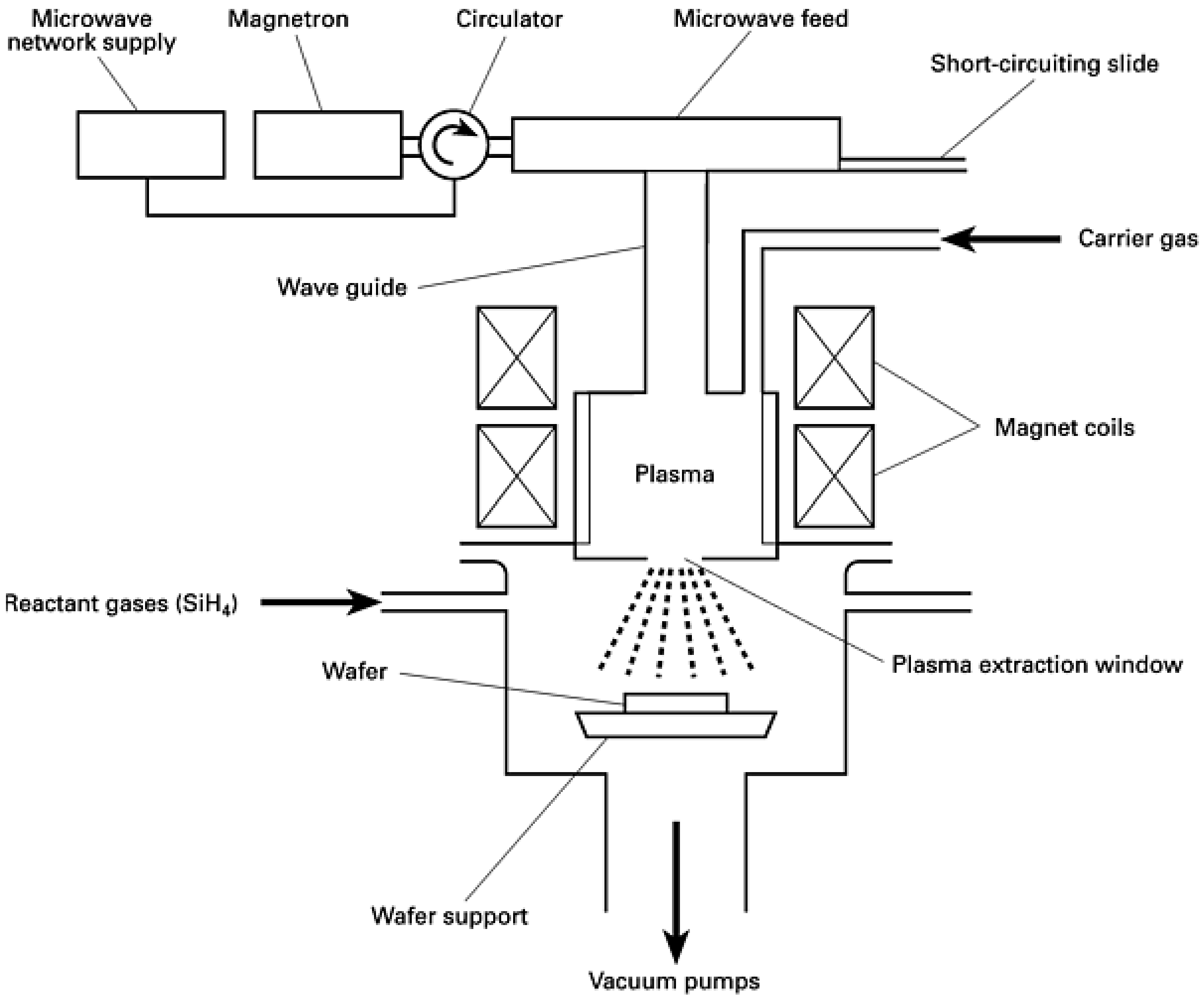


Fig. 3 Microwave/electron cyclotron resonance (ECR) plasma CVD reactor

Laser CVD. Two other activation methods based on a laser have recently been developed (Ref 8, 11). As of the mid-1990s, the thermal-laser and photo-laser CVD methods are still essentially in the experimental stage, but have great potential, at least in specialized areas. The materials that can be deposited include oxides, nitrides, tungsten, aluminum, and others.

Thermal-laser CVD (Ref 12), or laser pyrolysis, occurs when the laser thermal energy contacts and, thereby, heats an absorbing substrate. The wavelength of the laser can be such that little or no energy is absorbed by gas molecules. Because the substrate is locally heated, deposition is restricted to the heated area. Figure 4 illustrates the deposition of a thin stripe by moving a laser beam linearly across the substrate.

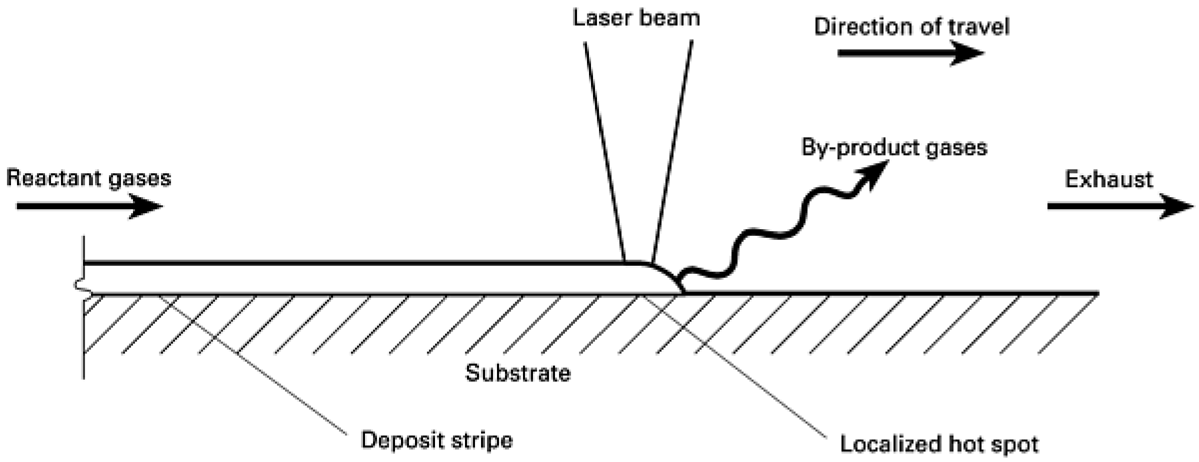


Fig. 4 Thermal-laser CVD growth mechanism

In photo-laser CVD, the chemical reaction is induced by the action of light, specifically ultraviolet (UV) radiation, which has sufficient photon energy to break the chemical bonds in the reactant molecules. In many cases, these molecules have a broad electronic absorption band and are readily excited by UV radiation. Although UV lamps have been used, more energy can be obtained from UV lasers, such as the excimer (e.g., excited dimer) lasers with photon energies ranging from 3.4 eV (XeFlaser) to 6.4 eV (ArFlaser). A typical photo-laser CVD system is shown in Fig. 5.

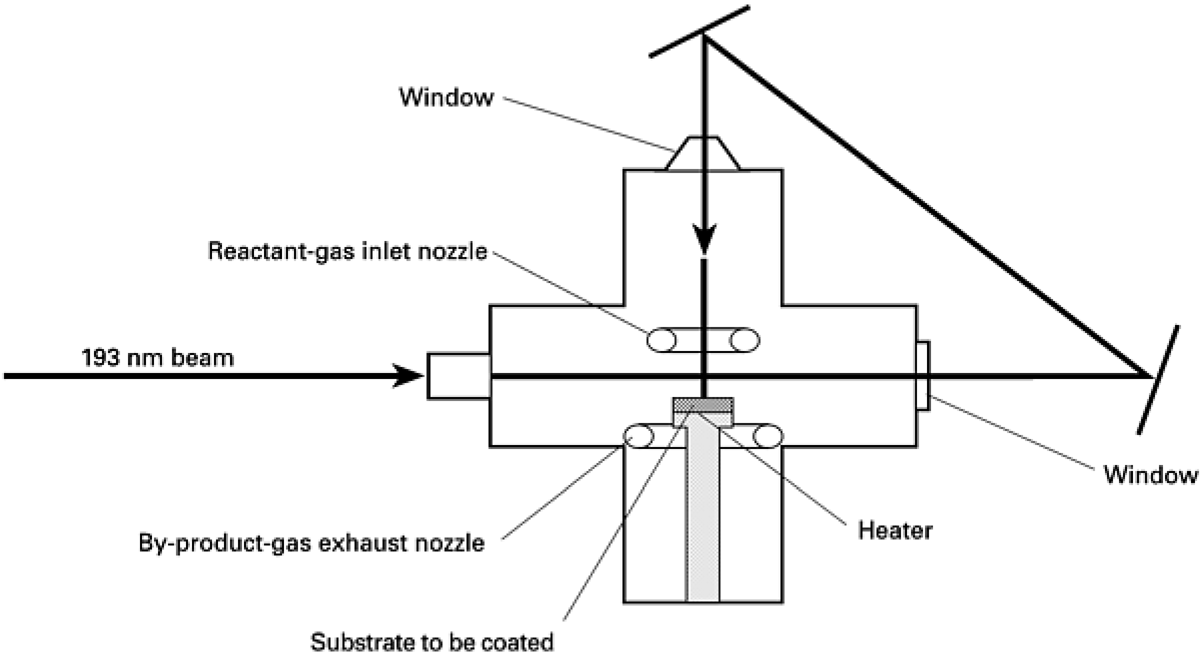


Fig. 5 Photo-laser CVD apparatus

Photo-laser CVD differs from thermal-laser CVD in that it does not require heat, because the reaction is photon-activated, and the deposition essentially occurs at room temperature. Moreover, there is no constraint on the type of substrate that can be used. It can be opaque, absorbent, transparent, or even temperature-sensitive.

A limitation of this method that has, to date, restricted its application is a slow deposition rate. If higher-power excimer lasers can be made more economical, then the process could compete with thermal CVD and thermal-laser CVD, particularly in critical applications where low temperature is essential.

Closed-Reactor CVD or Pack Cementation. The CVD systems described above use open reactors, in which reactants are introduced continuously and flow through the reactor (Ref 1). Another important system utilizes a closed reactor. The chemical vapor deposition in such a system is also known as pack cementation (Ref 13).

The entire process is carried out isothermally, because the driving mechanism for the reaction is not a difference in temperature, as in thermal CVD, but rather a difference in chemical activity between a metal in the free state and a metal in solution with another metal. A common reaction involves coating iron objects (such as turbine blades) with chromium, using chromium powder and ammonium iodide as reactants and aluminum oxide as an inert filler. Parts and chemicals are loaded in a molybdenum container that is then sealed, as shown schematically in Fig. 6. Pack cementation is a common industrial process with large-scale applications in chromizing, aluminizing, and siliconizing.

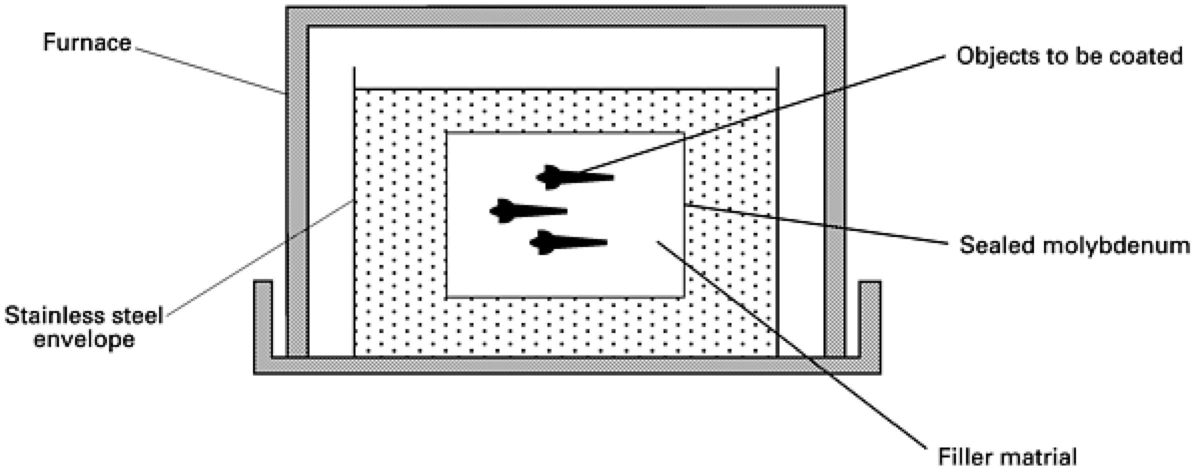


Fig. 6 Pack-cementation chromizing/siliconizing apparatus. Pack material composed of 3 wt% Cr, 11 wt% Si, 0.25 wt% NH_4I, and balance, Al_2O_3

Chemical vapor infiltration (CVI) refers to the particular CVD process in which gaseous reactants infiltrate a porous structure, such as an inorganic open foam or a fiber array. Deposition occurs on the foam or fiber, and the structure is gradually densified to form a composite (Ref 14).

In a typical CVI system (Fig. 7), both the gas inlet and substrate are water cooled, and only the top of the substrate is heated. Under pressure, the gaseous precursors enter the cool side of the substrate and flow through it to reach the hot zone, where the deposition reaction occurs.

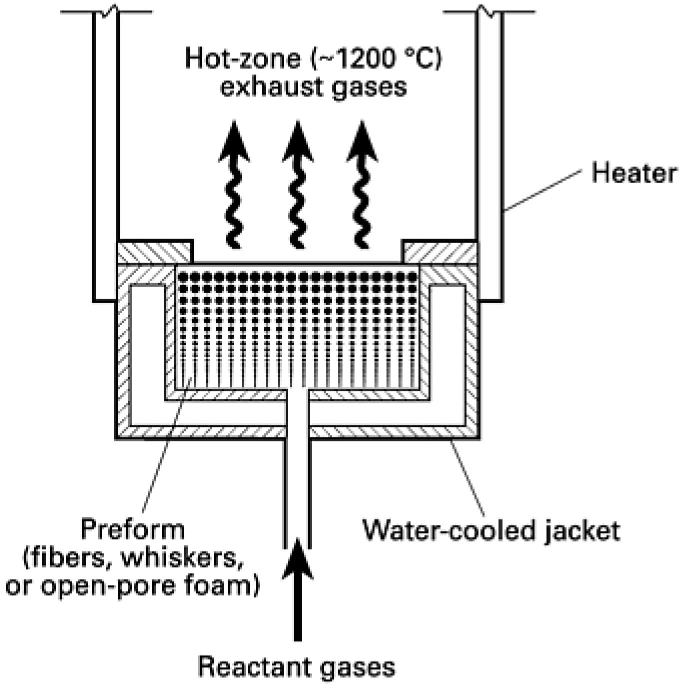


Fig. 7 Chemical vapor infiltration apparatus. Source: Ref 15

This process is used to produce high-strength silicon carbide and carbon-carbon composites, as well as other reinforced metal or ceramic composites. As contrasted with sintering, CVI does not require high pressure, and the processing temperatures are lower. As a result, mechanical and chemical damage to the substrate is minimized.

The major limitation of this method is the necessity for the interdiffusion of reactants and byproducts through relatively long and narrow channels. Chemical vapor infiltration is a slow process that can take several weeks. Full densification is nearly impossible to obtain because of the formation of closed porosity.

Metal-organic CVD (MOCVD) is a specialized process that utilizes organometallic compounds as precursors, usually in combination with hydrides or other reactants. Most MOCVD reactions occur at temperatures between 600 and 1000 °C (1110 and 1830 °F). When the most precise controls and high-purity gases are used, extremely thin deposits (<10 nm, or 0.4 μin.) with abrupt interfaces (<1 nm, or 0.04 μin.) can be produced. Because MOCVD equipment and chemicals are expensive and production costs are high, this method is considered most often when high performance is essential or when substrates are temperature sensitive.

The MOCVD method is being used extensively in microwave and optoelectronic applications, as discussed in detail in the article "Chemical Vapor Deposition of Semiconductor Materials" in this Section of the Volume. In addition, it is being introduced in wear and corrosion applications. An example of a nonsemiconductor application of MOCVD is the deposition of iridium via the decomposition of iridium acetylacetonate for oxidation protection (up to 2200 °C, or 3990 °F) of the maneuvering thruster nozzle of a spacecraft satellite (Ref 16). Additional information on the use of MOCVD in nonsemiconductor applications is provided in Ref 8.

References cited in this section

1. H.O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, 1992
6. T.M. Besmann et al., Chemical Vapor Deposition Techniques, *MRS Bulletin,* Nov 1988, p 45-50
7. P.K. Bachman, G. Gartner, and H. Lydtin, Plasma Assisted CVD Processes, *MRS Bulletin,* Dec 1988, p 51-59
8. D. Bhat, Techniques of Chemical Vapor Deposition, *Surface Modification Technologies--An Engineer's*

Guide, T. Sudarshan, Ed., Marcel Dekker, 1989

9. Y.Z. Hu, M. Li, J. Sunko, J. Andrews, and E. Irene, Characterization of Microwave ECR Plasma for Low Temperature Chemical Vapor Deposition, *Proc. 11th Int. Conf. on CVD,* K. Spears and G. Cullen, Ed., Electrochemical Society, 1990, p 166-172
10. R.F. Bunshah, Ed., *Handbook of Deposition Technologies for Films and Coatings,* 2nd ed., Noyes Publications, 1994
11. D. Bauerle, Laser Induced Chemical Vapor Deposition, *Laser Processing and Diagnostics,* D. Bauerle, Ed., Springer-Verlag, 1984
12. R. Solanki et al., Laser-Induced Chemical Vapor Deposition, *Solid State Technology,* Vol 28, June 1985, p 220-226
13. J.M. Blocher, Jr., Chemical Vapor Deposition, *Handbook of Deposition Technologies for Films and Coatings,* R.F. Bunshah, Ed., Noyes Publications, 1982
14. W.J. Lackey, Review, Status and Future of the CVI Process for Fabrication of Fiber-Reinforced Ceramic Composites, *Ceram. Eng. Sci. Proc.,* Vol 10 (No. 7-8), 1989, p 577-584
15. N. Tai and T. Chou, Modeling of an Improved Chemical Vapor Infiltration Process for Ceramic Composites Fabrication, *J. Am. Ceram. Soc.,* Vol 73 (No. 6), 1990, p 1489-1498
16. J.T. Harding, R.H. Tuffias, and R.B. Kaplan, "Oxidation Resistance of CVD Coatings," Technical Report 86-099, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, CA, 1987

Typical CVD Materials and Reactions

A wide variety of materials can be produced by CVD but, as mentioned earlier, only the most important of those related to hard, tribological, and high-temperature coatings and to free-standing structures are reviewed here. The CVD of other materials is described in Ref 1 and 17.

The metals most often deposited by the CVD technique include molybdenum, nickel, rhenium, and tungsten.

Molybdenum (Ref 17, 18). The hydrogen reduction of the chloride is most commonly used to deposit molybdenum:

$$MoCl_6 + 3H_2 \rightarrow Mo + 6HCl$$

The reaction temperature ranges from 400 to 1350 °C (750 to 2460 °F). The best deposits are obtained at the high end of this range and at low pressure (<2.7 kPa, or 20 torr).

Another well-established reaction is the decomposition of the carbonyl:

$$Mo(CO)_6 \rightarrow Mo + 6CO$$

The reaction temperature ranges from 300 to 700 °C (570 to 1290 °F), and pressure ranges from approximately 0.13 to 101 kPa (1 to 760 torr) in a hydrogen atmosphere.

Nickel (Ref 19, 20). The decomposition of nickel carbonyl is the most frequently used reaction to deposit nickel:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$

The reaction temperature ranges from 180 to 200 °C (355 to 390 °F), and the pressure can be as high as 101 kPa (760 torr). More ductile nickel is obtained at low deposition rates.

Rhenium (Ref 21, 22) is generally deposited by the hydrogen reduction of the fluoride:

$$ReF_6 + 3H_2 \rightarrow Re + 6HF$$

The reaction temperature ranges from 500 to 900 °C (930 to 1650 °F). The best deposits are obtained at 700 °C (1290 °F) and at low pressure (<2.7 kPa, or 20 torr).

Another common reaction is the pyrolysis of the chloride:

$$2ReCl_5 \rightarrow 2Re + 5Cl_2$$

The reaction temperature ranges from 1000 to 1250 °C (1830 to 2280 °F). The best deposits are obtained at low pressure (<2.7 kPa, or 20 torr). This reaction usually gives a more ductile and purer material than the reaction given in Eq 4, although a higher temperature is necessary.

Tungsten (Ref 23, 24, 25) is usually obtained by the hydrogen reduction of the halide:

$$WF_6 + 3H_2 \rightarrow W + 6HF$$

The reaction temperature ranges from 300 to 700 °C (570 to 1290 °F), and pressure ranges from 1.3 to 101 kPa (10 to 760 torr). Deposition at a lower temperature (500 °C, or 930 °F) gives a finer grain structure with high strength (83 MPa, or 12 ksi) than deposition at a high temperature (700 °C, or 1290 °F).

Another deposition reaction for tungsten is the hydrogen reduction of the chloride:

$$WCl_6 + 3H_2 \rightarrow W + 6HCl$$

The reaction temperature ranges from 900 to 1300 °C (1650 to 2370 °F), and the pressure ranges from 2.0 to 2.7 kPa (15 to 20 torr). This reaction, which yields high-purity deposits, is used to coat x-ray targets and to produce structural parts.

Graphite (Ref 26). The CVD of graphite, which is relatively simple, is obtained by the thermal decomposition of a hydrocarbon. The most common precursor is methane, which is generally pyrolyzed at 1100 °C (2010 °F) and at a pressure ranging from approximately 0.25 to 101 kPa (2 to 760 torr):

$$CH_4 \rightarrow C + 2H_2$$

Another common precursor is acetylene (C_2H_2), which decomposes at temperatures between 300 and 750 °C (570 and 1380 °F) and at pressures up to 101 kPa (760 torr) in the presence of a nickel catalyst. A third precursor is propylene (C_3H_6), which decomposes at temperatures between 1000 and 1400 °C (1830 and 2550 °F) and at low pressure (13 kPa, or 100 torr).

Diamond (Ref 26, 27, 28). The CVD of diamond requires the presence of atomic hydrogen, which selectively removes graphite and activates and stabilizes the diamond structure. To dissociate hydrogen requires a high-energy source. In addition to the need for atomic hydrogen, other factors, such as energy input and the presence of oxygen, have been shown to be important, as well.

The deposition mechanism is complex and not fully understood at this time. The basic reaction involves the decomposition of a hydrocarbon, such as methane:

$$CH_4 \rightarrow C(\text{diamond}) + 2H_2$$

The reaction can be activated by microwave plasma, thermal means (hot filament), or plasma arc.

Diamond-like carbon (DLC) represents a new form of carbon coating that is neither diamond nor graphite. A common deposition method is a high-frequency RF gas discharge (13.56 MHz) generated in a mixture of hydrogen and a hydrocarbon, such as methane (CH_4), *n*-butane (C_4H_{10}), or acetylene (C_2H_2).

The technology of CVD diamond and DLC has progressed considerably, and applications are reaching the production stage in electronics, optics, and tribology. Cutting tools coated with CVD diamond have performed remarkably well and should enter the market soon.

The deposition of ceramics usually involves titanium diboride, boron carbide, silicon carbide, titanium carbide, boron nitride, silicon nitride, titanium nitride, or alumina, each of which is described below.

Titanium diboride (Ref 29) is deposited by the hydrogen reduction of the halides. A typical reaction is:

$$TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl$$

The reaction temperature ranges from 800 to 1100 °C (1470 to 2010 °F), and the pressure ranges from approximately 0.25 to 101 kPa (2 to 760 torr) in a hydrogen atmosphere. Titanium diboride also can be deposited with diborane as the boron and hydrogen source in the same pressure range, but at a reaction temperature ranging from 600 to 1000 °C (1110 to 1830 °F):

$$TiCl_4 + B_2H_6 \rightarrow TiB_2 + 4HCl + H_2$$

Boron carbide (Ref 30) is commonly deposited by this reaction:

$$4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HCl$$

The reaction temperature ranges from 1200 to 1400 °C (2190 to 2550 °F), and pressure ranges from 1.3 to 2.7 kPa (10 to 20 torr).

Boron carbide also is deposited from diborane in a plasma:

$$2B_2H_6 + CH_4 \rightarrow B_4C + 8H_2$$

The reaction temperature is typically 400 °C (750 °F).

Silicon carbide (Ref 31, 32). Silicon carbide coatings and free-standing shapes are both important applications of the CVD process. A common CVD reaction is the decomposition of methyl trichlorosilane (MTS):

$$CH_3SiCl_3 \rightarrow SiC + 3HCl$$

The reaction temperature ranges from 900 to 1400 °C (1650 to 2550 °F), and pressure ranges from 1.3 to 6.7 kPa (10 to 50 torr) in a hydrogen atmosphere. The deposition rate and the crystallite size increase with the increasing partial pressure of MTS. Other precursor combinations are $SiCl_4/CH_4$, $SiCl_4/CCl_4$, SiH_2Cl_2/C_3H_8, and $SiHCl_3/C_3H_8$, usually in a hydrogen atmosphere.

Titanium carbide (Ref 33) is of major industrial importance in the coating of wear-resistant tools by the CVD process. The most common deposition system is the reaction of the metal chloride with a hydrocarbon:

$$TiCl_4 + CH_4 \rightarrow TiC + 4HCl$$

The reaction temperature ranges from 850 to 1050 °C (1560 to 1920 °F), and pressure varies from less than 0.13 to 101 kPa (1 to 760 torr) in a hydrogen atmosphere. Other carbon sources are toluene ($CH_3C_6H_5$) and propane (C_3H_8).

Boron nitride (Ref 34) is produced in a hydrogen atmosphere by the reaction of boron trichloride and ammonia:

$$BCl_3 + NH_3 \rightarrow BN + 3HCl$$

At a deposition temperature of 1300 °C (2370 °F), a low-density (1.5 g/cm^3) boron nitride is obtained. Density increases with increasing temperature and reaches 2.0 g/cm^3 at 1600 °C (2910 °F). Vapor-phase precipitation can be a problem in the high-temperature range. A more convenient reaction uses boron trifluoride:

$$BF_3 + NH_3 \rightarrow BN + 3HF$$

The reaction temperature ranges from 1100 to 1200 °C (2010 to 2190 °F), and the pressure is 101 kPa (760 torr).

Low-temperature deposition is possible with diborane:

$$B_2H_6 + 2NH_3 \rightarrow 2BN + 6H_2$$

The reaction temperature ranges from 300 to 400 °C (570 to 750 °F), and the pressure is less than 0.13 kPa (1 torr).

Silicon nitride (Ref 35) is deposited by the reaction of silicon tetrachloride with ammonia:

$$3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$$

The reaction temperature is 850 °C (1560 °F), and the pressure can go up to 101 kPa (760 torr). Silicon nitride also is deposited by the reaction of dichlorosilane and ammonia with a high nitrogen dilution:

$$3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$$

The reaction temperature ranges from 755 to 810 °C (1390 to 1490 °F). When a high-frequency (13.56 MHz) plasma is used, the deposition temperature is lowered (400 to 600 °C, or 750 to 1110 °F).

Titanium Nitride (Ref 36). A common reaction for the CVD of TiN uses N_2 $TiCl_4$ at temperatures above 900 °C (1650 °F) and at pressures up to 101 kPa (760 torr). Another reaction uses ammonia as a nitrogen source, as follows:

$$TiCl_4 + NH_3 + \frac{1}{2}H_2 \rightarrow TiN + 4HCl$$

Alumina (Ref 37, 38). A common reaction for the deposition of alumina is the hydrolysis of the aluminum trichloride:

$$2AlCl_3 + 3H_2 + 3CO_2 \rightarrow Al_2O_3 + 3CO + 6HCl$$

This reaction takes place in excess hydrogen, at an optimum temperature of 1050 °C (1920 °F) and at low pressure (approximately 0.13 kPa, or 1 torr).

References cited in this section

1. H.O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, 1992
17. N.J. Ianno and J.A. Plaster, Plasma Enhanced CVD of Molybdenum, *Thin Solid Films,* Vol 147 (No. 2), 2 March 1987, p 193-202
18. J.A. Sheward and W.J. Young, The Deposition of Molybdenum and Tungsten Coatings on Gun Steel Substrates by a Plasma Assisted CVD Technique, *Vacuum,* Vol 36 (No. 1-3), Jan-March 1986, p 37-41
19. T.R. Jervis and L.R. Newkirk, Metal Film Deposition by Laser Breakdown CVD, *J. Mater. Res.,* Vol 1 (No.

3), May/June 1986, p 420-424

20. M. Skibo and F. Greulich, Characterization of CVD Ni-(0.05-0.20wt%)B Alloys, *Thin Solid Films,* Vol 113, 1984, p 225-234
21. J.G. Donaldson, A Preliminary Study of the Vapor Deposition of Rhenium and Rhenium-Tungsten, *Journal of the Less Common Metals,* Vol 14, 1968, p 93-101
22. D. Bauerle, Laser Induced Chemical Vapor Deposition, *Laser Processing and Diagnostics,* D. Bauerle, Ed., Springer-Verlag, 1984
23. M.L. Green, Y. Ali, T. Boone, B. Davidson, L. Feldman, and S. Nakahara, The Formation and Structure of CVD W Films Produced by the Si Reduction of WF_6, *J. Electrochem. Soc.,* Vol 134 (No. 9), Sept 1987, p 2285-2292
24. C.C. Tang, Plasma Enhanced CVD of Beta-Tungsten, a Metastable Phase, *App. Phys. Lett.,* Vol 45 (No. 6), 15 Sept 1984, p 633-635
25. R. Kaplan and R. Tuffias, Large Seamless Tungsten Crucibles Made by CVD, *Int. J. Refract. Hard Metals,* Vol 3 (No. 3), 15 Sept 1984
26. H.O. Pierson, *Handbook of Carbon, Graphite, Diamond and Fullerenes,* Noyes Publications, 1994
27. K. Spear, Diamond: Ceramic Coating of the Future, *J. Am. Ceram. Soc.,* Vol 7 (No. 2), 1989, p 171-191
28. W.A. Yarborough, Diamond Growth with Locally Supplied Methane and Acetylene, *J. Mater. Res.,* Vol 7 (No. 2), 1992, p 379-383
29. H.O. Pierson, A Survey of the Chemical Vapor Deposition of Refractory Transition Metal Borides, *Chemical Vapor Deposited Coatings,* American Ceramic Society, 1981, p 27-45
30. A. Mellendore, Chemical Vapor Deposition of Boron-based Refractory Solids, *AIP Conf. Proc.,* 4-140, American Institute of Physics, 1986
31. F. Langlais and C. Prebende, On the Chemical Process of CVD of SiC-based Ceramics from the Si-C-H-Cl System, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 686-695
32. D. Stinton, T. Besmann, and R. Lowden, Advanced Ceramics by Chemical Vapor Deposition Techniques, *Ceram. Bull.,* Vol 67 (No. 2), 1988, p 350-355
33. M. Dariel, R. Aparicio, T. Anderson, and M. Sacks, CVD of TiC_x on Refractory Materials, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 659-669
34. L. Kempfer, The Many Faces of Boron Nitride, *Mater. Eng.,* Nov 1990, p 41-44
35. J. Marks, D. Witty, A. Short, W. Laford, and B. Nguyen, Properties of High Quality Nitride Films by Plasma Enhanced Chemical Vapor Deposition, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 368-373
36. D.G. Bhat, A Thermodynamic and Kinetic Study of CVD TiN Coating on Cemented Carbide, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 648-655
37. S. Choi, C. Kim, J. Kim, and J. Chun, Nucleation and Growth of Al_2O_3 on Si in the CVD Process, *Proc. 9th Int. Conf. on CVD,* M. Robinson et al., Ed., Electrochemical Society, 1984, p 233-241
38. G. Pauer, H. Altena, and B. Lux, Al_2O_3 CVD with Organic Al-Donors, *Int. J. Refract. Hard Metals,* Vol 5 (No. 3), Sept 1986, p 165-170

Applications

Wear-, erosion-, and corrosion-resistance applications extensively utilize CVD coatings, as do applications that require low friction characteristics. Table 2 lists the properties of typical CVD coating materials for these applications. Some materials, such as titanium diboride, titanium carbide, and silicon carbide, provide extremely low wear rates. Table 3 lists specific production applications for the wear-, erosion-, and corrosion protection provided by CVD coatings.

Table 2 Selected wear and corrosion properties of CVD coating materials

Material	Hardness		Thermal conductivity, W/m · K	Coefficient of thermal expansion at 25 °C (77 °F), 10^{-6}/K	Remarks
	GPa	10^6 psi			
Titanium carbide	31.4	4.5	17	7.6	High wear and abrasion resistance, low friction
Titanium nitride	20.6	3.0	33	9.5	High lubricity; stable and inert
Titanium carbonitride	24.5-29.4	3.5-4.3	20-30	8	Stable lubricant
Chromium carbide	22.1	3.2	11	10	Resists oxidation to 900 °C (1650 °F)
Silicon carbide	27.4	4.0	125	3.9	High conductivity, shock resistant
Titanium diboride	33.0	4.7	25	6.6	High hardness, high wear resistance
Alumina	18.8	2.7	34	8.3	Oxidation resistant, very stable
Diamond-like carbon	29-49	4.2-7.1	200	. . .	Very hard, high thermal conductivity
Diamond	98	14.2	180	2.9	Extreme hardness and high thermal conductivity

Table 3 Wear-, erosion-, and corrosion-resistance applications of CVD

Metal forming (noncutting)
Tube and wire-drawing dies (TiN) Stamping, chamfering, and coining tools (TiC) Drawing punches and dies (TiN) Deep-drawing dies (TiC) Sequential drawing dies (Cr_7C_3) Coating on dressing sticks for grinding wheels (B_4C)
Ceramic and plastic processing
Molding tools and dies for glass-filled plastics [Ti(CN)] Extrusion dies for ceramic molding (TiC) Kneading components for plastic mixing (TiC)
Chemical and general processing industries
Pump and valve parts for corrosive liquids (SiC) and abrasive liquids (TiB_2) Valve liners (SiC) Positive-orifice chokes (SiC, TiB_2) Packing sleeves, feed screws (TiC) Thermowells (SiC, Al_2O_3)

Abrasive-slurry transport (WC) Sandblasting nozzles (TiC, B_4C, TiB_2) Textile-processing rolls and shafts (Al_2O_3, TiC, WC) Paper-processing rolls and shafts (TiC) Valves for coal-liquefaction components (TiB_2) Cathode coating for aluminum production (TiB_2) Oxidation-resistant coatings for carbon-carbon composites (SiC)
Machine elements
Gear components (TiN) Coating on stainless-steel spray-gun nozzles (TiC) Components for abrasive processing (TiC) Coating on ball bearings (TiC) Turbine blades (SiC, TiC)
Nuclear
Coating for neutron flux control in nuclear reactors (B_4C) Coating for shielding against neutron radiation (B_4C) Coatings for fusion reactor applications (SiC) Nuclear waste container coatings (SiC)
Instruments
Radiation sensor (SiC) Thermionic cathodes (W-Th) Target coatings for x-ray cathodes (W-Re)

Note: TiN, titanium nitride; TiC, titanium carbide; B_4C, boron carbide; Ti(CN), titanium carbonitride; SiC, silicon carbide; TiB_2, titanium diboride; Al_2O_3, alumina; WC, tungsten carbide

The cutting-tool industry relies heavily on coatings. The technology associated with CVD has made some of its most important gains in this area. Major applications are represented by titanium carbide coatings on the majority of cemented (cobalt-bonded) tungsten carbide tools and both titanium nitride and carbonitride coatings on high-speed tool steel and cemented carbide tools.

The materials identified in Table 2 can be used as multilayer structures that utilize the strongest characteristics of each layer of material. Nearly all coatings are multilayer systems that combine titanium nitride for lubricity and galling resistance; alumina for chemical inertness and thermal insulation; and titanium carbide, as well as titanium carbonitride, for abrasion resistance. Selecting the optimum combination of materials depends on the type of machining operation, the material to be machined, and other factors. Criteria for such a selection are summarized in Table 4.

Table 4 Criteria for selecting coating materials for cutting tools

Property	**Best materials**[(a)]
Oxidation and corrosion resistance; high-temperature stability	Al_2O_3, TiN, TiC
Crater-wear resistance	Al_2O_3, TiN, TiC

Hardness and edge retention	TiC, TiN, Al_2O_3
Abrasion resistance and flank wear	Al_2O_3, TiC, TiN
Low coefficient of friction and high lubricity	TiN, Al_2O_3, TiC
Fine grain size	TiN, TiC, Al_2O_3

Source: Ref 39

(a) Al_2O_3, alumina; TiN, titanium nitride; TiC, titanium carbide. For each property, best material is identified first.

Titanium nitride, the most common coating material, is generally combined with a very thin undercoating of titanium carbide or titanium carbonitride to promote adhesion. Alumina coatings are preferred in high-speed machining applications in which oxidation resistance and high-temperature stability are the critical factors. Like titanium nitride, alumina is deposited on an intermediate titanium carbide layer.

A large variety of free-standing structures of refractory metals and ceramics are produced by the CVD process (Table 5).

Table 5 Free-standing structures produced by CVD

High-strength structural parts of nickel alloyed with small amount of boron
Shapes such as tubes, rods, and plates
Furnace muffles (tungsten)
Hollow spheres with thin walls (tungsten)
Boats and crucibles for liquid-phase and molecular-beam epitaxy (pyrolytic graphite), and crucibles for silicon single-crystal processing (silicon nitride)
Electrodes for plasma etching (pyrolytic graphite)
Trays for silicon-wafer handling (pyrolytic graphite)
Heating elements for high-temperature furnaces (pyrolytic graphite)
Aircraft disk brakes (carbon-carbon)
Re-entry heat shields, rocket nozzles, and other aerospace components (carbon-carbon)
High-temperature turbine blades and components for internal combustion engines (silicon nitride)
Heart valves and dental implants (pyrolytic carbon)

Note: Pyrolytic carbon is a generic term commonly used for CVD carbon, but usually applied to the low-temperature form (900 to 1400 °C, or 1650 to 2550 °F) with limited preferred orientation. Pyrolytic graphite is the higher-temperature product (1900 to 2300 °C, or 3450 to 4170 °F) with a high degree of preferred orientation in the "C" direction.

Ultrafine Powders by CVD. Powder is precipitated from the gas phase if the temperature and supersaturation of a CVD reaction are sufficiently high. The powder has few impurities, small diameter, and great uniformity, which are important factors in the production of high-quality hot-pressed or sintered ceramic bodies with good mechanical and electrical properties. In addition, the sintering temperatures required for CVD powders are lower than those for conventional powders.

The following powders are made experimentally or on a production basis:

- Beta SiC powder from methyl-trichlorosilane in the presence of hydrogen in an argon plasma or from tetramethylsilane in a flow-through reactor between 850 and 1500 °C (1560 and 2730 °F) (Ref 40)
- An amorphous silicon nitride powder produced by laser CVD from halogenated silanes and ammonia with an inert sensitizer such as SF_6 (Ref 41)

- Aluminum nitride produced from aluminum alkyl, and magnesium oxide produced from magnesium vapor and O_2 at 800 °C (1470 °F) and tungsten carbide (Ref 42)
- Iron, nickel, cobalt, molybdenum, and tungsten powders produced by the pyrolysis of the metal carbonyls or halides

CVD ceramic powders, such as SiC and Si_3N_4, are used either experimentally or in production in applications such as reciprocating engines, gas turbines, turbochargers, bearings, machinery, and process equipment.

Metallic and ceramic powders as small as 5 μm (200 μin.) in diameter can be coated with nickel or iron by CVD by the fluidized bed technique. A typical application is the coating of tungsten particles to promote sintering in powder metallurgy. Sintering time, sintering temperature, and grain growth are reduced, contamination is lessened, and properties are improved (Ref 43).

Boron and silicon carbide fibers are produced industrially by CVD (Ref 44, 45, 46). A monofilament starter core is required that is capable of being heated resistively, such as a tungsten or graphite fiber.

Boron fibers are produced by the hydrogen reduction of boron chloride at 1300 °C (2370 °F). The "boron" fiber actually consists of a boron envelope surrounding a tungsten boride core, which typically occupies 5% of the fiber cross section. The fiber has high strength, high modulus, and low density, but it also has a tendency to further grain growth at high temperatures, is highly reactive with many metals, and is costly.

CVD silicon carbide fibers are a recent development that show promise, and if the production cost can be reduced they may take over some of the applications of CVD boron fibers or other refractory fibers. They are generally produced by the reaction of silane and a hydrocarbon in a tubular glass reactor (Fig. 1). The substrate is a carbon monofilament that is precoated with a 1 μm (40 μin.) layer of pyrolytic graphite to ensure a smooth deposition surface and a constant resistivity.

SiC fibers have properties similar to those of CVD boron fibers, except that SiC is more refractory and less reactive than boron. The fibers retain much of their mechanical properties when exposed to high temperatures in air, up to 800 °C (1470 °F) for as long as 1 h. Most applications of CVD silicon carbide fibers are still under development, including:

- Reinforcement for ceramic and polymer composites
- Reinforcement for metal-matrix composites with such metals as titanium, titanium aluminide, aluminum, magnesium, and copper. Applications for these fibers are found mostly in advanced aerospace programs and include fan blades, drive shafts, and other components.

References cited in this section

39. D.G. Bhat and P.F. Woerner, Coatings for Cutting Tools, *J. Metals,* Feb 1986, p 68
40. H.D. Wu and D.W. Ready, Silicon Carbide Powders by Gaseous Pyrolysis of Tetramethylsilane, *Silicon Carbide 87,* Vol 2, *Ceramic Transactions,* 1987, p 35-46
41. R. Bauer, R. Smulders, E. Geus, J. van der Put, and J. Schoomman, Laser Vapor Phase Synthesis of Submicron Silicon and Silicon Nitride Powders from Halogenated Silanes, *Ceram. Eng. Sci. Proc.,* Vol 9 (No. 7-8), 1988, p 949-956
42. A. Kato, Study of Powder Preparation in Japan, *Ceramic Bulletin,* Vol 66 (No. 4), 1987, p 647-650
43. S. Mulligan and R.J. Dowding, "Sinterability of Tungsten Powder CVD Coated with Nickel and Iron," Technical Report 90-56, U.S. Army Mater. Tech. Lab., Watertown, MA, 1990
44. L.M. Sheppard, Progress in Composites Processing, *Ceramic Bulletin,* Vol 69 (No. 4), 1990, p 666-673
45. J.E. Gatica and V. Hlavacek, Laboratory for Ceramic and Reaction Engineering: A Cross-Disciplinary Approach, *Ceramic Bulletin,* Vol 69 (No. 8), 1990, p 1311-1318

46. "AVCO Silicon Carbide Fiber," Textron, Lowell, MA, 1990

Advantages and Disadvantages of CVD

The CVD process has a number of important advantages that often make it the preferred method when producing hard, tribological, and high-temperature coatings and free-standing structures:

- Refractory materials can be deposited at temperatures far below their melting point or sintering temperatures.
- Near-theoretical density is readily achieved.
- Preferred grain orientation and grain size can be controlled.
- Processing at atmospheric pressure is possible.
- Good bonding to a substrate is generally obtained.

Furthermore, the process is not restricted to line-of-sight deposition, as it is for most PVD processes. Deep recesses, high-aspect-ratio holes, and other difficult three-dimensional configurations can usually be coated with relative ease.

In addition, the deposition rate is high and thick coatings can be readily obtained (in some cases, centimeters thick). The process also is generally competitive and, sometimes, even more economical than other coating processes.

Finally, the equipment is relatively simple, does not require ultrahigh vacuum, and generally can be adapted to many process variations. Its flexibility allows many composition changes during deposition, and the codeposition of compounds is readily achieved.

However, the CVD process is not the universal coating panacea. Because it is most versatile at a temperature of 600 °C (1110 °F) or higher, its applications are limited to substrates that are thermally stable at such a temperature. (The development of the plasma and metal-organic CVD processes partially offsets this problem.)

A second problem is that some chemical precursors are hazardous or extremely toxic, which necessitates a closed system.

A third problem is that many reactions either leave solid byproducts or generate solid byproducts with neutralizing solutions. These byproducts can be toxic and corrosive, which necessites the careful consideration of disposal procedures and incurs additional costs. The Environmental Protection Agency (EPA) has been very active, even stringent, in this regard, as have the state regulators of the EPA and Occupational Safety and Health Administration.

A fourth problem is that energy requirements can be high, especially when high deposition temperatures are required.

Finally, the efficiency of the process is sometimes low, resulting in high costs.

Chemical Vapor Deposition of Semiconductor Materials

Manijeh Razeghi, Northwestern University

Introduction

CHEMICAL VAPOR DEPOSITION (CVD) is the deposition of thin, solid films from gas-phase precursors. Growth usually occurs through heterogeneous reactions catalyzed by a heated surface, although homogeneous reactions also can occur in the gas phase. Gas-phase, or parasitic, reactions should be avoided, because they deplete the precursor process and may produce deleterious solid particles, or "dust."

Epitaxial deposition is a process that produces single-crystal films with the same crystallographic orientation as the underlying substrate. Epitaxial growth from a CVD process is sometimes referred to as vapor-phase epitaxy (VPE). Other epitaxial processes that have been developed since 1960 include molecular-beam epitaxy (MBE) and liquid-phase epitaxy.

The vapor-phase methods that are discussed in this article have several advantages, when compared with liquid-phase epitaxy. One is the flexibility of depositing films with distinctly different compositions than the substrates. Even disparate chemistries can be used to deposit epitaxial films, as long as the lattice constant is matched sufficiently to the substrate. An example is the growth of gallium arsenide on silicon. A second advantage is the availability of high-purity gaseous precursors. The refinement of liquid sources is much more difficult, and it limits the quality of the resultant films. Vapor-phase techniques permit the growth of multilayered structures with excellent compositional and dimensional control, as well as abrupt interfaces. A third advantage is that selected gas-phase processes can be scaled to large areas and batch processing for commercial production.

The ability to grow thin, epitaxial films and multilayers on a variety of substrates has led to the development of new devices and technologies. Silicon epitaxial films are used routinely in the manufacture of high-performance bipolar and complementary metal-oxide semiconductor (CMOS) integrated circuits. The deposition of compound semiconductors with direct bandgaps has led to the production of millimeter and microwave devices, as well as optoelectronic devices, such as lasers, light-emitting diodes, and high-efficiency photovoltaic cells. The ability to grow thin, multilayered structures with very fine dimensional and compositional control has made possible quantum-well devices and strained-layer superlattices. The development of devices with novel capabilities and higher performance levels will certainly continue as the control and understanding of the growth process matures.

This article describes vapor-phase growth techniques that are applied to the epitaxial deposition of semiconductor films. The growth of Group III-V compounds via the metal-organic CVD (MOCVD) method is emphasized, because that method has become the most widely used and commercially important process for depositing these materials. The advantages of MOCVD, when compared with techniques such as MBE and VPE, are defined. The thermodynamic and kinetic processes responsible for epitaxial growth also are presented.

Technique Principles

Vapor-Phase Epitaxy. Tietjen and Amick (Ref 1) demonstrated the growth of gallium arsenide phosphide (GaAsP) by VPE in 1966. The growth of materials based on indium phosphide (InP) can be achieved in a horizontal reactor with two temperature zones, such as a fused-silica tube surrounded by multiple furnace windings. High-purity hydrogen (H_2) is a common carrier gas, and arsine (AsH_3) and phosphine (PH_3) are used as the arsenic and phosphorus sources, respectively. Pure indium metal is used as the Group III elemental source. Gaseous species are generated in the first zone (source zone), which is held at a higher temperature than the second zone (deposition zone). For the growth of InP, gaseous species are generated at 750 to 800 °C (1380 to 1470 °F), according to the reactions:

$$2\ In + 2\ HCl \rightarrow 2\ InCl + H_2 \qquad \textbf{(Eq 1)}$$

$$4PH_3 \rightarrow P_4 + 6H_2 \qquad \textbf{(Eq 2)}$$

Deposition occurs in the temperature range of 650 to 750 °C (1200 to 1380 °F) in the second zone, according to the reaction:

$$P_4 + 4\ InCl + 2\ H_2 \rightarrow 4\ InP + 4\ HCl \qquad \textbf{(Eq 3)}$$

To achieve the growth of multilayered structures, the substrate must be moved between reactors that use different chemistries. It is therefore difficult, if not impossible, to achieve layer thicknesses on the order of 5 nm (50 Å), as required for quantum-well or superlattice structures. Fine compositional manipulation favors the techniques of MBE or MOCVD, where the transport of source materials, rather than substrates, is controlled.

The MOCVD process uses at least one metal-organic chemical as a deposition precursor. The growth of Group III-V compounds from metal-organic and hydride sources was first reported by Manasevit in 1960 (Ref 2). In that experiment, InP was deposited from trimethylindium (TMIn) and PH_3 in a closed-tube system. Later, it was established that many common compound semiconductors could be deposited from metal-organic materials (Ref 3, 4, 5, 6). Manasevit coined the MOCVD acronym, which is used in this article. Other authors refer to organometallic CVD (OMCVD). When applied to the growth of epitaxial films, this technique is sometimes called metal-organic vapor-phase epitaxy or organometallic VPE. As used for the epitaxial growth of compound semiconductors, MOCVD has advanced rapidly since the mid-1980s. It has become established as a unique and important epitaxial crystal growth technique, yielding high-quality, low-dimension structures for fundamental semiconductor physics research and production of useful electronic and photonic semiconductor devices.

A typical MOCVD reactor is shown in Fig. 1. Gaseous precursors are introduced to the reaction chamber from the gas manifold. To achieve the growth of Group III-V compound semiconductors, Group III alkyls and Group V hydrides can be introduced to the reaction chamber. The substrate, located on a hot susceptor, has a catalytic effect on the decomposition of the gaseous products. Growth occurs primarily on this hot surface. The MOCVD technique is attractive because of its relative simplicity, when compared with other growth methods. Excellent control over film composition can be achieved by precisely metering the amounts of gaseous species introduced to the chamber. Thus, MOCVD can be used to produce heterostructures, multiquantum wells, and superlattices with very abrupt transitions in composition, as well as alloys with tailored doping profiles.

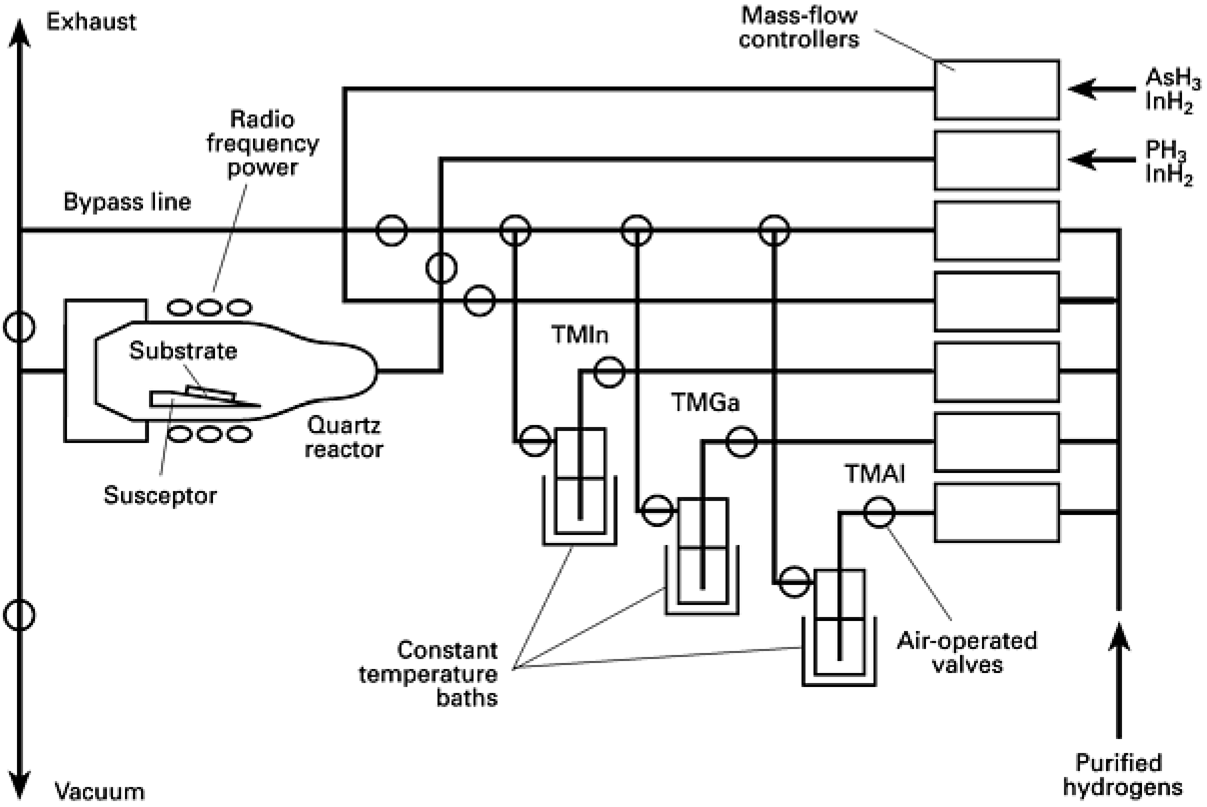


Fig. 1 Typical reactor design for metal-organic chemical vapor deposition. Source: Ref 7

Uniform layers with low background doping densities and sharp interfaces have been grown using MOCVD. Some reactor configurations in use are scalable to large areas, and are therefore attractive for commercial applications. This technique also has been used to produce multilayer structures with layers as thin as a few atomic layers (Ref 8, 9). These abrupt changes in composition produce quantum size effects (Ref 10, 11), and permit the study of two-dimensional electron gases (Ref 12, 13, 14, 15), two-dimensional hole gases (Ref 16, 17), and other charge-transport effects observed in a variety of Group III-V compound semiconductors, heterojunctions, and multilayers (Ref 18, 19). It is also possible to tailor the doping level or alloy composition of ternary and quaternary compounds. Varying the film composition results in a change in the bandgap (Ref 20). This ability to engineer the bandgap has created entirely new classes of electronic and photonic devices (Ref 21). Another recent advance is the ability to grow strained-layer superlattices, in which the crystal lattices of the two materials are purposely mismatched to produce a built-in strain in each layer (Ref 22, 23, 24, 25, 26).

A major disadvantage of MOCVD is the need for large quantities of toxic gases, such as AsH_3 and PH_3. However, less hazardous precursors, such as tertiarybutylphosphine (TBP) (Ref 27, 28) and tertiarybutylarsine (TBAs) (Ref 29, 30), are being developed to address this problem.

The MBE technique has been used to prepare epitaxial films of Group IV (Ref 31, 32), III-V (Ref 33, 34), and II-VI (Ref 35, 36) semiconductors, as well as metals (Ref 37, 38). In this technique, elemental sources are evaporated at controlled rates by heating and then condensed onto a crystalline substrate surface held at a suitable temperature. This is an ultrahigh vacuum (UHV) technique, in which the beams of evaporated molecules or atoms are focused on the substrate. UHV conditions are necessary to ensure sufficient film purity. The use of UHV has two advantages. First, atoms and molecules reach the growth surface in a very clean condition. Second, the growth process can be monitored by in-situ diagnostic techniques as the crystal grows one atomic layer at a time (Ref 39). The diagnostic techniques that are used include reflection high-energy electron diffraction (RHEED), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), secondary-ion mass spectroscopy (SIMS), and ellipsometry.

The MBE technique is recognized as an excellent crystal growth technology for the production of complex and varied structures, especially for GaAs-based multilayer structures. It provides extremely precise control of layer thickness and doping profile. However, this technique is expensive because it requires UHV apparatus.

Another major problem is the incorporation of specific dopants. The typical approach is to add dopants by effusion of the elemental impurity, which leads to difficulty when the dopant vapor pressure is either too high (Ref 40) or too low (Ref 41) to be handled conveniently in an ultrahigh vacuum system. Because the MBE process is a near-equilibrium one, dopant incorporation can be hindered by low incorporation probabilities (Ref 42) or surface segregation effects (Ref 43). Phosphorus is one such dopant that suffers from a low incorporation probability. Instead of becoming incorporated into the growing film, it tends to "bounce around" the system, and eventually collects in the vacuum pumps. In addition, the growth of alloys containing both arsenic and phosphorus is particularly difficult because of surface segregation effects.

Hybrid MBE and CVD Techniques. Versatile growth techniques have been developed by combining the beneficial aspects of MBE and CVD. These hybrid techniques employ the gas-handling system of MOCVD and the growth chamber of MBE.

To overcome the limitations of growing phosphide compounds, elemental Group V sources are replaced by those that can decompose AsH_3 and PH_3. This technique is called gas-source molecular-beam epitaxy (Ref 44). In addition, Group III elemental sources can be replaced by simple metal-organic compounds to create the metal-organic molecular-beam epitaxy growth technique (Ref 45, 46). This technique is also known as chemical-beam epitaxy or metal-organic chemical-beam deposition (MOCBD).

The MOCBD technique has numerous advantages, when compared with MOCVD, including:

- Use of a fraction of the amount of PH_3 and AsH_3 for the growth of GaAs- and InP-based materials and the elimination of chemical waste-disposal systems, such as the scrubbers normally used in MOCVD
- Elimination of parasitic reactions in the gas phase because of UHV conditions
- Possible use of in-situ surface diagnostic techniques
- Improvement in homogeneity, composition uniformity, and reproducibility of InP-based materials over large-area substrates
- In-situ etching and removal of oxide during the growth of InP on silicon substrates
- Reduction of contamination from previous chemistries (the memory effect) during *p*-type doping
- Reduction of boundary-layer thickness on hot substrate surfaces
- Compatibility with other high-vacuum, thin-film processing techniques, such as plasma etching, metal evaporation, ion-beam etching, and ion implantation

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References cited in this section

1. J.J. Tietjen and J.A. Amick, *J. Electrochem. Soc.,* Vol 113, 1966, p 724
2. R. Didchenko, J.E. Alix, and R.H. Toeniskoetter, *J. Inorg. Nucl. Chem.,* Vol 14, 1960, p 35
3. H.M. Manasevit, *Appl. Phys. Lett.,* Vol 12, 1968, p 156
4. H.M. Manasevit and W.I. Simpson, *J. Electrochem. Soc.,* Vol 116, 1969, p 1725
5. H.M. Manasevit, *J. Electrochem. Soc.,* Vol 118, 1971, p 647
6. H.M. Manasevit, F.M. Erdmann, and W.I. Simpson, *J. Electrochem. Soc.,* Vol 118, 1971, p 1864
7. R.D. Dupuis, *Science,* Vol 226, 1984, p 623

8. R.D. Dupuis, P.D. Dapkus, C.M. Garner, C.Y. Su, and W.E. Spicer, *Appl. Phys. Lett.,* Vol 34, 1979, p 335
9. P.M. Frijlink and J. Malvenda, *Jpn. J. Appl. Phys.,* Vol 21, 1982, p L574
10. M. Razeghi, *Rev. Tech. Thomson-C.S.F.,* Vol 15, 1983, p 1
11. R.D. Dupuis, P.D. Dapkus, N. Holonyak, and R.M. Kolbas, *Appl. Phys. Lett.,* Vol 35, 1979, p 487
12. M. Razeghi, *Lightwave Technology for Communication,* W.T. Tsang, Ed., Academic Press, 1985
13. F. Delahaye, D. Dominguez, F. Alexandre, J.P. Andre, J.P. Hirtz, and M. Razeghi, *Metrologia,* Vol 22, 1986, p 103
14. Y. Guldner, J.P. Vieren, M. Voos, F. Delahaye, D. Dominguez, J.P. Hirtz, and M. Razeghi, *Phys. Rev. B,* Vol 23 (No. 6), 1986, p 3990
15. M. Razeghi, P. Maurel, F. Omnes, S. Ben Amor, L. Dmowski, and J.C. Portal, *Appl. Phys. Lett.,* Vol 48, 1986, p 1267
16. M. Razeghi, P. Maurel, A. Tardella, L. Dmowski, D. Gauthier, and J.C. Portal, *Appl. Phys. Lett.,* Vol 60, 1986, p 2453
17. D.C. Rogers, R.J. Nicholas, J.C. Portal, and M. Razeghi, *Semicon. Sci. Technol.,* Vol 1, 1986, p 350
18. M. Razeghi, J.P. Duchemin, J.C. Portal, L. Dmowski, G. Remeni, R.J. Nicholas, and A. Briggs, *Appl. Phys. Lett.,* Vol 48, 1986, p 712
19. R.J. Nicholas, L.C. Brunel, S. Huant, K. Karrai, J.C. Portal, M.A. Brummell, M. Razeghi, K.Y. Chang, and A.Y. Cho, *Phys. Rev. Lett.,* Vol 55, 1985, p 8883
20. M. Razeghi, P. Maurel, F. Omnes, and J.P. Pochell, *Appl. Phys. Lett.,* Vol 49, 1986, p 1110
21. M. Razeghi, A. Hosseini, J.P. Vilcot, and D. Decoster, *Proc. 1987, GaAs and Related Compounds Conf.,* Creta, 1987
22. J.W. Matthews and A.E. Blakeless, *J. Cryst. Growth,* Vol 27, 1974, p 119
23. J.W. Matthews and A.E. Blakeless, *J. Cryst. Growth,* Vol 29, 1975, p 273
24. J.W. Matthews and A.E. Blakeless, *J. Cryst. Growth,* Vol 32, 1976, p 265
25. G.C. Osbourn, *Mater. Res. Soc. Symp. Proc. 37,* 1985, p 220-237
26. A.P. Roth, M. Sacilotti, R.A. Masut, P.J. D'Arch, B. Watt, G.T. Sproule, and D.F. Mitchell, *Appl. Phys. Lett.,* Vol 48, 1986, p 1452
27. C.H. Chen, C.A. Larse, G.B. Stringfellow, D.W. Brown, and A.J. Robertson, *Appl. Phys. Lett.,* Vol 48, 1986, p 1531
28. S.R. Kurtz, J.M. Olson, and A. Kibbler, *J. Electron. Mater.,* Vol 18, 1989, p 15
29. C.H. Chen, C.A. Larsen, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 50, 1987, p 218
30. A. Brauers, M. Weyers, and P. Balk, *Chemtronics,* Vol 4, 1989, p 8
31. Y. Ota, *J. Appl. Phys.,* Vol 51, 1980, p 1102
32. S. Shimizu and S. Komiya, *J. Vac. Sci. Technol.,* Vol 17, 1980, p 489
33. C.T. Foxon, B.A. Joyce, and M.T. Norris, *J. Cryst. Growth,* Vol 49, 1980, p 132
34. K. Ploog, *Crystals: Growth, Properties, and Applications,* Vol 3, *III-V Semiconductors,* H.C. Freyhardt, Ed., Springer, 1980, p 78
35. A.Y. Cho and J.R. Arthur, *Prog. Solid State Chem.,* Vol 10, 1975, p 157
36. D.L. Smith and V.Y. Pickhardt, *J. Appl. Phys.,* Vol 46, 1975, p 2366
37. C. Argile and G.E. Phead, *Surf. Sci.,* Vol 78, 1978, p 115
38. C. Argile and G.E. Phead, *Surf. Sci.,* Vol 78, 1978, p 125
39. E.H.C. Parker, *The Technology and Physics of Molecular Beam Epitaxy,* Plenum Press, 1985
40. C.E.C. Wood, *Appl. Phys. Lett.,* Vol 33, 1978, p 770
41. M. Ilegems and R. Dingle, *Proc. Symp. GaAs and Related Compounds 1974,* Institute of Physics and Physical Society, London, 1975
42. J.R. Arthur, *Surf. Sci.,* Vol 38, 1973, p 394
43. F. Alexandre, C. Raisin, M.I. Abdalla, A. Brenac, and J.M. Masson, *J. Appl. Phys.,* Vol 51, 1980, p 4296

44. M.B. Panish, *J. Electrochem. Soc.,* Vol 127, 1980, p 2729

45. N. Vodjdani, "These de Doctorate 3e Cycle University Paris XI," Ph.D. dissertation, 1982

46. W.T. Tsang, *Appl. Phys. Lett.,* Vol 45, 1984, p 11

Fundamentals of CVD

The fundamental processes that occur during crystal growth are commonly categorized into thermodynamic and kinetic components. Thermodynamics determine the driving force behind the overall growth process, whereas kinetics define the rates at which the various processes occur. Figure 2 depicts the fundamental processes involved in MOCVD. A study of the dependence of a macroscopic quantity, such as growth rate, on external parameters, such as substrate temperature and input precursor (source) flow rates, provides insight into the overall growth mechanism.

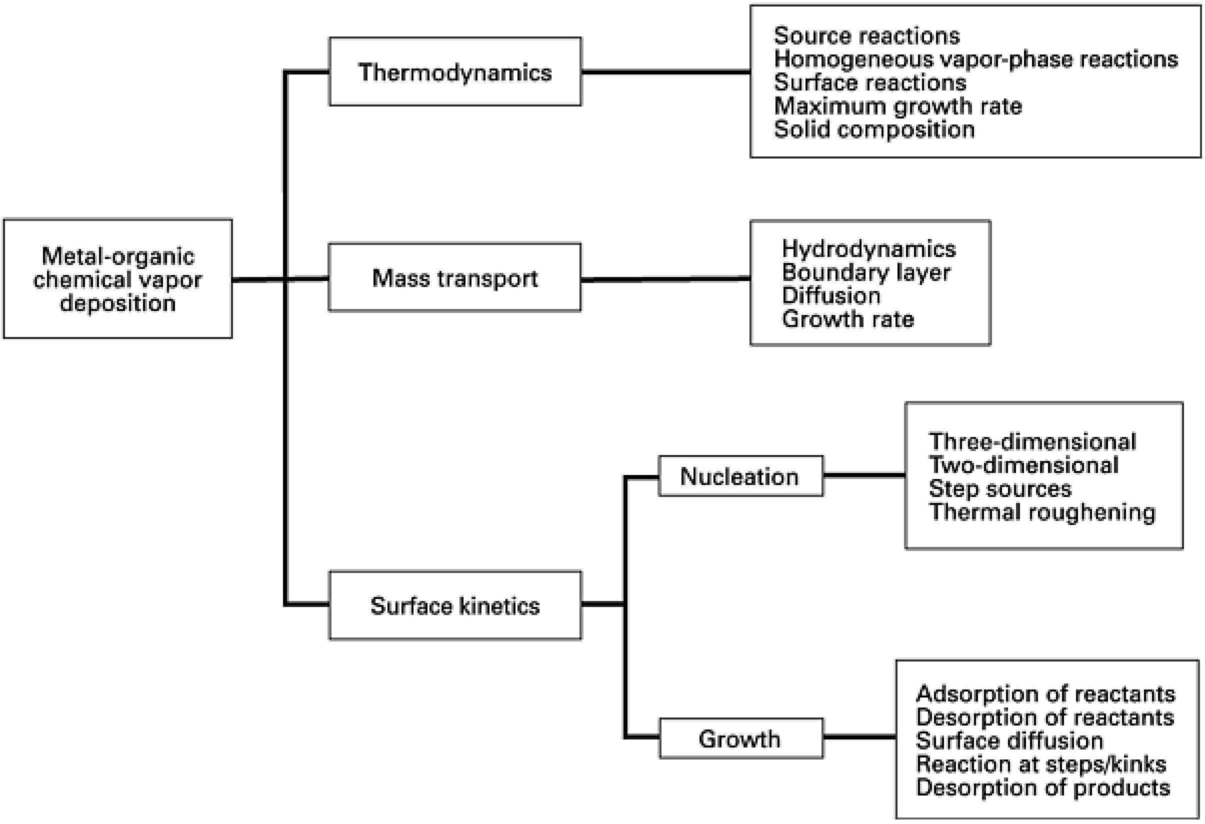

Fig. 2 Fundamental processes involved in metal-organic chemical vapor deposition. Source: Ref 47

Thermodynamics

The goal of thermodynamics is to define the composition of various phases in an equilibrium system at a constant temperature and pressure. Although many aspects of MOCVD growth are nonequilibrium, thermodynamics limits the possible outcomes. Thermodynamics can be used to describe the driving force for epitaxy and to specify the maximum growth rate. In addition, thermodynamic calculations often give an accurate account of the composition of multicomponent solids grown by MOCVD.

Equilibrium is the state that minimizes the Gibbs free energy, G, of the system:

$$G = H - TS$$ **(Eq 4)**

where H is the enthalpy, S is the entropy, and T is the temperature of the system. Entropy is a measure of the degree of randomness in a system, and enthalpy is a measure of the heat content, which can be defined as:

$$H = E + PV \qquad \textbf{(Eq 5)}$$

where E is the internal energy and V is the volume. The quantities G, H, S, E, and V are all extensive quantities, that is, they depend on the size of the system. They are therefore expressed on a per mole basis. For a system containing two phases, α and β, equilibrium is attained when a redistribution between phases causes no further decrease in free energy. This can be expressed mathematically as:

$$\left(\frac{\partial G'}{\partial n_i}\right)^{a}_{T,P,n_j} - \left(\frac{\partial G'}{\partial n_i}\right)^{b}_{T,P,n_j} = 0 \qquad \textbf{(Eq 6)}$$

where G' is the total free energy of the system (as opposed to the free energy per mole). The change in G' with respect to n_i is considered as all other variables (temperature, pressure, and molar amount of other components) are held constant. The partial derivative of G' with respect to n_i is such an important thermodynamic concept that it is given its own name, the chemical potential (μ_i). Thus, equilibrium is reached when:

$$m_i^a = m_i^b \qquad \textbf{(Eq 7)}$$

for each component, i, in the system.

When a system is not at equilibrium, the thermodynamic driving force to restore equilibrium is:

$$\Delta\mu = m_i^a - m_i^b \qquad \textbf{(Eq 8)}$$

This also is the driving force for epitaxial growth. In MOCVD, a nonequilibrium situation is intentionally created, in which the chemical potential of the solid phase differs from that of the vapor. The system restores equilibrium by producing the desired solid phase. The maximum quantity of solid produced is that which is needed to establish equilibrium. It is thus limited by the thermodynamics and size of the system.

The growth rate observed in MOCVD is almost always less than that calculated from thermodynamic principles. Kinetic factors, that is, either surface reaction rates or the diffusion of gas species through the vapor phase, are what limits the growth rate because they hinder the establishment of equilibrium. Driving forces for epitaxial growth are created in the vapor phase and the diffusion boundary layer, and at the interface between the solid and vapor, as depicted in Fig. 3(a). This diagram shows the driving forces necessary to sustain the flux for mass-transport processes ($\Delta\mu_D$) and surface reactions ($\Delta\mu_s$).

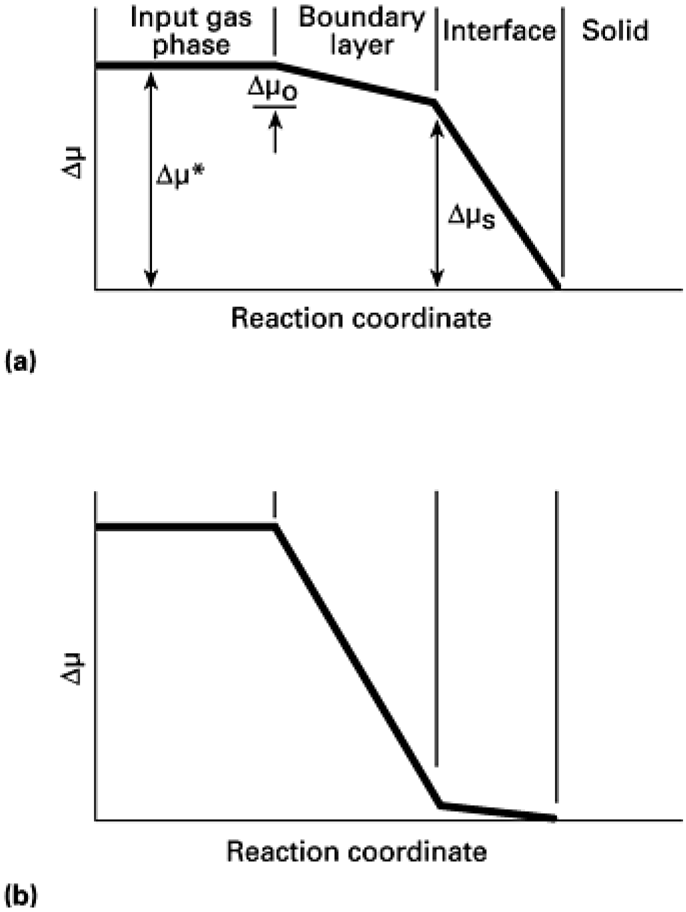

Fig. 3 Chemical potential in metal-organic chemical vapor deposition processes. (a) General case. (b) Mass-transport limited growth. Source: Ref 48

In any given MOCVD process, the shape of the Fig. 3(a) diagram depends on whether growth is limited by mass transport or by surface reactions. Even when there is a large supersaturation in the input vapor phase (a high degree of nonequilibrium), near-equilibrium conditions can exist near the growing surface. This occurs when the surface reactions are much faster than mass transport through the vapor. This situation, termed mass-transport limited growth, is depicted in Fig. 3(b).

Besides describing the driving force for epitaxy, thermodynamic calculations often give an accurate indication of the composition of multicomponent solids grown by MOCVD. Phase diagrams, calculated from the free energy of mixing, specify the number and composition of the phases in equilibrium at a constant temperature, pressure, and overall composition. An important quantity needed for the calculation of solid-solid, solid-liquid, and solid-vapor-phase equilibria is the heat of mixing in the solid, ΔH^{M}. This quantity, coupled with the assumption that constituents distribute randomly on their respective sublattices, allows calculation of the free energy of mixing of the solid alloy.

The simplest model that describes the free energy of mixing of semiconductor liquid and solid solutions is the regular-solution model. A regular solution, as defined by Hildebrand (Ref 49), is nonideal, but comprises a random arrangement of constituents. Two additional assumptions are that interactions occur only between nearest neighbors, and that atoms reside on a lattice, where each atom is surrounded by Z neighbors. For a solution consisting only of A and C atoms, the nearest neighbor bond energies that must be considered are H_{AC}, H_{AA}, and H_{CC}. The entropy of mixing is simply the ideal configurational entropy of mixing:

$$\Delta S^{\mathrm{M}} = -R[x\ln x + (1 - x)\ln(1 - x)] \qquad \textbf{(Eq 9)}$$

The enthalpy of mixing is obtained by summing the nearest neighbor bond energies:

$$\Delta H^{\mathrm{M}} = x(1 - x)\Omega \qquad \textbf{(Eq 10)}$$

where the interaction parameter, Ω, is:

$$\Omega = ZN^{\circ}\left[H_{AC} - \frac{1}{2}(H_{AA} + H_{cc}\right] \qquad \textbf{(Eq 11)}$$

where N^0 is Avogadro's number.

Phase-diagram calculations are based on the free energy of mixing:

$$\Delta G^{\mathrm{M}} = \Delta H^{\mathrm{M}} - T\Delta S^{\mathrm{M}} \qquad \textbf{(Eq 12)}$$

where the values for ΔH^{M} and ΔS^{M} are provided by Eq 9 and 10.

The regular-solution model does not provide much physical insight into the bonding and mixing of semiconductor solutions. As an empirical model, however, it can be used to interpolate and extrapolate phase-diagram information from limited experimental data. The regular-solution model has been used to calculate the phase diagrams in binary, ternary, and quaternary semiconductor systems.

Phase diagrams of many multicomponent systems are available in the literature (Ref 50, 51, 52). Thermodynamic analyses of solid composition against vapor composition have been published for the systems $\mathrm{GaAs}_{1\text{-}x}\mathrm{P}_x$, $\mathrm{InAs}_{1\text{-}x}\mathrm{P}_x$, $\mathrm{In}_{1\text{-}x}\mathrm{Ga}_x\mathrm{As}$ (Ref 53), and for the quaternary $\mathrm{Ga}_{1\text{-}x}\mathrm{In}_x\mathrm{As}_{1\text{-}y}\mathrm{P}_y$ (Ref 54). Generally, good agreement between calculations and experimental results is obtained.

Kinetics and Gas-Phase Transport

Thermodynamics determine the state of a closed system at equilibrium and indicate what to expect from the reactants on a surface (substrate) at a given temperature. However, the MOCVD process is not, by definition, an equilibrium process. Thermodynamics can only define certain limits for the growth process. It is not possible to use thermodynamics to predict the time required to attain equilibrium, what steps to take to achieve the lowest energy state, or the rates at which various processes occur during the transition from precursors to solid. These problems can only be approached in terms of kinetics (Ref 48).

Deposition Reactions. Several types of reactions occur in the CVD growth process. Reactions that occur entirely in the gas phase are called homogeneous, whereas those that occur at a solid surface are called heterogeneous. Homogeneous and heterogeneous reactions are usually either unimolecular or bimolecular. The unimolecular process involves a single energetically activated species, and the bimolecular process requires the collision of two species to produce an activated complex. The probability of higher-order reactions is extremely low.

A simplified depiction of the growth processes for Group III-V compounds that occur near and at the substrate surface is shown in Fig. 4. This figure exemplifies the growth of GaAs by trimethylgallium (TMGa) and $\mathrm{AsH_3}$. Several steps are involved in the growth of GaAs. First, both $\mathrm{AsH_3}$ and TMGa, which are carried by hydrogen gas, diffuse through the boundary layer to reach the substrate. Second, gas-phase reactants are adsorbed on the surface through a series of surface reactions. Third, these species are incorporated into the solid GaAs film. Finally, the reaction products are removed. This four-step description is an oversimplification, because many individual reactions actually occur in the gas phase and at the substrate surface to achieve thin-film growth. Table 1 lists those gas-phase and surface reactions that likely operate in the growth of GaAs from TMGa and $\mathrm{AsH_3}$.

Table 1 Gas-phase and surface reactions operative in the growth of gallium arsenide from trimethylgallium and arsine

Gas-phase reactions

(G1)	$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3*$
(G2)	$Ga(CH_3)_2 \rightarrow GaCH_3 + CH_3*$
(G3)	$CH_3* + AsH_3 \rightarrow AsH_2 + CH_4$
(G4)	$CH_3* + H_2 \rightarrow CH_4 + H*$
(G5)	$H* + H* + M \rightarrow H_2 + M$
(G6)	$CH_3 + H* + M \rightarrow CH_2 + M$
(G7)	$CH_3* + CH_3* \rightarrow C_2H_6$
(G8)	$GaCH_3 + CH_3* \rightarrow GaCH_2 + CH_4$
(G9)	$GaCH_2 + H* \rightarrow GaCH_3$
(G10)	$Ga(CH_3)_3 + CH_3 \rightarrow Ga(CH_3)_2CH_2 + CH_4$
(G11)	$Ga(CH_3)_2CH_2 + H* \rightarrow AsH_2 + Ga(CH_3)_3$
(G12)	$Ga(CH_3)_2CH_2 \rightarrow Ga(CH_3)_2 + CH_3*$
(G13)	$Ga(CH_3)CH_2 \rightarrow Ga(CH_2) + CH_3*$
(G14)	$Ga(CH_3)_3 + H* \rightarrow Ga(CH_3)_2 + CH_4$
(G15)	$Ga(CH3)_2 + H* \rightarrow Ga(CH_3) + CH_4$
(G16)	$Ga(CH_3)_2 + CH_3* \rightarrow Ga(CH_3) + CH_4$
(G17)	$Ga(CH_3)CH_2 + H* \rightarrow Ga(CH_3)_2$
Surface reactions	
(S1)	$H* + S_G \rightarrow H_G*$
(S2)	$H* + S_A \rightarrow H_A*$

(S3)	$CH_3 + S_G \leftrightarrow (CH_3)_G*$
(S4)	$CH_3 + S_A \leftrightarrow (CH_3)_A*$
(S5)	$GaCH_3 + S_G \leftrightarrow CH_3*$
(S6)	$Ga(CH_3)_2 + S_G \rightarrow GaCH_3* + CH_3*$
(S7)	$Ga(CH_3)_3 + S_G \rightarrow GaCH_3* + 2CH_3*$
(S8)	$GaCH_2 + S_G + S_A \rightarrow GaC + H_2$
(S9)	$Ga(CH_3)CH_2 + S_G + S_A \rightarrow GaC + CH_3* + H_2$
(S10)	$Ga(CH_3)_2CH_2 + S_G + S_A \rightarrow GaC + 2CH_3* + H_2$
(S11)	$AsH + S_A \leftrightarrow AsH*$
(S12)	$AsH_2 + S_A \rightarrow AsH* + H*$
(S13)	$AsH_3 + S_A \rightarrow AsH* + H_2$
(S14)	$CH_3* + H_G* \rightarrow CH_4 + S_G$
(S15)	$CH_3* + H_A* \rightarrow CH_4 + S_A$
(S16)	$H* + (CH)_G* \rightarrow CH_4 + S_G$
(S17)	$H* + (CH)_A* \rightarrow CH_4 + S_A$
(S18)	$H_G* + (CH)_A* \rightarrow CH_4 + S_A + S_G$
(S19)	$H_A* + (CH)_G* \rightarrow CH_4 + S_A + S_G$
(S20)	$H_A* + H_G* \rightarrow H_2 + S_A + S_G$
(S21)	$(CH_3)_A* + (CH_3)_A* \rightarrow C_2H_6 + S_A + S_G$
(S22)	$GaCH_3* + AsH* \rightarrow GaAs + CH_4 + S_A + S_G$

(S23)	$AsH^* + AsH^* \rightarrow As_2 + H_2 + 2S_A$
(S24)	$CH_3^* + AsH_G^* \rightarrow As^* + CH_4$
(S25)	$As^* + As^* \rightarrow As_2 + CH_4$
(S26)	$GaCH_3^* + As^* \rightarrow GaAs + CH_3^* + S_G + S_A$

Note: * refers to surface adsorption, S_A to arsenic site, and S_G to gallium site.

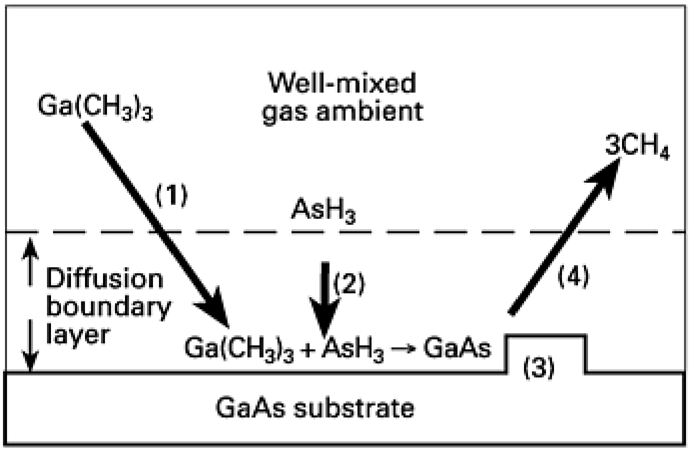

Fig. 4 Processes involved in the growth of gallium arsenide from trimethylgallium and arsine

A physicochemical model of the MOCVD process that combines models of fluid flow and heat transfer for a typical horizontal MOCVD has been presented by Jensen (Ref 55). This model predicts GaAs growth rates and carbon incorporation trends as a function of temperature, pressure, and Group V/III ratio.

In the general case of film growth from precursors, the chemical reaction pathways are not clearly understood. The surface reaction mechanism for growth is complicated by the large number of possible reactions. In Table 1, the general reaction pathway involves chemical reaction processes such as multistep pyrolytic decomposition of metal-organics and reactions with hydrogen radicals in the gas phase (G1 to G17) (Ref 56, 57, 58, 59), heterogeneous decomposition (S11 to S13), and surface adsorption and desorption (S1 to S13). The growth of the GaAs solid phase occurs via reactions between gallium- and arsenic-containing surface precursors (S22 and S26). Volatile reaction byproducts are removed from the surface by adsorption, interaction with colliding gas-phase radicals (S14 to S17, S24) and bimolecular surface recombination reactions (S18 to S21, S23, S25). Carbon incorporation occurs because of reactions S8 to S10.

Gas Flow Patterns. The gas velocities and temperature gradients in the vicinity of the hot susceptor play a significant role in the deposition process. The problems of reactor cell design and their solutions are best discussed in terms of the hydrodynamics of the reactant gas flowing into the cell. Important parameters include pressure, viscosity, volume, and temperature variation.

Laminar and Turbulent Flow. Consider a case of steady fluid flow through a uniform pipe. The flow may start uniformly, but can soon become nonuniform. After traversing a distance, *z*, which is the velocity entry length, the flow velocity *v*(*r*) attains a parabolic profile, as shown in Fig. 5(a):

$$v(r) = -\frac{1}{4h}\frac{dp}{dz}(a^2 - r^2),\ for (0 \le r \le a) \qquad \textbf{(Eq 13)}$$

where dp/dz is the pressure gradient, a is the cross-section radius, r is the radial axis, and $\eta$is the dynamic viscosity. The flow in Fig. 5(a) is steady, nonuniform, and laminar. In laminar flow, the velocity is always the same at a fixed position. Each element of the reactive species travels smoothly along a simple, well-defined path, and each element starting at the same place follows the same path.

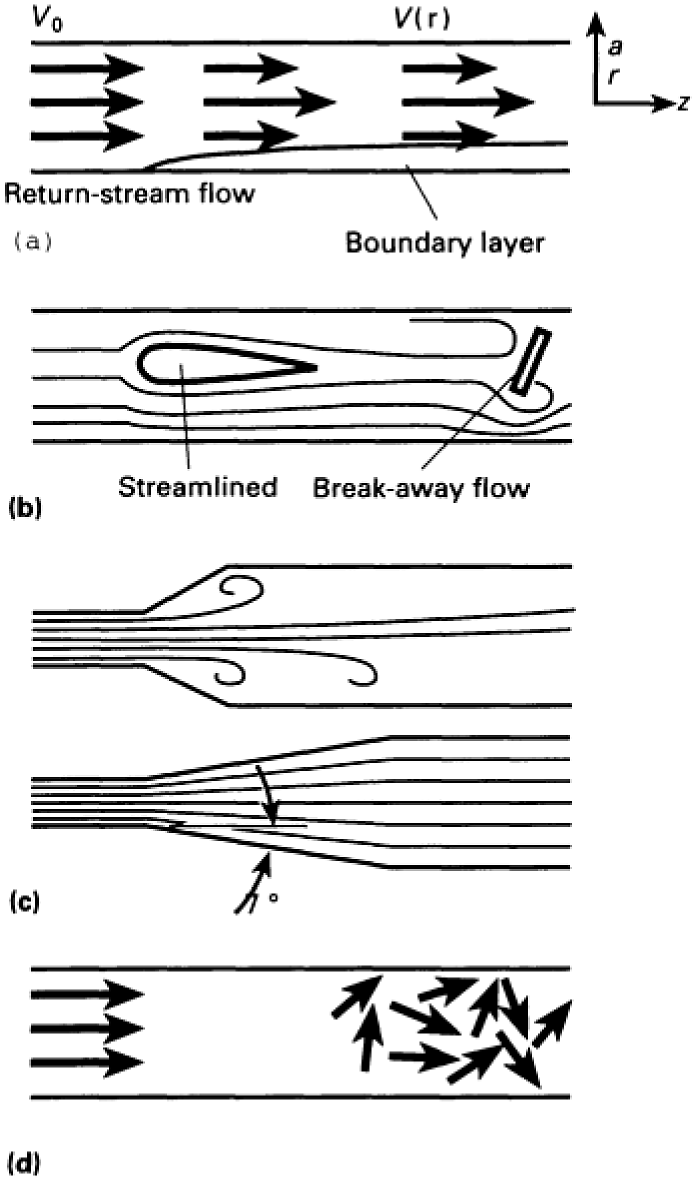

Fig. 5 Different gas flow patterns possible in chemical vapor deposition reactors. (a) Boundary layer of a gas flowing in a pipe and velocity distribution. (b) Stream lines showing adhered flow and break-away flow. (c) Flow patterns effected by expansion angle of tubes. (d) Effect of Reynolds number on flow properties. Source: Ref 48

The laminar pattern can easily be disturbed by either putting a barrier in the flow path (Fig. 5b) or changing the tube diameter (Fig. 5c). Stream lines are used to show the direction of gas molecules. In Fig. 5(b), the stream lines illustrate gas molecules that both break away from, and adhere to, the wall. In the first barrier in Fig. 5(b), a stream line adheres along the whole of its surface. The second barrier produces a break-away flow. The stream line that touches the edge of the barrier does not touch the plate anywhere else. The flow breaks away from the surface at this point. The wave behind the break-away flow may rotate slowly and form a stable eddy wave. When a susceptor is placed inside the reactor chamber at a large angle with respect to the flow direction, a break-away and return-stream flow is produced. This type of flow should be avoided because it can produce a "memory effect," that is, the composition of the growing layer is contaminated by residual gases used to grow previous layers.

Figure 5(c) illustrates gas flowing in a pipe that has a sudden change in cross-sectional area. When the cross-sectional area either increases or decreases, the gas will experience either a decrease or an increase in pressure, respectively. This kind of sudden momentum change can produce vortices. More importantly, vortices can be created by high flow velocities. As the mean velocity becomes larger, the velocity gradients also increase. The friction between adjacent layers of flow can become so high that local velocity components normal to the flow direction are no longer smoothed out. Instead, they progressively develop into turbulent or chaotic flow. When a pipe expands, the rate of decrease in pressure determines whether or not flow is smooth or turbulent. The rule of thumb for maintaining laminar flow is to avoid linear expansion angles, θ greater than 7° (Ref 55, 60).

When the flow becomes turbulent, it develops a highly random character with rapid, irregular fluctuations of velocity in both space and time. In this case, an element of gas flow will follow a highly irregular, distorted path (Fig. 5d). Different elements starting at the same place will follow different paths, because the pattern of irregularities changes all the time (Ref 61). The irregular motions do not affect all the molecules at the same instant, so that when the velocity is averaged out, it can still be thought of as a steady flow with a steady average velocity. The criteria that establish whether a gas will flow in a turbulent or laminar regime are characterized by the Reynolds number, R_e, which is defined as:

$$R_e = \frac{r v d}{h} \qquad \textbf{(Eq 14)}$$

where ρ is the density in kg/m^3, ν is the average flow rate in m/s, and d is the diameter of the tube in m. When R_e is small (< 100), the flow regime is laminar.

Consider the case of parallel flow over a flat plate. The velocity distribution in the fluid phase is shown in Fig. 6. The flow is uniform, with velocity V_0, before the plate is inserted into the system. After the plate is introduced, a contiguous, low-velocity boundary layer develops. The width of the resulting boundary a layer for the condition $z > \delta_0$ is given by:

$$\delta_0 \approx 4.56\ (Dz/V_0)^{1/2} \qquad \textbf{(Eq 15)}$$

where z is the distance measured from the leading edge of the susceptor, D is the diffusion coefficient, and V_0 is the entry velocity (Ref 62). The boundary layer width is proportional to the square root of z and inversely proportional to the square root of V_0.

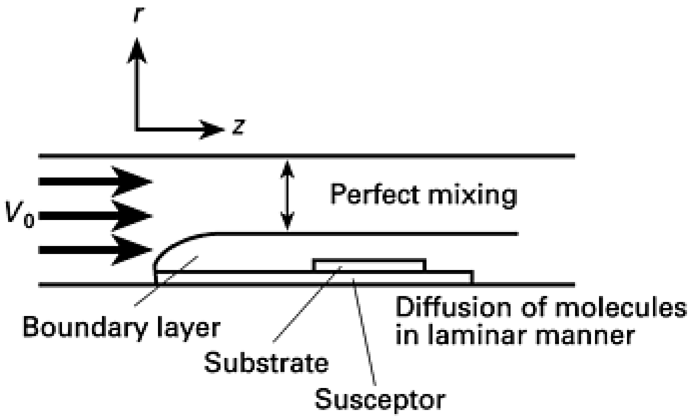

Fig. 6 Gas flow in a horizontal reactor

Effect of Substrate Heating. The introduction of heat adds another dimension of complexity to the gas flow, because convection is important in controlling gas flow along length of pipe. In a horizontal reactor chamber, the temperature difference from the chamber wall to the heated susceptor is enough to influence the flow of gas. When the thermal diffusivity is large and the temperature difference is small, the exchange of momentum is so fast, on a microscopic scale, that no real macroscopic gas-density gradients can develop. Hence, no buoyancy is observed, and the gas is said to be metastable. For higher temperature gradients and smaller heat diffusivities, the heavy, cold gas moves downward and the light, hot gas near the susceptor moves upward. The buoyancy forces are so large that free convection occurs. The onset of free convection is characterized by the Rayleigh number, *Ra*:

$$\mathrm{R}a = \frac{a\, g C_p\, r^2 h^3 \Delta T}{h\, k} \qquad \textbf{(Eq 16)}$$

where α is the coefficient of thermal expansion in 1/K, g is the gravitational constant in m/s^2, C_p is the specific heat in J/kg · K, ρ is the gas density in kg/m^3, h is the free height above the susceptor in m, ΔT is the difference in temperature between the susceptor and the reactor wall, η is the dynamic viscosity in kg/ms, and k is the thermal conductivity in J/m · s · K). When *Ra* is less than or equal to 1700, the gas is stable. When *Ra* is greater than 1700, free convection occurs.

The flux, J_i, of a chemical species, μ_i, toward the susceptor surface now depends on the local temperature, the local temperature gradient, and the creation or annihilation of molecules during the reaction (Ref 63). Flux can be expressed as:

$$J_i = \frac{D_i}{RT}\left(\frac{P_1}{P_1 + (n-1)P_i} \frac{\partial P_i}{\partial z} + a \frac{\partial T}{\partial z} \right) \qquad \textbf{(Eq 17)}$$

where $D_i(T) = D_0(T/T_0)^2$ is the binary diffusion coefficient of species i as a function of T, R is a gas constant equal to 8.31 J/mol · K, P_t is the total pressure, P_i is the partial pressure of component i, n is the ratio of the number of molecules after and before the reaction, z is the direction normal to the susceptor surface, and α_i is the thermal diffusion factor for species i.

Modeling Gas Flow Patterns to Optimize Reactor Design. Two approaches are used to study gas flow patterns and the effect of reactor geometry on those patterns. The first approach is based on experimental observations, whereas the second is based on numerical calculation.

Flow patterns can be visualized by using smoke particles (Ref 64, 65, 66). Generally, titanium dioxide smoke is used. These experiments provide information about the existence of a boundary layer adjacent to the susceptor, the presence of temperature gradients perpendicular to the flow, and additional evidence of a convection-induced gas motion. Flow visualization experiments also provide a qualitative insight into the momentum transfer in the gas phase. The problem with a smoke test is that it does not give a clear boundary layer thickness, because smoke is heavier than the process gases.

Giling used holographic interference techniques to visualize temperature gradients (Ref 63). In this method, a light beam that passes through the reactor is compared with a reference beam that does not pass through the reactor. Small differences in the light paths become visible as interference patterns. If the flow is turbulent, then all fringe lines will move around, giving an incoherent image. When the flow is convective, the isotherms will be curved such that an upward or downward flow can be recognized. When the flow is laminar and stable against convection, fringes parallel to the hot surface will be formed. Giling analyzed flow images for hydrogen, nitrogen, argon, and helium carrier gases.

Berkman et al. (Ref 67) developed a detailed model of the flow dynamics, mass, and thermal gradients in a horizontal cold-walled reactor heated from below. The engineering formulas derived from hydrodynamic flow theories are easy to apply and correlate well with experimental observations.

There are two distinct zones above the susceptor in a reactor. The gas near the susceptor flows in a nearly laminar manner. Above that, the gas flow is turbulent, with oscillations of 3 to 5 Hz. The turbulence is caused by both thermal entry effects and buoyancy forces originating at the leading edge of the hot susceptor. The Berkman model treats the upper turbulent zone as a cold finger of well-mixed gas that acts as a reservoir of reactants. The lower zone acts like a laminar boundary layer, with a velocity profile that has average characteristics of both laminar and turbulent flow, through which the reactant is transported by diffusion. For a flat susceptor, the growth rate decreases exponentially along the susceptor as:

$$\exp(-Az) \qquad \textbf{(Eq 18)}$$

where

$$A = {}^{2D_T}\!\Big/_{VTb_o^2} \qquad \textbf{(Eq 19)}$$

and where V_T is the temperature-corrected gas velocity, D_T is the reactant diffusion coefficient at temperature T, and b_0 is the initial channel height above the susceptor. The exponential variation can be nullified by tilting the susceptor at an angle, θ_c (3 to 5°), such that:

$$\sin(q_c) = \frac{2D0}{b_0 V_0}\left(\frac{T_a}{T_0}\right)^{0.88} \qquad \textbf{(Eq 20)}$$

where D_0 is the diffusion coefficient of the precursor molecule measured at room temperature (T_0), T_a is the average temperature of the gas above the susceptor, and V_0 is the initial horizontal gas velocity at T_0 in front of the susceptor. Low-pressure MOCVD (~10 kPa, or 0.1 atm) increases V_0, allowing $\sin(\theta_c)$ to approach zero.

The rigorous simulation of mass transport in epitaxial systems involves solving the mass continuity equation and the Navier-Stokes equation of momentum conservation, according to the appropriate boundary conditions set by the geometry of the reactor, the heating method, and gas inlet and outlet flow (Ref 68). With the rapid advances in computation speed and memory over the last decade, numerical models have expanded from simple boundary-layer descriptions, to two-dimensional models, to three-dimensional descriptions of horizontal reactors (Ref 55).

The numerical modeling effort has focused on different reactor cells, such as return cells (Ref 69, 70), horizontal reactors (Ref 71, 72), and recirculation cells in the vertical reactor configuration (Ref 73, 74). The influence of inlet flow rate, pressure, and geometry on the flow pattern has been studied to understand the origin and nature of mixed-convection flows. Two-dimensional simulations of flow patterns have been generated for both horizontal and vertical reactor configurations (Ref 73, 74, 75).

The modeling of three-dimensional flow patterns for the growth of GaAs using TMGa and AsH_3 has been reported (Ref 55). The following boundary conditions were used to simplify the solution of the partial differential equations:

- No slip at solid walls
- Constant wall temperature or insulated side walls
- No flux on nonreacting surfaces or a flux balanced by the rate at which the species is incorporated into the growing film

Surface adsorptions are also considered in boundary conditions. The partial differential equations and the associated boundary conditions were transformed into a large set of nonlinear algebraic equations (on the order of 40,000 to 90,000) that were solved on a supercomputer using Newton's method.

References cited in this section

47. G.B. Stringfellow, *Crystal Growth of Electronic Materials,* E. Kaldis, Ed., Elsevier Science, 1985, p 247
48. G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice,* Academic Press, 1989, p 8, 18
49. J.H. Hildebrand, *J. Am. Chem. Soc.,* Vol 51, 1929, p 66
50. G.B. Stringfellow, *Semiconductors and Semimetals,* Vol 22A, W.T. Tsang, Ed., Academic Press, 1985, p 209
51. G.B. Stringfellow, *Inter. Rev. Science, Inorganic Chemistry,* Series 2, Vol 10, Butterworths, London, 1975, p 111-145
52. M. Razeghi, *The MOCVD Challenge,* A. Hilger, 1989, p 14
53. J.B. Mullin and D.T.J. Hurle, *J. Luminesc.,* Vol 7, 1973, p 176

54. A. Koukitu and H. Seki, *J. Cryst. Growth,* Vol 49, 1980, p 325
55. K.F. Jensen, *J. Cryst. Growth,* Vol 107, 1991, p 1-11
56. G.A. Hebner, K.P. Kileen, and R.M. Biefeld, *J. Cryst. Growth,* Vol 98, 1989, p 293
57. D.K. Gaskill, V. Kolubeyev, N. Bottka, R.S. Sillmon, and J.E. Butler, *J. Cryst. Growth,* Vol 93, 1988, p 127
58. C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 52, 1988, p 480
59. M. Yoshida, H. Watanabe, and F. Uesugi, *J. Electrochem. Soc.,* Vol 132, 1985, p 677
60. J.L. Fitzjohn and W.L. Holstein, *J. Electrochem. Soc.,* Vol 137, 1990, p 699
61. A.H. Shapiro, *Shape and Flow,* Heinemann, London, 1961
62. H. Schlicting, *Boundary Layer Theory,* 6th ed., McGraw-Hill, 1968
63. L.J. Giling, *Crystal Growth of Electronic Materials,* E. Kaldis, 1985, p 83
64. F.C. Eversteijn, *Philips Res. Rep.,* Vol 29, 1974, p 45
65. R. Takahashi, Y. Koga, and K. Sugawara, *J. Electrochem. Soc.,* Vol 119, 1972, p 1406
66. V.S. Ban, *J. Electrochem. Soc.,* Vol 125, 1978, p 317
67. S. Berkman, V.S. Ban, and N. Goldsmith, *Heterojunction Semiconductors for Electronic Devices,* G.W. Cullen and C.C. Wang, Ed., Springer, 1977, p 264
68. F. Rosenberger, *Fundamentals of Crystal Growth,* Springer-Verlag, Berlin, 1979
69. E.P. Visser, C.R. Kleijn, C.A.M. Govers, C.J. Hoogendoorn, and L.J. Giling, *J. Cryst. Growth,* Vol 95, 1989, p 929
70. D.I. Fotiadis, M. Boekholt, K.F. Jensen, and W. Richter, *J. Cryst. Growth,* Vol 100, 1990, p 577
71. J. Quazzani and F. Rosenberger, *J. Crys. Growth,* Vol 100, 1990, p 545
72. H.K. Moffat and K.F. Jensen, *J. Electrochem. Soc.,* Vol 135, 1988, p 459
73. S. Patnaik, R.A. Brown, and C.A. Wang, *J. Cryst. Growth,* Vol 96, 1989, p 153
74. D.I. Fotiadis, S. Kieda, and K.F. Jensen, *J. Cryst. Growth,* Vol 102, 1990, p 441
75. K.F. Jensen, *J. Cryst. Growth,* Vol 98, 1989, p 148

The MOCVD Growth Technique

This section describes not only the reactor systems and hardware, but the engineering considerations that optimize growth, the MOCVD starting materials, and the growth parameters for a variety of Group III-V, II-VI, and IV semiconductors.

Reactor Systems and Hardware

The growth of Group III-V or II-VI compound semiconductors is achieved by introducing source materials into a reaction chamber (quartz tube or stainless steel) that contains a substrate on a heated susceptor. The hot susceptor has a catalytic effect on the decomposition of the gaseous products. Therefore, growth occurs primarily on this hot surface A typical MOCVD system (Fig. 1) consists of a gas-handling system, a reactor chamber, a heating system for pyrolysis temperatures, and an exhaust system and safety apparatus.

The purpose of the gas-handling system is to deliver the source alkyls and hydrides to the reaction chamber in precise, measured amounts. Gas manifolds, valves, flow controllers, and vacuum pumps are necessary to control the flow and mixture of gas. To grow high-quality layers, the gas-handling system must be clean. Stainless steel tubes are used to transport alkyls from the source to the reactor chamber, and electronic mass-flow controllers and thermal bath systems deliver precisely controlled amounts of gas.

Starting-material purity is one of the most important issues in modern semiconductor technology. Every material used in an MOCVD process is purified to avoid any kind of contamination. Gases used in an MOCVD reactor, including hydrogen, nitrogen, and helium carrier gases, can introduce contaminants to the semiconductor films. Contaminants can also be introduced by following improper procedures for gas-cylinder changing and vacuum-system maintenance.

Tubing, fitting, and valve selection is essential for the growth of high-purity films. Because some of the metal-organic sources and gases used in MOCVD are highly corrosive, components must be constructed of corrosion-resistant materials. Most MOCVD reactors use seamless 316 stainless steel tubing that has been electropolished inside. Selecting the proper gasket materials in fittings and valves is equally important. More information on the selection of tubes and fittings is given in Ref 76.

Hydrogen Purifier. The standard purity of the hydrogen supplied by many gas companies is 99.99 vol%. The major impurities are oxygen and water. Standard purity is inadequate for the growth of high-quality semiconductors. Research-grade hydrogen gas, with a purity on the order of 99.9995 vol%, is an expensive solution. The normal practice is to use standard-purity hydrogen gas that is run through a purifier at the point of delivery. Besides economics, this approach minimizes any water contamination introduced in the tubing between the cylinder and purifier.

In a hydrogen purifier, the impure hydrogen is passed through a palladium alloy membrane that serves as the diffusion medium. The palladium is inside a cell, which is heated to between 400 and 425 °C (750 and 800 °F). At these temperatures, only hydrogen diffuses through the membrane; all other elements are blocked. This type of purifier effectively delivers ultra-pure hydrogen gas to the system.

Thermal Bath. The vapor pressure of metal-organic sources is a sensitive function of temperature. To ensure controlled and reproducible source delivery, the source must be kept in a well-regulated thermal bath. Commercial thermal baths are able to control the temperature with an accuracy of ±0.1 °C (0.2 °F). Temperatures can be varied in the range of -30 to 100 °C (-20 to 210 °F).

Electronic mass-flow controllers are used to regulate the amount of gas flowing into the chamber. The carrier gas flows through the metal-organic bubbler to transport the source vapor into the chamber. Gaseous hydrides are delivered directly. Each must be precisely controlled to dictate the composition of the semiconductor film. Mass-flow controllers use a closed-loop control system that compares the requested flow to the actual flow and adjusts accordingly. The typical accuracy of a mass-flow controller is ±1% of full scale. A significant advantage of electronic mass-flow controllers is the ease of automation and programming for the growth of individual layers. Mass-flow controllers from various vendors operate under different physical principles. Each has different strengths and weaknesses with respect to calibration, drift, temporal response, and maintenance.

The gas-mixing manifold is an important component of the MOCVD system. The proper design of this manifold is crucial for growing superlattices and quantum-well structures, and for reducing the memory effect associated with some dopant sources (Ref 77). Because the manifold must not introduce additional contaminants into the system, it is constructed of electropolished stainless steel tubing. Welding is used in lieu of compression fittings to avoid leakage. Because the manifold also must deliver uniformly mixed gases to the reactor, it is connected both directly to the chamber and through a bypass line to the exhaust. A process flow is first established and stabilized through the bypass line before being introduced into the chamber. The gas manifold utilizes pneumatically actuated valves to permit process automation.

Susceptor Heat System. Any of three types of heating methods are used to heat the susceptor: radio-frequency (RF) induction heating, radiant heating, and resistance heating. In RF induction heating, the graphite or silicon-carbide graphite susceptor is inductively coupled to an RF coil. This type of heating, which is used in big industrial reactors, is usually very complex. In order to avoid the complexity of RF heating, radiant heating is often used. Here the graphite susceptor is heated by absorbing the radiant energy from lamps. In resistance heating, metallic susceptors (aluminum and molybdenum) are heated by the resistance to electrical current flow. The temperature of the susceptor can be measured by using embedded thermocouples or a pyrometer. The temperature of the substrate on the susceptor usually cannot be measured directly, but is less than the susceptor temperature because of poor thermal contact.

The exhaust system is the most critical part of the MOCVD configuration in terms of safety. The two main functions of this system are to remove unreacted gases and byproducts from the reaction chamber and to provide a path for reactants to bypass the reaction zone. Unreacted gases can react in the exhaust system, creating solid particles. Because these particles can collect and block the exhaust system, great care must be taken to remove them. In addition, a blocked exhaust line can lead to sudden pressure changes in the reactor, creating a back diffusion of particles, which affects the growth quality and uniformity. The vented gas can contain unreacted sources that may be toxic, pyrophoric, or flammable. Various cleaning systems are available, such as scrubbing systems, particle filters, and burn boxes.

Effluent Scrubbing Systems. The semiconductor wafer fabrication industry uses a variety of corrosive, toxic, pyrophoric, and flammable chemicals. In order to control pollution by toxic materials, different types of scrubbers are used. In the past, it was commonly believed that many chemicals could be released into the environment without hazard if they were diluted to a safe concentration level, as determined by a regulating agency and dictated by the detection limits of instrumentation or standards developed in response to exposure risks at the release site. The function of a scrubber was simply to reduce the concentration of contaminants produced to "safe levels." However, scientists have since demonstrated the negative impact of environmental contaminants at ever-diminishing levels. As a result, there has been a shift from scrubbers that simply dilute process gases to a new type of scrubber that can capture, isolate, and transform pollutants before allowing them to reach the environment.

As an example, a typical process for the epitaxial deposition of silicon requires the reaction of dichlorosilane (SiH_2Cl_2) and AsH_3. The scrubber is designed to remove the unreacted process gases in two stages. In the first stage, water removes unreacted SiH_2Cl by converting it to a complex mixture of solid silicon oxides. At the same time, hydrochloric acid (HCl) dissolves in the water and then exits the scrubber as aqueous HCl, which is neutralized. This reaction is summarized as:

$$SiH_2Cl_2 + AsH_3 + HCl \xrightarrow{H_2O} (SiO_2)_x + HCl_{(aq)} + AsH_3 + H_2 \qquad \textbf{(Eq 21)}$$

In the second stage, an oxidizing agent (e.g., potassium permanganate solution) oxides the arsenic to a solid residue, which then can be safely recovered for recycling. This reaction is written as:

$$AsH_3 + H_2 \xrightarrow{KMnO_{4(aq)}} As_2O_5 + MnO_2 + H_2 \qquad \textbf{(Eq 22)}$$

Because the solution used to remove toxic gases is expensive and its disposal difficult, scrubbers that use solid agents have been developed. By utilizing activated carbon, the toxic compounds from the effluent stream of MOCVD processes are adsorbed. In addition, controlled oxidation turns potentially harmful gases into solid oxides that have safer and easier disposal methods. This solid scrubbing is preferable to other methods, such as liquid scrubbers, burn boxes, and incinerators, which can cause back streaming or produce byproducts that are not wanted or have excessive disposal costs.

Burn boxes represent another way to dispose of unreacted materials from the exhaust. These boxes contain a furnace heated to a high temperature (900 to 1000 °C, or 1650 to 1830 °F), which cracks and oxidizes unreacted materials into less harmful compounds. Radical reaction products also condense on the quartz tube walls and are then removed as solids.

Particulate filters are used in conjunction with burn boxes or in front of pumping systems in low-pressure MOCVD systems. They must be able to remove particulates, resist clogging, minimize the exposure of maintenance personnel to arsenic dust, and contribute minimal internal outgassing.

Toxic-Gas Detectors. In the mid-1990s, almost all Group III-V growth systems use toxic gases such as AsH_3 and PH_3. Monitoring systems that are used to detect the presence of both AsH_3 and PH_3 provide a nearly instantaneous readout of concentration and initiate both warning and alarm signals whenever the preprogrammed concentration level for a particular gas and location is exceeded.

The solid-state gas sensors contain a heated resistor that is supplied with a specific voltage. When a gas enters the sensor, a voltage change is sensed because of the change in resistance. This voltage change is proportional to the concentration of the detected gas. The voltage is precalibrated in the factory for different gases and corresponding concentrations. The warning and alarm signals are set by the users, based on the safety level of each gas. Other types of toxic-gas detectors use chemically treated tape. Although they are more sensitive, they do not respond as quickly as solid-state detectors.

Engineering Considerations to Optimize Growth

Based on the study by Giling, as well as MOCVD growth practices (Ref 52), certain parameters are recommended for the growth of high-quality Group III-V semiconductor materials with sharp interfaces. First, laminar flows that are free of convection should exist by using a horizontal reactor, working at low pressure, and decreasing the reactor diameter. Second, temperature gradient should be present across the susceptor. Third, the memory effect should be eliminated by reactor geometries that prevent the development of vortices, and present no dead volumes. These conditions are designed to avoid parasitic reactions in the gas phase and condensation at the inlet of the deposition zone. Dead volumes should be avoided because they and the vortices will act as sources of unwanted materials that cannot be removed easily.

There have been at least 60 publications since the mid-1970s on the design of reactor cells and configurations. The essential factors in the design of horizontal cells have been established more recently (Ref 78, 79, 80, 81, 82, 83, 84). The ability to grow highly uniform compound semiconductors by MOCVD is influenced by a number of parameters in the gas-handling manifold and the growth cell. Several reactor design modifications have been reported to improve uniformity. First, the manifold must incorporate a pressure-balanced vent-run system (Ref 78). In addition, gas mixing must occur on the atomic level to ensure sufficient homogeneity across the susceptor. Compositional nonuniformity is eliminated by using a variety of gas-mixing devices (Ref 85), including vanes, meshes, mixing jets, spray tubes, silica frits and orifices, and perforated plates that are either stationary or rotating (Ref 78). The expansion region must prevent flow separation from the cell walls that leads to recirculation, upstream deposition, and nonuniform layers (Ref 70, 84, 86, 87, 88, 89, 90). The space between the substrate and reactor wall must be small enough to prevent return flow (Ref 70).

To overcome gas-phase depletion and geometrical effects, the substrate can be rotated (Ref 91, 92, 93, 94). Another approach to this engineering problem is to levitate the wafer carrier on a gas foil (Ref 92). To avoid parasitic gas reactions and to improve layer quality (Ref 95), some reactors use two separate inlets.

The understanding of the MOCVD process, including gas flow patterns and chemical-reaction pathways, is still immature. Growth parameters, such as temperature, pressure, total gas flow, and Group III/V ratio, are optimized empirically. Material is grown and characterized by ex-situ techniques. These results are correlated with the deposition conditions to predict the best processing parameters.

MOCVD Starting Materials

The alkyls of Group II and III metals and the hydrides of Group V and VI elements are generally used as precursors in MOCVD. Dilute vapors of these chemicals are transported at or near room temperature to a hot zone, where pyrolysis reactions occur. For example, GaAs is formed by heating trimethylgallium, $(CH_3)3Ga$, or triethylgallium, $(C_2H_5)3Ga$, and AsH_3 over a suitable substrate, usually a single crystal of GaAs or silicon, at temperatures near 600 °C (1110 °F). The decomposition reactions can be expressed as:

$$(C_2H_5)_3Ga + AsH_3 \rightarrow GaAs + 3C_2H_6 \qquad \textbf{(Eq 23)}$$

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4 \qquad \textbf{(Eq 24)}$$

The reaction for Group III-V compounds can be generalized as:

$$R_3M + EH_3 \rightarrow ME + 3RH \qquad \textbf{(Eq 25)}$$

where M is the Group III metal (such as gallium, indium, or aluminum), E is the Group V element (such as arsenic, phosphorus, or antimony), and R is the alkyl radical (either CH_3 or C_2H_5).

Acceptable starting materials for MOCVD must be stable at room temperature and must not spontaneously decompose or polymerize. They also must vaporize in hydrogen, nitrogen, or helium gases without decomposing, be capable of purification, and have the lowest possible toxicity. Suitable starting materials and their physical properties are listed in Table 2. Each item in this table is either an alloy constituent or a dopant. Group III-V source materials will be discussed in detail, because they are primarily used in optoelectronic and high-frequency device applications.

Table 2 Physical properties of selected metal-organic materials used in metal-organic chemical vapor deposition

Compound	**Formula**	**Abbreviation**	**Melting point**		**Boiling point**		**Log$_{10}$ vapor pressure, Pa (torr); Temperature, *T*, in kelvin**	**Pressure, Pa (torr); Temperature, *T*, in kelvin**
			°C	**°F**	**°C**	**°F**		
Group II sources								
Diethylberyllium	$(C_2H_5)_2Be$	DEBe	12	54	194	381	1012 (7.59); *T*,	. . .

							2200	
Dimethylberyllium	$(CH_3)_2Be$	DMBe	. . .	. . .	. . .	. . .	. . .	. . .
Bis(cyclopentadienyl)magnesium	$(C_5H_5)_2Mg$	Cp_2Mg	176	349	. . .	. . .	3351 (25.14); *T*, 4198(a)	1.33 (0.01); *T*, 273
Group IIB sources								
Dimethylzinc	$(CH_3)_2Zn$	DMZn	-42	-44	46	115	1040 (7.802); *T*, 1560	16,529 (124); *T*, 273(b)
Diethylzinc	$(C_2H_5)_2Zn$	DEZn	-28	-18	118	244	1104 (8.280); *T*, 2190	480 (3.6); *T*, 273(c)
Dimethylcadmium	$(CH_3)_2Cd$	DMCd	-4.5	24	105.5	222	1035 (7.764); *T*, 1850	1293 (9.7); *T*, 273(d)
Group III sources								
Trimethylaluminum	$(CH_3)_3Al$	TMAl	15.4	59.7	126	259	1096 (8.224); *T*, 2134	293 (2.2); *T*, 273(e)
Triethylaluminum	$(C_2H_5)_3Al$	TEAl	-58	-72	194	381	1438 (10.784); *T*, 3625	67 (0.5); *T*, 328
Trimethylgallium	$(CH_3)_3Ga$	TMGa	-15.4	4.28	55.7	132	1075 (8.07); *T*, 1703	8598 (64.5); *T*, 273(f)
Triethylgallium	$(C_2H_5)_3Ga$	TEGa	-82.3	-116	143	289	1096 (8.224); *T*, 2222	453 (3.4); *T*, 293(g)
Trimethylindium	$(CH_3)_3In$	TMIn	88.4	191	133.8	272.8	1402 (10.520); *T*, 3014	40 (0.3); *T*, 273(h)
Triethylindium	$(C_2H_5)_3In$	TEIn	-32	-26	184	363	160 (1.2); . . .	160 (1.2); *T*, 313
Dimethylaluminum hydride	$(CH_3)_2AlH$	DMAlH	. . .	. . .	154	309	1189 (8.92); *T*, 2575	267 (2); *T*, 298
Triisobutylgallium	$(C_4H_9)_3Ga$	TIBGa	. . .	. . .	. . .	. . .	636 (4.769); *T*, 1718	67 (0.5); *T*, 310
Group III adducts								

Trimethylindium-trimethyl nitrogen	. . .	TMIn-TMN	94-96	201-205	. . .	. . .	. . .	0.4 (0.003); *T*, 273(i)
Trimethylindium-trimethylphosphorus	. . .	TMIn-TMP	43-45	109-113	. . .	. . .	. . .	5.3 (0.04); *T*, 273(j)
Trimethylindium-triethylphosphorus	. . .	TMIn-TEP	33-36	91-97	. . .	. . .	. . .	0.05 (0.0004); *T*, 273(k)
Trimethylindium-trimethylarsenic	. . .	TMIn-TMAs	28-29	82-84	. . .	. . .	. . .	36 (0.27); *T*, 273(l)
Group IV sources								
Tetramethylgermanium	$(CH_3)_4Ge$	TMGe	-88	-126	43.6	110.5	18.529 (139); . . .	. . .
Tetramethyltin	$(CH_3)_4Sn$	TMSn	-53	-63	78	172	999 (7.495); *T*, 1620	. . .
Tetraethyltin	$(C_2H_5)_4Sn$	TESn	-112	-170	181	357	. . .	. . .
Group V sources								
Trimethylphosphorus	$(CH_3)_3P$	TMP	-85	-120	37.8	100	1031 (7.7329); *T*, 1512	50.787 (381); *T*, 293
Triethylphosphorus	$(C_2H_5)_3P$	TEP	-88	-126	127	260	1048 (7.86); *T*, 2000	6198 (46.5); *T*, 323
Trimethylarsenic	$(CH_3)_3As$	TMAs	-87.3	-125	50-52	122-126	1028 (7.7119); *T*, 1563	31,725 (238); *T*, 293
Triethylarsenic	$(C_2H_5)_3As$	TEAs	-91	-132	140	284	2066 (15.5); . . .	666 (5); *T*, 293(m)
Trimethylantimony	$(CH_3)_3Sb$	TMSb	-86.7	-124	80.6	177.1	1030 (7.7280); *T*, 1709	. . .
Triethylantimony	$(C_2H_5)_3Sb$	TESb	-98	-144	116	240	2266 (17); . . .	533 (4); *T*, 298
Isobutylphosphine	. . .	IBP	-20	-4	78	172	1010 (7.578); *T*, 1648	14,930 (112); *T*, 298

Tertiarybutylphosphine	. . .	TBP	4	39	54	129	1004 (7.532); *T*, 1443	23,460 (176); *T*, 273
Dimethylarsenic	$(CH_3)_2As$	DMAs	. . .	. . .	36.3	97.3	978 (7.339); *T*, 1680	5332 (40); *T*, 293
Diethylarsenic	$(C_2H_5)_2As$	DEAs	. . .	. . .	102	216	965 (7.243); *T*, 1509	10,797 (81); *T*, 283
Tertiarybutylarsenic	. . .	TBAs	-1	30	65	149	1129 (8.47); *T*, 2410	240 (1.8); *T*, 293
Phenylarsine	. . .	$PhAsH_2$	. . .	. . .	. . .	. . .	. . .	. . .
Group VI sources								
Diethylselenium	$(C_2H_5)_2Se$	DESe	. . .	. . .	108.00	226	. . .	. . .
Dimethyltellurium	$(CH_3)_2Te$	DMTe	-10	14	82.00	180	1062 (7.97); *T*, 1865	(65); *T*, 303
Diethyltellurium	$(C_2H_5)_2Te$	DETe	. . .	. . .	137-138	278-280	1065 (7.99); *T*, 2093	(12); *T*, 303

Source: Ref 48, 96

(a) ln *T*, 2.18.

(b) 40,790 Pa (306 torr); *T*, 293 K.

(c) 2000 Pa (15 torr); *T*, 293 K.

(d) 3732 Pa (28 torr); *T*, 293 K.

(e) 1200 Pa (9 torr); *T*, 293 K.

(f) 23,727 Pa (178 torr); *T*, 293 K.

(g) 2133 Pa (16 torr); *T*, 316 K.

(h) 227 Pa (1.7 torr); *T*, 293 K.

(i) 4 Pa (0.03 torr); *T*, 293 K.

(j) 29 Pa (0.22 torr); *T*, 293 K.

(k) 0.4 Pa (0.003 torr); *T*, 293 K.

(l) 160 Pa (1.2 torr); *T*, 293 K.

(m) 2066 Pa (15.5 torr); *T*, 310.

Group III Sources. Trimethyl and triethyl alkyls have been used exclusively in the early development of MOCVD. The trimethyl sources are used most often because of their high vapor pressure and good stability. The triethyl sources, such as triethylaluminum (TEAl), triethylgallium (TEGa), and triethylindium (TEIn), are only marginally stable. The latter material has been observed to decompose in storage containers. It was also discovered that TEIn reacts with the Group V hydrides, AsH_3 and PH_3, to form nonvolatile adducts upstream from the substrates (Ref 50) in atmospheric-pressure MOCVD reactors. However, in low-pressure MOCVD reactors, TEGa and TEAl were used successfully to reduce the carbon concentrations in GaAs and AlGaAs (Ref 97). These materials evidently pyrolyze without producing the highly reactive methyl radicals that are generally believed to be the main source of carbon in the epitaxial layers. Recently, triisobutylgallium (TIBGa), which has an even lower thermal stability than TEGa, has been used to grow GaAs (Ref 98).

Trimethylindium is currently the most widely used source of indium. It avoids the stability problems associated with the use of TEIn. Parasitic reactions are not observed in atmospheric-pressure MOCVD growth when TMIn is used. However, TMIn has a nonuniform evaporation rate, because it is a solid at room temperature. It also has a tendency to explode. Alternative indium sources that are liquid below room temperature, have adequate vapor pressure, and exhibit good chemical stability are still being sought.

Knauf et al. combined the advantages of TMIn (less parasitic reactions) with those of TEIn (liquid during use) by producing a new compound, ethyldimethylindium (EDMIn) (Ref 99). This material is liquid at room temperature and has a vapor pressure of 115 Pa (0.85 torr) at 17 °C (63 °F), which is similar to the value for TMIn at 135 Pa (1 torr) and an order of magnitude greater than the vapor pressure of TEIn. In early experiments, EDMIn was not as pure as TMIn. However, it is now available in high-purity form, which makes it an attractive indium source.

The growth of semiconductors containing aluminum has always been difficult because aluminum is highly reactive and readily incorporates carbon and oxygen into the solid (Ref 100). The incorporation of carbon is particularly likely when trimethylaluminum (TMAl) is used, because it pyrolyzes to form aluminum carbide. Other alkyl sources, such as triethylaluminum (TEAl) and triisobutylaluminum (TIBAl), which decompose to aluminum metal, can be used to minimize carbon incorporation. However, they have low vapor pressures at room temperature. Heating to increase the vapor pressure requires that the gas lines and the reactor tube be heated along with the source. In addition, these compounds are not sufficiently stable to be effective. Kuech et al. has reported reduced growth efficiency, when these compounds are compared with other sources (Ref 97). This indicates the occurrence of parasitic reactions, predominantly premature pyrolysis, that create wall deposits upstream from the substrate. The most unstable of these compounds is TIBAl, which can decompose in storage containers at room temperature.

In order to provide an acceptable source of aluminum, new molecules with the appropriate properties must be developed. Dimethylaluminumhydride (DMAlH) has an acceptable vapor pressure of 265 Pa (2 torr) at 25 °C (77 °F) and pyrolyzes at a temperature as low as 250 °C (480 °F) (Ref 101). Both AES and SIMS analyses of films grown from DMAlH indicate little carbon contamination. It has been shown that DMAlH can produce excellent aluminum gallium arsenide (AlGaAs) epitaxial layers. The only problem is that the layers have a high background doping level, with an approximate *n*-type carrier concentration of $2 \times 10^{18}/\text{cm}^3$ ($33 \times 10^{18}/\text{in.}^3$). The background doping level is due to silicon and sulfur impurities in the DMAlH source. Preliminary photoluminescence data indicate that the carbon concentration is substantially less than levels produced in layers grown from TMAl.

Alternative sources for the MOCVD growth of Group III-V compounds are adducts. An adduct is a compound formed between a Group III alkyl, such as MR_3, that acts as an electron-acceptor molecule (Lewis acid) and a Group V alkyl, such as ER_3, that acts as an electron-donor molecule (Lewis base), according to the following reaction:

$$MR_3 + ER_3 \rightarrow R_3MER_3 \qquad \textbf{(Eq 26)}$$

Adducts were first proposed by Harrison and Tompkins for the growth of indium antimonide (InSb) and GaAs (Ref 102).

Since 1980, acid-base adducts, for example, TMIn-triethylphosphine (TEP) (Ref 103) and TMIn-trimethylphosphine (TMP) (Ref 104), have been used as alternative metal sources to eliminate parasitic reactions in the atmospheric-pressure MOCVD growth of InP (Ref 105, 106, 107). Adducts produce fewer parasitic reactions because of their high chemical stability. Today, trimethyl and triethyl alkyls produce less parasitic reactions because of their higher purity and improved, safer handling facilities. Nevertheless, the adducts are still used in many laboratories to produce high-quality InP (Ref 107, 108), GaInAs on InP quantum-well structures (Ref 109), and InP on silicon layers (Ref 106). The films exhibit almost the same quality and background doping levels as films grown from the alkyls using the same deposition conditions. The main advantages of adducts are their low reactivity with oxygen and water vapor, and their liquid form at room temperature. The adduct TEGa-TEP is used in place of TEGa because of its higher vapor pressure, compared to the gallium alkyls (Ref 110). The indium adducts, however, have rather low vapor pressures. They are normally used at temperatures above 60 °C (140 °F), and the gas lines of the MOCVD system must be heated to prevent condensation.

The development of new precursors with tailored physiochemical properties (vapor pressure, melting point, stability) is an emerging field of research. New, intramolecularly saturated dimethyl-3-dimethylaminopropylindium $(CH_3)_2In(CH_2)3N(CH_3)_2$ and the adduct trimethylindium-diisopropylamine, $(CH_3)3In\text{-}NH(C_3H_7)_2$, have been synthesized (Ref 111). The first epitaxial results with these compounds are very promising. Indium phosphide layers with electron mobilities of 50,000 $cm^2/V \cdot s$ (7750 $in.^2/V \cdot s$) at 77 K have been produced. Aluminum- and gallium-based semiconductors also have been successfully grown using these new sources. Moreover, such sources are expected to reduce carbon incorporation when combined with organometallic Group V sources, because they can be cracked to form stable organic molecules even in the absence of atomic hydrogen. For less stable organometallics, carbon incorporation seems to be lower. Plass et al. have employed TlBGa as a starting material, but impurities in the source caused the resulting layers to show a relatively high n-type conduction (Ref 98). Another type of alternative source has been investigated in order to provide a single source for both the metal and the Group V element. Maury et al. successfully grew GaAs layers using $(ClMe_2Ga\text{-}AsEt_2)_2CH_2$ and $(C_6F_5)_3Ga\text{-}AsEt_3$ without an additional arsenic source (Ref 112, 113, 114, 115, 116). However, the importance of such compounds is limited to the growth of binary materials. For atomic-layer epitaxy by MOCVD, More and Sasaoka et al. used $Ga(C_2H_5)_2Cl$ as a starting material (Ref 117, 118). Such reactants have not previously been used in a normal MOCVD process.

Group V Sources. The hydride gases commonly used as precursors for Group V elements are extremely hazardous and toxic. Both AsH_3 and PH_3 have threshold level values of 0.05 and 0.3 ppm, respectively. A summary of the effects on human exposure to arsenic and phosphorus hydrides is given by Hess and Riccio (Ref 119). In addition, these gases must be stored in high-pressure cylinders (equilibrium vapor pressures at 20 °C, or 70 °F, are 140 and 410 kPa, or 14 and 41 bars, for arsine and phosphine, respectively). Consequently, large quantities of these toxic gases may accidentally be released in a very short time. They must be handled very carefully, especially when changing cylinders. Thus, the utilization of AsH_3 and PH_3 requires costly and delicate equipment to protect the operators and the environment from hazards, and the products from atmospheric contamination. Less toxic and hazardous alternative sources are desired for safety reasons. A number of organometallic Group V sources are less toxic than the hydrides. Another advantage of the organometallic sources is that they have moderate vapor pressures. This results in a less hazardous working environment, because computer studies show that the dispersion of these materials is approximately two orders of magnitude slower than for the release of gases from high-pressure cylinders. A good review of nonhydride Group V sources is provided by Stringfellow (Ref 120).

Finding alternatives to the highly toxic AsH_3 has been the subject of recent research. Organoarsenic materials normally have much lower vapor pressures and threshold level values, which enable safer handling (Ref 121). The commonly used reactants are trimethylarsenic (TMAs) (Ref 122, 123) and triethylarsenic (TEAs). (Ref 52, 120, 122, 123, 124, 125). It was shown that TEAs is less stable than AsH_3 under normal growth conditions, enabling lower Group V-III ratios in the MOCVD process. However, in most cases, carbon incorporation is significant ($\geq 5 \times 10^{16}/cm^3$) (Ref 80, 126). In addition, epitaxial layer morphology is inferior, probably because of the incorporation of carbon and other atomic or molecular impurities.

Other materials, such as tertiarybutylarsine (TBAs) (Ref 30, 122, 127, 128), isobutylarsine (IBAs) (Ref 29, 129), dimethylarsine (DMAsH) (Ref 130), diethylarsine (DEAsH) (Ref 105), and phenylarsine ($PhAsH_2$) (Ref 122), have been used to overcome this problem. Some of them, especially TBAs and $PhAsH_2$, have shown promising results (Ref 30, 128). Most of the organoarsenic compounds mentioned above are commercially available. In addition to excess carbon incorporation, other disadvantages include their limited purity and high cost. The use of elemental arsenic seems to be unsuitable for a reliable epitaxial process (Ref 131).

Alternative phosphorus sources are also desired to minimize toxic waste and safety hazards. Initially, experiments were carried out using TMP and triethylphosphine TEP (Ref 132). However, they must be precracked before being introduced to the growth chamber because of their high thermal stability. This rather nonreproducible technique is therefore not suitable for MOCVD. The same holds true for elemental phosphorus sources, which were investigated by Naitoh et al. (Ref 133).

Larger organophosphorus molecules, such as TBP and IBP, have exhibited better growth results (Ref 28, 134, 135, 136). Tertiarybutylphosphine, in particular, has a favorable vapor pressure and is found to pyrolyze several hundred degrees lower than PH_3 (Ref 134). This can be an advantage when growing quaternary compounds (e.g., InGaAsP), which require arsenic and phosphorus sources with comparable thermal stability. Because the toxicity of TBP is much lower than that of PH_3, it is a good candidate for future investigations (Ref 120).

Group III-V Semiconductor Growth Parameters

Group III-V semiconductors are the major materials used in optoelectronic and high-frequency electronic device applications. The ability to tailor the band structure and lattice constant in ternary and quaternary alloys by varying the composition represents one of the desirable features of these materials.

The GaAs-based materials described below include not only GaAs, but gallium indium phosphide (GaInP), gallium aluminum arsenide (GaAlAs), and gallium indium arsenide phosphide (GaInAsP).

GaAs layers can be grown either at atmospheric or low pressure in the temperature range from 500 to 550 °C (Ref 52). TEGa or TMGa and AsH_3 have been used as gallium and arsenic sources. Pure hydrogen can be used as a carrier gas. The growth rate depends linearly on the flow rate of Group III (gallium) elements and is independent of AsH_3 flow rate, substrate temperature, and substrate orientation. This suggests that epitaxial growth is controlled by the mass transport of Group III species.

The growth of GaAs layers has been carried out on <100> GaAs substrates misoriented up to 2° toward the <011> plane. The substrates were etched in a $H_2SO_4:H_2O_2:H_2O$ (5:1:1) solution for 20 s at 40 °C (105 °F), rinsed with deionized water, and dried under pure nitrogen. Before the growth process, the substrates were initially heated to the growth temperature under hydrogen and AsH_3 for 5 min to remove any surface oxides. Table 3 lists the optimum conditions for the low-pressure MOCVD growth of GaAs.

Table 3 Optimum growth conditions of gallium arsenide (GaAs), gallium indium phosphide (GaInP), and gallium indium arsenide phosphide (GaInAsP)

	GaAs	**$Ga_{0.51}In_{0.49}P$**	**$Ga_{0.87}In_{0.13}As_{0.73}P_{0.27}$**
Growth pressure, Pa (torr)	10,130 (76)	10,130 (76)	10,130 (76)
Growth temperature, °C (°F)	510 (950)	510 (950)	510 (950)
Total hydrogen flow rate, L/min (gal/min)	3 (0.8)	3 (0.8)	3 (0.8)
Arsine, cm^3/min ($in.^3$/min)	30 (1.8)	. . .	20 (1.2)

Trimethylindium, cm^3/min ($in.^3$/min)	. . .	200 (12)	150 (9)
Triethylgallium, cm^3/min ($in.^3$/min)	120 (7)	120 (7)	170 (10)
Phosphine, cm^3/min ($in.^3$/min)	. . .	300 (18)	200 (390)
Growth rate, nm/min (μin./min)	15 (0.6)	20 (0.8)	25 (1.0)

Note: For 808 nm (31.5 μin.) materials

Epitaxial GaAs layers are of the *n*-type in a wide range of Group V/III ratios and substrate temperatures. Suitable conditions, such as growth temperature, growth rate, total flow rate, purity of starting materials, and reactor design, are responsible for the high quality of the epitaxial layers.

GaInP layers can be grown on GaAs using MOCVD, either at atmospheric pressure or low pressure, in the temperature range from 500 to 600 °C (930 to 1110 °F) (Ref 137). Different Group III alkyls can be used for gallium and indium sources, whereas hydrides or alkyls can be used for the Group V phosphorus source. Chemical reactions that occur among these sources are:

$$0.51R_3Ga + 0.49\ R'_3In + EH_3 \\ -Ga_{0.51}In_{0.49}P + nC_nH_{2n} \qquad \textbf{(Eq 27)}$$

where *R*, *R*', and *E* can be methyl, ethyl, alkyl, or hydride.

For example, one can use:

$$0.49(C_2H_5)_3In + 0.51(C_2H_5)_3Ga + PH_3 \rightarrow InGaP \\ + nC_2H_6\text{, or} \qquad \textbf{(Eq 28)}$$

$$0.49(CH_3)_3In + 0.51(CH_3)_3Ga + PH_3 \rightarrow InGaP \\ + nCH_4\text{, or} \qquad \textbf{(Eq 29)}$$

$$0.49(CH_3)_3In + 0.51(C_2H_5)_3Ga + PH_3 \rightarrow InGaP \\ + nC_2H_6\text{, or} \qquad \textbf{(Eq 30)}$$

$$0.49(C_2H_5)_3In + 0.51(CH_3)_3Ga + PH_3 \rightarrow InGaP \\ + nC_2H_6 \qquad \textbf{(Eq 31)}$$

The GaInP layers can be grown at the lower temperatures of 500 to 550 °C (930 to 1020 °F), by using TEGa, TMIn, and PH_3 in a hydrogen carrier gas. At optimum conditions (Table 3), the growth rate (dx/dt) of GaInP depends on the flow rates of TMIn and TEGa and is independent of the PH_3 flow rate and growth temperature. The undoped GaInP layer grown as specified has a free electron carrier concentration of $5 \times 10^{14}/cm^3$ ($80 \times 10^{14}/in.^3$), with a mobility of 6000 $cm^2/V \cdot s$ (930 $in.^2/V \cdot s$) at 300 K and 40,000 $cm^2/V \cdot s$ (6200 $in.^2/V \cdot s$) at 77 K. No GaAs buffer layer was grown in this case.

GaAlAs layers can be grown on a GaAs substrate in the temperature range of 600 to 750 °C (1110 to 1380 °F) by using TMGa, TMAl, and AsH_3 as the sources of gallium, aluminum, and arsenic, respectively. Oxygen incorporation, produced by the strong reactivity of aluminum with oxygen, can deteriorate the optical and electrical properties of the GaAlAs epitaxial layer (Ref 138). To solve this problem, graphite baffles are used for internal gettering. They absorb TMAl, which then reacts with oxygen to form the extremely stable, nonvolatile Al_2O_3 (Ref 139). It was later discovered that high-quality aluminum gallium arsenide (AlGaAs) can be grown at higher temperatures (<780 °C, or 1440 °F) without using oxygen-gettering techniques (Ref 140). This is because the aluminum suboxide that absorbs on surfaces at high temperatures is more volatile. It was demonstrated that at low aluminum concentrations, the photoluminescence intensity increases by three orders of magnitude as the substrate temperature increases from 600 to 750 °C (1110 to 1380 °F). No effect occurs at high aluminum concentrations (Ref 141).

GaInAsP layers can be grown on GaAs by using low-pressure MOCVD within the entire composition range in which the quaternary is lattice matched to GaAs. Both TMIn and TEGa are used as the sources of indium and gallium, whereas AsH_3 and PH_3 are used as the sources of arsenic and phosphorus. The optimum conditions for the growth of GaInAsP (composition having a bandgap of 808 nm, or 31.5 μin.) on GaAs are listed in Table 3. The quality of the quaternary is comparable with that of the quaternary grown on InP substrates (Ref 142).

The InP-based materials described below include not only InP, but gallium indium arsenide (GaInAs) and gallium indium arsenide phosphide (GaInAsP) grown on InP.

High-quality InP layers have been grown by using MOCVD (Ref 52). Both TEIn and PH_3 are used as indium and phosphorus sources, respectively. A mixture of hydrogen and nitrogen is used as the carrier gas. The presence of hydrogen is necessary to avoid the deposition of carbon, and the presence of nitrogen is necessary to avoid the parasitic reaction between TEIn and PH_3.

The InP layers have been grown at 10 kPa (76 torr) and at low temperatures (between 500 and 650 °C, or 930 and 1200 °F) by using TEIn, PH_3, and a mixture of hydrogen and nitrogen as the carrier gas. The growth rate (ranging from 200 to 800 cm^3/min, or 12 to 48 in.^{3}/min) is linearly dependent on the TEIn flow rate, and is independent of PH_3 flow rate, substrate temperature, and substrate orientation. This suggests that epitaxial growth is controlled by the mass transport of Group III species.

Razeghi and Duchemin (Ref 18) have studied the growth of InP layers by using 100% hydrogen and mixtures of hydrogen and nitrogen as the carrier gas. The best morphology and the highest photoluminescence intensity were obtained by using 50% hydrogen and 50% nitrogen. Using argon instead of nitrogen produced InP layers with the same surface quality. Table 4 lists the optimum conditions used in this study for the MOCVD growth of InP in the temperature range of 550 to 650 °C (1020 to 1200 °F). The InP layers grown by MOCVD are less compensating at lower growth temperatures.

Table 4 Optimum growth conditions of indium phosphide

Growth temperature		Nitrogen-triethylindium bubbler flow rate		Phosphine flow rate		Total flow rate		Growth rate	
°C	°F	cm^3/min	in.^{3}/min	cm^3/min	in.^{3}/min	L/min	gal/min	nm/min	μin./min
550	1020	450	27	260	16	6	1.6	20±1	0.8±0.04
		225	14	200	12	6	1.6	10±1	0.4±0.04
650	1200	450	27	520	32	6	1.6	22±1	0.9±0.04
		225	14	400	24	6	1.6	11±1	0.4±0.04

GaInAs layers can be grown on InP substrates at 10 kPa (76 torr) in the temperature range of 500 to 650 °C (930 to 1200 °F), using either TEIn or TMIn, TEGa, and AsH_3 (Ref 52). When TEIn is used as the indium source, then pure hydrogen is used as the carrier gas. When TMIn is used, then a mixture of hydrogen and nitrogen is used as the carrier gas. The growth rate is linearly dependent on the combined flow rates of TEGa and TEIn. It is independent of the AsH_3 flow rate within the range of 60 to 90 cm^3/min (3.5 to 5.5 in.^{3}/min). This suggests, as in the case of InP, that epitaxial growth is controlled by the mass transport of Group III species. Uniform layers of $Ga_{0.47}In_{0.53}As$ have been deposited over large areas (10 cm^2, or 1.5 $in.^2$) of InP substrates. The quality of the epitaxial layer is sensitive to the alloy composition, as in the case of GaInAs grown by other techniques.

The surface morphology of GaInAs grown on InP depends on the pretreatment of the substrate and is independent of the lattice mismatch, even when the mismatch is 0.01 or more. $Ga_{0.47}In_{0.53}As$ grown on InP exhibits an excellent surface morphology and state-of-the-art electron mobility when grown under the optimum conditions listed in Table 5.

Table 5 Optimum growth conditions of gallium indium arsenide/indium phosphide

Growth temperature, °C (°F)	550 (1020)
Total flow rate, L/min (gal/min)	7 (1.8)
Hydrogen-triethylindium bubbler flow rate, cm^3/min ($in.^3$/min)	450 (27)
Hydrogen-triethylgallium bubbler flow rate, cm^3/min ($in.^3$/min)	180 (11)
Phosphine flow rate, cm^3/min ($in.^3$/min)	90 (5)
Growth pressure, Pa (torr)	76 (0.6)
Growth rate, nm (μin.)	27 (1.05)

Note: Stoichiometry of material is $Ga_{0.47}In_{0.53}As$.

$Ga_xIn_{1-x}As_yP_{1-y}$ layers can be grown on InP substrates in the range of compositions that are lattice matched. Growth occurs at 10 kPa (76 torr) and at a substrate temperature between 630 and 650 °C (1170 and 1200 °F) using TEIn, TEGa, AsH_3, and PH_3 in a mixture of hydrogen and nitrogen carrier gas (Ref 52). The growth rate is linearly dependent on the sum of the partial pressures of TEIn and TEGa, and is independent of the arsenic and phosphorus partial pressures. The epitaxial layer quality is sensitive to the pretreatment of the substrate and the alloy composition. The optimum growth conditions for the lattice-matched composition, $Ga_{0.23}In_{0.77}As_{0.51}P_{0.49}$, are listed in Table 6.

Table 6 Optimum growth conditions of gallium indium arsenide phosphide/indium phosphide

Source	**Partial pressure**		**Temperature**	
	Pa	**mbar**	**°C**	**°F**
Triethylindium	0.85	0.0085	31	88
Triethylgallium	0.3	0.003	0	32
Arsine	31	0.31	25	77
Phosphine	700	7	25	77

nitrogen, 7 L/min (1.8 gal/min). Stoichiometry of material is $Ga_{0.28}In_{0.72}As_{0.61}P_{0.39}$.

Source: Ref 52

The nitride semiconductors described below include gallium nitride (GaN) and aluminum nitride (AlN).

High-quality GaN films have been very difficult to obtain because of the large mismatch in lattice constant and coefficient of thermal expansion with available substrates. The (001) plane of sapphire is often used, although the mismatch is large. Sun et al. recently discovered that the (012) plane is better matched with GaN and produces higher-quality GaN films (Ref 143). In the cited study, GaN was grown at atmospheric pressure in the temperature range of 900 to 1000 °C (1650 to 1830 °F), using TMGa and ammonia (NH_3) as the sources of gallium and nitrogen. The carrier gas was hydrogen. The precursors were mixed just before entering the reactor, in order to reduce the parasitic reactions between the metal-organics and NH_3. The total gas flow rate of 1600 sccm comprised 3 to 10 standard cm^3/min (sccm) TMGa, 500 to 1100 sccm NH_3, and carrier gas. The bubbler was kept at -10 °C (15 °F) for TMGa.

Aluminum nitride has been grown by using atmospheric-pressure MOCVD, with TMAl and NH_3 as the aluminum and nitrogen sources, respectively. The flow rates of each precursor were: 5 sccm of TMAl, 400 sccm of NH_3, and 1200 sccm of N_2. The TMAl was maintained in a bubbler at 25 °C (77 °F). The growth temperature was 1050 °C (1920 °F). Both the (001) and (012) planes of sapphire and the (100) plane of silicon were used as substrates. Thermal annealing under hydrogen and nitrogen caused no degradation of the crystalline quality, and improved the optical quality of the films (Ref 144).

The antimony-based materials described below include indium antimonide (InSb) and indium thallium antimonide (InTlSb).

Indium antimonide can be grown by using low-pressure MOCVD, with TMIn and trimethylantimony (TMSb) as sources for indium and antimony, respectively (Ref 145). Both InSb and GaAs (100) substrates were used in the growth process. Optimum growth conditions are listed in Table 7. The full width at half maximum of an x-ray rocking curve of 174 arc · s and a Hall mobility of 76,200 $cm^2/V \cdot s$ (11,820 $in.^2/V \cdot s$) at 240 K have been observed for a layer of 4.85 μm (190 μin.) grown under the optimum conditions.

Table 7 Optimum growth conditions of indium antimonide

Growth pressure, Pa (torr)	10,130 (76)
Growth temperature, °C (°F)	465 (870)
Total hydrogen flow rate, L/min (gal/min)	1.5 (0.40)
Hydrogen flow rate through trimethylindium bubbler, cm^3/min ($in.^3$/min)	50 (3.1)
Hydrogen flow rate through trimethylantimony bubbler, cm^3/min ($in.^3$/min)	20 (1.2)
Growth rate, μm/h (μin./h)	1.2 (47)

Source: Ref 145

Indium thallium antimonide was grown for the first time by using low-pressure MOCVD, with TMIn and TMSb as sources of indium and antimony, respectively, and cyclopentadienylthallium as the source of thallium (Ref 146). The optimum growth conditions are listed in Table 8.

Table 8 Optimum growth conditions of indium thallium antimonide

Growth pressure, Pa (torr)	10,130 (76)
Growth temperature, °C (°F)	455 (851)
Total hydrogen flow rate, L/min (gal/min)	1.5 (0.4)
Hydrogen flow rate through trimethylindium bubbler, cm^3/min (in.^{3}/min)	50 (3.1)
Hydrogen flow rate through trimethylantimony bubbler, cm^3/min (in.^{3}/min)	20 (1.2) 60 (3.7)

Source: Ref 146

Other Group III-V materials that have been grown by using MOCVD are listed in Table 9.

Table 9 The principal Group III-V materials grown by metal-organic chemical vapor deposition

Film	**Substrate**	**Precursors**	**Reference**
Gallium phosphide	Gallium phosphide	TMG, PH_3	147
Gallium antimonide	Gallium antimonide	TMG, TMSb	148
Indium arsenide	Indium arsenide	TEI, AsH_3	149
Gallium aluminum phosphide	Gallium phosphide	TMG, TMAl, PH_3	147
Gallium aluminum antimony	Gallium arsenide	TMG, TMAl, TMSb	150
Gallium indium arsenide	Gallium arsenide	TMG, TEI, TMAs	151
Aluminum indium arsenide	Indium phosphide	TMAl, TMI, AsH_3	152
Indium arsenide antimonide	Indium antimonide	TMI, TMSb, AsH_3	153
Gallium aluminum arsenide antimonide	Gallium arsenide	TMG, TMAl, TMAs, TMSb	151
Indium arsenide antimonide phosphide	Indium arsenide	TEI, TESb, AsH_3, PH_3	154

Note: TMG, trimethylgallium; PH_3, phosphine; TMSb, trimethylantimony; TEI, triethylindium; AsH_3, arsine; TMAl, trimethylaluminum; TMAs, trimethylarsenic; TMI, trimethylindium; TESb, triethylantimony

Group II-VI Semiconductor Growth Parameters

The Group II-VI semiconductors have been used for electroluminescent films (zinc sulfide and zinc selenide), infrared and far-infrared photodetectors (mercury cadmium telluride), thin-film photovoltaic devices (cadmium telluride), and, most recently, blue semiconductor lasers (zinc selenide).

The wide-bandgap materials described below include zinc selenide (ZnSe), zinc sulfide (ZnS), and zinc sulfide selenide (ZnS_xSe_{1-x}).

Both ZnSe and ZnS can be grown on GaAs or GaP substrates by using diethylzinc (DEZn) or dimethylzinc (DMZn) as the source of zinc, and either hydrogen sulfide (H_2S) or hydrogen selenide (H_2Se) respectively. However, the MOCVD growth of wide-bandgap selenides and sulfides has two major problems that are not encountered in the growth of Group III-V materials. The first is a premature reaction between DMZn and DEZn and H_2Se or H_2S, and the second is the formation of native defects, such as zinc, selenium, and sulfur vacancies at high growth temperatures. The first problem leads to poor surface morphology, whereas the second problem seems to be inherent to wide-bandgap semiconductors, especially materials that contain relatively high vapor pressure elements, such as ZnSe and ZnS.

The first problem can be solved by using both Group II and Group VI dialkyl sources, such as DMZn or DEZn and dimethylselenium (DMSE) or diethylselenium (DESe) because of the high decomposition temperature of these sources. The second problem can be reduced by decreasing the growth temperature. By using laser- or plasma-assisted MOCVD growth techniques, the growth temperature can be reduced to the range of 350 to 400 °C (660 to 750 °F) (Ref 155). Alternate precursors, such as Lewis acid-base adducts of dialkylzincs with dialkyl selenides or dialkyl sulfides and either H_2Se or H_2S, also reduce the growth temperature, although the premature reaction is not completely eliminated with these source combinations (Ref 156).

ZnS_xSe_{1-x} layers are lattice matched to GaAs and GaP substrates at $x = 0.06$ and $x = 0.83$, respectively. They can be grown at 500 °C (930 °F) using the precursors diethylsulfur (DES), DEZn, and DESe. The epitaxial layer shows excellent morphology, as evidenced by a narrow x-ray rocking curve (Ref 157). The growth temperature can be lowered by using an alternative source combination of the adduct, such as DMZn-DMSe, H_2S, and H_2Se, but it then becomes more difficult to control the alloy composition and attain lattice-matched layers. The growth mechanism that impedes control of the composition in this case is not clear. Photo-assisted CVD using alkyls of zinc, sulfur, and selenium as source materials is an effective low-temperature technique for the deposition of lattice-matched ZnSSe layers.

The narrow-bandgap materials described below include cadmium telluride (CdTe), mercury telluride (HgTe), and mercury cadmium telluride (HgCdTe).

Cadmium telluride can be grown by directly combining the vapors of the two elements, which are carried by hydrogen or nitrogen. Cadmium vaporizes at 756 °C (1390 °F), and tellurium, at 990 °C (1815 °F) (Ref 158). This material also can be grown by MOCVD through this reaction:

$$(C_2H_5)_2Te + Cd\ (vapor) + H_2 \rightarrow CdTe + 2C_2H_6 \qquad \textbf{(Eq 32)}$$

which takes place in the temperature range of 325 to 350 °C (620 to 660 °F), or through the reaction:

$$(C_2H_5)_2\ Te + (CH_3)_2Cd + nH_2 \rightarrow CdTe + \text{hydrocarbons} \qquad \textbf{(Eq 33)}$$

which takes place at substrate temperatures between 150 and 250 °C (300 and 480 °F) under the activation of an excimer laser (Ref 159).

Mercury telluride can be grown by using plasma-enhanced CVD, with dimethylmercury (DMHg) and dimethyltellurium (DMTe) as the mercury and tellurium sources, respectively. Williams et al. demonstrated a growth rate of 4 μm/h (160 μin./h) at a deposition temperature of 85 °C (185 °F), a pressure of 65 Pa (0.5 torr) and an RF power of 2 W at 15 MHz (Ref 160).

For HgCdTe, the selection of MOCVD growth temperature is a problem. The most commonly used tellurium precursor, diethyltellurium (DETe), pyrolyzes effectively only at a temperature of approximately 410 °C (770 °F). This is higher than the pyrolysis temperature of dimethylcadmium (DMCd), the Group II alkyl commonly used. The high temperatures require a very high mercury pressure, which is supplied by heating elemental mercury. The combination of a high mercury concentration and a high molecular weight leads to convection cells in the vapor. It also results in the creation of large concentrations of mercury vacancies, which act as acceptors. Finally, the self-diffusion coefficients at 400 °C (750 °F) are large, precluding the growth of superlattice structures with abrupt interfaces. Lowering the growth temperature becomes the major consideration of the growth of HgCdTe. This material has been grown at 440 °C (825 °F) on GaAs and InSb substrates by using DETe and DMCd (Ref 161).

Group IV Semiconductor Growth Parameters

Silicon is the foundation of the present electronics industry. Epitaxial layers are used routinely in high-performance CMOS and bipolar technologies. Not surprisingly, the CVD process for silicon is the most mature. Germanium is another important Group IV semiconductor. Because both of these materials are grown from either chloride or hydride sources, they are categorized as CVD, rather than MOCVD, processes.

Epitaxial silicon (Si) layers can be grown at atmospheric pressure in the temperature range of 1050 to 1250 °C (1920 to 2280 °F), using either silicon tetrachloride ($SiCl_4$) or dichlorosilane (SiH_2Cl_2) as the source gas. Because this growth method is a high-temperature process, it is conducted during the initial stages of integrated-circuit manufacture. Lowering the deposition temperature minimizes dopant redistribution via solid-stage diffusion. Autodoping (the evaporation of dopants for the substrate and subsequent incorporation into the epitaxial layer) is reduced by operating at low temperatures and reduced pressures (Ref 162). Enhanced control of vertical dopant profiles permits the growth of thinner layers, which are necessary to achieve higher levels of integration. To achieve low-temperature growth, researchers have used lower-pressure processing and plasma-enhanced CVD (PECVD) methods, as well as silane (SiH_4) as a source gas.

The deposition temperature can be reduced to 825 °C (1520 °F) by using SiH_2Cl_2 in the pressure range of 1 to 3 kPa (8 to 25 torr) (Ref 163). By using SiH_4 as the source gas and utilizing very low pressures of 0.13 to 2.0 Pa (1 to 15 mtorr) to prevent parasitic reactions, epitaxial silicon can be deposited in the temperature range of 750 to 800 °C (1380 to 1470 °F) (Ref 164, 165). The growth temperature can be reduced to approximately 600 °C (1110 °F) by using a plasma-enhanced process (Ref 166). A review of PECVD methods is given by Reif and Kern (Ref 167).

Single-crystal germanium (Ge) can be grown by hydrogen reduction of the chloride in the temperature range of 600 to 900 °C (1110 to 1650 °F), according to the reaction (Ref 168):

$$GeCl_4 + 2H_2 \rightarrow Ge + 4\ HCl \qquad \textbf{(Eq 34)}$$

It is more widely grown by the decomposition of germane (GeH_4), usually at atmospheric pressure and at temperatures ranging from 600 to 900 °C (1110 to 1650 °F), according to the reaction:

$$GeH_4 \rightarrow Ge + 2H_2 \qquad \textbf{(Eq 35)}$$

Under low pressure (<130 Pa, or 1 torr), crystalline germanium can be grown in the temperature range of 350 to 400 °C (660 to 750 °F), using the above reaction (Ref 169).

Germanium also can be grown by using low-pressure MOCVD, with tetrapropylgermanium, $Ge(C_3H_7)_4$, and tetraethylgermanium, $Ge(C_2H_5)_4$, as the precursor and helium or hydrogen as the carrier gas. Growth temperatures range from 575 to 700 °C (1070 to 1290 °F) (Ref 170).

Silicon carbide (SiC) can be grown by the reaction of silane with a hydrocarbon such as propane or benzene, as expressed by the reactions:

$$3SiH_4 + C_3H_8 \rightarrow 3SiC + 10\ H_2 \qquad \textbf{(Eq 36)}$$

$$6SiH_4 + C_6H_6 \rightarrow 6SiC + 15\ H_2 \qquad \textbf{(Eq 37)}$$

The reaction temperature is about 800 °C (1470 °F), with a pressure of 1.3 KPa (10 torr) (Ref 171). The decomposition of methyl silane (Ch_3SiH_3) can be used to produce amorphous silicon carbide at 800 °C (1470 °F) and crystalline silicon carbide at 900 °C (1650 °F) (Ref 172).

References cited in this section

18. M. Razeghi, J.P. Duchemin, J.C. Portal, L. Dmowski, G. Remeni, R.J. Nicholas, and A. Briggs, *Appl. Phys. Lett.,* Vol 48, 1986, p 712
28. S.R. Kurtz, J.M. Olson, and A. Kibbler, *J. Electron. Mater.,* Vol 18, 1989, p 15
29. C.H. Chen, C.A. Larsen, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 50, 1987, p 218
30. A. Brauers, M. Weyers, and P. Balk, *Chemtronics,* Vol 4, 1989, p 8
48. G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice,* Academic Press, 1989, p 8, 18
50. G.B. Stringfellow, *Semiconductors and Semimetals,* Vol 22A, W.T. Tsang, Ed., Academic Press, 1985, p 209
52. M. Razeghi, *The MOCVD Challenge,* A. Hilger, 1989, p 14
70. D.I. Fotiadis, M. Boekholt, K.F. Jensen, and W. Richter, *J. Cryst. Growth,* Vol 100, 1990, p 577
76. F.J. Callahan, *Swagelok Tube Fitting and Installation Manual,* 1985
77. L. Hollan, M. Boulon, and J.P. Chane, *J. Electron. Mater.,* Vol 10, 1981, p 193
78. N.J. Mason and P.J. Walker, *J. Cryst. Growth,* Vol 107, 1991, p 181
79. J.S. Roberts, N.J. Mason, and M. Robinson, *J. Crystal Growth,* Vol 68, 1984, p 422
80. C. Blaauw, C. Mincr, B. Emrnerstorfer, A.J. SpringThorpe, and M. Gallant, *Can. J. Phys.,* Vol 63, 1985, p 664
81. G. Landgren, S.G. Andersson, J.Y. Anderson, L. Samuelson, P. Silverberg, and P. Tolkien, *J. Crystal Growth,* Vol 77, 1986, p 67
82. E.J. Thrush, J.E.A. Whiteway, G. Wale-Evans, D.R. Wight, and A.G. Cullis, *J. Cryst. Growth,* Vol 68, 1984, p 412
83. R.J.M. Griffiths, N.G. Chew, A.G. Cullis, and G.C. Joyce, *Electron. Lett.,* Vol 19, 1983, p 319
84. L.J. Giling, *J. Electrochem. Soc.,* Vol 129, 1982, p 634
85. C. Blaauw, B. Emmerstorfer, and A.T. SpringThorpe, *J. Cryst. Growth,* Vol 84, 1987, p 431
86. J. van de Ven, H.G. Schoot, and L.J. Giling, *J. Appl. Phys.,* Vol 60, 1986, p 1648
87. J. van de Ven, G.J.M. Rutten, M.J. Raaymakers, and L.J. Giling, *J. Crystal Growth,* Vol 76, 1986, p 352
88. C. Goodings, N.J. Mason, P.J. Walker, and D. Jebb, *J. Cryst. Growth,* Vol 96, 1989, p 13
89. Yu.N. Makarov and A.I. Zhmakin, *J. Crystal Growth,* Vol 94, 1989, p 537
90. D. Schmitz, G. Strauch, H. Jürgensen, and M. Heyen, *J. Crystal Growth,* Vol 107, 1991, p 188
91. P.M. Frijink, *J. Crystal Growth,* Vol 93, 1988, p 207
92. E. Woelk and H. Beneking, *J. Cryst. Growth,* Vol 93, 1988, p 216
93. G.S. Tompa, M.A. McKee, C. Beckham, P.A. Zawadski, J.M. Colabella, P.D. Reinert, K. Capuder, R.A. Stall, and P.E. Norris, *J. Cryst. Growth,* Vol 92, 1988
94. A. Mircea, A. Ougazzaden, P. Daste, Y. Gao, C. Kazmierski, J.-C. Bouley, and A. Carenco, *J. Cryst. Growth,* Vol 92, 1988, p 235
95. M. Mpaskoutas, C. Morhaïm, J.N. Patillon, and J.P. Andréo, *J. Cryst. Growth,* Vol 107, 1991, p 192
96. M.J. Ludowise, *J. Appl. Phys.,* Vol 58 (No. 8), 1985, p R33
97. T.F. Kuech, E. Veuhoff, T.S. Kuan, V. Deline, and R. Potemski, *J. Cryst. Growth,* Vol 77, 1986, p 257
98. C. Plass, H. Heinecke, O. Kayser, H. Luth, and P. Balk, *J. Cryst. Growth,* Vol 88, 1988, p 455
99. J. Knauf, D. Schmitz, G. Strauch, H. Jurgensen, and M. Heyen, *J. Cryst. Growth,* Vol 93, 1988, p 34
100. G.B. Stringfellow, *J. Cryst. Growth,* Vol 55, 1981, p 42
101. R. Bhat, M.A. Koza, C.C. Chang, A. Schwarz, and T.D. Harris, *J. Cryst. Growth,* Vol 77, 1986, p 7
102. B.C. Harrison and E.H. Tompkins, *Inorg. Chem.,* Vol 1, 1962, p 951

103. K.W. Benz, H. Renz, J. Wiedlein, and N.H. Pilkuhn, *J. Electron. Mater.,* Vol 10, 1981, p 185
104. R.H. Moss and J.S. Evans, *J. Cryst. Growth,* Vol 55, 1981, p 129
105. R. Bath, M.A. Koza, and B.J. Skromme, *Appl. Phys. Lett.,* Vol 50, 1987, p 1386
106. M.K. Lee, K.C. Huang, D.S. Wuu, H.H. Tung, and K.Y. Yu, *J. Cryst. Growth,* Vol 93, 1988, p 539
107. P. Wolfram, F.W. Reier, D. Franke, and H. Schumann, *J. Cryst. Growth,* Vol 96, 1989, p 691
108. G. Laube, U. Kohier, J. Weidlein, F. Schol, K. Streubel, R.J. Dieter, N. Karl, and M. Gerdon, *J. Cryst. Growth,* Vol 93, 1985, p 45
109. K. Streubel, F. Scholz, G. Laube, R.J. Dieter, E. Zielinski, and F. Keppler, *J. Cryst. Growth,* Vol 93, 1988, p 347
110. R.H. Moss, private communication, 1985
111. T.S. Moss and S. Mahajan, *Handbook on Semiconductors,* Vol 3(a), North Holland, 1994, p 183
112. F.A. Maury and G. Constant, *J. Cryst. Growth,* Vol 62, 1983, p 568
113. F.A. Maury, A. El Hammadi, and G. Constant, *J. Cryst. Growth,* Vol 68, 1984, p 88
114. F.A. Maury, G. Constant, P. Fontaine, and J.P. Biberian, *J. Cryst. Growth,* Vol 78, 1986, p 185
115. F.A. Maury and A. El Hammadi, *J. Cryst. Growth,* Vol 91, 1988a, p 97
116. F.A. Maury and A. El Hammadi, *J. Cryst. Growth,* Vol 91, 1988b, p 105
117. K. Mori, M. Yoshida, and A. Usui, *Inst. Phys. Conf. Ser. 91,* 1988, p 187
118. C. Sasaoka, M. Yoshida, and A. Usui, *Jpn. J. Appl. Phys. Lett.,* Vol 27, 1988, p L190
119. K.L. Hess and R.J. Riccio, *J. Cryst. Growth,* Vol 77, 1966, p 95
120. G.B. Stringfellow, *J. Electron. Mater.,* Vol 17, 1989b, p 327
121. T.H. Chui, W.T. Tsang, E.F. Schubert, and E. Agyekum, *Appl. Phys. Lett.,* Vol 51, 1987, p 1109
122. A. Brauers, O. Kayser, R. Kall, H. Heinecki, P. Balk, and H. Hofmann, *J. Cryst. Growth,* Vol 93, 1988, p 7
123. L.M. Fraas, P.S. McLeod, R.E. Weiss, L.D. Partain, and J.A. Capc, *J. Appl. Phys.,* Vol 62, 1987, p 299
124. R.M. Lum, J.K. Klingert, and M.G. Lamont, *J. Cryst. Growth,* Vol 89, 1988a, p 137
125. S. Fujita, M. Imaizumi, S. Araki, Y. Takeda, and A. Sasaki, *J. Cryst. Growth,* Vol 93, 1988, p 1
126. R.M. Lum, J.K. Klingert, A.S. Wynn, and M.G. Larnont, *Appl. Phys. Lett.,* Vol 52, 1988b, p 1475
127. G. Haacke, S.P. Watkins, H. and Burnhard, *Appl. Phys. Lett.,* Vol 54, 1989, p 2029
128. H. Tanaka, T. Kikkawa, K. Kasai, and J. Komeno, *Jpn. J. Appl. Phys.,* Vol 28, 1989, p L901
129. R.H. Lum, J.K. Klingert, and M.G. Lamon, *Appl. Phys. Lett.,* Vol 50, 1987, p 284
130. C.H. Chen, E.H. Reihlen, and G.B. Stringfellow, *J. Cryst. Growth,* Vol 96, 1989, p 497
131. R. Bath, *J. Electron. Mater.,* Vol 14, 1985, p 433
132. K.W. Benz, H. Haspeklo, and R. Bosch, *J. Phys., Coll. CS,* Suppl. 43, 1982, p C5-393
133. M. Naitoh, T. Soga, T. Jimbo, and M. Umeno, *J. Cryst. Growth,* Vol 93, 1988, p 52
134. C.H. Chen, C.A. Larsen, G.B. Stringfellow, D.W. Brown, and A.J. Robertson, *J. Cryst. Growth,* Vol 77, 1986, p 11
135. R.R. Saxena, J.E. Fouquet, V.M. Sardi, and R.L. Moon, *Appl. Phys. Lett.,* Vol 53, 1988, p 26
136. F.G. Kellert, J.S. Whelan, and K.T. Chan, *J. Electron. Mater.,* Vol 18, 1989, p 355
137. M. Razeghi, F. Omnes, J. Nagle, M. Defour, D. Acher, and P. Bove, *Appl. Phys. Lett.,* Vol 55, 1989b, p 1677
138. D. Kisker, J.N. Miller, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 40, 1982, p 614
139. G.B. Stringfellow and G. Hom, *Appl. Phys. Lett.,* Vol 34, 1979, p 794
140. M.J. Tsai, M.M. Tashima, and R.L. Moon, *J. Electron. Mater.,* Vol 13, 1984, p 437
141. T.F. Kuech, E. Veuhoff, D.J. Wolford, and J.A. Bradley, *Inst. Phys. Conf. Ser. 74,* 1985, p 181
142. M. Razeghi, X.G. He, J. Diaz, J. Hoff, M. Erdtmann, and E. Kolev, *Proc. SPIE,* 1994

143. C.J. Sun and M. Razeghi, *Appl. Phys. Lett.,* Vol 63, 1993, p 973
144. P. Kung, C.J. Sun, A. Saxler, H. Ohsato, and M. Razeghi, *J. Appl. Phys.,* Vol 75, 1994 p 4515
145. C. Besikci, Y.H. Choi, R. Sudharsanan, and M. Razeghi, *J Appl. Phys.,* Vol 73, 1993, p 5009
146. Y.H. Choi, C. Besikci, R. Sudharsanan, and M. Razeghi, *Appl. Phys. Lett.,* Vol 63, 1993, p 361
147. H. Beneking and H. Roehle, *J. Cryst. Growth,* Vol 55, 1981, p 79
148. H. Manasevit and K. Hess, *J. Electrochem. Soc.,* Vol 126, 1979, p 2031
149. H. Manasevit and K. Hess, *J. Electrochem. Soc.,* Vol 120, 1973, p 135
150. C. Cooper, M. Ludovik, and V. Achi, and R. Moon, *Electron. Lett.,* Vol 16, 1980, p 892
151. B. Baliga and S. Gandhi, *J. Electrochem. Soc.,* 1975, p 683
152. L. Aina and M. Mattingly, *Appl. Phys. Lett.,* Vol 51, 1987, p 1637
153. R.M. Biefeld, *J. Cryst. Growth,* Vol 75, 1986, p 255
154. T. Fukui and Y. Horikoshi, *Jpn. J. Appl. Phys.,* Vol 19, 1980, p L551
155. T. Yasuda, Y. Koyama, J. Wakitani, J. Yoshino, and H. Kukimoto, *Jpn. J. Appl. Phys.,* Vol 28, 1989, p L1628
156. T. Yasuda, K. Hara, and H. Kukimoto, *J. Cryst. Growth,* Vol 77, 1986, p 485
157. H. Mitsubashi, I. Mitshishi, and H. Kukimoto, *Jpn. J. Appl. Phys.,* Vol 24, 1989, p L864
158. S. Chu, T. Chu, K. Han, Y. Liu, and M. Mantravadi, *Proc. 10th Int. Conf. CVD,* Electrochemical Society, 1987, p 982
159. R.L. Gentilman, B. Bibendetto, R. Tustison, and J. Pappis, *Chemically Vapor Deposited Coatings,* H. Pierson, Ed., American Ceramic Society, 1981, p 47
160. L.M. Williams, P.Y. Lu, C.H. Wang, J.M. Partsey, and S.N.G. Chu, *Appl. Phys. Lett.,* Vol 21, 1987, p 1738
161. W.E. Hoke, P.J. Lemonias, and Traczewski, *Appl. Phys. Lett.,* Vol 44, 1984, p 1046
162. E. Krullman and W.L. Engl, *IEEE Trans. Electron. Dev.,* Vol ED-29, 1982, p 491
163. J. Borland and C. Drowley, *Solid State Technol.,* Aug, 1985, p 141
164. J.H. Comfort, L.M. Gaverick, and R. Reif, *J. Appl. Phys.,* Vol 62, 1987, p 3388
165. L.M. Gaverick, J.H. Comfort, T.R. Yew, R. Reif, F.A. Baiocchi, and H.S. Luftman, *J. Appl. Phys.,* Vol 62, 1987, p 3398
166. J.H. Comfort and R. Reif, *J. Electrochem. Soc.,* Vol 136 (No. 8), 1989, p 2386
167. R. Reif and W. Kern, *Thin Film Processes II,* W. Kern and J. Vossen, Ed., Academic Press, 1991, p 525
168. E.F. Cave and B.R. Czorny, *RCA Review,* Vol 24, 1963, p 523
169. J. Murota, A. Kobayashi, M. Kato, N. Mikoshiba, and S. Ono, *Proc. 11th Conf. CVD,* Electrochemical Society, 1990, p 325
170. R. Morancho, G. Constant, C. Gallon, J. Boucham, P. Mazerolles, and C. Bernard, *Proc. 5th European Conf. on CVD,* Sweden, 1985, p 526
171. H. Komiyama, H. Oyamada, S. Tanaka, and Y. Shimogaki, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Gullen, Ed., Electrochemical Society, 1990, p 361
172. P. Angelini, *Diss. Abst. Int.,* Vol 46, 1986, p 170

Plasma-Enhanced Chemical Vapor Deposition

Prabha K. Tedrow, Consultant; Rafael Reif, Massachusetts Institute of Technology

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Introduction

PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION (PECVD), also known as plasma-assisted CVD, is an important technique used for depositing films of a wide variety of crystalline and noncrystalline materials. Examples of films that are commonly deposited using the PECVD process are noncrystalline materials such as oxides, nitrides, and oxynitrides of silicon (Ref 1), and crystalline materials such as polycrystalline silicon (Ref 2, 3, 4), epitaxial silicon (Ref 5, 6, 7), and refractory metals and their silicides. All of these materials are extensively used in microelectronic device fabrication, and PECVD is a critical process step in the fabrication of modern silicon devices. PECVD is also used in depositing optical coatings and other crystalline compounds such as titanium nitride, which is used in highly wear-resistant coatings on cutting tools (Ref 8).

Thermally driven atmospheric-pressure and low-pressure chemical vapor deposition (APCVD and LPCVD, respectively) are well understood and established methods for depositing films in integrated circuit (IC) fabrication technology (see the article "Chemical Vapor Deposition of Semiconductor Materials" in this Volume). However, the deposition temperatures in a thermally driven CVD process can be quite high (e.g., 700 to 900 °C, or 1300 to 1650 °F, for LPCVD silicon nitride deposition) (Ref 1, 9) and thus are detrimental to modern silicon devices. Plasma enhancement of the CVD process makes it possible to lower the deposition temperature significantly (e.g., to 250 to 300 °C, or 480 to 570 °F, for PECVD of silicon nitride) (Ref 1, 9) while maintaining a reasonable rate of deposition and film quality. Thus, some of the advantages of PECVD are that:

- Films can be deposited on substrates that would be unstable at higher temperatures (e.g., intermetallic dielectric layers deposited on aluminum or the encapsulation of ICs).
- Lower-temperature film deposition in microelectronic circuits allows precise control of dopant migration. The dimensions of modern microelectronic devices are getting smaller, increasing the importance of this control.

This article discusses application of the PECVD process in the deposition of amorphous and crystalline films from the point of view of microelectronic device fabrication. Plasma enhancement of the CVD process is discussed briefly, followed by a description of various types of PECVD reactors. Deposition techniques and the properties of some of the amorphous and crystalline films deposited by the PECVD process for IC fabrication are also described.

References

1. B. Gorowitz, T.B. Gorczyca, and R.J. Saia, in *Solid State Technology,* Vol 28 (No. 6), 1985, p 197
2. T.I. Kamins and K.L. Chiang, in *J. Electrochem. Soc.,* Vol 129, 1982, p 2326, 2331
3. W.R. Burger, T.J. Donahue, and R. Reif, in *VLSI Science and Technology,* C.J. Dell'Oca and W.M. Bullis, Ed., The Electrochemical Society, 1982, p 87
4. J.-J. Hajjar, R. Reif, and D. Adler, in *J. Electronic Materials,* Vol 15, 1986, p 279
5. S. Suzuki and T. Itoh, in *J. Appl. Phys.,* Vol 54, 1983, p 1466
6. S.R. Shanfield and R. Reif, in *The Electrochem. Soc. Extended Abstracts,* Vol 83-1, Abs. 144, 1983, p 230
7. J.H. Comfort, L.M. Garverick, and R. Reif, in *J. Appl. Phys.,* Vol 62, 1987, p 3388
8. N. Kikuchi, Y. Oosawa, and A. Nishiyama, in *Proceedings of the Ninth International Conference on Chemical Vapor Deposition,* McD. Robinson, C.W. Cullen, C.H.J. van den Brekel, and J.M. Blocher, Jr., Ed., The Electrochemical Society, 1984, p 728
9. A.C. Adams, *Solid State Technology,* in Vol 26 (No. 4), 1983, p 135; also in *VLSI Technology,* S. Sze, Ed., McGraw-Hill, 1983, Chapter 3

Process Description

In a thermally driven CVD process, component elements of the film to be deposited are introduced into the reaction chamber via gaseous precursor reactants. The reactants are mass-transported to the surface of the hot substrate, where they are adsorbed. If the substrate is heated to an appropriate temperature for the desired chemical reaction to take place, films of the material to be deposited form on the substrate surface while the reaction byproducts are pumped out of the system. Thus the quality and the rate of film deposition are a function of, among other things, reactor geometry, partial pressures of the reactants, and the substrate temperature. Although the thermally driven CVD process is thermodynamically quite well understood and is widely used for the deposition of some films (e.g., undoped polycrystalline silicon), high deposition temperatures could be quite prohibitive for other applications (e.g., deposition of intermetallic dielectrics).

In the PECVD process, the gaseous precursors are most commonly subjected to time-varying electric fields of frequencies in the range of 50 kHz to 13.5 MHz. In some designs, microwave frequencies are also used. The electric field initially reacts primarily with the free electrons present in the gas. Although the electric field also reacts with the ions, these species remain initially unaffected because of their higher mass. The electrons undergo elastic and inelastic collisions with the gas molecules, but the electrons do not lose much energy during the elastic collisions because they are much lighter than the gas molecules. Loss of electronic energy during inelastic collisions with the gas molecules occurs only if the electrons, accelerated by the electric field, acquire energy that is higher than the threshold energies for excitation and ionization for a particular gas species (e.g., 11.56 eV for excitation and 15.8 eV for ionization of argon) (Ref 10). The inelastic collisions between these energetic electrons and gas molecules generate highly reactive species such as excited neutrals, free radicals, and ions, as well as more electrons. By this mechanism, the energy of the electrons is used to create reactive and charged species, while the gas temperature does not increase substantially.

In the PECVD environment, only a fraction of the precursor species in the gas phase undergo electron impact ionization and excitation, thereby generating the reactive species. The latter have a lower energy barrier to physical and chemical reactions than the parent species and consequently react at lower temperatures. Thus in the PECVD process, these reactive species lead to lower deposition temperatures and higher deposition rates than are possible with only thermally driven CVD. In film growth with the PECVD process, in addition to the unchanged parent species, these highly reactive species also diffuse to the surface of the substrate, where they are adsorbed and undergo a sequence of processes similar to that of thermal CVD. But these reactive species follow an alternate deposition pathway that proceeds parallel to the thermal pathway, because:

- The reactive species created during the inelastic collisions of gas molecules with energetic electrons have a sticking coefficient closer to unity (Ref 10); that is, once they reach the surface of the substrate, they tend not to escape.
- The activation energy for chemical dissociation is typically lower for these plasma-enhanced reactions (Fig. 1).

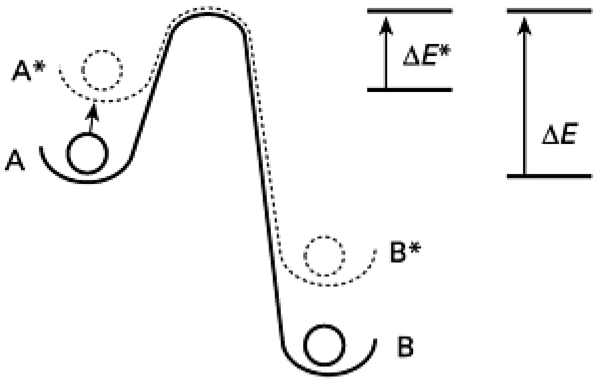

Fig. 1 Activation energy diagram for thermally driven (solid line) and plasma-enhanced (dashed line) chemical vapor deposition reactions. A and B, initial and final energy states, respectively, for the thermally driven reaction; ΔE, activation energy; A*, B*, ΔE*, corresponding parameters for the plasma-enhanced reaction. Source: Ref 11

Some heat is needed to drive the reaction over E*, but as shown in Fig. 1, this energy is typically lower than the energy needed for a purely thermally driven reaction to proceed at a reasonable rate. If the substrate is kept at a temperature such that the deposition proceeds at a very slow rate without the plasma but at a reasonable rate once the plasma is switched on, a plasma can be used as a "switch" to turn the deposition reaction on and off (Ref 12). Switching the plasma on and off can be used to start and stop the deposition process. Extremely abrupt layers can be grown by this technique, because the time required for the plasma to switch is equivalent to that between gas molecule collisions (e.g., 1 ms at 1 torr) (Ref 13). The thermal energy in a PECVD process, in addition to driving the surface reaction, is also needed for desorption of the reaction byproducts, minimizing adsorption and the inclusion of undesired gases in the deposited film, thereby lowering film contamination.

Typically, radio-frequency (rf) glow discharges used for the deposition of thin films operate at frequencies between 50 kHz to 13.56 MHz and at pressures of 0.1 to 2.0 torr. The plasma density (i.e., the density of ions and free electrons) is in the range of 10^8 to 10^{12} cm^{-3}. The degree of ionization is 10^{-4}. Typical average electron energies are in the range of 1 to 3 eV, but the fastest electrons may reach energies as high as 10 to 30 eV (Ref 14).

In a PECVD deposition system, many factors can affect the growth, composition, and the properties of deposited films, in addition to conditions such as the substrate temperature, reactor geometry, and reactant partial pressures, which are important in thermally driven CVD film growth. Some of these factors are plasma power, frequency, electrode spacing, and substrate positioning. In these plasma glow discharges, the PECVD environment is not in thermal equilibrium because the average electron energies are much higher than the ion energies. Consequently, thermodynamic calculations cannot reliably predict the product of a PECVD reaction (Ref 13).

References cited in this section

10. M. Rand, in *J. Vac. Sci. Technol.,* Vol 16, 1979, p 420
11. R. Reif, in *Handbook of Plasma Processing Technology,* S. Rossnagel, J. Cuomo, and W. Westwood, Ed., Noyes Publications, 1990, Chapter 10
12. A.D. Huelsman, L. Zien, and R. Reif, in *Appl. Phys. Lett.,* Vol 52, 1988, p 726
13. R. Reif and W. Kern, Plasma Enhanced Chemical Vapor Deposition, *Thin Film Processes II,* Academic Press, Inc., 1991
14. J.R. Hollahan and A.T. Bell, Ed., *Techniques and Applications of Plasma Chemistry,* John Wiley, 1974

Types of PECVD Systems

As with thermal CVD reactors, PECVD systems can be either the hot-wall type, in which the reactor walls, the substrate, and the reactant gases are all at the same temperature, or the cold-wall type, in which only the substrate is heated to the desired temperature. In addition, PECVD reactors can be of direct or remote plasma type, where consideration is given to the plasma generation and what is coupled to this plasma. Numerous articles in the published literature (Ref 15, 16, 17, 18, 19, 20, 21) describe in detail the different geometries of commercial PECVD reactors and their use in the deposition of specific films.

In a direct PECVD system, all the reactant gases as well as the substrate are exposed to the rf plasma glow. A schematic of a direct plasma cold-wall reactor is shown in Fig. 2. The upper electrode is connected to the high-frequency rf power generator through an impedance-matching network. The reactants are introduced through the upper electrode, which is perforated, and directly enter the plasma region. The gases are pumped out at the bottom of the chamber. The lower electrode is a continuous plate and has a resistive heating element to heat the substrates. Substrates (wafers) are placed on the lower electrode and are thus immersed in the plasma as well as heated to the desired temperature of deposition.

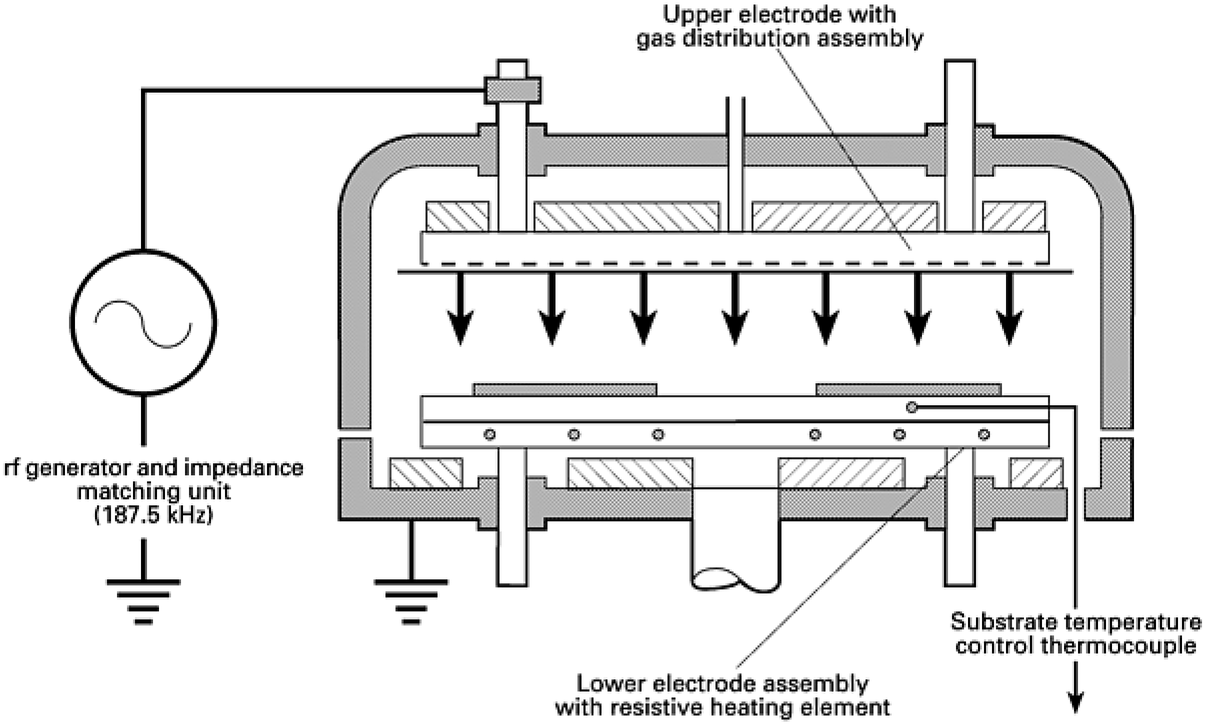

Fig. 2 Schematic of a direct plasma cold-wall reactor. Source: Ref 17, 22

Remote PECVD Systems. In a direct PECVD system, the substrate is exposed to the plasma discharge environment, which may cause radiation damage in the film being deposited. In a remote PECVD system, the substrate is removed from the plasma glow, and the reactant gases may be selectively excited by the plasma. The excited species are then carried to the substrate surface, where they react with other adsorbed gaseous reactants and the desired chemical reaction for deposition takes place. Keeping the substrate out of the plasma glow eliminates the deleterious effects of radiation. Moreover, this technique allows independent optimization of plasma, reactant gas chemistries, and wafer parameters.

One example of a remote PECVD system is shown in Fig. 3. This reactor was designed and built at the Massachusetts Institute of Technology (Ref 23) for metallo-organic CVD (i.e., CVD where some of the source gases are metallo-organic compounds) of gallium arsenide. The reactor consists of three vertically aligned concentric regions. The group III source gases enter through the center tube, the group V source gases enter between the inner and center tubes, and the reaction byproducts are exhausted between the inner and outer tubes. The substrate rests horizontally on a SiC-coated graphite disk, which is heated from below by a 750 W quartz halogen lamp with an elliptical reflector. The reactor can be equipped with internal electrodes fabricated of either aluminum or tantalum that can be connected via feedthroughs to an external power source to generate the plasma. The electrode configuration consists of an aluminum cylinder, 5 cm (2 in.) in diameter and 4 cm (1.6 in.) long, placed parallel to the gas stream. The distance between the wafer and the plasma can be varied by moving the electrode up or down in the inner quartz tube. In this design, the substrate receives a uniform distribution of plasma species and uniform infrared heat.

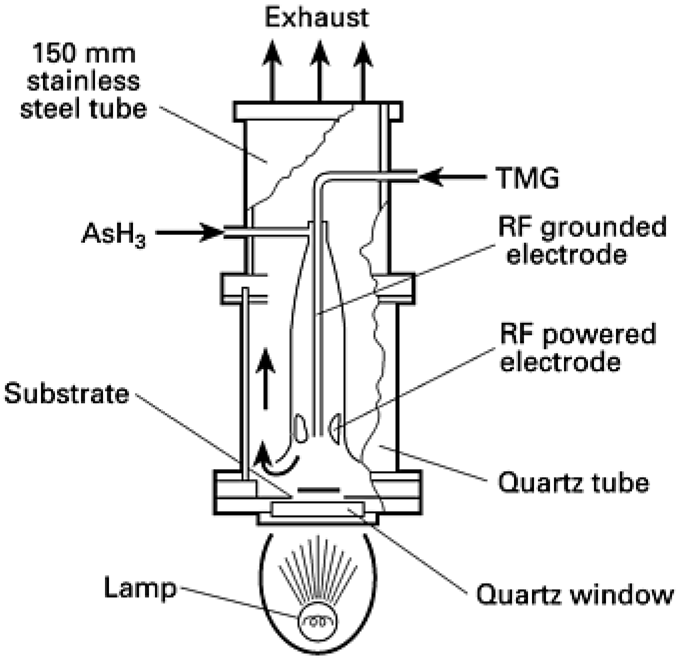

Fig. 3 Schematic of a remote plasma-enhanced chemical vapor deposition reactor for depositing compound semiconductor films. TMG, trimethylgallium. Source: Ref 23

Hybrid PECVD systems are a combination of the direct and remote PECVD systems. One example of such a system is a reactor designed for the deposition of amorphous hydrogenated silicon (Ref 24). In this reactor, one of the electrodes is replaced by a grid and the substrate is positioned directly under it. The substrate is thus shielded from the direct plasma glow while the reactant gases are subjected to the plasma discharge.

In some PECVD systems, microwave power is used to generate plasma. The plasma is excited by the resonance of microwaves and electrons through a microwave discharge across a magnetic field of 800 to 1200 G. This process, called electron cyclotron resonance, allows the film to grow at high rates of deposition at very low gas pressures (!10^{-4} torr) and at very low temperatures (<275 °C, or 525 °F) (Ref 25). The plasma is contained magnetically in the system and the deposition occurs outside the glow region, while all the gases are subject to plasma excitation.

References cited in this section

15. A.R. Reinberg, in *The Electrochem. Soc. Extended Abstracts,* Vol 74-1, Abs. No. 6, 1974
16. W. Kern, in *Microelectronic Materials and Processes,* C.R. Levey, Ed., NATO ASI Series E, Vol 164, Kluwer Academic Publishers, 1989, Chapter 5; see also *Semiconductor International,* Vol 8 (No. 7), 1985, p 121
17. A. Kiermasz, A.A. Chambers, and A. McQuarrie, in *Research and Development,* Vol 29 (No. 12), 1987, p 71
18. R.S. Rosler and G.M. Engle, *Solid State Technol.,* Vol 24 (No. 4), 1981, p 172
19. A.D. Weiss, *Semiconductor International,* Vol 6, July 1983, p 88
20. Novellus Systems Inc., San Jose, CA
21. E.R. van de Ven, I.-W. Connick, and A.S. Harrus, in *Proceedings of the Seventh International IEEE Multi-Level Interconnection Conference* (Santa Clara, CA), Institute of Electrical and Electronics Engineers, June 1990, p 194
22. Electrotech, Hauppauge, NY
23. A.D. Huelsman and R. Reif, in *J. Vac. Sci. Technol. A,* Vol 7, 1989, p 2554

24. A. Matsuda and K. Tanaka, Investigation of the Growth Kinetics of Glow-Discharge Hydrogenerated Amorphous Silicon Using a Radial Separation Technique, *J. Appl. Phys.*, Vol 60, 1986, p 2351
25. W.R. Snow, in *Proceedings of the Tenth International Conference on Chemical Vapor Deposition,* G.W. Cullen, Ed., The Electrochemical Society, Inc., 1987, p 810

PECVD of Dielectric Films

One of the most important uses of PECVD is in the deposition of dielectric films used in microelectronic device fabrication. The ability to deposit films of a dielectric such as silicon nitride, silicon oxide, or silicon oxynitride at lower temperatures is critical in the manufacture of modern very-large-scale integration (VLSI) chips. Fabrication of devices with smaller dimensions requires precise control of dopant movement during the multistep processing sequences. In addition, deposition of dielectrics used in intermetallic layers and/or chip encapsulations also requires low-temperature depositions.

Silicon nitride films provide an excellent barrier against alkali ions and moisture and are thus the material of choice as a final passivation and coating layer for ICs. The PECVD technique makes it possible to deposit silicon nitride films at temperatures in the range of 250 to 400 °C (480 to 750 °F), which is low enough to be deposited over device wafers with aluminum metallization and interconnects. Silicon nitride films deposited by the PECVD process are generally represented as $Si_xN_yH_z$ because they are not stoichiometric and contain bonded hydrogen. The films can be deposited by using silane (SiH_4) and ammonia (NH_3) as source gases for silicon and nitrogen, respectively. The depositions are normally carried out at pressures of 0.2 to 3 torr, and film growth rates at these pressures are about 200 to 500 Å/min. These films contain 15 to 30 at.% H bonded to either silicon or nitrogen (Ref 9, 26, 27).

Another choice of reactant gases can be silane and nitrogen (N_2). In this case, the deposition rates are low and the films tend to be silicon-rich. The SiH_4-N_2 chemistry tends to yield films that have less hydrogen and an excess of nitrogen, and that have poorer step coverage of the underlying metal.

Film properties such as refractive index, stress, and optical absorption edge are greatly affected by the concentration and chemical bonding of the hydrogen in the film. Other film properties (e.g., electric breakdown strength, etch rates in hydrofluoric acid, diffusion barrier to alkali ions and moisture, and stress) are also functions of the film composition and are very sensitive to the reactor geometry and deposition conditions.

Both bonded hydrogen and a high level of stress are harmful to the chips on which the films are deposited. Hydrogen tends to escape from the films when further processing is done at temperatures higher than the deposition temperature, and this can change the electrical properties of underlying devices (Ref 28). Stress in the PECVD nitride films can vary from 10^{10} dyn/cm^2, compressive, to 10^{10} dyn/cm^2, tensile. Excessive stress can cause the films to crack and peel (Ref 29). It is possible to choose the stress type and control the stress level by selecting the right deposition conditions (Ref 21).

Silicon oxide films are used as intermetallic dielectric layers in microelectronic circuits. Some of the important advantages that PECVD silicon oxide films offer are that:

- The deposition temperatures are low (200 to 300 °C, or 390 to 570 °F), so that PECVD silicon oxide films can be deposited over low-melting-point metals such as aluminum.
- The dielectric constant of PECVD oxide is relatively low (4 to 6, versus 6 to 9 for silicon nitride films) (Ref 30).
- The dry etch rate of PECVD oxide films is much higher than that of thermal CVD films.

The last factor is used to advantage in the process called planarization. During IC device fabrication, the surface needs to be planarized at some point before the next processing step. One method involves depositing the PECVD oxide film over the processed wafer, followed by deposition and flow of photoresist. The photoresist and the oxide films are then dry etched. The etch rate of the PECVD oxide may be 20 to 40% higher than that of thermal oxide. This high etch rate allows the planarization process to succeed, because the latter depends on having equal etch rates of photoresist and oxide (Ref 31).

Properties of PECVD silicon oxide films are a function of deposition conditions, reactor geometry, and the reaction chemistry (but to a lesser degree than in PECVD silicon nitride films) (Ref 13). Some of the source gas combinations that can be used for the deposition of PECVD silicon oxide films are (Ref 1, 32):

- SiH_4, used as the silicon source, and nitrous oxide (N_2O), used as the source of nitrogen. SiH_4 is usually diluted with argon.
- SiH_4 diluted with oxygen (alone or in combination with N_2O)
- Tetraethylorthosilicate (TEOS) as the source of silicon in an O_2-N_2 ambient

The SiH_4-N_2O process tends to yield films with better uniformity and less particle contamination. Hydrogen occurs in PECVD silicon oxide films in the bonded form as Si-H, Si-O-H, or H-O-H in concentrations ranging from 2 to 9 wt% (Ref 30). The hydrogen in oxide films is less of a problem than in PECVD nitride films. If the films are heated substantially beyond their deposition temperatures, the hydrogen in the films escapes by outdiffusion, whereas the PECVD silicon nitride films may be destroyed by blistering because they are relatively impermeable.

Some of the properties of silicon oxide films deposited by PECVD process are:

- Compressive stress, 0.07 to 2.4×10^9 dyn/cm^2
- Breakdown strength, 2 to 6×10^6 V/cm
- Resistivity, 10^{13} to 10^{17} $\Omega \cdot$ cm

Effects of deposition variables on the properties of PECVD silicon oxide films are reported in Ref 33, 34, 35, 36.

Silicon oxynitride films combine some of the best properties of PECVD silicon nitride and oxide films. Deposition of silicon oxynitride film is based on SiH_4 (diluted with helium), NH_3, and N_2O as reactants in various ratios at 300 °C (570 °F) (Ref 37). Properties such as stress, dielectric constant, and resistance to the diffusion of sodium ions and moisture can be modified by changing the gas flow ratios during film growth. The presence of oxygen in these films lowers the values of properties such as stress and dielectric constant, whereas the presence of nitrogen increases the impermeability to sodium ions and moisture (Ref 13). PECVD oxynitride films are also used in the planarization process, where the difference in etch rates of oxynitrides, photoresist, and nitride films is used advantageously (Ref 1).

References cited in this section

1. B. Gorowitz, T.B. Gorczyca, and R.J. Saia, in *Solid State Technology,* Vol 28 (No. 6), 1985, p 197
9. A.C. Adams, *Solid State Technology,* in Vol 26 (No. 4), 1983, p 135; also in *VLSI Technology,* S. Sze, Ed., McGraw-Hill, 1983, Chapter 3
13. R. Reif and W. Kern, Plasma Enhanced Chemical Vapor Deposition, *Thin Film Processes II,* Academic Press, Inc., 1991
21. E.R. van de Ven, I.-W. Connick, and A.S. Harrus, in *Proceedings of the Seventh International IEEE Multi-Level Interconnection Conference* (Santa Clara, CA), Institute of Electrical and Electronics Engineers, June 1990, p 194
26. A.K. Sinha, in *Solid State Technol.,* Vol 23 (No. 4), 1980, p 133
27. J.L. Vossen, in *J. Electrochem. Soc.,* Vol 126, 1979, p 319
28. S.J. Fijita, N.S. Zhon, H. Toyoshima, T. Ohishi, and A. Sasaki, in *IEDM Tech. Digest,* Vol 84, 1984, p 630
29. W. Kern and R.S. Rosler, in *J. Vac. Sci. Technol.,* Vol 14 (No. 5), Sept/Oct 1977, p 1082
30. A.C. Adams, in *Reduced Temperature Processing for VLSI,* R. Reif and G.R. Srinivasan, Ed., The Electrochemical Society, 1986, p 111
31. A.C. Adams and C.D. Capio, in *J. Electrochem. Soc.,* Vol 128, 1981, p 423
32. I.T. Emesh, G. D'Asti, J.S. Mercier, and P. Leung, in *J. Electrochem. Soc.,* Vol 136, 1989, p 3404

33. E.P.G.T. van den Ven, in *Solid State Technol.,* Vol 24 (No. 4), 1981, p 167

34. J.R. Hollahan, in *J. Electrochem. Soc.,* Vol 126, 1979, p 930

35. A.C. Adams, F.B. Alexander, C.D. Capio, and T.E. Smith, in *J. Electrochem. Soc.,* Vol 128, 1981, p 1545

36. A.C. Adams, in *Reduced Temperature Processing for VLSI,* R. Reif and G.R. Srinivasan, Ed., The Electrochemical Society, 1986, p 111

37. V.S. Nguyen, S. Burton, and P. Pan, in *J. Electrochem. Soc.,* Vol 131, 1984, p 2349

PECVD of Amorphous and Polycrystalline Silicon Films

Amorphous Silicon Films. The PECVD process is extensively used to deposit amorphous silicon films. Amorphous hydrogenated silicon (a-Si:H) films are deposited by the PECVD process by the decomposition of monosilane, disilane, or chlorosilane in a glow discharge plasma at temperatures in the range of 200 to 300 °C (390 to 570 °F) (Ref 38). The amorphous-to-polycrystalline transition temperature is sensitive to reactor design and deposition conditions and has to be controlled carefully. The a-Si:H films have important applications in the fabrication of solar cells (Ref 39), as photoreceptors in photolithography, and in Vidicon-type photoconductive image tubes (Ref 40).

Polycrystalline Silicon Films. Polycrystalline silicon is used as the gate electrode in metal-oxide semiconductor devices and as the emitter in bipolar devices. It is also used as interconnect material in ICs. In commercial manufacturing of ICs, polycrystalline silicon is deposited by thermally driven LPCVD at 625 °C (1150 °F). The PECVD process is rarely used for polycrystalline silicon film deposition, because deposited polycrystalline silicon films are intrinsic and have very high resistivity. Most applications in the microelectronic industry require the polycrystalline films to be highly conductive, which is achieved by doping the films after deposition. The number of processing steps can be reduced if the films are doped in situ. Application of PECVD for in-situ doping of polycrystalline silicon films is being explored. Thickness, uniformity, and deposition rates are very much affected when relatively high concentrations of dopant species are introduced in the LPCVD reactor during film growth. When PECVD is used to dope the polycrystalline silicon films in situ, the conductivity of these films can be modulated by six orders of magnitude for both p-type (by adding diborane) and n-type (by adding arsine) (Ref 41).

In other applications of polycrystalline silicon films, for example in the fabrication of thin-film transistors, PECVD is very desirable. Thin-film transistors are being explored for use in flat-panel displays and require much lower deposition temperatures, which can be achieved by PECVD. In addition, the growth rate of PECVD polycrystalline silicon films is less sensitive to the deposition temperature (Ref 4), as shown in Fig. 4, and so uniform film deposition requires less stringent control of the wafer temperature.

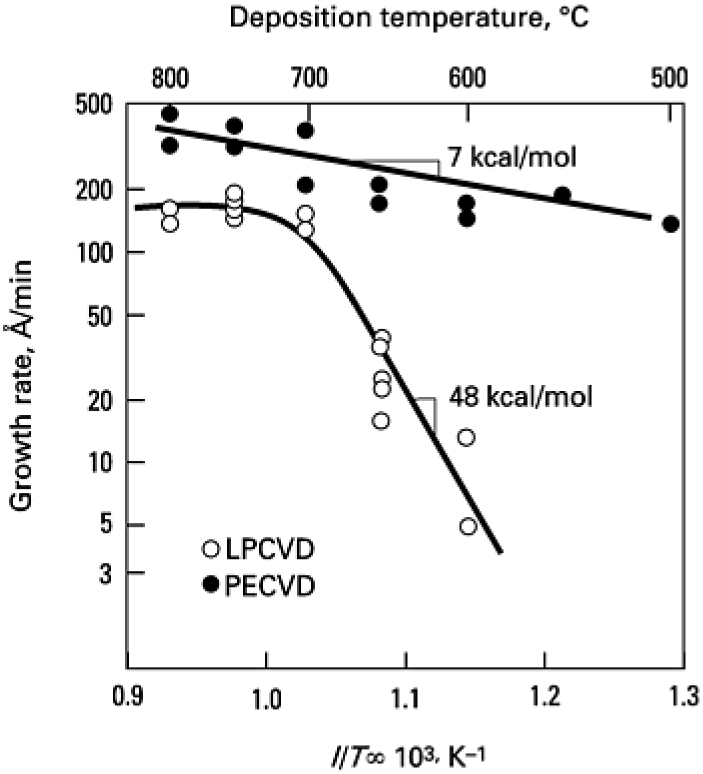

Fig. 4 Arrhenius plots of growth rates of polycrystalline silicon films deposited on oxidized silicon wafers with and without plasma enhancement. LPCVD, low-pressure chemical deposition; PECVD, plasma-enhanced chemical vapor deposition. Source: Ref 41

Epitaxial Films. In microelectronic devices, epitaxial films have extensive applications in both bipolar technology (as subcollector) and complementary metal-oxide semiconductor technology (to prevent latch-up). They are commercially deposited by APCVD at 1050 to 1200 °C (1920 to 2190 ° F) (Ref 42). Other deposition techniques can be used to deposit epitaxial silicon films at temperatures lower than in LPCVD, namely, molecular beam epitaxy (Ref 43), ion beam epitaxy (Ref 44), ultrahigh-vacuum CVD (Ref 45), and photo-enhanced CVD (Ref 46). The PECVD process is another exciting option for depositing homoepitaxial or heteroepitaxial films at lower temperatures. PECVD offers other potential advantages, such as flexibility in the deposition of in-situ doped films (Ref 47).

Deposition of silicon epitaxial films with and without plasma enhancement has been reported (Ref 48). The films were deposited in a very-low-pressure CVD system at temperatures as low as 650 °C (1200 °F) with SiH_4 as the source gas. A schematic of this reactor, which was designed and built at the Massachusetts Institute of Technology, is shown in Fig. 5. The substrate or wafer sits vertically on a graphite susceptor and faces a bank of infrared lamps, which heat both the wafer and the susceptor to the desired deposition temperature. The reactant gases can be pure SiH_4 for intrinsic deposition or SiH_4 mixed with other reactants (e.g., arsine or diborane) for epitaxial deposition of doped silicon. The gases enter the reactor from the top and are pumped out at the bottom. The reactor could be evacuated to a hydrocarbon-free base pressure about 10^{-8} torr, and epitaxial films are deposited at operating pressures of 1 to 100 mtorr. Plasma powers from 2.5 to 100 W could be used at a frequency of 13.56 MHz. In this reactor, a direct-current power supply was also used to bias the susceptor relative to ground and to decouple the substrate biasing from rf plasma power or electrode self-bias. At low plasma power (2.5 W) and in the temperature range of 750 to 800 °C (1380 to 1470 °F), the plasma-enhanced depositions were 20% faster, and at higher power (20 W), an additional 10% increase in the growth rate was observed.

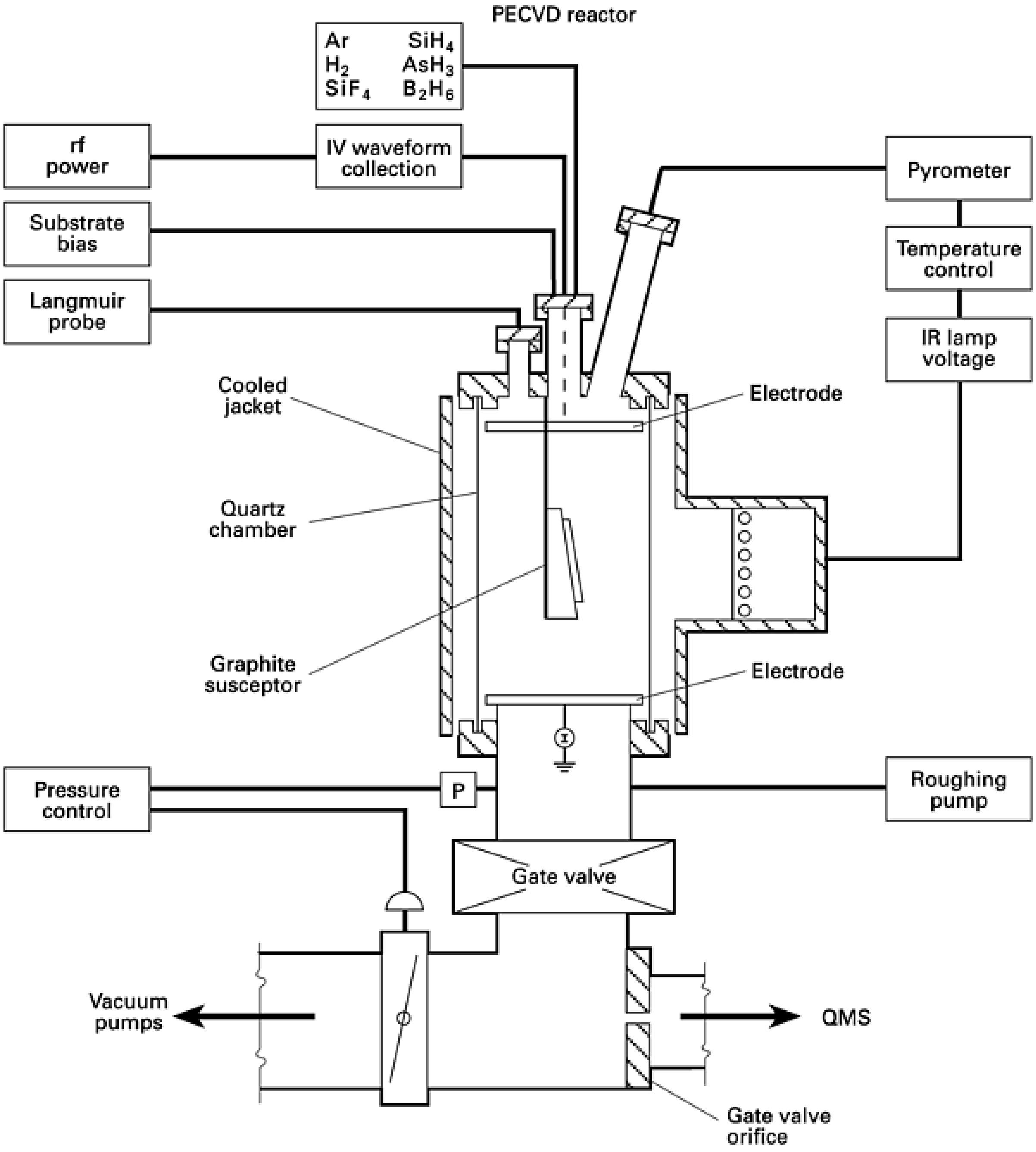

Fig. 5 Reactor for plasma-enhanced chemical vapor deposition of epitaxial silicon films. QMS, quadruple mass spectrometer. Source: Ref 48

Conductive Films. The deposition of refractory metals and their silicides with the PECVD process has been a subject of investigation by many researchers (Ref 49, 50, 51, 52). Refractory metals such as tungsten and molybdenum and their silicides--for example, tungsten silicide (WSi_2), molybdenum silicide ($MoSi_2$), and titanium silicide ($TiSi_2$)--have resistivities greater than that of aluminum but much less than that of doped polycrystalline silicon. Typical resistivities of the refractory metals are !15 μΩ· cm, while those of the refractory metal silicides have a range of 16 to 40 μΩ· cm (as compared to aluminum, which has a resistivity of 2.6 μΩ· cm, and doped polycrystalline silicon, which has a resistivity of about 500 μΩ· cm). When aluminum is used as the interconnect material in ICs, all the postaluminum processing steps have to be kept below about 450 °C (840 °F) (aluminum melts at about 600 °C, or 1220 °F). The refractory metals and their silicides are compatible with higher-temperature processing steps and can be used as interconnects or gates (in conjunction with polycrystalline silicon or alone). They are most commonly deposited by thermally driven CVD (Ref 13).

The resistivities of both the refractory metals and their silicides are very sensitive to factors such as impurities, which can be trapped in the film during the PECVD process, and grain size. When the PECVD process is used to deposit films of refractory metals or their silicides, even though the actual deposition temperatures can be as low as 400 °C (750 °F), a high-temperature postdeposition anneal is always necessary to bring down the resistivity. This high-temperature annealing step also presumably helps in the outdiffusion of impurities, in increasing the grain size, and in the annealing-out of radiation-induced defects in the films created during the PECVD process.

Refractory metal films are usually deposited at 400 °C (750 °F) with metal halides as the source gases (Ref 49, 50), for example, tungsten hexafluoride (WF_6) for tungsten deposition, and molybdenum pentachloride ($MoCl_5$) and H_2 for molybdenum deposition. Deposition of refractory metal silicides is carried out by introducing a silicon source (e.g., SiH_4) along with the metal halides into the reaction chamber. Usually an inert gas is also used to dilute the mixture. Table 1 gives a description of source gases, deposition temperatures, and the required postdeposition anneals when various refractory metal films and their silicides are deposited by the PECVD process.

Table 1 Plasma-enhanced chemical vapor deposition of refractory metal films

Material	**Reactant gases**	**Deposition temperature**		**Post-deposition anneal**	**References**
		°C	**°F**		
W	WF_6, H_2	350-400	660-750	1000 °C (1830 °F) for 30 min	49, 50
WSi	WF_6 + SiH_4 diluted with He	230	450	1000 °C (1830 °F) for 60 min in N_2	52
Mo	$MoCl_5$, H_2	170-430	340-800	800 °C (1470 °F) for 30 min in N_2	53
$MoSi_2$	$MoCl_5$, SiH_4 + Ar	400	750	1000 °C (1830 °F) for 20 min in N_2	51
$TaSi_2$	$TaCl_5$, SiH_2Cl_2 + H_2	580	1080	900 °C (1650 °F) for 60 min in Ar	54

References cited in this section

4. J.-J. Hajjar, R. Reif, and D. Adler, in *J. Electronic Materials,* Vol 15, 1986, p 279
13. R. Reif and W. Kern, Plasma Enhanced Chemical Vapor Deposition, *Thin Film Processes II,* Academic Press, Inc., 1991
38. H. Fritzsche, in *Thin Solid Films,* Vol 90, 1982, p 119
39. D.E. Carlson, in *Solid Energy Mat.,* Vol 3, 1980, p 503
40. I. Shimizu, T. Komatsu, K. Saito, and E. Inoue, in *J. Non-Cryst. Solids,* Vol 35-36, 1980, p 773
41. J-J. Hajjar and R. Reif, in *J. Electrochem. Soc.,* Vol 137, 1990, p 2888
42. J.O. Borland and C. Drowley, in *Solid State Technol.,* Vol 28 (No. 8), 1985, p 141
43. Y. Ota, in *J. Appl. Phys.,* Vol 51, 1980, p 1102
44. P.C. Zalm and L.J. Beckers, in *Appl. Phys. Lett.,* Vol 41, 1982, p 167
45. B.S. Meyerson, in *Appl. Phys. Lett.,* Vol 48, 1986, p 797
46. A. Ishitani, Y. Ohshita, K. Tanigaki, K. Takada, and S. Itoh, in *J. Appl. Phys.,* Vol 61, 1987, p 2224

47. J.H. Comfort and R. Reif, in *J. Appl. Phys.,* Vol 65, 1989, p 1053, 1067
48. T.J. Donahue and R. Reif, in *J. Appl. Phys.,* Vol 19, Supplement 19-1, 1979, p 647
49. J.K. Chu, C.C. Tang, and D.W. Hess, in *Appl. Phys. Lett.,* Vol 41, 1982, p 75
50. C.C. Tang, J.K. Chu, and D.W. Hess, in *Solid State Technol.,* Vol 26 (No. 3), 1983, p 125
51. A. Tabuchi, S. Inoue, M. Maeda, and M. Takagi, in *Proceedings of the 23rd Symposium on Semiconductors and IC Technology of the Electrochemical Society of Japan,* 1-2 Dec 1982, p 60
52. K. Akitmoto and K. Watanabe, in *Appl. Phys. Lett.,* Vol 39, 1981, p 445
53. S. Inoue, N. Toyokura, T. Nakamura, M. Maeda, and M. Takagi, in *J. Electrochem. Soc.,* Vol 130, 1983, p 1603
54. K. Hieber, M. Stolz, and C. Wieczorik, in *Proceedings of the Ninth International Conference on Chemical Vapor Deposition,* McD. Robinson, C.H.J. van den Brekel, G.W. Cullen, and J.M. Blocher, Jr., Ed., The Electrochemical Society, 1984, p 205
55. T. Hara, Y. Ishizawa, H.M. Wu, D.G. Hemmes, and R.S. Rosler, in *Proceedings of the Tenth International Conference on Chemical Vapor Deposition,* G.W. Cullen and J. Blocher, Jr., Ed., The Electrochemical Society, 1987, p 867

Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition

Donald M. Mattox, IP Industries

Introduction

THE PROPERTIES of atomistically deposited films depend strongly on the material being deposited, the substrate surface chemistry and morphology, the surface preparation process, and the details of the deposition process and the deposition parameters. The origin of the unique properties of physical vapor deposition (PVD) film can be understood by understanding the film formation process.

The formation of a useful and commercially attractive engineered surface using any PVD process (vacuum deposition, sputter deposition, or ion plating) involves several stages:

1. Choice of the substrate ("real surface") and development of an appropriate surface preparation process
2. Selection of the film material(s) to produce the surface properties required
3. Choice of the PVD process to provide reproducible properties, compatibility with subsequent processing, and long-term stability
4. Development of the fabrication process parameters, parameter limits, and the monitoring/control techniques
5. Development of appropriate characterization techniques to determine the film properties and stability of the product
6. Creation of written specifications and manufacturing processing instructions to cover the substrate material, surface preparation, deposition process, and characterization procedures

The properties of a film of a material formed by any PVD process depends on four factors:

- *Substrate surface condition*--e.g., surface morphology (roughness, inclusions, particulate contamination), surface chemistry (surface composition, contaminants), mechanical properties, surface flaws, outgassing, preferential nucleation sites, and the stability of the surface
- *Details of the deposition process and system geometry*--e.g., angle-of-incidence distribution of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, and concurrent energetic particle bombardment (flux, particle mass, energy)
- *Details of film growth on the substrate surface*--e.g., substrate temperature, nucleation, interface

formation, interfacial flaw generation, energy input to the growing film, surface mobility of the depositing adatoms, growth morphology of the film, gas entrapment, reaction with deposition ambient (including reactive deposition processes), and changes in the film properties during deposition
- *Postdeposition processing and reactions*--e.g., reaction of film surface with the ambient, thermal or mechanical cycling, corrosion, interfacial degradation, burnishing of soft surfaces, shot peening, and overcoating ("topcoat")

In order for the film to have reproducible properties, each of these factors must be reproducible.

Technological (Real) Surfaces

Technological surfaces or *engineering surfaces* are terms that are used to describe the real surfaces of engineering materials. These layers, along with the underlying bulk material, are the real substrate that must be altered to produce the desired surface properties. Invariably the real surface differs chemically from the bulk material by having surface layers of reacted and adsorbed material such as oxides and hydrocarbons. The surface chemistry, morphology, and mechanical properties of the real surface can be very important to the adhesion and film formation process. The underlying bulk material can be important to the performance of the surface. For example, a wear coating on a soft substrate will not function well if, under load, it is fractured by the deformation of the underlying substrate. Also, good film adhesion cannot be obtained when the substrate surface is mechanically weak, because failure can occur in the near-surface material. The bulk material can influence the surface preparation and the deposition process by continual outgassing and outdiffusion of internal constituents.

Some of the surface properties that affect the formation and properties of the deposited film are:

- *Surface chemistry*--affects the adatom-surface reaction and nucleation density. Chemistry can affect the stability of the interface formed by the deposition.
- *Contamination* (particulate and film, local or uniform)--affects surface chemistry and nucleation of the adatoms on the surface. Particulate contamination generates pinholes in the deposited film.
- *Surface morphology*--affects the angle-of-incidence of the depositing atoms and thus the film growth. Geometrical shadowing of the surface from the depositing adatom flux reduces surface coverage. Surface morphology can affect the film properties and stability.
- *Mechanical properties*--affects film adhesion and deformation under load
- *Outgassing and outdiffusion*--affects nucleation and film contamination
- *Homogeneity of the surface*--affects uniformity of film properties over the surface

In particular, the surface morphology can have an important effect on the film properties. Figure 1 shows the effect of surface morphology and particulate contamination on surface coverage and pinhole formation. Also, the surface morphology can affect the average angle-of-incidence of the adatom flux, which has a large effect on the development of the columnar morphology in atomistically deposited films.

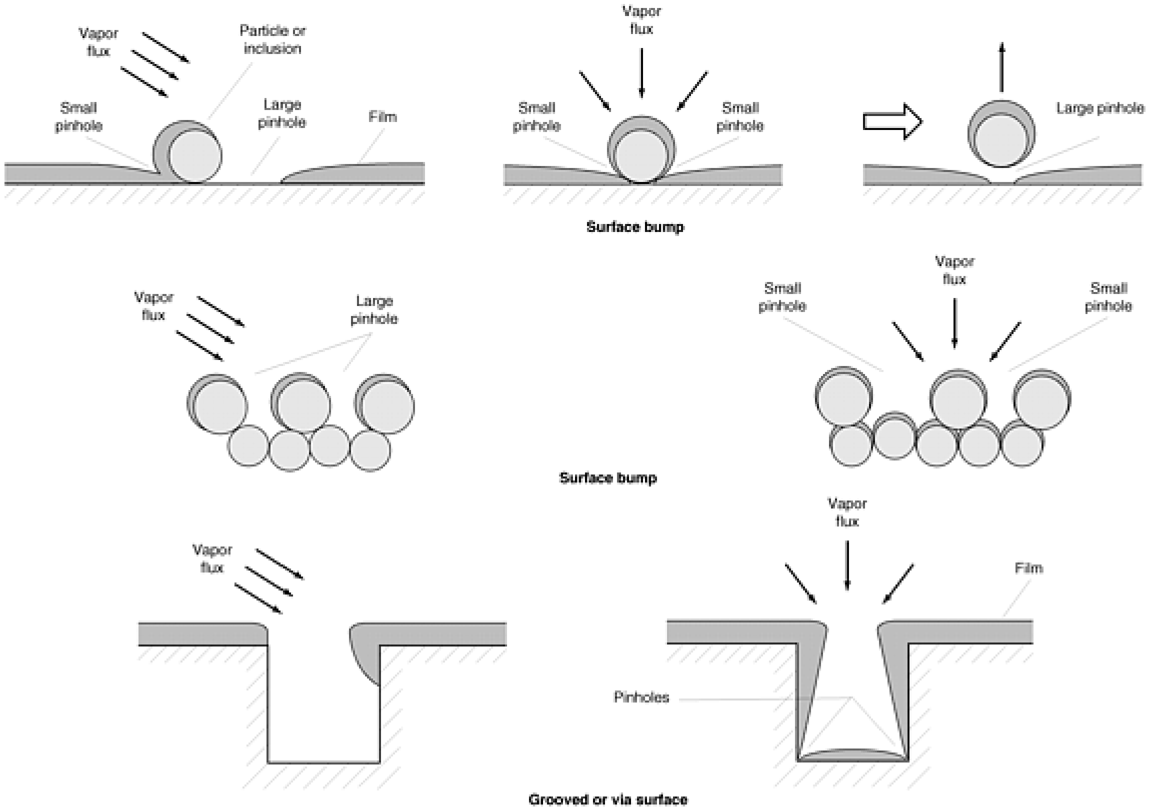

Fig. 1 Surface morphology effects on pinhole formation

The nature of the real surface depends on its formation, handling, and storage history. In order to have reproducible film properties, the substrate surface must be reproducible. This reproducibility is attained by careful specification of the substrate material, careful incoming inspection procedures, careful surface preparation, and appropriate handling and storage of the material.

Surface preparation is the process of preparing a surface for the film/coating deposition process (Ref 1). Surface preparation may mean cleaning (removal of contaminants), but it can also include surface treatments to change the properties of the surface in a desirable way, such as roughening or smoothing the surface, making a harder surface by plasma treatment (i.e., plasma nitriding) or shot peening, or "activating" the surface, such as the oxygen plasma treatment of a polymer surface. Often surface preparation consists of two distinct stages. The first is "external cleaning," which takes place outside the deposition system in a controlled environment. This processing environment is designed to control recontamination after cleaning. For example, to control recontamination by particulates, a filtered air "cleanroom" is used. External cleaning can consist of both "gross cleaning," which removes a portion of the substrate surface material, and "specific cleaning," which removes specific contaminants such as hydrocarbons or salts. The second stage of surface preparation is "in situ cleaning," which is performed in the deposition system. For example, hydrocarbon contamination can be removed from some surfaces by exposing them to an oxygen plasma in the deposition system.

Care must be taken to ensure that the surface preparation process does not change the surface in an undesirable or uncontrolled manner, such as selective leaching of one phase of a two-phase surface. One objective of any surface preparation procedure is to produce as homogeneous a surface as possible. Reproducible surface preparation, as well as associated handling and storage techniques, are obtained by having appropriate specifications for the process, handling, and storage procedures used. In addition, recontamination of the prepared surface in the deposition chamber and by the deposition process is a major consideration.

Reference cited in this section

1. D.M. Mattox, Surface Preparation for Film and Coating Deposition Processes, Chapter 3, *Deposition*

Processes for Films and Coating, 2nd ed., R. Bunshah, Ed., Noyes Publications, 1994

Atomistic Film Growth

Atomistic film growth occurs as a result of the condensation of atoms ("adatoms") on a surface. The stages of film formation are:

1. Vaporization of the material (adatoms) to be deposited
2. Transport of the material to the substrate
3. Condensation and nucleation of the adatoms
4. Nuclei growth
5. Interface formation
6. Film growth--nucleation and reaction with previously deposited material
7. Changes in structure during the deposition process--interface and film
8. Postdeposition changes due to postdeposition treatments, exposure to the ambient, subsequent processing steps, in-storage changes, or in-service changes

All of these stages are important in determining the properties of the deposited film material (Ref 2, 3, 4, 5).

Vaporization

In physical vapor deposition, vapors can be formed by thermal and nonthermal techniques. Thermal techniques require heating, such as vacuum evaporation and sublimation (see the article "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume). Nonthermal vaporization includes sputtering (see the article "Sputter Deposition" in this Volume), arc vaporization, laser ablation, and others.

Transport

The vaporized material can be transported through a vacuum, gas, or plasma. The vacuum environment allows control of the contamination in the ambient environment to any desired level. The gaseous environment may thermalize energetic particles and cause vapor phase nucleation, depending on the gas density (see the article "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume). The plasma environment "activates" reactive species, making them more chemically reactive.

Condensation and Nucleation

Atoms that impinge on a surface in a vacuum environment either are reflected immediately, reevaporate after a residence time, or condense on the surface. The ratio of the condensing atoms to the impinging atoms is called the *sticking coefficient*. If the atoms do not immediately react with the surface, they will have some degree of surface mobility over the surface before they condense. Re-evaporation is a function of the bonding energy between the adatom and the surface, the surface temperature, and the flux of mobile adatoms. For example, the deposition of cadmium on a steel surface having a temperature greater than about 200 °C (390 °F) will result in total re-evaporation of the cadmium.

Surface Mobility. The mobility of an atom on a surface will depend on the energy of the atom, atom-surface interactions (chemical bonding), and the temperature of the surface. The mobility on a surface can vary due to changes in chemistry or crystallography. The different crystallographic planes of a surface have different surface free energies that affect the surface diffusion. For example, for face-centered cubic metals the surface free energy of the (111) surface is less than that of the (100) surface, and the surface mobility of an adatom is generally higher on the (111) surface than on the (100) surface. This means that different crystallographic planes will grow at different rates during adatom condensation. Various techniques have been developed to study surface mobility and the surface diffusion rate of adatoms on a surface (Ref 6, 7).

The surface mobility of adatoms can be an important factor in surface coverage. For example, the surface coverage of a silicon device is improved by depositing an Al/Cu metallization on a TiN barrier layer at 500 °C (930 °F). The Al/Cu has a higher surface mobility on the TiN surface than on the silicon surface and is able to completely fill a 0.5 μm diameter by 0.8 μm deep "via" holes. Also, by direct current magnetron sputter-depositing the Al-5Ga eutectic alloy at 300 °C (570 °F), "via" holes with aspect ratios of up to 4:1 have been successfully filled.

Nucleation. Atoms condense on a surface by losing energy. They lose energy by:

- Making and breaking chemical bonds with the substrate surface atoms
- Finding preferential nucleation sites (e.g., lattice defects, atomic steps, impurities)
- Colliding with other diffusing surface atoms (same species)
- Colliding or reacting with adsorbed surfacespecies

Nucleation by Surface Reaction. The condensing atoms react with the surface to form atom-to-atom chemical bonds. The chemical bonding may be by metallic (homopolar) bonding where the atoms share orbital electrons, by electrostatic (coulombic, heteropolar) bonding where ions are formed due to electron loss/gain, or by electrostatic attraction (van der Waals forces) due to polarization of molecules. If the atom-atom interaction is strong, surface mobility is low and each surface atom can act as a nucleation site. If the reaction is strong, the atom is said to be *chemisorbed*. In some cases the chemisorbed adatom displaces the surface atoms, giving rise to a "pseudomorphic" surface structure.

The bonding energy of atoms to surfaces can be studied by thermal desorption techniques. The chemisorption energy for some materials on clean surfaces are:

Material	**Energy, eV**
Rb on W	2.6
Cs on W	2.8
B on W	6.1
N_2 on Fe	3.0
Ni on Mo	2.1
Ag on Mo	1.5
Au on W	3.0
O_2 on Mo	7.5

Note: 1 eV/atom = 23 kcal/mole.

Source: Ref 8

The bonding between a metal atom and an oxide surface is proportional to the metal-oxygen free energy of formation, with the best adhesion produced by the formation of an intermediate oxide interfacial layer. In many instances the surface composition can differ significantly from that of the bulk of the material, and/or the surface can have an nonhomogeneous composition. Examples are the glass-bonded (Si-O) sintered, alumina ceramics shown in Fig. 2. Film atoms prefer to nucleate and react with the glassy Si-O phase, and if this material is leached from the surface during surface preparation, the film adhesion suffers (Ref 9). Preferential sputtering of a compound or alloy substrate surface can change the surface chemistry. For instance, preferential sputtering of an Al_2O_3 surface removes oxygen, leaving an aluminum-rich surface (Ref 10). Surface contamination can greatly influence the nucleation density, interfacial reactions, and nuclei orientation. When a two-phase binary alloy is deposited, the two materials may react differently with the surface, resulting in segregation on the surface.

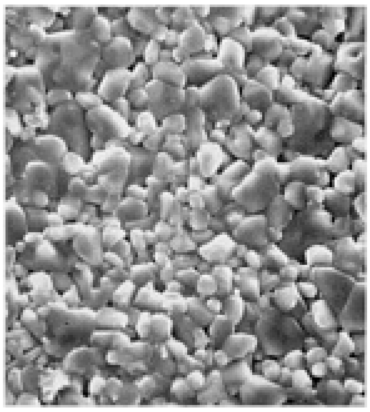

Fig. 2 Surface morphology of an as-sintered 96% alumina ceramic such as is used in hybrid circuitry. 1000×

Nucleation at Preferential Nucleation Sites. If the adatom-surface interaction is weak, the adatom will have a high surface mobility and will condense at preferential nucleation sites where there is stronger bonding due either to a change in chemistry (element or electronic) or an increase in coordination number (e.g., at a step). Preferential nucleation sites can be:

- Morphological surface discontinuities such as steps or scratches
- Lattice defects in the surface such as point defects or grain boundaries
- Foreign atoms in the surface
- Charge sites in insulator surfaces
- Surface areas that have a different chemistry or crystallographic orientation

Steps on a surface can act as preferential nucleation sites. For example, gold deposited on cleaved single-crystal NaCl or KCl shows preferential nucleation on cleavage steps. Steps on Si (100) and GaAs (100) surfaces can be produced by polishing at an angle of several degrees to a crystal plane. This procedure produces an "off-cut" or "vicinal" surface (Ref 11) comprised of a series of closely spaced steps. These steps aid in dense nucleation for epitaxial growth of GaAs on Si and Al_xGa_{1-x} As on GaAs. Scratches on the substrate surface provide nucleation sites in the deposition of diamond films.

Lattice defects can act as preferential nucleation sites. For example, amorphous carbon films have a high density of defects that act as nucleation sites for gold deposition. When depositing adatoms on electrically insulating substrates, charge sites on the surface can act as preferential nucleation sites. Electron irradiation, ultraviolet radiation (UV), and ion bombardment can be used to create charge sites.

Nucleation by Collision. Mobile surface adatoms can nucleate by collision with other mobile surface species to form stable nuclei. Thus the nucleation density can depend on the deposition (arrival) rate. For example, in the deposition of silver on lead it has been shown that at a deposition rate of 0.1 nm/min, the silver is completely re-evaporated, while at 10 nm/min, the atoms are completely condensed. When depositing silver on glass, improved adhesion can be obtained by a rapid initial deposition rate, followed by a lower rate to build up the thickness.

Nucleation by Reaction with Adsorbed Atoms. Mobile surface species can react with adsorbed surface species such as oxygen. For example, chromium deposition after oxygen plasma cleaning of glass generally results in improved adhesion compared to a glass surface that has not been oxygen-plasma cleaned. This is probably due to the adsorption of oxygen on glass, which increases the nucleation density of deposited gold (Ref 12). The adsorption of reactive species can also have an important effect in reactive deposition processes (Ref 13).

Nucleation of Unstable Surfaces. Some surfaces are unstable and change their nature when atoms are added to the surface. For example, the adatom may interact with the surface lattice and cause atomic rearrangement such that a pseudomorphic surface is formed that presents a different surface to atoms subsequently deposited (Ref 8). Some polymers, particularly glassy polymers (i.e., those above their glass transition temperatures), have surfaces that are unstable and into which the depositing adatom will sink and possibly even nucleate below the polymer surface (Ref 14). Polyethylene and polypropylene are examples of polymers that are glassy at room temperature.

Nucleation Density. In general, the number of nuclei per unit area, or "nucleation density," should be high in order to form a dense film and obtain complete surface coverage at low film thickness. The nucleation density and growth behavior can vary with different substrate locations due to phase distribution, surface morphology, or crystallographic orientation of the substrate surface. The variation of nucleation density and subsequent film growth can result in film property variations over the surface.

Characterization of Nucleation Density. The relative and absolute nucleation density can be determined by a number of techniques (Ref 15), including:

- Optical density of the deposited film as a function of mass deposited
- Behavior of the thermal coefficient of resistivity (TCR) as a function of mass deposited
- Transmission electron microscopy (TEM) and ultrahigh vacuum TEM
- Auger electron spectroscopy (AES)
- Low-energy electron diffraction (LEED)
- Reflection high-energy electron diffraction (RHEED)
- Work function change as a function of mass deposited
- Scanning electron microscopy (SEM)
- Scanning tunneling microscopy (STM) (Ref 16)
- Atomic force microscopy (AFM)
- Photon tunneling microscopy (PTM) (Ref 17)

Optical Adsorption. On transparent substrate materials, the optical density of a film formed by depositing a given amount of material can be used to measure the comparative nucleation density. The optical density (OD) is defined as: OD = log [(% visual light transmitted through the substrate)/(% visual light transmitted through a metallized substrate)]. A good electrical conductor having a high nucleation density is optically opaque to the human eye when the film thickness is about 1000 Å (100 nm). A comparison of optical densities is often a good "quick check" on process reproducibility.

The temperature coefficient of resistance (TCR) of very thin metal films on electrically insulating substrates depends on the growth of the nuclei. Isolated nuclei result in a negative TCR (increasing temperature/decreasing resistance) due to thermally activated tunneling conduction between nuclei. Connected nuclei, which form a continuous film, have a positive TCR as would be expected in a metal. Thus TCR measurements can be used to provide an indication of nucleation density and growth mode by determining the nature of the TCR as a function of mass deposited.

Surface Analytical Techniques. Using low-energy electron diffraction (LEED) it has been shown that very low coverages of contamination can inhibit interfacial reaction and epitaxial growth. The field ion microscope has been used to field-evaporate deposited material and observe the "recovered" substrate surface. Using this technique to study the deposition of copper on tungsten, it was shown that electroplating results in interfacial mixing similar to that produced by high-temperature vacuum deposition processing.

Modification of Nucleation Density. There are a number of ways to modify the nucleation of depositing atoms on substrate surfaces, including:

- Change deposition temperature (increasing temperature can increase reaction with surface and increases

surface mobility; decreasing temperature can decrease surface mobility)
- Increase deposition rate to increase collision probability of diffusing species
- Change surface chemistry to make the surface more reactive
- "Sensitizing" the surface by the addition of "nucleating agents"
- Generate nucleation sites on the surface (lattice defects, charge sites on insulators) by mechanically disrupting the surface to produce defects and disturb contaminant layers ("mechanical activation"), using ion bombardment to produce lattice defects (Ref 18), incorporating species by ion implantation or chemical substitution, or using electron bombardment or photon bombardment (Ref 19) to charge centers on insulator surfaces
- Produce codeposition or absorption of reactive species
- Change surface roughness
- Create a new surface--"basecoat" or "glue layer"

Adsorption and Codeposition or Reactive Species. Adsorbed or codeposited reactive species can affect the surface chemistry and thus the nucleation of the deposited species. The presence of adsorbed oxygen or oxygen in a plasma or bombarding oxygen ion beam during deposition has been shown to aid in the adhesion of gold (Ref 20) and oxygen-active film materials (Ref 21) to oxide substrates. The increased adhesion is attributed to the increased nucleation density. In the case of a plasma system such as plasma-enhanced chemical vapor deposition (PECVD), the radicals, unique species, and excited species formed in the plasma may play an important role in adsorption and deposition from a gaseous precursor. For example, in the deposition of silicon from silane by PECVD, it has been proposed that the formation of disilane and trisilane in the plasma and its adsorption on the surface, along with low-energy particle bombardment, is important to the low-temperature, high-rate deposition of amorphous silicon (Ref 22).

Surface roughness can also play an important role in nucleation. The typical 94% alumina used in microelectronics has a surface roughness that looks like a field of boulders several microns in diameter (see Fig. 2). Deposition on such a surface results in a high nucleation density on the tops of the "boulders" and a lower nucleation density on the sides and in the pores. Flowed glass surfaces, on the other hand, are smooth and the nucleation density can be uniform over the surface.

Establishing a New Surface. In the extreme case, a new surface layer ("glue layer," basecoat) can be used to provide a better surface for the deposition of the desired material. This is often done in the metallization systems used in microelectronics and for interconnects in integrated circuit technology. In these cases a material is deposited on the oxide/semiconductor surface that forms a desirable oxide interface (e.g., titanium or chromium). Then a surface layer is deposited that alloys with the first layer and provides the desired property (e.g., gold, copper, silver). The new surface can also be used to smooth or "planarize" the initial surface (e.g., a "flowed" basecoat layer).

Growth of Nuclei

When atoms condense they form nuclei. If the surface is of the same material as the depositing atoms, the process is called *homogeneous nucleation*; if they are of different materials, the process is call *heterogeneous nucleation*. In semiconductor terminology, heterogeneous nucleation forms *heterojunctions*. Three types of nucleation mechanisms have been identified; they differ according to nature of interaction between the deposited atoms and the substrate material (Ref 23): (a) the van der Merwe mechanism leading to a monolayer-;by-monolayer growth; (b) the Volmer-;Weber (V-;W) mechanism, characterized by a three-dimensional nucleation and growth; and (c) the Stranski-Krastanov (S-K) mechanism, where an altered surface layer is formed by reaction with the deposited material to generate a strained or pseudomorphic structure, followed by nucleation on this altered layer. The S-K nucleation is common with metal-on-metal deposition and at low temperatures where the surface mobility is low. The conditions for these types of growth is generally given in terms of thermodynamics and surface energy considerations.

Often the adsorption is accompanied by surface reconstruction, surface lattice strain, or surface lattice relaxation, which change the lattice atom spacing or the surface crystallography to give a pseudomorphic structure. The interaction of the depositing material with the surface can form a structure on which subsequent depositing atoms nucleate and grow in a manner different from that of the initially depositing material. This may alter the subsequent film structure. For example, the unique beta-tantalum structured films are stabilized by deposition on an as-grown tantalum silicide interfacial material.

Nuclei Coalescence and Agglomeration. The nuclei grow by collecting atoms that diffuse over the surface. Isolated nuclei grow laterally and vertically on the surface to form a continuous film (Ref 24). The higher the nucleation density, the less the amount of material needed to form a continuous film. The principal growth mode of the nuclei may be laterally over the substrate surface ("wetting growth"), or the nuclei may prefer to grow in a vertical mode ("dewetting growth"). Examples of wetting growth are: gold on copper and chromium, iron on W-O surfaces, and titanium on SiO_2. Examples of dewetting growth are nickel and copper on W-O surfaces, and gold on carbon, Al_2O_3, and SiO_2. Growth and coalescence of the nuclei can leave interfacial voids or structural discontinuities at the interface, particularly if there is no chemical interaction between the nuclei and the substrate material and dewetting growth occurs.

In cases where there is little chemical interaction between the nucleating atoms and the substrate, the isolated nuclei grow together, giving the so-called island-channel-continuous film growth stages. Before coalescence the nuclei can have a "liquid-like" behavior that allows them to rotate and align themselves crystallographically with each other, giving an oriented (epitaxial) overgrowth.

Agglomeration of nuclei occurs when the temperature of the nuclei is high enough to allow atomic diffusion and rearrangement such that the nuclei "ball-up" to minimize the surface area. Agglomeration of evaporated gold films is increased at high deposition rates, at high substrate temperatures, and in high-rate electron beam evaporation. Gold is often used for replication in electron microscopy, and agglomeration of pure gold can be a problem; therefore, gold alloys such as 60Au:40Pd are used to reduce the agglomeration tendencies and provide better replication. Agglomeration can occur after deposition if there is appreciable columnar growth (high surface area) in the film and the film is heated.

Where there is strong interaction between the adatoms and the substrate but little diffusion or compound formation with the substrate, the crystal orientation of the deposited material can be influenced by the substrate crystallographic orientation, producing a preferential crystallographic orientation in the nuclei. This type of oriented overgrowth is called *epitaxial growth.* Lattice mismatch between the nuclei and the substrate at the interface can be accommodated by lattice strain or by the formation of "misfit" dislocation networks, and under proper conditions a single crystal epitaxial film can be grown. This is often the goal in molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) of semiconductor thin films. In the growth of semiconductor materials it is desirable to form an interface that is defect-free so that electronically active sites are not generated. Such an interface can be formed if there is lattice parameter matching between the deposited material and the substrate, or if the deposited material is thin enough to allow lattice strains to accommodate the lattice mismatch without producing dislocation networks. This latter condition produces a "strained layer superlattice" structure (Ref 25).

At the other extreme of growth are amorphous materials where rapid quenching, bond saturation, limited surface diffusion, and the lack of substrate influence results in a highly disordered material. Comparison between amorphous materials formed by coevaporation and those formed by rapid quenching show some indication of a lower degree of short range ordering in the codeposited material, as indicated by the lower crystallization temperature and lower activation energy for crystallization than in the low-temperature deposited films. Amorphous conductive materials, such as $W_{75}Si_{25}$, have been proposed as a diffusion barrier film in semiconductor metallization. Because amorphous films have no grain boundaries, they are expected to show lower diffusion rates than films that have grain boundaries, in that grain boundary diffusion rates are generally higher than bulk diffusion rates.

Heating by Condensation. At high deposition rates, the condensation energy can produce appreciable substrate heating. When a thermally vaporized atom condenses on a surface it releases energy from several sources, including:

- *Heat of vaporization or sublimation* (enthalpy of vaporization)--a few electron volts per atom
- *Energy to cool to ambient*--depends on heat capacity and temperature change
- *Energy associated with reaction*, which may be exothermic, where heat is released, or endothermic, where heat is adsorbed--heat of reaction (Table 1)
- *Energy released on solution*--heat of solution

Table 1 Heats of reaction

Material	Heat, kcal/mole

Ni_2Si	-11
NiSi	-18
Pt_2Si	-11
PtSi	-15
$ZrSi_2$	-35
Ta_2O_5	-500
Al_2O_3	-399
V_2O_3	-290
Cr_2O_3	-270
TiO_2	-218
WO_3	-200
MoO_3	-180
Cu_2O	-40
SiC	-15
Au in Si	-2.3(a)
Ni_3C	+16
Au_2O_3	+19

(a) Heat of solution

The thermal vaporization energy for gold from tungsten is about 3 eV per atom, and the kinetic energy of the vaporized atom is about 0.3 eV per atom. Thus the kinetic energy is only a small part of the energy being released during deposition. However, it has been shown, using mechanical velocity filters, that the kinetic energy of the depositing gold particles is important to the film structure, properties, and annealing behavior.

If the depositing atom has greater than thermal energy, due either to being vaporized by sputtering (and not "thermalized" during transport from source to substrate), or to being accelerated as an ion (film ion), the kinetic energy that it releases will be greater than thermal. If the depositing species is excited or ionized, it also releases the excitation energy or the ionization energy. In these situations the energy released also includes excess kinetic energy, excitation energy (if an excited species), or ionization energy (if an ionized species).

Interface Formation

The depositing film material can diffuse and react with the substrate to form an "interfacial region." The material in the interfacial region has been called the "interphase material," and its properties are important to the adhesion, electrical, and electronic properties of film-;substrate systems. The type and extent of the interfacial region can change as the deposition process proceeds or be modified by postdeposition treatments. Interfacial regions are categorized as (Ref 26):

- Abrupt
- Mechanical (specific type of the abrupt interface)
- Diffusion
- Compound (also requires diffusion)
- Pseudodiffusion (physical mixing, ion implantation, recoil implantation)
- Reactively graded
- Combinations of the above

Figure 3 schematically shows the types of interfacial regions.

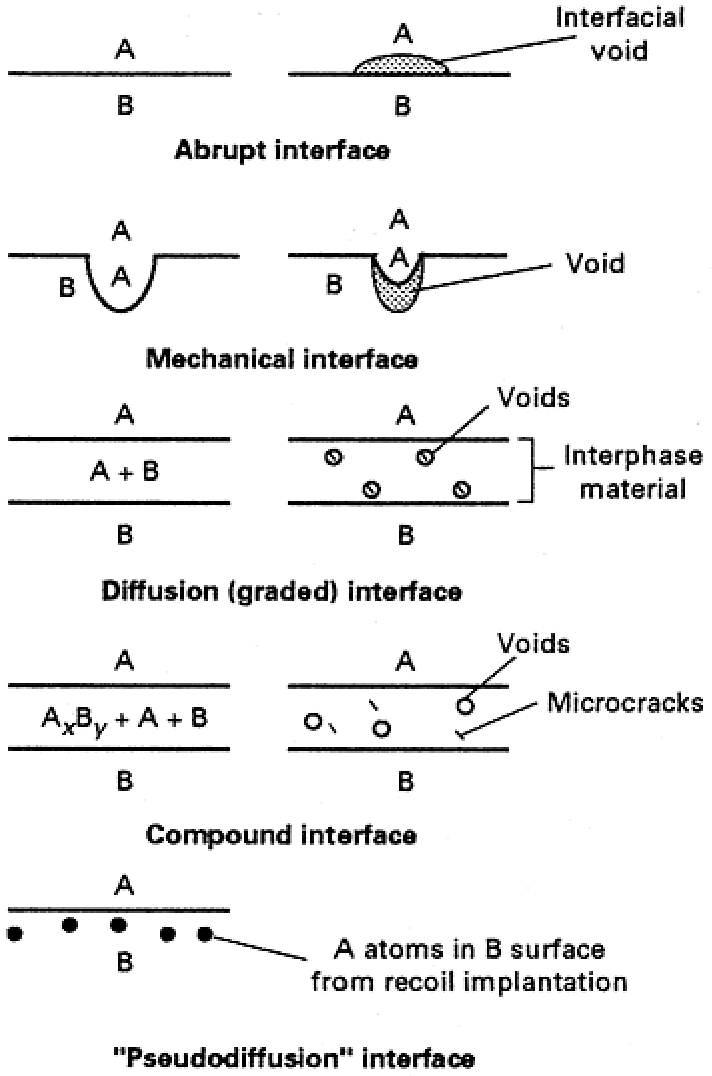

Fig. 3 Types of interfacial regions

The abrupt interface is characterized by an abrupt change from the film material to the substrate material in a distance of the order of the atomic spacing (i.e., 0.2 to 0.5 nm), with concurrent abrupt changes in material properties. This type of interface is formed when there is no bulk diffusion, and it generally signifies weak chemical reaction between the depositing atoms and the substrate, a low deposition temperature, surface contamination, or no solubility between film and substrate materials. The formation of this type of interfacial region generally means that the nucleation density is low and that the film will have to grow to appreciable thickness before it becomes continuous. This results in the formation of interfacial voids along the interface. Typically the adhesion in this system is low because of interfacial voids and an easy fracture path.

Mechanical Interlocking Abrupt Interface. The mechanical interface is an abrupt interface on a rough surface where the deposited material forms a conformal surface to the roughness and the rough surface is "filled in" to give mechanical interlocking. The strength of the interface depends on the mechanical properties of the materials. To fracture along the interface requires following a tortuous path with changing stress tensors, and the adhesion of the film to the surface can be high. Surfaces can be made rough or porous to increase the degree of mechanical interlocking. The adhesion of this couple is limited by the deformation and/or fracture properties of the materials involved. If the roughness is not filled in, the adhesion will be low due to the lack of contact and interfacial voids. The filling in of the roughness can be aided by having a dispersed adatom flux distribution, concurrent energetic particle bombardment, or high surface mobility of the deposited material.

The diffusion interface is characterized by a gradual change or gradation in composition across the interfacial region with no compound formation. The diffusion interface is formed when there is mutual solid solubility between the film and substrate material and the temperature and time are sufficient to allow diffusion to occur. This type of interfacial system is often found in metallic systems. Some systems, such as silver on iron and indium, or gallium on GaAs, have no solubility and an abrupt interface is formed. If contamination is present on the surface, diffusion can be suppressed.

The extent of diffusion in the interface depends on time and temperature. Differing diffusion rates of the film and substrate materials can create porosity in the interfacial material. Porosity formed by this mechanism is called *Kirkendall porosity*. This porosity can weaken the interfacial material and provide an easy fracture path for adhesion failure.

In some cases, diffusion barriers are used at the interface to reduce diffusion. For example, tungsten plus titanium or the electrically conductive nitride, TiN, is used as a diffusion barrier in silicon metallization to inhibit aluminum diffusion into the silicon during high-temperature processing. The presence of compound-forming species in the depositing material reduces the diffusion rate. Alternatively, the depositing material can be alloyed with substrate material to reduce diffusion rates.

In high-temperature processing the substrate material near the interface can be weakened by the diffusion of a constituent of the substrate into the depositing film material. For example, the diffusion of carbon from cemented carbide tools during CVD deposition of coating forms a weak eta phase at the interface. Conversely the diffusion from the substrate can result in increased adhesion. For example, it has been shown that in the deposition of carbides on oxide surfaces the oxygen intermixes and reacts with the carbide material, producing a "keying" action.

Compound Interface. Diffusion, along with chemical reaction, forms a compound interfacial region. The compounds formed are often brittle, and high stresses are often introduced due to the volumetric changes involved in forming the new phase(s). Sometimes these stresses are relieved by microcracking in the interfacial region, thus weakening the interphase material. The compound interface is generally conducive to good adhesion, but if the reaction region is too thick, the development of porosity and the formation of microcracked brittle compounds can lead to poor adhesion.

The compound interface is the type of interface found in reactive systems, such as oxygen-active metal films on oxide substrates (Ref 27), or in intermetallic-forming metal-on-metal systems such as Au-Al and Al-U. In the case of Au-Al, the interdiffusion and reaction forms both Kirkendall voids and a brittle intermetallic phase termed "purple plague" that causes easy bond failure (Ref 28).

Table 1 lists heats of reactions of various materials in forming compounds. An exothermic reaction is one in which heat is released and is indicated by a negative heat of formation. An endothermic reaction is one in which heat is taken up and is indicated by a positive heat of reaction. In some layered film systems there can be an exothermic reaction such that large amounts of heat are generated after the reaction has been "triggered." Such systems are Pd-Sn, Al-Pd, and Al-Zr, which have increasingly higher "triggering" temperatures. Multilayer composite structures of these materials can be used to rapidly release heat (Ref 29).

Interfacial Boundary. It should be remembered that diffusion and reaction can continue during the deposition process, particularly if an elevated deposition temperature and long times are used. For example, with aluminum on platinum an Al-Pt intermetallic is formed, and as the intermetallic layer thickness increases it removes the aluminum preferentially from grain boundaries at the Al/Al-Pt interface. This leads to void formation at the grain boundaries and the formation of "capillary voids."

As diffusion proceeds, the interfacial boundary becomes "rough." Rapid diffusion can occur at grain boundaries and dislocations, giving a "spiked" interfacial surface that aids in the bonding of some coatings to surfaces but can cause shorting in semiconductor junctions ("pipe diffusion"). Rapid heating and cooling can also limit diffusion and in ion plating, where heat is introduced directly into the surface, a cold substrate can be used. As a postdeposition process, heating by rapid thermal processing can be used to limit preferential diffusion along lattice defects.

The interphase material formed by diffusion and reaction often contains a graded composition with properties that vary throughout the layer. If the material becomes thick, it can develop high residual stress, voids, and microcracks that weaken the material and result in poor adhesion. The interphase material is important in film adhesion, contact resistance, and the electronic "interfacial states" of metal-semiconductor contacts.

In the extreme the film material can completely react with the substrate, thus forming a film of the interphase material. This is usually an effect of high substrate temperature during deposition or postdeposition processing. For example, it has been reported that sputter-deposited tungsten on silicon forms a silicide film that has the same properties as 900 °C (1650 °F) furnace-diffused tungsten-on-silicon silicide films. Platinum on silicon can also be completely reacted to form silicide electrodes on the silicon.

Metal-Polymer Interfaces. In the case of polymer surfaces, particularly glassy polymers, the depositing atoms can diffuse into the surface, then nucleate, forming nuclei of the material in the subsurface region. For example, in the deposition of copper on polyimide at low deposition rates (1 monolayer/min), copper nuclei are formed beneath the surface while chromium, which forms a chemical bond with the polymer chain, does not diffuse into the surface. The nucleation and chemical bonding of the adatoms to the polymer surface determine the adhesion strength (Ref 30).

Pseudodiffusion Interfaces. In deposition processes, an interface with a graded composition and materials properties can be formed by "grading" the deposition from one deposited material to the other. For example, in depositing Ti-Au or Ti-Cu metallization, the gold or copper deposition can begin before the titanium deposition has ended. This produces a graded interface similar to the diffusion interface, called a *pseudodiffusion interface*. This can be formed between insoluble materials, such as silver and iron, and at low temperatures where the phases do not segregate. This method of grading the interface also avoids the potential problem of oxidation of the titanium film before the gold or copper is deposited. If oxidation occurs, the adhesion between the titanium and the gold or copper layers will be poor. The pseudodiffusion type of interface can also be formed by "recoil implantation" during concurrent or subsequent ion bombardment.

Reactively Graded Interface. A compound-containing interfacial region that consists of a graded compound-matrix material can be formed by controlling the availability of reactive gases during reactive deposition. For example, a TiN hard coating can be deposited with a graded interfacial layer of Ti to TiN_x, to improve adhesion, by controlling the availability of the reactive nitrogen.

Characterization of Interfaces. Generally the interphase material is difficult to characterize because it usually consists of a small amount of material buried under a relatively thick film. In 1988 the National Science Foundation conducted a workshop on adhesion, and one of the principal determinations was that the properties of the interphase material were poorly characterized and understood (Ref 31).

In some cases the compositional profile of the interfacial region can be determined using Auger electron spectroscopy in combination with sputter etching or Rutherford backscatter spectrometry (Ref 15). Cross section TEM can be used with proper care not to introduce artifacts due to sample preparation.

Modification of Interfacial Regions. Interface composition, structure, and extent can be modified by:

- Substrate surface cleaning and surface preparation
- Changing the substrate temperature and deposition time
- Introducing energy into the surface region during deposition by concurrent ion bombardment, laser heating, and so on

Surface preparation is an important factor in interface formation in that the interface reactions can be drastically modified by the presence of strongly bound contaminants such as oxygen, carbon, and nitrogen, whereas weakly bound contaminants such as H_2O, CO, and hydrogen, can be displaced from the surface during deposition.

Ion bombardment, before and during deposition, can introduce defects into the surface region, and diffusion can be enhanced by mechanisms similar to those found in "radiation enhanced diffusion." For example, in the aluminum metallization of silicon it has been shown that there is little diffusion of aluminum into silicon during high-temperature processing if the silicon surface is undamaged. However, extensive diffusion occurs if the surface is damaged by ion bombardment.

Film Growth

Films grow by the continuous nucleation of depositing atoms on previously deposited material. The film growth, as well as the nucleation mode, determines many film properties, such as density, surface area, surface morphology, and grain size. Important aspects of film growth are:

- Continual burial of the surface under newly depositing material
- Substrate surface roughness--initially, and as the film develops
- Surface temperature--initially, and as the film develops
- Adatom surface mobility
- Geometrical shadowing effects (angle-of-incidence effects)
- Reaction and mass transport during deposition, such as segregation effects and void agglomeration

Developing Surface Roughness. On an atomistic scale, surface morphology can vary from very smooth, such as that of a flowed glass surface, to very rough, such as is found with sintered materials (see Fig. 2). Generally, as the film grows the surface roughness increases because some features or crystallographic planes grow faster than others. The roughness may not be uniform over the surface, or there can be local areas of roughness due to scratches, vias, embedded particles, particulate contamination, and so on that lead to variations of the film properties in these areas.

Structure-Zone Model (SZM). Typically the film near the interface is influenced by the substrate and/or interface material, and it takes an appreciable thickness before the film establishes a particular growth mode. After a growth mode has been established, the film morphology can be described by a structure zone model (SZM). The SZM was first applied to vacuum-deposited coatings by Movchan and Demchishin in 1969 (Ref 32). Later the SZM was extended to sputter-deposited films by Thornton (Ref 33), as shown in Fig. 4, and was later modified by Meissier (Ref 34) to include point defect agglomeration and void coarsening with thickness. The details of the condensation processes that determine the film morphology at low temperatures where atom mobility is low are not well understood, although there are a number of factors involved, including:

In vacuum:

- Angle-of-incidence of the adatom flux effects (i.e., geometrical shadowing)
- Ratio of the deposition temperature (in K) to the melting temperature (in K) of the film material
- Energy released on condensation
- Adatom surface mobility on surfaces and crystallographic planes
- Surface roughness
- Deposition rate
- Void coalescence
- Mass transport and grain growth during deposition

In sputter deposition and ion plating (Ref 13):

- Adsorption of inert and/or reactive gaseous species on the surface
- Gas scattering of vaporized particles
- Concurrent bombardment by high-energy particles, which can be from reflected high-energy neutrals from the sputtering target that are not thermalized by collisions in the gas phase, accelerated negative ions from the sputtering target, accelerated positive ions from a plasma, or energetic neutrals formed by charge exchange processes

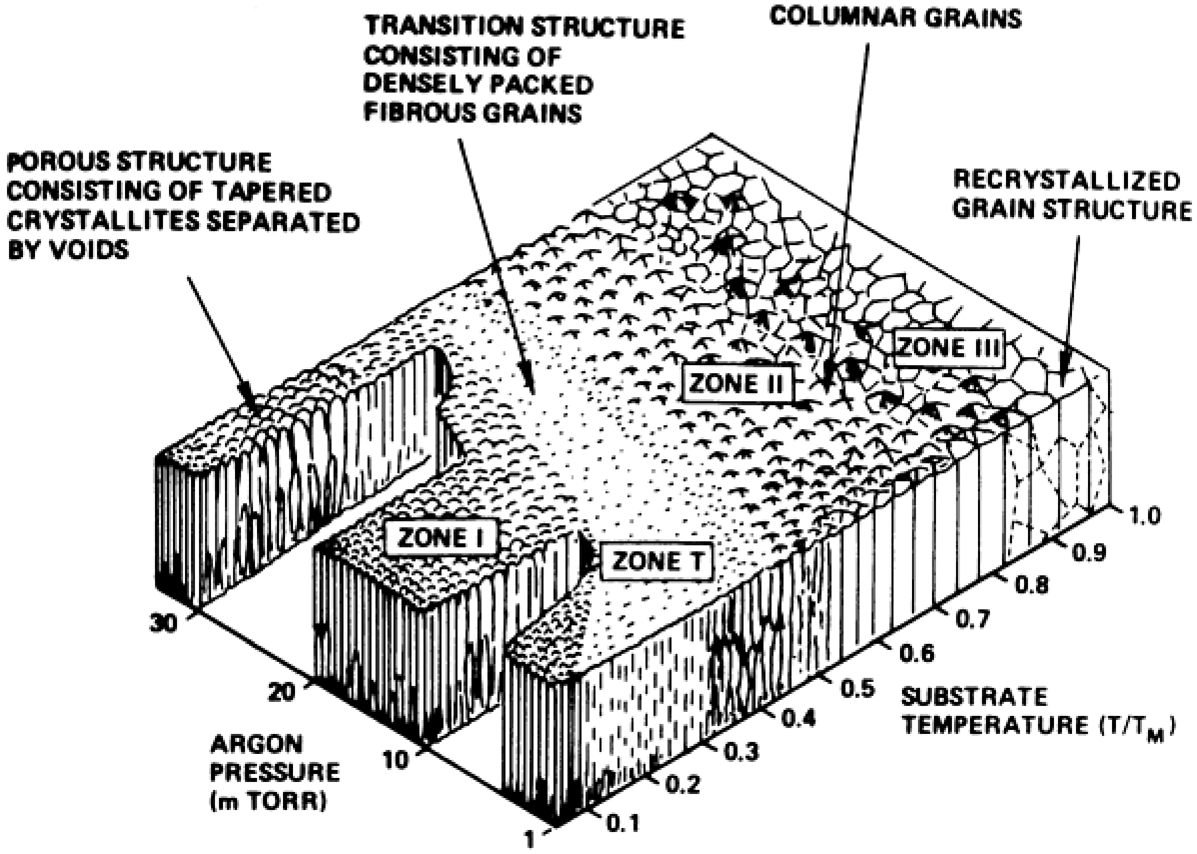

Fig. 4 Structure-zone model for sputter-deposited films (Ref 33)

The morphology of the depositing film is determined by the surface roughness and the surface mobility of the depositing atoms, with geometrical shadowing and surface diffusion competing to determine the morphology of the depositing material. When the surface is rough, the peaks receive the adatom flux from all directions, and if the surface mobility of the adatoms is low, the peaks grow faster than the valleys due to geometrical shadowing. This shadowing effect is exacerbated if the adatom flux is off-normal so that the valleys are in "deeper shadows" than when the flux is normal to the surface. Adsorbed gaseous species decrease the adatom surface mobility, while concurrent energetic particle bombardment can increase or decrease the surface mobility.

SZM Zone 1. In Zone 1 of the Movchan and Demchishin model and in the Thornton model, the adatom surface diffusion is insufficient to overcome the geometrical shadowing by the surface features. This results in open boundaries between the columns that are formed. This morphology produces a film with a high surface area and a film surface that has a "mossy" appearance. Higher gas pressures extend this zone to higher temperatures due to gas scattering, and surface mobilities decrease due to gas adsorption and collisions on the surface. The columnar morphology that develops has been computer modeled for depositing spheres (Ref 35). The columns can have different shapes such as round columns for aluminum (as shown in Fig. 5) and platelets for beryllium. The columns are not single grains. The columns can be microns in size, but the grain size can be less than 1000 Å (100 nm) or even amorphous within the columns. Because the columnar growth is strictly a function of surface geometry and adatom surface mobility, amorphous as well as crystalline materials show the columnar growth mode.

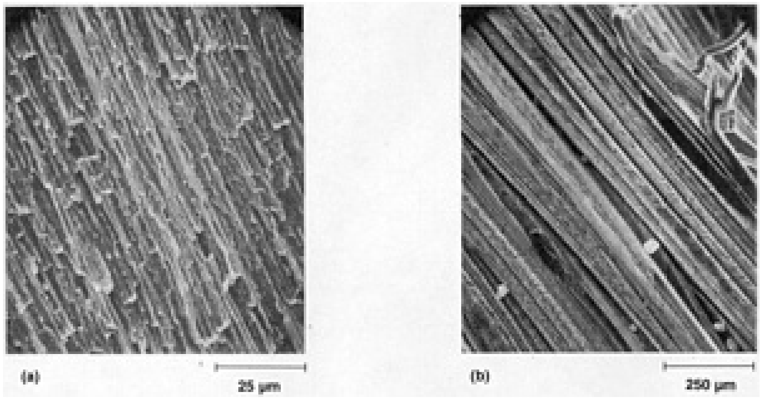

Fig. 5 Columnar morphologies of (a) sputter-deposited stainless steel and (b) vacuum-deposited aluminum films

The development of the columnar morphology begins very early in the film growth stage and generally becomes prominent after about 100 nm of thickness. For example, in the sputter deposition of MoS_2 solid film lubricants, the growth is such that, irrespective of the thickness of the deposited film, during wear, all the columns shear off at their base, leaving a surface layer of about 200 nm thickness. Another example is the vacuum deposition or sputter deposition of CoCr, a magnetic recording material that is very sensitive to film growth. The film consists of columnar grains with the hexagonal close-packed (hcp) *c*-axis, which is the easy magnetization direction, perpendicular to the substrate surface. TEM studies of the growth of sputter-deposited CoCr on NaCl at 100 °C (212 °F) show the following stages of columnar morphology development as a function of film thickness (Ref 36):

- Less than 5 nm: Poor crystal quality--substrate effects
- 10 nm: Good hcp with clear grain boundaries--grain size 2 to 8 nm, various crystallographic orientations
- 80 nm: Well-developed columnar grain orientation
- 100 nm: *c*-axis becomes perpendicular to growth direction, grain size 15 to 25 nm

Angle-of Incidence Effects. The columnar growth is exacerbated by oblique deposition flux orientations because now the valleys get no flux. The oblique angle of incidence can be due to a rough surface, a surface with features such as steps, scratches, or vias, or an off-normal deposition on a relatively smooth surface. For an off-normal incident flux, the columns do not grow normal to the surface but grow toward the adatom source with a change in column shape. The off-normal growth gives an even more open morphology with a lower density than that of the normal-deposited columnar morphology. The off-normal incidence can vary over the surface due to local surface morphologies such as that of a sintered material (see Fig. 2), scratches, via sidewalls, particulates, steps (Ref 37), etc. Figure 6 shows a "nodule" in a sputter-deposited chromium film that developed on particulate contamination on the substrate surface.

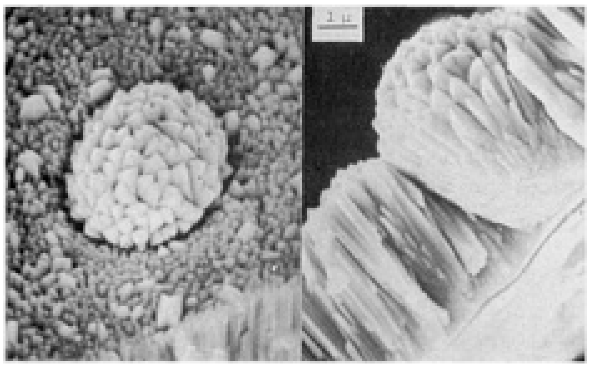

Fig. 6 Picture of a "nodule" in a thick sputter-deposited chromium film

Angle-of-incidence effects can be apparent when the substrate is moved in front of the vaporization source, as in the case of the use of a pallet fixture. In this case the angle of incidence starts very low, goes through normal incidence, then exits at a low angle of incidence. The initial growth at high angle can influence the growth at normal incidence.

SZM Zone T. In the zone model for sputter-deposited films, Thornton introduced the zone T. In zone T the coating has a fibrous morphology and is considered to be a transition from zone 1 to zone 2. The formation of the zone T material is due to the energetic bombardment from reflected high-energy neutrals from the sputtering target at low gas pressures. These energetic high-energy neutrals erode the peaks and fill in the valleys to some extent.

SZM Zone 2. In zone 2 the growth process is dominated by adatom surface diffusion. In this region, surface diffusion during deposition allows the densification of the intercolumnar boundaries. However, the basic columnar morphology remains. The grain size increases and the surface features tend to be faceted.

SZM Zone 3. In zone 3, bulk diffusion allows recrystallization, grain growth, and densification. Often the highly modified columnar morphology is detectable, with the columns being single crystals of material.

Surface Morphology Effects on Film Morphology. A columnar morphology will develop on a smooth substrate surface as it roughens with film thickness during growth. If the surface is not smooth, the variation in the angle of incidence and the general roughness will produce a more complex morphology and generally a less dense film than on a smooth surface. For example, a film grown on the surface shown in Fig. 2 will consist of a "microcolumnar" morphology of columns grown in films on each of the individual "boulders" and a "macrocolumnar morphology" resulting from shadowing effects by the boulders. The result will be a very complicated morphology that will depend on the surface morphology. If the surface has some morphology pattern, such as the patterned metallization on a smooth silicon wafer, the angle of incidence will vary with position on the surface, and differing film properties with position can be expected over the surface. For example, the film on the sidewall of a via can be expected to be less dense than the surface facing the vapor source directly (Ref 37). This effect is easily demonstrated using chemical etch rate tests. It is important to remember that the film growth can vary over the surface due to surface inhomogeneities, angle-of-incidence variation, and variations in the process variables.

Particulates on the surface present very local changes in surface morphology, and local features develop such as those shown in Fig. 6. These features are poorly bonded to the film and the surface and easily come out, leaving a pinhole in the film. The resulting pinhole will be larger than the initiating particulate. This "pinhole flaking" from film deposited on surfaces and fixtures in the deposition system can be a major source of particulate contamination in the deposition system. It is particularly evident when the surfaces and fixtures have been cleaned by glass bead blasting and glass chards have been embedded in the surfaces.

Residual Gas Effects on Film Growth. Residual gases in the deposition system can influence the growth, structure, morphology, and properties of the deposited films. The origins of these effects are poorly understood, but some portion can be attributed to changing the surface mobility of the adatom. In the case of reactive deposition, the residual gas partial pressure is high and has a major effect on the surface mobility and the development of columnar morphologies at high deposition temperatures.

Changes in Microstructure and Morphology during Deposition

Film microstructure, morphology, and properties can be influenced by processes that occur after adatom condensation but during film growth. The processes that change the film properties include:

- Mass transport, such as growth of the interfacial region and crystal defect formation and void coalescence
- Recrystallization and grain growth
- Phase precipitation and growth
- Chemical reaction of codeposited species

- Stress annealing

Many of these changes are time- and temperature-dependent and therefore depend on the thermal history of the film during deposition. This thermal history depends on the deposition temperature, condensation energy release, deposition rate, deposition time, thermal conductivity of the film and substrate materials, heat removal mechanisms, and so on.

Modification of Film Morphology. The film morphology and microstructure can be modified during growth. Methods of modifying the columnar growth include continuous or periodic:

- Bulk or surface heating by laser or radiant heating
- Codeposition of alloying species
- Reaction with ambient gaseous species
- Changing angle of incidence of adatom flux
- Mechanical disruption of the growth
- Changing deposition rate
- Changing gas pressure
- Bombardment by massive energetic particles

Heating. Increasing the deposition (substrate) temperature changes the film morphology, as shown in Fig. 4. Surface heating by a laser or by a radiant heat source can change the surface mobility of the adatom, thereby changing the growth mode of the deposited material.

Codeposition of Alloying, Impurity, or Dopant Species. Codeposition of alloying species can change the surface mobility and thus the film morphology. Alloying species that lower the melting point of the deposited material are particularly effective.

Impurities are small amounts of material incorporated into the structure unintentionally. The addition of small amounts of an impurity can have a significant influence on the microstructure and properties of the growing film. Small amounts of nitrogen in aluminum films change the electromigration properties. Residual gases present during deposition can affect film stress.

Dopants are small amounts of materials that are deliberately incorporated into the structure to affect microstructure or film properties. For example, the inclusion of gold, nickel, or cobalt (5 wt%) in sputter-deposited MoS_2 films for solid film lubricants produces "compact" films that are physically stronger to greater thicknesses than MoS_2 films sputtered without the additions.

Periodic Injection of Reactive Gas. Periodic reaction of the surface of the growing film with ambient species generates a new surface chemistry. This can force the adatoms to renucleate on the "foreign" surface, thereby changing the film morphology. For example, the periodic injection of oxygen during aluminum deposition suppresses the columnar growth morphology (Ref 38). The same effect is seen for nitrogen on beryllium films. The effect is similar to the "brightening agents" used in electrodeposition.

The angle of incidence of the adatom flux is important to the growth of the columnar morphology. The angle of incidence can be modified by proper fixturing and position control. Generally it is not possible to optimize the angle of incidence for all surface features.

Mechanical Disruption during Deposition. Mechanical disruption of the growing surface can be used to change the columnar morphology. Periodic mechanical brushing of a surface during deposition has been used to densify and eliminate porosity in sputter-deposited aluminum films and in CVD-tungsten deposits.

Changing Gas Pressure during Deposition. For gaseous environments, where vapor phase collision processes are important, changes in the ambient pressure change the scattering and thermalization of the adatom flux, and, in the case of sputter deposition, the flux and energy of reflected high-energy neutrals. These factors are important in determining the film morphology, stress (Ref 39), and other properties.

Concurrent Massive Energetic Particle Bombardment. In ion plating, the growing film is subjected to continuous or periodic energetic particle bombardment during deposition. When massive energetic particles bombard a surface, they release their energy rapidly by physical collisions with the near-surface atoms. These physical collisions cause a number of effects, some of which modify the columnar morphology of the growing film. These effects include:

- Sputtering and redeposition
- Input of "heat" into the surface and the near-surface region
- Increased or decreased surface mobility of the depositing atoms
- Generation of point defects that act as nucleation sites

Typically, a film sputtering rate of 20 to 40% of the deposition rate or an energy input of about 20 eV per depositing atom is necessary to completely disrupt the columnar growth process.

References cited in this section

2. C.A. Neugebauer, Condensation, Nucleation and Growth of Thin Films, Chapter 8, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, McGraw-Hill, 1970
3. J.E. Greene, Film Growth and Structure of PVD Deposits, Chapter 13, *Deposition Processes for Films and Coating,* 2nd ed., R. Bunshah, Ed., Noyes Publications, 1994
4. J.A. Thornton, High Rate Thick Film Growth, *Ann. Rev. Mater. Sci.,* Vol 7, 1977, p 239
5. J.A. Venables, Nucleation and Growth Processes in Thin Film Formation, *J. Vac. Sci. Technol. B,* Vol 4, 1986, p 870
6. A.G. Naumovets and Y.S. Vedula, Surface Diffusion of Adsorbates, *Surf. Sci. Rep.,* Vol 4 (No. 7/8), 1984, p 365
7. V.T. Binh, Ed., *Surface Mobilities on Solid Materials--Fundamental Concepts and Applications,* NATO ASI Series, Series B: Physics, Vol 86, Plenum Press, 1983
8. G. Somorjai, *Principles of Surface Chemistry,* Wiley, 1969
9. R.C. Sundahl, Relationship between Substrate Surface Chemistry and Adhesion of Thin Films, *J. Vac. Sci. Technol.,* Vol 9 (No. 1), 1971, p 181
10. R. Kelly, Bombardment-Induced Compositional Changes with Alloys, Oxides, Oxysalts and Halides, Chapter 4, *Handbook of Plasma Processing Technology Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 91
11. J.E. Griffith and G.P. Kochanski, The Atomic Structure of Vicinal Si(001) and Ge(001), *Crit. Rev. Solid State Mater. Sci.,* Vol 16 (No. 4), 1990, p 255
12. G.G. Paulson and A.L. Friedberg, Coalescence and Agglomeration of Gold Films, *Thin Solid Films,* Vol 5, 1970, p 47
13. D.M. Mattox, Surface Effects in Reactive Ion Plating, *Appl. Surf. Sci.,* Vol 48/49, 1991, p 540, and references therein
14. F.K. LeGoues, B.D. Silverman, and P.S. Ho, The Microstructure of Metal-Polyimide Interfaces, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2200
15. *Materials Characterization,* 9th ed., Vol 10, *Metals Handbook,* 1986, ASM International
16. H. Neddermeyer, STM Studies of Nucleation and the Initial Stages of Film Growth, *Crit. Rev. Solid State Mater. Sci.,* Vol 16 (No. 5), 1990, p 309
17. J.M. Guerra, Photon Tunneling Microscopy, *Appl. Optics,* Vol 29 (No. 26), 1990, p 3741
18. J.E. Greene, T. Motooka, J.-E. Sundgren, D. Lubbens, S. Gorbatkin, and S.A. Barnett, The Role of Ion/Surface Interactions and Photo-Induced Reactions during Film Growth from the Vapor Phase, *Nucl. Instrum. Methods Phys. Res. B,* Vol 27, 1987, p 226, and references therein

19. J.E. Greene, T. Motooka, J.-E. Sundgren, A. Rockett, S. Gorbatkin, D. Lubben, and S.A. Barnett, A Review of the Present Understanding of the Role of Ion/Surface Interactions and in Photo-Induced Reactions during Vapor Phase Crystal Growth, *J. Cryst. Growth,* Vol 79, 1986, p 19
20. A.M. Klumb, C.R. Aita, and N.C. Tran, Sputter Deposition of Gold in Rare-Gas (Ar,Ne)-O_2 Discharges, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1697, and references therein
21. P.H. Holloway, Gold/Chromium Metallization for Electronic Devices, *Solid State Technol.,* Vol 23 (No. 2), 1980, p 109, and references therein
22. S. Veprek and M. Heintz, The Mechanism of Plasma-Induced Deposition of Amorphous Silicon from Silane, *Plasma Chem. Plasma Process.,* Vol 10 (No. 1), 1990, p 3
23. J.A. Venables, G.D.T. Spiller, and M. Hanbucker, Nucleation and Growth of Thin Films, *Rep. Prog. Phys.,* Vol 47, 1984, p 399
24. M.A. Listvan, Determination of the Time Dependence of Domain Growth by Direct Observation of Small Metal Clusters, *Surf. Sci.,* Vol 173, 1986, p 294
25. C. Mailhoit and D.C. Smith, Strained-Layer Semiconductor Superlattices, *Crit. Rev. Solid State Mater. Sci.,* Vol 16 (No. 2), 1989, p 131
26. D.M. Mattox, Thin Film Adhesion and Adhesive Failure--A Perspective, *ASTM Proc. Conf. Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings,* STP 640, ASTM, 1978, p 54
27. D.M. Mattox, Thin Film Metallization of Oxides in Microelectronics, *Thin Solid Films,* Vol 18, 1973, p 173
28. E. Philofsky, Intermetallic Formation in Gold Aluminum Systems, *Solid State Electronics,* Vol 13 (No. 10), 1970, p 1391
29. F. Bordeaus and A.R. Yavari, Ultra Rapid Heating by Spontaneous Mixing Reactions in Metal-Metal Multilayer Composites, *J. Mater. Res.,* Vol 5 (No. 8), 1990, p 1656
30. R.W. Burger and L.J. Gerenser, Understanding the Formation and Properties of Metal/Polymer Interfaces via Spectroscopic Studies of Chemical Bonding, *Society of Vacuum Coaters Ann. Tech. Conf. Proc.,* SVC Publications, 1991, p 162
31. G.G. Fuller and K.L. Mittal, Ed., *Opportunities and Research Needs in Adhesion Science and Technology,* National Science Foundation Workshop on Adhesion, 14-16 Oct 1987 (Lake Tahoe, CA), Hitex Publication, 1988
32. B.A. Movchan and A.V. Demchishin, Study of the Structure and Properties of Thick Vacuum Condensates of Nickel, Titanium, Tungsten, Aluminum Oxide and Zirconium Oxide, *Phys. Met. Metallogr. (USSR),* Vol 28, 1969, p 83
33. J.A. Thornton, High Rate Thick Film Growth, *Ann. Rev. Mater. Sci.,* Vol 7, 1977, p 239
34. R. Messier, A.P. Giri, and R.A. Roy, Revised Structure Zone Model for Thin Film Physical Structure, *J. Vac. Sci. Technol. A,* Vol 2, 1984, p 500
35. R.N. Tait, T. Smy, and M.J. Brett, Modeling and Characterization of Columnar Growth in Evaporated Films, *Thin Solid Films,* Vol 226 (No. 2), 1993, p 196
36. M. Futamoto, Y. Honds, H. Kakibayashi, T. Shimotsu, and Y. Uesaka, Microstructure of CoCr Thin Films Prepared by Sputtering, *Jpn. J. Appl. Phys.,* 1985, p L460
37. R.N. Tait, T. Smy, and M.J. Brett, Simulation and Measurement of Density Variation in Mo Films Sputter Deposited over Oxide Steps, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1593
38. R.W. Springer and D.S. Catlett, Structure and Mechanical Properties of Al/Al_xO_y Vacuum Deposited Laminates, *Thin Solid Films,* Vol 54, 1978, p 197
39. R.E. Cuthrell, D.M. Mattox, C.R. Peeples, P.L. Dreike, and K.P. Lamppa, Residual Stress, Stress Anisotropy, Stress Control and Resistivity in Post Cathode Magnetron Sputter-Deposited Molybdenum Films, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2914

Reactive Deposition

Reactive deposition is the formation of a film of a compound, either by codeposition and reaction of the constituents or by the reaction of a deposited species with the ambient gaseous environment. If the reacting species form a volatile compound, etching results. If the reaction results in a nonvolatile species, a compound film is formed (Ref 40).

Codeposition of reactive species does not necessarily mean that they will chemically react to form a compound. For example, a mixture of titanium and carbon may not have any TiC, or it may be partially TiC and the rest an unreacted mixture of titanium and carbon, substoichiometric TiC_{1-x}, or TiC with excess titanium or carbon, each of which will have different properties. Generally, for low-temperature deposition, the best situation for reactive deposition is where one of the reacting species is condensable and the other is gaseous (e.g., titanium plus nitrogen). If both are condensable (e.g., titanium plus carbon), the best deposition condition is to have a high substrate temperature to promote reaction or use postdeposition heat treatment to promote reaction. Reactively deposited films of oxides and nitrides are commonly used in the optics, electronics, decorative, and mechanical applications, with TiN being one of the more common film materials.

There are a number of techniques for performing reactive atomistic film deposition. The simplest way is to thermally evaporate the material in a partial pressure of a reactive gas in the process called *reactive evaporation* (see the article "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume). This generally gives poor-quality films because the materials are not completely reacted and the high gas pressures necessary for reaction result in gas phase collision and vapor phase nucleation, giving a low-density deposit. Better-quality films are obtained by promoting the chemical reaction by some means, such as activating the reactive gas or using concurrent energetic particle bombardment to promote the chemical reaction (Ref 13).

Reactive Species

Molecular Species. Typically gaseous reactive species are in the molecular form (i.e., N_2, O_2, H_2, etc.). The molecular species is less chemically reactive than the atomic species of the gas.

Activated Reactive Species. The gaseous reactive species can be "activated" to make them more chemically reactive and/or more readily adsorbed on surfaces (Ref 13). The reactivity of the species can be increased by adding internal energy to form "excited species," by fragmenting the species to form uncharged "radicals," such as O, N, or F, by forming ions, which are charged species such as O^+, N_2^+, or N^+, or by forming a new volatile reactive species, such as ozone (O_3) from O_2 + O or Si_2H_6 from SiH_4. Activation is most often done in a direct current, radio frequency, or microwave plasma, in a plasma arc, or by radiation adsorption (e.g., "photoexcitation") from a source such as a mercury vapor lamp or an excimer laser. Such activation is done in reactive sputter deposition, reactive ion plating, PECVD, and activated reactive evaporation. Activation of the gaseous species can also be done using other means, such as the hot filament decomposition of NH_4, F_2, and H_2.

A plasma provides a very complicated chemical environment that can give reactive deposition processes that are not normally expected. For example, the sputter deposition of gold on oxide surfaces in an oxygen-containing plasma gives rise to very adherent gold films. It has been shown that the deposition of gold in an oxygen plasma gives rise to Au-O bonding. This may be due to the formation of activated oxygen species in the plasma or the formation of a more readily adsorbed reactive species (i.e., O_3) (Ref 41, 42).

Reaction Probability

In reactive deposition, the depositing material is continually being buried and the time available for reaction is limited. The probability of chemical reaction of the growing film surface depends on a number of factors, including:

- Temperature of the surface
- Chemical reactivity of the species
- Extent of prior reaction on the surface (e.g., whether the surface composition is $TiN_{0.1}$ or $TiN_{0.95}$)
- Relative fluxes of condensing species and incident gaseous species (i.e., the "availability" of the reactive species)
- Residence time (adsorption) of reactive species on the surface
- Radiation by electrons capable of stimulating chemical reactions on the surface
- Radiation by photons capable of stimulating photochemical reactions
- Energy of the incident reactive species
- Concurrent bombardment by energetic species not involved in the reaction (e.g., concurrent argon ion bombardment during titanium plus nitrogen deposition)

In many cases, surface reaction occurs first at active sites on a surface providing a nonhomogeneous growth mode. The extent to which this occurs in reactive deposition is not known.

Adsorption on a Surface. For an ambient pressure of 10^{-3} torr (0.13 Pa) and 25 °C (77 °F), gaseous particles will impinge on a surface at about 10^3 monolayers/s, compared to a typical atomistic deposition rate of 10 or so monolayers per second. The impinging species may be reflected with little residence time, or they may be adsorbed with an appreciable residence time (Ref 42). Adsorbed species will be available for reaction for a longer period of time than the reflected species. The adsorption probability and adsorbed film thickness will depend on a number of factors, such as the impinging species, nature of the surface, adsorption sites, and so on. For instance, it has been shown that atomic oxygen on silicon will adsorb with a higher probability and to a greater thickness than molecular oxygen and that ozone (O_3) is strongly adsorbed on Al_2O_3, whereas O_2 is not (Ref 41). It has also been shown that the surface stoichiometry affects the adsorption. For example, stoichiometric TiO_2 surfaces do not adsorb oxygen but substoichiometric surfaces do, with the amount depending on the degree of substoichiometry. In plasma CVD of silicon from silane (SiH_4), it has been shown that the disilane species formed in a plasma has a high adsorption probability and is important in the deposition of the silicon at low temperatures (Ref 22). Oxygen molecules will react with a pure aluminum film, but nitrogen molecules will not react. The probability that the oxygen molecules will react with the aluminum decreases as the aluminum reacts with the oxygen molecules and the oxygen coverage increases.

Reaction Extent. The extent of the reaction before the surface is buried also depends on the factors listed above. For example, in the case of atomic oxygen on silicon surfaces, the reaction probability will decrease monotonically with coverage through several monolayer coverages. If the material can form a series of compounds (e.g., TiN, T_2N) the probability of reaction is further decreased as the extent of reaction increases, making it more difficult to form the higher compound (i.e., TiN will be more difficult to form than the Ti_2N).

Reactant Availability. The degree of reaction of codepositing species depends on the availability of the reactive species; therefore, the relative fluxes of the reactants are important. This gives rise to the "loading factor," which means that there is a relationship between the surface area for reaction (deposited film area) and the amount of reaction gas available.

Stoichiometry. Many materials form a series of stable compounds that have different crystal structures. For example, titanium and oxygen form TiO, Ti_2O_3, TiO_2 (brookite), TiO_2 (anatase), and TiO_2 (rutile). By controlling the availability of the reactive gas, the stoichiometry of the resulting film material can be controlled. The stoichiometry of the material can be changed during the deposition by changing the reactant gas availability.

Reactively Graded Interface. The composition of the reactively deposited material can be controlled by controlling the availability of the reactive species. This allows the gradation of composition from an elemental phase to the compound phase. For example, in the deposition of titanium nitride TiN, the deposition may start by having no nitrogen available, so as to deposit pure titanium, and then increase the nitrogen availability so as to grade the composition to TiN. This technique is often helpful in obtaining good adhesion of compound films to surfaces. Another example is the deposition of a nitride on an oxide where the deposited material is graded from an oxide through an oxynitride composition to the nitride by controlling the availability of both oxygen and nitrogen.

Free electrons can enhance chemical reactions in the vapor phase and on a surface. Electron energies of about 50 eV are the most effective. The effect of electrons on reactive deposition is relatively unknown.

Photon radiation can enhance chemical reactions by exciting the reacting species (photoexcitation), thereby providing internal energy to aid in chemical reactions (Ref 18).

Energetic Inert Particle Bombardment Effects. The reactivity between codeposited or adsorbed species can be increased by using concurrent energetic particle bombardment by a reactive species or with an inert species that does not enter into the reaction. Concurrent energetic particle bombardment during reactive film deposition has been shown to have a substantial effect on the composition, structure, and properties of compound films (Ref 43, 44). In general, the bombardment:

- Introduces heat into the surface
- Generates defects that can act as adsorption and reaction sites
- Dissociates adsorbed molecular species
- Produces secondary electrons that can assist chemical reactions

- Selectively desorbs or sputters unreacted or weakly bound species

This process has been termed "bombardment-enhanced chemical reaction" (Ref 44). It is of interest to note that Coburn and Winters attribute the major portion of bombardment-enhanced etching of silicon with fluorine to the development of the volatile high-fluoride compound (SiF_4) (i.e., more complete reaction) under bombardment conditions. Periodic bombardment of a depositing species by energetic reactive species can accomplish many of the same effects (Ref 45). For example, oxide films can be formed by depositing several monolayers of aluminum, then alternately bombarding the film with energetic oxygen ions and depositing more aluminum to form an aluminum oxide film.

Beam Deposition Using Activated Species. Ions of an activated species can be produced in a separate source, accelerated, and then used to bombard the depositing material in a vacuum environment to give "reactive ion beam" deposition. For particle energies greater than a few tens of electron volts, the energetic particle will physically penetrate into the surface, thereby increasing its "residence time." For example, it has been shown that for N_2^+, ions having an energy of 500 eV impinging on a depositing aluminum film, all of the nitrogen will react with the aluminum up to a N:Al deposition ratio of 1:1 (Ref 46).

Deposition of Composite Materials

Composite materials are materials that consist of several phases in the form of either layers or phases dispersed in a matrix.

Layered Composites. In many applications, multilayer film structures are used. One of the most common uses is to produce an adhesion layer next to the substrate with the functional layer(s) on top, such as the Ti-Au metallization on oxides. In some cases several layers are used. Examples are Ti-Pd-Au (Ref 47, 48), where the palladium inhibits corrosion, and the Ti-Pd-Cu-Au metallization, where the copper acts as an economical electrical conductor and the gold is present to prevent surface reaction.

Dispersed Phase Composites. Dispersed phase materials can be formed by codepositing insoluble materials. If the temperature is high enough for mass transport, the phases will separate, resulting in a two-phase material. Composite materials can also be formed by codepositing materials where the phase formed by reaction is dispersed in a matrix of the unreacted material (Ref 49). For example, a reactive material such as titanium can be codeposited with a less reactive material such as nickel in a reactive environment of oxygen or carbon to give dispersed phases of oxides (TiO_2) or carbides (TiC) in nickel. Composite films can be formed by a minor constituent reacting with the major constituent to form an intermetallic phase that is dispersed in the major phase. For example, in the Al-2Cu metallization, on heating, the Al_2Cu phase will precipitate to form a dispersion in the aluminum. This precipitate phase then acts as segregation sites for voids formed due to film stress. In cases where two or more materials are depositing at the same time on nonreactive surfaces, there may be changes in composition in the early stages of nucleation due to differing segregation effects.

The presence of second-phase materials in a film can lead to galvanic corrosion problems when an electrolyte is present. For example, Al-Al_2Cu composite films have been found to be more susceptible to intergranular and pitting corrosion than pure aluminum films (Ref 50). The Al_2Cu acts as a cathode (-0.73 volts) while the aluminum acts as the anode (-0.85 volts). The corrosion effects become more important with increasing copper concentration, so the copper in the Al-Cu metallization is limited to 2 to 4% when a homogeneous distribution of the Al-Cu particles is desirable.

Composite materials of metal particles in a polymer matrix can be formed by deposition of the metallic phase during plasma polymerization. Such a composite film has been shown to have a better wear durability than the polymer film alone (Ref 51) and to have interesting optical properties.

Deposition of Intermetallic Materials

Intermetallic compounds are formed from relatively electropositive and electronegative metals that chemically bond to form compounds with a specific composition and crystalline structure. Intermetallic films are often formed by depositing the film material on a hot surface so that the adatoms diffuse and react with the surface material, converting it into a silicide, aluminide, or whatever. Very corrosion-resistant intermetallic materials can be formed by codeposition processes at high temperatures. These include the very chemically stable compounds Mo_5Ru_3 and W_3Ru_2 (Ref 52) and $ZrPt_3$ and $ZrIr_3$, which are d-orbital bonded intermetallic compounds (Ref 53).

"Amphoteric" metals are those that may gain or lose electrons, that is, act as either an acid (electron donor) or a base (electron acceptor) in chemical reactions.

References cited in this section

13. D.M. Mattox, Surface Effects in Reactive Ion Plating, *Appl. Surf. Sci.,* Vol 48/49, 1991, p 540, and references therein
18. J.E. Greene, T. Motooka, J.-E. Sundgren, D. Lubbens, S. Gorbatkin, and S.A. Barnett, The Role of Ion/Surface Interactions and Photo-Induced Reactions during Film Growth from the Vapor Phase, *Nucl. Instrum. Methods Phys. Res. B,* Vol 27, 1987, p 226, and references therein
22. S. Veprek and M. Heintz, The Mechanism of Plasma-Induced Deposition of Amorphous Silicon from Silane, *Plasma Chem. Plasma Process.,* Vol 10 (No. 1), 1990, p 3
40. W.D. Westwood, Reactive Sputter Deposition, Chapter 9, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Noyes Publications, 1990, p 233
41. A.O. Klimovskii, A.V. Bavin, V.S. Tkalich, and A.A. Lisachenko, Interaction of Ozone with Gamma-Al_2O_3 Surface, *React. Kinet. Catal. Lett.,* Vol 23 (No. 1-2), 1983, p 95-98 (trans. from Russian)
42. P.A. Dowben, A Review of the Halogen Adsorption Process on Metal Surfaces, *Crit. Rev. Solid State Mater. Sci.,* Vol 13 (No. 3), 1987, p 191
43. J.E. Greene and S.A. Barnett, Ion-Surface Interactions during Vapor Phase Crystal Growth by Sputtering, MBE and Plasma-Enhanced CVD: Applications to Semiconductors: Critical Review, *J. Vac. Sci. Technol.,* Vol 21 (No. 2), 1982, p 285
44. G.A. Lincoln, M.W. Geis, S. Pang, and N. Efremow, Large Area Ion Beam Assisted Etching of GaAs with High Etch Rates and Controlled Anisotropy, *J. Vac. Sci. Technol. B,* Vol 1, 1983, p 1043
45. S. Schiller, U. Heisig, and K. Goedicke, Alternating Ion Plating--A Method of High Rate Ion Vapor Deposition, *J. Vac. Sci. Technol.,* Vol 12 (No. 4), 1975, p 858
46. J.M.E. Harper, J.J. Cuomo, and H.T.G. Hentzell, Quantitative Ion Beam Process for the Deposition of Compound Thin Films, *Appl. Phys. Lett.,* Vol 43, 1983, p 547
47. J.D. Speight and M.J. Bill, Observations on the Aging of Ti-Based Metallizations in Air/HCl Environments, *Thin Solid Films,* Vol 15, 1973, p 325
48. D.J. Sharp, Corrosion Inhibition in Sputter-Deposited Thin-Film Systems using an Intermediary Layer of Palladium, *J. Vac. Sci. Technol.,* Vol 16 (No. 2), 1979, p 204
49. B.V. Movchan, Composite Materials Deposited from the Vapour Phase under Vacuum, *Surf. Coat. Technol.,* Vol 46 (No. 1), 1991, p 1
50. S. Thomas and H.M. Berg, Micro-Corrosion of Al-Cu Bonding Pads, *IEEE/IRPS,* 1985, p 153
51. H. Biedwermann and L. Martinu, Plasma Polymer-Metal Composite Films, Chapter 4, *Plasma Deposition, Treatment and Etching of Polymers,* R. d'Agostino, Ed., Academic Press, 1990
52. L.R. Testardi, W.A. Royer, D.D. Bacon, A.R. Storm, and J.H. Wernick, Exceptional Hardness and Corrosion Resistance of Mo_5Ru_3 and W_3Ru_2 Films, *Metall. Trans.,* Vol 4, 1973, p 2195
53. L. Brewer, A Most Striking Confirmation of the Engel Metallic Correlation, *Acta Metall.,* Vol 15, 1967, p 553

Postdeposition Processing

Postdeposition heating of films can be done in a furnace, by flash lamp heating such as is used in RTP techniques, or by laser irradiation. In the extreme, the heating can be used to melt and "reflow" the film to planarize the surface.

Postdeposition heating can create film stresses due to differences in the coefficient of thermal expansion between the film and substrate and between different phases in the film. These stresses can result in plastic deformation of the film or substrate material, create stress-related changes in the film properties such as voids (Ref 54), or create interfacial fractures.

Diffusion. Heating is used to promote mass transport so as to anneal the residual stress and defect structure in deposited films. For example, it has been shown that glass films exhibit strain points far lower than those of the bulk material (Ref 55), that grain growth can take place in sputter-deposited copper films at very low temperatures (Ref 56), and that stress relief in TiB_2 films occurs far below the annealing temperature of the bulk material. Postdeposition heating has been shown to modify the structure and electrical properties of deposited SiO_2 films. These effects are probably due to the residual film stress and high defect concentrations in the deposited films.

Postdeposition heat treatments can be used to induce grain growth or phase changes, but care must be taken because the changes can result in increased film stress or fracture. The substrate material and structure can influence the kinetics of the phase change by influencing the nucleation of the new phase. Postdeposition heating rarely allows densification of columnar films, because the surfaces of the columnar structure react with the ambient and the surface layers that are formed prevent the diffusion needed for densification. Typically, heating during deposition or in situ heating in the deposition chamber is more effective in densifying deposits than ex situ heating.

Agglomeration. Postdeposition heating can cause the film structure to agglomerate into islands generating porosity and changing the optical and electrical properties of the films (Ref 57). Agglomeration also occurs by grain boundary grooving of the film material (Ref 58).

Heating with Reaction and Diffusion. Postdeposition heat treatments are used to promote reaction between unreacted codeposited materials and to promote reaction of the deposited material with an ambient gas. For instance, it is common practice to heat deposited high-temperature oxide superconductor films in an oxygen atmosphere to improve their performance, and transparent, electrically conductive indium-tin-oxide films are heated in "forming gas" to increase their electrical conductivity. Heating can also cause the formation of internal dispersed phases (e.g., Ni-B, Cu-Al) to give dispersion strengthening.

Heating is used to alloy the deposited material with the substrate surface. Postdeposition diffusion and reaction can form a more extensive interfacial region and induce compound formation in semiconductor metallization. Postdeposition heating and diffusion can be used to completely convert the deposited material to interfacial material. For example, a platinum film on silicon can be heated to form a platinum silicide layer. Postdeposition interdiffusion can result in the failure of metallized semiconductor devices by diffusion and shorting of the junctions.

Alloying and reaction between films and substrates can be limited by:

- Deposition of refractory metal diffusion barriers such as tungsten or W-Ti alloy
- Deposition of electrically conductive diffusion barrier layers of compounds such as carbide (e.g., TiC), nitrides (e.g., TiN), or silicides (Ref 59)
- Formation of compounds that act as diffusion barriers when the film and substrate materials react
- Doping of the film or substrate materials with a material that retards mass-transport (e.g., rare earth metals in aluminum)
- Rapidly heating and cooling the surface region

Melting. The XeCl (308 nm) excimer laser has been used to melt and planarize thin films of gold, copper, and aluminum on silicon devices with submicron features.

Postdeposition ion bombardment using reactive or nonreactive bombarding species can be used to change the composition or properties of the film material or to increase the interfacial adhesion by interfacial mixing or "stitching" (Ref 60).

To "recoil mix" or "stitch" an interface, the films must be rather thin (<100 nm) and the ion energies are selected to give the peak range just beyond the interface. In recoil mixing at an interface, if the materials involved are miscible, the ion mixing results in interfacial reaction and diffusion. If the materials are not miscible, the interfacial region is not mixed but the adhesion is increased. Generally adhesion improvement is dose dependent, with the best result being for doses of 10^{15} to 10^{17} ions/cm^2, while excessive bombardment induces interfacial voids. Part of the observed increase in adhesion may be due to the elimination of interfacial voids by "forward sputtering."

Deformation. In the case of films of soft materials, the film structure can be densified and porosity closed by postdeposition burnishing (Ref 61) or shot peening of the surface. For example, the MCrAl (where M can be a metal of various types) films deposited on turbine blades are routinely shot peened to increase their corrosion resistance.

Chemical and Electrochemical Treatments. Deposited films may be subjected to various chemical and electrochemical treatments to convert all or part of the film to another material. For example, aluminum films can be anodized (Ref 62) or chemically converted by a chromate conversion process for increased corrosion resistance.

Pore Filling. Porosity of the deposited films is often a limiting factor in their use. Various techniques may be used to fill the pores in the film. For example, electrophoretic deposition of polymer particles has been used to selectively fill the pores in a dielectric film on a conductive substrate (Ref 62), and corrosion of the substrate through the pores has been used to plug the pores with corrosion products.

Topcoats are often applied to deposited films to increase abrasion and corrosion resistance. An example of a fluid topcoat is the dip-coated polysiloxane coating used on aluminum-coated polycarbonate automotive headlight reflectors.

Fluid Topcoats. Often deposited coatings are overcoated with a thin (<1μm) protective film of highly cross-linked polymeric material. Many topcoat materials require heat for curing. The heating is necessary to remove the solvents and cross-link the polymeric materials. Due to environmental concerns this type of topcoat material is being modified to give a higher "solids content" (i.e., less solvent will be released into the environment). Another class of polymeric topcoat materials are the organo-siloxanes, which consist of an organic host polymer containing siloxane coupling agents and colloidal silica. The coatings can be applied by spraying, spinning, or dip coating and can be cross-linked by UV radiation or electron irradiation (e.g., UV-curable acrylics).

Plasma-Deposited Topcoats. Some topcoat material can be deposited by plasma polymerization. For example, plasma polymerization of polysiloxane is used to form organo-silicon coatings, which are sometimes heat treated in oxygen to increase the Si-O content of the films. The plasma-polymerized organo-silicon films have excellent surface coverage ability and are hydrophobic, hard, and relatively pinhole-free. The films are being used as clear protective topcoats on optical reflective films. Plasma-deposited organo-carbon films are used as conductive films.

References cited in this section

54. F.G. Yost, D.E. Amos, and A.D. Romig, Stress Driven Diffusion Voiding of Aluminum Conductor Lines, *Proc. IEEE/IRPS '89,* 1989, p 193
55. G.J. Kominiak and D.M. Mattox, Physical Properties of Thick Sputter-Deposited Glass Films, *J. Electrochem. Soc.,* Vol 120, 1973, p 1535
56. J.W. Patten, E.D. McClanahan, and J.W. Johnson, Room-Temperature Recrystallization in Thick Bias-Sputtered Copper Deposits, *J. Appl. Phys.,* Vol 42, 1971, p 4371
57. R.R. Zito, W.S. Bickel, and W.M. Bailey, The Physical and Optical Properties of Agglomerated Gold Films, *Thin Solid Films,* Vol 114, 1984, p 241
58. Y.-K. Chao, S.K. Kurinec, I. Toor, H. Shillingford, and P.H. Holloway, Porosity in Thin Ni/Au Metallization Layers, *J. Vac. Sci. Technol. A,* Vol 5, 1987, p 337
59. M.-A. Nicolet, Diffusion Barriers in Thin Films, *Thin Solid Films,* Vol 52, 1978, p 415
60. J.E.E. Baglin, Ion Beam Effects on Thin Film Adhesion, Chapter 15, *Ion Beam Modification of Insulators,* P. Mazzoldi and G. Arnold, Ed., Elsevier, 1987
61. A.T. English and P.A. Turner, Use of Vibratory Finishing for Occlusion of Pinholes and for Surface Smoothing in Thin Films on Ceramic Substrates, *Plating,* Sept 1972, p 851
62. J.K.G. Panitz, D.J. Sharp, and F.E. Martinez, Electrophoretic Coatings for Capacitor Applications, *Plat. Surf. Finish,* Vol 75, 1988, p 23

Growth-Related Film Properties

Films deposited by PVD processes invariably have properties that differ from those of the bulk materials (Ref 63). For this reason the specific film properties should be determined for films made with controlled and reproducible materials and processes. The columnar morphology and the residual film stress developed during film growth are important to a number of the film properties and the stability of the deposited film structure, including:

- *Density*--mechanical deformation, electrical resistivity
- *Porosity*--corrosion rate, etch rate
- *Surface area and morphology*--contaminant adsorption, optical reflectivity, electrical resistivity

Residual Film Stress

Invariably, atomistically deposited films have a residual film stress that can be tensile or compressive and that can approach the yield or fracture strength of the materials involved. Generally, vacuum-deposited films and sputter-deposited films prepared at a high sputtering gas pressure have a tensile stress that can be anisotropic with off-normal angle-of-incidence depositions. Compressive stresses are generally encountered in films deposited under conditions where there is concurrent high-energy particle bombardment, such as in ion plating and in low-pressure sputtering where high-energy reflected neutrals from the target bombard the growing film (Ref 39). Figure 7 shows the residual film stresses generated in one direction in the film during postcathode magnetron sputter deposition of molybdenum. The film stress is anisotropic and is related to the configuration of the sputtering cathode. At low pressures, where there is bombardment by high-energy reflected neutrals, the stress is compressive. At higher pressures the stress is tensile, and at even higher pressures, where the morphology is more columnar and the film density is lower, the stress decreases. The origin of these stresses is poorly understood, though several phenomenological models have been proposed (Ref 64).

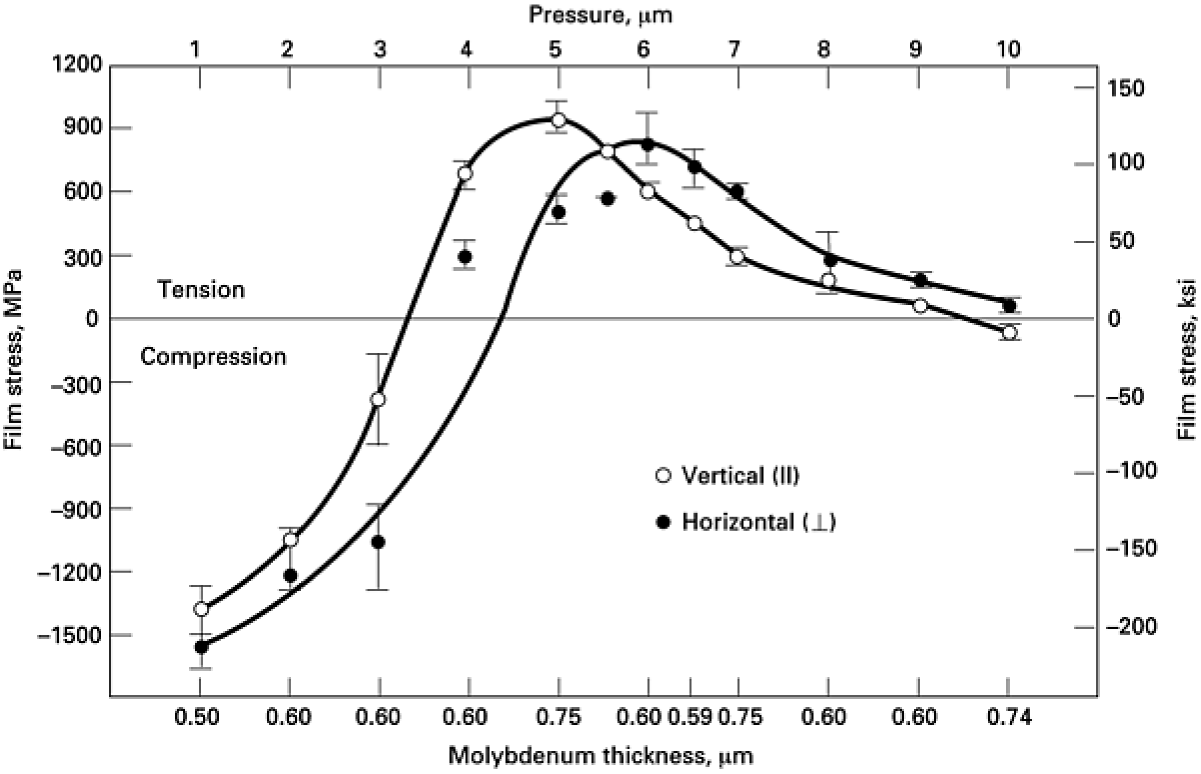

Fig. 7 Film stress as a function of gas pressure in postcathode magnetron sputter-deposited molybdenum films (Ref 39)

Tensile stresses can be developed when the growth mechanism does not allow the depositing atoms to attain their lowest energy positions. The Klockholm-Berry model is based on a constrained shrinkage of deposited material resulting in lattice parameters greater than normal. The grain boundary model attributes the stress to the development of grain boundary material. It has been proposed that the coalescence of lattice defects into "microvoids" causes the tensile stresses. It has been shown that the mechanical properties of the grain material are important to the resulting stresses and that impurity incorporation and reaction with the depositing film material can also be important factors in the stress generation. Tensile stresses can also be generated by phase changes and recrystallization, which result in volumetric shrinkage.

For high-temperature deposition conditions, the differences in the coefficients of thermal expansion of the substrate and film material can produce thermal (shrinkage) stresses that put the film in tension or in compression, depending on which material has the greater thermal expansion.

Film stress can change with film thickness. Stress gradients can exist in the deposited film due to the growth mode and differing thermal histories of the various layers of the film. These stresses can give the outermost layer of the film a tensile stress compared to the rest of the film. This film stress profile leads to "curling" of a film when it is detached from the substrate. If the adhesion failure is such that some of the substrate material remains attached to the film, the film can curl because of the constrained surface. Local stresses can be found in films where there is nonhomogeneous growth, such as over steps and defects in the substrate.

On a thin substrate that is in the form of a thin, long beam, the sum of all these stresses in the film causes the "beam" to bend. From the degree of bending and the material properties, the film stress can be calculated. The force on a substrate due to the film stress is a function of the film thickness. Film stress can also be determined by x-ray diffraction measurements of lattice strain, but this does not fully take into account boundary effects. The film morphology affects the stress buildup with a columnar morphology resulting in a low total stress.

Film stress and the resulting force and shear stresses are important factors in the adhesion and stability of films. High isotropic compressive film stresses produce "blistering" of the film from the surface in "worm-track" patterns. High isotropic tensile film stresses produce microcracking of the film. The cracks tend to meet orthogonally and form polygon "islands" or "chips" such as are seen in dried "mudflats" (Ref 65). Because the interface is constrained, the mudflat islands will tend to curl at the edges. If the compressive stresses are highly anisotropic, the "worm-track" pattern changes to line-shape blisters. If the tensile stresses are highly anisotropic, the "mud-flatting" pattern changes to linear cracks. If the adhesion between the film and the substrate is high, the stress can cause fracture in the film or substrate material. The film buckling or cracking can be time-dependent and can also depend on the moisture available in the ambient environment. This time/environment-related failure is called *static fatigue* (Ref 66). Fractures and fracture patterns in films can be detected by the use of fluorescent tracers. Generally, residual film stress should be minimized to prevent failure.

Modification of Film Stress. There are several methods of modifying the mechanical stresses developed in films during growth:

- Limiting the thickness of the stressed film
- Using concurrent energetic particle bombardment during deposition to maintain a near-zero-stress condition (Ref 67)
- Periodically alternating the concurrent bombardment conditions (Ref 39)
- Periodically adding alloying or reacting materials
- Mixing materials
- Deliberately generating an open columnar morphology that cannot transmit a stress

Limiting the film thickness is generally the most easily accomplished approach. As a "rule-of-thumb," the thickness of high-modulus materials such as chromium and tungsten should be limited to less than 50 nm to avoid excessive residual stress. If the film thickness is to exceed that value, some technique for stress monitoring and control should be developed.

One technique to control film stress is to use concurrent ion bombardment during deposition to create compressive stress to offset the tensile stress (Ref 67). By carefully controlling the bombardment parameters it is possible to find a zero-stress condition. Unfortunately this condition is usually very dependent on the process parameters and the proper conditions are hard to control and maintain. A more flexible technique is to alternately deposit layers having tensile and compressive stresses that offset each other (Ref 39). This can be done by varying the concurrent bombardment from the reflected high-energy neutrals in low-pressure sputter deposition, bombardment from a plasma or bombardment from an ion gun.

Adhesion

Adhesion is a fundamental requirement of almost all film systems. It is determined by the nature of the stresses that appear at the interface and the energy needed to propagate a fracture and/or cause deformation. Film adhesion is intimately connected with the film and substrate properties as well as the properties of the interfacial (interphase) materials (Ref 26). Good adhesion is promoted by high fracture toughness of the interface and the near-surface material, presence of fracture blunting and deflecting features, low stresses and stress gradients, absence of fracture-initiating features, and an absence of operational adhesion-degradation mechanisms.

Poor adhesion can be attributable to low degree of chemical bonding, poor interfacial contact, low fracture toughness (brittle materials, flaws), high residual film stresses, fracture-initiating features, and/or operational adhesion-degradation mechanisms. Poor adhesion may be localized so as to give local failure (i.e., pinholes). In many systems where direct adhesion is difficult to attain, an intermediate material is introduced onto the substrate surface to bond to both the substrate and the film material. Substrate surface roughness can improve or degrade the adhesion, depending on the ability of the deposition technique to fill in the surface roughness and the film morphology generated. The generation of a good interface is also important to other properties such as thermal transport and electrical contact resistance. The lack or loss of adhesion is often called *deadhesion*.

Modeling of Adhesion. The principal models used for explaining adhesion are:

- Surface energy reduction, wettability, and spreading--commonly used with polymer bonding
- Interfacial fracture and deformation--used in inorganic systems (Ref 26)

In the latter case the fracture toughness or fracture energy is the relevant physical parameter. This depends on the stress at the interface and the properties of the interface, the "interphase material," and the nearby material of the film and substrate. The failure modes for ductile materials will be quite different from those of brittle materials.

Causes of Deadhesion. The stresses that appear at the interface and can cause adhesion failure (deadhesion) include:

- *Mechanical*--tensile, shear, compressive, shock, fatigue
- *Chemical and electrochemical*--corrosion, solution
- *Thermal*/*time*--diffusion, reaction

These stresses can cause loss of adhesion at or near the interface by:

- Fracture and deformation at the interface--mechanical
- Generation or propagation of flaws in the interface region--mechanical, static fatigue
- Corrosion at the interface--chemical
- Dissolution of interfacial material--chemical
- Diffusion of material away from the interface--thermal (Ref 21)
- Diffusion of species to the interface--thermal
- Phase change of material at the interface giving flaws and stress--thermal, diffusion

These stresses can originate externally to the film from the environment, subsequent processing, storage, or use, or they can be internal to the film-substrate structure. In addition, residual ionic species in the film can cause interfacial corrosion if exposed to humidity, or dissolved mobile species, such as gases, can migrate to the interface, causing deadhesion.

Deadhesion due to Fracture. The loss of adhesion under mechanical stress (tensile, compressive, shear) occurs by deformation and fracture of material at or near the interface. The fracture mode (brittle or ductile) depends on the properties of the materials. The fracture path depends on the applied tensor stress, the presence of flaws, the interface configuration, "easy fracture paths," and the properties of the materials involved.

The fracture toughness (K_c) of a material is a measure of the energy necessary for fracture propagation and is thus an important adhesion parameter. In fracture, energy is adsorbed in the material and at the propagating crack tip by elastic deformation, plastic deformation, generation of defects, phase changes, and the generation of new surfaces. If this fracture occurs at an interface or in the nearby material, then loss of adhesion (deadhesion) occurs. Fracture mechanics approaches to measuring, describing, modeling, and/or predicting thin film (or any interface) adhesion are few. Some work has been published on the fracture of thick film and thin film systems. Thouless (Ref 68) has described the problem of critical and subcritical crack growth in thin film systems. Very little has been done to elucidate the effects of environment (subcritical crack growth) and film properties (Ref 69) on fracture and adhesion of thin film systems.

The fracture toughness of a material depends on the material composition, the microstructure, the flaw concentration, and the nature of the applied stresses. If an interphase material has been formed in the interfacial region it will be involved in the fracture process. Such interphase material is formed by diffusion, by diffusion plus compound formation, and by physical processes such as physical mixing and recoil implantation. The interphase material may be weaker or stronger than the nearby film and/or substrate material. For example, carbon lost from high-carbon steel substrates by diffusion into the film material during high-temperature processing can weaken the substrate and strengthen the film material. A National Science Foundation workshop in 1987 determined that the properties of the "interphase" (interfacial) material are some of the critical concerns in quantifying, measuring, and modeling the adhesion failure process (Ref 31). At present there are few if any good characterization techniques for determining the properties of interfacial materials that affect adhesion, such as fracture toughness, deformation properties, interfacial stress, presence of microscopic flaws, or effects of degradation mechanisms.

When a fracture surface (crack) advances, energy is needed for the creation of new crack surfaces and the deformation processes around the crack tip. This energy is supplied by the applied stress and the internal strain energy stored in the film-substrate system (residual film stress). The path of crack propagation is determined by the mechanical properties of the materials and by the resolved tensor stresses (tensile and shear) on the crack tip. The crack may progress along a plane of weakness, through weak material, or it can be diverted into stronger materials by the resolved stress. The fracture path is also determined by the presence of features that can blunt or change the fracture propagation direction.

Interfacial Morphology Effects on Fracture. In atomistic film deposition, the nucleation of depositing atoms on a smooth surface is controlled by various factors such as surface chemistry and nucleation sites. If the film-substrate interface is smooth, then any interfacial growth defects, such as interfacial voids, will lie in a plane that will then be a plane of weakness or "easy fracture path" along which fracture will easily propagate.

If the surface is rough and the deposited film material "fills in" the roughness, the propagating fracture must take a circuitous path with the likelihood that the fracture will be arrested and have to be reinitiated, as in the case of fiber-reinforced composite materials. If the roughness is not "filled in," there will be weakness (voids and low contact area) built into the interfacial region. Therefore the nature of the substrate surface roughness and the ability of the deposition process to fill in this roughness is important to the development of good adhesion.

The energy necessary for fracture propagation (fracture energy) can be lessened by mechanisms that weaken the material at the crack tip or reduce the elastic-plastic deformation in the vicinity of the crack tip. These mechanisms can be dependent on the environment in the case of ionically bonded materials. If time is involved in reducing the strength of the crack tip, the loss of strength is called *static fatigue* (Ref 66). Static fatigue depends strongly on mechanical (stress) and environmental (chemical) effects, particularly moisture and hydrogen (Ref 70).

Brittle surfaces and interfaces can be strengthened by placing them in compressive stress. This can be done by chemically replacing some surface ions with larger ions (chemical strengthening), by ion implantation, by putting the interior of the bulk material into tensile stress, or by placing the film in a state of compressive stress.

Residual Film Stress Effects on Adhesion. Invariably, atomistically deposited films have a residual stress that can be either tensile or compressive and can approach the yield or fracture strength of the materials involved. These stresses can arise from high-temperature deposition when there are differences in the thermal coefficients of expansion between the film and substrate, thermal gradients formed in the depositing film, and/or stresses due to the growth of the film. These stresses can enhance or retard fracture propagation.

In thin-film systems, high residual stress can be relieved by plastic deformation, blistering of the film from the surface in the case of compressive stress, or by microcracking and flaking in the case of high tensile stresses. If the film adhesion is high or the strength of the surface or film is low, the actual fracture path can be in the substrate or film and not at the interface. In many cases, in order to obtain good adhesion the residual film stress must be minimized and controlled. In some cases, film adhesion can increase with time due to the relief of high residual film stress.

Localized regions of high intrinsic stress can be found in films due to growth discontinuities or defects such as pinholes, nodules, or surface features such as edges or inclusions. These stressed areas can lead to localized adhesion failure under applied stress, producing pinholes.

Static fatigue is the slow growth of a crack under ambient stress and environmental conditions (Ref 66). The static fatigue failure mode due to moisture can be accelerated by breathing on the films to condense moisture at the crack tip. This moisture condensation method is an easy method of quickly determining if the residual film stresses are high, if the adhesion is poor, and whether the stresses in a failed film are compressive or tensile.

Corrosion. Interfacial corrosion/dissolution occurs when chemical or electrochemical (galvanic) effects create a solid or soluble corrosion product at the interface. An example of the loss of adhesion due to corrosion effects is the degradation of Ti-Au metallization in an HCl environment. This electrochemical degradation can be prevented by the addition of a thin intermediate layer of palladium between the titanium and the gold. The presence of chloride ions is generally to be avoided; they are often present as residues from cleaning and processing steps. Corrosion products can aggravate failure by a "wedging" action at the crack tip, either by solid corrosion products or by gas accumulation.

The diffusion of material away from the interface can weaken the interface by producing voids or in the extreme the complete removal of a bonding layer. For example, in the case of Cr-Au metallization, heating the system to higher than 200 °C in air will cause the chromium to diffuse from the interface to the surface, where it is tied up as the oxide (Ref 21). If all of the chromium diffuses from the interface, the gold film will not adhere. This "out-diffusion" of the interfacial material is dependent on the gaseous ambient, and a nonoxidizing ambient reduces the diffusion. The incorporation of a small amount of oxygen in the gold during deposition (by deposition in an oxygen plasma) reduces the chromium diffusion rate and gives a more thermally stable metallization.

Diffusion to the Interface. Interfaces generally act as preferential condensation regions for diffusion species. Diffusion of species to the interface can weaken or strengthen the interface. The deposition process may have influence on this effect. For instance, plasma cleaning of glass surfaces prior to silver deposition has been shown to give a time-dependent improvement in the adhesion of the silver films after deposition. Precipitation of gas at the interface to form voids will reduce adhesion. The diffusion of hydrogen through a film to an interface where it precipitates has been used by the electroplating community as an adhesion test. Diffusion and precipitation of vacancies form voids at interfaces that can cause adhesion loss.

Diffusion of water vapor through a polymer film to the interface can lead to the degradation of metal-polymer adhesion (Ref 71). Interfacial mixing can improve the moisture degradation properties of polymer-metal film systems.

Interdiffusion and reaction at the interface can generate an undesirable interphase material that results in a loss of adhesion. For example, in Au-Al metallization, interdiffusion and reaction form both Kirkendall voids and a brittle intermetallic phase ($AuAl_2$), termed "purple plague," that causes loss of adhesion (Ref 28).

Film Morphology Effects on Adhesion. Film properties can influence the apparent adhesion of a film-substrate couple (Ref 72). The mechanical, microstructural, and morphological properties of the film material determine the ability of the material to transmit mechanical stress and to sustain internal stresses. For example, a columnar film morphology can exhibit good adhesion because each column is separately bonded to the substrate and the columns are poorly bonded to each other. The columnar morphology is generally not desirable because of its low density and high surface area.

Deliberate Nonadhering Coatings. In some situations, adhesion is not desirable. For example, one technique to form freestanding films or shapes is to deposit a coating on a mandrel and then separate the coating from the mandrel. The coating can be deposited on a substrate to which it will not adhere, or a "parting layer" (release layer) can be used (Ref 73). In the electrodeposition of freestanding copper or gold structures, stainless steel or carbon is often used as a mandrel, because the chromium oxide and carbon are good electrical conductors but copper and gold will not adhere to the oxide or carbon surface. Easily dissolved materials such as sodium chloride or polymers can be used as parting layer materials. In some cases, particularly for complex shapes, the mandrel must be completely dissolved to release the structure.

Film Density and Surface Area

The presence of porosity in the columnar structure, closed and open voids, and pinholes means that the film density is lower than that of the bulk material and that the surface area exposed to the ambient is much higher than the geometrical surface area. This low density and high surface area influence many film properties, such as hardness, deformation, chemical etch rate, resistivity, and index of refraction.

Open porosity features pores that connect to the free surface and contribute to the surface area of the film. The coalescence of lattice defects along surfaces such as grain boundaries and the open space between the columns in the columnar microstructure are sources of such porosity. Process parameters that affect the growth of the columnar microstructure affect the film porosity. For example, the porosity of vacuum-deposited films can be varied by controlling the substrate surface roughness, angle of incidence of the adatom flux, or the gas pressure during deposition.

Through porosity is a special case of open porosity where the porosity is aligned in such a manner as to allow an open space to exist between the film surface and the substrate surface. Through porosity develops from the columnar growth, particularly on rough surfaces, and the growth on surface contaminants such as particulates (see Fig. 6). Such porosity causes pinholes in the film and allows corrosion of the substrate through the pinholes, electrical "opens" in patterned electrical circuits, optical transmission, and high surface diffusion rates from the interface to the film surface.

Crystallographic Orientation

The crystallographic orientation of the grains in the film is determined by the preferential growth of certain crystal planes over others. This orientation can be altered by epitaxial growth on a substrate or by concurrent energetic ion bombardment.

Even when single crystal films are not formed, it is often found that a preferential crystallographic orientation or texture develops in deposited films. This texturing can lead to nonisotropic film properties in materials that do not have cubic crystal forms.

Epitaxial Film Growth. *Epitaxy* is defined as the oriented overgrowth of film material and typically refers to the growth of single crystal films (Ref 74). *Homoepitaxy* is the epitaxial growth of a deposit on a substrate of the same material (e.g., doped Si on Si). *Heteroepitaxy* is the epitaxial growth of a deposit on a substrate of a different material (e.g., Au on Ag, GaAs on Si). Epitaxial growth requires some degree of mobility of the atoms and nuclei on the surface. An "epitaxial temperature" necessary for epitaxial growth in specific systems and under specific deposition conditions is sometimes specified.

Single crystal overgrowth can be accomplished with large mismatches in lattice parameters between the film and substrate, either by keeping the thickness of the deposited material small, so that the mismatch can be taken up by straining the film lattice without forming lattice defects ("strained layer superlattice"), or by using a "buffer" layer to grade the strains from the substrate to the film. For example, thick single crystal SiC layers can be grown on silicon by CVD techniques even though the lattice mismatch is large (20%). This is accomplished by forming a buffer layer by first carbonizing the silicon surface and grading the composition from the substrate to the film. However, in general, if the lattice mismatch is large, the interface has a high density of dislocations and the resulting film is polycrystalline.

Oriented growth can be enhanced by "seeding" of the substrate surface with oriented nuclei. Such "seeds" can be formed by depositing a small amount of material, heating the surface to form isolated oriented grains, and then using these grains as seeds for the deposition of an oriented film.

Energetic adatoms and low-energy ion bombardment during deposition can be used as partial substitutes for increased substrate temperature in the epitaxial growth process. Carefully controlled bombardment can lower the temperature at which epitaxy can be obtained. This is probably due to increased surface mobility of the adatoms. Ion beams of the depositing material (film ions) have also been used to deposit epitaxial films.

Lattice Defects and Voids

Lattice defects are point defects in the lattice and the microstructures, such as dislocations, that arise from coalescence of point defects or the relaxation of elastic strains. Voids are internal pores that do not connect to a free surface of the material and thus do not contribute to the surface area but do affect film properties such as density. During film growth, vacancies can agglomerate into "microvoids" in the crystal structure. Defects in the films can be reduced by:

- Increased substrate heating during deposition

- Controlled concurrent ion bombardment during deposition--use of low enough particle energies such that the bombarding species are not incorporated into the growing film

Point defects in the film can affect the electrical conductivity and electromigration in metallic films, and carrier mobility and lifetime in semiconductor materials. Generally, high-defect concentrations result in poor electromigration properties. Lattice defects have been shown to be important to the properties of the high-transition-temperature superconductor films.

Surface Coverage

Surface geometry affects the growth of films by shadowing the surfaces from the depositing flux of atoms. Steps, vias, and grooves are of particular importance, and in order to get conformal coverage over such surfaces, the deposition often must be done at an elevated temperature to increase surface mobility or by using backsputtering/redeposition. Off-normal incidence of the depositing flux makes conformal coverage more difficult. The ability of concurrent ion bombardment to improve step-coverage is of great interest in microelectronic fabrication. The improved coverage by concurrent ion bombardment is due to a number of factors, including:

- Forward sputtering (Ref 75)
- Gas scattering--randomizing of direction of adatom flux
- Backscattering of sputtered material
- Ionization and return of sputtered material

Graded Properties

There are a number of effects that lead to changes of film properties with thickness (graded properties). As previously discussed, the film growth mode is continually changing with thickness in the early stages of growth, particularly on rough surfaces. The initial deposition may have reacted with residual gases, giving a changing composition with thickness. In addition, the initially deposited material is being heated while the film is growing, thus allowing annealing during growth. The degree of this annealing differs with deposition time, deposition rate, thickness, and the thermal transport properties of the film and substrate material.

Postdeposition Changes (Stability) in Film Properties

High surface areas and high residual film stress are major factors in the change of film properties with time. The high surface areas allows corrosion and adsorption to play major roles in the stability of film properties. Residual stress represents stored energy that can give long-term stability problems.

Adhesion. In some cases, film adhesion can increase or decrease with time under ambient conditions. The increase in adhesion can be due to diffusion of reactive species to the interface or the relief of residual stresses. The film adhesion may decrease with time, and it can be due to static fatigue fracture at the interface due to residual stress, promoted by the presence of moisture, or to corrosion of the interface by ambient species.

Microstructure. High residual stress and high point defect concentrations can lead to time-dependent changes in the microstructure of the deposited material. This may lead to low-temperature grain growth and recrystallization in sputter-deposited copper and the generation of voids ("stress voiding") at room temperature.

Electromigration (Ref 76) and stress-induced void formation (Ref 54, 77) in aluminum metallization can be reduced by the addition of a material that will react with the aluminum to form finely dispersed second-phase materials that act as sinks for migrating defects and coalescing voids. Copper is the common material added to aluminum metallization to reduce stress-induced voiding and electromigration (Ref 77). The copper forms the theta Al-Cu phase Al_2Cu.

Residual Stress. A high internal concentration of defects along with high intrinsic stress can lead to time-dependent changes of stress ("stress relaxation") in films.

Electrical Properties. Changes of the electrical resistivity of a film can be due to oxidation of the columnar surfaces. The combination of metallic conduction in the columns and the tunneling conduction through oxide layers on the column surfaces, allows the formation of films that have a low-temperature coefficient of resistivity.

References cited in this section

21. P.H. Holloway, Gold/Chromium Metallization for Electronic Devices, *Solid State Technol.,* Vol 23 (No. 2), 1980, p 109, and references therein
26. D.M. Mattox, Thin Film Adhesion and Adhesive Failure--A Perspective, *ASTM Proc. Conf. Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings,* STP 640, ASTM, 1978, p 54
28. E. Philofsky, Intermetallic Formation in Gold Aluminum Systems, *Solid State Electronics,* Vol 13 (No. 10), 1970, p 1391
31. G.G. Fuller and K.L. Mittal, Ed., *Opportunities and Research Needs in Adhesion Science and Technology,* National Science Foundation Workshop on Adhesion, 14-16 Oct 1987 (Lake Tahoe, CA), Hitex Publication, 1988
39. R.E. Cuthrell, D.M. Mattox, C.R. Peeples, P.L. Dreike, and K.P. Lamppa, Residual Stress, Stress Anisotropy, Stress Control and Resistivity in Post Cathode Magnetron Sputter-Deposited Molybdenum Films, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2914
54. F.G. Yost, D.E. Amos, and A.D. Romig, Stress Driven Diffusion Voiding of Aluminum Conductor Lines, *Proc. IEEE/IRPS '89,* 1989, p 193
63. M. Ohring, *The Material Science of Thin Films,* Academic Press, 1991, and references therein
64. H. Windischmann, Intrinsic Stress in Sputter-Deposited Thin Films, *Crit. Rev. Solid State Mater. Sci.,* Vol 17 (No. 6), 1992, p 547
65. R. Pestrong, Nature's Angles, *Pacific Discovery--Calif. Academy of Sciences,* Vol 44 (No. 3), Summer 1991, p 28
66. S.M. Wiederhorn and L.H. Bolz, Stress Corrosion and Static Fatigue of Glass, *J. Am. Ceram. Soc.,* Vol 53, 1970, p 543
67. D.M. Mattox, Particle Bombardment Effects on Thin Film Deposition: A Review, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1105, and references therein
68. M.D. Thouless, The Role of Fracture Mechanics in Adhesion, *Adhesion in Solids,* Symp. Proc., Vol 119, D.M. Mattox, J.E.E. Baglin, C. Batich, and R. Gottschall, Ed., Materials Research Society, p 51
69. T.S. Oh, R.M. Cannon, and R.O. Ritchie, Subcritical Crack Growth along Ceramic-Metal Interfaces, *J. Am. Ceram. Soc.,* Vol 70, 1987, p C352
70. R.E. Cuthrell, Influence of Hydrogen on the Deformation and Fracture of the Near Surface Region of Solids: Proposed Origin of the Rehbinder-Westwood Effect, *J. Mater. Sci.,* Vol 14, 1979, p 6123
71. V.D. Venables, Adhesion and Durability of Metal-Polymer Bonds: A Review, *J. Mater. Sci.,* Vol 19, 1984, p 2431
72. J.T. Prater and R.W. Moss, Effect of the Coating Structure on the Adherence of Sputter-Deposited Oxide Coatings, *Thin Solid Films,* Vol 107, 1983, p 455
73. A.H.F. Muggleton, Deposition Techniques for Preparation of Thin Film Nuclear Targets: Invited Review, *Vacuum,* Vol 37, 1987, p 785
74. M. Simpson, P. Smith, and G.A. Dederski, Atomic Layer Epitaxy: State of the Art Review, *Surf. Eng.,* Vol 3, 1987, p 343
75. D.W. Skelly and L.A. Grunke, Significant Improvement in Step Coverage using Bias Sputtered Aluminum, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 457
76. L. Berenbaum and R. Rosenberg, Electromigration Damage in Al-Cu Thin Films, *IEEE/IRPS,* 1971, p 136
77. J.G. Ryan, J.B. Riendeau, S.E. Shore, G.J. Slusser, D.C. Beyar, D.P. Bouldin, and T.D. Sullivan, The Effects of Alloying on Stress Induced Void Formation in Aluminum Based Metallizations, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1474

Unique Materials Formed by Atomic Deposition Processes

Amorphous materials are those that have no detectable crystal structure. Materials can be naturally amorphous, such as the nonmetallic glasses. Some normally crystalline materials can be formed in the solid amorphous condition by rapidly cooling ("quenching") from the liquid phase (Ref 78).

Amorphous film materials can be formed by:

- Deposition of a natural "glassy" material such as a glass composition
- Deposition at low temperatures where the adatoms do not have enough mobility to form a crystalline structure
- Ion bombardment of high-modulus materials (Ref 79)
- Deposition of materials some of whose bonds are partially saturated by hydrogen (e.g., a-Si:H, a-C:H, and a-B:H, where "a" stands for *amorphous*)
- Deposition of complex metal alloys

Hydrogen seems to play a very unusual role in the growth of some materials. In the case of depositing silicon from the silane (SiH_4) precursor gas in CVD, the incomplete decomposition of the precursor results in the deposition of a-Si, which can contain 10 to 15 at.% H. The hydrogen prevents Si-Si bonding, thus causing the film material to be amorphous in much the same way as "glass formers" do in forming glasses by melting. The a-Si seems to deposit much like a polymer film, giving very good surface replication and low void density in the early stages of film growth.

The unique applications of amorphous materials arise because of:

- Absence of grain boundaries--no grain boundary diffusion
- Low void/pinhole content
- Considerable compositional latitude
- Unique optical properties
- Unique electronic properties
- Ease of fabrication

Some semiconductor materials grow with some of their bonds unsaturated ("dangling"). This can lead to unacceptable electron trapping. It has been demonstrated that the unsaturated bonds in a-Si can be passivated by hydrogen doping, thus raising the electron mobility in the material. Hydrogen ion bombardment is now used to treat polycrystalline silicon photovoltaic materials to improve photoconversion efficiency.

Metastable or labile phases are unstable phases of materials that are easily changed if energy is available for mass transport processes to occur. Deposition processes allow the development of metastable forms of the material. Metastable crystal structures can be formed by rapid quenching of high-temperature phases of the deposited material, or they can be stabilized by residual stresses or impurities in the film. For example, diamond is a metastable phase of carbon that is formed naturally in a high-pressure and high-temperature environment and changes to graphitic carbon on heating. However, diamond films can be deposited using the proper deposition techniques. Metastable film compositions can also be formed under deposition conditions that do not allow precipitation of material when it is above the solubility limit of the system. For example, concurrent low-energy ion bombardment using "dopant ions" allows doping of semiconductor films to a level greater than that obtainable by diffusion-doping techniques (Ref 80).

Diamond and Diamond-like Carbon (DLC) Films. Recently great progress has been made in the deposition of diamond and diamond-like carbon (DLC) coatings for industrial applications. Natural diamond, with its high hardness, low coefficient of friction, high thermal conductivity (1.5 times that of silver), high packing density, good visible and infrared transparency, and chemical inertness, has long provided a goal for the thin film deposition community.

Diamond is a carbon material with a specific crystallographic structure (diamond structure) and specific chemical bonding (sp^3 bonding). DLC is an amorphous carbon material with mostly sp^3 bonding that exhibits many of the desirable properties of crystalline diamond. DLC material is sometimes called "amorphous diamond," but that term is an oxymoron and should be avoided.

The property of the carbon sp^3 bonding that allows the deposition of both diamond and DLC coatings is its relative chemical inertness to hydrogen reduction. The sp^3 bonds formed during deposition are stable against hydrogen etching. Any sp^2 (graphite) bond formed, however, is susceptible to hydrogen etching.

Polycrystalline diamond films can be formed if the deposition temperature is high enough (>600 °C, or 1100 °F) to allow atomic rearrangement during deposition. DLC films are formed at lower temperatures (room temperature and even below) where the atoms cannot arrange themselves into the diamond structure, giving an amorphous material. The DLC films have varying amounts of sp^2 bonding and included hydrogen that affect their properties. The sp^3-bonded material can be deposited by a number of techniques, all of which involve "activating" both a hydrocarbon species, to allow carbon deposition, and hydrogen, to provide the etchant species.

Polycrystalline diamond films are most often deposited by the hot filament CVD technique, the combustion flame technique, or PECVD using a microwave plasma. In all cases, the diamond film that is formed is polycrystalline and has a rough surface. This is due to the method of film nucleation on the substrate surface and the nature of the film growth. This rough surface gives a high coefficient of friction, and a great deal of work is being done to try to improve this surface morphology for wear and friction applications. Other properties can approach those of natural diamond.

DLC films are made primarily using PECVD or ion beam techniques with low substrate temperatures (Ref 81). The DLC films are smooth with properties approaching those of natural diamond, except that thermal conductivity is much lower. DLC films can also be deposited by ion bombardment processes that do not involve hydrogen. These films are sometimes called "i-C" films (Ref 79). DLC films are being used as coatings on optical products such as eyeglasses, sunglasses and IR optics, and as wear-resistant coatings on storage media and cutting surfaces.

References cited in this section

78. K.H.J. Buschow, Amorphous Alloys, *J. Less-Common Met.,* Vol 110, 1985, p 205
79. C. Weismantel, Preparation, Structure and Properties of Hard Coatings on the Basis of i-C and i-BN, Chapter 4, *Thin Films from Free Atoms and Particles,* K.J. Klabunge, Ed., Academic Press, 1985, p 153, and references therein
80. J.E. Greene, A Review of Recent Research on the Growth and Physical Properties of Single Crystal Metastable Elemental and Alloy Semiconductors, *J. Vac. Sci. Technol. B,* Vol 1 (No. 2), 1983, p 229
81. H.-C. Tsai and D.B. Bogy, Critical Review: Characterization of Diamond-Like Carbon Films and Their Applications as Overcoats on Thin Film Media for Magnetic Recording, *J. Vac. Sci. Technol. A,* Vol 5 1987, p 3287, and references therein

Vacuum Deposition, Reactive Evaporation, and Gas Evaporation

Donald M. Mattox, IP Industries

Introduction

VACUUM DEPOSITION, or vacuum evaporation, is a physical vapor deposition process in which the atoms or molecules from a vaporization source reach the substrate without colliding with residual gas molecules. Generally, the vaporization source is one that vaporizes materials by thermal means (that is, evaporation or sublimation), but other vapor sources can be used. The advantage of vacuum evaporation is that films of a variety of materials can be deposited at high rates over large areas in a very pure form. Limitations of vacuum evaporation are that often the films do not have optimum properties and that there are relatively few deposition parameters that can be modified to improve the film properties.

Vacuum deposition requires a vacuum of better than 13 mPa (0.1 mtorr). At this pressure, there is still a large amount of concurrent bombardment of the substrate by potentially undesirable residual gases that can contaminate the film. If film contamination is a problem, a high (13 μPa, or 10^{-7} torr) or ultrahigh (0.13 μPa, or 10^{-9} torr) vacuum environment can be used to produce a film with the desired purity, depending on the deposition rate, reactivities of the residual gases and depositing species, and the tolerable impurity level in the deposit.

Vacuum deposition of a film was first reported by Faraday in 1857 using exploding wires. Nahrwold was the first to use thermal evaporation in a vacuum to produce a thin film, in 1887. Vacuum deposition was not routinely used until about 1929, when it was first used for optical coatings (Ref 1). Strong, for example, metallized the 100 in. mirror for the Mount Wilson Observatory in 1935. The subject of vacuum deposition was thoroughly investigated by Glang in 1970 (Ref 2), and most review articles and book chapters on the subject since that time have drawn heavily on his work.

In reactive evaporation, a partial pressure of reactive gas is used to deposit compounds of the vaporized material by the reaction of deposited atoms with ambient gases. Reactive evaporation was first reported by Auwarter in 1952 and Brinsmaid et al. in 1953. In 1971, Heitmann used reactive evaporation to deposit oxide films by evaporating the film material through a plasma of the reactive gas, and this technique is now generally called activated reactive evaporation. With this method, either a gas, such as oxygen or nitrogen, or a hydrocarbon is metered into the vacuum chamber, where it reacts with the vapor from a metallic evaporant to form a metal oxide, nitride, or carbide coating.

In gas evaporation, a high residual gas pressure causes the formation of ultrafine (100 nm, or 1000 Å) particles by gas phase collision and nucleation. Gas evaporation is a term given to the deposition of ultrafine particles ("smokes"), which are formed by gas phase nucleation due to collision of the evaporated atoms with residual gas molecules. This typically requires an ambient gas pressure greater than about 1.3 mPa (10 torr). The formation of useful films of ultrafine particles formed by gas evaporation was reported by Pfund, who produced "zinc black" infrared absorbing films in 1933.

References

1. W.P. Strickland, "Optical Thin Film Technology: Past, Present and Future," *Society of Vacuum Coaters 33rd Ann. Tech. Conf. Proc.,* 1990, p 221
2. R. Glang, Vacuum Evaporation, Chapter 1, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, Ed., McGraw-Hill, 1970, p 1-26

Vacuum Deposition

In the vacuum deposition process, elements, alloys, or compounds are vaporized and deposited in a vacuum. The process is carried out at pressures of less than 0.1 Pa (1 mtorr) and usually in vacuum levels of 10 to 0.1 mPa (100 to 1 μtorr). The substrate temperature typically ranges from ambient to 500 °C (930 °F). Figure 1 shows a typical batch vacuum deposition system. Vacuum deposition is commonly used to deposit pure metals (for example, aluminum, silver, gold, nickel, chromium, titanium, molybdenum, and tungsten), some alloys (for example, stainless steel, nickel-chromium, lead-tin, and M-Cr-Al-Y), and selected compounds (for example, Al_2O_3, TiC, and TiB_2).

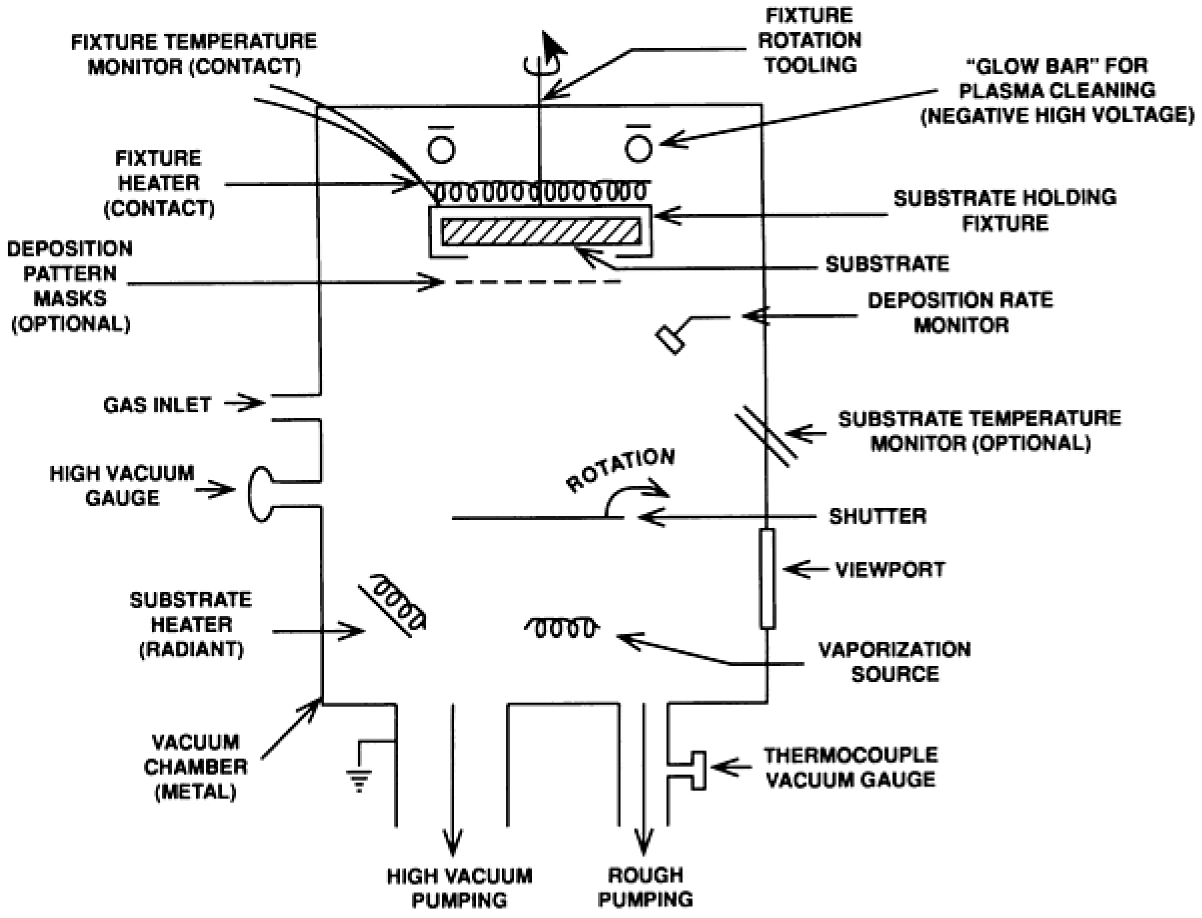

Fig. 1 Schematic diagram of a typical vacuum deposition chamber

Fundamentals of Thermal Vaporization

Equilibrium Vapor Pressure. The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface. At equilibrium, as many atoms return to the surface as leave the surface. The vapor pressure is measured by the use of a Knudsen cell, which consists of a closed volume with a small orifice of known conductance. When the container is held at a constant temperature the material that escapes through the hole depends on the pressure differential. In a vacuum environment and knowing the rate of material escaping, the equilibrium vapor pressure in the container can be calculated. The vapor pressures of the elements have been presented in tabular and graphical form (Ref 3). The Knudsen cell is often used as a source for molecular beam epitaxy, where the deposition rate can be carefully controlled by controlling the temperature of the source (Ref 4) or by mechanically interrupting the beam (Ref 5).

Figure 2(a) and 2(b) shows the vapor pressure of selected materials as a function of temperature. Note that the slopes of the vapor pressure curves are strongly temperature dependent (about 13 mPa/100 °C for cadmium and 13 mPa/250 °C for tungsten). The vapor pressures of different materials at a given temperature can differ by many orders of magnitude. For vacuum deposition, a reasonable deposition rate can be obtained only if the vaporization rate is fairly high. A vapor pressure of 1.3 Pa (10^{-2} torr) is typically considered the value necessary to give a useful deposition rate. Materials with that vapor pressure above the solid are described as subliming materials, and materials with that vapor pressure above the liquid are described as evaporating materials. Figure 3 shows the equilibrium vapor pressure curves of lithium and silver in detail and shows that at 800 K (527 °C) the vapor pressures differ by a factor of 10^7.

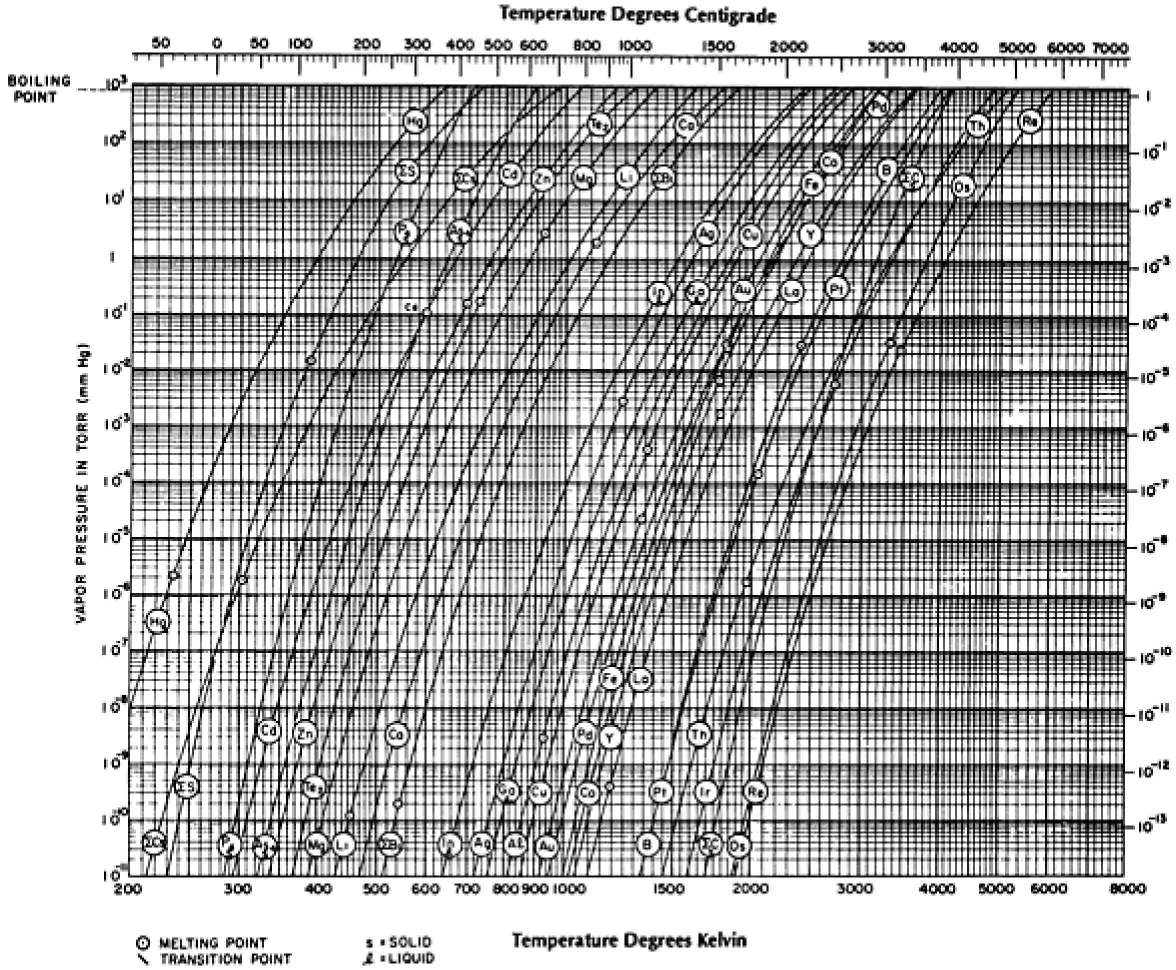

Fig. 2(a) Vapor pressure curves of the elements

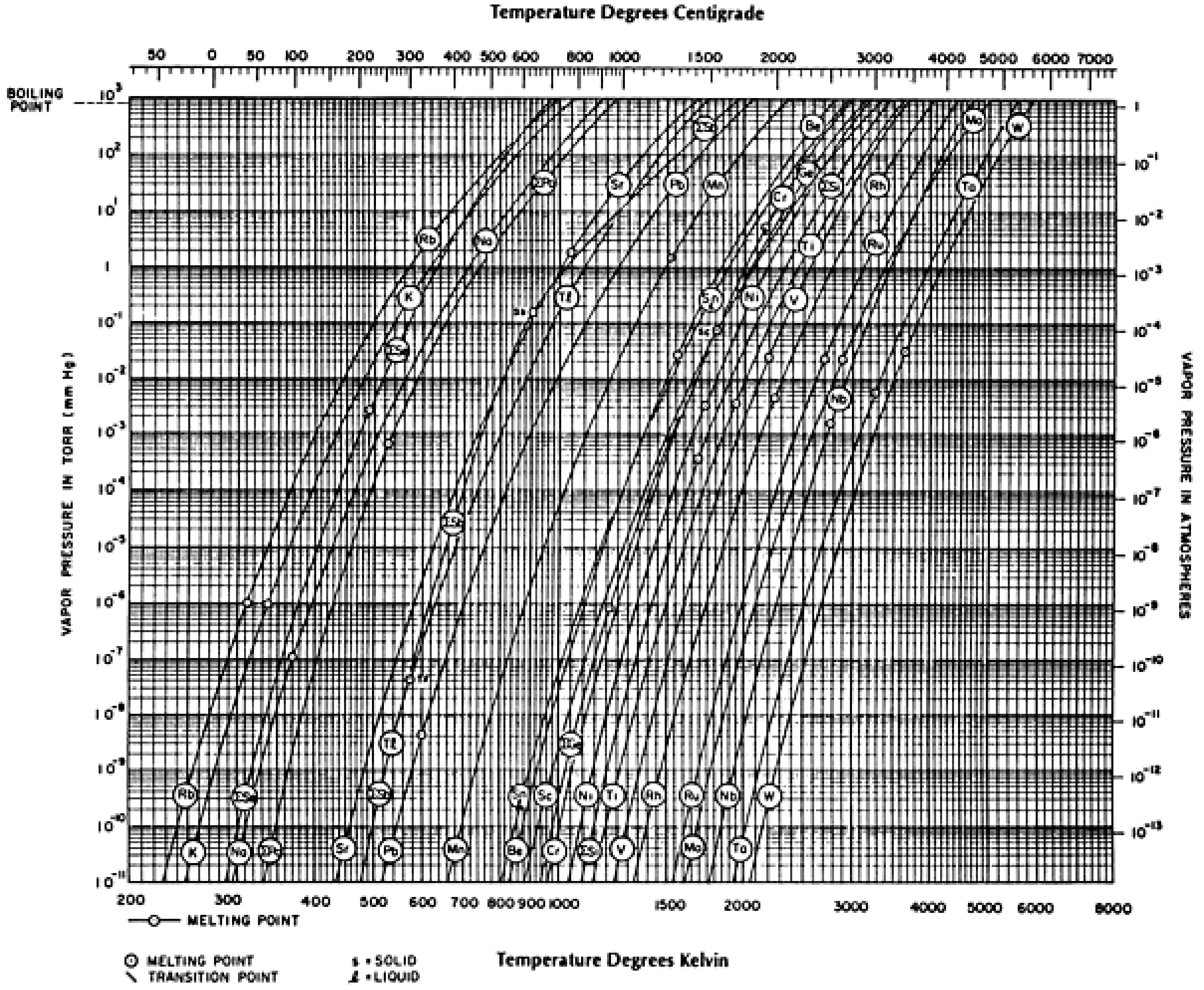

Fig. 2(b) Vapor pressure curves of the elements

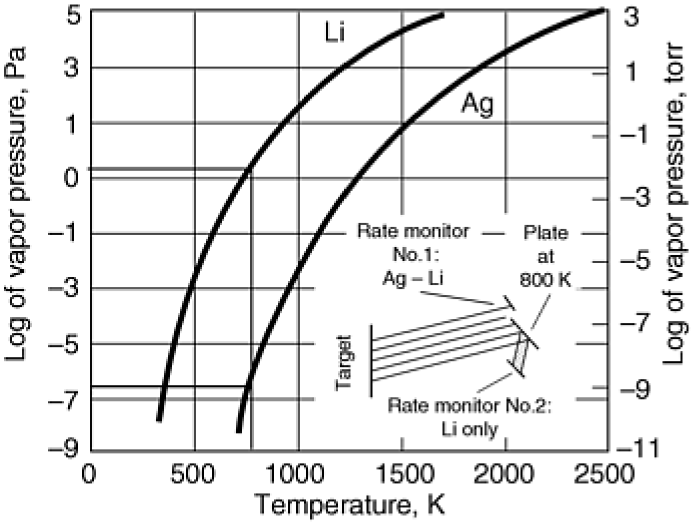

Fig. 3 Plot of equilibrium vapor pressure vs. temperature for lithium and silver

Vaporization Rate. A material vaporizes freely from a surface when the vaporized material leaves the surface with no collisions above the surface. The free surface vaporization rate, dN/dt (in s^{-1}) is proportional to the vapor pressure and is given by the Hertz-Knudsen vaporization equation (Ref 2, 6):

$$dN/dt = C\,(2\pi mkT)^{-1/2}\,(p^* - p) \qquad \textbf{(Eq 1)}$$

where dN/dt is the number of evaporating atoms per cm^2 of surface area per second, C is a constant that depends on the rotational degrees of freedom in the liquid and the vapor, p^* is the vapor pressure of the material at temperature T, p is the hydrostatic pressure of the vapor above the surface, k is Boltzmann's constant, T is the absolute temperature, and m is the mass of the vaporized species. The maximum vaporization rate is when $p = 0$ and $C = 1$. The actual vaporization rate will be one-third to one-tenth of this maximum rate because of collisions in the vapor above the surface (that is, $p > 0$ and $C \neq 1$), surface contamination, and other effects (Ref 7). Figure 4 shows some calculated maximum vaporization rates.

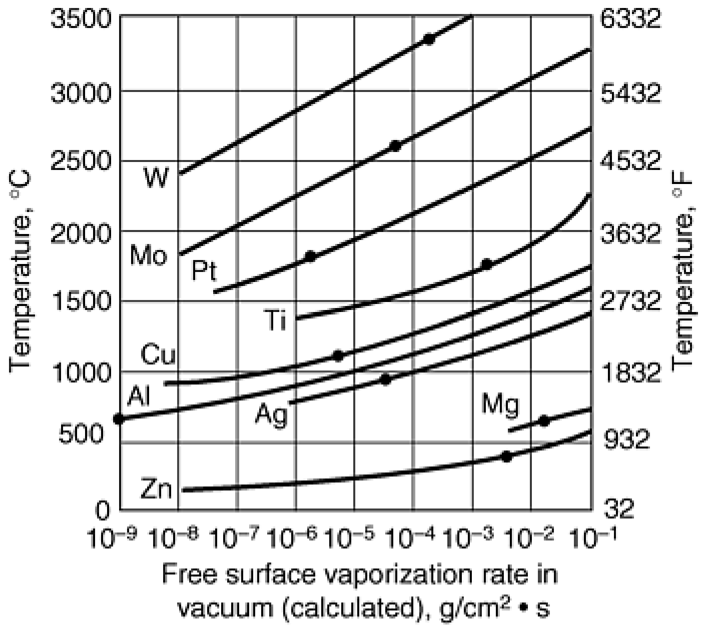

Fig. 4 Plot of temperature vs. free surface vaporization rate in a vacuum for selected elements. The symbol • indicates the melting point.

Vapor Flux Distribution on Vaporization. For low vaporization rates, the flux distribution can be described by a cosine distribution (Ref 2, 6). With no collisions in the gas phase, the material travels in a straight line between the source and the substrate (that is, line-of-sight deposition). The material from a point deposits on a surface with a distance and substrate orientation dependence given by the cosine deposition distribution equation:

$$dm/dA = (E/\pi r^2)\cos\theta\,\cos j \qquad \textbf{(Eq 2)}$$

where dm/dA is the mass per unit area, E is the total mass evaporated, r is the distance from the source to the substrate, $\theta$is the angle from the normal to the vaporizing surface, and j is the angle from the source-substrate line.

Figure 5 shows the distribution of atoms vaporized from a point source and the thickness distribution of the film formed on a planar surface above the source based on Eq 2.

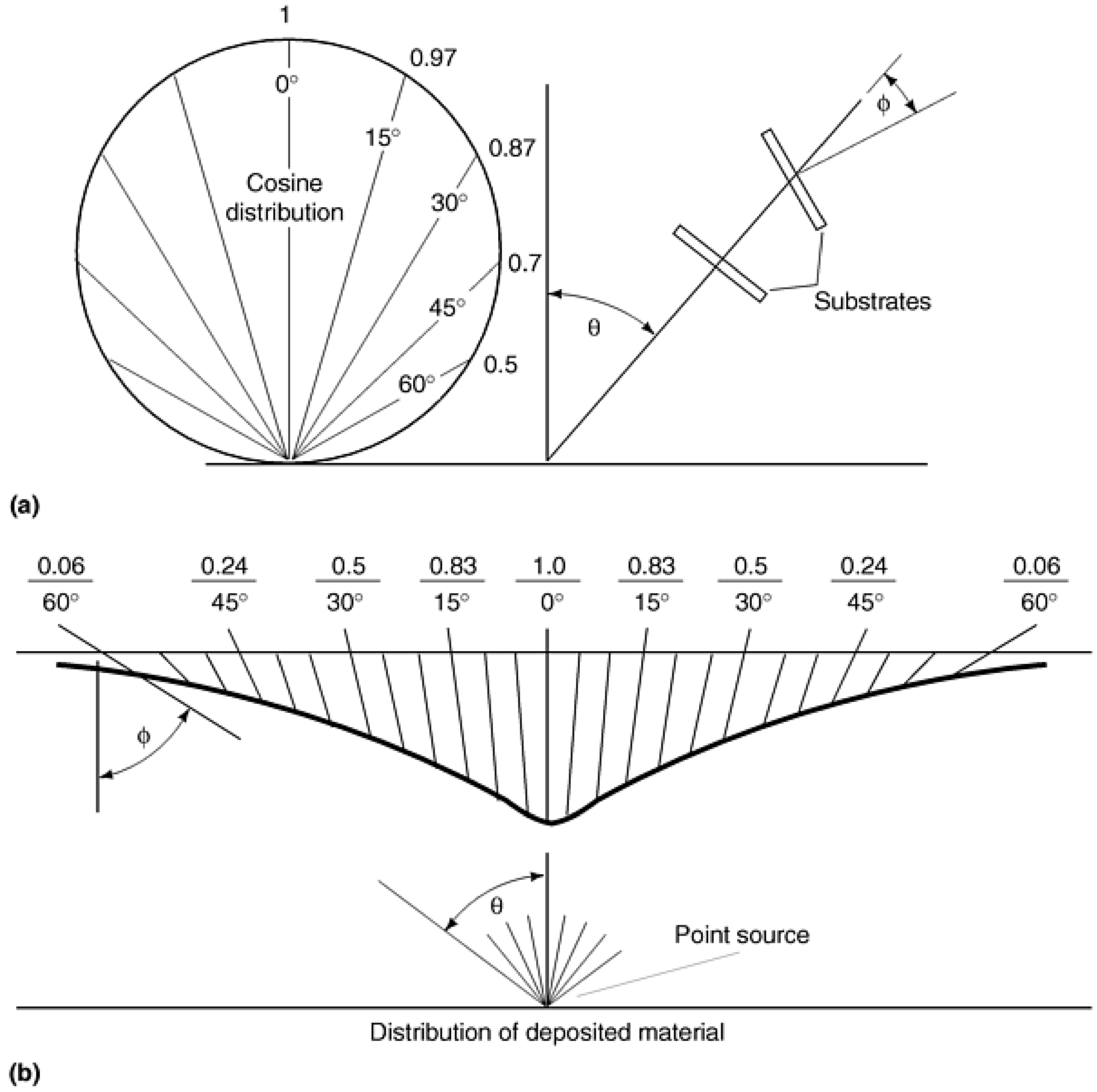

Fig. 5 Flux distribution above a point source, based on cosine deposition distribution equation. (a) Distribution of atoms vaporized from a point source. (b) Thickness distribution of film formed on planar surface above source

In actuality the flux distribution from a free surface may not be cosine but can be modified by source geometry, collisions associated with a high vaporization rate, level of evaporant in the source, and so on. In such cases, the flux distribution must be measured directly (Ref 8). A more complete model for the flux distribution from a Knudsen (orifice) source is given by the Knudsen effusion model proposed by Ruth and Hirth (Ref 9).

Particle Energies. Atoms leave a hot surface with thermal energies given by 3/2 kT, where k is Boltzmann's constant and T is the absolute temperature (Ref 2, 6). The atoms have a Maxwell-Boltzmann distribution in velocities. For example, for a 1500 °C evaporation temperature for copper, the mean energy of the vaporized copper atoms is 0.2 eV, and the mean atom velocity is about 1 km/s.

Shutters. Because the particles from a vaporizing source travel in straight lines in a vacuum, a shutter can be used to intercept vaporized material and prevent it from reaching the substrate. By opening and closing the shutter the deposition time can be precisely controlled.

Vaporization of Materials

Elements. Many elements evaporate, but many (for example, chromium, cadmium, magnesium, arsenic, and carbon) sublime, and many others (for example, antimony, selenium, and titanium) are on the borderline between evaporation and sublimation. Chromium has a vapor pressure of 1.3 Pa (10^{-2} torr) at 600 °C (1080 °F) below its melting point, and carbon cannot be melted except under high hydrostatic pressure. Materials such as aluminum, tin, gallium, and lead have very low vapor pressures above the just-molten material. Tin, for example, has a vapor pressure of 1.3 Pa (10^{-2} torr) at 1000 °C (1800 °F) above its melting point. Aluminum and lead have vapor pressures of about 1.3 Pa (10^{-2} torr) at 500 °C (900 °F) above their melting points.

Most elements vaporize as atoms, but some (for example, antimony, tin, carbon, and selenium) have a significant portion of the vaporized species as clusters of atoms. For materials that evaporate as clusters, special vaporization sources called *baffle sources* can be used to ensure that the depositing vapor is in the form of atoms. It should be noted that as a material is heated, the first materials that are volatilized are high-vapor-pressure surface contaminants, absorbed gases, and high-vapor-pressure impurities.

Alloys vaporize in a ratio that is the same as their vapor pressures (that is, the high vapor pressure constituent vaporizes more rapidly than the low vapor pressure material). This relationship is called Raoult's Law, and the effect can be used to purify materials by selective vaporization/condensation. When an alloy is evaporated from a molten pool, the higher-vapor-pressure material steadily decreases in proportion to the lower-vapor-pressure material in the melt. For example, when an Al:Mg (6.27 at.%) alloy is evaporated at 1919 K, the magnesium is totally vaporized in about 3% of the total vaporization time (Ref 10). Vaporization of alloys produces a gradation of film composition as the evaporant is selectively vaporized. This can be desirable or undesirable. For example, when copper-gold is deposited on polymers by evaporation of a copper-gold alloy, copper, which has a higher vapor pressure than gold, is deposited at a higher initial rate than the gold. This results in copper enrichment at the interface, which is conducive to better adhesion between the deposited film and the polymer.

In some cases, the nature of vaporization of an element can be changed by alloying it with another material. For example, chromium (melting point of 1863 °C, or 3385 °F), which normally sublimes, can be alloyed with zirconium (melting point of 1855 °C, or 3371 °F) to give a liquid melt from which the chromium evaporates. The eutectic alloy of zirconium-chromium (14 wt%) melts at 1332 °C (2430 °F), at which temperature chromium has a vapor pressure of approximately 1.3 Pa (10^{-2} torr) and zirconium has a vapor pressure of approximately 0.13 μPa (10^{-9} torr). Another eutectic alloy of zirconium-chromium (72 wt%) has a melting point of 1592 °C (2898 °F).

Compounds. Many compounds (for example, SiO, MgF_2, Si_3N_4, HfC, SnO_2, BN, PbS, and VO_2) sublime. Compounds often vaporize with a range of species, from clusters of molecules to dissociated or partially dissociated molecules (Ref 2). The degree of dissociation is strongly dependent on the temperature and composition of the compound (Ref 11). For example, in the thermal vaporization of SiO_2, a number of species are formed in addition to SiO_2, including $(SiO_2)_x$, SiO_{2-x}, SiO, Si, and O.

Evaporation from a very hot surface or by electron beams can give ionization of some of the molecular fragments. These charged species can be detrimental to the electrical properties of the deposited material. The ionized species can be deflected from the vapor flux using electrically charged plates above the source.

Fundamentals of Condensation

Thermally vaporized atoms may not condense when they impinge on a surface, but may rather be reflected or re-evaporate. Re-evaporation is a function of the surface temperature and the flux of depositing atoms. A hot surface can act as a mirror for atoms. For example, the deposition of cadmium on a steel surface having a temperature greater than 200 °C (390 °F) results in total re-evaporation of the cadmium. Figure 3 shows how this "hot mirror effect" can be used to monitor the deposition of the separate constituents of a depositing Ag-50Li alloy. The lithium is re-evaporated from the hot collector surface to deposit on the cold collector surface, while the silver remains on the hot surface. Hot surfaces can be used to reflect the evaporant flux of some materials, such as cadmium or zinc, into non-line-of-sight locations on a substrate to improve surface coverage and uniformity.

Nucleation and Nucleation Density. When adatoms (atoms adsorbed on a surface so that they migrate over the surface) move over a surface, they lose energy by making and breaking chemical bonds formed with the surface atoms, by colliding with other atoms, or by chemically reacting with an adsorbed species. If there is little chemical interaction between the surface atoms and the adatoms, the surface mobility will be high and the adatoms will nucleate on preferential nucleation sites such as steps, charge centers, impurities, grain boundaries, and so on. If the chemical reaction is strong, the adatoms will have low surface mobility and the nucleation density will be high. The nucleation density plays an important role in determining film properties.

Condensation Energy. When a thermally vaporized atom condenses on a surface, it gives up energy, including:

- Heat of vaporization or sublimation (enthalpy change on vaporization): a few eV per atom, including the kinetic energy of the particle, which is typically 0.3 eV or less
- Energy to cool to ambient temperature: depends on heat capacity and temperature change
- Energy associated with chemical reaction (heat of reaction), which can be exothermic (when heat is released) or endothermic (when heat is adsorbed)
- Energy released on solution (alloying): heat of solution

The heat of vaporization for gold is about 3 eV/atom, and the mean kinetic energy of the vaporized gold atom is about 0.3 eV. This means that the kinetic energy is only a small part of the energy released at the substrate during deposition. However, it has been shown, using mechanical velocity filters, that the kinetic energy of the depositing gold atoms is important to the film structure, properties, and annealing behavior (Ref 12). At high deposition rates, the condensation energy can produce appreciable substrate heating (Ref 13).

Deposition rates for vacuum deposition processes vary greatly. They range from less than one monolayer per second (MLS) (<0.3 nm/s, or 3 Å/s) to more than 10^4 MLS (>3 μm/s, or 3×10^4 Å/s). The rate depends on the thermal power input to the source, the system geometry, and the material. Generally, the power input to the source is controlled by monitoring the deposition rate.

Deposition Uniformity. As shown in Fig. 5, the deposition thickness uniformity from a vaporizing point onto a plane is poor. A more uniform deposit over a planar surface can be obtained by using multiple sources with overlapping patterns. However, this produces source control and flux distribution problems (Ref 8). By moving the substrate farther away, the uniformity over a given area can be improved; however, the deposition rate is decreased. The most common technique to improve uniformity is to move the substrate in a random manner over the vapor source(s). Because the vaporization rate can change during the deposition process, the movement should sample each position a number of times during deposition. Often the substrates are rotated on a hemispherical fixture (calotte) with the evaporant source at the center of the sphere to give a constant r (see Eq 2). Specially designed movable masks can be used to provide specific thickness distributions over a surface (Ref 14, 15, 16), or the substrate movement can be controlled to give a specific film thickness distribution.

Surface Coverage. Because the deposition is line-of-sight, deposition on a rough or nonplanar surface can give geometrical shadowing effects resulting in nonuniform film thickness and variable film morphology. This is particularly a problem at sharp steps and at oblique angles of deposition. Figure 6 shows the effect of the angle of incidence in covering a surface having a particle on the surface. These geometrical problems can be alleviated by extended vaporization sources, multiple sources, or substrate movement.

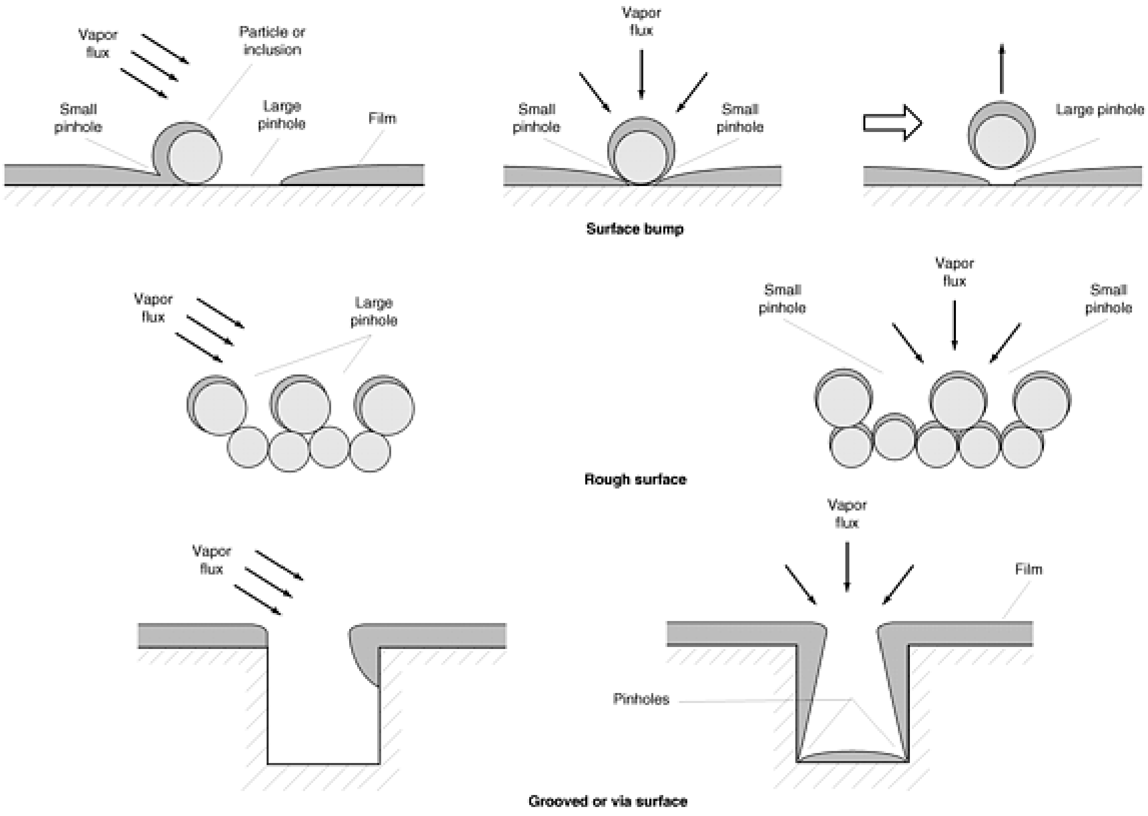

Fig. 6 Geometrical shadowing of the deposition flux by a particle on the surface relative to the angle of incidence and the surface morphology

Attempts to use gas scattering (that is, scatter plating, pressure plating, or gas plating) to randomize the flux distribution and improve the surface covering ability of evaporated films (Ref 17) have been singularly unsuccessful because of the poor density of the deposited material.

Additional information on condensation and growth is available in the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" in this Volume.

Deposition of Materials

Deposition of Elements. Elements are typically deposited by vaporization of the elemental material directly. The purity of the deposited film depends on the purity of the starting material and contaminant gases in the ambient.

Deposition of Alloys. Alloys can be deposited directly by the vaporization of the alloy material if the vapor pressures of the constituent are comparable. However, if the vapor pressures differ, the composition of the film will change as the deposition proceeds and the composition of the melt changes.

Rod-Fed Source. One technique for depositing a constant composition alloy film is to use a rod-fed electron beam evaporation source and to keep the temperature and volume of the molten pool constant. After an equilibration time, the composition of the vapor flux is the same as the composition of the material being melted, even though the composition of the molten pool is not the same as that of the bulk material (Ref 18, 19). Using this technique, alloys whose constituents vary in vapor pressure by as much as 10^3 are being deposited on aircraft engine turbine blades.

Sequential Layers. Alloy films can be formed by depositing alternating layers of the different materials from different sources. The layers are then diffused to form the alloy film. The alloy composition then depends on the relative amounts of materials in the films.

Multiple Sources. Alloy films can be deposited using multiple separate vaporization sources with individual deposition rate controllers. In this case, the vapor flux distribution from each source must be taken into account. The multiple source technique can also be used to deposit layered composite films (Ref 2, 20). Sources with overlapping flux distributions can be used to form films having a range of compositions over the substrate surface.

Flash Evaporation. A constant-composition alloy film can be deposited using flash evaporation techniques, where a small amount of the alloy material is periodically completely vaporized (Ref 2, 21, 22, 23). Flash evaporation uses a very hot surface and requires dropping a pellet or periodically touching a wire tip to the surface, so that the molten pellet or tip is completely vaporized.

Deposition of Compounds. When compounds are vaporized, some of the lighter fragments, such as oxygen, may be lost by scattering in the gas phase and by not reacting with the deposited material when it reaches the substrate. In the vaporization of SiO_2, this results in an oxygen-deficient SiO_{2-x} film that is yellowish in color. The composition of the deposited material is determined by the degree of dissociation, the loss of materials in the mass transport process, and the reaction coefficient of the reactive species at the film surface. The lost oxygen can be replaced by reactive deposition in an oxygen environment (see the section "Reactive Evaporation" in this article), or postdeposition heat treatments in oxygen (Ref 24).

In some cases, the state of reaction can be increased by concurrent bombardment with a reactive species from a plasma (activated reactive ion plating) (Ref 25) or an ion source (reactive ion beam assisted deposition). For example, SiO, which is easily evaporated, can be bombarded with oxygen ions to give $SiO_{1.8}$, which is of interest as a transparent, insulating, permeation-barrier coating on polymers for the packaging industry.

Graded Interfaces. When layered structures are deposited, the interface between the layers can be graded from one composition to the other by beginning the second deposition before the first is completed. This forms a "pseudo-diffusion" interface between the two layers and prevents possible contamination/reaction of the first layer by the ambient environment before the second layer begins depositing. Grading the interface between deposited films often provides better adhesion than abruptly changing from one material to another.

Vaporization Sources

Common heating techniques for evaporation/sublimation include resistive heating, high-energy electron beams, low-energy electron beams, and inductive (radio frequency) heating. Figures 7, 8(a), and 8(b) show some vaporization source configurations. Resistive heating is the most common technique for vaporizing materialat temperatures below about 1800 °C (3270 °F), while focused electron beams are most commonly used above 1800 °C (3270 °F).

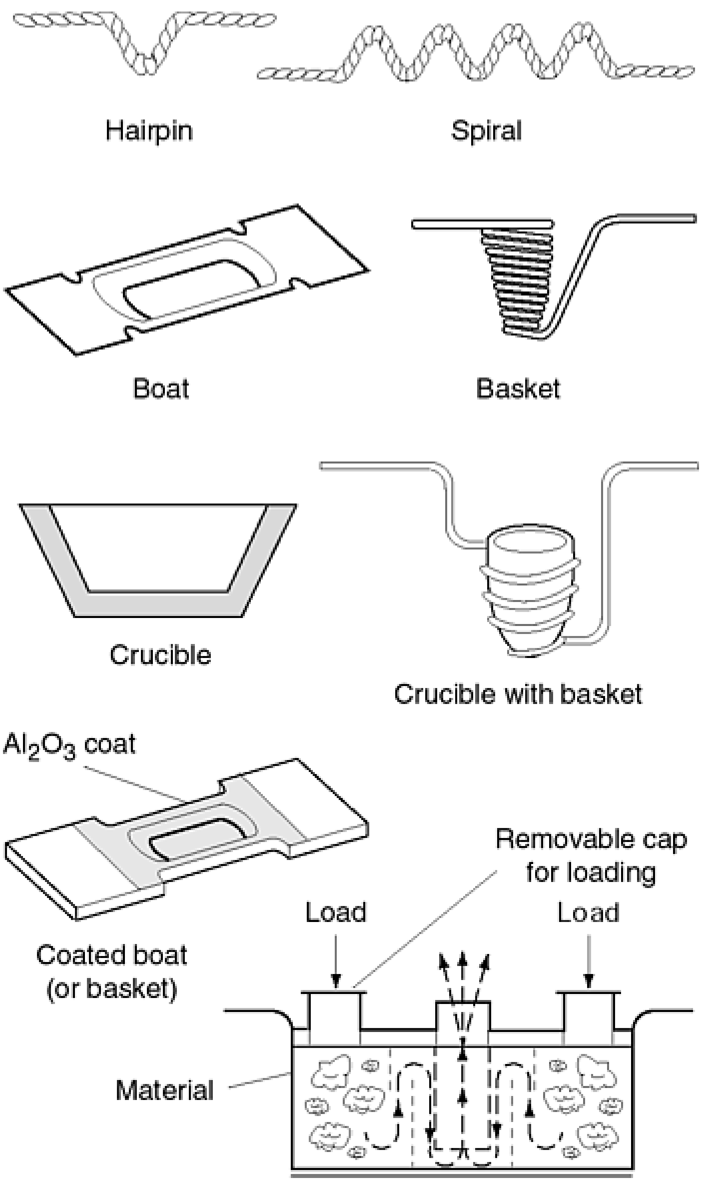

Fig. 7 Sources used for resistive heating of materials in evaporation processing

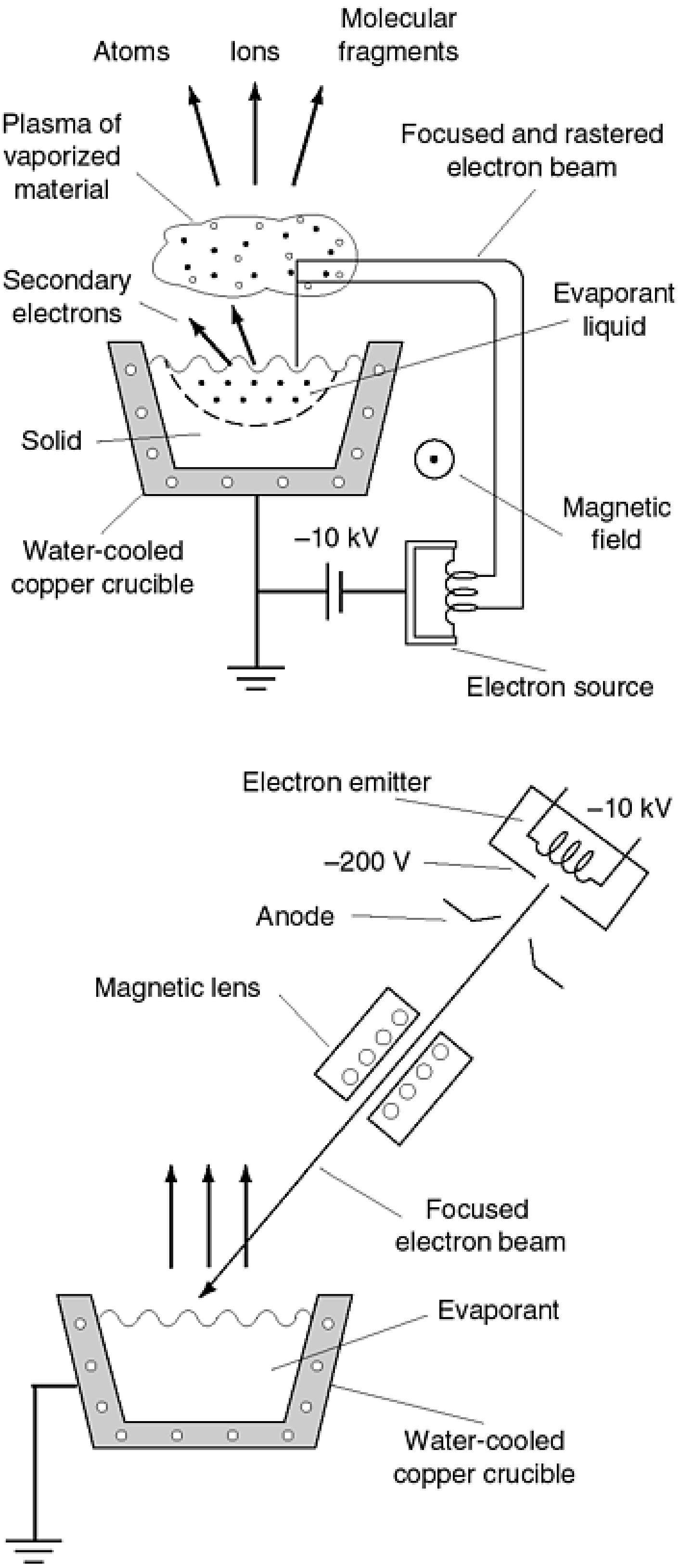

Fig. 8(a) Focused electron-beam sources used for evaporation processing. Bent-beam electron gun (top); long-focus gun (bottom)

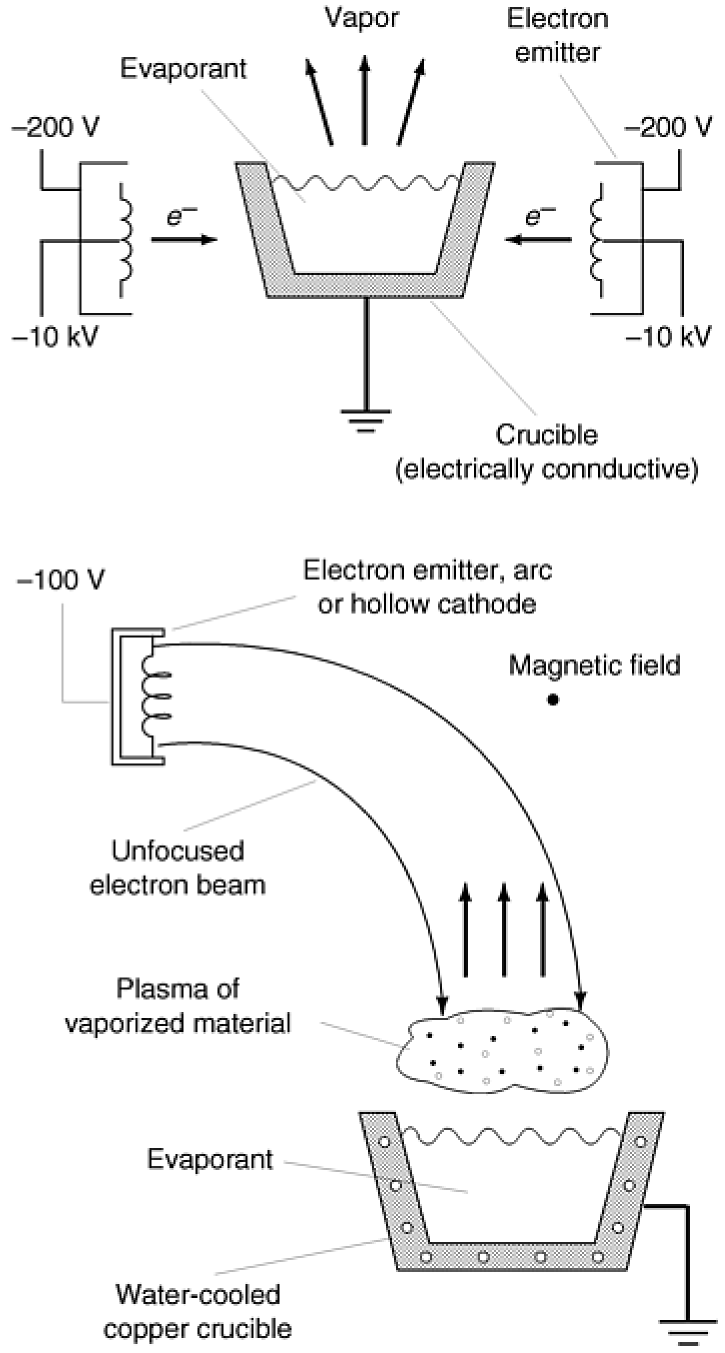

Fig. 8(b) Unfocused electron-beam sources used for evaporation processing. Work-accelerated gun (top); setup with magnetic confinement of electrons (bottom)

Resistive Heating. Resistively heated sources are the most widely used vaporization sources (Ref 26, 27). Typical conductive source materials are tungsten, tantalum, molybdenum, carbon, and BN/TiB_2 composite ceramics. Resistive heating of electrically conductive heater is typically by low voltage (<10 V), very high alternating current (several hundred amperes) transformer supplies. It is generally better to slowly increase the heater current than to suddenly turn on full heater power. Due to the low voltages used in resistive heating, contact resistance is an important factor in source design. As the temperature increases, thermal expansion causes the evaporator parts to move; this movement should be accounted for in the design of the heater fixturing. Because metals expand on heating, the contacting clamps between the fixture and the source may have to be water cooled to provide consistent clamping and contact resistance (Ref 27). Figure 7 shows some typical resistively heated source configurations. The resistively heated vaporization sources are typically operated near ground potential. If the sources are to be operated much above ground, filament isolation transformers must be used.

Electron-beam heating sources can be classified as being either focused or unfocused.

Focused, high-energy electron beams are necessary to provide local high temperatures when required for the evaporation of refractory materials, such as most ceramics, glasses, carbon, and refractory metals. This electron-beam heating is also useful for evaporating large quantities of materials. Graper has tabulated the electron-beam vaporization characteristics of a large number of materials (Ref 28). Figure 8(a) and 8(b) shows two sources that use focused electron-beam heating: the deflected electron gun and the long-focus gun (Fig. 8(a)).

With the deflected or bent-beam electron gun source, the high-energy electron beam is formed using a thermionic-emitting filament to generate the electrons, high voltages (typically 10 to 20 kV) to accelerate the electrons, and electric or magnetic fields to focus and deflect the beam (Ref 29, 30, 31). Electron-beam guns for evaporation typically require 10 to 50 kW of power. Using high power electron-beam sources, deposition rates as high as 50 μm/s (0.002 in./s) have been attained (Ref 32) from sources capable of vaporizing aluminum at rates of up to 10 to 15 kg/h (22 to 33 lb/h). Electron-beam evaporators can be made compatible with ultrahigh vacuum (UHV) processing (Ref 33). Electron-beam evaporators are typically built to deposit material in the vertical direction, but high-rate electron-beam source installations that deposit material in a horizontal direction are being used (Ref 34).

In many applications, the electron beam is magnetically deflected through greater than 180°, to avoid deposition of evaporated material on the filament insulators and to focus the beam onto the source material, which is contained in a water-cooled copper hearth "pocket". The electron beam can be rastered over the surface to produce heating over a large area. The electron bombardment produces secondary electrons that are magnetically deflected to ground. The high-energy electron bombardment also produces soft x-rays that can be detrimental to sensitive semiconductor devices (Ref 35, 36, 37). The electrons ionize a portion of the vaporized materials and these ionscan be used to monitor the evaporation rate. With the electron-beam evaporation of some materials (for example, beryllium), a significant number of ions are produced that can be accelerated to the substrate to modify the film microstructure (Ref 38).

Electron gun sources can have multiple pockets so that several materials can be evaporated. By moving the beam or the crucible, more than one material can be heated with the same electron source.

The long-focus gun uses electron optics to focus the electron beam on a surface that can be an appreciable distance from the electron emitter (Ref 32, 39). The optic axis is often a straight line from the emitter to the evaporant, and therefore the gun must be mounted off-axis from the source-substrate axis.

Unfocused, high-energy electron-beam heating can be accomplished with an electron source by applying a voltage between the electron emitter and the source material or source container, which is usually at ground potential (Fig. 8(b)). Such a source is referred to as a work-accelerated gun (Ref 40, 41). Magnetic confinement of the electrons along the emitter-source axis (Fig. 8(b)) can also be used to increase the electron path length and so increase the ionization probability (Ref 42, 43).

Unfocused, Low-Energy Electron-Beam Heating. High-current, low-energy electron beams can be produced by thermionic-emitting surfaces, plasma arcs (Ref 44), or hollow cathodes (Ref 45, 46, 47, 48, 49). They can be accelerated to several hundred volts and magnetically deflected onto the source, which is at ground potential. Low-energy electron beams are typically not very well focused, but they can have high current densities. The vaporization of a surface by the low-energy electron beam can provide appreciable ionization of the vaporized material because the vaporized atoms pass through a high-density, low-energy electron cloud as they leave the surface.

Electron-Beam Guns in a Plasma Environment. Electron-beam guns are not generally used in a plasma environment because of sputter erosion of the filament by positive ions. There are also problems with the reaction of the hot emitting filaments in reactive gases. In order to use an electron-beam evaporator in a plasma or reactive gas environment, the electron-emitter region can be differentially pumped by being isolated from the deposition environment. This is accomplished by having a septum between the differentially pumped electron-emitter chamber and the deposition chamber. This septum incorporates a small orifice for the electron beam to pass from one chamber to the other (Ref 50).

Inductive Heating. Inductive heating couples radio frequency (rf) energy directly into electrical conductors such as metals or carbon (Ref 51). The rf source can be used either to heat the source material directly or to heat the container ("susceptor") that holds the source material. This technique has been particularly useful in evaporating aluminum from boron nitride and BN/TiB_2 crucibles (Ref 52). When the source material is heated directly, the containing crucible can be cooled.

Evaporation sources must contain molten liquid without extensive reaction and prevent the molten liquid from falling from the heated surface. This is accomplished by having a wetted surface or by using a container (Ref 53). Commercial evaporation source manufacturers provide lists of recommended sources for various materials.

Wetted Sources. Wetting is desirable to obtain good thermal contact between the hot surface and the material being vaporized. Wetted sources are also useful for depositing downward, sideways, or from nonplanar surfaces. Metallic stranded wire, coils, and baskets are relatively cheap and can be used in many applications. Wires for evaporation are typically tungsten (Ref 2, 54, 55) but can be molybdenum or tantalum. Wire meshes and porous metals, through which the molten metals wet and wick by capillary action, can be used for large-area vaporization sources.

Wire and coil filaments have the often-frustrating property that the molten material runs to the low spots, where it can drop off. To help alleviate this problem, stranded wire is used to hold the molten material by capillary action. Bends or kinks can be put in the wire at selected points to collect the molten material, or coils of tantalum wire can be wrapped on the filament to hold the molten material at specific points.

Solid evaporants have poor thermal contact with the heater surface until they melt and wet the surface. To obtain wetting of the evaporant on the heater surface, it is often necessary to have a temperature in excess of that needed for a reasonable evaporation rate. When the material becomes molten and wets the surface, the vaporization rate is very high and can cause "spitting" as the molten evaporant spreads over the superheated surface. Refractory metals used for vaporization are covered with oxides, which volatilize at temperatures lower than the vaporization temperatures of many source materials. If film contamination by these oxides is to be avoided, the heater material should be cleaned before installation, shutters should be used, or the surface should be prewetted by the source material.

Premelting and wetting of the evaporant on the heater surface prior to the beginning of the deposition has several benefits:

- Good thermal contact can be established.
- There is volatilization of volatile impurities and contaminants from the evaporant and from the surface of the heater.
- Overheating of the heater surface is avoided, thereby minimizing spitting and radiant heating from the source.

Premelting can be done external to the deposition system if care is used in handling the source afterwards, to prevent surface contamination. Premelting can be done in the evaporator system by using shutters to prevent the deposition of undesirable material on the substrate before film deposition begins.

Crucible containers can hold large amounts of molten evaporant, but the vapor flux distribution changes as the level of the molten material changes. Electrically conductive crucibles can be heated resistively and are available in the form of boats, canoes, dimpled surfaces, crucibles, and so on (Ref 56). Typical refractory metals used for containers are tungsten, molybdenum, and tantalum, as well as refractory metal alloys such as TZM (titanium and zirconium added to molybdenum for improved high-temperature strength) and tungsten with 5 to 20% rhenium added for improved ductility. Metallic containers are often wetted by the molten material, and the material can spread to areas where it is not desired. This spreading can be prevented by having nonwetting areas on the surface. Such nonwetting areas can be formed by plasma spraying Al_2O_3 on the surface.

Commonly used crucible construction includes water-cooled copper, ceramics (both conductive and insulating), and glasses:

- *Water-cooled copper* is used as a crucible material when the evaporant materials are heated directly, as with electron-beam heating. The design of the coolant flow is important in high-rate evaporation from a copper crucible, because a great deal of heat must be dissipated (Ref 57). The water-cooled copper solidifies the molten material near the interface, forming a "skull" of the evaporant material so that the molten material is actually contained in a like material. This prevents reaction of the evaporant with the crucible material. On cooling, the evaporant "slug" shrinks and can be easily removed from the pocket of the electron-beam evaporator. In some cases, a liner can be used with a water-cooled crucible. Typical liner materials include pyrolytic graphite, pyrolytic boron nitride, BN/TiB_2, BeO, Al_2O_3, and other such materials. In general, the liner materials have poor thermal conductivity. This property, along with the poor thermal contact that the liner makes with the copper, allows the liner to heat significantly. Liners can be fabricated in special shapes to obtain specific characteristics (Ref 58).

- *Electrically conductive ceramics* can be used as containers. Carbon and glassy carbon are commonly used container materials, and when a carbon-reactive material is evaporated from such a container, a carbide skull forms that limits the reaction with the container. For example, titanium in a carbon crucible forms a titanium carbide skull. An electrically conductive composite ceramic that is used for evaporating aluminum is BN-50TiB_2 composite ceramic (known by the tradename UCAR) (Ref 59). This composite ceramic is stable in contact with molten aluminum, whereas most metals react rapidly with the molten aluminum at vaporization temperature.
- *Glasses and electrically insulating ceramics* can be used as crucibles and are often desirable because of their chemical inertness with many molten materials. Typical crucible ceramics are ThO_2, BeO, stabilized ZrO_2 (additions of HfO_2 and CaO to ZrO_2), Al_2O_3, MgO, BN, and fused silica. Kohl has written an extensive review of the oxide and nitride materials that may be of interest as crucible materials (Ref 60). The ceramics can be heated by conduction or radiation from a hot surface though these are very inefficient methods of heating. For more efficient heating, the material contained in the electrically insulating crucible can be heated directly by electron bombardment of the surface or by rf inductive heating from a surrounding coil. Isotopic boron nitride is a good crucible material for containing molten aluminum for rf heating because most other ceramics are attacked by molten aluminum. Metal sources, such as boats, can be coated with a ceramic (for example, plasma-sprayed Al_2O_3) in order to form a ceramic surface in contact with the molten material.

Feeding sources are sources where additional evaporant material is added to the molten pool without opening the processing chamber. Feeding sources can use pellets (Ref 61), powder, wires, tapes, or rods of the evaporant material. Pellet and powder feeding is often done with vibratory feeders, while wires and tapes are fed by friction and gear drives. Multiple wire-fed electron-beam evaporators are often aligned to give a line source for deposition in a web coater (Ref 62, 63). Rod feeds are often used with electron-beam evaporators where the end of the rod, whose side is cooled by radiation to a cold surface, acts as the crucible to hold the molten material (Ref 18). Feeding sources are used to deposit large amounts of material.

Baffle Sources. Some elements vaporize as clusters of atoms, and some compounds vaporize as clusters of molecules. Baffle sources are designed so that the vaporized material must undergo several evaporations from heated surfaces before it leaves the source, to ensure that the clusters are decomposed. Baffle sources can also be used to allow deposition downward from a molten material. Baffle sources are desirable when evaporating silicon monoxide or magnesium fluoride for optical coatings, to ensure the vaporization of monomolecular SiO or MgF_2. Drumheller made one of the first baffle sources, called a "chimney source," for the vaporization of SiO (Ref 64).

Focused vaporization sources can be used to confine the vapor flux to a beam. Focusing can be done using wetted curved surfaces or by using defining apertures. A beam-type evaporation source that uses apertures has been developed to allow the efficient deposition of gold on a small area (Ref 65). This source forms a $2\frac{1}{2}°$ beam of gold and gives a deposition rate of 4 nm/s (40 Å/s) at 50 mm (2 in.).

Confined vapor sources confine the vapor in a heated cavity and pass the substrate through the vapor. The vapor that is not deposited stays in the cavity. Such a source uses material very efficiently and can produce very high rates of deposition. For example, a wire can be coated by having a heated cavity source such that the wire is passed through a hole in the bottom and out through a hole in the top. By having a raised stem in the bottom of the crucible, the molten material can be confined in a doughnut-shaped melt away from the moving wire. The wire can be heated by passing a current through the wire as it moves through the crucible.

Porous Evaporation Sources. Porous materials and meshes can be used to evaporate materials that wet and wick through the material. Examples of such materials are porous tungsten, tungsten meshes, and porous ceramics. These types of sources are sometimes called *dispenser sources* and are similar to the electron-emitted cathodes in electronic devices (Ref 60).

Radiation shields can be used to surround the hot vaporization source to reduce radiant heat loss (Ref 56). Generally radiation shields consist of several layers of refractory metal sheet separated from each other and from the heated surface. These radiation shields:

- Reduce the power requirements of the source
- Reduce radiant heating from the source
- Allow the source to reach a higher temperature
- Have a more uniform temperature over a larger volume

Source Degradation. Vaporization sources can degrade with time due to reaction of the evaporant material with the heated surface. When there is reaction between the molten source material and the heater material, the vaporization should be done rapidly. For example, palladium, platinum, aluminum, iron, and titanium should be evaporated rapidly from tungsten heaters. When tungsten is used as the heater material, crystallization at high temperatures makes the tungsten brittle and causes microcracks, which create local hot spots that result in burnout. On burnout, the tungsten is vaporized and can contaminate the film. In general, it is better to replace tungsten wire heaters after each deposition if such contamination poses a problem. When large masses of material that have wet the surface are allowed to cool in brittle containers (crucibles or boats), the stresses can crack the container material.

Sublimation Sources. Vaporization from solid sources has the advantage that the vaporizing material does not melt and flow. Vaporization from a solid can be sublimation from a chunk or pellet, or sublimation from a solid composed of a subliming phase and a nonvaporizing phase (for example, Ag-50Li and Ta-25Ti alloy wire, known by the tradename KEMET). Heating can be by resistive heating, direct contact with a hot surface, radiant heating from a hot surface, or bombardment by electrons.

A problem with sublimation of a solid material from a heated surface is the poor thermal contact with the surface. This is particularly true if the evaporant can "jump around" due to system vibration during heating. Changing the source setup can often alleviate the problem (for example, changing from a boat to a basket source, eliminating mechanical vibration, using mesh "caps" on open-top sources, etc.). Direct electron-beam heating of the material is generally more desirable than contact heating for heating a subliming material.

Better thermal contact between the subliming material and the heater can be obtained when forming the material in contact with the heater by pressing powders around the heater or by electroplating the material onto the heater surface. Powder pressing generally produces a porous material that has appreciable outgassing. Chromium is often electrodeposited on a tungsten heater. Electroplated chromium has an appreciable amount of trapped hydrogen, and such a source should be heated slowly to allow outgassing of the material before deposition commences.

Exploding Wires. Flash evaporation can be accomplished by "exploding wire" techniques, where very high currents are pulsed through a small wire by the discharge of a capacitor (Ref 66). The majority of the vaporized material is in the form of molten globules. This technique has the interesting feature that the wire can be placed through a small hole and the vaporized material can be used to coat the inside of the hole.

Radiant Heating from the Source. The radiant energy, *E*, from a hot surface is given by:

$$E = \varepsilon T^4 A \qquad \textbf{(Eq 3)}$$

where ε is the emittance of the surface, *T* is the absolute temperature, and *A* is the area of emitting surface. Radiant energy heats all of the surfaces in the deposition chamber, leading to a rise in the substrate temperature, desorption of gases from surfaces, and surface creep of contaminants. Radiant heating of the substrate and interior surfaces can be minimized by:

- Using small heated areas (*A*)
- Using prewetted evaporant surfaces
- Using radiation shields
- Using shutters over the source until the vaporization rate is established
- Rapid vaporization of the source material onto the substrate

Some materials, such as gold, are good heat reflectors; as soon as a gold film is formed, a high percentage of the incident radiant heat is reflected from the coated surface. Some materials, such as silicon dioxide, do not adsorb infrared radiation very well and are not easily heated by radiation.

Spits and Comets. In the evaporation of materials from heated surfaces, "spits" and "comets" are often encountered. Spits are solidified globules of the source material found on the deposited film. When these poorly bonded globules are disturbed, they fall out, leaving large pinholes in the film. Comets are seen in the system during vaporization as the hot molten globules are ejected from the source.

Molten globules can originate from the molten material by any one of several processes. During heating, particularly rapid heating, gases and vapors in the molten source material agglomerate into bubbles and explode through the surface, giving spits. For example, silver can have a high content of dissolved oxygen and give spitting problems. The source of spits can be continual if new material is continually being added to the melt. Spits can be reduced by using pure vacuum-melted source material, handled and stored in an appropriate way, and by degassing the evaporant charge by premelting with slow heating to melting.

If the molten evaporant is held in a heated crucible, vapor bubbles can form on the crucible surfaces, where they grow and break loose. As the bubbles rise through the molten material, the hydrostatic pressure decreases and the bubbles grow in size. When the bubbles reach the surface they "explode," giving rise to globules of ejected molten material. Materials that have high vapor pressures at their melting points are more likely to give spits than materials that have low vapor pressures at their melting points. Spitting is common in boiling water; in high school chemistry, students are taught to add boiling beads to the water to reduce the violence and splashing. The same approach can be used to prevent spitting from molten material. For example, chunks of tantalum are placed in molten gold to prevent gold spits. The tantalum does not react with the gold and does not vaporize at the gold evaporation temperatures.

Spits from crucibles can be minimized by:

- Using source materials that are free of gases and high-vapor-pressure impurities
- Polishing the crucible surfaces so that bubbles do not stick well and break loose when they are small
- Using "boiling beads" in the molten material to prevent large bubbles from forming
- Using baffle-type sources so that the source material must be vaporized several times before the vapor leaves the source
- Using specially designed crucibles (Ref 58)
- Using electron-beam evaporation where the surface of the evaporant is heated
- Reducing source power if spitting occurs

Spits can also occur during melting and flowing of a material on a hot surface. A solid material placed on a surface has poor thermal contact with the surface, so the tendency is to heat the surface to a very high temperature. When the evaporant melts and spreads over the surface, the very hot surface creates vapor that "explodes" through the spreading molten material. This source of spits can be eliminated by premelting the charge on the surface, to give good thermal contact, and by using shutters in the system, to prevent the substrate from "seeing" the source until the molten charge has wetted the surface and is vaporizing uniformly.

Additional Vaporization Methods

Vaporization can also be produced by vacuum arc, laser, electric field, and polymer evaporation methods.

Vacuum Arc Vaporization. Arc vaporization was first reported by Robert Hare in 1839 and has been used to deposit carbon (Ref 67) and metal (Ref 68) films. Arc vaporization in vacuum occurs when a high-current, low-voltage arc passes between slightly separated electrodes in a vacuum, vaporizing the electrode surfaces and forming a plasma of the vaporized material (Ref 69, 70, 71, 72). In order to initiate the arc, a high voltage "trigger" arc is used. A high percentage of the vaporized material is ionized in the arc, and the ions are often multiply charged. A negative space charge is generated in the plasma, and the ions are accelerated away from the plasma to energies that are much higher than thermal energies. This means that the deposition is accompanied by concurrent bombardment from the high-energy film ions. This concurrent bombardment can have beneficial effects on the film density, as is found in ion plating.

If the arc anode is cooled or has a large area, vaporization primarily occurs from the solid cathode surface by arc erosion. At the present time,the principal arc vapor source in thin-film technology is the solid cathode. Problems with this deposition technique include stabilization and movement of the arc on the solid surface and the formation of globules of the ejected material. Arc confinement and controlled arc movement using magnetic fields have given rise to the "steered arc" source. The globules can be filtered from the arc using various means (for example, the "plasma duct") (Ref 73), all of which reduce the deposition rate. Carbon ions (500 eV) from a vacuum arc source have been used to deposit hydrogen-free, diamond-like carbon films (Ref 74).

If the anode is allowed to melt, material evaporates from the molten (consumable) anode surface. This vaporization technique is essentially the same as the vacuum-arc-remelting (VAR) process (Ref 75, 76). Some studies have been done using the vapor from the molten anode of a vacuum arc. This has the advantage that globules are formed to a lesser degree than in cathodic erosion (Ref 77, 78). A commercial source of metal ions from a vacuum arc is the metal vapor vacuum arc (MVVA) source (Ref 79).

Additional information is available in the article "Arc Deposition" in this Volume.

Globules. The number of globules produced from the cathode surface depends on the melting point of the cathode material and the arc movement. The distribution of globule emission is nonisotropic, with the maximum number being found at angles greater than 60° from the normal to the surface. The neutral atoms found in the arc vapor are thought to be produced by thermal evaporation from the ejected globules. This effect causes the composition of the deposited film to vary with thickness and position when an alloy material is deposited (Ref 80).

Laser Vaporization. Flash evaporation can also be done with pulsed laser heating of surfaces (Ref 81, 82). This technique is sometimes called laser ablation deposition (LAD) (Ref 83). Typically an excimer laser (yttrium-aluminum-garnet, or YAG, or argon-fluorine) is used to deposit energy in pulses. The YAG lasers typically deliver pulses (5 ns pulse length, 5 Hz frequency) with an energy of about 1 J/pulse (9×10^{-4} Btu/pulse), and the argon-fluorine lasers typically deliver pulses (20 ns, 50 Hz) with about 300 nJ/pulse (2.7×10^{-10} Btu/pulse). The vaporized material forms a plume above the surface, where some of the laser energy is adsorbed and ionization and excitation occur. In laser vaporization the ejected material is highly directed; this creates a problem with forming a uniform thickness over large areas. During vaporization molten globules are ejected, and these can be eliminated by using a velocity filter. Laser vaporization, combined with the passage of a high electrical current along the laser-ionization path to give heating and ionization, has been used to deposit hydrogen-free, diamond-like carbon films at an ablation energy density greater than 5×10^{14} W/m^2 (1.6×10^{14} Btu/ft^2 · h) (Ref 83). Laser vaporization with concurrent ion bombardment has been used to deposit a number of materials (Ref 84, 85), including high-quality, high-temperature superconductor oxide films (Ref 86), at low substrate temperatures. Laser vaporization can be used to vaporize material from a film on a transparent material onto a substrate facing the film, by shining the laser through the "backside" of the transparent material, vaporizing a controlled film area, and thus depositing a pattern directly onto the substrate (Ref 87).

Field Evaporation. Surface atoms of metals can be vaporized by a high electric field. This technique is known as field evaporation and can be directly observed in the field ion microscope (Ref 88). This vaporization technique is used to clean emitter tips in field ion microscopy and to form metal ions from liquid-metal-coated tips. Field evaporation has been used to directly deposit nanometer-size gold structures (Ref 89). The very sharp tips necessary to obtain the high field can be formed in a variety of ways (Ref 90).

Polymer Evaporation. Many monomers and polymers can be evaporated to produce thin organic films on a substrate surface. Some organics can be cross-linked in the vapor phase inside a heated furnace before condensing on the substrate surface (paralyene process) (Ref 91). Condensed polymers can be cross-linked on the surface by exposing them to an electron beam (Ref 92) or ultraviolet radiation (Ref 93).

Materials for Vaporization

Material placed in the vaporization source is called a *charge* and can be in the form of powder, chunks, wire, slugs, and so on. The desired purity of the source material depends on the application and the effect of purity on film properties and process reproducibility. It is possible to obtain some material with extremely high purity (>99.999%), although the cost increases rapidly with the purity level. Often impurities such as oxygen, nitrogen, carbon, and hydrogen are not specified by the supplier. They can be present in significant quantities as oxidized surfaces of reactive metals, hydrogen incorporated into electrorefined chromium, carbon monoxide in nickel purified by the carbonyl process, and helium in natural quartz. Generally, it is better to specify vacuum-melted materials from the supplier when possible. Very reactive metals should be nitrogen-packed in glass ampules to prevent oxidation, and the ampules should be opened and handled in an inert gas dry box where the reactive gas content is kept low by the use of getter materials such as liquid NaK [K:Na (20-50%)].

Careful specification of purity, allowable impurities, fabrication method, postfabrication treatments, and packaging of the source materials purchased is important to obtaining a reproducible process. Using inexpensive material or material of unknown origin often creates problems. Source material should be carefully cleaned and handled, because on heating, the impurities and surface contaminants are the first materials to be vaporized. The source and source material can be outgassed and premelted prior to film deposition.

Materials Utilization. Often material utilization in an evaporation process is poor unless proper fixturing and tooling is used to intercept the maximum amount of the flux. This can be accomplished by having the substrates as close as possible to the vaporization source, though this can result in excessive heating of the substrate during deposition. Deposition on large numbers of parts or over large areas can be done using large chambers with many (or large) vaporization sources.

Excess deposited material builds up on walls and fixtures and can flake off, producing particulate contamination in the processing chamber. The deposit buildup on surfaces also generates high surface areas that can absorb contaminants and are slow to desorb the contaminants. This results in changes in the pumping characteristics of the deposition system with use. It is desirable to have an easy way to collect and remove the excess evaporated material, and it can also be important to collect the excess material for reclamation. Excess evaporant can be collected by surrounding the source with a removable collector that defines the flux of evaporant to the substrate and collects excess evaporant. The chamber can have a removable liner to collect excess material, and the fixtures can be surrounded with panels or foil that can be easily removed.

References cited in this section

2. R. Glang, Vacuum Evaporation, Chapter 1, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, Ed., McGraw-Hill, 1970, p 1-26
3. R.E. Honig and H.G. Cook, "RCA Review 23," 1962, p 567
4. K.-G. Wagner, A Brief Review of Knudsen Cells for Application in Experimental Research, *Vacuum,* Vol 34 (No. 8/9), 1984, p 743
5. A. Beck, H. Jurgen, B. Bullemer, and I. Eisele, A New Effusion Cell Arrangement for Fast and Accurate Control of Material Evaporation under Vacuum Conditions, *J. Vac. Sci. Technol. A,* Vol 2 (No. 1), 1984, p 5
6. H.K. Pulker, Chapter 6, *Coatings on Glass,* Elsevier, 1984
7. E. Rutner, Some Limitations on the Use of the Langmuir and Knudsen Techniques for Determining Kinetics of Evaporation, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 149
8. J.A. Dobrowolski, M. Ranger, and R.L. Wilkerson, Measure the Angular Evaporation Characteristics of Sources, *J. Vac. Sci. Technol. A,* Vol 1, 1983, p 1403
9. V. Ruth and J.P. Hirth, The Angular Distribution of Vapor from a Knudsen Cell, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 99
10. A.D. Romig, A Time Dependent Regular Solution Model for the Thermal Evaporation of an Al-Mg Alloy, *J. Appl. Phys.,* Vol 62, 1987, p 503
11. S. Otani, T. Tanaka, and Y. Ishizawa, Evaporation from Molten TiC_x, *J. Mater. Sci.,* Vol 21, 1986, p 176
12. H. Fuchs and H. Gleiter, The Significance of the Impact Velocity of Vacuum-Deposited Atoms for the Structure of Thin Films, *Thin Films: The Relationship of Structure to Properties Symposium,* C.R. Aita and K.S. Sreeharsha, Ed., MRS Symp. Proc., Vol 47, MRS Publications, 1985, p 41
13. A.N. Pergellis, Evaporation and Sputtering Substrate Heating Dependence on Deposition Rate, *J. Vac. Sci. Technol. A,* Vol 7 (No. 1), 1989, p 27
14. J. Strong, *Procedures in Experimental Physics,* Prentice-Hall, 1938, p 183
15. K.H. Behrndt, Films of Uniform Thickness from a Point Source, *Trans. 9th AVS Symposium,* Macmillan,

1962, p 111

16. I.J. Hodgkinson, Vacuum-Deposited Thin Films with Specific Thickness Profiles, *Vacuum,* Vol 28, 1978, p 179
17. K.D. Kennedy, G.R. Scheuermann, and H.R. Smith, Jr., Gas Scattering and Ion Plating Deposition Methods, *R&D Mag.,* Vol 22 (No. 11), 1971, p 40
18. R. Nimmagadda, A.C. Raghuram, and R.F. Bunshah, Preparation of Alloy Deposits by Electron Beam Evaporation from a Single Rod-Fed Source, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1406
19. D.H. Boone, S. Shen, and R.M. McKoon, Electron Beam Evaporation of Low Vapor Pressure Elements in the M-Cr-Al Coatings Compositions, *Thin Solid Films,* Vol 63, 1979, p 299
20. H.Q. Yang, H.K. Wong, J.Q. Zheng, and J.B. Ketterson, Dual Electron Beam Evaporator for the Preparation of Composition-Modulated Structures, *J. Vac. Sci. Technol. A,* Vol 2 (No. 1), 1984, p 1
21. T. Strahl, Flash Evaporation--An Alternative to Magnetron Sputtering in the Production of High-Quality Aluminum-Alloy Films, *Solid State Technol.,* Vol 21 (No. 12), Dec 1978, p 78
22. F. Jansen, The Flash Evaporation of Low Melting Point Materials, *J. Vac. Sci. Technol.,* Vol 21 (No. 1), 1982, p 106
23. G. Adachi, H. Sakaguchi, K. Niki, N. Naga, and J. Shimokawa, Preparation of $LaNi_5$ Films and Their Electrical Properties under a Hydrogen Atmosphere, *J. Less-Common Met.,* Vol 108, 1985, p 107
24. A. Gupta, P. Gupta, and V.K. Srivasteva, Annealing Effects in Indium Oxide Films Prepared by Reactive Evaporation, *Thin Solid Films,* Vol 123, 1985, p 325
25. E. Moll, R. Buhl, H.K. Pulker, and E. Bergmann, Activated Reactive Ion Plating (ARIP), *Surf. Coat. Technol.,* Vol 39/40 (No. 1-3), 1990, p 475
26. L. Watts, 20 Years of Resistant Source Development, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 118
27. B. Ruisinger and B. Mossner, Evaporation Boats--Properties, Requirements, Handling, and Future Development, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 335
28. E.B. Graper, Evaporation Characteristics of Materials from an Electron Beam Gun II, *J. Vac. Sci. Technol. A,* Vol 5 (No. 4), 1987, p 2718
29. R.A. Denton and A.D. Greene, in *Proc. 5th Electron Beam Symp.,* Alloyd Electronics Corp., 1963, p 180
30. J. Knall, J.-E. Sundgren, L.C. Market, A. Rockett, and J.E. Greene, Influence of the Si Evaporation Sources on the Incorporation of In During Si Molecular-Beam Epitaxy Growth: Comparative Study of Magnetically and Electrostatically Focused Electron-Gun Evaporators, *J. Vac. Sci. Technol. B,* Vol 7 (No. 2), 1989, p 204
31. S. Schiller, U. Heisig, and S. Panzer, *Electron Beam Technology,* Wiley, 1982
32. S. Schiller and J. Jusch, Deposition by Electron Beam Evaporation with Rates of up to 50 Microns s^{-1}, *Thin Solid Films,* Vol 54, 1978, p 9
33. M. Heilblum, J. Bloch, and J.J. O'Sullivan, Electron-Gun Evaporators of Refractory Metals Compatible with Molecular Beam Epitaxy, *J. Vac. Sci. Technol. A,* Vol 3, 1985, p 1885
34. H.R. Smith, Jr., High Rate Horizontally Emitting Electron Beam Vapor Source, *Society of Vacuum Coaters 21st Annual Technical Symposium Proceedings,* 1978, p 49
35. T.H. Ning, Electron Trapping in SiO_2 due to Electron-Beam Deposition of Aluminum, *J. Appl. Phys.,* Vol 49, 1978, p 4077
36. D.R. Collins and C.T. Sah, Effect of X-Ray Irradiation on the Characteristics of the Metal-Oxide Silicon Structure, *Appl. Phys. Lett.,* Vol 8, 1966, p 124
37. J.R. Davis, *Instabilities in MOS Devices,* Gordon and Breach, 1981, p 74
38. R.F. Bunshah and R.S. Juntz, The Influence of Ion Bombardment on the Microstructure of Thick Deposits Produced by High Rate Physical Vapor Deposition Processes, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1404
39. J.R. Pierce, *Theory and Design of Electron Beams,* D. Van Nostrand, 1954
40. K.L. Chopra and M.R. Randlett, Modular Electron Beam Sources for Thin Film Deposition, *Rev. Sci. Instr.,* Vol 37, 1966, p 1421

41. J.R. Waldrop and R.W. Grant, Simple Evaporator for Refractory Metal Thin Film Deposition in Ultrahigh Vacuum, *J. Vac. Sci. Technol. A,* Vol 1, 1983, p 1553
42. H. Kaufmann, "Method of Depositing Hard Wear-Resistant Coatings on Substrates," U.S. Patent 4,346,123, 24 Aug 1982
43. H.K. Pulker, "Methods of Producing Gold-Color Coatings," U.S. Patent 4,254,159, 3 Mar 1981
44. J.R. Morley and H.R. Smith, High Rate Ion Production for Vacuum Deposition, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1377
45. Y.S. Kuo, R.F. Bunshah, and D. Okrent, Hot Hollow Cathode and Its Application in Vacuum Coating: A Concise Review, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1983, p 397
46. C. Schalansky, Z.A. Munir, and D.L. Walmsley, An Investigation on the Bonding of Hot-Hollow Cathode Deposited Silver Layers on Type 304 Stainless Steel, *J. Mater. Sci.,* Vol 22, 1987, p 745
47. H.R. Kaufman and R.S. Robinson, Broad-Beam Electron Source, *J. Vac. Sci. Technol. A,* Vol 3 (No. 4), 1985, p 1774
48. C.M. Horwitz, Hollow Cathode Etching and Deposition, Chapter 12, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Noyes Publications, 1989
49. J.J. Rocca, J.D. Meyer, M.R. Farrell, and G.J. Collins, Glow-Discharge-Created Electron Beams: Cathode Materials, Electron Gun Designs and Technological Applications, *J. Appl. Phys.,* Vol 56 (No. 3), 1984, p 790
50. D.L. Chambers and D.C. Carmichael, Development of Processing Parameters and Electron-Beam Techniques for Ion Plating, *Society of Vacuum Coaters 14th Ann. Tech. Conf. Proc.,* 1971, p 13
51. F.W. Curtis, *High Frequency Induction Heating,* Lindsay Publications reprint, 1990
52. I. Ames, L.H. Kaplan, and P.A. Roland, Crucible Type Evaporation Source for Aluminum, *Rev. Sci. Instr.,* Vol 37, 1966, p 1737
53. K.H. Behrndt, in *Techniques of Materials Research,* Vol I, Pt. 3, R.F. Bunshah, Ed., Interscience, 1968, p 1225
54. P. Dixit and R.W. Vook, A Highly Efficient Source for Vapor Deposition of Platinum, *Thin Solid Films,* Vol 110, 1983, p L133
55. J.L. Walter and C.L. Briant, Tungsten Wire for Incandescent Lamps, *J. Mater. Res.,* Vol 5 (No. 9), 1990, p 2004
56. J.A. Dobrowolski, A. Waldorf, and R.A. Wilkinson, A Practical High Capacity, High Evaporation Rate Resistance-Heated Source, *J. Vac. Sci. Technol.,* Vol 21, 1982, p 881
57. G. Crumley, Improved Cooling for an Electron Beam Crucible, *Society of Vacuum Coaters 33rd Ann. Tech. Conf. Proc.,* 1990, p 29
58. M.L. Rappaport and B. Berkovitz, A Graphite Crucible for Splitting-Free High Rate e-gun Evaporation of Ge, *J. Vac. Sci. Technol.,* Vol 21, 1982, p 102
59. H.J. Wilder, Application of Intermetallic Evaporation Sources, *Society of Vacuum Coaters 25th Ann. Tech. Symp. Proc.,* 1982, p 103
60. W.H. Kohl, Ceramics, Chapter 2, *Handbook of Materials and Techniques for Vacuum Devices,* Reinhold, 1967
61. N.B. Brennan, T. Pilkington, N.M. Samin, and A. Matthews, A Pellet Feeder for Pulsed Evaporation, *Vacuum,* Vol 34, 1984, p 805
62. K.A. Taylor and E.G. Ferrari, Design of Metallization Equipment for Web Coating, *Thin Solid Films,* Vol 109, 1983, p 295
63. F. Casey, Recent Advances in Source Design in Resistive Evaporation Web Coaters, in *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 124
64. C.E. Drumheller, Silicon Monoxide Evaporation Techniques, *Trans. 7th AVS Symp.,* Pergamon Press, 1960, p 306
65. R.J. Ney, Nozzle Beam Evaporant Source, *J. Vac. Sci. Technol. A,* Vol 1 (No. 1), 1983, p 55

66. D.M. Mattox, A.W. Mullendore, and F.N. Rebarchik, Film Deposition by Exploding Wires, *J. Vac. Sci. Technol.,* Vol 4, 1967, p 123
67. B.J. Massey, Production of Self-Supporting Carbon Films, *Trans. 8th AVS Nat. Symp.,* 1962, p 922
68. M.S.P. Lucas, C.R. Vail, W.C. Stewart, and H.A. Owen, A New Deposition Technique for Refractory Metal Films, *Trans. 8th AVS Nat. Symp.,* 1962, p 988
69. D. Sanders, Vacuum Arc-Based Processing, Chapter 18, *Handbook of Plasma Processing Technology,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
70. D.M. Sanders, A Review of Ion-Based Coating Processes Derived from Cathodic Arc, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 2339
71. R.L. Boxman and S. Goldsmith, Cathode-Spot Arc Coating: Physics, Deposition and Heating Rates and Some Examples, *Surf. Coat. Technol.,* Vol 33, 1987, p 153
72. R.L. Boxman and S. Goldsmith, Characterization of a 1 kA Vacuum Arc Plasma Gun for Use as a Metal Vapor Deposition Source, *Surf. Coat. Technol.,* Vol 44, 1990, p 1024
73. P.J. Martin, R.P. Netterfield, and T.J. Kinder, Ion-Beam-Deposited Films Produced by Filtered Arc Evaporation, *Thin Solid Films,* Vol 193/194, 1990, p 77
74. J.-P. Hirvonen, R. Lappalainen, J. Koskinen, A. Anttila, T.R. Jervis, and M. Trkula, Tribological Properties of Diamond-Like Films Deposited with an Arc-Discharge Method, *J. Mater. Res.,* Vol 5 (No. 11), 1990, p 2524 (This journal issue is largely devoted to diamond films.)
75. F.J. Zanner and L.A. Bertam, Vacuum Arc Remelting--An Overview, in *Proc. 8th Int. Conf. Vacuum Metallurgy,* Vol I, 1985, p 512
76. F.J. Zanner, Metal Transfer during Consumable Arc Remelting, *Metall. Trans. B,* Vol 10, 1979, p 133
77. H. Ehrich, B. Hasse, M. Mausbach, and K.G. Muller, The Anodic Vacuum Arc and Its Application to Coating, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 2160
78. H. Ehrich, B. Hasse, M. Mausbach, and K.G. Muller, Plasma Deposition of Thin Films Utilizing the Anodic Vacuum Arc, *IEEE Trans. Plas. Sci.,* Vol 18 (No. 6), 1990, p 895
79. B.L. Gehman, G.D. Magnuson, J.F. Tooker, J.R. Treglio, and J.P. Williams, High Throughput Metal-Ion Implantation System, *Surf. Coat. Technol.,* Vol 41 (No. 3), 1990, p 389
80. D.M. Poirier and P.A. Lindfors, Non-Isotropic Deposition from a 304 Stainless Steel Cathodic Arc Source, *J. Vac. Sci. Technol. A,* Vol 9 (No. 2), 1991, p 278
81. H.M. Smith and A.F. Turner, Vacuum Deposited Thin Films Using a Ruby Laser, *Appl. Optics,* Vol 4, 1965, p 147
82. J. Cheung and J. Horwitz, Pulsed Laser Deposition History and Laser-Target Interactions, *MRS Bull.,* Vol 17 (No. 2), 1992, p 30 (This issue is devoted to laser deposition.)
83. D.C. Paine and J.C. Bravman, Ed., *Laser Ablation for Material Synthesis,* MRS Proc., Vol 191, MRS Publications, 1990
84. *Laser Assisted Deposition, Etching and Doping,* SPIE, Vol 459, 1984
85. J.T. Cheung and H. Sankur, Growth of Thin Films by Laser-Induced Evaporation, *Crit. Rev. Solid State/Material Sci.,* Vol 15, 1988, p 63
86. A. Kumar, L. Ganapath, P. Chow, and J. Narayan, In-Situ Processing of Textured Superconducting Thin Films of Bi(-Pb)-Ca-Sr-Cu-O by Excimer Laser Ablation, *Appl. Phys. Lett.,* Vol 56 (No. 20), 1990, p 2034
87. T. Bohandy, B.F. Kim, and F.J. Adrian, Metal Deposition from a Supported Metal Film Using an Excimer Laser, *J. Appl. Phys.,* Vol 60, 1986, p 1538
88. M. Wada, On the Thermally Activated Field Evaporation of Surface Atoms, *Surf. Sci.,* Vol 145, 1984, p 451
89. H.J. Mamin, S. Chiang, H. Birk, P.H. Guenther, and D. Rugar, Gold Deposition from a Scanning Tunneling Microscope Tip, *J. Vac. Sci. Technol. B,* Vol 9 (No. 2), 1991, p 1398
90. A.J. Melmed, The Art and Science and Other Aspects of Making Sharp Tips, *J. Vac. Sci. Technol. B,* Vol 9 (No. 2), 1991, p 601
91. R.A. Olsen, The Application of Thin, Vacuum-Deposited Poly Parxylyene to Provide Corrosion Protection for Thin Porous Inorganic Films, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 317

92. D.G. Shaw, A New High Speed Vapor Deposition Process, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 180
93. R.T. Lake, Ultraviolet Curing of Organic Coatings, *Society of Vacuum Coaters 25th Ann. Tech. Symp.,* 1982, p 87

Reactive Evaporation

Films of compounds can be deposited by reactive deposition, in which the elemental constituents of the compound are vaporized and codeposited, or in which the deposited material reacts with a reactive gaseous ambient on the surface of the depositing film. Most reactive deposition involves a condensible species (that is, titanium, zirconium, or aluminum) and a gaseous species (O_2, N_2), although some compounds of two or more condensible species can be deposited (for example, titanium and carbon). When codepositing two reactive species, obtaining the correct composition is often difficult, because the relative fluxes must be carefully controlled and generally the substrate temperature must be high to ensure reaction (for example, TiC from titanium plus carbon).

In reactive evaporation the reactive gas is in its natural (that is, molecular) state (Ref 94, 95, 96). This technique generally requires that there be many more reactive gas molecules striking the depositing film than are needed for forming the compound, because the reaction coefficient is generally much less than one.

Activated Reactive Evaporation. If the reactive gas is "activated" by forming new molecular species (that is, ions, radicals, and excited species), the reactive deposition process is termed activated reactive evaporation (ARE) (Ref 97, 98, 99, 100). Because the reactive gas is activated, the gas density needed for reaction is less than that needed for reactive evaporation. The reactive gas can be activated by a plasma (Fig. 9), thermal decomposition, photoadsorption, or some other means. The use of atomic or radical beams of the reactive gas, directed toward the depositing material during deposition, allows reactive deposition to take place at a relatively low chamber pressure. An example of activated reactive evaporation that does not use a plasma is the deposition of a thin layer of titanium nitride to reduce secondary electron emission, by evaporating titanium in ammonia where the ammonia is decomposed by the hot evaporating filament to provide reactive nitrogen radicals (Ref 101).

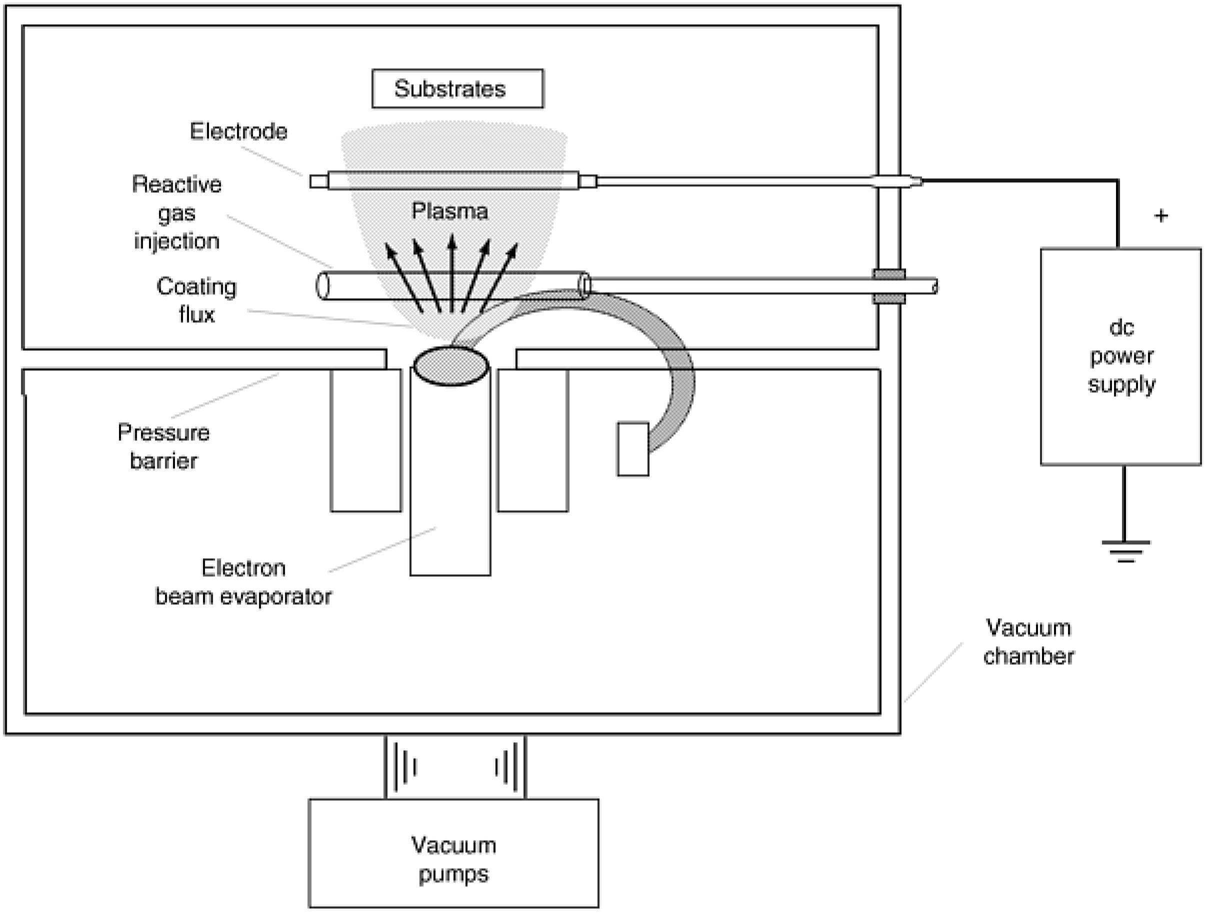

Fig. 9 Schematic of the activated reactive evaporation process using an electron-beam gun as an evaporation source. Source: Ref 99

In reactive evaporation, the interface can be graded by controlling the availability of the reactive gas. For example, in depositing titanium nitride the material can be graded from titanium to titanium nitride by controlling the availability of the nitrogen. Reactive evaporation can be used to form compounds when the evaporant is another compound. For example, cubic boron nitride (CBN) has been formed by the evaporation of H_3BO_3 in a plasma of NH_3 (Ref 102).

References cited in this section

94. E. Ritter, Deposition of Oxide Films by Reactive Evaporation, *J. Vac. Sci. Technol.,* Vol 3, 1966, p 225
95. L. Holland, Substrate Treatment and Film Deposition in Ionized and Reactive Gases (Invited review), *Thin Solid Films,* Vol 27, 1975, p 185
96. Martin, R.P. Netterfield, and W.G. Sainty, Optical Properties of TiN_x Produced by Reactive Evaporation and Reactive Ion Beam Sputtering, *Vacuum,* Vol 32, 1982, p 359
97. W. Heitmann, Reactive Evaporation in Ionized Gases, *Appl. Opt.,* Vol 10, 1971, p 2414
98. R.F. Bunshah and A.C. Raghurm, Activated Reactive Evaporation Process for High Rate Deposition of Compounds, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1385
99. C.V. Deshpandey and R.F. Bunshah, The Activated Reactive Evaporation (ARE) Process, Chapter 15, *Handbook of Plasma Processing Technology Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
100. R.F. Bunshah and C. Deshpandey, The Activated Reactive Evaporation Process, *Physics of Thin Films,* Vol 13, 1987, p 59
101. R.J. Greiggs and W.D. Cornelius, Titanium Nitridation of Metallic Surfaces, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 2515
102. K.L. Chopra, V. Agarwal, V.D. Vankar, C.V. Deshpandey, and R.F. Bunshah, Synthesis of Cubic Boron Films by Reactive Evaporation of H_3BO_3, *Thin Solid Films,* Vol 126, 1985, p 307

Additional Evaporative Vacuum Deposition Techniques

Other deposition processes that use the vacuum environment to control contamination and provide a long mean free path for vaporized material can be defined as *vacuum deposition* processes:

- Molecular beam epitaxy
- Ionized cluster beam deposition
- Ion beam sputter deposition
- Jet vapor deposition

Molecular Beam Epitaxy. Probably the most sophisticated vacuum deposition system/process is that used for molecular beam epitaxy (MBE), or vapor phase epitaxy (VPE) (Ref 103). Molecular beam epitaxy is used to form epitaxial films of semiconductor materials. A vacuum environment of better than 0.13 μPa (10^{-9} torr) is used to deposit atoms from carefully rate-controlled vapor sources (Knudsen-type sources) (Ref 9). The MBE deposition chamber can also contain a wide range of analytical instruments for in situ analysis of the growing film. These analytical techniques include methods for measuring crystal parameters, such as reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED).

Gaseous or vaporized metal-organic compounds can also be used as the source of film material in MBE. The molecular species are decomposed on the hot substrate surface to provide the film material. The use of metal-organic precursor chemicals is called metal-organic molecular beam epitaxy (MOMBE) (Ref 104). MOMBE is used in low-temperature formation of compound semiconductors with low defect concentrations.

Ionized Cluster Beam Deposition. Clusters of atoms (approximately 1000) can be charged and accelerated to such high velocities that the average kinetic energy of the depositing atom is greater than that associated with thermal vaporization. This is the basis of the ionized cluster beam (ICB) deposition process (Ref 105, 106). There is some controversy about how and if clusters are formed and what actually happens at the surface in this deposition process (Ref 107, 108, 109). There are numerous technical papers detailing the advantages of the ICB deposition process in forming epitaxial films at low temperatures that are defect free, have good adhesion, and have good surface coverage.

Ion-Beam Sputter Deposition. Ion guns can be used to sputter deposit films in a vacuum environment (Ref 110). This technique has limited applications because high-energy neutrals reflected from the sputtering target can bombard the growing film during deposition, giving rise to uncontrolled film property variations.

Jet Vapor Deposition. In the "jet vapor deposition" process, evaporated atoms/molecules are "seeded" in a supersonic jet flow of inert carrier gas into a rapidly pumped vacuum chamber (Ref 111, 112). The jet transports the atoms/molecules to the substrate surface, where they are deposited. The vapor source can be in the form of thermal evaporation or sputtering and is located in the jet nozzle. The deposition chamber pressure is about 130 Pa (1 torr) and is pumped using high-capacity mechanical pumps.

References cited in this section

9. V. Ruth and J.P. Hirth, The Angular Distribution of Vapor from a Knudsen Cell, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 99
103. P. Chow, Molecular Beam Epitaxy, Chapter II-3, *Thin Films Processes II,* J.L. Vossen and W. Kern, Ed., Academic Press
104. L.M. Fraas, P.S. McLeod, L.D. Partain, and J.A. Cape, Epitaxial Growth from Organometallic Sources in High Vacuum, *J. Vac. Sci. Technol. B,* Vol 4, 1986, p 22
105. T. Takagi, *Ionized-Cluster Beam Deposition and Epitaxy,* Noyes Publications, 1988
106. I. Yamada, Ionized Cluster Beam (ICB) Deposition Techniques, Chapter 14, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 356
107. F.K. Urban and A. Bernstein, Formation of Gold Clusters in Ionized Cluster Beam Deposition Technique, *Thin Solid Films,* Vol 193/194, 1990, p 92
108. F.K. Urban, Effects of Space Charge on Ion Energy in Ionized Cluster Beam Film Deposition Technique, Paper TF-WeP11 in 38th National AVS Symp., to be published in *J. Vac. Sci. Technol.*
109. W. Knauer, Formation of Large Metal Clusters by Surface Nucleation, *J. Appl. Phys.,* Vol 62, 1987, p 841
110. J.M.E. Harper, Ion Beam Deposition, Chapter II-4, *Thin Film Processes,* J.L. Vossen and W. Kern, Academic Press, 1978
111. J.J. Schmitt, "Method and Apparatus for the Deposition of Solid Films of Material from a Jet Stream Entraining the Gaseous Phase of Said Material," U.S. Patent No. 4,788,082, 29 Nov 1988
112. B.L. Halpern, J.J. Schnidtt, J.W. Golz, Y. Di, and D.L. Johnson, Gas Jet Deposition of Thin Films, *Appl. Surf. Sci.,* Vol 48/49, 1991, p 19

Advantages and Limitations of Vacuum Deposition Processes

Vacuum deposition has advantages and limitations relative to other physical vapor deposition (PVD) techniques.

Advantages of vacuum deposition include:

- Line-of-sight deposition allows the use of masks to define the area of deposition.
- Large-area sources can be used for some materials (for example, "hog trough" boat crucibles for aluminum and zinc).

- High deposition rates can be obtained.
- Deposition rate monitoring is relatively easy.
- Vaporization source material can be in many forms (for example, chunks, powder, wire, chips, and so on).
- Vaporization source material of high purity is relatively inexpensive.
- High-purity films are easily deposited from high-purity source material, because the deposition ambient can be made as noncontaminating as required.
- The technique is relatively inexpensive compared to other PVD techniques.

Limitations of vacuum deposition include:

- Line-of-sight deposition gives poor surface coverage, thus requiring elaborate tooling and fixturing.
- Line-of-sight deposition prevents uniform deposits over a large surface area unless complex fixturing and tooling are available.
- Deposition of many alloys and compounds is difficult.
- Capital equipment costs are high relative to those of other deposition techniques (for example, electroplating).
- High radiant heat loads are required during processing.
- Vaporized material is used inefficiently.
- Film properties are suboptimal (typical defects include pinholes, less than bulk density, columnar morphology, high residual film stress, and so on).
- Few processing parameters are available to control film properties.

Vacuum Deposition Applications

Applications of evaporation processes include:

- Electrically conductive coatings for ceramic metallization (for example, Ti-Au, Ti-Pd-Au, Al, Al-Cu-Si, Cr-Au, Ti-Ag), semiconductor metallization (for example, Al-2Cu on silicon), and metallization of capacitor foils (for example, zinc and aluminum)
- Optical coatings for reflective, antireflective, and abrasion-resistant topcoat (for example, SiO, MgF_2) applications
- Decorative coatings (for example, aluminum and gold)
- Moisture and oxygen permeation barriers for packaging materials (for example, aluminum and $SiO_{1.8}$ on polymer webs)
- Corrosion resistance (for example, aluminum on steel)
- Insulating layers for microelectronics (Ref 113)
- Coating of engine turbine blades (M-CrAl alloys) (Ref 19, 114, 115)
- Avoiding the pollution problems associated with electroplating (that is, "dry processing")
- Vacuum plating of high-strength steels to avoid the hydrogen embrittlement associated with electroplating (for example, cadmium on steel, or "vacuum cad plating")

Freestanding Structures. Evaporation processes can be used to form freestanding structures by depositing the film on an appropriately shaped mandrel. On the mandrel, either there is a "parting layer" (for example, evaporated NaCl) or the surfaces may be nonadhering (for example, copper on the oxide on stainless steel). In some cases, the mandrel must be dissolved to release the deposited form. This technique is used to fabricate thin-wall structures and windows (Ref 116).

Multilayer Structures. Many applications of evaporation processes require deposition of layered structures. These applications range from simple two- to three-layer metallization systems to x-ray diffraction gratings that consist of alternating low-mass material (carbon) and high-mass material (tungsten) and form a stack of thousands of layers with each layer only 3 to 4 nm (30 to 40 Å) thick.

References cited in this section

19. D.H. Boone, S. Shen, and R.M. McKoon, Electron Beam Evaporation of Low Vapor Pressure Elements in the M-Cr-Al Coatings Compositions, *Thin Solid Films,* Vol 63, 1979, p 299
113. H. Oetzmann, N.-J. Krokoszinski, H. Gernoth, and C. Schmidt, Evaporated Insulating Layers for Thin Film Circuits, *Thin Solid Films,* Vol 140, 1986, p 209
114. D.H. Boone, T.E. Strangman, and L.W. Wilson, Some Effects of Structure and Composition on the Properties of Electron Beam Vapor Deposited Coatings for Gas Turbine Superalloys, *J. Vac. Sci. Technol.,* Vol 11, 1974, p 641
115. H. Lämmermann and G. Kienel, PVD Coatings for Aircraft Turbine Blades, *Adv. Mater. Proc.,* Dec 1991, p 18-23
116. A.H.F. Muggleton, Deposition Techniques for Preparation of Thin Film Nuclear Targets: Invited Review, *Vacuum,* Vol 37, 1987, p 785

Gas Evaporation and Ultrafine Particles

Vapor phase nucleation can occur in a dense vapor cloud by multibody collisions. The nucleation can be encouraged by passing the atoms to be nucleated through a gas to provide the necessary collisions and cooling for nucleation. These particles have a size range of 1 to 100 nm (10 to 1000 Å) and are called *ultrafine particles* or *ultrafine clusters*. The process of forming the particles is called *gas evaporation* (Ref 117, 118, 119). The size and size distribution of the particles depend on the gas density, the gas species, the evaporation rate, and the geometry of the system. When these particles deposit on a surface the resulting film is very porous and can be used as an optical radiation trap; for example, "black gold" infrared radiation bolometer films, germanium film solar absorber coatings (Ref 120) and low secondary electron emission surfaces (Ref 121). The particles themselves are used for various powder metallurgical processes, such as low-pressure, low-temperature sintering (Ref 122). Ultrafine particles of reactive materials are very pyrophoric because of their high surface area.

Evaporation into a plasma causes the ultrafine particles to have a negative charge and to be suspended in the plasma near walls where they can grow to appreciable size (Ref 123, 124, 125). Ultrafine particles of alloys can be formed by evaporation from a single source, or they can be evaporated from separate sources and nucleated in the gas. Ultrafine particles of compounds can be formed by having a reactive gas present during nucleation or by decomposing and reacting precursor gases in an arc or plasma.

Buckminster Fullerenes. Recent gas evaporation techniques have allowed the formation of the Buckminster fullerenes (C^{60} and C^{70} "Buckeyballs"), a newly discovered form of the carbon molecule that resembles the shape of a soccer ball (Ref 126, 127). The synthesis involves arcing two pure graphite electrodes in a partial vacuum containing helium. The carbon "soot" that forms contains from 3 to 40% fullerenes, depending on the experimental conditions. The fullerenes are extracted from the soot by dissolving them in boiling benzene or toluene, and then this extract is vacuum dried.

References cited in this section

117. A.H. Pfund, The Optical Properties of Metallic and Crystalline Powders, *J. Opt. Soc. Am.,* Vol 23, 1933, p 375
118. R. Uyeda, The Morphology of Fine Metal Crystallites, *J. Cryst. Growth,* Vol 24/25, 1974, p 69
119. J.K.G. Panitz, D.M. Mattox, and M.J. Carr, Salt Smoke: The Formation of Submicron Sized RbCl Particles by Thermal Evaporation in 0.5-100 Torr of Argon and Helium, *J. Vac. Sci. Technol. A,* Vol 6 (No. 6), 1988, p 3105
120. D.M. Mattox and G.J. Kominiak, Deposition of Semiconductor Films with High Solar Absorptivity, *J. Vac. Sci. Technol.,* Vol 12 (No. 1), 1975, p 182
121. S. Thomas and E.B. Pattinson, The Controlled Preparation of Low SEE Surfaces by Evaporation of Metal Films under High Residual Gas Pressure, *J. Phys. D, Appl. Phys.,* Vol 3, 1970, p 1469

122. C. Hayashi, Ultrafine Particles, *Physics Today,* Vol 40, 1987, p 44

123. W.J. Yoo and Ch. Steinbruchel, Kinetics of Growth of Silicon Particles in Sputtering and Reactive Ion Etching Plasmas, *J. Vac. Sci. Technol. A,* Vol 10 (No. 4), 1992, p 1041

124. G.S. Selwyn and E.F. Patterson, Plasma Particle Generation Control II. Self-Cleaning Tool, *J. Vac. Sci. Technol. A,* Vol 10 (No. 4), 1992, p 1053

125. D.M. Mattox, Fundamentals of Ion Plating, *J. Vac. Sci. Technol.,* Vol 10, 1973, p 47

126. W. Krätschmer, L.D. Lamb, L.B. Fostiropoulos, and D.R. Huffman, Solid C^{60}: A New Form of Carbon, *Nature,* Vol 347 (No. 6291), 1990, p 354-358

127. P.E. Ross, Buckeyballs, *Sci. Am.,* Vol 263 (No. 7), 1991, p 114-116

Evaporation Process Equipment

The primary function of the vacuum system associated with evaporation processing is to reduce contaminating residual gases and vapors to an acceptable level. Potential sources of the gases and vapors in the processing chamber and related systems include:

- Residual atmospheric gases and vapors
- Desorption from surfaces in the vacuum (for example, water vapor and oils)
- Outgassing from materials in the vacuum (for example, water vapor and oxygen)
- Vaporization of construction materials (especially at high temperatures)
- Leakage from real and virtual leaks
- Permeation through materials such as rubber O-rings
- Desorption, outgassing, and vaporization from fixtures, tooling, substrates, and deposition source materials introduced into the system

In all cases, specifications for system performance, deposition procedures, and vacuum conditions should be established when the system and procedures produce a reproducible workpiece with the desired properties. Figure 10 shows a vacuum deposition system that can use a plasma discharge for plasma cleaning or the ARE process. Usually there are tradeoffs between the optimum design for achieving a good vacuum and the practicality of design for processing. For example, processing may require a large access door so that fixturing and substrates can be assembled externally and installed in the chamber.