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Surface Engineering

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Foreword

Improving the performance, extending the life, and enhancing the appearance of materials used for engineering components are fundamental--and increasingly important--concerns of ASM members. As the performance demands placed on materials in engineering applications have increased, the importance of surface engineering (cleaning, finishing, and coating) technologies have increased along with them.

Evidence of the growing interest in (and complexity of) surface engineering processes can be found in the expansion of their coverage in ASM handbooks through the years. The classic 1948 Edition of *Metals Handbook* featured a total of 39 pages in three separate sections on surface treating and coating. In the 8th Edition, surface technologies shared a volume with heat treating, and the number of pages jumped to over 350. The 9th Edition of *Metals Handbook* saw even further expansion, with a separate 715-page volume devoted to cleaning, finishing, and coating.

Surface Engineering, the completely revised and expanded Volume 5 of *ASM Handbook,* builds on the proud history of its predecessors, and it also reflects the latest technological advancements and issues. It includes new coverage of testing and analysis of surfaces and coatings, environmental regulation and compliance, surface engineering of nonmetallic materials, and many other topics.

The creation of this Volume would not have been possible without the early leadership of Volume Chairperson Fred A. Smidt, who passed away during the editorial development of the handbook. Two of his colleagues at the Naval Research Laboratory, Catherine M. Cotell and James A. Sprague, stepped in to see the project through to completion, and they have done an excellent job of shaping the content of the book and helping to ensure that it adheres to high technical and editorial standards. Special thanks are also due to the Section Chairpersons, to the members of the ASM Handbook Committee, and to the ASM editorial and production staffs. Of course, we are especially grateful to the hundreds of authors and reviewers who have contributed their time and expertise to create this outstanding information resource.

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Preface

In the 9th Edition of *Metals Handbook,* the title of this Volume was *Surface Cleaning, Finishing, and Coating;* for the new *ASM Handbook* edition, the title has been changed to *Surface Engineering.* A useful working definition of the term *surface engineering* is "treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material." These surface-specific functions include protecting the bulk material from hostile environments, providing low- or high-friction contacts with other materials, serving as electronic circuit elements, and providing a particular desired appearance.

Although the surface normally cannot be made totally independent from the bulk, the demands on surface and bulk properties are often quite different. For example, in the case of a turbine blade for a high-performance jet engine, the bulk of the material must have sufficient creep resistance and fatigue strength at the service temperature to provide an acceptably safe service life. The surface of the material, on the other hand, must possess sufficient resistance to oxidation and hot corrosion under the conditions of service to achieve that same component life. In many instances, it is either more economical or absolutely necessary to select a material with the required bulk properties and specifically engineer the surface to create the required interface with the environment, rather than to find one material that has both the bulk and surface properties required to do the job. It is the purpose of this Volume to guide engineers and scientists in the selection and application of surface treatments that address a wide range of requirements.

Scope of Coverage. This Volume describes surface modifications for applications such as structural components, in which the bulk material properties are the primary consideration and the surface properties must be modified for aesthetics, oxidation resistance, hardness, or other considerations. It also provides some limited information on surface modifications for applications such as microelectronic components, in which the near-surface properties are paramount and the bulk serves mainly as a substrate for the surface material.

The techniques covered may be divided broadly into three categories:

- Techniques to prepare a surface for subsequent treatment (e.g., cleaning and descaling)
- Techniques to cover a surface with a material of different composition or structure (e.g., plating, painting, and coating)
- Techniques to modify an existing surface topographically, chemically, or microstructurally to enhance its properties (e.g., glazing, abrasive finishing, and ion implantation)

Two significant surface-modification techniques that are not covered extensively in this Volume are conventional carburizing and nitriding. Detailed information on these processes is available in *Heat Treating,* Volume 4 of the *ASM Handbook.*

The materials that are suitable for surface engineering by the techniques addressed in this Volume include metals, semiconductors, ceramics, and polymers. Coverage of the classes of surfaces to be engineered has been broadened in this edition, reflecting the trend toward the use of new materials in many applications. Hence, this Volume provides information on topics such as high-temperature superconducting ceramics, organic-matrix composites that are substituted for metals in many automotive parts, diamond coatings that are used for either their hardness or their electronic properties, and surfaces that are implanted on medical prostheses for use in the human body. While a number of new materials and processes have been added to the coverage of this Volume, every attempt has been made to update, expand, and improve the coverage of the established surface treatments and coatings for ferrous and nonferrous metals.

In this edition, a section has been added that specifically addresses the environmental protection issues associated with the surface treatment of materials. These issues recently have become extremely important for surface treatment technology, because many surface modification processes have the potential to create major environmental problems. For some technologies, such as cadmium and chromium plating, environmental concerns have prompted intensive research efforts to devise economical alternative surface treatments to replace the more traditional but environmentally hostile methods. This Volume presents the current status of these environmental protection concerns and the efforts underway to address them. This is a rapidly developing subject, however, and many legal and technological changes can be expected during the publication life of this Volume.

Organization. Depending on the specific problem confronting an engineer or scientist, the most useful organization of a handbook on surface engineering can be by technique, by material being applied to the surface, or by substrate material being treated. The choice of an appropriate technique may be limited by such factors as chemical or thermal stability, geometrical constraints, and cost. The choice of material applied to a surface is typically dictated by the service environment in which the material will be used, the desired physical appearance of the surface, or, in the case of materials for microelectronic devices, the electrical or magnetic properties of the material. The substrate material being treated is usually chosen for its mechanical properties. Although the surface modification technique and the material being applied to the surface can be changed, in many cases, to take advantage of benefits provided by alternative techniques or coatings, the choice of a substrate material is generally inflexible. For example, if the problem confronting the materials engineer is the corrosion protection of a steel component, the most direct approach is to survey the processes that have been successfully applied to that particular base material. Once candidate processes have been identified, they can be examined in more detail to determine their suitability for the particular problem.

To serve as wide a range of needs as possible, this Volume is organized by both treatment technique and base material. Wherever possible, efforts have been made to cross-reference the technique and material sections to provide the reader with a comprehensive treatment of the subject.

The first several sections are organized by technique, covering surface cleaning, finishing, plating, chemical coating, vapor deposition, ion implantation, and diffusion treatment. The first of the process-oriented sections, "Surface Cleaning," covers techniques for removing various types of foreign substances. In addition to the mature technologies that have been applied routinely for decades, this section describes a number of processes and innovations that have been developed recently, prompted by both technological demands and environmental concerns. The section "Finishing Methods" addresses processes used to modify the physical topography of existing surfaces. These processes also have a lengthy history, but they continue to evolve with the development of new materials and applications. New information has been added to this section on methods used to assess the characteristics of finished surfaces.

The section "Plating and Electroplating" describes processes used for electrolytic and nonelectrolytic deposition of metallic coatings. Coverage of these techniques has been significantly expanded in this edition to include a larger number of metals and alloys that can be plated onto substrate materials. This section also contains an article on electroforming, a topic that spans surface and bulk material production. The next section, "Dip, Barrier, and Chemical Conversion Coatings," contains articles on physically applied coatings, such as paints and enamels, as well as on coatings applied by chemical reactions, which are similar in many cases to plating reactions. The final technique-related section, "Vacuum and Controlled-Atmosphere Coating and Surface Modification Processes," covers techniques that apply coatings from the vapor and liquid phases, plus ion implantation, which modifies the composition near the surface of materials by injecting energetic atoms directly into the substrate. Several new technologies involving deposition of energetic atoms have been added to this section. Reflecting the rapid development of electronic materials applications since the last edition was published, articles have been added on processes specifically applicable to semiconductors, superconductors, metallization contacts, and dielectrics.

Following the technique-oriented sections, a new section has been added for this edition specifically to address methods for the testing and characterization of modified surfaces. This information is similar to that provided in *Materials Characterization,* Volume 10 of *ASM Handbook,* but it is extrapolated to surface-specific applications. Because of the functions performed by engineered surfaces and the limited thickness of many coatings, materials characterization techniques must be specifically tailored to obtain information relevant to these problems.

The next four sections of the book focus on then selection and application of surface modification processes for specific bulk or substrate materials. The section "Surface Engineering of Irons and Steels" is new to this edition and provides a convenient overview of applicable processes for these key materials. The articles in the section "Surface Engineering of Nonferrous Metals" provide updated information on the selection and use of surface treatments for widely used nonferrous metals. Reflecting the increased importance of a variety of materials to engineers and scientists and the integration of different classes of materials into devices, a section entitled "Surface Engineering of Selected Nonmetallic Materials" has been added to this edition.

The final section of this Volume, "Environmental Protection Issues," deals with regulatory and compliance issues related to surface engineering of materials. In recent years, concerns about the impact of many industrial processes on local environments and the global environment have joined economic and technological questions as significant drivers of manufacturing decisions. The surface engineering industry, with its traditional reliance on toxic liquids and vapors for many processes, has been especially affected by these concerns. Environmental protection in surface engineering of materials is a rapidly developing field, and this final section attempts to assess the current status of these issues and give some bases for predicting future trends.

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Classification and Selection of Cleaning Processes

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Introduction

CLEANING PROCESSES used for removing soils and contaminants are varied, and their effectiveness depends on the requirements of the specific application. This article describes the basic attributes of the most widely used surface cleaning processes and provides guidelines for choosing an appropriate process for particular applications.

The processing procedures, equipment requirements, effects of variables, and safety precautions that are applicable to individual cleaning processes are covered in separate articles that follow in this Section of the handbook. Additional relevant information is contained in the articles "Environmental Regulation of Surface Engineering," "Vapor Degreasing Alternatives," and "Compliant Wipe Solvent Cleaners" in this Volume. Information about considerations involved in cleaning of specific metals is available in the Sections

Cleaning Process Selection

In selecting a metal cleaning process, many factors must be considered, including:

- The nature of the soil to be removed
- The substrate to be cleaned (i.e., ferrous, nonferrous, etc.)
- The importance of the condition of the surface to the end use of the part
- The degree of cleanliness required
- The existing capabilities of available facilities
- The environmental impact of the cleaning process
- Cost considerations
- The total surface area to be cleaned
- Effects of previous processes
- Rust inhibition requirements
- Materials handling factors
- Surface requirements of subsequent operations, such as phosphate conversion coating, painting, or plating

Very few of these factors can be accurately quantified, which results in subjective analysis. Frequently, several sequences of operations may be chosen which together produce the desired end result. As in most industrial operations, the tendency is to provide as much flexibility and versatility in a facility as the available budget will allow. The size and shape of the largest predicted workpiece is generally used to establish the cleaning procedure, equipment sizes, and handling techniques involved.

Because of the variety of cleaning materials available and the process step possibilities, the selection of a cleaning procedure depends greatly on the degree of cleanliness required and subsequent operations to be performed. Abrasive blasting produces the lowest degree of cleanliness. Solvent, solvent vapor degrease, emulsion soak, alkaline soak, alkaline electroclean, alkaline plus acid cleaning, and finally ultrasonics each progressively produces a cleaner surface. In addition to these conventional methods, very exotic and highly technical procedures have been developed in the electronics and space efforts to produce clean surfaces far above the normal requirements for industrial use.

Cleaning Media. Understanding the mechanics of the cleaning action for particular processes can help guide the selection of an appropriate method.

Solvent cleaning, as the name implies, is the dissolution of contaminants by an organic solvent. Typical solvents are trichloroethylene, methylene chloride, toluene, and benzene. The solvent can be applied by swabbing, tank immersion, spray or solid stream flushing, or vapor condensation. Vapor degreasing is accomplished by immersing the work into a cloud of solvent vapor; the vapor condenses on the cooler work surface and dissolves the contaminants. Subsequent flushing with liquid solvent completes the cleaning process. Temperature elevation accelerates the activity.

One major drawback of solvent cleaning is the possibility of leaving some residues on the surface, often necessitating additional cleaning steps. Another more significant disadvantage is the environmental impact of solvent cleaning processes. In fact, much effort is being expended on replacing solvent-based processes with more environmentally acceptable aqueous-based processes (see the article "Vapor Degreasing Alternatives" in this Volume).

Emulsion cleaning depends on the physical action of emulsification, in which discrete particles of contaminant are suspended in the cleaning medium and then separated from the surface to be cleaned. Emulsion cleaners can be water or water solvent-based solutions; for example, emulsions of hydrocarbon solvents such as kerosene and water containing emulsifiable surfactant. To maintain stable emulsions, coupling agents such as oleic acid are added.

Alkaline cleaning is the mainstay of industrial cleaning and may employ both physical and chemical actions. These cleaners contain combinations of ingredients such as surfactants, sequestering agents, saponifiers, emulsifiers, and chelators, as well as various forms of stabilizers and extenders. Except for saponifiers, these ingredients are physically active and operate by reducing surface or interfacial tension, by formation of emulsions, and suspension or flotation of insoluble particles. Solid particles on the surface are generally assumed to be electrically attracted to the surface. During the cleaning process, these particles are surrounded by wetting agents to neutralize the electrical charge and are floated away, held in solution suspension indefinitely, or eventually are settled out as a sludge in the cleaning tank.

Saponification is a chemical reaction that splits an ester into its acid and alcohol moieties through an irreversible base-induced hydrolysis. The reaction products are more easily cleaned from the surface by the surface-active agents in the alkaline cleaner. Excessive foaming can result if the alkalinity in the cleaner drops to the point where base-induced hydrolysis cannot occur; the reaction of the detergents in the cleaner with oil on the work surface can make soaps, which causes the characteristic foaming often seen in a spent cleaner.

Electrolytic cleaning is a modification of alkaline cleaning in which an electrical current is imposed on the part to produce vigorous gassing on the surface to promote the release of soils. Electrocleaning can be either anodic or cathodic cleaning. Anodic cleaning is also called "reverse cleaning," and cathodic cleaning is called "direct cleaning." The release of oxygen gas under anodic cleaning or hydrogen gas under cathodic cleaning in the form of tiny bubbles from the work surface greatly facilitates lifting and removing surface soils.

Abrasive cleaning uses small sharp particles propelled by an air stream or water jet to impinge on the surface, removing contaminants by the resulting impact force. A wide variety of abrasive media in many sizes is available to meet specific needs. Abrasive cleaning is often preferred for removing heavy scale and paint, especially on large, otherwise inaccessible areas. Abrasive cleaning is also frequently the only allowable cleaning method for steels sensitive to hydrogen embrittlement. This method of cleaning is also used to prepare metals, such as stainless steel and titanium, for painting to produce a mechanical lock for adhesion because conversion coatings cannot be applied easily to these metals.

Acid cleaning is used more often in conjunction with other steps than by itself. Acids have the ability to dissolve oxides, which are usually insoluble in other solutions. Straight mineral acids, such as hydrochloric, sulfuric, and nitric acids, are used for most acid cleaning, but organic acids, such as citric, oxalic, acetic, tartaric, and gluconic acids, occupy an important place in acid cleaning because of their chelating capability.

Phosphoric Acid Etching. Phosphoric acid is often used as an etchant for nonferrous metals (such as copper, brass, aluminum, and zinc) to enhance paint adhesion. A detergent-bearing iron phosphating solution is often ideal for this sort of combined cleaning and etching approach.

Molten salt bath cleaning is very effective for removing many soils, especially paints and heavy scale. However, the very high operating temperatures and high facility costs discourage widespread use of this process.

Ultrasonic cleaning uses sound waves passed at a very high frequency through liquid cleaners, which can be alkaline, acid, or even organic solvents. The passage of ultrasonic waves through the liquid medium creates tiny gas bubbles, which provide a vigorous scrubbing action on the parts being cleaned. Although the mechanism of this action is not completely understood, it yields very efficient cleaning. It is ideal for lightly soiled work with intricate shapes, surfaces, and cavities that may not be easily cleaned by spray or immersion techniques. A disadvantage of ultrasonic cleaning processes is the high capital cost of the power supplies and transducers that comprise the system. Therefore, only applications with the most rigorous cleaning requirements are suitable for this technique.

Substrate Considerations. The selection of a cleaning process must be based on the substrate being cleaned as well as the soil to be removed. Metals such as aluminum and magnesium require special consideration because of their sensitivity to attack by chemicals. Aluminum is dissolved rapidly by both alkalis and acids. Magnesium is resistant to alkaline solutions with pH values up to 11, but is attacked by many acids. Copper is merely stained by alkalis, yet severely attacked by oxidizing acids (such as nitric acid) and only slightly by others. Zinc and cadmium are attacked by both acids and alkalis. Steels are highly resistant to alkalis and attacked by essentially all acidic material. Corrosion-resistant steels, also referred to as *stainless steels*, have a high resistance to both acids and alkalis, but the degree of resistance depends on the alloying elements. Titanium and zirconium have come into common use because of their excellent chemical resistance. These two metals are highly resistant to both alkalis and acids with the exception of acid fluorides which attack them rapidly and severely.

Table 1 summarizes the comparative attributes of the principal cleaning processes.

Table 1 Comparative attributes of selected cleaning processes

Rated on a scale where 10 = best and 1 = worst

Attribute	Hand wiping	Immersion	Emulsion	Batch spray	Continuous conveyor	Ultrasonic
Handling	2	7	7	5	9	7
Cleanness	4	3	5	7	7	10
Process control	3	6	6	8	9	9
Capital cost	7	8	7	5	4	1
Operating cost	5	8	8	7	6	6

Types of soil may be broadly classified into six groups: pigmented drawing compounds, unpigmented oil and grease, chips and cutting fluids, polishing and buffing compounds, rust and scale, and miscellaneous surface contaminants, such as lapping compounds and residue from magnetic particle inspection. These six types of soil are dealt with separately in the order listed.

Removal of Pigmented Drawing Compounds

All pigmented drawing lubricants are difficult to remove from metal parts. Consequently, many plants review all aspects of press forming operations to avoid the use of pigmented compounds. Pigmented compounds most commonly used contain one or more of the following substances: whiting, lithopone, mica, zinc oxide, bentonite, flour, graphite, white lead (which is highly toxic), molybdenum disulfide, animal fat, and soaplike materials. Some of these substances are more difficult to remove than others. Because of their chemical inertness to acid and alkali used in the cleaners and tight adherence to metal surfaces, graphite, white lead, molybdenum disulfide, and soaps are the most difficult to solubilize and remove.

Certain variables in the drawing operation may further complicate the removal of drawing lubricants. For example, as drawing pressures are increased, the resulting higher temperatures increase the adherence of the compounds to the extent that some manual scrubbing is often an essential part of the subsequent cleaning operation. Elapsed time between the drawing and cleaning operations is also a significant factor. Drawing lubricants will oxidize and loosely polymerize on metal surfaces over time, rendering them even more resistant to cleaning.

Table 2 indicates cleaning processes typically selected for removing pigmented compounds from drawn and stamped parts such as Parts 1 through 6 in Fig. 1.

Table 2 Metal cleaning processes for removing selected contaminants

Type of production	In-process cleaning	Preparation for painting	Preparation for phosphating	Preparation for plating
Removal of pigmented drawing compounds(a)				
Occasional or intermittent	Hot emulsion hand slush, spray emulsion in single stage, vapor slush degrease(b)	Boiling alkaline blow off, hand wipe	Hot emulsion hand slush, spray emulsion in single stage, hot rinse, hand wipe	Hot alkaline soak, hot rinse (hand wipe, if possible) electrolytic alkaline, cold water rinse
		Vapor slush degrease, hand wipe		

Type of production	**In-process cleaning**	**Preparation for painting**	**Preparation for phosphating**	**Preparation for plating**
		Acid clean(c)		
Continuous high production	Conveyorized spray emulsion washer	Alkaline soak, hot rinse alkaline spray, hot rinse	Alkaline or acid(d) soak, hot rinse, alkaline or acid(d) spray, hot rinse	Hot emulsion or alkaline soak, hot rinse, electrolytic alkaline, hot rinse
Removal of unpigmented oil and grease				
Occasional or intermittent	Solvent wipe	Solvent wipe	Solvent wipe	Solvent wipe
	Emulsion dip or spray	Vapor degrease	Emulsion dip or spray, rinse	Emulsion soak, barrel rinse, electrolytic alkaline rinse, hydrochloric acid dip, rinse
	Vapor degrease	Phosphoric acid etch	Vapor degrease	
	Cold solvent dip		Alkaline spray	
	Alkaline dip, rinse, dry or dip in rust preventative			
Continuous high production	Automatic vapor degrease	Automatic vapor degrease	Emulsion power spray, rinse	Automatic vapor degrease, electrolytic alkaline rinse, hydrochloric acid dip, rinse(e)
	Emulsion, tumble, spray, rinse, dry		Vapor degrease	
			Acid clean(c)	
Removal of chips and cutting fluid				
Occasional or intermittent	Solvent wipe	Solvent wipe	Solvent wipe	Solvent wipe
	Alkaline dip and emulsion surfactant	Alkaline dip and emulsion surfactant	Alkaline dip and emulsion surfactant(f)	Alkaline dip, rinse, electrolytic alkaline(g), rinse, acid dip, rinse(h)
	Stoddard solvent or trichlorethylene	Solvent or vapor	Solvent or vapor	
	Steam			
Continuous high production	Alkaline (dip or spray) and emulsion surfactant	Alkaline (dip or spray) and emulsion surfactant	Alkaline (dip or spray) and emulsion surfactant	Alkaline soak, rinse, electrolytic alkaline(g), rinse, acid dip and rinse(h)

Type of production	In-process cleaning	Preparation for painting	Preparation for phosphating	Preparation for plating
Removal of polishing and buffing compounds				
Occasional or intermittent	Seldom required	Solvent wipe	Solvent wipe	Solvent wipe
		Surfactant alkaline (agitated soak), rinse	Surfactant alkaline (agitated soak), rinse	Surfactant alkaline (agitated soak), rinse, electroclean(i)
		Emulsion soak, rinse	Emulsion soak, rinse	Alkaline spray
Continuous high production	Seldom required	Surfactant alkaline spray, spray rinse	Surfactant alkaline spray, spray rinse	Surfactant alkaline soak and spray, alkaline soak, spray and rinse, electrolytic alkaline(i), rinse, mild acid pickle, rinse
		Agitated soak or spray, rinse(j)	Emulsion spray, rinse	

(a) For complete removal of pigment, parts should be cleaned immediately after the forming operation, and all rinses should be sprayed where practical.

(b) Used only when pigment residue can be tolerated in subsequent operations.

(c) Phosphoric acid cleaner-coaters are often sprayed on the parts to clean the surface and leave a thin phosphate coating.

(d) Phosphoric acid for cleaning and iron phosphating. Proprietary products for high-and low-temperature application are available.

(e) Some plating processes may require additional cleaning dips.

(f) Neutral emulsion or solvent should be used before manganese phosphating.

(g) Reverse-current cleaning may be necessary to remove chips from parts having deep recesses.

(h) For cyanide plating, acid dip and water rinse are followed by alkaline and water rinses.

(i) Other preferences: stable or diphase emulsion spray or soak, rinse, alkaline spray or soak, rinse, electroclean; or solvent presoak, alkaline soak or spray, electroclean.

(j) Third preference: emulsion spray rinse

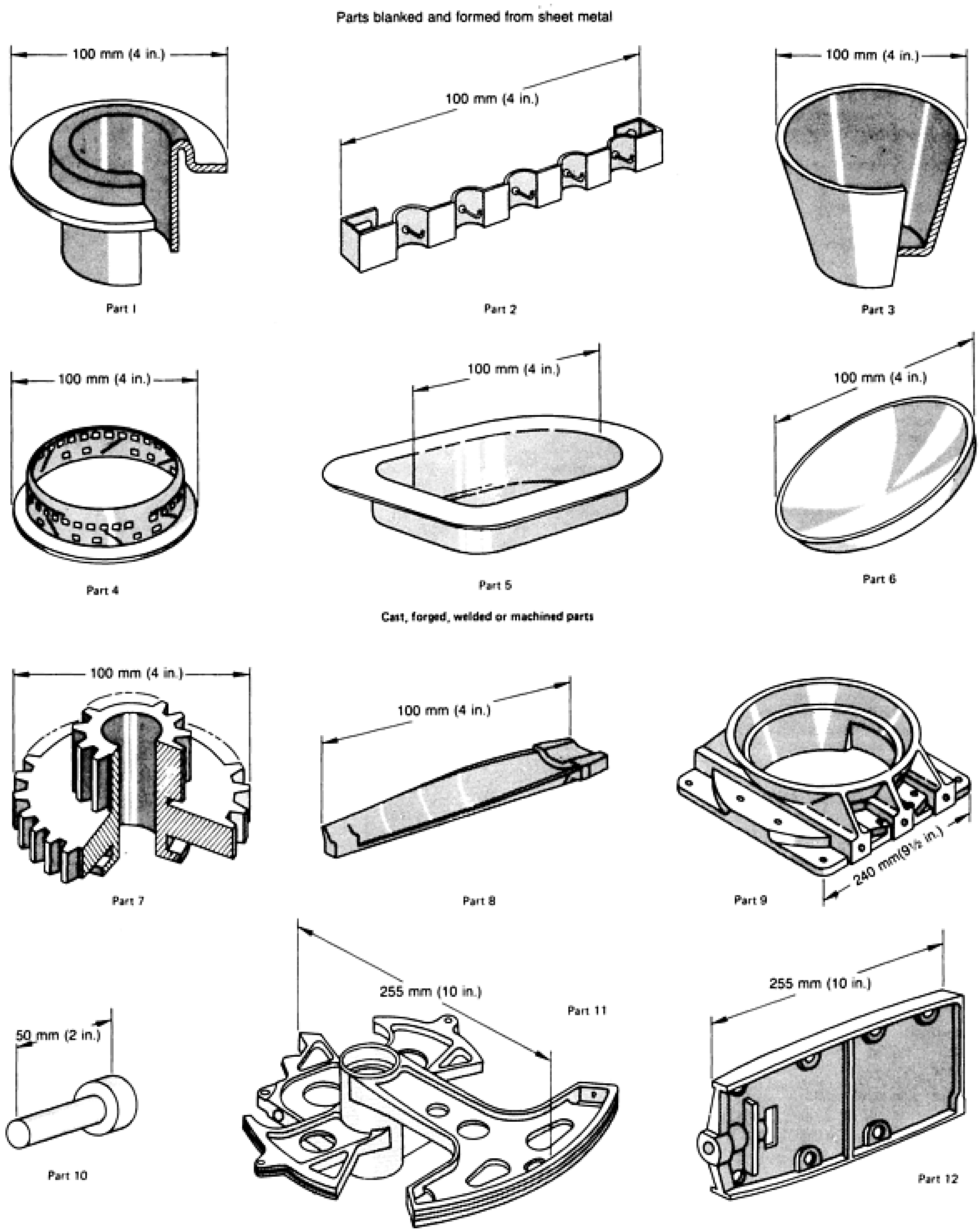

Fig. 1 Sample part configurations cleaned by various processes. See text for discussion.

Emulsion cleaning is one of the most effective methods for removing pigmented compounds, because is relies on mechanical wetting and floating the contaminant away from the surface, rather than chemical action which would be completely ineffective on such inert materials. However, emulsions alone will not do a complete cleaning job, particularly when graphite or molybdenum disulfide is the contaminant. Emulsion cleaning is an effective method of removing pigment because emulsion cleaners contain organic solvents and surfactants, which can dissolve the binders, such as stearates, present in the compounds.

Diphase or multiphase emulsions, having concentrations of 1 to 10% in water and used in a power spray washer, yield the best results in removing pigmented compounds. The usual spray time is 30 to 60 s; emulsion temperatures may range from 54 to 77 °C (130 to 170 °F), depending on the flash point of the cleaner. In continuous cleaning, two adjacent spray zones or a hot water (60 to 66 °C, or 140 to 150 °F) rinse stage located between the two cleaner spraying zones is common practice.

Cleaning with an emulsifiable solvent, a combination of solvent and emulsion cleaning, is an effective technique for removing pigmented compounds. Emulsifiable solvents may either be used full strength or be diluted with a hydrocarbon solvent, 10 parts to 1 to 4 parts of emulsifiable solvent. Workpieces with heavy deposits of pigmented compound are soaked in this solution, or the solution is slushed or swabbed into heavily contaminated areas. After thorough contact has been made between the solvent and the soil, workpieces are rinsed in hot water, preferably by pressure spray. Emulsification loosens the soil and permits it to be flushed away. Additional cleaning, if required, is usually done by either a conventional emulsion or an alkaline cleaning cycle.

Most emulsion cleaners can be safely used to remove soil from any metal. However, a few highly alkaline emulsion cleaners with pH higher than 10 must be used with caution in cleaning aluminum or zinc because of chemical attack. Low alkaline pH (8 to 9) emulsion cleaners, safe on zinc and aluminum, are available. Emulsion cleaners with a pH above 11 should not be used on magnesium alloys.

Alkaline cleaning, when used exclusively, is only marginally effective in removing pigmented compounds. Success depends mainly on the type of pigmented compounds present and the extent to which they have been allowed to dry. If the compounds are the more difficult types, such as graphite or white lead, and have been allowed to harden, hand slushing and manual brushing will be required for removing all traces of the pigment. Hot alkaline scale conditioning solutions can be used to remove graphite and molybdenum disulfide pigmented hot forming and heat treating protective coatings. The use of ultrasonics in alkaline cleaning is also highly effective in removing tough pigmented drawing compounds.

The softer pigmented compounds can usually be removed by alkaline immersion and spray cycles (Table 2). The degree of cleanness obtained depends largely on thorough mechanical agitation in tanks or barrels, or strong impingement if a spray is used. A minimum spray pressure of 0.10 MPa (15 psi) is recommended.

Parts such as 1 to 6 in Fig. 1 can be cleaned effectively by immersion or immersion and spray when the parts are no longer than about 508 mm (20 in.) across. Larger parts of this type can be cleaned more effectively by spraying. Operating conditions and the sequence of processes for a typical alkaline cleaning cycle are listed in Table 3. This cycle has removed pigmented compounds effectively from a wide variety of stampings and drawn parts. Energy saving low-temperature solventized-alkaline cleaners are available for soak cleaning. Similarly low-temperature electro-cleaners also are effectively employed in industry, operating at 27 to 49 °C (80 to 120 °F).

Table 3 Alkaline cleaning cycle for removing pigmented drawing compounds

Process sequence	Concentration		Time, min	Temperature		Anode current		Remarks
	g/L	oz/gal		°C	°F	A/dm^2	A/ft^2	
Alkaline soak clean								
Barrel[(a)]	65 to 90	9 to 12	3 to 5	Boiling	Boiling	. . .	. . .	. . .
Rack[(b)]	65 to 90	9 to 12	3 to 5	Boiling	Boiling	. . .	. . .	. . .
Hot water rinse, immersion, and spray								
Barrel[(a)]	. . .	. . .	3[(c)]	43	110	. . .	. . .	Spray jet if barrel is open type

Process sequence	Concentration		Time, min	Temperature		Anode current		Remarks
	g/L	oz/gal		°C	°F	A/dm^2	A/ft^2	
Rack[b]	. . .	. . .	2[c]	43	110	. . .	. . .	Spray rinse, immerse, and spray rinse
Electrolytic alkaline clean								
Barrel[a]	55 to 65	7 to 9	2	82 to 99	180 to 210	4 to 6	40 to 60	. . .
Rack[b]	65 to 90	9 to 12	2	82 to 99	180 to 210	4 to 6	40 to 60	. . .
Hot water rinse, immersion, and spray[d]								
Barrel[a]	. . .	. . .	3[c]	43	110	. . .	. . .	Spray jet if barrel is open type
Rack[b]	. . .	. . .	2[c]	43	110	. . .	. . .	Spray rinse, immerse, and spray rinse
Cold water rinse, immersion, and spray[e]								
Barrel[a]	. . .	. . .	2[c]	. . .	. . .	. . .	. . .	Spray jet if barrel is open type
Rack[b]	. . .	. . .	1[c]	. . .	. . .	. . .	. . .	Spray rinse, immerse, and spray rinse

(a) Rotate during entire cycle.

(b) Agitate arm of rack, if possible.

(c) Immersion time.

(d) Maintain overflow at approximately 8 L/min (2 gal/min).

(e) Clean in cold running water.

Electrolytic alkaline cleaning is seldom used as a sole method for the removal of pigmented compounds. Although the generation of gas at the workpiece surface provides a scrubbing action that aids in removal of a pigment, the cleaner becomes contaminated so rapidly that its use is impractical except for final cleaning before plating (Table 2).

Copper alloys, aluminum, lead, tin, and zinc are susceptible to attack by uninhibited alkaline cleaners (pH 10 to 14). Inhibited alkaline cleaners (pH below 10), which have reduced rates of reaction, are available for cleaning these metals. These contain silicates and borates.

Acid Cleaning. Acid cleaners, composed of detergents, liquid glycol ether, and phosphoric acid have proved effective in removing pigmented compounds from engine parts, such as sheet rocker covers and oil pans, even after the pigments have dried. These acid compounds, mixed with water and used in a power spray, are capable of cleaning such parts without hand scrubbing.

A power spray cycle used by one plant is given in Table 4. A light blowoff follows the rinsing cycle. Parts with recesses should be rotated to allow complete drainage. This cleaning procedure suitably prepares parts for painting, but for parts to be plated, the acid cleaning cycle is conventionally followed by electrolytic cleaning which is usually alkaline, but sometimes done with sulfuric or hydrochloric acid. Phosphoric acid cleaners will not etch steel, although they may cause some discoloration.

Table 4 Power spray acid cleaning for removing pigmented compounds

Steel parts cleaned by this method are suitable for painting, but electrolytic cleaning normally follows if parts are to be electroplated; solventized, phosphoric acid-based, low-temperature (27 to 49 °C, or 80 to 120 °F) products are successfully used for power spray cleaning.

Cycle	Phosphoric acid		Solution temperature		Cycle time, min
	g/L	oz/gal	°C	°F	
Wash	15-19	2-2.5	74-79	165-175	3-4

Aluminum and aluminum alloys are susceptible to some etching in phosphoric acid cleaners. Chromic acid or sodium dichromate with either nitric or sulfuric acid is used to deoxidize aluminum alloys. Nonchromated deoxidizers are preferred environmentally. Ferric sulfate and ferric nitrate are used in place of hexavalent chromium. However, nonchromated deoxidizers tend to produce smut on the workpiece, especially 2000- and 7000-series alloys, when the deoxidizer etch rate is maintained (normally with fluoride) above 0.003 μm/side per hour (0.1 μin./side per hour). For more information on removing smut from aluminum, see the article "Surface Engineering of Aluminum and Aluminum Alloys" in this Volume.

Vapor degreasing is of limited value in removing pigmented compounds. The solvent vapor will usually remove soluble portions of the soil, leaving a residue of dry pigment that may be even more difficult to remove by other cleaning processes. However, modifications of vapor degreasing, such as slushing, spraying, ultrasonic, or combinations of these, can be utilized for 100% removal of the easier-to-clean pigments, such as whiting, zinc oxide, or mica.

The latter practice is often used for occasional or intermittent cleaning (Table 2). However, when difficult-to-clean pigments such as graphite or molybdenum disulfide are present, it is unlikely that slush or spray degreasing will remove 100% of the soil.

Vapor degreasing of titanium should be limited to detailed parts and should not be used on welded assemblies that will see later temperatures in excess of 290 °C (550 °F) because degreasing solvents are known to cause stress-corrosion cracking of titanium at these temperatures. Subsequent pickling in nitric-fluoride etchants may relieve this concern.

Solvent cleaning, because of its relatively high cost, lack of effectiveness, rapid contamination, and health and fire hazards, is seldom recommended for removing pigmented compounds, except for occasional preliminary or rough cleaning before other methods. For example, parts are sometimes soaked in solvents such as kerosene or mineral spirits immediately following the drawing operation to loosen and remove some of the soil, but the principal effect of the operation is to condition parts for easier cleaning by more suitable methods, such as emulsion or alkaline cleaning.

Removal of Unpigmented Oil and Grease

Common shop oils and greases, such as unpigmented drawing lubricants, rust-preventive oils, and quenching and lubricating oils, can be effectively removed by several different cleaners. Selection of the cleaning process depends on production flow as well as on the required degree of cleanness, available equipment, and cost. For example, steel parts in a clean and dry condition will rust within a few hours in a humid atmosphere. Thus, parts that are thoroughly clean and dry must go to the next operation immediately, be placed in hold tanks, or be treated with rust preventatives or water displacing oils. If rust preventatives are used, the parts will probably require another cleaning before further processing. Accordingly, a cleaner that leaves a temporary rust-preventive film might be preferred.

Table 2 lists cleaning methods frequently used for removing oils and greases from the 12 types of parts in Fig. 1. Similar parts that are four or five times as large would be cleaned in the same manner, except for methods of handling. Variation in shape among the 12 parts will affect racking and handling techniques.

Advantages and disadvantages of the cleaners shown in Table 2, as well as other methods for removing common unpigmented oils and greases, are discussed in the following paragraphs.

Emulsion Cleaning. Emulsion cleaners, although fundamentally faster but less thorough than alkaline cleaners, are widely used for intermittent or occasional cleaning, because they leave a film that protects the steel against rust. Emulsion cleaners are most widely used for inprocess cleaning, preparation for phosphating, and precleaning for subsequent alkaline cleaning before plating (Table 2).

Vapor degreasing is an effective and widely used method for removing a wide variety of oils and greases. It develops a reproducible cleanliness because the degreasing fluid is distilled and filtered.

Vapor degreasing has proved especially effective for removing soluble soil from crevices, such as rolled or welded seams that may permanently entrap other cleaners. Vapor degreasing is particularly well adapted for cleaning oil-impregnated parts, such as bearings, and for removing solvent-soluble soils from the interiors of storage tanks.

Solvent cleaning may be used to remove the common oils and greases from metal parts. Methods vary from static immersion to multistage washing. Eight methods of solvent cleaning listed in increasing order of their effectiveness are as follows:

- Static immersion
- Immersion with agitation of parts
- Immersion with agitation of both the solvent and the parts
- Immersion with scrubbing
- Pressure spraying in a spray booth
- Immersion scrubbing, followed by spraying
- Multistage washing
- Hand application with wiper

A number of solvents and their properties are found in the articles on vapor degreasing and solvent cleaning in this Volume. Solvent cleaning is most widely used as a preliminary or conditioning cleaner to degrease both the time required in and contamination of the final cleaner.

Shape of the part influences the cycle and method selected. For example, parts that will nest or entrap fluids (Parts 3 and 6 in Fig. 1) are cleaned by dipping in a high-flash naphtha, Stoddard solvent, or chlorinated hydrocarbon for 5 to 30 s at room temperature. Time depends on the type and amount of soil. Parts that are easily bent or otherwise damaged, such as Part 2 in Fig. 1, are now sprayed for 30 s to 2 min at room temperature. Complex parts, such as Part 9 in Fig. 1, are soaked at room temperature for 1 to 10 min.

Acid Cleaning. Acid cleaners such as the phosphoric acid-ethylene glycol monobutyl ether type are efficient in the removal of oil and grease. Also, they remove light blushing rust and form a thin film of phosphate that provides temporary protection against rusting and functions as a suitable base for paint (Table 2).

Acid cleaners are usually used in a power spray washer. The cycle shown for removing pigmented compounds in Table 4 also removes unpigmented compounds.

Although acid cleaners are comparatively high in cost, they are often used on large ferrous components, such as truck cabs, before painting. Acid cleaners will etch aluminum and other nonferrous metals.

Alkaline Cleaning. Alkaline cleaners are efficient and economical for removing oil and grease and are capable of cleaning to a no-water-break surface. They remove oil and grease by saponification or emulsification, or both. The types that saponify only are quickly exhausted.

Mineral, lard, and synthetic unpigmented drawing compounds are easily removed by alkaline cleaners. Silicones, paraffin, and sulfurized, chlorinated, oxidized, or carbonized oils are difficult, but can be removed by alkaline cleaners. Alkaline cleaners will etch aluminum and other nonferrous metal parts unless inhibitors are used, and aqueous solutions of alkaline cleaners cannot be tolerated on some parts or assemblies. On assemblies comprised of dissimilar metals, this presence of alkaline solution in crevices may result in galvanic corrosion, and even a trace of alkali will contaminate paint and phosphate coating systems; therefore, rinsing must be extremely thorough. However, very hot rinsing will promote flash drying and flash rusting of work. Parts should be kept wet between stages, and delays before subsequent processing should be kept to a minimum. Cold water rinsing is recommended.

Electrolytic alkaline cleaning is effective as a final cleaning process for removing oil and grease from machined surfaces when extreme cleanness is required. It is almost always used for final cleaning before electroplating of items such as precision steel parts (fitted to ±0.0076 mm, or ±0.0003 in.) in refrigeration and air conditioning equipment. Electrolytic alkaline cleaning provided a cleanness of 0.0005 g/10 parts on the small plate assembly (Part 13) in Fig. 2, and of 0.003 g/10 parts on the 165 mm (6.5 in.) diameter part (Part 14). This degree of cleanness was obtained by using a conveyor system and the following cycle:

1. Soak in alkali, 45 to 60 g/L (6 to 8 oz/gal) at 77 to 88 °C (170 to 190 °F) for 1 to 2 min. Energy saving, solventized-alkaline low-temperature soak cleaners, suitable for ferrous and nonferrous metals are available. Similarly, low-temperature electrocleaners are also used. Both operate at 27 to 49 °C (80 to 120 °F).
2. Alkaline clean with reverse current, using current density of 5 A/dm^2 (50 A/ft^2), same time, concentration, and temperature as in step 1. Avoid making the part cathodic when cleaning high-strength steels or titanium to avoid hydrogen embrittlement.
3. Rinse in cold water containing chromic acid for rust prevention.
4. Rinse in cold water containing ammonia.
5. Rinse in hot water containing 0.1% sodium nitrate.
6. Dry in hot air.
7. Place parts in solvent emulsion prior to manganese phosphate coating.

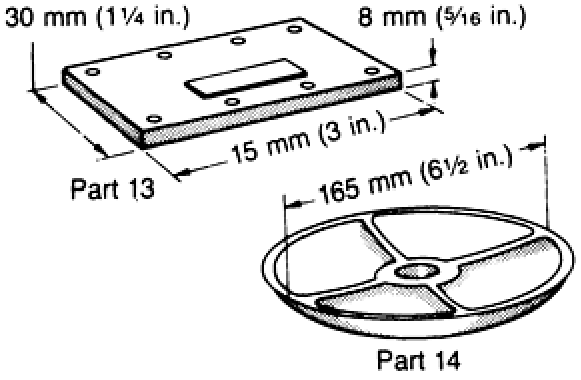

Fig. 2 Parts for refrigerators or air conditioners that are cleaned using electrolytic alkaline processes

Removal of Chips and Cutting Fluids from Steel Parts

Cutting and grinding fluids used for machining may be classified into three groups, as follows:

- Plain or sulfurized mineral and fatty oils (or combination of the two), chlorinated mineral oils, and sulfurized chlorinated mineral oils.
- Conventional or heavy-duty soluble oils with sulfur or other compounds added and soluble grinding oils with wetting agents.
- Chemical cutting fluids, which are water-soluble and generally act as cleaners. They contain soaps, amines, sodium salts of sulfonated fatty alcohols, alkyl aromatic sodium salts of sulfonates, or other types of soluble addition agents.

Usually, all three types of fluids are easily removed, and the chips fall away during cleaning, unless the chips or part become magnetic. Plain boiling water is often suitable for removing these soils, and in some plants, mild detergents are added to the water to increase its effectiveness. Steam is widely used for in-process cleaning, especially for large components. Table 2 indicates cleaning processes typically used for removing cutting fluids to meet specific production requirements.

Emulsion cleaning is an effective and relatively inexpensive means of removing all three types of cutting fluids. Attendant fire hazard is not great if operating temperatures are at least 8 to 11 °C (15 to 20 °F) below the flash temperature of the hydrocarbon used. Parts may be cleaned by either dipping or spraying. Many parts are immersed and then sprayed, particularly parts with complex configurations, such as Part 9 in Fig. 1.

It is has often proved economical to remove a major portion of the soil by alkaline cleaning first and then to use an emulsion surfactant, an emulsion containing surface-activating agent. This sequence prevents the possible contamination of painting or phosphating systems with alkaline solution.

Most emulsion cleaners can be safely used for removing these soils from nonferrous metals. Only the emulsions having pH values higher than 10 are unsafe for cleaning nonferrous metals.

Alkaline Cleaners. Alkaline cleaners are effective for removing all three types of cutting and grinding fluids. Alkaline cleaning is usually the least expensive process and is capable of delivering parts that are clean enough to be phosphate coated or painted. Inhibited alkaline cleaners are required for removing cutting and grinding fluids from aluminum and zinc and their alloys.

Electrolytic alkaline cleaning, which invariable follows conventional alkaline cleaning for parts that are to be plated, is also recommended for removing cutting fluids when extra cleanness is required. For example, Parts 7 and 9 in Fig. 1 would be cleaned electrolytically before scaleless heat treating.

Vapor degreasing will remove cutting fluids of the first group easily and completely, but fluids of the second and third groups may not be completely removed and are likely to cause deterioration of the solvent. Water contained in these soluble fluids causes the hydrolysis of the degreasing solvent and produces hydrochloric acid, which will damage steel and other metals. Vapor degreasing solvents have inhibitors to reduce corrosion by stabilizing the pH. A potential fire hazard exists when water or moisture and aluminum chips are allowed to accumulate in a vapor degreaser.

If vapor degreasing is used to remove water-containing soils, perchloroethylene may be the preferred solvent because its higher boiling point (120 °C or 250 °F) causes most of the water to be driven off as vapor. However, prolonged immersion at 120 °C (250 °F) may also affect the heat treated condition of some aluminum alloys. Used exclusively, the vapor phase will not remove chips or other solid particles. Therefore, combination cycles, such as warm liquid and vapor, are ordinarily used. An air blowoff also aids in removing chips.

Solvent cleaning by soaking (with or without agitation), hand wiping, or spraying is frequently used for removing chips and cutting fluids. Solvents preferentially remove cutting fluids of the first group. Solvent cleaning is commonly used for cleaning between machining operations, to facilitate inspection or fixturing.

Acid Cleaning. Phosphoric or chromic acid cleaners used in a power spray or soak cleaning when followed by pressure spray rinsing are effective in removing most types of cutting fluids. However, they are expensive and are seldom used for routine cleaning. In some applications, acid cleaners have been used because they also remove light rust from ferrous metals and oxide and scale from aluminum alloys.

Removal of Polishing and Buffing Compounds

Polishing and buffing compounds are difficult to remove because the soil they deposit is composed of burned-on grease, metallic soaps, waxes, and vehicles that are contaminated with fine particles of metal and abrasive. Consequently, cleaning requirements should be considered when selecting polishing and buffing compounds. Compounds used for obtaining buffed and polished finishes may be classified by cleaning requirements:

- *Liquids:* mineral oils and oil-in-water emulsions or animal and vegetable oils with abrasives
- *Semisolids:* oil based, containing abrasives and emulsions, or water based, containing abrasives and dispersing agents
- *Solids:* greases containing stearic acid, hydrogenated fatty acid, tallow, hydrogenated glycerides, petroleum waxes, and combinations that produce either saponifiable or unsaponifiable materials, in addition to abrasives

Table 2 lists preferred and alternate methods for removing polishing and buffing compounds from sheet metal parts. However, some modification may be required for complete removal of all classes of these soils. Characteristics of polishing compounds and their effects on cleaning for the three broad classifications of soil are described in the following paragraphs.

Liquid compositions are oil based and flow readily, leaving a thin film of oil that contains particles of metal and abrasive on the work. Under extreme heat and pressure, some oils polymerize and form a glaze that is difficult to remove.

Mineral oils are usually unsaponifiable and are not readily removable by conventional alkaline cleaners. Solvent wiping, alkaline, or emulsion cleaning, using surfactant cleaners containing surface-activating agents, are more effective in removing residues from mineral oils.

Most animal and vegetable oils can be saponified at a slow rate. These oils are insoluble in water, but can be removed by soaking or spraying in hot alkaline solutions (82 °C, or 180 °F). Spraying is preferred because it removes adhering particles more effectively. Surfactants are suitable also, but their higher cost cannot always be justified.

Semisolid compounds are mixtures of liquid binders and abrasives that contain emulsifying or dispersing agents to keep the abrasive in suspension. When subjected to heat and pressure, these compounds usually form a heavy soil on the surface and may cake and fill in depressions and corners. Such compounds vary from unsaponifiable to completely saponifiable. Hand wiping with solvent or emulsion cleaner is effective in removing these compounds. Impingement from power washers usually removes most of the soil, regardless of the cleaner used. If power washers are not available, soak in agitated solutions containing surfactants, followed by a thorough rinsing, for satisfactory results.

Solid Compounds. The oil phases of solid compounds are easily removed, but the remaining residues cling tenaciously to metal surfaces and must be dislodged by scrubbing action. Power washers are the most effective. Most agitated surfactant cleaners are also effective, but the agitation must be strong enough to dislodge the soils.

Removal Methods

Solvent cleaning is effective for precleaning but is more costly than alkaline or emulsion methods. Cleaning with chlorinated solvents in a mechanical degreaser or brushing or spraying with petroleum solvents quickly removes most of the gross soil after buffing or polishing.

Emulsion Cleaning. Emulsion cleaners containing one part of emulsion concentrate to 50 to 100 parts of water, and operated at 54 to 60 °C (130 to 140 °F) are effective for removing mineral oils and other unsaponifiable oils from polished work. To effectively remove semisolid compounds, the temperature must be raised to 66 to 71 °C (150 to 160 °F) and the concentration increased to one part concentrate to 10 to 20 parts water. Agitation helps dislodge soil from corners or grooves. Table 5 describes cleaning cycles for removing polishing and buffing compounds. Thickened emulsion cleaners may be applied with an airless spray pump. Allow 5 to 10 min dwelling time before cold water rinsing. Emulsion cleaners applied manually at ambient temperature are suitable for many applications, especially for buffed aluminum parts.

Table 5 Emulsion cleaning cycles for removing polishing and buffing compounds

All workpieces were rinsed using water spray.

Type of compound	Temperature		Time, min	Concentration, emulsion to water	Agitation
	°C	°F			
Oil	66-71	150-160	3-5	1:10-20	Soak
Semisolid	54-60	130-140	3-5	1:50-100	Solution movement
Solid	71-82	160-180	1 $\frac{1}{2}$	1:20-50	Spray wash

Note: All emulsion cleaned parts should be subsequently cleaned by alkaline soaking and electrolytic alkaline cleaning before

Removal of solid soils or those containing grit requires the use of higher temperature (71 to 82 °C, or 160 to 180 °F) and increased concentration (one part concentrate to ten parts water). If the soil is heavy, caked, or impacted in corners, a spray washer is required, and the proper ratio of concentrate to water is between 1 to 20 and 1 to 50 (Table 5).

All emulsion methods must be followed by a thorough water spray rinse. The cleaner will loosen and remove most of the soil, but only a strong water spray can remove the remainder. Warm water is preferred, but cold water can be used. A rust inhibitor additive may be required in the rinse after emulsion cleaning to control flash rusting.

In spray equipment, concentration must be controlled to avoid foaming or breaking the emulsion. When soil removal requires a critical concentration, a foam depressant may be added to the cleaner. Polishing compounds containing soap or soap-forming material will cause excessive foaming during agitation, which may reduce the efficiency of the cleaner and the washer. The performance of emulsion cleaners can sometimes be improved by using them in conjunction with alkaline solutions, particularly in spray washers. Alkaline cleaning compounds at a concentration of about 4 g/L ($\frac{1}{2}$ oz/gal) may be used, but the surface being cleaned will still have an oily film after rinsing.

Although the preceding information is applicable primarily to ferrous metal parts, it can be applied also to brass and to zinc-based die castings. The following is a cycle that proved successful for removing polishing and buffing soil from zinc-based die castings in high-volume production:

1. Preclean by soaking for 4 min in diphase cleaner, using kerosene as the solvent; temperature, 71 °C (160 °F); concentration, 1 to 50; plus a 75 mm (3 in.) layer of kerosene. Parts are sprayed with a solution as they are being withdrawn from the tank.
2. Fog spray rinse.
3. Alkaline spray cleaner, 7.5 g/L (1 oz/gal), 71 °C (160 °F), for 1 $\frac{1}{2}$ min.
4. Alkaline soak cleaner, 30 to 45 g/L (4 to 6 oz/gal), 71 °C (160 °F), for 4 min.
5. Spray rinse.
6. Transfer to automatic plating machine or electrolytic alkaline cleaning.

Alkaline cleaning, or one of its modifications, is an effective and usually the least expensive method for removing soils left by polishing and buffing. Mineral oils and other saponifiable oils are difficult to remove by soak cleaning. Oil that floats to the surface redeposits on the work unless the bath is continually skimmed. Agitation of the bath to minimize oil float and proper rinsing of parts as there are withdrawn from the tank minimizes the retention of oil by cleaned parts.

Removing liquid or solid compounds that contain abrasives requires agitation. Most soak cleaners foam if agitated sufficiently to dislodge hardened soil from recesses or pockets. A mildly agitated surfactant cleaner, followed by a strong water spray, can loosen these soils (Table 2).

Operating conditions for soak, spray, and electrolytic alkaline cleaning methods for removing polishing and buffing compounds are listed in Table 6. When the soil is charged with abrasive, alkaline cleaners must be renewed more frequently to prevent the accumulation of dirt that will clog screens and nozzles.

Table 6 Alkaline cleaning for removing polishing and buffing compounds

Soak and spray cleaning are followed by electrolytic cleaning if parts are to be electroplated; electrolytic cleaning is usually preceded by soak or spray cleaning.

Method of cleaning	Concentration		Temperature		Time, min
	g/L	oz/gal	°C	°F	
Soak(a)	30-90	4-12	82-100	180-212	3-5
Spray(b)	4-15	$\frac{1}{2}$ -2	71-82	160-180	1-2
Electrolytic(c)	30-90	4-12	82-93	180-200	1-3

Note: Use great care in cleaning brass and zinc die cast, because these materials are easily attacked at high concentration, temperature, and current density of alkaline cleaners. Anodic cleaning is best, using a concentration of 30 to 45 g/L (4 to 6 oz/gal) at a temperature

(a) For removing light oils, semisolid compounds, and solid compounds if not impacted or burned on work; must be followed by a strong spray rinse.

(b) For removing light mineral oils, semisolids, and solids if impacted or caked on work; followed by a rinse.

(c) For removing light oil films and semisolids. Solids are difficult to remove, especially if combined with grit or metal particles.

Electrolytic alkaline cleaning provides a high level of agitation close to the work surface because of the gas generated and is an effective method for removing polishing and buffing residues. Electrocleaners can be easily contaminated by polishing and buffing compounds as well as steel particles which may be attracted to the work and cause surface roughness during plating. Precleaning is necessary. Parts on which mineral oil has been used as a polishing compound should always be precleaned before being electrocleaned. Use of both heavy duty alkaline soak cleaners and electrocleaners is often necessary to provide a water-break-free surface necessary for good plating quality and adhesion. The presence of large amounts of animal or vegetable oils or fatty acids and abrasives in the polishing and buffing compounds will react with free caustic and form soaps in the electrocleaner and shorten its life.

Acid Cleaning. Acid cleaners are chemically limited in their ability to remove polishing and buffing compounds. Soaps and other acid-hydrolyzable materials present in these compounds are decomposed by acid cleaners into insoluble materials, which precludes the use of acid cleaners in most instances.

Acid cleaners can be used alone for the more easily removed polishing and buffing compounds, such as fresh and unpolymerized liquids. In these applications, the acid cleaner must be used at the maximum operating temperature recommended for the specific cleaner in conjunction with the maximum agitation obtainable by spraying or scrubbing.

Acid cleaners may be desirable for removing acid-insensitive soils in special instances such as: where slight surface attack (short of pickling) is needed for dislodging particles or smut, and in conjunction with alkaline or alkaline emulsion cleaners, when successive reversal of pH proves to be advantageous. A light pickle in dilute hydrochloric, hydrofluoric, or sulfuric acid may be added to the cleaning sequence to remove fine metal particles, tarnish, or light scale to activate the surface for electroplating.

Removal of Rust and Scale

The seven basic methods used for removing rust and scale from ferrous mill products, forgings, castings, and fabricated metal parts are:

- Abrasive blasting (dry or wet)
- Tumbling (dry or wet)
- Brushing
- Acid pickling
- Salt bath descaling
- Alkaline descaling
- Acid cleaning

The most important considerations in selecting one of the above methods are:

- Thickness of rust or scale
- Composition of metal
- Condition of metal (product form or heat treatment)
- Allowable metal loss
- Surface finish tolerances
- Shape and size of workpieces
- Production requirements
- Available equipment
- Cost
- Freedom from hydrogen embrittlement

Combinations of two or more of the available processes are frequently used to advantage.

Abrasive blast cleaning is widely used for removing all classes of scale and rust from ferrous mill products, forgings, castings, weldments, and heat treated parts. Depending on the finish requirements, blasting may be the sole means of scale removal, or it may be used to remove the major portion of scale, with pickling employed to remove the remainder. Glass bead cleaning (blasting) is used for cleaning threaded or precision parts, high-strength steel, titanium, and stainless steel.

Tumbling is often the least expensive process for removing rust and scale from metal parts. Size and shape of parts are the primary limitations of the process. Tumbling in dry abrasives (deburring compounds) is effective for removing rust and scale from small parts of simple shape, such as Part 10 in Fig. 1. However, parts of complex shape with deep recesses and other irregularities cannot be descaled uniformly by tumbling and may require several hours of tumbling if that method is used. Adding descaling compounds rather than deburring compounds often decreases the required tumbling time by 75%.

Brushing is the least used method of descaling parts, although it is satisfactory for removing light rust or loosely adhering scale. It is better suited for workpieces formed from tubing than for castings or forgings.

Pickling in hot, strong solutions of sulfamic, phosphoric, sulfuric, or hydrochloric acid is used for complete removal of scale from mill products and fabricated parts. However, pickling is declining in use as a single treatment for scale removal. With increasing frequency, pickling, at acid concentrations of about 3% and at temperatures of about 60 °C (140 °F) or lower, is being used as a supplementary treatment following abrasive blasting or salt bath descaling. Use of deoxidizing aluminum alloys in room-temperature chromic-nitric-sulfuric acid solutions to remove heat treat scale is common practice.

Electrolytic pickling, although more expensive than conventional pickling, can remove scale twice as fast and may prove economical where the time is limited. In an automatic plating installation, electrolytic pickling removes light scale and oxidizes during the time allowed in the pickling cycle and eliminates a preliminary pickling operation. For this purpose, a solution of 30% hydrochloric acid is used at 55 °C (130 °F) and 3 to 6 V for 2 to 3 min. Cathodic current is used.

Sulfuric acid formulas also are used electrolytically. A cycle for removing light scale from spot-welded parts is a solution of 10% sulfuric acid at 82 °C (180 °F) and 3 to 6 V for 5 to 20 s.

The main objection to electrolytic pickling is high cost. In addition to the requirement for more elaborate equipment, all workpieces must be racked.

Salt bath descaling is an effective means of removing or conditioning scale on carbon, alloy, stainless, and tool steels, heat-resisting alloys, copper alloys, nickel alloys, titanium, and refractory metals. Several types of salt baths either reduce or oxidize the scale. Various baths operate within a temperature range of 400 to 525 °C (750 to 975 °F).

Except in the descaling of pure molybdenum, molten salt baths are seldom used alone for scale removal. Usually, salt bath descaling and quenching are followed by acid pickling as a final step in removing the last of the scale. The supplementary pickling is done with more dilute acids at lower temperatures and for shorter times than are used in conventional pickling. A solution of 3% sulfuric acid at a maximum temperature of about 60 °C (140 °F) is commonly used for pickling after salt bath descaling. Other acids are used at comparable concentrations. Metal loss and the danger of acid embrittlement are negligible in this type of pickling.

Alkaline descaling or alkaline derusting is used to remove rust, light scale, and carbon smut from carbon, alloy, and stainless steels and from heat-resisting alloys. Alkaline descaling is more costly and slower in its action than acid pickling of ferrous alloys, but no metal is lost using the alkaline method, because chemical action stops when the rust or scale is removed. Alkaline descaling also allows complete freedom from hydrogen embrittlement. Alkaline etch cleaning of aluminum alloys is less expensive than acid pickling solutions for descaling, removing shot peen residue, removing smeared metal prior to penetrant inspection, chemical deburring, and decorative finishing of nonclad surfaces.

A number of proprietary compounds are available. They are composed mainly of sodium hydroxide (60% or more) but also contain chelating agents.

Immersion baths are usually operated from room temperature to 71 °C (160 °F), but can be used at 93 to 99 °C (200 to 210 °F) with concentrations of about 0.9 kg (2 lb) of compound to 4 L (1 gal) of water. Required immersion time depends on the thickness of the rust or scale.

The rate of removal of oxide can be greatly increased by the use of current in the bath, either continuous direct or periodically reversed. In one instance, an electrolyzed bath descaled steel parts in $1\frac{1}{2}$ min, as compared to 15 min for a nonelectrolytic bath doing the same job. However, parts must be racked for electrolytic descaling, increasing cost because of the additional equipment, increased power requirement, and decreased bath capacity.

The addition of about 0.5 kg (1 lb) of sodium cyanide per 4 L (1 gal) of water increases the effectiveness of electrolyzed baths. However, when cyanide is used, the bath temperature should be kept below 54 °C (130 °F) to prevent excessive decomposition of the cyanide. One manufacturer descales heat treated aircraft parts in an alkaline descaling bath, using direct current and cyanide additions. Another manufacturer descales similar work in an alkaline bath operated at 82 to 93 °C (180 to 200 °F) with a lower concentration of descaling compound, 60 to 90 g/L (8 to 12 oz/gal), and no cyanide. The latter bath is operated at a current density of 2 to 20 A/dm^2 (20 to 200 A/ft^2) and with periodic current reversal (55 s anodic, followed by 5 s cathodic). Alkaline permanganate baths are also used for descaling. Proprietary products available are used at about 120 g/L (1 lb/gal), 82 to 93 °C (180 to 200 °F), 30 min or longer, depending on scale thickness and condition

Despite the high cost of alkaline descaling baths, they can be economical. Because alkaline descaling baths are compounded for detergency as well as derusting, chemical cleaning and derusting are accomplished simultaneously.

Paint, resin, varnish, oil, grease, and carbon smut are removed along with rust and scale. Thus, in a single operation, work is prepared for phosphating, painting, or electroplating. If parts are to be plated, the cost of electrolytic descaling may be comparable to that of the nonelectrolytic process, because in either case workpieces must be racked before final cleaning and plating. An electrolytic descaling bath may serve as the final cleaner.

Alkaline descalers are used for applications on critical parts such as turbine blades for jet engines where risk of hydrogen embrittlement, loss of metal, or etched surfaces cannot be tolerated. Alkaline descaling may also be chosen for parts made of high-carbon steel or cast iron, because acid pickling will leave smut deposits on these metals. Because of the time required, alkaline descaling is seldom used for removing heavy scale from forgings.

Acid Cleaning. Acid cleaners more dilute than acid pickling solutions are effective for removing light, blushing rust, such as the rust that forms on ferrous metal parts in storage under conditions of high humidity or short-time exposure to rain. Acid deoxidizing solutions specifically designed for use on aluminum remove oxides and should be used before electroplating or chemical coating. Various organic acid-based solutions, such as citric acid, are used to remove rust from stainless steels, including the 400 series and the precipitation hardening steels.

The following examples illustrate the considerations that influence the choice of process for removing rust and scale. Additional criteria for selection of process are included in Table 7, which compares advantages and disadvantages of abrasive blast cleaning, pickling, and salt bath descaling.

Table 7 Advantages and disadvantages of the three principal processes for removing scale and rust from steel parts

Advantages

Abrasive blast cleaning
A variety of equipment and abrasives is available
Does not interfere with properties established by heat treatment
Size of workpiece is limited only by available equipment
A wide variety of shapes can be blasted
All metals can be safely blasted
Adaptable to either intermittent low or continuous high production
Pickling
Formulations can be adjusted to meet individual requirements in removing scale from various ferrous and nonferrous alloys
Equipment required is simple and relatively inexpensive
Materials are relatively low in cost, and process control usually is not difficult
Adaptable to products of virtually any size or shape
Installations can be adapted to either low or high, intermittent or continuous production
Temperatures used will not affect properties of heat treated steel
Salt bath descaling
Reduction or oxidation of the scale is almost instantaneous after workpieces reach bath temperature
No loss of metal and no danger of hydrogen embrittlement
Preliminary cleaning is unnecessary unless there is so much oil on the work that a fire hazard is involved as workpieces enter the bath
Different metals can be descaled in the same bath
Workpieces of complex shape can be processed, although special handling may be required to obtain complete removal of salt
Processing temperature may provide useful stress relieving
For some heat-resisting and refractory metals, molten salt is the only satisfactory method
Will not damage sensitized stainless steels, whereas acid pickling would be harmful

Disadvantages

Abrasive blast cleaning
Some of the metal will be abraded from workpieces, especially from corners
May alter dimensions of machined parts or damaged corners
If sufficiently drastic to remove scale, process may cause more surface etching or roughness than can be tolerated

Complex configurations will not receive equal blasting on all surfaces without special handling, which may be too costly

Pickling

Potential source of hydrogen embrittlement in some metals such as carbon and alloy steels of high carbon content, especially if these materials have been heat treated to high strength levels

Up to 3% of the metal may be lost in pickling--particularly significant for the more costly metals such as stainless steels or heat-resisting alloys

Fume control and disposal of spent acids are major problems

Process is likely to deposit smut on cast iron

Excessive pitting may occur in the pickling of cast steels and irons

Salt bath descaling

Not economical for intermittent production, because high operating temperatures necessitate special heating and handling equipment, and because the bath must be kept molten between production runs

The required water quenching may cause cracking or excessive warping of complex workpieces

The process is not suitable for metals (such) as some grades of stainless steel) that precipitation harden at the temperature of the salt bath

Operating temperature of the bath can cause carbide precipitation in unstabilized stainless steels

Properties of heat treated workpieces may be impaired if their tempering temperature is below that of the salt bath

Subsequent acid cleaning is usually required to neutralize remaining salts, complete the descaling, and brighten the finished product

Example 1:

Barrel or vibratory tumbling is probably the most economical method for removing scale or rust from steel parts like Part 10 in Fig. 1, if they are no larger than about 50 to 75 mm (2 to 3 in.). For similar but larger parts, abrasive blasting is usually a better choice.

However, if such parts are close to finished dimensions and these dimensions are critical, a nonabrasive method of cleaning should be chosen. If parts are made of low-carbon steel and are not heat treated, pickling in inhibited hydrochloric or sulfuric acid is satisfactory and less expensive, and hydrogen embrittlement is not a factor. However, if such parts are made of high-carbon (or carburized) steel and are heat treated, acid pickling would be hazardous and alkaline descaling would be preferred.

Example 2:

The gear illustrated as Part 7 in Fig. 1 is made of 8620 steel, carburized, and hardened to about 56 to 58 HRC. Although the part is processed in a controlled atmosphere, a descaling operation is required. Abrasive blasting with fine steel grit or chilled iron shot (SAE G40 or S170) proved the most economical method for cleaning large tonnages of such parts used in the manufacture of trucks, tractors, and similar vehicles. Acid pickling was precluded because of hydrogen embrittlement, and descaling in molten salt was unsuitable because of the softening effect of the high-temperature bath.

Conventional abrasive blasting may deleteriously affect the dimensions of precision gears or pinions. In these special applications, alkaline descaling or wet blasting with a fine abrasive, such as glass beads, under carefully controlled conditions, is indicated.

Example 3:

The turbine blade shown as Part 8 in Fig. 1 is made of type 403 stainless steel. If such parts are made in continuous production, molten salt bath descaling would be the preferred cleaning method. If production is intermittent, the molten salt method would be too costly, and alkaline descaling would be more practical. Abrasive blasting is unsuitable for this application because of close dimensional requirements; pickling cannot be used because of metal loss and the risk of hydrogen embrittlement.

Example 4:

Scale resulting from welding of the low-carbon steel component shown as Part 12 in Fig. 1 could be removed satisfactorily and economically by either abrasive blasting or acid pickling. Because the part is phosphated and painted, surfaces are not critical. Acid pickling would probably be preferred, because it would make more uniform contact with all areas without the need for special handling. Even if a large quantity of parts were to be cleaned, salt bath descaling would not be used, because the water quench from about 425 °C (800 °F) would cause excessive warpage. The cost of alkaline descaling in an aqueous solution would not be justified for this class of work.

Example 5:

Normally, abrasive blasting would be the preferred method for removing rust and scale from a rough ferrous metal casting like Part 11 in Fig. 1. Chilled iron shot or steel abrasives are usually the most economical abrasives for this purpose.

Pickling is seldom used for descaling castings, such as cast iron, because smut is deposited and must be removed by another cleaning operation. Severe pitting is also likely to result.

Salt baths have been successfully used for descaling ferrous castings, but there is danger of cracking and excessive distortion for configurations such as Part 11.

Removal of Residues from Magnetic Particle and Fluorescent Penetrant Inspection

Successful removal of the iron oxide particles deposited on ferrous parts during magnetic particle inspection requires complete demagnetization of the part. After demagnetization, emulsion cleaning is an effective and practical means of removing both the iron oxide residues and oil. Fluorescent pigments used for similar inspection of aluminum parts can be removed with hot alkaline cleaners.

For low-to-moderate production, an efficient procedure consists of immersing parts in a light, undiluted, oil-based emulsion cleaner at room temperature or slightly above. Parts are then drained to remove excess cleaner and rinsed in water, using either agitation or forced spray at room temperature or slightly above. For higher-volume production, power washers are successful. Parts can be handled singly or in baskets or carriers.

Parts with complex configurations such as Part 9 in Fig. 1, fine threads, or serrations are difficult to clean thoroughly. As-cast or as-forged surfaces also cause the magnetic oxide particles to cling tenaciously. However, immersion in a cleaning emulsion with sufficient agitation or the use of a power washer, with properly placed nozzles and with suitable handling equipment, will clean almost any part. All oxide particles must be removed before the part is dried, or hand wiping or brushing will be required.

A type of emulsion cleaner that incorporates a rust preventative is usually preferred, because it provides protection until the next operation is performed. If rust-preventive films are objectionable in the next operation, they can be removed easily with alkaline cleaners.

Special Procedures for the Removal of Grinding, Honing, and Lapping Compounds

Residues remaining on parts after honing or grinding are usually mixtures of metallic and abrasive particles with oil-based or water-based cutting fluids. Thus, the methods recommended earlier in this article for the removal of chips and cutting fluids are applicable also for the removal of grinding residues in a majority of instances.

Lapped parts are usually more difficult to clean than honed or ground parts. Lapping residues are composed of extremely fine particles of various abrasives, minute metal particles, semi-solid greases and oils, and some graphite. Even if graphite is not a part of the original lapping compound, it accumulates from the wear of cast iron laps. Allowing compounds to dry increases cleaning difficulty. In many instances, methods used for removing polishing and buffing compounds are applicable also for removing lapping compounds. However, parts that are precision ground, honed, or lapped present special cleaning problems because: such parts are commonly used in precision machinery, and consequently the degree of cleanness required is higher than for most commercial work; they are frequently intricate in design (an example in Part 15 in Fig. 3); and they are commonly susceptible to damage and frequently require special handling.

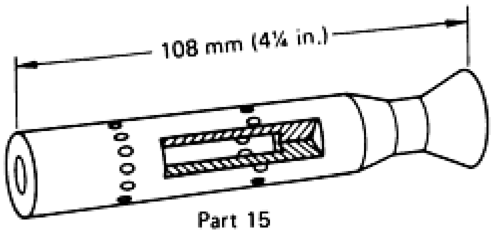

Fig. 3 Part for fuel control mechanism that requires special modification of solvent cleaning to remove grinding and lapping compounds

An extremely high degree of cleanness without damage is required on some expensive delicate parts (e.g., fuel injection equipment). Ultrasonic cleaning with alkaline solution, followed by spray with alkaline and immersion/spray rinsing is ideal for this application. Ultrasonic cleaning is rapidly replacing the old pressure solvent spray/agitated immersion technologies, which were only partially effective. Parts which normally took an hour or more to clean using solvent cleaning processes are now effectively cleaned in just a few minutes of ultrasonic cleaning. Other inherent advantages of this approach are that it is nondestructive to the parts; it uses more environmentally friendly cleaning solutions, and it is much safer with respect to the explosion dangers that are characteristic of many solvent cleaning technologies. As always, the primary drawback to ultrasonic cleaning is the comparative high up-front capital cost.

Room-Temperature Cleaning

Room-temperature or cold cleaners are aqueous solutions for removing soil without the aid of heat other than that resulting from pumping and circulating the solution or being transferred from the surrounding atmosphere. The operating range of such cleaners is usually from 21 to 46 °C (70 to 115 °F). For additional information, see the article "Alkaline Cleaning" in this Volume.

Cold alkaline cleaners, such as the silicate or phosphate types (orthosilicate or tetrasodium pyrophosphate), are chiefly used for cleaning where heat is not available, where heated solutions are not permitted, or when heating the parts above about 46 °C (115 °F) is not desirable. In a cold process for iron phosphating, for example, parts that have been cleaned in a heated solution and have not cooled sufficiently before entering the phosphate solution will yield an unacceptable phosphate coat. In some applications, an unheated cleaning solution is preferred in order to facilitate the checking of part dimensions at room temperature without the delay involved in cooling the parts after cleaning. This procedure is used for cam shafts, honed cylinder walls, and valve-guide holes in engine heads. One automotive plant utilizes a cold alkaline cleaner for removing soil from engine blocks in a power washer at the rate of 300 per hour. In another application, carburetor parts are cleaned at a rate of 600 to 700 per hour. Table 8 provides several detailed examples of the application of cold alkaline cleaners.

Table 8 Examples of application of room-temperature alkaline cleaners

Part	Surface from last operation	Relative amount of original soil on part	Residual soil on part after cleaning, mg
Aluminum alloy piston	Ground	Heavy, up to 0.75 g per part	0.1
Pinion gear, ferrous	Ground and lapped	Heavy	0.1
Ring gear, ferrous	Ground and lapped	Heavy	0.1

Part	Surface from last operation	Relative amount of original soil on part	Residual soil on part after cleaning, mg
Engine heads, ferrous	Fully machined	Heavy	1.5
Engine intake manifold, ferrous	Fully machined	Heavy	10
Carburetor throttle body, ferrous	Fully machined	Medium to heavy	0.5
Automatic transmission pump, ferrous	Fully machined	Medium to heavy	6

Cold cleaners may also reduce costs by using simpler equipment, eliminating the expense of energy for heating, and reducing maintenance requirements.

Cold acid cleaners, such as monosodium phosphate containing a detergent, are also available. Their chief use is for cleaning immediately before iron phosphating, where the advantage of a lower pH is significant. These acid cleaners have a pH of about 6 and thus impart a surface compatible with the iron phosphate bath, which has a pH of 4.5 to 5.5.

Some proprietary products now offer simultaneous cleaning and iron phosphating at room or low temperatures. In a few other isolated applications, cold acid cleaners perform satisfactorily, but in most instances heated solutions are much more efficient.

Ultrasonic Cleaning

Ultrasonic energy can be used in conjunction with several types of cleaners, but it is most commonly applied to chlorinated hydrocarbon solvents, water, and water with surfactants. Ultrasonic cleaning, however, is more expensive than other methods, because of higher initial cost of equipment and higher maintenance cost, and consequently the use of this process is largely restricted to applications in which other methods have proved inadequate. Areas of application in which ultrasonic methods have proved advantageous are:

- Removal of tightly adhering or embedded particles from solid surfaces
- Removal of fine particles from powder-metallurgy parts
- Cleaning of small precision parts, such as those for cameras, watches, or microscopes
- Cleaning of parts made of precious metals
- Cleaning of parts with complex configurations, when extreme cleanness is required
- Cleaning of parts for hermetically sealed units
- Cleaning of printed circuit cards and electronic assemblies

Despite the high cost of ultrasonic cleaning, it has proved economical for applications that would otherwise require hand operations.

Part size is a limitation, although no definite limits have been established. The commercial use of ultrasonic cleaning has been limited principally to small parts. The process is used as a final cleaner only, after most of the soil is removed by another method. Ultrasonic cleaning, in some cases, has resulted in fatigue failure of parts. Proper racking and isolation from tank wall will often solve this problem.

Surface Preparation for Phosphate Coating

Because the chemical reaction that results in the deposit of a phosphate coating depends entirely on good contact between the phosphating solution and the surface of the metal being treated, parts should always be sufficiently clean to permit the phosphating solution to wet the surface uniformly. 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, at worst, completely preventing solution contact. Some soils can be coated with the phosphate crystals, but adherence of the coating will be poor, and this will in turn affect the ability of a subsequent paint film to remain continuous or unbroken in service.

Soils such as cutting oils, drawing compounds, coolants, and rust inhibitors can react with the substrate metal and form a film that substantially changes the nature of the coating. 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. Additional information can be found in the article "Phosphate Coatings" in this Volume.

Surface Preparation for Painting

Surface preparation has a direct effect on the performance of paint films. The best paint available will fail prematurely if applied to a contaminated or improperly prepared surface. The surface will also influence the final appearance of the paint film. Surface irregularities may not be hidden by the paint, but they may instead be reflected as apparent irregularities of the paint film. The principal surface contaminants that are deleterious to the performance of paint films include oil, grease, dirt, weld spatter, alkaline residues, rust, mill scale, water, and salts such as chlorides and sulfides.

Mechanical and chemical cleaning operations may be used in combination to meet a rigid requirement of surface cleanliness. For example, on scale-bearing steel intended for an application involving exposure to chemical environments, complete removal of all oil, grease, rust, mill scale, and any other surface contaminants is mandatory. Nonferrous alloys such as aluminum require chemical conversion pretreatment plus chromated primers for maximum life and corrosion protection.

Further discussion can be found in the article "Painting" in this Volume.

Surface Preparation for Electroplating

Preparation for plating is one of the most critical of all cleaning operations, because maximum adhesion of the plated coating to the substrate is the major requirement for quality work. Maximum adhesion depends on both the elimination of surface contaminants in order to induce a metallurgical bond whenever possible and the generation of a completely active surface to initiate plating on all areas. In addition to pickling or other descaling operations, adequate cleaning requires multistage cycles, usually comprised of the following steps: (1) precleaning with a solvent to remove most of the soil; (2) intermediate cleaning with alkaline cleaners; (3) electrocleaning to remove the last traces of solids and other contaminants that are especially adherent; (4) acid treatment and surface conditioning to remove light oxide films formed during previous cleaning processes and to microetch the surface; and (5) electrolytic (anodic) desmutting to remove any smut formed during acid pickling of heat treated high-carbon steel parts. Low-carbon steels do not require this desmutting step. Anodic electrocleaning also offers oxidation or conditioning of scale. The oxidized or softened scale is easily removed in subsequent acid pickling. The types of cleaning usually employed in the above steps are:

- *Precleaning:* cold solvent, vapor degreasing, emulsifiable solvent, solvent emulsion spray, or alkaline spray with or without solvent emulsion
- *Intermediate alkaline cleaning:* soak cleaning with 30 to 90 g/L (4 to 12 oz/gal) of cleaner at 82 °C (180 °F) to boiling, spray cleaning with 4 to 15 g/L (0.5 to 2 oz/gal) at 66 to 82 °C (150 to 180 °F), and barrel cleaning with 7.5 to 45 g/L (1 to 6 oz/gal) at temperatures below 82 °C (180 °F)
- *Electrocleaning:* cathodic, anodic, or periodic-reverse
- *Acid treatment:* practice is highly specific for the metal being processed
- *Anodic desmutting:* necessary to remove carbon smut

ASTM recommended practices for cleaning various metals prior to plating are given below:

A 380	Descaling and cleaning of stainless steel surfaces
B 183	Preparation of low-carbon steel for electroplating
B 242	Preparation of high-carbon steel for electroplating
B 252	Preparation of zinc-based die castings for electroplating
B 253	Preparation of and electroplating on aluminum alloys
B 254	Preparation of and electroplating on stainless steel
B 281	Preparation of copper and copper-based alloys for electroplating
B 319	Preparation of lead and lead alloys for electroplating
B 480	Preparation of magnesium and magnesium alloys for electroplating
B 322	Cleaning metals before electroplating

Process sequences and operating details in surface preparation for electroplating are presented in articles in this Volume on cadmium plating, finishing of stainless steel, finishing of aluminum alloys, finishing of copper alloys, finishing of magnesium alloys, and finishing of titanium alloys. The procedures used for preparing the surfaces of high-carbon and low-alloy steels, low-carbon steel, and zinc-base die castings are discussed below.

Steels may be cleaned and otherwise prepared for electroplating according to the procedures outlined by the flow charts in Fig. 4 and operating conditions in Table 9. The preparation of low-carbon steel for electroplating consists essentially of cleaning to remove oil and caked-on grease, pickling to remove scale and oxide films, cleaning to remove smut left on the surface, and reactivating the surface for plating.

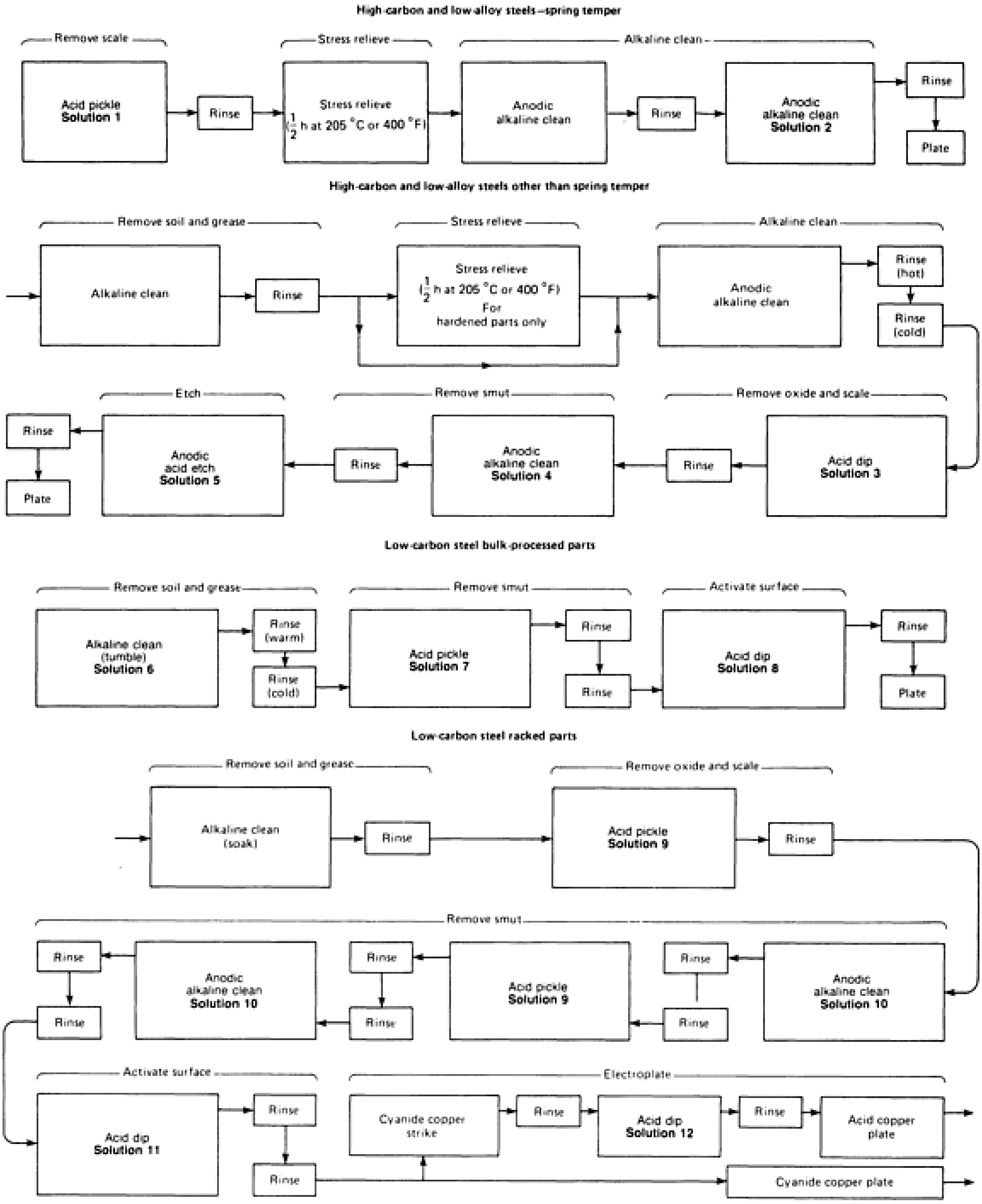

Fig. 4 Process flow charts for preparation of steels for electroplating. See Table 9 for operating conditions.

Table 9 Solutions and operating conditions for preparation of steels for electroplating

See Fig. 4.

Solution no.	Type of Solution	Composition	Amount	Operating temperature		Cycle time, s
				°C	°F	
High-carbon and low-alloy steels, spring tempter						

1	Acid pickle	HCl HNO_3	20-80 vol% 1-5 vol%	Room temperature		[(a)]
2	Anodic alkaline cleaner[(b)]	NaCN	20-45 g/L (3-6 oz/gal)	49-54	120-130	30-60
High-carbon and low-alloy steels other than spring temper						
3	Acid dip	HCl	1-10 vol%	Room temperature		[(a)]
4	Anodic alkaline cleaner[(b)]	NaCN	20-45 g/L (3-6 oz/gal)	Room temperature		30-60
5	Anodic acid etch[(c)]	H_2SO_4	250-1005 g/L (33.5-134 oz/gal)	30 max	86 max	60 max
Low-carbon steel bulk-processed parts						
6	Alkaline cleaner[(d)]	Alkali	30-60 g/L (4-8 oz/gal)	82-99	180-210	60-120
7	Acid pickle	HCl	25-85 vol%	Room temperature		5-15
8	Acid dip	H_2SO_4	4-10 vol%	Room temperature		5-15
Low-carbon steel racked parts[(e)]						
9	Acid pickle	HCl	25-85 vol%	Room temperature		[(a)]
10	Anodic alkaline cleaner[(f)]	Alkali	60-120 g/l (8-16 oz/gal)	93-99	200-210	60-120
11	Acid dip	H_2SO_4	4-10 vol%	Room temperature		5-15
12	Acid dip	H_2SO_4	1 vol%	Room temperature		5-10

(a) Minimum time for removal of scale.

(b) Current density, 1.5 to 2.0 A/dm^2 (15 to 20 A/ft^2).

(c) Current density, 1.50 A/dm^2 (150 A/ft^2).

(d) Tumble, without current.

(e) Cycles for copper plating included in chart are applicable to all steels here, except that for high-carbon and low-alloy steels, a cyanide copper strike precedes cyanide copper plating.

(f) Current density, 5.0 to 10.0 A/dm^2 (50 to 100 A/ft^2)

Plating on low-carbon steels represents the bulk of industrial plating. The steps generally used before plating low-carbon steels are:

1. Vapor degrease, if necessary
2. Alkaline soak clean
3. Water rinse
4. Descale, if necessary
5. Water rinse
6. Alkaline electroclean
7. Water rinse
8. Acid activate
9. Water rinse
10. Plate, as required

These steps are a general guideline and should not be construed as firm recommendations. The actual required cycle would depend on extent of grease and oil contamination, type of scale, and facilities available for the plating operation. Some of the options available to the plater are:

- Emulsion cleaning may be used in place of vapor degreasing. In this case, additional water rinsing is required.
- Anodic electrocleaning is preferred over cathodic cleaning which can cause smut on parts because of plating of polar soils in the cleaner. Electrocleaners are generally used at 60 to 75 g/L (8 to 10 oz/gal) and at 8.0 to 10.0 A/dm^2 (80 to 100 A/ft^2). Temperature will depend on the type of cleaner. Low-temperature cleaners operate at 27 to 49 °C (80 to 120 °F); high-temperature cleaners operate at 82 to 93 °C (180 to 200 °F).
- If parts are not excessively dirty, soak cleaning can be used instead of electrocleaning. Specially compounded alkaline cleaners are sometimes used to remove slight amounts of oxides. Elevated temperatures are recommended for all alkaline cleaning.
- Alkaline cleaners are difficult to rinse. Carryover of residues can produce staining, skip plating, or loss of adhesion. Warm water is recommended in the first rinse along with good agitation. Two or more countercurrent (cascade) rinses are highly desirable both from the standpoint of good rinsing and conservation of water. If both alkaline soak cleaning and alkaline electrocleaning are used, the two cleaning steps should be separated with a thorough rinse.
- Plating is initiated on an active surface. A wide variety of activators is available, and most are acidic in nature. Hydrochloric, sulfuric, or fluoboric acids are commonly used.
- Water rinse after activation is critical to avoid contaminating the sensitive plating solution. Countercurrent rinsing with two or more rinse tanks is desirable.
- High-carbon and low-alloy steels are susceptible to hydrogen embrittlement.
- Proprietary inhibited acid pickles are available for the effective removal of scale and rust with reduced danger of hydrogen embrittlement and base metal attack.

Unless the acids used contain inhibiting agents, the acid treatments for surface preparation must be very mild and of short duration. If electrolysis is necessary, it should be used with anodic current. This is especially significant for spring-temper parts and parts that have been case hardened. Mechanical methods of descaling can often eliminate the need for pickling.

During the anodic etch, a high acid content, low solution temperature, and high current density will minimize smut formation. Carryover of water into the anodic etching solution should be held to a minimum, and long transfer times after the anodic etch should be avoided.

Cold rolled steel that has been subjected to deep drawing and certain prepickled hot rolled steels with glazed brownish-colored surfaces may be exceedingly difficult to clean. For these materials, a solution of 25 to 85 vol% nitric acid has proved effective.

Paint Stripping

Infrequently, parts have to be stripped and repainted. Possibly there is a problem with appearance; the wrong paint or color may have been used. Tools, fixtures, and automatic spray line fixtures must be periodically cleaned of old paint buildup as well. Some paints are easier to strip than others, and some paint stripping methods are incompatible with some metals. A hot alkaline cleaning bath, which is a part of a metal process line, should not be used as a paint stripping tank. Even if the cleaning bath works, the bath quality would be degraded and uncontrolled impurities introduced. Paint cannot be effectively removed from a soiled part, so any part should first be cleaned. Table 10 compares various stripping methods and lists appropriate financial considerations. Selection of strippers is summarized in Table 11. In paint stripping, two processes are widely used, hot stripping and cold stripping.

Table 10 Methods of stripping paint

Method	**Facility**	**Cost factors**
Immersion	One or more tanks, water rinse capability required	Slow removal rate, low labor, costly facility, disposal cost
Spray or brush-on	Area, ventilation, rinse capability required	Slow removal rate, higher labor, lesser cost facility, disposal cost
Abrasive	Sand or shot blast facility	Slow removal, high labor, may use existing facility, disposal cost
Molten salt	Specialized facility for steel only	Rapid removal rate, costly facility, low labor, very efficient, lower disposal cost, fume collection required

Table 11 Selection of strippers for removing organic coatings

Type of organic finish to be removed	**Approved metal substrates**	**Means of application**	**Approved strippers and methods**	**Operating temperature**		**Remarks**
				°C	**°F**	
Epoxy primer epoxies polyurethanes	All[(a)]	Spray or brush on	Proprietary phenolic chromated methylene chloride	10-38[(b)]	50-100[(b)]	Good ventilation and protective clothing. Must be approved for high-strength steels
All others	Steel	Immersion	Low viscosity[(c)]	10-38[(b)]	50-100[(b)]	Good ventilation and protective clothing
	All[(a)]	Spray or brush on	High viscosity[(c)]	10-38[(b)]	50-100[(b)]	Must be approved for high-strength steels

All	Steel(d)	Immersion	Proprietary molten salt	As specified by vendor		2-5 min follow with water quench and rinse. Smoke and fume control required
Primers, wax, overspray, and temporary coatings	All	Wipe or squirt on	Butyl cellosolve methyl isobutyl ketone, ethyl alcohol xylene, toluene	Room temperature(e)		Xylene and toluene are normally only effective on waxes and some temporary coatings
All except epoxy based	All	Immersion	Caustic stripper	10-38(b)	50-100(b)	Water base 10-12 pH
Epoxy	All	Dry abrasive blast	MIL-G-5634 Type III	Room temperature		Adjust pressure to part fragility
	Aluminum	Immersion	Chromic acid solution,360-480 g/L (3-4 lb/gal)	74 ± 3	165 ± 5	Maximum allowable immersion time is 15 min. Water rinse parts as soon as possible on removal from solution.
			Chromic acid plus nitric acid solution			CrO_3 360-480 g/L (3-4 lb/gal), HNO_3 5% total volume
All	Aluminum	Immersion	Nitric acid solution 50-78% HNO_3	34 ± 6	110 ± 10	Maximum allowable immersion time, 20 min

Note: Heavy metals plus stripping chemicals require appropriate means of disposal to meet EPA regulations.

(a) Except steel heat treated above 1500 kPa (220 psi).

(b) Optimum temperature range: 18 to 29 °C (65 to 85 °F).

(c) Proprietary: phenolic, chromated, methylene chloride.

(d) Except heat treated steel.

(e) Do not exceed 32 °C (90 °F)

Hot stripping uses high caustic level and high temperatures. Alkaline paint strippers contain caustic soda, sodium gluconate, phenols, or cresols. The bath is used at 80 to 95 °C (180 to 200 °F). Depending on the type of paint and coating thickness, stripping can be done in 30 min to 6 to 8 h. Hot stripping is slow, but economical and environmentally safe. Hot alkaline paint strippers will attack brass, zinc, and aluminum. These strippers are safe for steel and copper.

Cold stripping, as the name indicates, is done without any heating. The stripping bath consists of powerful organic solvents, such as methylene chloride; also organic acids, such as phenols or cresols. Many of the organic solvent strippers available in the market contain two layers. The heavier bottom layer is the organic solvent layer, in which the actual paint stripping takes place. The lighter top layer is the aqueous layer which prevents the evaporation of the highly volatile organic solvents from the bottom layer.

Cold solvent stripping, when applicable, is fast. The process, however, is very expensive and waste disposal could be a problem. Unlike hot strippers, the organic cold strippers can be used on all base metals such as steel, copper, aluminum, brass, and zinc.

Newer paint stripping technologies strive to combine advantages of both the hot and cold stripping techniques. These paint strippers, called *diphase* or *multiphase* strippers, allow hot alkaline stripping and solvent-based stripping to occur in the same tank via formation of a stable paint stripping emulsion. The emulsion stripper is best run hot with high agitation to keep the emulsion stable. This process is often able to strip paint that cannot be stripped by either hot alkaline or cold solvent methods, and it is comparatively fast.

Glass Bead Cleaning

Glass bead cleaning is a low energy, nonpolluting method for use with both small and delicate parts as well as large turbines and engines. Glass bead air systems equal or surpass the finish quality provided by liquid abrasive slurry. Other benefits include no measurable amount of metal removed from close tolerance surfaces (fine threaded screws) and noncontamination of work surfaces with wide range of bead sizes (170 to 400+ grit). Glass bead cleaning has been successfully applied to a wide diversity of uses such as: preparation of surfaces for painting, plating, brazing, welding, bonding; finishing of castings; production of matte finish on metal, glass, and plastics for decorative purposes; reclamation of tools such as files and saws; stripping of paint; and removal of solder from electrical assemblies.

Air pressures recommended for this procedure range from 70 to 415 kPa (10 to 60 psi). An angle of 40 to 60° for nozzle to work direction should be used to minimize bounce back and reduce bead consumption because of breakage. The selection of bead size should be based on the smallest particle that will give the desired surface. This provides the maximum number of impacts per pound. Working distances of 100 to 200 mm (4 to 8 in.) from nozzle to work will provide greatest impact (velocity) with the best pattern.

Pollution Control and Resource Recovery

The increasing cost of waste disposal has a great impact on process cost and should be considered in selecting cleaning processes. Treatment of waste within the plant should be considered to reduce cost, reduce liability, permit reuse of the raw material, and improve process control. A good example of closed-loop recycling is the distillation purification of vapor degreasing solvent. The federal EPA has established compliance guidelines, but state and local regulations are often more stringent. For more information, see the article "Environmental Regulation of Surface Engineering" in this Volume.

Safety

In the use of any metal cleaning process, there are possible safety, health, and fire hazards which need to be considered. The degree of hazard is dependent upon such factors as the specific materials and chemicals involved, the duration of employee exposure, and the specific operating procedures.

Information is presented in Table 12 on the types of hazards which may be associated with each cleaning process and the general control measures which would be used for each hazard.

Table 12 Safety and health hazards of cleaning processes

Cleaning process	Hazard/air contaminant	Control measures	OSHA/NFPA references
Abrasive blasting	Silica dust/total dust exposures	Local exhaust ventilation	(29 CFR)
		Respiratory protection	1910.94(a)
		Goggles or face shield	1910.95

Cleaning process	**Hazard/air contaminant**	**Control measures**	**OSHA/NFPA references**
	Noise exposures	Noise exposures	1910.133
		Hearing protective devices	1910.134
	Skin abrasion	Leather protection garments	1910.1000
			Table Z-3
Acid cleaning	Acid gas or mist exposure	Local exhaust ventilation	1910.94(L)
		Respiratory protection	1910.133
		Goggles or face shield	1910.134
	Skin contact	Impervious gloves and garments	1910.1000
			Table Z-1
Alkaline cleaning	Alkaline mist exposure	Local exhaust ventilation	1910.94(d)
		Respiratory protection	1910.133
		Goggles or face shield	1910.134
	Skin contact	Impervious gloves and garments	1910.1000
			Table Z-1
Emulsion cleaning	Petroleum or chlorinated hydrocarbons	Local exhaust ventilation	1910.94(d)
		Respiratory protection	1910.132
	Alkaline mist exposures	Local exhaust ventilation	1910.133
			1910.134
			1910.1000

Cleaning process	**Hazard/air contaminant**	**Control measures**	**OSHA/NFPA references**
			Tables Z-1, Z-2
Emulsion cleaning	Alkaline mist exposures	Respiratory protection	
		Goggles or face shield	
	Skin contact	Impervious gloves and garments,	
Pickling	Acid gas or mist exposures	Local exhaust ventilation	1910.94(d)
		Respiratory protection	1910.133
		Goggles or face shield	1910.134
	Skin contact	Impervious gloves and garments	1910.1000
			Table A
Salt bath descaling	Burns	Heat resistant gloves and garments	1910.132
		Face shield	1910.133
	Toxic gases	Local exhaust ventilation	1910.134
		Respiratory protection	1910.1000
			Table Z-1
	Fire/explosion	Proper facility design, construction, maintenance	NFPA 86C, Chapter 11
		Proper controls for tank	
		Proper work procedures	
Solvent cleaning	Petroleum or chlorinated hydrocarbon exposure	Local exhaust ventilation	1910.94(d)
			1910.132

Cleaning process	Hazard/air contaminant	Control measures	OSHA/NFPA references
			1910.133
		Respiratory protection	1910.134
			1910.1000
	Skin contact	Impervious gloves and garments	Tables Z-1, Z-2
Tumbling	Noise exposure	Noise enclosure for equipment	1910.95
		Hearing protective devices	
Vapor degreasing	Chlorinated hydrocarbon exposure	Condenser cooling system and appropriate thermostats	1910.94(d)
		Minimize dragout	
		Local exhaust ventilation	
	Solvent decomposition products	Eliminate hot surfaces above 400 °C (750 °F) in the vicinity	
		Eliminate sources of ultraviolet radiation in the vicinity	
		Proper monitoring of solvent for acid buildups to prevent exothermic decomposition	

The Occupational Safety and Health Administration has established in its General Industry Standards (29 CFR 1910) regulations pertaining to a variety of safety and health hazards. Those sections of the standards which may apply to each cleaning process are referenced in Table 12. Because of the unusual fire hazard associated with salt bath descaling, an applicable chapter of the NFPA standards has also been referenced.

Tests for Cleanliness

The final evaluation of the effectiveness of a cleaning process should come from a performance test. Eight well-known methods of determining the degree of cleanness of the work surface are discussed below.

Water-break test is a simple test, widely used in industry. It consists of dipping the work into clean water to reveal a break in the water film in the soiled area. However, because the test depends on the thickness of the applied water film, a factor which cannot be controlled, false results can be obtained because of bridging of residues. A mild acid dip before testing for water break has been found advantageous.

Nielson method requires that ten soiled panels be processed individually to determine the time required for each to be cleaned. Panels are checked by the water-break test and then by the acid copper test. In the acid copper test, the ferrous panel is immersed in a copper sulfate solution (typical composition, 140 g [5 oz] of copper sulfate and 30 cm^3 [1 fluid oz] of sulfuric acid per gallon of water). On clean surface areas, copper will be deposited by chemical activity, forming a strongly adherent, semibright coating that is free of spots.

An average of the times required to clean the ten panels is taken as a measure of the effectiveness of the cleaning solution.

Atomizer Test. In the atomizer test, panels are cleaned, acid dipped, dried, placed in a vertical position, and sprayed with an atomizer containing a blue dye solution. Just before the droplets begin to run, the spray is stopped and the panel is placed in a horizontal position. Heat is applied to freeze the pattern. The cleaning index is the percentage of the total area that appears clean. This is determined by placing a grid over the panel, estimating the cleaning for several random squares, and then averaging for the reported value. The atomizer test is 10 to 30 times as sensitive as the water-break test.

Fluorescent method requires soiling with a fluorescent oil, cleaning, and inspecting under ultraviolet light. It is very slow and is less sensitive than the water-break and atomizer tests.

Weight of residual soil is also an evaluation of cleanness. The cleaned panel is washed with ether, the washings are evaporated, and the residue is then weighed. A modified method is to clean, dry, and weigh the test panel, then soil, clean, dry, and reweigh it. The increase in weight represents the amount of residual soil present.

Wiping method is a qualitative test. A panel is coated with pigmented soil, cleaned, and then wiped with a white cloth or paper. The presence of soil on the cloth or paper indicates poor cleaning.

In the residual pattern method, cleaned panels are dried at 49 °C (120 °F) for 20 min. After drying, the presence of a stained area indicates residual soil and incomplete cleaning.

Radioisotope tracer technique requires that radioactive atoms be mixed with the soil. Panels are coated uniformly with the soil, and their radioactivity is determined. The panels are then subjected to various cleaning cycles, after which their radioactivity is again determined. The cleaning ability of each of the various cycles can be evaluated by the amount of radioactivity remaining on the panels. This is the most sensitive test; however, dealing with radioactive materials requires an AEC license, trained personnel, and special types of equipment.

Alkaline Cleaning

Revised by Gerald J. Cormier, Parker+Amchem, Henkel Corporation

Introduction

ALKALINE CLEANING is a commonly used method for removing a wide variety of soils from the surface of metals. Soils removed by alkaline cleaning include oils, grease, waxes, metallic fines, and dirt. Alkaline cleaners are applied by either spray or immersion facilities and are usually followed by a warm water rinse. A properly cleaned metal surface optimizes the performance of a coating that is subsequently applied by conversion coating, electroplating, painting, or other operations. The main chemical methods of soil removal by an alkaline cleaner are saponification, displacement, emulsification and dispersion, and metal oxide dissolution.

Alkaline Cleaner Composition

Alkaline cleaners have three major types of components: builders, which make up the bulk of the cleaner; organic or inorganic additives, which promote better cleaning or affect the rate of metal oxide dissolution of the surface; and surfactants.

Builders are the alkaline salts in an alkaline cleaner. Most cleaners use a blend of different salts chosen from:

- Orthophosphates, such as trisodium phosphate
- Condensed phosphates, such as sodium pyrophosphate and sodium tripolyphosphate
- Sodium hydroxide
- Sodium metasilicate
- Sodium carbonate

- Sodium borate

The corresponding (and more expensive) potassium versions of these salts are also commonly used, especially in liquid cleaner formulations. The choice of salts for a given cleaner is based on the metal being cleaned, the cleaning method, performance requirements, and economics. Table 1 shows a few common formulations for specific combinations of metals and cleaning methods.

Table 1 Alkaline cleaning formulas for various metals

Constituent	**Formula, wt%, for cleaning:**					
	Aluminum		**Steel**		**Zinc**	
	Immersion	**Spray**	**Immersion**	**Spray**	**Immersion**	**Spray**
Sodium hydroxide	. . .	. . .	38	50	. . .	. . .
Sodium carbonate	55	18	36	17	10	20
Sodium metasilicate, anhydrous	37	. . .	12	. . .	15	10
Sodium metasilicate, hydrated	. . .	60	. . .	. . .	. . .	. . .
Tetrasodium pyrophosphate	. . .	20	9	20	20	65
Sodium tripolyphosphate	. . .	. . .	. . .	. . .	50	. . .
Trisodium phosphate	. . .	. . .	. . .	10	. . .	. . .
Fatty acid esters	1	. . .	3	0.6	. . .	. . .
Ethoxylated alkylphenol	. . .	. . .	2	0.2	. . .	. . .
Ethoxylated alcohol	. . .	2	. . .	2	. . .	5
Sodium lauryl sulfonate	5	. . .	. . .	. . .	5	. . .

Phosphates are of great importance in the builder packages of alkaline cleaners. A key function of phosphates is their ability to complex with hard water salts. By "softening" these hard water salts, they eliminate the formation of flocculate precipitation caused by calcium, magnesium, and iron. Phosphates are also effective as dispersants for many types of soils. Additionally, they provide alkalinity and prevent large changes in the pH of the cleaning solution.

Silicates are also versatile as builders for cleaners. They provide alkalinity, aid detergency, and most importantly, protect metals such as aluminum and zinc from attack by other alkaline salts. However, silicates are difficult to rinse away and therefore may cause trouble in subsequent plating operations.

Carbonates are an inexpensive source of alkalinity and buffering. They are useful in powdered cleaners as adsorbents for liquid components. Hydroxides are relatively inexpensive and are the strongest form of alkalinity available.

Borates provide strong buffering at a moderately alkaline pH. They have been used extensively in the cleaning of aluminum. Borates provide a degree of metal inhibition and aid detergency.

Additives are organic or inorganic compounds that enhance cleaning or surface modification. Chemical compounds such as glycols, glycol ethers, corrosion inhibitors, and chelating agents should be considered additives.

- *Glycols and glycol ethers* are solvents that remove certain oily soils.
- *Corrosion inhibitors* can be incorporated into a cleaner to help decrease the occurrence of oxidation of the metal surface during water rinsing.
- *Chelating agents* are specialized chemicals for counteracting the negative effects of hard water salts and metal ions.

Some widely used chelating agents are sodium gluconate, sodium citrate, tetrasodium ethylenediaminetetraacetic acid (EDTA), trisodium nitrilotriacetic acid (NTA), and triethanolamine (TEA).

Surfactants are organic and are the workhorses of alkaline cleaners. They are key in displacing, emulsifying, and dispersing many of the soils found on a metal surface. Surfactants lower the surface tension of the cleaner at the metal surface, allowing it to cover the surface uniformly. There are four major types:

- *Anionic* (e.g., sodium alkylbenzene sulfonate)
- *Cationic* (e.g., quaternary ammonium chloride)
- *Amphoteric* (e.g., alkyl substituted imidazoline)
- *Nonionic* (e.g., ethoxylated long chain alcohol)

These major types differ in the type of charge found on the individual surfactant molecule, which has both a water-soluble portion and an oil-soluble portion. In anionic surfactants, the water-soluble portion of the molecule is negatively charged. Cationic surfactants have a positively charged entity. Amphoteric surfactants have both a positively and a negatively charged entity on each molecule. Nonionic surfactants are free of any charge; they are neutral.

For spray cleaners, nonionic surfactants are used almost exclusively, because in general this is the only type that can provide both low foaming and good cleaning ability. For immersion cleaning, anionic or nonionic surfactants are most often used. Alkaline immersion cleaners can use any of the four types, because the foaming properties of surfactants do not cause a problem. Amphoteric surfactants behave like anionic surfactants when used in an alkaline medium, so it is usually more cost-effective to use an anionic surfactant directly. Cationic surfactants are rarely used in the alkaline cleaning of metal because they are the weakest cleaners. In addition, certain cationics react with the metal surface and form a counterproductive film.

Cleaning Mechanisms

Cleaning is accomplished using saponification, displacement, emulsification and dispersion, and metal oxide dissolution. When a particular part is cleaned, any one or more of these mechanisms may be at work.

Saponification is limited to the removal of fats or other organic compounds that react chemically with alkaline salts. Fatty compounds, both animal and vegetable, react with the alkaline cleaner salts in the cleaning solution to form water-soluble soaps. The soap formed may be either beneficial or detrimental to the performance of the cleaner.

Displacement is the lifting of oily soils from a surface by the action of surfactants. By their chemical nature, surfactants have an affinity for metal surfaces that is stronger than the oil's affinity. The surfactant in the cleaning solution lifts the oil from the surface and replaces it with itself. Once the oil is in solution, dispersion and emulsification phenomena act on it.

Dispersion and emulsification hold oily materials in solution. These two mechanisms have the same goal: to allow mutually insoluble liquids, such as oil and water, to stay together.

Emulsification is the use of a surfactant as a connector to keep oil and water together as if they were one unit. As stated above, one portion of a surfactant molecule is water soluble, and this allows it to move freely in water-based cleaners. The oil-soluble portion of the surfactant molecule allows it to hold on to oil-soluble molecules. In a typical water-based cleaner, the surfactant captures and holds oil in solution.

Dispersion is the ability of the cleaner to break oil down into tiny droplets and prevent it from regrouping (reassembling). Both the surfactants and the alkaline salts of the cleaning solution aid in keeping the oil dispersed.

Metal Oxide Dissolution. Surface oxide dissolution is the direct reaction of the alkaline cleaner salts on the metal surface. Metal oxide dissolution targets the removal of undesirable oxides and inorganic contaminants (e.g., light mill scale, corrosion products, and superficial oxides) from a metal surface. The type of metal being cleaned and the concentration, composition, and temperature of the cleaner all play a role in the speed and degree of metal dissolution. The rate should be controlled to minimize the loss of base metal beneath the oxide. Excessive base metal removal will result in localized corrosion and pitting of the surface.

Rinsing

A good water rinse is essential for good cleaning. The temperature of the water rinse may be hot, warm, or cold, but regardless of the temperature the solution should be kept clean. Warm water is usually the best for rinsing. Cold rinses are less efficient than warm rinses, while hot rinses may promote the rapid formation of an oxide film commonly known as "flash rust."

The water rinse should contain no more than 3% of the concentration of the cleaner solution. For example, if the cleaner is prepared at 30 g/L (4 oz/gal), the rinse water should contain no more than 0.9 g/L (0.12 oz/gal). The water rinse is mainly responsible for removing residual cleaner, but it may also remove a small amount of soil. Water rinsing can be done by either immersion, spray, or a combination.

Method of Application

Immersion Cleaning. When an alkaline cleaner is applied by immersion, the parts to be cleaned are immersed in the solution and allowed to soak. As the alkaline cleaner acts on the parts, convection currents (due to heating or mechanical agitation) help to lift and remove soils from the metal surface. The efficiency of removal by the soak cleaner is greatly enhanced by agitation.

There are several approaches to immersion cleaning:

- *Barrel cleaning,* in which small parts are agitated inside a barrel that rotates in the cleaner solution
- *Moving conveyor cleaning,* in which solution flow is created as parts are dragged through the cleaner
- *Mechanical agitation,* in which the cleaner is circulated using pumps, mechanical mixers, or ultrasonic waves
- *Mechanical contact,* in which the cleaner is applied with external forces such as brushes or squeegees

Spray Cleaning. The effectiveness, low cost of equipment, and high degree of flexibility associated with spray cleaning has made this method popular for many years. Specialized methods of spray cleaning include *steam cleaning,* in which the cleaning solution is injected into a stream of high-pressure steam, and *flow cleaning,* in which the cleaning solution is flooded onto the part at high volume but at relatively low pressure.

Spray cleaning is accomplished by pumping the cleaning solution from a reservoir through a large pipe ("header"), through a series of smaller pipes ("risers"), and finally out of spray nozzles onto the part to be cleaned (Fig. 1). The pressure at which the solution is applied to the part can vary from as low as 14 kPa (2 psi) to as much as 13,800 kPa (2,000 psi). On a typical cleaning line the application pressure will range from 70 to 210 kPa (10 to 30 psi). In general, higher spray pressure produces greater mechanical forces for removing soils from a metal surface. Mechanical effects are especially important for the removal of insoluble particles such as dust, metal fines, and carbon smut.

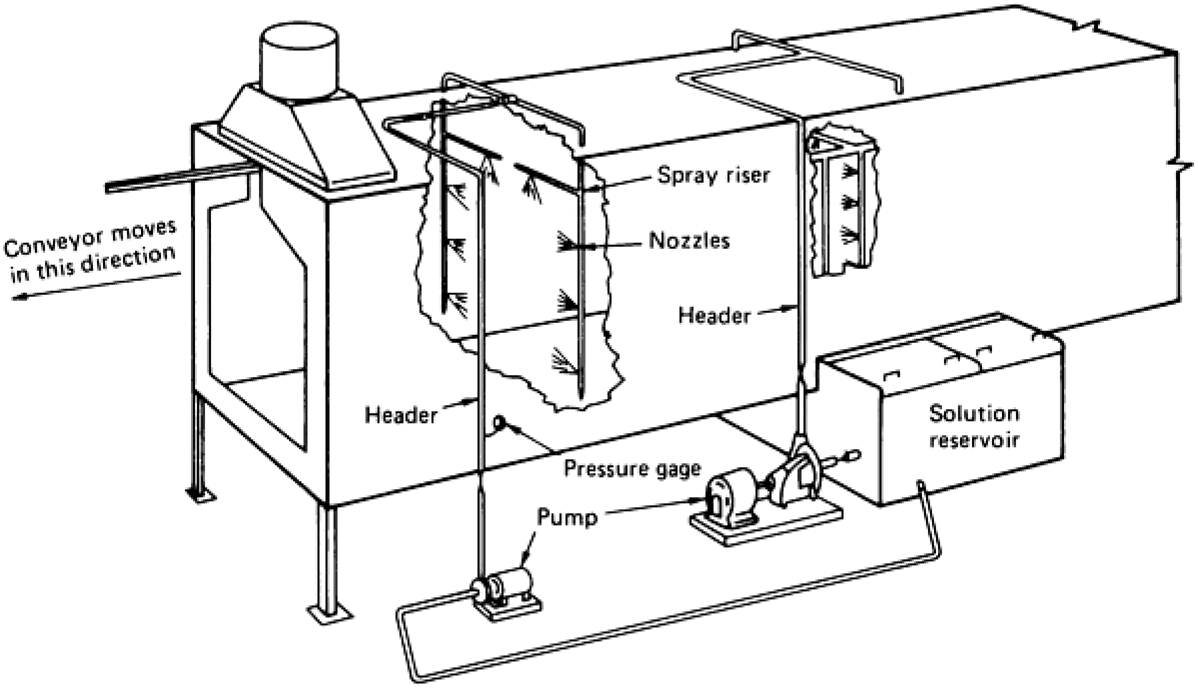

Fig. 1 Equipment for spray cleaning operation

Spray cleaners are prepared with low foaming surfactants that minimize foam formation, even at high spray pressure. Over the last few years, low-foaming surfactants designed for spray cleaning have achieved cleaning performance comparable to that of surfactants used for immersion cleaning.

While spray cleaning is effective on most parts, certain parts, such as the interior of an enclosed section, have soiled areas inaccessible to the sprayed cleaning solution. In these instances, immersion cleaning is more effective because all surfaces of the part can be brought in contact with the cleaning solution.

Operating Conditions

The operating conditions for applying an alkaline cleaner by spray are very different from those used for immersion cleaning. The following table shows typical operating conditions for spray and immersion cleaners.

Operating condition	Immersion cleaners	Spray cleaners
Concentration	7.5-90 g/L (1-12 oz/gal)	1.9-22.5 g/L (0.25-3 oz/gal)
Application temperature	50-100 °C (122-212 °F)	40-71 °C (140-160 °F)

Processing time	1-5 min	0.5-3 min
Spray pressure	. . .	35-210 kPa (5-30 psi)

Considerable progress has been made in recent years to lower the operating temperature of alkaline cleaners. Improved nonionic surfactants, especially for spray-applied cleaners, have allowed for a reduction in cleaner temperature of 15 °C (25 °F) or more without a loss in cleaning performance. A considerable cost savings results from this decrease in energy demand. For example, the cost of heating a solution by steam to 88 °C (190 °F) is about three times that of heating to 49 °C (120 °F). Research in this area is being directed at further reducing the temperature necessary to provide top-quality cleaning of metal surfaces in both spray and immersion applications.

Testing and Control of Cleaners

Alkaline cleaners lose strength through use and dilution, as well as through the necessity of replacing lost cleaning solution with water, so a reliable method of determining cleaner concentration is necessary. The most commonly used method is acid-base titration. In this procedure, an accurately measured amount of alkaline cleaner is placed in a container, and then an acid of specific concentration is slowly added (titrated) to the solution with stirring until a specific pH is achieved. The equipment to determine when the sample has reached the proper pH may be as exacting as a pH meter, or it may use a less precise method such as the addition of a colored indicator solution. (An indicator solution changes the color of the titrated solution at or near the desired pH.) The acid added to achieve the final test pH is generally measured in millimeters (commonly referred to as "points"). The amount of acid that must be added to the alkaline cleaner solution to achieve the proper pH relates directly to the cleaner's strength.

Cleaners age as they react with atmospheric carbon dioxide, as soils are removed, and as water is added due to cleaner dragout and evaporation. The increase in total alkalinity indicates the degree of contamination in the cleaner, and this can be determined by two titrations of the cleaning solution. The pH values used for measuring the age of a cleaner are 8.2 and 3.9. The amount of acid required to change the pH of an alkaline cleaner to 8.2 is called the *free alkalinity*. The amount of acid required to increase the pH of an alkaline cleaner to 3.9 is the *total alkalinity*. If indicators are used, phenolphthalein is used for pH 8.7 (changes from pink to clear) and methyl orange is used for pH 3.9 (changes from yellow to orange). The relationship between the free and total alkalinity will change as a cleaner ages. For instance, if the free alkalinity of a fresh cleaner sample was 5.0 and the total alkalinity was 6.0, the ratio of total alkalinity to free alkalinity would be 6:5, or 1.2. Cleaner manufacturer guidelines differ, but a rule of thumb for disposing of a cleaner is that a cleaner should be rebuilt when the ratio of total alkalinity to free alkalinity of the solution has doubled relative to its starting ratio.

Equipment for Alkaline Cleaners

All equipment for alkaline cleaners can be constructed of low-carbon steel. However, construction from 300 series stainless steel will significantly increase life and simplify maintenance. Stainless steel is recommended for areas that are exposed to highly corrosive environments, such as circulation pumps and heat exchangers. For cleaner stage piping, plastic is used increasingly often due to its excellent resistance to corrosion.

The simplest type of cleaning line is immersion, where the equipment consists of a tank, a source of heat (such as gas, electricity, steam, or a heat exchanger), and an exhaust system to draw off the steam being generated by the hot cleaner. For a spray system, additional equipment includes a spray pump, riser, nozzles, and a spray zone enclosure. Periodically, the cleaning tank and spray equipment must be cleaned in order to remove the scale and contaminants that build up during normal operations. The cleaning method consists of circulating an inhibited acid throughout the cleaning system until the scale and hard water deposits are removed. These deposits cause reduced spray pressures and inefficient heating. If not removed, they could permanently damage the equipment. After acidic cleaning, the tank is thoroughly rinsed and charged with fresh cleaner.

Safety and Environmental Concerns

The handling and use of alkaline cleaners follows general, common chemical handling rules. A person handling powdered cleaners should wear not only gloves and aprons, to prevent skin contact, but also appropriate goggles and a particle mask, to prevent eye contact and inhalation. Liquid cleaners are becoming more popular due to their ease of handling and increased safety. Alkaline cleaners are also becoming more popular as an alternative for hydrocarbon and fluorocarbon solvent degreasing operations.

Environmental regulations continue to affect the direction of cleaner development and cleaner use. Three major issues confront cleaner formulators: reducing or eliminating phosphate effluent; reducing the aquatic toxicity and increasing the biodegradability of cleaners; and "recycling" of cleaners to extend bath life and therefore reduce cleaner dump frequencies and their associated costs. These regulation-driven issues are being approached in a number of ways. For instance, the reduction of phosphate salt use is being addressed by partial or complete replacement of phosphate salts (e.g., with polyacrylic-acid-base polymers). These polymers provide good hard water control and are easy to waste treat. The pursuit of lowering aquatic toxicity and increasing biodegradability of alkaline cleaners is being accomplished by reformulating with biodegradable surfactants. Recycling of cleaners includes the use of ultrafiltration to remove dispersed oil, thereby extending bath life and decreasing the frequency of cleaner discharge. Thermal oil separators have also been useful for removing emulsified or dispersed oil in cleaner baths.

Solvent Cold Cleaning and Vapor Degreasing

Revised by Vicki L. Rupp and Ken Surprenant, Dow Chemical USA

Introduction

SOLVENT CLEANING is a surface preparation process that is especially adept at removing organic compounds such as grease or oil from the surface of a metal. Most organic compounds are easily solubilized by organic solvent and removed from the workpieces. In some cases, solvent cleaning before other surface preparations can extend the life of cleaning operations and reduce costs. In other cases, solvent cleaning prepares workpieces for the next operation, such as assembly, painting, inspection, further machining, or packaging. Before plating, solvent cleaning is usually followed by an alkaline wash or another similar process that provides a hydrophilic surface. Solvent cleaning can also be used to remove water from electroplated parts, a common procedure in the jewelry industry.

Solvent cleaning can be accomplished in room-temperature baths or by using vapor degreasing techniques. Room-temperature solvent cleaning is referred to as *cold cleaning. Vapor degreasing* is the process of cleaning parts by condensing solvent vapors of a solvent on workpieces.

Parts may also be degreased by immersion in the hot solvent, as well as by exposure to the solvent vapor. Drying is accomplished by evaporating the solvent from the parts as they are withdrawn from the hot solvent vapor. In cold cleaning, parts are dried at room temperature or by the use of external heat, centrifuging, air blowing, or an absorptive medium.

The use of many industrial solvents is being severely restricted because of health, safety, and environmental concerns. These concerns are discussed to some degree in this article; additional information is available in the articles "Environmental Regulation of Surface Engineering" and "Vapor Degreasing Alternatives" in this volume.

Cold Cleaning

Cold cleaning is a process for removing oil, grease, loose metal chips, and other contaminants from the surfaces of metal parts. Common organic solvents such as petroleum distillate fractions, chlorinated hydrocarbons, chlorofluorocarbons, hydrofluorocarbons, or blends of these classes of solvents are used. Cleaning is usually performed at, or slightly above, room temperature. Parts are cleaned by being immersed and soaked in the solvent, with or without agitation. Parts that are too large to be immersed are sprayed or wiped with the solvent. Ultrasonic agitation is sometimes used in conjunction with solvent cleaning to loosen and remove soils, such as abrasive compounds, from deep recesses or other difficult-to-reach areas. This reduces the time required for solvent cleaning of complex shapes.

Cold cleaning is chosen when one or more special conditions exist: water will not remove the soils, water would promote corrosion or rusting, or soil must be removed from temperature-sensitive parts. Equipment for cold cleaning can be as simple as a small tank or a pail with a cover. Thus, cold cleaning is a convenient choice for temporary operations,

operations where each machinist must be able to clean parts, or operations where capital intensive equipment cannot be justified.

Solvents

Table 1 lists aliphatic petroleums, chlorinated hydrocarbons, chlorofluorocarbons, alcohols, and other solvents commonly used in cold cleaning. Stoddard solvent, mineral spirits, and VM&P naphtha are widely used because of their low cost and relatively high flash points. The chlorinated hydrocarbons and chlorofluorocarbons exhibit a wide range of solvency and are nonflammable, but most are far more expensive than the aliphatic petroleums. Blends of solvents are offered to provide improved solvency, reduce cost, reduce fire hazard, adjust evaporation rates, and so on. The alcohols are used alone, or in conjunction with chlorocarbons or chlorofluorocarbons, for special cold cleaning applications such as removing activated soldering fluxes. Acetone and other solvents having low flash points are used for special purposes only, such as cleaning the components of precision instruments, but may pose a serious fire hazard. Their storage and use require strict observance of all safety precautions.

Table 1 Properties of cold cleaning solvents

Solvent	**Flash point**[(a)]		**OSHA TWA, ppm**[(b)]
	°C	**°F**	
Aliphatic petroleums			
Kerosene	63	145	. . .
Naphtha, hi-flash	43	110	. . .
Mineral spirits	14	57	500
Naphtha, VM&P	9	48	500
Stoddard solvent	41	105	100
Chlorinated hydrocarbons[(c)]			
Methylene chloride	None	None	500
Perchloroethylene	None	None	100
Trichloroethane (1,1,1)	None	None	350
Trichloroethylene	None	None	100
Trichlorotrifluoroethane	None	None	1000
Alcohols			

Ethanol, SD	14	57	1000
Isopropanol	10	50	400
Methanol	12	54	200
Other solvents			
Acetone	-18	0	750
Benzol	-11	12	10
Cellosolve(d)	40	104	50
Toluol	4	40	100

(a) Tag closed cup.

(b) OSHA exposure values expressed as parts of vapor or gas per million parts of air by volume at 25 °C (77 °F) and 760 mm Hg pressure. These values should not be regarded as precise boundaries between safe and dangerous concentrations. They represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. The values refer to time-weighted average concentrations for a normal workday.

(c) Also used for vapor degreasing.

(d) 2-ethoxyethanol

In choosing an organic solvent for a particular operation, the most important characteristics to consider are its:

- Toxicity
- Solvency for soils, water, and salts
- Evaporation rate
- Purity
- Biodegradability
- Ease of conservation/recovery/distillation
- Compatibility with part or assembly materials
- Cost
- Ease of disposal
- Associated regulatory requirements

The importance of any specific characteristic is related to the cleaning required, the sophistication of the equipment engineering, and other properties of the candidate solvent. For example, a more toxic solvent might be acceptable if the equipment prevents overexposure of workers. Solvency for the soil to be removed is usually essential, but solubility of water may be preferred for drying parts. On the other hand, solubility of water could be a disadvantage if the discharge water contains excessive amounts of solvent. A low-vapor-pressure solvent is lost through evaporation more slowly, and may be more easily controlled below its acceptable worker exposure standard, than a solvent with greater volatility. However, slow evaporation causes prolonged drying time. Removal of one soil only to have it replaced by a different soil from the solvent is normally not desirable. Therefore, initial solvent purity is important, and a means is required (usually distillation) of maintaining a level of purity to prevent redeposition of soil from previously cleaned parts. Highly biodegradable solvents may be more acceptable in discharge to public water treatment plants, but even so they could cause fish kills due to oxygen depletion in ponds or lakes. Tight equipment may conserve solvent to the extent that a preferred higher-price solvent may be a practical choice. Greater conservation results in less addition of fresh solvent to the system and increases the need for purification by distillation. Identification markings, paint, or plastic components may require a solvent that is selective in dissolving the soil without damaging the parts. Critical factors in cost control may be the use of a minimum of labor, elimination of reject parts, and reduction of disposal costs, rather than the price of the solvent. Disposal costs are another factor in the overall operating costs. Regulations have become another major consideration in the solvent selection process. The best illustration of this is the production ban on 1,1,1-trichloroethane and trichlorotrifluoroethane, beginning January 1, 1996, because they deplete stratospheric ozone. Table 1 provides some information that can be used in choosing a solvent.

Process Control Variables

Cold cleaning is chosen for its simplicity and the low capital cost for the great majority of its uses. It is not surprising that most operations are conducted in a simple tank or pail with a cover at room temperature. A course spray, mechanical agitation (usually manual), brushing, and ultrasound are used to speed cleaning and assist in the removal of insoluble matter. Increasing the solvent temperature will increase its solvency, but this option is infrequently used. Elevated temperatures can significantly increase the fire hazard of flammable solvents, and control of worker vapor exposures becomes difficult as the solvent evaporates more rapidly.

Cleanness of Solvent. As contamination of the solvent increases, cleaning efficiency and the cleanness of processed parts decrease correspondingly. Cleanness requirements prescribe the time at which the solvent must be replaced. For example, a service business that has become quite popular, especially in automotive repair shops, provides the tank equipment and solvent, periodically removes the dirty solvent, and replaces it with clean solvent.

Solvent Reclamation. All solvents can be reclaimed by either a factory-operated still or a licensed reclamation service. In general, the reclamation process is one of simple distillation. However, explosion-proof equipment is essential for the distillation of flammable solvents.

Factory distillation equipment must be selected on the basis of the volume of solvent used, whether the solvent is flammable, the boiling point of the solvent, the nature of the contaminants, and the degree of purity required. A still may service multiple cold cleaning locations, or it may be incorporated into the large sizes of dip or soak equipment on a semiautomated basis.

Standards for recovered solvent usually relate to color, clarity, moisture content, and neutrality, although tests for specific contaminants may be included. Chlorinated hydrocarbons contain stabilizers, added during manufacture; many times, distillation necessitates supplemental inhibition.

The time to replace dirty solvent with clean solvent is determined by the degree of redeposition. Each part placed in a dip solvent comes out of the solvent with a thin film of soil redeposited on its surface. The permissible degree of redeposition determines the practical limit of usefulness of a solvent and the rate at which fresh solvent must be introduced. Alternatively, immersion in sequentially cleaner solvent baths can prolong the useful life of the solvent. In spray wipe applications in which the solvent is aided by strong mechanical action, there is a nearly continuous use of fresh solvent, which is seldom reused.

Each solvent typically has a temperature range where ultrasonic energy optimally agitates it. If the solvent bath is heated too close to the boiling point of the solvent by the sonic energy, the mechanical action diminishes. Control of the bath temperature is important to effective use of ultrasonic cleaning, which is often employed to remove insoluble matter that would need to be filtered from the solvent to maintain cleaning effectiveness.

Tests of cleanness made directly on parts generally are more practical for determining the reclamation point than are measurements of soil buildup in the solvent. Although checking the cleaned item for satisfactory performance in subsequent operations is a practical method for determining whether a required degree of cleanness has been obtained, various other methods of testing for cleanness are also available. In order of increasing degree of cleaning requirements, they are:

1. Visual observation of parts and solvent condition
2. Wiping parts with a clean dry white cloth and then examining the cloth for adhering soil
3. Applying tape to the cleaned surface, removing it, and examining it for adhering soil (Scotch tape test)
4. Tests for the adhesion of paints, ranging from special low-adhesion test paints to conventional paint
5. Microscopic examination of parts
6. Resoaking parts in fresh solvent and weighing the nonvolatile residue
7. Chemical analysis for specific soils
8. Electrical test (on combinations of conductors and nonconductors only)
9. Use of radioactive tracers

Methods from the above list generally are used for specific purposes according to the following table:

Method No.	Purpose of cleaning
1, 2, 3	Preclean only
4	Preparation for paint or adhesive
5, 6, 7, 8	Precision instrument parts
6, 7, 8, 9	Initial studies on precision parts

Drying the Work. Cold cleaning solvents are selected so that the evaporation of the solvent film on parts does not require an excessively long time. In all drying operations, solvent fumes must be exhausted to prevent the possibility of fire, explosion, or health hazards.

Equipment

Pails, tanks, and spray equipment are used in solvent cleaning. Pails with covers are the simplest containers and are often used to contain kerosene, mineral spirits, or chlorinated hydrocarbons for hand brush cleaning or wiping.

Soaking tanks of various designs and sizes are used, depending on the nature of the work. Such tanks may be heated by steam coils, but more often they are used at room temperature. Agitation is sometimes provided by mixer impellers or forced air. For in-process cleaning of small parts, such as those encountered on subassembly lines, a variety of specially made safety tanks are available. Some are designed to permit quick opening and closing by means of a foot pedal, minimizing evaporation and fire hazard. Some are equipped to supply fresh solvent quickly to the work zone and dispense contaminated solvent to another reservoir for subsequent discarding or reclamation.

Small bench sprayers, similar to the unit shown in Fig. 1, are used on assembly lines for cleaning delicate components.

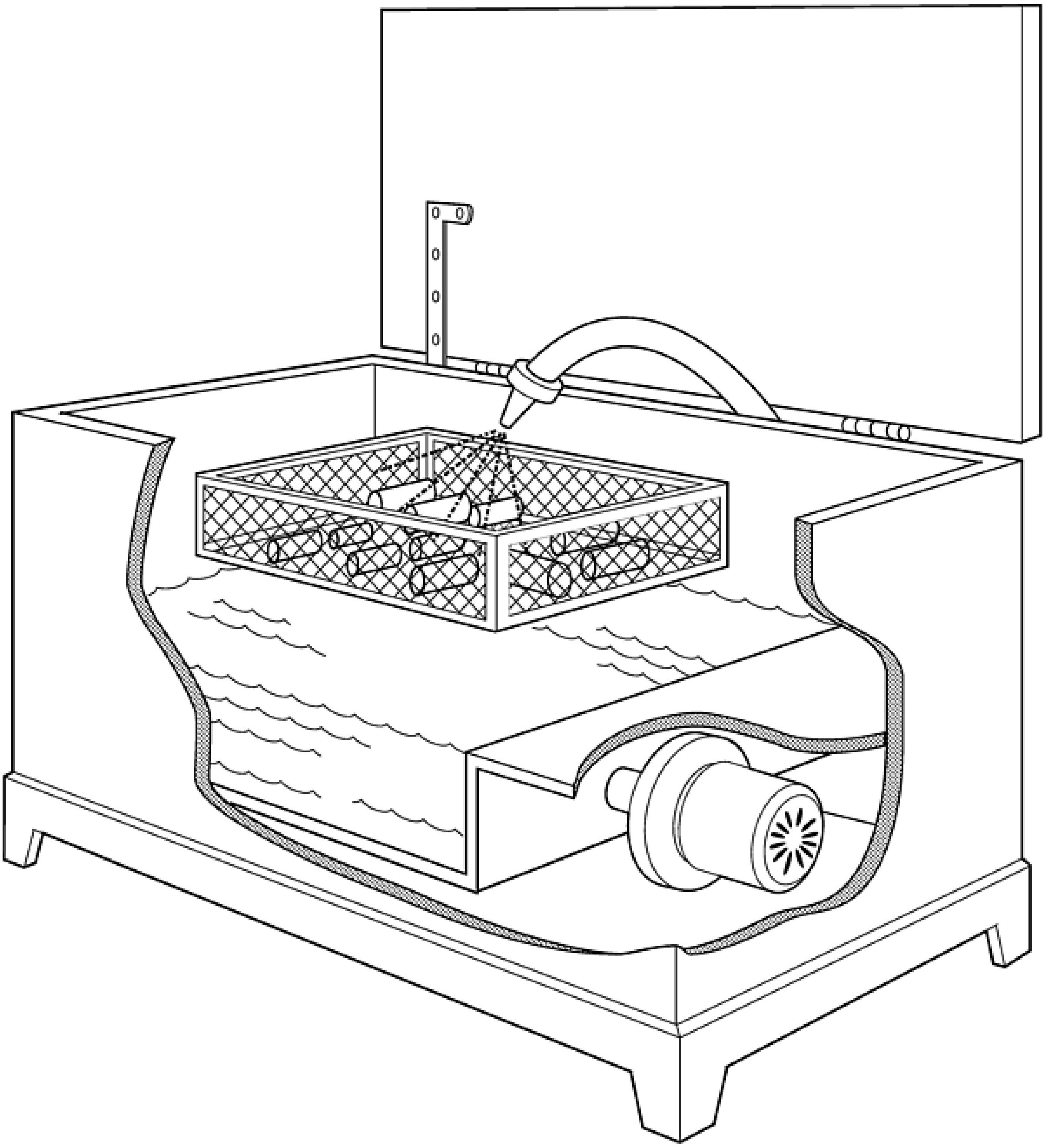

Fig. 1 Spray cleaning equipment

Washing machines also are available for cleaning small precision parts. Some of these machines are similar to home laundry machines in design. Parts are placed on trays, and the agitated solvent provides a constant washing action. In many applications in which the removal of oil and grease is not the main purpose, the equipment is used to remove the residue of polishing or lapping compounds. A filtering system on the machine continuously removes solid particles from the solvent as they are washed from the workpieces.

Equipment requirements for solvent cleaning vary with the size, shape, and quantity of workpieces, as well as the amount of soil to be removed. No matter what equipment is selected, proper covers to minimize solvent loss should be used. Regulations controlling the emissions of smog producing volatile organic compounds require specific designs of cold cleaning equipment and operating procedures in most states. Permits may also be required for construction/installation and operation.

Specific Applications

Solvent cleaning has traditionally been regarded as a method for precleaning or as one reserved for special applications. However, with the rise in the manufacture of electronic components and other assemblies that comprise many small parts, the use of solvents as a final cleaner has increased. At present, most solvent cleaning applications fall within one of the following categories:

- Inexpensive precleaning of parts
- Hand cleaning of parts too large for immersion or spray machine cleaning
- Cleaning heat-sensitive, water-sensitive, or chemical-sensitive parts
- Removal of organic materials such as plating stopoffs, marking crayons, or soldering flux
- Cleaning of precision items in a succession of steps in which the work is first cleaned in nonpolar solvent to remove oil
- Temporary general cleaning where the cost of vapor degreasing equipment is not justified
- Cleaning electrical or electronic assemblies in which the presence of inorganic salt deposits may cause current leakage

Process Limitations

Virtually all common industrial metals can be cleaned in the commonly used cleaning grade solvents without harm to the metal, unless the solvent has become contaminated with acids or alkalis. Cleaning cycles should be adjusted to minimize the immersion time. Certain plastic materials can be affected by cleaning solvents, and tests must be conducted to determine compatibility.

Solvent degreasing is ineffective in removing such insoluble contaminants as metallic salts and oxides; sand; forging, heat treat or welding scale; carbonaceous deposits; and many of the inorganic soldering, brazing, and welding fluxes. Likewise, fingerprints can resist solvent removal.

Size and shape of the workpiece is seldom a limitation. Highly intricate parts have been solvent cleaned by devising techniques of handling that allow the solvent to reach and drain from all areas.

Quantity of Work. Although many high-production applications regularly use cold cleaning, it is more likely to be used for maintenance and intermittent cleaning of small quantities. Because cold cleaning is usually done at or near room temperature, the problem of heating, or otherwise preparing, equipment for a small quantity of work is eliminated. Unless there is some special requirement, other methods of cleaning, such as vapor, alkaline, emulsion, or acid, are usually cheaper and more satisfactory for cleaning large quantities in continuous production.

Lack of uniformity is often a severe limitation of cold cleaning. The process is basically one of dissolving a contaminant in a solvent; therefore, immersion cleaning causes resoiling as the solvent is reused. The work parts do not receive a final rinse in pure solvent as they do in vapor degreasing. The parts are seldom, if ever, perfectly clean. Therefore, except in special applications where spray techniques are used, solvent cleaning is more likely to be used as a preliminary, rather than as a final, cleaning method. The amount of soil that remains on the part depends on how much was there initially and on the quality of the solvent (how often the solvent was reclaimed). In some applications, the use of two or more consecutive solvent baths serves to provide more uniform cleaning results.

Applicability to Soils. The range of soils on which solvents are highly effective is greater than for vapor degreasing because: (a) lower temperatures permit a wider choice of solvents; and (b) lower drying temperatures usually used in solvent cleaning do not bake on insolubles, such as polishing or buffing compounds. Mechanical agitation, ultrasonics, and sometimes hand scrubbing are used in solvent cleaning to help loosen and float away insolubles.

Safety and Health Hazards

Fire and excessive exposure are the greatest hazards entailed in the use of solvents for cleaning. The flash points and permissible vapor concentrations of the solvents adopted for specific operations must be known (Table 1). All flammable solvents should be stored and used in metal containers, such as groundable safety cans.

Adequate ventilation should be provided to prevent accumulation of vapor or fumes. No solvents should be used close to an open flame or heaters with open coils.

Operators should be cautioned against repeated exposure of the skin to solvents. The use of basket, hangers, and other devices that prevent skin exposure is common practice and is recommended. Protective gloves or protective hand coatings should be used to prevent extraction of natural oils from the skin, which can cause cracking of the skin and dermatitis.

Common solvents vary in relative toxicity, and the vapors of these solvents are capable of exerting a potentially lethal anesthetic action when excesses are inhaled. Common solvents have a relatively slight toxic effect, but maintenance workers have lost their lives after working inside tanks containing very high concentrations of vapor, as a result of its strongly narcotic effect. When working in an enclosed space, such as tanks or pits, workers should follow confined space entry procedures.

- Drain and vent thoroughly.
- Check air for adequate oxygen and the absence of flammable or toxic vapor concentrations.
- Always use an air-supplying respirator and life belt.

Any person working with a solvent should be familiar with its material safety data sheet, which can be obtained from the supplier.

Vapor Degreasing

Vapor degreasing is a generic term applied to a cleaning process that uses the hot vapors of a chlorinated or fluorinated solvent to remove soils, particularly oils, greases, and waxes. A vapor degreasing unit consists of an open steel tank with a heated solvent reservoir, or sump, at the bottom and a cooling zone near the top. Sufficient heat is introduced into the sump to boil the solvent and generate hot solvent vapor. Because the hot vapor is heavier than air, it displaces the air and fills the tank up to the cooling zone. The hot vapor is condensed when it reaches the cooling zone, thus maintaining a fixed vapor level and creating a thermal balance. The temperature differential between the hot vapor and the cool workpiece causes the vapor to condense on the workpiece and dissolve the soil.

The soils removed from the workpieces usually boil at much higher temperatures than the solvent, which results in the formation of essentially pure solvent vapors, even though the boiling solvent may be quite contaminated with soil from previous work parts. Vapor degreasing is an improvement over cold solvent cleaning, because the parts are always washed with pure solvent. By contrast, in cold cleaning, the solvent bath becomes more and more contaminated as repeated work loads are processed and redeposition of soil increases. In vapor degreasing, the parts are heated by condensation of the solvent vapors to the boiling temperature of the degreasing solvent, and they dry instantly as they are withdrawn from the vapor zone. Cold-cleaned parts dry more slowly.

To supplement vapor cleaning, some degreasing units are equipped with facilities for immersing work in warm or boiling solvent and for spraying workpiece surfaces with clean solvent. The efficiency of the liquid phase of the cleaning cycle can be augmented by the application of ultrasonic energy.

Solvents

Only halogenated solvents are used in vapor degreasing, and they have the following characteristics in varying degrees:

- Nonflammability and nonexplosiveness under proper vapor degreasing operating conditions. This critical requirement makes solvents with flash points unacceptable.
- High solvency for oil, grease, and other contaminants to be removed
- Low heat of vaporization and low specific heat, to maximize the amount of solvent that condenses on a given weight of metal and to minimize heat requirements
- Boiling point high enough so that sufficient solvent vapor is condensed on the work to ensure adequate final rinsing in clean vapor
- Boiling point low enough to permit the solvent to be separated easily from oil, grease, or other contaminants by simple distillation
- Toxic properties low enough to permit control of worker exposures to Occupational Safety and Health Administration (OSHA) permissible exposure levels
- High vapor density, in comparison with air, and low rate of diffusion into air, to minimize loss of

solvent to the atmosphere

- Chemical stability in the process, which requires the solvents be inhibited or stabilized with chemical additives, if required
- Noncorrosiveness to metals used in workpieces and in construction of equipment for the process, and to plastic parts

Table 2 lists pertinent properties of halogenated solvents used for vapor degreasing. Table 3 is a comparative evaluation of these solvents for vapor degreasing applications.

Table 2 Vapor degreasing solvent properties

Property	**Methylene chloride**	**Perchloroethylene**	**1,1,1-trichloroethane**	**Trichloroethylene**	**Trichloro-trifluoroethane**
Flammability					
Flash point	None	None	None	None	None
Flammable limits at 25 °C[a]	14.5-22	None	7.5-15	8.0-10.5	None
Boiling point, °F(°C)	104 (40)	250 (121)	165 (74)	189 (87)	118 (63)
Specific gravity	1.32	1.62	1.32	1.46	1.57
Density					
Liquid, lb/gal at 25 °C	11.0	13.5	11.0	12.1	13.2
Relative vapor: Air	2.93	5.72	4.6	4.53	6.46
Specific heat (liquid), BTU/lb °F (kj/kg °C)	0.28 (1.2)	0.21 (0.88)	0.25 (1.0)	0.23 (0.96)	0.21 (0.88)
Latent heat, BTU/lb (kj/kg)	142 (330)	90 (209)	102 (237)	103 (240)	63 (147)
Azeotrope with water					
Boiling point, °F (°C)	100.6 (38)	190 (88)	149 (65)	164 (73)	. . .
wt% water	1.5	15.8	4.3	5.4	. . .
Molecular weight	84.9	165.8	133.4	131.4	187.4

Vapor pressure at 25 °C, mm Hg	436	18	124	70	334

(a) vol% in mixtures with air

Table 3 Comparative evaluation for vapor degreasing applications

Property	**Trichloroethylene**	**Perchloroethylene**	**1,1,1-trichloroethane**	**Methylene chloride**
General stability	Good	Excellent	Selective	Good
Solvency	Aggressive	Selective	Selective	Aggressive
Recoverability (steam stripping and carbon adsorption)	Good	Good	Unsuitable	Limited
Parts handling (based on temperature after vapor rinse)	Little delay	Delay	Little delay	Immediate
Removal of high melting waxes	Good	Excellent	Good	Fair
Removal of water (spot free dryer)	Fair	Excellent	Poor	Poor
Cooling water availability and cost	Good	Good	Good	Poor
Cost to vaporize (heat of vaporization)	Moderate	Good	Moderate	High
Cleaning of light-gage parts	Good	Excellent	Good	Poor
Use with water-soluble oils	Good	Excellent	Poor	Poor
Stability towards white metals	Good	Good	Fair	Good
Stability towards caustics	Hazardous	Good	Hazardous	Good
Nonflammability	Good	Excellent	Good	Good
Steam pressures needed	Moderate	High	Fair	Low
Temperature effect on work area	Good	Fair	Good	Excellent
Use history	Very extensive	Extensive	Very extensive	Very limited

Air pollution classification	Nonexempt some areas	Nonexempt	Exempt	Exempt
Cost per pound	Medium	Lower	Higher	Higher

Trichloroethylene (C_2HCl_3) historically has been the major solvent used in industrial vapor degreasing and cleaning applications. Beginning in 1966, air pollution control regulations led to its partial replacement by 1,1,1-trichloroethane. The classification of trichlorotrifluoroethane and 1,1,1-trichloroethane as stratospheric-ozone-depleting chemicals has stimulated interest in returning to trichloroethylene, which is still frequently an excellent solvent choice. It has a very aggressive solvent action on oils, greases, waxes, tars, gums, and rosins and on certain resins and polymers. Its fast, efficient action leaves no residue or film to interfere with subsequent metal treatment such as welding, heat treating, electroplating, or painting.

Trichloroethylene can be safely used with iron, steel, aluminum, magnesium, copper, brass, and various plating metals without harm to the parts or to the degreasing equipment. The listed vapor degreasing solvents should be used with some caution with titanium and its alloys. Residual solvent or chlorides could cause hot salt stress-corrosion cracking if the workpieces are subsequently welded or experience service temperatures of 280 °C (550 °F) or higher. Care must be taken to remove any residuals. Dipping in nitric or nitric-hydrofluoric acid is recommended.

Always avoid the use of strong caustic (sodium hydroxide) around the degreasing operation, because trichloroethylene can react vigorously with this chemical to produce spontaneously flammable dichloroacetylene. Because of the moderate boiling temperature of trichloroethylene, the degreased parts can be handled soon after the vapor rinse is complete. Normal operation uses steam at 69 to 105 kPa (10 to 15 psig).

Perchloroethylene (C_2Cl_4) has been used for many years as an important specialized solvent for difficult industrial cleaning applications. For vapor degreasing, it effectively resists chemical decomposition under heavy work loads and adverse operating conditions. Steam at 345 to 415 kPa (50 to 60 psig) is required for heating. Because of its high boiling point, it has found particular use for removal of high melting waxes, because these are melted for easy solubilization. Perchloroethylene has also been of particular value for spot-free drying of metal parts having a bright finish or an intricate design. Frequently, in such cases, water that is brought into the degreaser is trapped in recessed parts and blind holes even under normal operating conditions. Because the boiling solvent is at a higher temperature than the boiling point of solvent and water, water quickly forms an azeotrope and is swept away. The rather high operating temperature of perchloroethylene also aids in the degreasing of light-gage metals by permitting a longer and more thorough rinsing action with minimum staining. It can be used effectively with iron, steel, aluminum, magnesium, copper, brass, zinc, and various plating metals, without harm to the metal parts or to the degreasing equipment.

Because of the high boiling point of perchloroethylene, vapor degreasing produces work that is too hot for immediate hand processing. This can be dealt with if the work cycle is adjusted to allow for a cooling period after degreasing. Another related problem is that the degreaser itself, operating at the boiling point of perchloroethylene, is a source of extra heat in the work area. This may cause considerable discomfort (and even danger of burns) to the operating personnel. Often the best solution is to insulate the degreaser. At other times, a little extra local ventilation, coupled with the installation of a guard rail, is all that is needed.

1,1,1-trichloroethane ($C_2H_3Cl_3$) was once the most widely used degreasing solvent because it was exempted in most states from regulations controlling chemicals that cause smog (ozone). The current trend is away from this solvent because it has been categorized as a stratospheric-ozone-depleting chemical. Production of 1,1,1-trichloroethane will be progressively limited until it is phased out by 31 Dec 1995 (Table 4).

Table 4 Applicability of key regulations to selected cleaning solvents

Solvent	**CAS No.(a)**	**OSHA PEL, ppm(b)**	**ACGIH TWA, ppm(c)**	**Regulated as**		**Drinking water Standard MCL, µg/L(f)**	**NFPA Code(g)**	**Hazardous waste(h)**	**SARA 313(i)**	**Spill reportable quantity, lb(j)**
				VOC(d)	**ODS(e)**					

Methylene chloride	75-09-2	500 (25)	50	No	No	(5)	2-1-0	Yes	Yes	1000
Methyl chloroform	71-55-6	350	350	No	Yes	200	2-1-0	Yes	Yes	1000
Perchloroethylene	127-18-4	100	25	(No)	No	5	2-0-0	Yes	Yes	100
Trichlorotrifluoroethane	354-58-5	1000	1000	No	Yes	. . .	. . .	Yes	Yes	1000
Trichloroethylene	79-01-6	100	50	Yes	No	5	2-1-0	Yes	Yes	100

Note: Parentheses indicate proposed standards.

(a) Chemical Abstract Service numbers.

(b) Occupational Safety and Health Administration permissible exposure limits.

(c) American Conference of Governmental Industrial Hygienists time-weighted averages.

(d) Volatile organic compounds, chemicals that react to form smog (ozone) in the lower atmosphere. *No* means *not regulated.*

(e) Ozone-depleting substance. *No* means *not regulated.*

(f) Drinking water standards of the Environmental Protection Agency (EPA). Clean Water Act 40 CFR 100-149, 400-690 MCL, maximum contaminant level.

(g) National Fire Protection Association code for health, flammability, and reactivity under fire conditions.

(h) According to EPA Resource Conservation and Recovery Act, 40 CFR 190-299.

(i) EPA Superfund Amendments and Reauthorization Act (SARA), 40 CFR 300-399. Yes indicates that the substance is subject to the SARA toxic chemical release reporting requirements and community right-to-know regulations.

(j) According to SARA

This solvent has properties similar to those of trichloroethylene. It is an excellent solvent for many oils, greases, waxes, and tars, while at the same time it has a unique specificity toward individual plastics, polymers, and resins. Steam pressure usually ranges from 20 to 40 kPa (3 to 6 psig) because it has a lower boiling point than trichloroethylene.

1,1,1-trichloroethane hydrolyzes slowly with free water to produce acidic byproducts. Thus, in a vapor degreasing application, water being introduced on the workpieces should be limited by an efficiently operating water separator. Such a separator, with provisions for cooling the solvent condensate as it leaves the trough or by a coil within the water separator, is recommended for all degreasers. 1,1,1-trichloroethane suitably stabilized for vapor degreasing has been widely used with all types of metal parts. However, stabilizer additives are essential for this solvent in vapor degreasing due to its susceptibility to react with aluminum.

Methylene chloride (CH_2Cl_2) is a versatile solvent, aggressive toward many oils, fats, greases, waxes, tars, plastics, resins, polymers, lacquers, and both synthetic and natural rubber. Use of methylene chloride should be considered particularly where the work parts might be damaged by the higher boiling temperatures of the other chlorinated degreasing solvents or where its aggressive solvency powers are specifically required. In this latter connection, some plastics and elastomers normally used in chlorinated solvents service for hose, gaskets, and containers undergo degradation when continuously in contact with methylene chloride.

For general utility, methylene chloride has the inherent limitations associated with its low boiling point. For economy of use, refrigeration rather than plant water may be needed for efficient condensing of the solvent in the machine. Care should also be exercised that the parts are allowed to dry fully before leaving the freeboard area of the vapor degreaser. Recently, the use of methylene chloride has been boosted by the need for solvents to replace trichloroethane that do not contribute to smog in the lower atmosphere and do not significantly deplete stratospheric ozone.

Trichlorotrifluoroethane ($C_2Cl_3F_3$) is a highly stable solvent requiring little or no additives to maintain its stability in use. It is often referred to as fluorocarbon 113 (FC 113). Fluorocarbon 113 boils only slightly above methylene chloride, and, as with methylene chloride, refrigeration is normally required for vapor condensation and control. While methylene chloride is the strongest solvent, fluorocarbon 113 is the gentlest. This property permits its use in cleaning some assemblies containing sensitive plastic components; however, the gentle solvency is not sufficient for some soils. To compensate and to provide special solvent properties, fluorocarbon 113 is available in azeotropic composition with methylene chloride and acetone. Other admixtures are also available.

Stabilization of the azeotropes is needed for vapor degreasing, particularly for zinc. Fluorocarbon 113 and its blends are more costly, so they are chosen for special applications where other solvents are not suitable. Fluorocarbon 113 is among the select group of solvents identified as not causing smog in the lower atmosphere. Unfortunately, it is a stratospheric-ozone-depleting chemical, and its production will be phased out by 31 Dec 1995.

Solvent stability is usually controlled by the addition of stabilizers when the solvent is manufactured. Trichloroethylene, methylene chloride, 1,1,1-trichloroethane, and perchloroethylene all require stabilizers to perform successfully in vapor degreasing. Quality control of vapor degreasing operations can be conducted by analyzing the stabilizer levels by gas chromatography. The boiling point and/or specific gravity of used solvent can be used to estimate the level of contamination.

Severe degradation problems may result from permitting cross-contamination of solvents during transportation, storage, or use. Particular care should be taken to prevent 1,1,1-trichloroethane contamination of the other solvents, even at levels of 1% or less.

Degreasing Systems and Procedures

Procedures used for cleaning various classes of work and soils by degreasing systems are indicated schematically in Fig. 2. Regardless of the system used, the distinctive features of vapor degreasing are the final rinse in pure vapors and a dry final product.

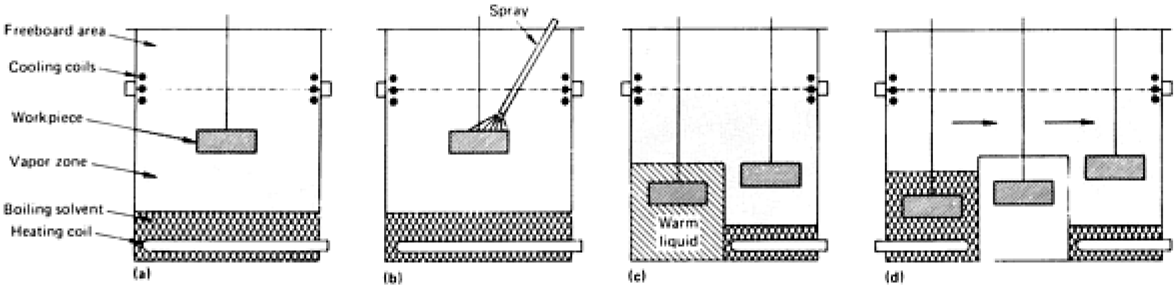

Fig. 2 Principal systems of vapor degreasing. (a) Vapor phase only. (b) Vapor-spray-vapor. (c) Warm liquid-vapor. (d) Boiling liquid/warm liquid-vapor

Vapor Phase Only. The simplest form of degreasing system uses the condensation of solvent vapor only (Fig. 2a). The work to be cleaned is lowered into the vapor zone, where the relative coolness of the work causes the vapor to condense on its surface. The condensate dissolves the soil and removes it from the surface of the work by dripping back into the boiling solvent. When the work reaches the temperature of the hot vapor, condensation and cleaning action cease. Workpieces are dry when removed from the tank.

Vapor-Spray-Vapor. If the workpiece contains blind holes or recesses that are not accessible to the vapor, or if the soil cannot be removed by the vapor, a spray stage may be added. The system then consists of vapor, spray, vapor (Fig. 2b).

Usually, the work to be cleaned is lowered into the vapor zone, where the condensing solvent does the preliminary cleaning; when condensation ceases, the work remains in the vapor zone and is sprayed with warm solvent. The pressure of the spray forces the liquid solvent into blind holes and effects the removal of stubborn soils that cannot be removed by vapor alone. The warm spray also lowers the temperature of the work; after spraying, the work is cool enough to cause further condensation of vapor for a final rinse.

The hot vapor may bake on some soils, such as buffing compounds, and make them difficult to remove. For complete removal of these soils, the work must be sprayed immediately upon entering the vapor and before the heat of the vapor can affect the compounds. The spray nozzle must be below the vapor line, and all spraying takes place within the vapor zone. Normal spray pressure for standard degreasers is 40 kPa (6 psi) and should not exceed 55 kPa (8 psi). Excessive spray pressure disturbs the vapor zone, resulting in a high rate of vapor emission.

Warm Liquid-Vapor. Small parts with thin sections may attain temperature equalization before the work is clean. For these parts, and for other small parts that are packed in baskets, the warm liquid-vapor system is recommended. In the degreasing unit shown in Fig. 2(c), work may be held in the vapor zone until condensation ceases, and then be lowered into the warm liquid, or the work may be lowered directly into the warm liquid. Agitation of the work in the warm liquid mechanically removes some additional soil. From the warm liquid, the work is transferred to the vapor zone for a final rinse.

Boiling Liquid/Warm Liquid-Vapor. For cleaning parts with particularly heavy or adherent soil or small workpieces that are nested or packed closely together in baskets, the boiling liquid/warm liquid-vapor system is recommended. In the unit shown in Fig. 2(d), the work may be held in the vapor zone until condensation ceases and then be lowered into the boiling liquid, or the work may be lowered directly into the boiling liquid. In the boiling liquid, the violent boiling action scrubs off most of the heavy deposit, as well as metal chips and insolubles. Next, the work is transferred to the warm liquid, which removes any remaining dirty solvent and lowers the work temperature. Finally, the work is transferred to the vapor zone, where condensation provides a final rinse.

Ultrasonic Degreasing. Ultrasonic transducers, which convert electrical energy into ultrasonic vibrations, can be used in conjunction with the vapor degreasing process. The transducer materials used are of two basic types, electrostrictive (barium titanate) and magnetostrictive. The latter is capable of handling larger power inputs. Barium titanate transducers generally are operated over a range of 30 to 40 kHz; magnetostrictive transducers usually operate at about 20 kHz, but they may operate at frequencies up to about 50 kHz.

Cleaning efficiency in the liquid phase of a vapor degreasing cycle can be considerably augmented by the application of ultrasonic energy. However, ultrasonic cleaning is expensive and is seldom used in a degreasing cycle unless other modifications have failed to attain the desired degree of cleanness. It is often applied to parts that are too small or too intricate to receive maximum benefit from conventional degreasing cycles.

The inside walls of hypodermic needles can be thoroughly cleaned by ultrasonic degreasing. Other examples of parts cleaned by ultrasonics because they failed to respond to conventional degreasing methods are small ball bearing and shaft assemblies, printed circuit boards (for removal of soldering flux), intricate telephone relays, plug valve inserts (contaminated with lapping compounds), and strands of cable (for removal of oil and other manufacturing contaminants trapped between the strands).

Rustproofing. When a ferrous metal is vapor degreased, organic films are usually removed, and the metal is highly susceptible to atmospheric corrosion. If the surrounding atmosphere is humid or contains products of combustion or other corrosive contaminants, immediate steps must be taken to provide exposed metal surfaces with a protective film. When precision steel parts with a high surface finish (antifriction bearings, for example) are being degreased and complete rust prevention is desired, rustproofing by flushing or immersion should be included as an integral part of the degreasing system.

Control of Solvent Contamination

The cleanness and chemical stability of the degreasing solvent are important influences on the efficiency of vapor degreasing. For example, an excess of contaminant oil raises the boiling point of the solvent and detracts from its effectiveness in cleaning.

Oils. The chlorinated solvents used in degreasers are stabilized or inhibited to resist the harmful effects of many contaminants. However, certain cutting oils with a high content of free fatty acid can overcome the effects of stabilization and may contribute to a sour, acidic condition. Oils with high contents of sulfur or chlorine as additives have the same effect. These oils and greases accumulate in the boiling or vapor chamber and cause foaming and a reduction in solvent evaporation. Baked sludge accumulates on the steam coils and other heated areas, thus reducing the efficiency of the degreaser.

When the oil content of the solvent reaches 25 vol%, the solvent should be replaced and the oily solvent reclaimed. The percentage of mineral oil in trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, and methylene chloride can be determined from the boiling temperatures given in Table 5.

Table 5 Physical properties of mineral oil-in-solvent mixtures

Solvent	**Boiling point for vol% oil loading:**								**Specific gravity at 25/25 °C for vol % oil loading:**			
	0		**10**		**20**		**30**					
	°C	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**0**	**10**	**20**	**30**
Perchloroethylene	121	250	122	252	124	255	126	259	1.619	1.542	1.464	1.395
Trichloroethylene	87	189	88	190	89	192	90	194	1.457	1.406	1.345	1.288
1,1,1-trichloroethane	74	165	76	169	77	171	79	174	1.320	1.272	1.227	1.180

Paint Pigments. Pigments from painted surfaces that are washed into the degreaser should be filtered or removed by other mechanical means. The oils in pigment or paint dissolve in the degreasing solvent, but the remaining material is insoluble. This material usually floats on the surface of the degreaser solution and adheres to the work. In addition to reducing cleaning efficiency, these pigments may bake out on the heating coils and the work.

Chips washed from parts into the degreaser should be removed periodically, because they contaminate other parts entering the degreaser. Such contamination is possible even in ultrasonic degreasers when the solution is not filtered continuously. An excessive amount of chips in the vapor or boiling tank reduce heat transfer and evaporation rates. An accumulation of fine aluminum particles may also result in solvent breakdown.

Water can be present in degreasers as a result of the presence of water on parts being degreased or the accumulation of condensate on the cooling coil or jacket of the degreaser. Most chlorinated degreasing solvents are inhibited against the effects of hydrochloric acid formation in the presence of water; nevertheless, to avoid stains, spotting, and rusting of parts, all water must be removed from the degreaser. To accomplish this, degreasers should be equipped with one or more water separators that continuously remove free water from the circulating recondensed solvent (Fig. 3).

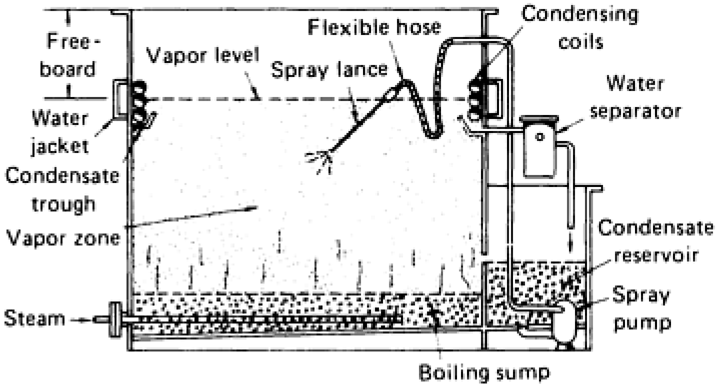

Fig. 3 Vapor degreasing unit designed specifically for a vapor-spray-vapor system

Other contaminants, such as silicones, should not be allowed to enter the degreaser, because they cause foaming at the surface of the liquid solvent. All acids, oxidizing agents, cyanides, or strong alkalis must be prevented from entering the degreasing solvent.

Conservation of Solvent

The maintenance of an adequate volume of solvent in the degreasing tank is important to the efficiency of the degreasing process. Loss of solvent can be minimized by observing the following precautions:

- The vapor degreaser wall (freeboard) should extend above the top of the vapor zone by at least 75% of the width of the degreaser.
- The degreaser should not be located in an area subject to drafts from doors, windows, or fans.
- Dragout loss should be minimized by proper drainage. Specially designed racks or rotating baskets made from wire mesh or round stock are effective.
- Where the work is small and tightly packed into a basket, the basket should be allowed to drain in the vapor area before being removed from the degreaser.
- Spraying, when required, should be held to a minimum and performed well below the vapor level.
- Work should remain in the vapor until all condensation has ceased.
- Work should not be rapidly introduced into or withdrawn from the degreaser. Vertical speed of mechanical handling equipment should not exceed about 3.4 m/min (11 ft/min).
- The degreaser should be covered when not in use. Well-designed manually operated degreasers are provided with suitable covers; conveyorized degreasers are provided with hoods.
- Plumbing, cleanout ports, valves, and pumps should be checked periodically for solvent leakage.

- Introduction of moisture into the degreaser should be avoided. Except in special situations, work that has been wetted in a previous process should not be brought into the degreaser until it is completely dry.
- Work loads should not occupy more than 50% of the open cross-sectional area of the degreasing tank. When work is lowered into the vapors, it absorbs the heat in the vapors, causing the vapor level to drop. Work load should be sized to minimize this fluctuation of the vapor level.
- Porous or absorbent materials should not be degreased.

Recovery of Solvent

Solvent can be recovered from the soils removed in cleaning parts and from solvent vapors in air. Used solvent may be transferred to a still and recovered by distillation with or without steam. Also, the solvent may be recovered by using the degreaser as its own still and drawing off the distillate to storage.

Distillation in the degreasing unit may be accomplished by operating the degreaser with the solvent return line closed. After being passed through the water separator, the distilled solvent may be collected in a clean drum or tank, leaving the sludge behind in the boiling compartment. Some degreasers have built-in tanks for this purpose. As the concentration of high boiling oils in the sludge increases, the amount of solvent recovered decreases sharply until it is no longer profitable to continue distillation.

At no time during distillation should the heating element be exposed. Such exposure may be detected by the copious white fumes generated. The high surface temperature developed by an exposed heater destroys the heater, deteriorates the solvent, and, in extreme cases, may cause a flash fire.

Solvent Still. The use of a special still for solvent recovery is usually justified when large amounts of soil must be removed from the solvent daily, when cleaning requires immersion in a solvent with very little contamination, or when downtime for maintenance must be held to an absolute minimum.

A still may be plumbed directly to a degreaser. A solvent level detector in the still senses when a pump drawing solvent from the degreaser should be turned on and off, in this arrangement. Alternatively, dirty solvent from multiple degreasers may be recovered in a centralized still or by a service company.

Solvent vapors captured in ventilation air streams may be recovered by adsorption on activated carbon. When the carbon becomes saturated with solvent, the solvent can be revaporized with steam, condensed to a liquid, separated from the steam condensate, and collected for reuse.

Vapor Degreasing Equipment

All vapor degreaser designs provide for an inventory of solvent, a heating system to boil the solvent, and a condenser system to prevent loss of solvent vapors and control the upper level of the vapor zone within the equipment. Heating the degreaser is usually accomplished by steam. However, electrical resistance ($\leq$ 3.0 W/cm^2 or $\leq$ 20 W/in.^{2}) heaters, gas combustion tubes, and hot water can be used. Gas combustion heaters with open flames located below the vapor degreaser are not recommended and are prohibited by OSHA regulations. Specialized degreasers are designed to use a heat pump principle for both heating and vapor condensation. In this instance, the compressed gases from the heat pump are used for heating the vapor degreasing solvent, and the expanded refrigeration gases are used for vapor condensation. Such a degreaser offers mobility that permits movement without having to be connected to water, steam, or gas for operation.

Normal vapor control is achieved with plant water circulation through the condensing coils. Refrigeration-cooled water or direct expansion of the refrigeration gases in the condenser coils are effective means of vapor control. Where a sufficient cool water supply is not available, or where plant water is excessively warm, a low boiling vapor degreasing solvent, such as methylene chloride or fluorocarbon 113, is chosen. Refrigerated cooling coils above the normal condenser coils (also called a *cold trap*) can reduce solvent losses.

For safety, economy, and in some cases, to comply with regulations, degreasers are usually equipped with a number of auxiliary devices:

- *Water separator:* a chamber designed to separate and remove water contamination from the degreaser.

Solvent and water condensate collected by the condenser coils are carried by the condensate collection trough and exterior plumbing to the water separator. The water separator is designed to hold 5 to 6 min of solvent and water condensate flow. This provides for nonturbulent flow and flotation of the insoluble water. This water is discharged from the equipment while the solvent condensate is returned to the degreasing equipment.

- *Vapor safety thermostat:* located just above the condensing coils, detects the heat of solvent vapors if they rise above the designed level in the equipment. This could occur with inadequately cool condensing water or condenser water flow interruption. The purpose of this device is to prevent massive solvent vapor escape into the plant atmosphere. When solvent vapors are detected, the heat input to the degreaser is turned off automatically. Manual resetting is preferred and used, because this demands attention and alerts the operator to a malfunction.
- *Boiling sump thermostat:* In the cleaning operation, high boiling oils and greases are removed and collect in the boiling chamber. These contaminants elevate the boiling temperature of the solvent and could cause solvent decomposition if left to accumulate without control. The boiling sump thermostat is located in the boiling chamber solvent and, like the vapor safety thermostat, turns off the heat to the degreaser if it senses temperatures higher than those appropriate for the solvent being used.
- *Condenser water thermostats and/or flow switches:* The water flow switch will not allow heat to be turned on unless condensing water is flowing into degreaser coils, and it will turn off the heat source if flow stops during operation. The condenser water thermostat shuts off the heat source if condensing water leaving the degreaser is too warm, indicating that the water flow through the condenser system is inadequate or that the water temperature is insufficiently cool to control the solvent vapors in the degreaser.
- *Solvent spray thermostat:* a temperature-sensing device, located just below the vapor-air interface in the degreaser and designed to prevent manual or automatic spraying if the vapor zone is not at or above the thermostat level. This device has been required by some regulations. Spraying above the vapor zone can exaggerate solvent losses by causing air and solvent vapor mixing.
- *Liquid level control:* This control shuts the heat off if the liquid level in the boiling chamber drops to within 50 mm (2 in.) of heaters. This control protects the heaters and reduces the possibility of thermal breakdown of solvent.

Modifications in this basic vapor degreaser are designed to permit various cleaning cycles, including spraying of the workpieces or immersion of the workpieces in boiling or cool solvent. Further, vapor degreaser designs are available to provide various conveyor and transport means through the cleaning cycles. Common conveyor systems include the monorail vapor degreaser, the crossrod vapor degreaser, the vibratory conveyorized degreaser, and the elevator degreaser. Open-top degreasers constitute over 80% of the vapor degreasers used in industry. Their sizes range from benchtop models with perhaps 0.2 m^2 (2 ft^2) of open-top area to tanks over 30 m (100 ft) long. The most common sizes range between 1.2 to 2.4 m (4 to 8 ft) long and 0.6 to 1.2 m (2 to 4 ft) wide. The most frequently used cleaning cycle is vapor-solvent spray-vapor. Among the conveyorized vapor degreasers, the monorail is the most prevalent. Generally, open-top degreasers are much lower in cost, permit greater flexibility in cleaning different workloads, occupy much less floor space, and are adaptable to both maintenance and production cleaning. Because of their relatively low cost and minimum space requirements, they are preferred for intermittent operations and for decentralized cleaning where transport of parts to be cleaned to a centralized location adds substantially to the cleaning cost.

Emerging technology combines vacuum autoclave with solvent cleaning. This system cleans in a sealed chamber, using either solvent spray or immersion to clean the parts. The solvent can be perchloroethylene, trichloroethylene, or HFC. After the parts are placed in the chamber to be cleaned, it is dried by evacuating the chamber to 29 mm/Hg. The vacuum reduces the boiling temperature of the residual solvent, flashing it off. The solvent vapors from the chamber are condensed (Fig. 4).

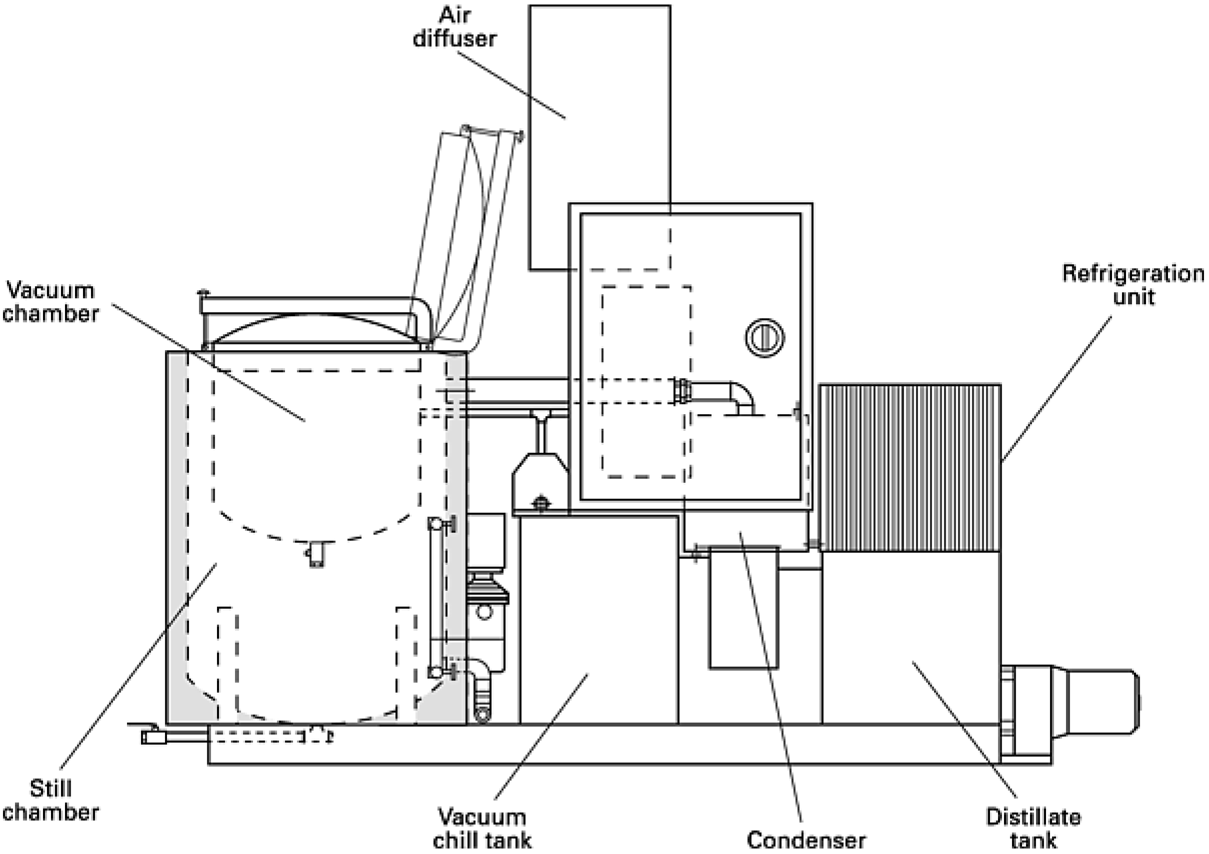

Fig. 4 Vacuum cleaning system. Courtesy of Baron-Blakeslee Company

Installation of degreasing equipment should be supervised by a qualified individual. Some important considerations relating to installation are:

- A degreaser should never be installed in a location that is subjected to drafts from ventilators, unit heaters, fans, doors, or windows. When units cannot be ideally located, such drafts should be reduced by the installation of baffles.
- No degreaser should be installed near open flames unless the combustion products of these flames are exhausted outside the building. Location near welding or other operations using high temperatures must be avoided, because exposure of solvent vapors to high temperatures and high-intensity ultraviolet light results in decomposition to toxic and corrosive substances such as phosgene and hydrogen chloride.
- The flue from the combustion chamber of a gas-fired unit should conform with local laws or ordinances. All exhausts should be discharged outside the building at an adequate distance from air intakes.
- Water outlets from condenser jackets or coils should not be connected directly to sewer lines, but instead should drain freely into a funnel or other open-to-view collecting device that is connected to sewer lines. This prevents back pressure and ensures maximum efficiency of the condensing coils. As water and sewage treatment costs continue to escalate, recirculating condenser water systems such as water chillers and cooling towers are being used. Many degreasers using low-temperature boiling solvents incorporate direct refrigeration. Several manufacturers offer heat recovery of heat recycling systems for use with low-boiling-temperature solvents.
- All degreaser containers should have a legible, highly durable sign attached to them that bears solvent label information (see ASTM D 3698) and operating procedures, as required by most state environmental protection agencies.

Baskets and racks should be constructed of open-mesh, nonporous material. When baskets are completely filled with closely packed small items, basket size should not exceed more than 50% of the work area of the degreaser. For baskets handling large parts with generous open spaces, however, the 50% maximum may be exceeded slightly. Baskets that are too large may act as pistons as they enter the tank and displace the vapor level, thus forcing the vapor from the unit into the atmosphere.

The placement of work in the basket is critical, particularly when the parts have blind holes, which may entrap solvent. Precautions must be taken to ensure that entrapped air does not prevent liquid solvent or vapor from reaching all surfaces. After cleaning, the solvent must be completely drained from the parts to reduce dragout. To satisfy these requirements, specially designed racks or rotating baskets may be necessary.

Operating and Maintaining the Degreaser

An effective operator training program and a routine maintenance program are important to safe and efficient vapor degreasing. Proper education and maintenance practices can greatly extend working life with assurance of smooth production. Following the checklist provided below should aid in beginning an efficient degreasing operation.

Startup

- Be sure the degreaser operator is adequately trained and equipped with the appropriate safety equipment and clothing. For emergency situations, such as power failures, condenser coolant stoppages, and ventilation interruptions, have organic vapor respirators or air-line masks available for immediate use. Also, be sure the operator knows how to use personal protective equipment, understands first aid procedures, and is familiar with the hazards of the operation.
- Check proper operation of the vent system and leave it on.
- Turn on the condensing water. Observe the rate of flow and check for leaks. Leave the condenser water on. If the cooling water supply of the degreaser is equipped with an outlet water temperature control or a flow control safety shutoff, check these for proper operation. It is easier to do this with the degreaser heat on.
- Adjust the high temperature cutoff control for the boiling sump and the vapor safety thermostat control to the temperatures recommended for the particular degreasing solvent to be used. The high temperature cutoff control setting should be about the boiling point of a 25% mineral oil-in-solvent mixture (Table 6). The vapor safety control setting should be at least 6 °C (10 °F) lower than the boiling point of the solvent-water azeotrope (Table 6). Do not turn on a gas or electrically heated degreaser unless the heaters are covered by solvent. If the machine is steam heated, turn steam on and check for leaks and for proper settings and functioning of pressure gages, reducer valves, and traps. Turn off and cool before adding solvent.
- Add some solvent to the degreaser and check the operation of the liquid level control, if the machine is so equipped. Finish filling the degreaser by adding enough solvent to cover the heating elements by 75 to 150 mm (3 to 6 in.), or up to the bottom of the work rest if the machine is so equipped.
- Turn on the heat and, as the temperature rises, ensure proper operation of the various heat controls that may be in use.
- As condensation begins, observe the flow of condensate from the coil and jacket, through the trough and water separator, and the returning stream to the degreaser. Interrupt the flow of condensing water and observe for proper operation of the vapor safety control.
- Adjust the heat input and/or the condenser water flow so that the vapor zone rises only halfway up the condenser coils.
- Check the functioning of the degreaser auxiliary equipment, such as the sprayer, conveyor, still feed pump, and the still. Look at the solvent levels in each degreaser compartment and adjust to operating levels.
- Begin supplying work to the unit.
- Check the first parts through for satisfactory cleanness and for any signs of machine malfunction.
- Adjust the condenser discharge water temperature to about 8 to 11 °C (15 to 20 °F) above the dew point of the surrounding atmosphere, that is, about 32 to 46 °C (90 to 115 °F), for all the chlorinated solvents except methylene chloride. For methylene chloride or fluorocarbon 113, do not allow the discharge water temperature to go above about 29 °C (85 °F). Degreasers for these two solvents often employ

refrigeration for vapor control.

Operation

- Check the upper level of the vapor zone. The vapor zone should not rise above the midpoint of the condenser.
- While the degreaser is operating, maintain a routine surveillance to see that the work is being cleaned properly and the various systems continue to function satisfactorily.
- Any time work is not being processed in the degreaser, the cover should be closed. Degreaser manufacturers supply covers for their degreasers. The cover should be relatively tight fitting but should allow the degreaser to breathe.
- Give some detailed attention to the arrangement of the work parts being cleaned. It may be necessary to reposition some of the parts to get proper cleaning and free draining. Cup-shape parts, for example, should be positioned as shown in Fig. 5.
- Observe the spraying operation. Be sure that the vapor-air interface is not being unnecessarily disturbed.
- Check to see that the amount of work being fed at one time is not so great that it causes vapor shock. The vapor level should not recede excessively. Be sure the rate of introduction of the work does not exceed 3.4 vertical m/min (11 vertical ft/min). A faster rate of entry increases vapor losses.
- Observe the vapor level as the work is being removed. The vapor level should not rise above the cooling coil or jacket. If the vapor level is rising too much, check the cross section of the work. This generally should not exceed 50% of the open area of the degreaser if the parts are traveling at a rate of about 3.4 vertical m/min (11 vertical ft/min). If the parts are larger than this, the rate of vertical movement should be reduced accordingly.
- Check to see that the parts are within the vapor zone long enough for condensation to cease before the parts are brought up into the freeboard area. Also, see that the parts are remaining in the freeboard area long enough for the solvent to evaporate completely.
- After the degreasing operation has continued for several hours, observe the water separator to see that any water entering the degreaser is being withdrawn efficiently by the separator. A cloudy ghost vapor in the vapor zone of the degreaser is a warning sign that water is not being properly removed. If water is allowed to accumulate in the degreaser, the boiling point of the solvent may drop due to the formation of the solvent-water azeotrope. The direct results are poor cleaning, greater solvent losses, water spotting, and more odor complaints.
- As the solvent level in the degreaser drops due to evaporation and leakage losses, fresh makeup solvent should be added to maintain a solvent level of about 150 mm (6 in.) above the heating elements. Particular care should be exercised that the solvent level in the boil chamber never drops lower than 25 mm (1 in.) above the heating elements. Makeup solvent should be added to the degreaser before startup, that is, while cold.
- On a periodic basis, perhaps every few days during initial operation, the acid acceptance inhibitor level of the solvent should be checked. The acid acceptance value should stabilize at no less than 40% of the original value. Should the inhibitor level show an unexpected drop, the trouble should be traced and eliminated. The problem might be excessive water in the degreaser, introduction of acid soils, soil buildup on, or exposure of, the heating surfaces, or accumulation of excessive amounts of metal fines or soluble soils.
- Based on the total soil load and type, and taking into account work scheduling, regular periodic degreaser cleanouts should be performed. The frequency of cleanout can sometimes be extended by removal of particulate soils from the degreasing solvent by use of an external filtration system. Nevertheless, at intervals varying from a few days to a few months, it is necessary to shut down the degreaser and clean it out. The oily soil level of the degreaser should not be allowed to go higher than 25 vol%.

Shutdown

- A scheduled shutdown should be planned so that work is not inconveniently backlogged. The degreaser, of course, should be shut down only after the last parts in process have cleared the machine.

- Turn off the heat supply to the degreaser. Wait for solvent condensation on the cooling surfaces to cease and the vapor zone to collapse.
- Turn off the cooling water and any unneeded pump.
- If the degreaser is being used to partially distill the solvent, the solvent condensate from the water separator should be directed to storage rather than returned to the degreaser. Heating should be stopped when the boiling chamber solvent level approaches 25 mm (1 in.).
- Additional information is available in the *Manual on Vapor Degreasing* published by ASTM.

Maintenance

- Routine cleanout operations can and should be conducted from outside the equipment. Workers entering vapor degreasing equipment or associated pits should follow the confined-space-entry procedures outlined in the next section.
- For a routine cleanout, allow the machine to cool completely and then drain the soil-laden solvent. Ventilate the interior to outside the plant to remove solvent vapors and dry any remaining solvent.
- Remove any auxiliary equipment from the degreaser that may interfere with the cleaning or might be damaged in the process.
- Clean out the trough, water separator, spray pump sump, and associated piping.
- Scrape and brush out the metal fines and other particulate soils. Pay particular attention to corners and recesses where residues tend to collect.
- Clean off excess rust and corrosion, paying particular attention to the heating elements. Consider replacing mild steel piping with stainless steel if heavy rust is noted.
- Inspect and repair any defective auxiliary equipment. Lubricate pumps and conveyor drives.
- Install a new cleanout door gasket, using as a sealant either plain or litharge-thickened glycerol or ethylene glycol. Reinstall all auxiliary equipment items removed during cleanout.
- If the degreaser has experienced an acid condition, the cleaning procedure should be augmented by charging the compartment with water containing 30 g/L (4 oz/gal) sodium carbonate (soda ash), to a depth of about 300 mm (12 in.). The solution should be boiled for about 15 min, and the compartment should be rinsed and thoroughly dried. The degreasing unit is then ready for recharging with clean solvent. If acid conditions persist, contact the solvent supplier or degreaser manufacturer for detailed procedures to cope with the condition and prevent its recurrence.

Table 6 Applications of vapor degreasing by vapor-spray-vapor systems

Note: Degreasing by vapor only is applicable to the cleaning of flat parts with light soils and little contamination. Anything that can be cleaned by vapor degreasing usually can be cleaned better by liquid-vapor systems

Parts	**Metal**	**Production rate**		**Soil removed**	**Subsequent, operation**	**Notes on processing**
		kg/h	**lb/h**			
Spark plugs	Steel	270	600	Machining oil	. . .	Special fixture and conveyor
Kitchen utensils	Aluminum	450	1000	Buffing compound	Inspection	Special fixture and conveyor
Valves (automotive)	Steel	540	1200	Machining oil	Nitriding	Automatic conveyor
Valves (aircraft)	Steel	590	1300	Machining oil	Aluminum coating	Automatic conveyor

Parts	Metal	Production rate		Soil removed	Subsequent, operation	Notes on processing
		kg/h	lb/h			
Small-bore tubing	Aluminum	680	1500	Wax extrusion lubricant	Annealing	Hoist-operated unit
Builders' hardware	Brass	2270	5000	Buffing compound; rouge	Lacquer spray	Racked work on continuous monorail
Acoustic ceiling tile	Steel	2720	6000	Light oil (stamping lubricant)	Painting	Monorail conveyor
Gas meters	Terneplate	4540	10,000	Light oil	Painting	Monorail conveyor
Continuous strip, 0.25-4.1 mm (0.010-0.160 in.)	Cold rolled and stainless steels; titanium	13,600	30,000	Oil emulsion (steels); palm oil (titanium)	Annealing	Continuous processing at up to 0.6 m/s (120 ft/min)
Automatic transmission components	Steel	18,100	40,000	Machining oil; light chips; shop dirt	Assembly	Double monorail conveyor
Degreasing by warm liquid-vapor system						
Aircraft castings	Magnesium	230	500	Polyester resin (from impregnating)	Curing	Solvent: methylene chloride
Speedometer shafts and gears	Steel; brass	340	750	Machining oil; chips	Inspection; assembly	Rotating baskets (drainage and chip-removal)
Screws	Steel; brass	680	1500	Machining oil; chips	Painting; finishing	Flat and rotating baskets; conveyorized
Automotive die castings	Zinc-base	910	2000	Light oils, grease; tapping lubricants; chips	Assembly	Flat and rotating baskets; conveyorized
Electron-tube components	Steel	910	2000	Light oils	Dry hydrogen fire	Conveyorized unit
Tractor gears and shafts	Steel	910	2000	Machining oil; chips; quenching oil	Nitriding	Elevator-type conveyor handling of work in heat treating trays
Flexible hose connectors	Steel; brass	1250	2750	Machining oil; chips	Assembly	Conveyorized unit

Parts	**Metal**	**Production rate**		**Soil removed**	**Subsequent, operation**	**Notes on processing**
		kg/h	**lb/h**			
Wire, 0.8-3.2 mm (0.030-0.125 in.) diam	Aluminum	1810	4000	Drawing lubricants; light oil	Shipment	Processed at 3 m/s (500 ft/min)
Hand power-tool components	Cast iron; aluminum	2270	5000	Machining oil; chips; polishing; buffing compounds	Painting or plating; assembly	Rotating and flat baskets on conveyorized machine
Tubing, 6-76 mm ($\frac{1}{4}$ -3 in.) diam; 762-1270 mm (30-50 in.) long	Aluminum	5670	12,500	Drawing lubricants	Annealing	Hoist-operated 1134 kg (2500 lb) loads
Degreasing by boiling liquid-warm liquid-vapor system						
Transistors	Gold and tin plated	25	50	Silicone oil; light oil	Painting; branding	Manual; mesh basket
Electron-tube components	Stainless steel	90	200	Light oil	Dry hydrogen oil	Manual; mesh basket
Calculating-machine components	Steel	450	1000	Stamping oil	Painting	Manual operation
Valves (automotive, aircraft)	Steel	450	1000	Machining oil	Welding	Manual operation
Knife blades	Steel	820	1800	Oil; emery	Buffing	Manual operation
Carbide-tip tool holders	Steel	910	2000	Lubricant; chips	Recess milling	Conveyorized unit
Tubing, 60 cm (2 ft) long	Aluminum	910	2000	Drawing lubricants; quench oil	Satin finishing	Conveyorized; tube handled vertically
Calculating-machine components	Steel	1360	3000	Stamping oil	Plating	Conveyorized unit
Hand-tool housings, die-cast	Zinc-base	1360	3000	Tapping oil; chips	Assembly	Automatic conveyor; racks
Screw machine products	Steel; brass	1360	3000	Cutting lubricants; chips	Assembly	Flat and rotating basket; conveyor

Parts	**Metal**	**Production rate**		**Soil removed**	**Subsequent, operation**	**Notes on processing**
		kg/h	**lb/h**			
Cable fittings	Steel	1810	4000	Light oils	Inspection	Conveyorized
Stampings (miscellaneous)	Steel	2270	5000	Light oil; chips	Furnace brazing	Small stampings nested in baskets
Wafers	Silicon	. . .	. . .	Sealing wax; paraffin	Acid etch; diffusing	Manual, in beakers; fixtured

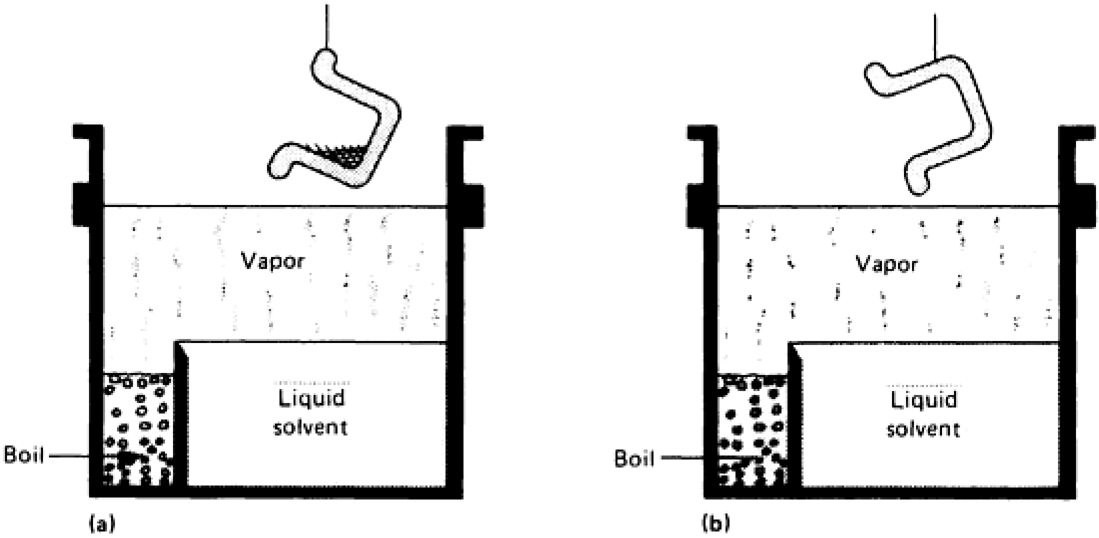

Fig. 5 Positioning of cup-shape parts to drain solvent. (a) Incorrect positioning. (b) Correct positioning

Confined Space Entry

Entering a confined space such as a vapor degreaser is potentially life threatening and requires adherence to OSHA regulations (Section 1910.146 of Title 29 of the *Code of Federal Regulations*). Another resource for information on confined space entry is ASTM D 4276-84. Some of the questions to consider are:

- Is entry required?
- Has management approval been obtained?
- Has the entire solvent volume been drained from all portions of the degreaser, and has all solvent vapor been vented? (Note: Ventilation should continue during tank entry.)
- Has the electric power to conveyors, pumps, and motors been turned off and locked?
- Have all liquid transfer lines been opened and capped?
- Has the atmosphere in the enclosed area been tested for flammable and toxic vapor concentrations and the presence of adequate (19.5%) oxygen in the air?
- Has a properly trained and equipped observer been assigned?

- Have nearby employees been alerted to the tank entry operation, and have enclosed area entry placards been posted?
- Have the person(s) entering the tank and the observer(s) been equipped with a rescue harness and lifeline, a self-contained breathing apparatus, and proper protective clothing (e.g., gloves)?
- Is a hoist or pulley system available in case rescue would require a vertical lift?

Process Applications

The wide range of applications in which vapor degreasing is used are indicated in Table 6, which lists parts and metals cleaned by the degreasing systems, as well as soils removed, production rates, and subsequent operations. The data in this table represent the experience of numerous manufacturing plants.

Process Limitations

The principal limitations of the vapor degreasing process are related to the materials it can clean without damaging effects and the soils it can remove effectively. Size and shape of workpieces, quantity of work, and degree of cleanness obtainable may also limit the applicability of vapor degreasing, but to a lesser extent. Normally, these variables merely determine the degreaser design selected.

Materials. All common industrial metals can safely be degreased with a minimum of difficulty, provided the chlorinated solvent is properly stabilized for vapor degreasing and the degreaser is properly operated. Iron parts are more susceptible to rusting after degreasing, especially in humid atmospheres.

Compatibility with Nonmetals. Some chlorinated solvents attack rubber, plastics, and organic dyes; this must be considered when degreasing assemblies with both metallic and nonmetallic components. Trichlorotrifluoroethane and 1,1,1-trichloroethane are less aggressive to many nonmetallic parts and have been the preferred solvents for these assemblies.

Solvent Stability. Vapor degreasing solvents can be decomposed, resulting in hydrogen chloride gas. This gas is very irritating, toxic, and corrosive to metals. Sources of solvent decomposition include:

- Exposure to surfaces hotter than about 175 °C (350 °F)
- Prolonged exposure to metal fines (particularly aluminum)
- Excessive soil accumulation in the boiling chamber
- Excessive and prolonged exposure to water
- Contamination with aluminum or iron chloride salts
- Exposure of the liquid or vapor to ultraviolet light

The vapor degreasing solvents have variable resistance to decomposition under the various conditions above. Trichlorotrifluoroethane is the most inherently stable of the group. Stabilizers or inhibitors are added to these solvents especially for this use. Solvent products made for other uses are likely to be insufficiently stabilized for the rigors of vapor degreasing. With proper stabilization of the degreasing solvent and good operating and maintenance practices, solvent stability is essentially secured.

Quantity of work to be processed is not a significant factor when considering the use of vapor degreasing, so long as the equipment was designed to mechanically handle the workload and has sufficient heat input. Available units range from those that are suitable for occasional cleaning of a few parts to completely automated installations geared to high-production operations.

Degree of Cleanness Obtainable. Under normal operating conditions, vapor degreasing provides a degree of cleanness that is suitable for subsequent polishing, passivating, assembly, phosphating, or painting. However, when parts are to be electroplated or subjected to other electrochemical treatments, vapor degreasing is seldom adequate and must be followed by another cleaning operation, such as electrolytic alkaline cleaning. Vapor degreasing is used immediately preceding the alkaline cleaners to remove most of the soil, thus prolonging the life of the final cleaners.

Radioactive and water-break testing techniques have indicated that a degree of cleanness between 0.1 and 1.0 monomolecular layers of soil is attainable in vapor degreasing. Under normal operating conditions, the degree of cleanness is usually near the upper level. Surface condition and section thickness may affect the degree of cleanness obtainable by vapor degreasing. For example, a polished surface is easier to clean than a grit-blasted surface. Thin sections receive less cleaning action than heavy sections, because the former equalize in temperature with the vapor zone in less time.

Removal of Difficult Soils

Virtually all ordinary oils and greases are soluble in chlorinated hydrocarbons and can be completely removed by one or more of the methods illustrated in Fig. 2. Other types of soils vary in responsiveness to vapor degreasing, from mild to almost total resistance to solvent cleaning.

Frequently, vapor degreasing is used to remove soils that do not dissolve in the solvents. Among these difficult soils are pigmented drawing compounds, water-based cutting fluids, chips, polishing and buffing compounds, and soldering fluxes. In some instances, it may be possible to substitute more easily cleaned materials. When insoluble soils are encountered, the solvent cleaning may need to be supplemented by mechanical cleaning. Impingement with a spray will remove some insolubles. Brushing may be practical in some situations. Finally, ultrasonic cavitation in the warm dip chamber can often remove the most tenacious soils.

Safety and Health Hazards

The chlorinated hydrocarbons used in vapor degreasing are modestly toxic when inhaled; gross overexposures result in anesthetic effects and may cause death. Prolonged or repeated exposure of the skin to these solvents should be avoided because they extract oils from the skin, causing cracking and dermatitis.

OSHA requires users to obtain Material Safety Data Sheets and to keep them on file and available to employees. They are useful information sources for operator training. Personnel operating degreasers or using chlorinated solvents should be warned of attendant potential hazards and observe proper operating instructions. They should be familiarized with the symptoms of excessive inhalation: headaches, fatigue, loss of appetite, nausea, coughing, and loss of the sense of balance. Maintenance workers have lost their lives climbing inside tanks containing extremely high concentrations of solvent vapors. Death was attributed to the strong anesthetic power or asphyxiation.

Every effort should be made to clean or maintain a degreaser without entering the tank. However, if tank entry is necessary, workers should follow the guidelines given in the section "Confined Space Entry" in this article.

OSHA has the primary responsibility for protecting worker health. Numerous general regulations apply to open tanks or heated equipment. For example, management must provide a cover, guardrails for platforms or walkways, an open-top edge or guardrail 1050 mm (42 in.) high, and enclosed combustion heaters with corrosion-resistant exhaust ducts. Where flammable solvents are used, special devices such as explosion-resistant equipment and fusible link cover supports are required. Solvent spraying in general must be conducted in an enclosure, to prevent spray discharge into the working area. Spraying in a vapor degreaser should be done only below the solvent vapor zone, to prevent forcing air into the vapor zone. Welding and chlorinated solvent cleaning operations must be located separately so that the solvent vapors are not drawn into welding areas. Exposure of the chlorinated solvent vapors to the high-intensity ultraviolet light radiated by welding can cause solvent decomposition to corrosive and toxic products.

The primary health hazard associated with solvent cleaning is the inhalation of excessive vapor concentrations. Acceptable time-weighted average vapor exposure standards have been adopted by OSHA, and it requires that worker exposures be maintained at or below these concentration limits. Mechanical ventilation may be required to control exposures below these concentrations. The measurement of actual exposures to vapor concentrations can be accomplished by industrial hygiene surveys using activated carbon collection tubes and calibrated air pumps, continuous reading vapor detectors, and detector tubes. Additional information can be found in the 29 May 1971 *Federal Register*, p 10466, and in the 27 June 1974 issue, p 23540.

Disposal of Solvent Wastes

The Resource Conservation and Recovery Act, also known as the Solid Waste Disposal Act, promotes the protection of health and the environment and the conservation of valuable material and energy resources. Virtually all chemical wastes have the potential to be defined as hazardous, because the EPA defines *solid waste* as any solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, or agricultural operations, or from community activities. There are exceptions, and a good background document appears in the *Code of Federal Regulations*, Title 40, sections 261-281 (especially section 261.31).

Most electroplating wastes, including solvent residues, require disposal according to these regulations. Quantity exemptions, such as less than 1000 kg (2200 lb) per month, exist in some states for some wastes, providing relief from paperwork; however, proper waste disposal is still required. Solvent distillation can reduce the quantity of waste to a minimum, particularly with the nonflammable vapor degreasing solvents. Under some circumstances, still bottoms (residues) can be used as a fuel in industrial boilers. Nonhazardous waste such as paper should be segregated from hazardous wastes to minimize disposal costs. Incineration is the best known ultimate disposal method for wastes from solvent cleaning operations. However, wastes containing reasonable quantities of solvent may be saleable to local reclaimers.

Introduction

EMULSION CLEANING is an industrial cleaning process that uses an organic solvent as the main active agent. The solvent is usually a hydrocarbon of distilled petroleum dispersed in water. The emulsion, which alone is potentially volatile, is suspended in a nonvolatile aqueous vehicle. Most emulsion cleaners include emulsifying agents, and some are aided by surfactants. Emulsion cleaners are generally used in situations where alkaline or acid cleaners are not applicable.

Emulsion means tiny droplets dispersed in large droplets. An emulsion is simply a colloidal suspension of one liquid into another immiscible liquid. (*Immiscible* means the liquids will not mix.) The oil-in-water emulsion has tiny droplets of an organic (hydrocarbon) solvent dispersed throughout a water solution. This is generally the type used in emulsion cleaning. The other is water-in-oil (natural petroleum), which has tiny droplets of a water solution dispersed throughout an oil. The oil-in-water type can easily be washed off with water and light detergent. The water-in-oil type leaves a greasy film that is much more difficult to remove.

The hydrocarbon can be distilled from any of any of different petroleum products, such as naphtha, kerosine, benzene, carbon tetrachloride, or other chlorinated solvents, including 1,1,1-trichloroethane. Most of these are no longer used because they are flammable and potentially carcinogenic and have been identified as causes of ozone depletion. Most emulsions are now based on a "mineral spirits" derivative, a hydrocarbon mixture with a relatively high boiling point (93 to 150 °C, or 200 to 300 °F). Compositions, operating temperatures, and production applications for emulsion cleaners are summarized in Tables 1 and 2.

Table 1 Compositions and operating temperatures for emulsion concentrates

Maximum safe temperature depends on the flash point of the hydrocarbon (petroleum) solvent used as the major component

Component	**Composition, parts by volume**		
	Stable(a)	**Unstable**(b)	**Diphase**(c)
Petroleum solvent(d)	250-300	350-400	250-300
Soaps(e)	10-15	15-25	None
Petroleum (or mahogany) sulfonates(f)	10-15	None	1-5
Nonionic surface-active agents(g)	5-10	None	1-5
Glycols, glycol ethers(h)	1-5	1-5	1-5

Aromatics[(i)]	5-10	25-50	5-10
Water[(j)]	5-10	None	None

(a) Operating temperature range: 4 to 66 °C (40 to 150 °F).

(b) Operating temperature range: 4 to 66 °C (40 to 150 °F).

(c) Operating temperature range: 10 to 82 °C (50 to 180 °F).

(d) Two frequently used solvents are deodorized kerosine and mineral seal oil.

(e) Most soaps are based on rosin or other short-chain fatty acids, saponified with organic amines or potassium hydroxide.

(f) Low molecular weight petroleum sulfonates (mahogany sulfonates) are used for good emulsification plus some rust protection. High molecular weight sulfonates, with or without alkaline-earth sulfonates, offer good rust inhibition and fair emulsification.

(g) Increased content improves stability in hard water, but increases cost.

(h) Glycols and glycol ethers are used in amounts necessary to act as couplers in stable and unstable emulsions. These agents are frequently used with diphase and detergent cleaners to provide special cosolvency of unique or unusual soils.

(i) Aromatic solvents are used to provide cosolvency for special or unique soils. They also serve to inhibit odor-causing or rancidifying bacteria.

(j) Water or fatty acids, or both, are used to adjust the clarity and the stability of emulsion concentrate, particularly those which are stable or unstable.

Table 2 Production applications of emulsion cleaning

Data represent practices reported by a number of plants

Part	**Soils removed**	**Cleaning cycles**	**Cleaning, time, min**	**Subsequent operations**
Stable emulsion, dip cleaning				
Cast iron parts and machined parts	Machining oil, chips	Alkaline clean, emulsion clean	1	Storage
Stable emulsion, spray cleaning				
Aluminum and brass carburetor parts	Machining oil, shop dirt	Clean, blow off[(a)]	1	Assembly, storage

Aluminum and brass	Dirt, machining oil	Clean, blow off	2	Assembly, storage
Aluminum cabinets	Machining oil, chips	Clean[(b)]	1	Assembly, storage
Aluminum housing (automatic transmission)	Alkali	Alkaline clean, emulsion clean[(c)]	1	Assembly, storage
Automobile wheel assembly, 0.103 m^2 (160 $in.^2$)	Drawing compound, chips	Clean, no rinse	1	Assembly, storage
Brass valves	Machining oil	Clean, blow off	2	Assembly, storage
Cast iron motor blocks	Machining oil, chips	Clean, no rinse	2	Assembly, storage
Cast iron motor heads	Machining oil, chips	Clean, no rinse	1	Assembly, storage
Retainer plate, 0.01 m^2 (16 $in.^2$)	Shop dirt, drawing compound	Clean	1	Assembly, storage
Steel rings, 100 mm (4 in.) diam	Machining oil	Clean, no rinse	1	Assembly, storage
Steel sinks	Drawing compound, oil	Clean	4	Alkaline soak, then enamel
Tractor parts	Machining oil, dirt	Clean, blow off	1	Wash, then paint
Valves (steel and brass)	Machining oil	Clean, blow off	1	Assembly, storage
Washing machine tubs	Drawing compound	Clean, no rinse	3	Alkaline soak, then paint
Unstable emulsion, spray cleaning				
Brake assembly, 0.01 m^2 (20 $in.^2$)	Shop dirt, chips	Clean, no rinse	1	Assembly, storage
Brake plates, 200 mm (8 in.) diam	Machining oil, chips	Clean, no rinse	1	Assembly, storage
Brake cases, 100 by 100 mm (4 by 4 in.)	Drawing compound	Clean, blow off	2	Assembly, storage
Diphase emulsion, dip cleaning				
Brass or zinc die castings	Buffing dirt	Soak, spray, electroclean,	4	Wash, then plate

		acid pickle		

(a) Emulsion does not plug holes of the needle valves and does not interfere with subsequent gaging operations.

(b) Emulsion does not spot or dull aluminum.

(c) Emulsion furnishes lubricity for interlocking gear parts.

Cleaning Action

In basic terms, cleaning is accomplished when the organic phase dissolves the oil contamination, breaking it up into tiny droplets. The hydrocarbon molecule has two ends. One end tends to bond with oils; the other bonds readily with water molecules. In effect, the hydrocarbon molecule bonds to the oil molecule, which breaks off and floats in the high-volume water phase. Once all of the oil bonds are broken and dispersed throughout the emulsion, the water-oriented end of the molecule remains free. When the rinse is applied it attaches to the "free" water-oriented ends of the surface active agents. As the molecules are rinsed away, the soil that is firmly held by the oil-oriented ends comes loose, too.

Emulsifiable solvent detergents are particularly well suited to the removal of such heavy soils as carbonized grease and oil deposits, and buffing and lapping compound residues. Where parts are very heavily soiled, solvent detergents are frequently used as precleaners before the work is put through the regular alkaline solution. The advantage of solvent precleaning is that heavy surface soil is removed from the alkaline tank, thus prolonging solution life. Precleaning of emulsifiable solvents shortens total cleaning time, and because it allows less frequent dumping of the alkaline tank, it also reduces total cleaning costs.

Applications

Emulsion systems are best used when rapid superficial cleaning is required and when some protection by light residual oil film is desired. Because the solvent phase of the emulsion is a petroleum derivative, a thin film is left behind when the rest of the emulsion dries. This film protects ferrous parts from rust and can aid lubrication in applications such as gears or bearings.

Emulsions are also used to remove heavy oils, because the solvent can clean with soil loading up to 50%. It is often considered more for gross cleaning than for producing a clean, water-break-free surface. (A *water-break-free surface* is clean enough that water runs freely off of it. If impurities such as oil or detergent residue are present, water will tend to bead up and stay on the surface.) The solvent phase of the emulsion is very effective in dissolving oils and grease without attacking the base metal. Thus, an emulsion system should be considered when evaluating the most appropriate cleaning method for:

- *Delicate parts with tenacious contaminants,* such as buffing and polishing compounds that cannot tolerate any mechanical agitation or impingement. The solvent will dissolve the binding agent, allowing the soils to flush away in a basic immersion bath (followed by an alkaline wash to clean off the emulsion).
- *Buffed soft metals:* Buffed or polished parts typically can be cleaned with an alkaline detergent but may require pH > 12. Brass and bronze tend to tarnish in solutions with pH > 10. Thus, emulsions have been widely used for buffed soft metals. (Detergents have recently been developed that clean buffed soft metals without tarnishing.)
- *Intricate internal cavities contaminated only with oils* could be cleaned with an immersion emulsion. Care must be taken to ensure that the emulsion can be thoroughly rinsed unless it is compatible with the subsequent process. For example, in one application, an emulsion was chosen for cleaning of aluminum and brass carburetor parts because it did not plug the needle valve holes or interfere with subsequent gaging.
- *Parts that cannot be heated* may be suitable for cold emulsion if they have light soils. Emulsions work most effectively when heated to 60 to 80 °C (140 to 180 °F), but they will accomplish some cleaning at

lower temperatures. This may be needed, for example, in a totally automated machining cell of tight tolerance parts followed by a coordinate measuring machine, where heat from a detergent washing operation may affect part dimensions.

- *Delicate parts in small volumes* may be suitable for hand wipe. A cold emulsion may be a strong enough cleaning agent.
- *Pigmented drawing lubricants*
- *Residues resulting from magnetic particle inspection*
- *Adhesives that may need an organic solvent to dissolve the gum binder*
- *Multiple-soil and multiple-part applications:* Emulsions can clean many different soils on ferrous and nonferrous parts that must go through one cleaning stage. The petroleum residue tends to protect ferrous metals from short-term rust, and it protects nonferrous parts from oxidation. Compromises will still be required in deciding what solution to use to clean off the emulsion residue.
- *Longevity:* Emulsions can be reclaimed and reused for many cleaning charges. Oils separate and can be decanted off, whereas other contaminants would require separate filtration. Emulsions contain other agents that may be removed in a reclamation process. (Emulsion suppliers can provide information about how to ensure proper regeneration.)

The hydrocarbon solvents in emulsion cleaners are generally safe for use on all metals and plastics. However, some rubbers and synthetic materials may absorb the hydrocarbon and become swollen, which can cause problems if they are being used as seals. Also, the solvent may attack and break down some types of rubber.

Emulsion Cleaning Process

Emulsion cleaners leave an oil-like residue on parts, and very often this is unacceptable to the next process, or the appearance is unacceptable if cleaning is the final process. The emulsion is usually followed with an alkaline detergent wash to remove the last traces of contaminants. Then a plain or deionized water rinse may be required to remove the alkaline. If parts must come out of the system dry, then an ambient or heated air drier must be included. Thus, many emulsion cleaning systems have four stages, which will be discussed below.

Concerns and Limitations

Oil-like Residue. If the oil-like residue is not desired for protection or is not compatible with the next process, it usually can be washed off with an alkaline detergent. Parts that cannot be thoroughly rinsed, such as sintered powdered metal and parts with blind holes, should not be cleaned with emulsion cleaning. On parts that will be plated or painted, it must be ensured that all of the emulsion has been removed, because emulsion can contaminate a plating line or prevent paint adhesion.

Safety. Heat aids the cleaning and drying process, but because emulsions are distilled from petroleum, they have a flash point and are potentially volatile. Depending on the emulsion, these flash points range from 40 to 99 °C (100 to 210 °F). Operating temperatures should be kept 15 °C (30 °F) below the flash point. (Some manufacturers indicate that it is safe to operate within 8 to 10 °C, or 15 to 20 °F, of the flash point.) The margin of safety may be determined by the process control capability of the equipment.

Volatile organic compounds (VOC) are emitted from the emulsion, particularly when it is heated, so adequate ventilation is vital. Depending on the type and volume of solvent discharge, the vent may need carbon absorption or scrubbers. In either case, the process may require a permit from the local air quality management authority.

Spray. Most emulsions should not be sprayed because spraying tends to atomize the solvent phase, which is highly susceptible to "flash." However, emulsions with flash points around 95 °C (200 °F) and used with higher water content can be sprayed in equipment with proper safety controls. These include close temperature control and possibly a backup temperature sensor, extra ventilation, and explosion-proof wiring.

Heat Source. Open fire gas burners should not be used. Steam heat is safest. Electric immersion heaters can be used safely with the proper solution level and electric spark controls.

Drying. Emulsions are generally slow-drying solutions because of the petroleum base. Heating the solution will aid drying, but temperature often needs to be held down due to safety concerns. Ambient air blowoffs are effective only if the air nozzle is very close to the part and is directed into any cavity. This can work with a manual air gun or proper setup on a conveyor belt. It generally does not work for batch processing. Heated air blowoff dryers will work, but caution must be taken to keep the system temperature 15 °C (30 °F) below the flash point.

Superfund Amendments and Reauthorization Act (SARA). Depending on the solvent base and concentration, the emulsion process may need to be reported to the Environmental Protection Agency under the terms of SARA, Title III.

Process Parameters

Process Selection. Determining the most appropriate cleaning method for a given application requires a thorough analysis of the manufacturing process, including:

- Part conformation
- Dirt to be cleaned
- Volume of parts
- Batch size
- Materials handling
- Process before cleaning
- Process following cleaning
- Cleanliness specifications
- Current method
- Budget
- Process limitations (e.g., time or chemistry constraints)

This information will guide the user to the balance of chemistry, method, and process parameters that will provide the proper cleanliness most economically.

Immersion Cleaning

Immersion is the cleaning method most widely used with emulsions, because of the solvent content required and because it provides full exposure of the part to the cleaning agent. Obviously, this method requires a tank large enough to contain the part or batch of parts and enough emulsion for complete immersion. It may be economical to clean small parts with this method, but for even small volumes of very large parts, the cost of thousands of gallons of emulsion may be prohibitive.

Processing Variables

Temperature. Although significant, bath temperature is less important in emulsion cleaning than in alkaline detergent washing. The dispersed oil (solvent) phase can accomplish much of its cleaning at ambient temperature. Higher temperatures are required for high-melting greases, buffing compounds, and waxes. The maximum safe operating temperature must be kept 8 to 15 °C (15 to 30 °F) below the flash point.

Agitation. Some of the oil-based soils can be cleaned in stagnant immersion. However, to ensure full coverage and increase effectiveness, the bath should be mechanically agitated. This can be accomplished with a recirculating "turbulating" pump, mechanical stirring, or air injection. Agitation helps to flush contaminants away from the part surface, allowing the cleaner to attack the next layer.

Ultrasonic energy is another form of agitation that can significantly improve immersion cleaning efficiency and effectiveness. Energy waves go through the solution at frequencies up to 50 kHz, creating millions of tiny bubbles on the part surface that then implode, creating a scrubbing action. Ultrasonics are particularly helpful in cleaning small-diameter or blind holes.

Concentration. In immersion, emulsions are usually used in concentrations of 20 to 30%. However, concentration is not a critical factor, as shown in Table 3. The capacity for dissolving soil increases proportionally with the concentration (volume) of the emulsion, but the solubilizing rates are not similarly affected by an increase in concentration. Some soils do react to varied concentrations, as shown in Fig. 1.

Table 3 Operating conditions for emulsion cleaners

Classification of cleaner	Concentration, %	Operating temperature		Time, min
		°C	°F	
Immersion systems				
General-purpose	5-15	10-71	50-160	2-8
Unstable single-phase[a]	10	21	70	1-10
Kerosine-based[b]	15-25[b]	21	70	2-10
Diphase, heavy-duty	15-25	21-54	70-130	2-10
Emulsifiable solvent	100	21-60	70-140	-2
Spray systems				
General-purpose	1-5	10-71	50-160	-3
General-purpose	2-5	10-77	50-170	-3
Light cleaning	1-2	10-71	50-160	1-3

(a) Requires vigorous agitation.

(b) Water-in-solvent emulsion, 15 to 25% water in kerosine

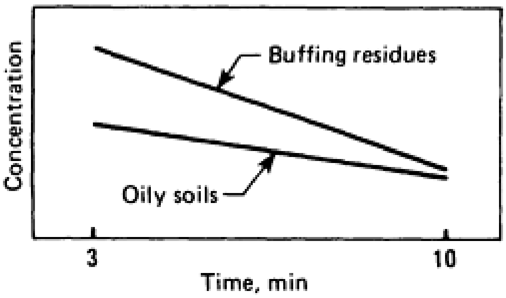

Fig. 1 Approximate relationship of time and concentration for emulsion cleaners used to remove two different soils

Emulsion cleanliness may affect cleaning effectiveness, which would relate to the concentration of the cleaning agent. If smut is seen on parts, then the emulsion is saturated with dirt and can absorb no more soils. To some extent, more emulsion can be added. Then the bath must be regenerated or replaced.

Time/Exposure. Generally an emulsion can accomplish its cleaning in 30 sec to 5 min. If cleaning requires much more time, then it is likely that the wrong emulsion was used or that immersion emulsion is not the proper cleaning method for the application. The length of time can be significantly altered by increasing the heat or changing or increasing the agitation. (Some typical process cycles are shown in Table 4.) Difficult applications may be accomplished with a combination of soak and spray rather than extended soaking time.

Table 4 Cycles for immersion and spray emulsion cleaning

Process sequence	Cycle time, min			
	Easy cleaning(a)		Difficult cleaning(b)	
	Immersion(c)	Spray(d)	Immersion(e)	Spray(f)
Clean(g)	2-4	-1	4-10	1-2
Rinse(h)	$\frac{1}{4}$ -	$\frac{1}{4}$ -	-	-
Rinse(i)	-1	-1	-1	-1

(a) Removing cutting oils and chips from machined surfaces, shop dirt and oil from sheet metals, and drawing compounds from automotive trim.

(b) Removing embedded buffing compounds, impregnated carbonized oils from cast iron motor blocks, and quenching oil from heat treated forgings.

(c) Concentration of cleaner, 1.5 to 6 vol%.

(d) Concentration, 0.6 to 1.5 vol%.

(e) Concentration, 3 to 9 vol%.

(f) Concentration, 0.75 to 1.5 vol%.

(g) 10 to 82 °C (50 to 180 °F).

(h) Unheated rinse.

(i) 54 to 71 °C (130 to 160 °F).

(j) 10 to 71 °C (50 to 160 °F)

Secondary Cleaning

Very often, emulsion cleaning is followed with an alkaline detergent wash, a secondary emulsion cleaning (usually at a lower concentration), or a water rinse. This step cleans off the emulsion residue and any particle contaminants not flushed away in the primary cleaning stage.

A detergent wash is used for secondary cleaning when all emulsion must be removed. This is generally run hot at 50 to 80 °C (120 to 180 °F), with mechanical action. Steel parts still need some rust inhibiting.

A final rinse is almost always used to flush off dirt that remains or has been redeposited since the primary or secondary cleaning. Some emulsions can be flushed off with plain water. In either case, the rinse water should be hot. Heat speeds the process and keeps the parts hot to aid drying. For applications in which absolutely no surface residue can be tolerated, deionized water must be used. Plain tap water contains salts that may adversely affect subsequent processes such as anodizing.

Spray Cleaning

Spray cleaning provides the advantages of power impingement, continuous flushing, and no redeposition of contaminants. The mechanical action of the spray tends to cut into soils to help break them away. The continuous flushing exposes the next dirt layer, allowing the emulsion to work through even heavy buildup quickly. The spray solution can be filtered in series with the wash pump prior to recirculating over parts. The rest of the contaminants are contained in the solution tank below the wash cabinet. Thus, it is possible to get an acceptably clean part in a single-stage spray machine, whereas this is unlikely in a single-stage immersion system.

The main drawback to spraying an emulsion is the increased exposure to VOC. Spraying releases more of the solvent to air and requires significantly more ventilation than an immersion application. In addition, like immersion, spray emulsion leaves an oil-like residue. If this is unacceptable, then subsequent alkaline wash and rinse stages are required, as discussed in the section "Immersion Cleaning" in this article.

Spraying can be done via two methods:

- *Manual spray/flush* over large parts in a vented tank at low pressure (only enough to deliver the emulsion to the work, approximately 35 kPa, or 5 psi). With the operator at the point of contact, there is still potential exposure, depending on the particular emulsion and the temperature. Fewer vapors are emitted at lower temperatures.

- *By machine,* either in-line or cabinet, usually at 100 to 700 kPa (15 to 100 psi). These pressures atomize the emulsion, which increases the flash potential, particularly at normal operating temperatures of 60 to 70 °C (140 to 160 °F). Explosion-proof cabinets and electrical controls should be critically analyzed before spray emulsion is attempted.

For very large parts, an emulsion can be flushed on manually at high concentrations, then rinsed off with a power spray.

Processing Variables

Temperature. Some cleaning is accomplished at ambient temperature, but spray emulsion is more efficient and effective at elevated temperatures. Temperatures should be kept 15 to 20 °C (25 to 40 °F) below the flash point.

Agitation. The mechanical power of spray significantly reduces cleaning time and increases the ability to flush out cavities. Spray pressure should be kept to the minimum required. If pressures greater than 515 kPa (75 psi) are required to accomplish cleaning, a different process may be more appropriate.

Concentration. For spray emulsion, emulsion cleaners are typically used in concentrations of 1 to 5% (Table 3) because the spray adds power and exposure speed. These concentrations, 85% less than those used for immersion, make spray emulsion a very economical process. Also, a low volume of emulsion (diluted in 95 to 99% water) does reduce the risk of VOC exposure and flash, and it results in less residue on the parts. This is a second reason that spray emulsion can sometimes be used without secondary cleaning.

Time. Power spray in-line or cabinet equipment reduces cleaning time up to 75% compared to the time required for immersion, even at lower concentrations (Table 4).

Emulsion Cleaners

Emulsion cleaners are broadly classified into four groups on the basis of stability:

- *A stable single phase, or permanent, emulsion* is one in which the discontinuous phase is dispersed throughout the continuous phase. This requires no more agitation to maintain a uniform dispersion than that provided by thermal gradients and the motion of the work being cleaned.
- *An unstable single phase emulsion* has a uniformly dispersed phase that tends to separate and form a solvent layer. Solvents with specific gravity of less than 1.0 form a top layer, and those with a specific gravity greater than 1.0 form a bottom layer. These cleaners require moderate to considerable agitation to maintain complete dispersion.
- *A diphase, multiphase, or floating layer emulsion* forms two layers in the cleaning tank and is used in this separated condition. Work is immersed through the solvent-rich surface layer into the water-rich lower layer, permitting both cleaning phases to come in contact with the surfaces to be cleaned. When used in a spray system, a diphase cleaner resembles an unstable single phase cleaner, because the solvent and water phases are mixed in the pumping action.
- *An emulsifiable-solvent system* is one in which the as-received, undiluted solvent is applied to the surface to be cleaned by hand or by use of a dip tank. It is followed by a water rinse that emulsifies and removes the solvent and soil.

Because *stability* is a relative term, the definitions of these four types of cleaners can overlap. The advantages and disadvantages of the first three types are as follows.

Stable emulsion cleaners are the most economical. They are practical for removing light shop soils, especially in applications where in-plant rust protection is required. These cleaners contain hydrocarbon solvents such as kerosine, which can dissolve and clean light soils. Two to three weeks of rust protection can be expected for ferrous metal parts cleaned by a properly constituted stable cleaner. Such a cleaner maintains an emulsion with water for many hours, requiring a minimum amount of agitation.

A 2% stable emulsion spray rinse often follows alkaline cleaning. This procedure has provided rust protection for as long as three to four weeks in storage areas where humidity is not excessive and unusual changes in temperature are not encountered.

Although 75 °C (170 °F) is the recommended maximum operating temperature, stable emulsions can be operated safely at temperatures up to 80 °C (180 °F). The higher temperatures, sometimes advantageous when rapid drying of the work is desired, increase evaporation rates and may cause polymerization of emulsion and the formation of a varnish-like film that is difficult to remove from work. When large quantities of parts are cleaned in a continuous production flow in automatic spray washers, stable emulsion cleaners are preferred because of their lower initial cost and ease of maintenance.

Stable emulsion cleaners do have disadvantages. Their efficiency is low in removing hydrocarbon soils if more than 10% of the soil has a solidification temperature within 10 °F of the temperature of the emulsion. In hard water, stable emulsions form insoluble precipitates that may plug drains and increase maintenance.

Unstable emulsion cleaners, although higher in cost than stable emulsion cleaners, perform more efficiently in removing heavy shop soils, such as oil-based rust preventatives and lubricants used in stamping and extruding. The hydrocarbon fraction of unstable emulsion cleaners makes more intimate contact with the work surface, permitting greater action of the solvent on soil. Unstable emulsions are also successful in hard waters that cause stable emulsions to break down.

Unstable emulsions, as well as the equipment required for using them, are less costly than diphase emulsions. However, their cleaning power approaches that of diphase systems, and they are widely used for the removal of heavy hydrocarbon soils. Phosphates may be added to hard waters to increase the efficiency of unstable emulsions.

The concentration of an unstable emulsion can generally be determined by gravimetric separation. Operation above or below the preferred concentration range lowers cleaning efficiency or causes excessive cleaner consumption. The operating temperature of an unstable emulsion is critical and must not exceed 70 °C (160 °F). The usual range is 63 to 68 °C (145 to 155 °F).

Diphase emulsion cleaners are used for removing the most difficult hydrocarbon soils, such as lapping compounds, buffing compounds, and oxidized oils. They provide a higher degree of cleanliness than can be obtained with stable or unstable emulsions. The flash points of diphase emulsion cleaners cover a wide range, permitting operating temperatures up to 80 °C (180 °F). The monomolecular layer of oil that remains after diphase cleaning provides good rust protection.

In diphase cleaning, the solvent in the bottom phase is very powerful and a 100% concentrated product. It is not an emulsion with water. Hence, these cleaners provide better cleaning than regular emulsion cleaners.

Diphase cleaners are most frequently used in dip tanks. However, with specially designed equipment or the addition of emulsifiers to retard separation into solvent and water layers, these cleaners can be used in recirculating spray washers. Diphase cleaners also have disadvantages:

- They are adversely affected by hard water, and preconditioning the water with phosphates is unsuccessful.
- They cost more than stable or unstable cleaners.
- Vaporization of hydrocarbon layers requires more ventilation than is needed for stable and unstable cleaners to avoid fire and health hazards.
- No easy test is available for determining diphase cleaner concentration.

Selecting an Emulsion System

Factors that influence the choice of a stable, unstable, or diphase emulsion system include:

- Type of soil to be removed
- Size and quantity of work
- Need for rust protection
- Water condition
- Cleaning sequence (especially if emulsion cleaning is preceded by alkaline cleaning)
- Cost

Production applications for the principal emulsion cleaners and pertinent operating data are given in Table 2.

Analysis

Analysis of the more stable emulsion cleaners can be made at the tank. However, distillation techniques are used for the unstable and diphase cleaners, requiring analysis in a laboratory. To obtain a good representative sampling, samples should be taken from various locations. In an immersion installation, samples should be taken from tanks with a glass tube. In a spray installation, samples should be taken from the jets after the washer has been in operation for some time, because soluble oils become more emulsified as spraying continues. One simple and rapid method of analysis is:

1. Place approximately 90 to 95 mL of emulsion in a 100 mL glass-stoppered graduated cylinder.
2. Measure and record the actual amount of sample.
3. Cautiously add 5 mL of sulfuric acid.
4. Place a stopper on the cylinder and shake until the emulsion begins to break.
5. Allow the emulsion to cool to 20 °C (70 °F) and separate completely.
6. Measure and record the amount of separated emulsifiable material or oil. The volume percentage of oil in the emulsion is the volume of soluble oil divided by the volume of original sample, multiplied by 100.

Composition

Stable, unstable, diphase, and other emulsion cleaners cover a wide range of solvent and emulsifier compositions. The solvent is generally of petroleum origin and may be heterocyclic (Mpyrol), naphthenic, aromatic, or of hydrocarbon nature (kerosine).

Solvents are available with boiling points of 60 to 260 °C (140 to 500 °F) and flash points ranging from room temperature to above 95 °C (200 °F). Because the solubility factor increases as the molecular weight of the solvent approaches that of water, low-to-medium molecular weight solvents are usually more effective in removing soils. However, fire hazards and evaporation losses increase as boiling and flash points decrease.

Emulsifiers include:

- Nonionic polyethers and high-molecular-weight sodium or amine soaps of fatty acids
- Amine salts of alkyl aryl sulfonates (anionic)
- Fatty acid esters of polyglycerides
- Glycerols
- Polyalcohols

Cationic ethoxylated long-chain amines and their salts are also used in emulsions.

Emulsifiers must have some solubility in the solvent phase. When solubility is low, it can be increased by adding a coupling agent (hydrotrope), such as a higher-molecular-weight alcohol, ester, or ether. These additives are soluble in oil and water.

Emulsion Types and Stability. The stability of emulsion cleaners depends on the properties of emulsifying agents that are capable of causing oil and water to mix uniformly. Because oil and water do not mix naturally, an oil-in-water mixture that does not contain an emulsifying agent or dispersant requires constant mechanical agitation to prevent the oil and water from separating into two layers. Emulsifying agents can be placed in two categories:

- Those that promote the formation of solvent-in-water emulsions, in which water constitutes the continuous phase and solvent constitutes the discontinuous phase
- Those that promote the formation of water-in-solvent emulsions, in which water is the dispersed discontinuous phase

Equipment for Immersion Systems

Tanks for cleaning solution should be constructed of hot-rolled steel. Depending on tank capacity , steel gage requirements are as follows:

- Up to 380 L (100 gal), 12 gage
- 380 to 1890 L (100 to 500 gal), 10 gage
- Over 1890 L (500 gal), 7 gage

All seams should be penetration welded and dye checked for leaks. Channel or angle iron reinforcements should be welded wherever they are required for strength or rigidity. All tanks should be built up on a frame so they can be insulated underneath and so they can be picked up. Tanks should have a minimum of 25 mm (1 in.) of insulation with light-gage, cold-rolled steel cover panels for energy efficiency.

Tanks can be heated with steam or immersion electric elements. Gas burners are not recommended because of potential flash. Where steam is used, coils are preferred to an open line. Condensate from an open line will dilute the solution. Coils must, of course, be fabricated of a substance compatible with the solution to be heated. Iron or steel tubing is recommended for alkaline solutions, while acid-resistant metals, graphite, and impervious carbon are recommended for acidic solutions. The steam coil length depends on the type of tank, the coil diameter (not less than 1 in.), the steam pressure available, and the speed with which the solution is expected to heat to optimum temperature. Commercially available plate coils are most efficient.

Electricity as a tank heating method is most efficiently applied by means of electrical resistance elements, encased in protective jackets and immersed within the solution. Where possible, the heat-transmitting medium should be readily removable from the tank. It should not be located on the tank bottom where scale or sludge can reduce its efficiency or where it could be damaged when sludge is shoveled out.

Emulsion solutions with pH > 8 will provide rust protection so the wash tanks can be carbon steel. Alkaline wash tanks can also be carbon steel. Rinse tanks should be stainless steel.

Provision of agitation is important. Agitation keeps bringing fresh solution into contact with the work and introduces a degree of physical force to supplement chemical activity. The result is faster cleaning.

Draining is an important consideration. An overflow surface drain permits surface grease and oil to be skimmed off, preventing rapid solution contamination. A bottom drain is also necessary, to discard solution.

Equipment for Spray Systems

Spray Washing Machines.

Where metal is washed in volume on an assembly line, spray application of the detergent solution in an automatic or semiautomatic spray washing machine is the faster possible cleaning method. It combines the mechanical force of spray jets with the chemical and physical action of the cleaning solution.

Spray washing machines are usually engineered to a particular installation. Part, size, volume, time necessary to clean and rinse, and subsequent operations are factors that influence individual machine design. Many machines provide for more than one washing stage, as well as for rinsing and forced air drying. They can be batch cabinet style or in-line conveyor. The proper type is the one that matches the materials handling and product flow of the rest of the manufacturing process.

Work is transported through the various spray washer stages on a flat conveyor belt, in a screwlike drum that keeps work moving forward, or suspended from an overhead monorail. Spray machines deliver a solution through fixed nozzles, to impinge on work from all angles as it passes through. Soiled work is typically exposed to a detergent spray solution for about one minute, sometimes less.

For batch washers, the sprays can be either fixed or moving. Most operations have fixed sprays with a rotary table turning relatively slowly (usually 2 to 10 rpm) through the sprays to ensure overall cleaning. The use of programmable logic controllers in batch cabinet spray washers can allow multistage processing in a single cabinet. The key is to keep solutions separate and develop a system to prevent cross-contamination. This includes using separate spray headers or having a way to evacuate one solution before second-stage processing. If a dry stage is required, the cabinet must be designed so that the solution tanks can be closed off from the spray cabinet; otherwise, moisture will continue to flow into the cabinet. Parts will not dry in a wet cabinet.

Solution tanks should be sized to hold a volume of two to three times the pump flow rate. The tank bottom should be sloped for easier cleanout, and the entire tank should be insulated for efficiency and operator safety. The pump intake should be above the bottom of the tank and should be equipped with a screen to prevent the intake of sediment and chips. In handling unstable emulsions, pump intakes should be located at the interfaces of oil and water. In some applications, more than one intake is necessary. The reservoir tank is usually constructed of low-carbon steel. The thickness of the steel depends on the size of the equipment, but it should not be less than 10 gage.

Piping System.

For effective spray cleaning, nozzle pressure should be at least 105 kPa (15 psi) to provide adequate mechanical action at the surface of the workpiece. Higher pressures can be used, but they tend to atomize more of the emulsion, which increases the risk of flash. The nozzles should be readily accessible and removable for cleaning. To prevent overspraying, end nozzles in the cleaning and rinsing chambers should be deflected inward approximately 30°. All nozzles should be staggered to ensure complete coverage of the workpiece.

Conveyor.

The use of a variable speed conveyor should be considered in the initial installation to permit some latitude in the retention time of parts in the cleaning cycle.

Heating.

Steam is widely used as a source of heat in spray cleaning units. Gas immersion burners are not recommended, because they prevent a fire hazard. The capacity of the steam coils or plates should be sufficient to heat the solution to operating temperature within 30 min to 1 h.

Air Drying.

Forced air is used to dry parts after cleaning and rinsing. It may be heated or kept at room temperature. Heated air has three advantages:

- Drying is hastened.
- Floor space is conserved.
- Less air is required for the same number of parts.

Safety

The potential exposure and flash of solvent emulsions has been mentioned several times in this article. This is not to say that these solutions are unsafe, only that they are safe when used properly, particularly those recently developed formulations with flash points above 95 °C (200 °F). Keeping the heat 8 to 20 °C (15 to 40 °F) below the flash point and using steam or electric heat are the main factors in reducing flash potential. Wiring used in the vicinity of emulsion cleaning operations should be explosion-resistant for immersion systems, explosion-proof for spray systems.

Emulsions are not highly toxic or carcinogenic. (Those currently sold in the market do not use a chlorinated solvent base.) Generally, manufacturers recommend that operators wear a minimum of rubber gloves and apron. Normal eye protection is suggested, but most emulsions do not require full face shields.

The type of proper ventilation varies with different emulsions. Some require special permits or exhaust stack controls.

Waste Disposal

One of the advantages in using emulsion cleaners is that they can be reused many times. However, when it is time to change solutions, disposal of spent emulsions is a problem. Most emulsions have an organic/oil base, and most local water authorities have reduced the acceptable concentration of oil permitted for sewer discharge well below 100 ppm.

Concentrated emulsions should be removed by an authorized hazardous waste hauler and incinerated in a fuels blending program. Most emulsified solutions separate when cooled, given enough settling time. The oils can be skimmed off, and the emulsion concentrate will float on the water so that it can be separated. The water portion may be neutralized and the particles filtered out. This may be able to be discharged into the sewer after checking with local authorities. If that is not permitted, it could perhaps be processed with an ultrafilter, depending on the particular emulsion and contaminants. In some areas, the water may be evaporated off to concentrate the volume for proper disposal.

Information on emulsion cleaning of specific metals and alloys can be found in the Sections "Surface Engineering of Irons and Steels" and "Surface Engineering of Nonferrous Metals" in this Volume.

Molten Salt Bath Cleaning

James C. Malloy, Kolene Corporation

Introduction

MOLTEN SALT BATHS are anhydrous, fused chemical baths used at elevated temperatures for a variety of industrial cleaning applications. Among the more common uses of these baths include:

- Removal of organic polymers and coatings
- Dissolution of sand, ceramic, and glassy materials
- Stripping of plasma carbide coatings

In addition, molten salt baths may be used to pretreat cast iron surfaces before brazing and bonding operations.

Molten salt baths for cleaning applications are chemically active or reactive fluids with unique process capabilities. They are quite distinct from other molten salt compositions that are used for simple heat transfer or heat treatment applications. Equipment requirements for successful use of these processes also differ from molten salt heat transfer or heat treatment equipment. Larger volumes of insoluble cleaning byproducts are usually formed that must be effectively and safely collected and removed from the baths.

Cleaning salt baths are formulated from a variety of inorganic chemical compounds. Among the more common ingredients are alkali hydroxides, alkali nitrates and nitrites, alkali chlorides, and alkali fluorides. By adjusting the ratios of the various ingredients, a wide range of melting points, operating temperature ranges, chemical reactivity, and other parameters can be obtained. As a whole, they offer combinations of reactivity, solvency, and speed unavailable in any other cleaning medium. The chemistry involved during various cleaning applications ranges from simple dissolution of contaminants to more complex reactions involving the thermochemical oxidation of organics and the electrolysis of molten salts.

Applications

As with any cleaning process, molten salt baths are used to remove some type of unwanted surface soil, contamination, coating, or other substance from a substrate to allow further processing or reclamation of the substrate. Due to the relatively high temperatures involved with molten salt processing (205 to 650 °C, or 400 to 1200 °F), substrates to be cleaned are restricted to those materials that are compatible with the operating temperatures of the various processes. Because these baths are also chemically active, the substrate must also be chemically compatible with the various molten salt systems. While most metals that are temperature compatible will also be chemically compatible, there are notable exceptions to this general statement. For example, magnesium and its alloys must not be processed in oxidizing salt baths because of the potent oxidation-reduction reaction that may occur at elevated temperatures. This would result in ignition of the metal and destruction of the component.

Paint stripping in molten salts is a simple immersion process and is applicable to a wide variety of organic coatings, including solvent-based, water-borne, cured powders and high-performance coatings such as fluorinated polymers. Depending on the type and thickness of the paint coating to be removed, the stripping reaction time can vary from several seconds to a few minutes. The operating temperature depends on the specific process used, but it normally falls in the range of 290 to 480 °C (550 to 900 °F). The lower-temperature processes are generally used to reclaim reject-coated products and on temperature-sensitive materials and components. The higher-temperature processes are used for stripping more robust components.

The higher temperatures are also used for "maintenance" paint stripping of hooks, racks, carriers, and similar fixtures that serve as extensions or add-ons to the conveyor system that carries components to be painted through the paint line. Hooks and racks generally hang down from an overhead conveyor system, while carriers generally "ride" on a floor track or floor conveyor. The components to be coated are affixed to the hooks, racks, and so on and are transported through the various coating operations such as surface pretreatment, coating area, and curing ovens. At the end of the line, the finished parts are removed and "raw" unpainted parts are placed on the fixtures. Because the hooks and racks may pass through the coating line numerous times between stripping operations, they may receive numerous layers of coatings.

Stripping is accomplished by a thermochemical reaction between the oxidizing molten salt and the organic portion of the paint. Alkali nitrate, usually present in an oxidizing salt bath, donates the oxygen required to allow the organic material to be completely oxidized to carbon dioxide while immersed in the bath:

$$\mathrm{C} + 2\mathrm{N}O_3^- \rightarrow \mathrm{CO_2} + 2\mathrm{N}O_2^- \qquad \textbf{(Eq 1)}$$

During the course of the reaction, nitrate is chemically reduced to nitrite. Contact with atmospheric oxygen then reoxidizes the nitrite back to nitrate, helping to regenerate the bath:

$$\mathrm{N}O_2^- + \frac{1}{2}\,\mathrm{O_2} \rightarrow \mathrm{N}O_3^- \qquad \textbf{(Eq 2)}$$

Alkali carbonates are formed as a result of the stripping from the reaction between carbon dioxide and caustic alkalis present in the bath:

$$\mathrm{CO_2} + \mathrm{OH^-} \rightarrow \mathrm{C}O_3^{2-} + \mathrm{H_2O}\uparrow \qquad \textbf{(Eq 3)}$$

The alkali carbonates continue to increase in the bath until the bath becomes saturated with them. After saturation has been reached, the bath continues to react with any additional organics introduced. The additional carbonates, however, begin to precipitate out of solution in the form of sludge. Molten salt stripping equipment typically is designed with collection devices into which the sludge, which is denser than the host salt, settles for subsequent removal from the bath. Along with the alkali carbonates, the sludges may also contain insoluble inorganic pigments, fillers and so on, that were present in the original paints that were stripped.

Upon removal from the molten salt, the components are rinsed in water to cool them and to remove the thin film of salt residue present on the components. Additional post-treatments, such as acid brightening, neutralizing, and so on, are also commonly used to prepare the components for recoating.

Polymer Removal. The removal of solidified synthetic polymer residues is another common use for oxidizing molten salts. Synthetic fiber production involves the use of intricate dies or spinnerets and associated components such as filter packs and distributor plates. The molten polymer (for example, nylon, polyester, or polypropylene) is extruded through the spinneret under pressure to form the fiber strand. It becomes necessary to disassemble and clean the packs and spinnerets when blockages are present or when production schedules dictate a "changeout" of the packs. The chemistry involved is the same as described above for paint stripping.

Great care must be taken when cleaning spinnerets because of their delicate hole geometries, low root-mean-square (rms) surface finishes, and high intrinsic value. To clean spinnerets and screens of polymeric material, the initial salt composition should be essentially neutral. Buildup of alkaline reaction products ultimately leads to some attack (pitting) of the workpieces and can cause an accumulation of undesirable ions (for example, chromate) in the salt. The spinneret with its solidified polymer residues is immersed in the cleaning bath and a polymer is quickly and completely removed via thermochemical oxidation, without harming the spinneret's properties.

Casting Cleaning. The cleaning of castings with molten salt processes is applicable to both investment castings (lost wax) and sand castings. Investment castings are processed in molten salt baths to remove residual external shell and to leach out preformed ceramic internal coring. Sand castings are processed to remove binder residues and burned-in core sand. Salt bath cleaning is usually used after preliminary cleaning operations such as shakeout and mechanical blasting.

Investment Castings. In the case of investment castings, a small amount of external shell is usually still present after mechanical cleaning operations. Salt bath processing is then used as a scavenger to remove these residues. Relying on the reaction between silica present in the shell and caustic alkalis in the salt bath, the silica is converted into an alkali silicate that is soluble in the bath:

$$\mathrm{SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O}\uparrow \qquad \textbf{(Eq 4)}$$

Within the bath's normal operating temperature range of 480 to 650 °C (895 to 1200 °F), the water formed during the reaction is released from the bath as vapor and is visible as a mild effervescence on the bath surface. Inert shell and core constituents such as zircon or aluminosilicates simply slough off the casting as the silica is removed from the shell or core.

Sand castings are cleaned using a method similar to that used to clean investment castings. Again, the principal reaction is between silica (sand) and the alkalis present in the molten salt. When cleaning cast iron, however, the process is usually performed electrolytically.

Incorporating direct current into the molten salt cast iron cleaning process allows simultaneous removal of sand, surface graphite, and scale. The casting to be cleaned is normally subjected to an initial reducing (cathodic) cycle to dissolve sand and produce an oxide-free casting. This procedure not only produces a casting that is free from any sand contamination, but also greatly improves the machinability (and machine tool life) of the casting by removing the tough, hard surface scale. The scale reduction also helps to expose any sand particles that may have been masked by scale at the metal surface; the now-exposed sand is then dissolved by the bath (Fig. 1a and b). To prepare cast iron surfaces (either as-cast or machined) for subsequent brazing, babbitting, or other metal coating operations, the electrolytic process becomes somewhat more involved.

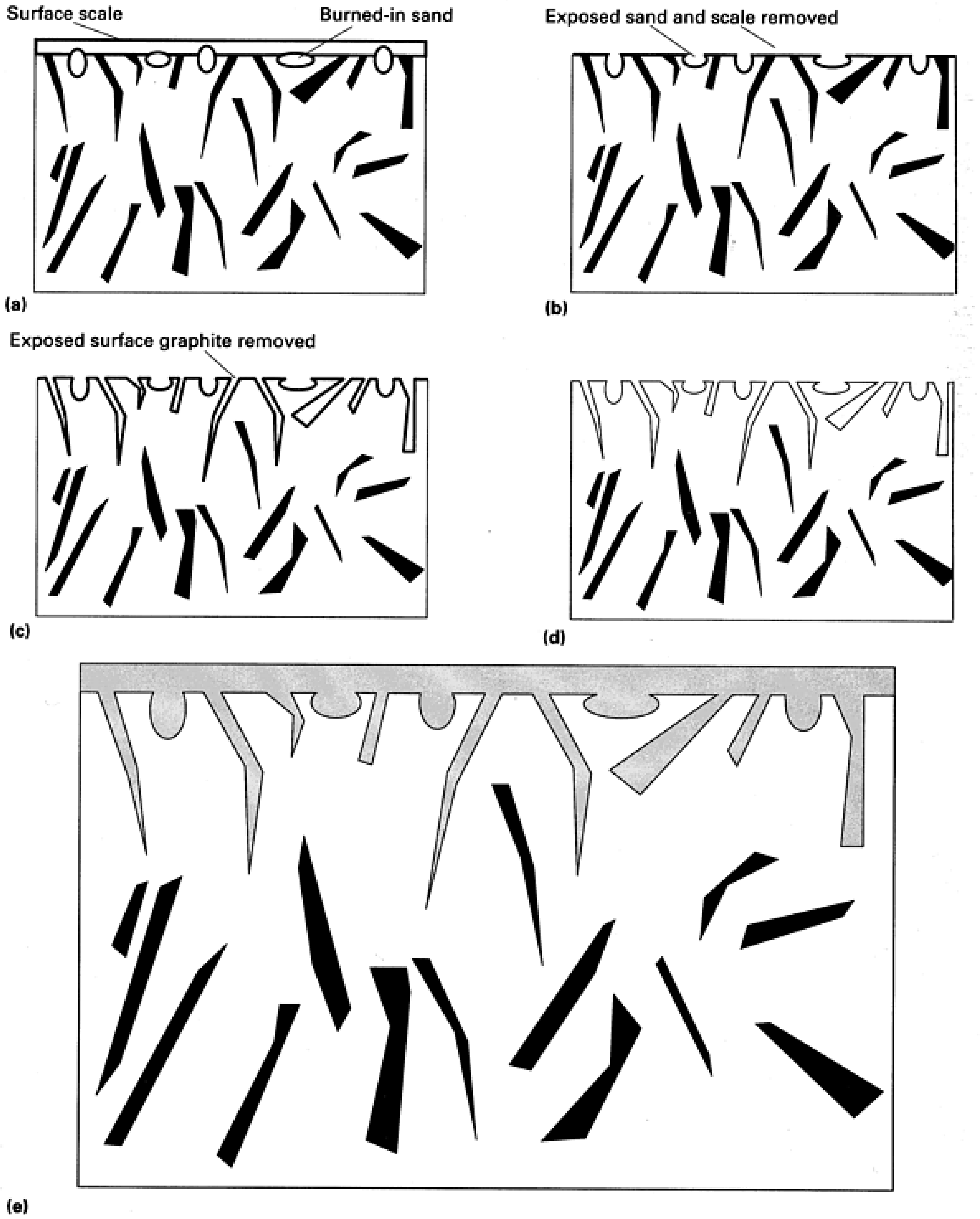

Fig. 1 Schematic cross section of the surface of a cast iron component as it is modified by cleaning in a molten salt bath. (a) As-cast. Note surface scale, burned-in core/mold sand particles, and flake graphite extending to surface. (b) After first reduction cycle. Exposed sand particles have been chemically dissolved, while the original casting oxide has been electrochemically reduced. The original flake graphite is unaffected and intact at this stage of processing. (c) After oxidation cycle. The original flake graphite has been electrochemically oxidized to carbon dioxide. The entire exposed cast surface is now covered with a very thin, uniform layer of iron oxide. (d) After second reduction cycle. The cast surface is now free of all original cast scale, sand inclusions, and exposed graphite flakes. The final reduction cycle also removes the thin layer of iron oxide that was formed during the oxidation cycle. (e) After brazing. The braze metal uniformly "wets" the surface of the metal and freely flows into the surface voids previously occupied by graphite flakes.

The initial cleaning cycle usually incorporates a reducing cycle to remove sand and surface scale as described above. The polarity of the direct current is then reversed, effectively electrolytically oxidizing the casting. This converts any exposed surface graphite to carbon dioxide (Fig. 1c). To remove the thin, uniform layer of iron oxide from the casting formed by the oxidizing treatment, the current is once again reversed to produce a final reducing cycle. This results in a scale-free, sand-free, graphite-free surface ready for coating or joining operations (Fig. 1d). When joined, the brazing alloy uniformly "wets" the metal surface and penetrates the voids previously occupied by the graphite flakes (Fig. 1e).

The amount of foreign material removed from a given casting will vary widely from application to application. In the case of investment castings, it will depend on the size of the casting, how much preliminary mechanical cleaning (e.g., shot blast) the casting receives prior to salt bath cleaning, and the geometry of the casting itself. It may range from as low as a fraction of an ounce to several pounds. Likewise, the amount of material removed from a sand casting will depend on the amount of burned-in mold and core sand that is present after mechanical shakeout. These amounts are somewhat more predictable and usually fall in the range of fractional ounces to a few ounces for a typical cast iron engine head or hydraulic valve body.

Glass Removal. Molten salts are an effective medium for removing both solidified glasses and glassy coatings from metals. They are commonly used for cleaning glass fiber production equipment, such as spinnerets and spinner disks, and removing the glassy lubricants commonly used in high-temperature forging operations. Reactions involved are analogous to those for sand removal (see the section "Sand Castings" in this article).

Plasma/Flame Spray Removal. Oxidizing molten salt baths are effective in removing a variety of flame spray or plasma coatings. It is necessary to strip these wear-resistant and protective coatings when jet-engine components are repaired or rebuilt, when tooling and jigs are cleaned during plasma coating, or whenever these tough coatings are not wanted.

The stripping reaction usually involves both the metallic and carbide portions of the coating. Soluble alkali salts are formed by the metallic constituent, while the carbide portion is oxidized to from carbon dioxide. In the case of chromium carbide, the net reaction products are alkali chromates and alkali carbonates. The simplified reaction is as follows:

$$\begin{array}{l} \mathrm{CrC} + 5\mathrm{N}O_3^- + 4\mathrm{OH}^- \rightarrow \\ \mathrm{Cr}O_4^{2-} + \mathrm{C}O_3^{2-} + 2\mathrm{H_2O} + 5\mathrm{N}O_2^- \end{array} \qquad \textbf{(Eq 5)}$$

Analogous reactions take place with tungsten carbide. Stripping rates are quite rapid, with typical stripping times of 15 to 30 min being common to remove a "full-thick" plasma coating. The actual coating thickness depends on the coating process but generally ranges from a few to several mils (0.001 to 0.015 in.). Removal of worn coatings during rework or overhaul requires correspondingly less time.

Salt Bath Equipment

Design Considerations. Basic design considerations for salt bath cleaning systems (see the article "Salt Bath Equipment" in *Heat Treating,* Volume 4 of the *ASM Handbook*) are similar to those of heat treatment salt bath furnaces. However, the actual process equipment is unique. Two main distinctions between heat treatment/heat transfer salts and cleaning salts are that the cleaning salts are chemically active and the byproduct generation in cleaning baths is potentially much greater. Both of these factors must be taken into account when designing and engineering appropriate salt bath equipment.

Basic design considerations such as throughput, heat capacity, and part geometries are similar to those for heat treating baths. Because the baths are chemically active, the materials of construction must be carefully selected. Materials commonly used for fabricating heat treatment transfer/heat salt bath equipment are generally not suitable as cleaning salt baths because of chemical interactions with the cleaning salts.

Heating systems for molten salt baths may be either electric or gas fired. Due to the generation and settling of reaction byproducts and their insulating effects, most heating designs use internal or immersion heating devices, as opposed to external heaters. (Certain higher-temperature cleaning processes, however, may require external heating systems to achieve good heating system longevity. Care must be taken when using outside heating, to prevent localized "hot spots" where reaction byproducts may accumulate and retard heat transfer in the salt bath furnace.)

Electric immersion heaters may be either resistance elements, enclosed in a tube or bayonet, or electrode configurations that rely on the conductivity and resistance of the molten salt itself to convert electrical energy to heat. Due to their higher energy efficiencies and simplified electrical circuits, resistance immersion elements are more commonly employed with cleaning salt bath equipment than are electrode-type heating systems. Resistance heaters also offer easier and safer start-up than electrode systems. Electrode systems require a molten pool of salt for electrical conduction. In a cold, solidified bath, this is formed by a "starting torch" or auxiliary resistance heater. Once an ample amount of salt has been melted, the auxiliary heater may be turned off and the main electrode system energized. Electrode systems also pose a potential safety hazard if a bath should partially "freeze over," forming an impermeable solid salt crust. The volume of a molten salt increases with increasing temperature, so if the electrode heating system is activated while the bath is crusted, the fluid or molten salt beneath the crust will attempt to expand against the crust. As the salt expands, its pressure increases until the crust ruptures. This sudden release of pressure may result in an eruption of the salt through the crust and possible injury of personnel and equipment.

Gas-fired immersion heating systems are very reliable and economical to use. Consisting of either an open-head or closed-head burner system, the ignited fuel mixture is drawn or forced through a burner tube immersed in the salt (Fig. 2).

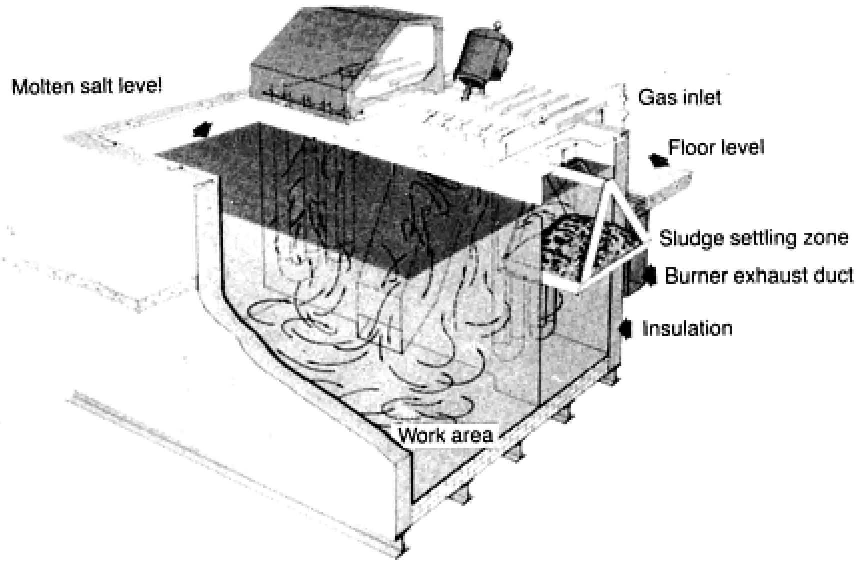

Fig. 2 Cutaway view of a salt bath furnace incorporating an agitated molten salt bath and a sludge settling zone

Byproduct Collection and Removal. Provisions must also be made for the effective collection of reaction byproducts formed during cleaning operations. In addition, subsequent removal of these byproducts from the bath must be accomplished in a convenient, safe, and efficient manner. Most cleaning baths do not require routine chemical monitoring, but rather rely on the removal of reaction byproducts and additions of fresh process chemicals to maintain proper chemical balance and performance. If the byproduct collection system is ineffective, or the removal of the collected byproducts is inconvenient or unsafe, this necessary routine maintenance function will not be performed. This will result in overall process degradation and will eventually necessitate the complete disposal of the spent molten salt and recharge with fresh product.

Molten salt bath processes require properly designed and engineered equipment for their safe operation. In most installations, it is highly desirable to have the salt bath furnace and its associated process tanks (quench water, rinse water, sludge, or byproduct discharge zone) situated under a common hood system (Fig. 3, 4). The ventilated hood, outfitted with observation windows, internal lighting, exhaust system, and so on, protects the operator from accidental contact with the molten salt. It also captures and exhausts the steam generated during the quenching and/or rinsing of hot workloads.

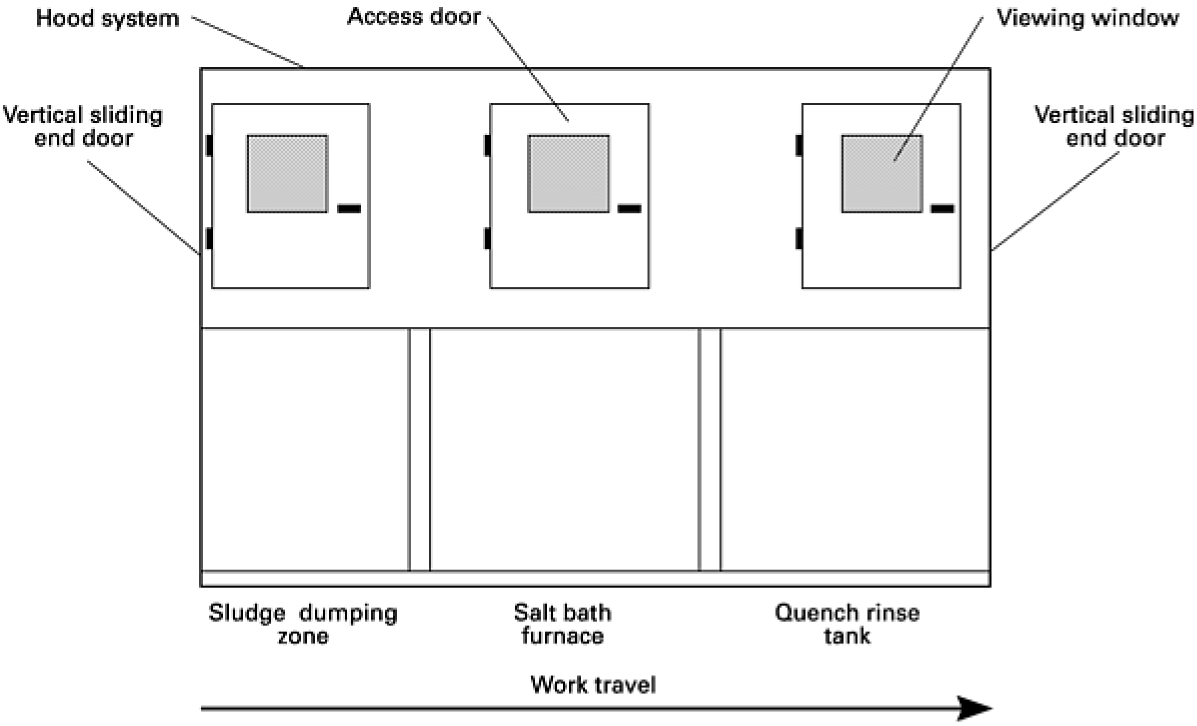

Fig. 3 Schematic of an enclosed molten salt bath cleaning line

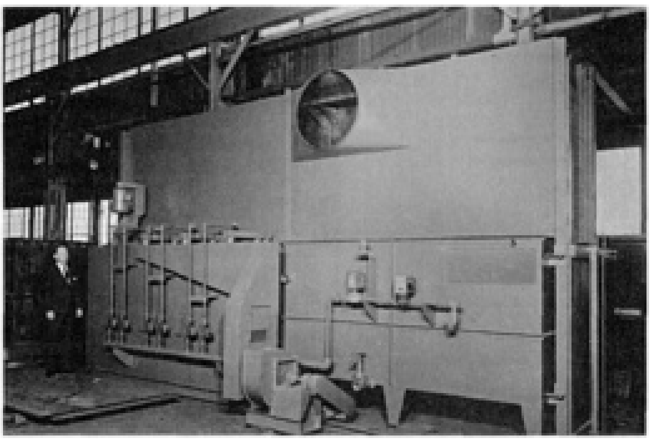

Fig. 4 Fused salt cleaning system that is completely enclosed by a hood to comply with Occupational Safety and Health Administration guidelines

Personnel Safety

One of the most important safety considerations with cleaning-type molten salts is properly designed equipment. As discussed in the section "Salt Bath Equipment" of this article, a common hood structure over the salt bath, quench and rinse tanks, and sludge removal zone forms an effective barrier between the operator and the process (Fig. 3, 4). Operators must have a thorough understanding of the process, receive adequate training, and comply with standard operating procedures and process user's guides.

The molten salt is both a thermal and a chemical hazard to the worker. As with any high-temperature molten process, the salt will burn human tissue. Because many of the compounds used in formulating these salts rely on caustic alkalis, contact with molten or dry salt also poses a risk of chemical burns. All operating personnel, along with plant safety and hygiene monitors, should be familiar with the proper handling procedures for these compounds and the appropriate response procedures. This information is generally contained in the supplier's Material Safety Data Sheet for the specific process chemical being used.

Environmental Impact

Most cleaning salts are formulated from alkali metal salts, as previously described. Some of these ingredients may be highly alkaline and corrosive. Process chemicals formulated for salt bath cleaning applications do not contain restricted or heavy metals in their "fresh" condition.

The byproducts or sludge that must be removed from an operating bath will contain the materials that were processed in it. For example, byproducts formed from paint stripping applications will contain heavy metals if the paints stripped in them contained heavy metals. Likewise, byproducts formed during the stripping of chromium carbide will contain significant amounts of hexavalent chromium (Cr^{6+}) due to the reaction between an oxidizing molten salt and the chromium content in the original coating being removed.

Once byproducts are removed from a bath, they solidify upon cooling into a dense solid. Most sludges are freely soluble in water, allowing subsequent treatment operations to be readily performed. In the absence of heavy or restricted metals, the pH level is often the only adjustment that is necessary. This is usually accomplished by the controlled addition of a mineral acid such as sulfuric acid. In facilities where other metal finishing operations are performed, the alkaline values of the sludge solution are often used to adjust the pH level of acidic streams from other processes. When heavy metals are present in the sludge, more involved waste treatment procedures are necessary. These commonly include reduction of oxidized metal species (for example, the reduction of hexavalent chromium to trivalent chromium, with subsequent pH adjustment, metals precipitation, and filtration/separation of solids). Numerous proprietary and nonproprietary approaches may be used for in-plant treatment of sludge. Sludges may also be disposed of off-site in an approved disposal facility. Representative samples would require testing for corrosivity, restricted metals, and so on, as dictated by applicable regulations, to determine their ultimate disposal classification.

Ultrasonic Cleaning

Jeff Hancock, Blue Wave Ultrasonics

Introduction

ULTRASONIC CLEANING involves the use of high-frequency sound waves (above the upper range of human hearing, or about 18 kHz) to remove a variety of contaminants from parts immersed in aqueous media. The contaminants can be dirt, oil, grease, buffing/polishing compounds, and mold release agents, just to name a few. Materials that can be cleaned include metals, glass, ceramics, and so on. Ultrasonic agitation can be used with a variety of cleaning agents; detailed information about these agents is available in the other articles on surface cleaning in this Section of the Handbook.

Typical applications found in the metals industry are removing chips and cutting oils from cutting and machining operations, removing buffing and polishing compounds prior to plating operations, and cleaning greases and sludge from rebuilt components for automotive and aircraft applications.

Ultrasonic cleaning is powerful enough to remove tough contaminants, yet gentle enough not to damage the substrate. It provides excellent penetration and cleaning in the smallest crevices and between tightly spaced parts in a cleaning tank.

The use of ultrasonics in cleaning has become increasingly popular due to the restrictions on the use of chlorofluorocarbons such as 1, 1, 1-trichloroethane. Because of these restrictions, many manufacturers and surface treaters are now using immersion cleaning technologies rather than solvent-based vapor degreasing. The use of ultrasonics enables the cleaning of intricately shaped parts with an effectiveness that corresponds to that achieved by vapor degreasing. Additional information about the regulation of surface cleaning chemicals is contained in the article "Environmental Regulation of Surface Engineering" in this Volume. The article "Vapor Degreasing Alternatives" in this Volume includes descriptions of cleaning systems (some using ultrasonics) that have been designed to meet regulatory requirements while at the same time providing effective surface cleaning.

Process Description

In a process termed *cavitation*, micron-size bubbles form and grow due to alternating positive and negative pressure waves in a solution. The bubbles subjected to these alternating pressure waves continue to grow until they reach resonant size. Just prior to the bubble implosion (Fig. 1), there is a tremendous amount of energy stored inside the bubble itself.

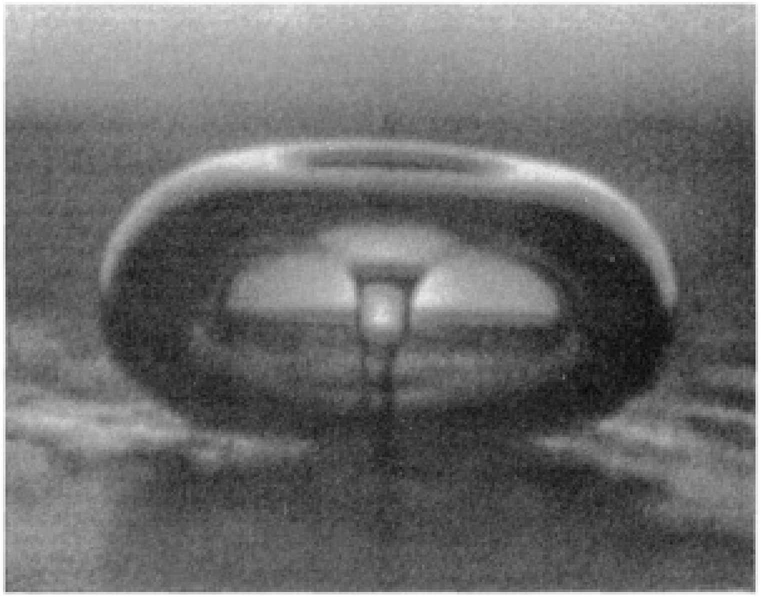

Fig. 1 Imploding cavity in a liquid irradiated with ultrasound captured in a high-speed flash photomicrograph. Courtesy of National Center for Physical Acoustics, University of Mississippi

Temperatures inside a caviting bubble can be extremely high, with pressures up to 500 atm. The implosion event, when it occurs near a hard surface, changes the bubble into a jet about one-tenth the bubble size, which travels at speeds up to 400 km/hr toward the hard surface. With the combination of pressure, temperature, and velocity, the jet frees contaminants from their bonds with the substrate. Because of the inherently small size of the jet and the relatively large energy, ultrasonic cleaning has the ability to reach into small crevices and remove entrapped soils very effectively.

An excellent demonstration of this phenomenon is to take two flat glass microscope slides, put lipstick on a side of one, place the other slide over top, and wrap the slides with a rubber band. When the slides are placed into an ultrasonic bath with nothing more than a mild detergent and hot water, within a few minutes the process of cavitation will work the lipstick out from between the slide assembly. It is the powerful scrubbing action and the extremely small size of the jet action that enable this to happen.

Ultrasound Generation In order to produce the positive and negative pressure waves in the aqueous medium, a mechanical vibrating device is required. Ultrasonic manufacturers make use of a diaphragm attached to high-frequency transducers. The transducers, which vibrate at their resonant frequency due to a high-frequency electronic generator source, induce amplified vibration of the diaphragm. This amplified vibration is the source of positive and negative pressure waves that propagate through the solution in the tank. The operation is similar to the operation of a loudspeaker except that it occurs at higher frequencies. When transmitted through water, these pressure waves create the cavitation process.

The resonant frequency of the transducer determines the size and magnitude of the resonant bubbles. Typically, ultrasonic transducers used in the cleaning industry range in frequency from 20 to 80 kHz. The lower frequencies create larger bubbles with more energy, as can be seen by dipping a piece of heavy-duty aluminum foil in a tank. The lower-frequency cleaners will tend to form larger dents, whereas higher-frequency cleaners form much smaller dents.

Equipment

The basic components of an ultrasonic cleaning system include a bank of ultrasonic transducers mounted to a radiating diaphragm, an electrical generator, and a tank filled with aqueous solution. A key component is the transducer that generates the high-frequency mechanical energy. There are two types of ultrasonic transducers used in the industry, piezoelectric and magnetostrictive. Both have the same functional objective, but the two types have dramatically different performance characteristics.

Piezoelectric transducers are made up of several components. The ceramic (usually lead zirconate) crystal is sandwiched between two strips of tin. When voltage is applied across the strips it creates a displacement in the crystal, known as the *piezoelectric effect.* When these transducers are mounted to a diaphragm (wall or bottom of the tank), the displacement in the crystal causes a movement of the diaphragm, which in turn causes a pressure wave to be transmitted through the aqueous solution in the tank. Because the mass of the crystal is not well matched to the mass of the stainless steel diaphragm, an intermediate aluminum block is used to improve impedance matching for more efficient transmission of vibratory energy to the diaphragm. The assembly is inexpensive to manufacture due to low material and labor costs. This low cost makes piezoelectric technology desirable for ultrasonic cleaning. For industrial cleaning, however, piezoelectric transducers have several shortcomings.

The most common problem is that the performance of a piezoelectric unit deteriorates over time. This can occur for several reasons. The crystal tends to depolarize itself over time and with use, which causes a substantial reduction in the strain characteristics of the crystal. As the crystal itself expands less, it cannot displace the diaphragm as much. Less vibratory energy is produced, and a decrease in cavitation is noticed in the tank. Additionally, piezoelectric transducers are often mounted to the tank with an epoxy adhesive, which is subject to fatigue at the high frequencies and high heat generated by the transducer and solution. The epoxy bond eventually loosens, rendering the transducer useless. The capacitance of the crystal also changes over time and with use, affecting the resonant frequency and causing the generator to be out of tune with the crystal resonant circuit.

Energy transfer of a piezoelectric transducer is another factor. Because the energy is absorbed by the parts that are immersed in an ultrasonic bath, there must be a substantial amount of energy in the tank to support cavitation. If this is not the case, the tank will be "load-sensitive" and cavitation will be limited, degrading cleaning performance. Although the piezoelectric transducers utilize an aluminum insert to improve impedance matching (and therefore energy transfer into the radiating diaphragm), they still have relatively low mass. This low mass limits the amount of energy transfer into the tank (as can be seen from the basic equation for kinetic energy, $\frac{1}{2}\ mv^2$). Due to the low mass of the piezoelectric transducers, manufacturers must use thin diaphragms in their tanks. A thick plate simply will not flex (and therefore cause a pressure wave) given the relatively low energy output of the piezoelectric transducer. However, there are several problems with using a thin diaphragm. A thin diaphragm driven at a certain frequency tends to oscillate at the upper harmonic frequencies as well, which creates smaller implosions. Another problem is that cavitation erosion, a common occurrence in ultrasonic cleaners, can wear through a thin-wall diaphragm. Once the diaphragm is penetrated, the solution will damage the transducers and wiring, leaving the unit useless and requiring major repair expense.

Magnetostrictive transducers are known for their ruggedness and durability in industrial applications. Zero-space magnetostrictive transducers consist of nickel laminations attached tightly together with an electrical coil placed over the nickel stack. When current flows through the coil it creates a magnetic field, and nickel has a unique property of expanding or contracting when it is exposed to the magnetic field. This is analogous to deformation of a piezoelectric crystal when it is subjected to voltage. When an alternating current is sent through the magnetostrictive coil, the stack vibrates at the frequency of the current.

The nickel stack of the magnetostrictive transducer is silver brazed directly to the resonating stainless steel diaphragm. This has several advantages over an epoxy bond. The silver braze creates a solid metallic joint between the transducer and the diaphragm that will never loosen. The silver braze also efficiently couples the transducer and the diaphragm together, eliminating the damping effect that an epoxy bond creates. The use of nickel in the transducers means there will be no degradation of the transducers over time; nickel maintains its magnetostrictive properties on a constant level throughout the lifetime of the unit. Magnetostrictive transducers also provide more mass, which is a major factor in the transmission of energy into the solution in the ultrasonic tank. Zero-space magnetostrictive transducers have more mass than piezoelectric transducers, so they drive more power into the tank, and this makes them less load-sensitive than piezoelectric systems.

A radiating diaphragm that uses zero-space magnetostrictive transducers is usually 5 mm ($\frac{3}{16}$ in.) or greater in thickness, eliminating any chance for cavitation erosion wearthrough. Heavy nickel stacks can drive a plate of this thickness and still get excellent pressure wave transmission into the aqueous solution.

In summary, the advantages of zero-space magnetostrictive transducers are:

- They are silver brazed for permanent bonding with no damping effect
- They provide consistent performance throughout the life of the unit with no degradation of transducers
- Their high mass results in high energy in the tank and less load sensitivity
- Their thick diaphragm prevents erosion wearthrough

The magnetostrictive transducer is not as efficient as a piezoelectric transducer. That is, for a given voltage or current displacement, the piezoelectric transducer will exhibit more deflection than the magnetostrictive transducer. This is a valid observation; however, it has offsetting disadvantages. The efficiency of concern should be that of the entire transducing system, including not only the transducer but also the elements that make up the transducer, as well as the diaphragm and the effectiveness of the bond to the diaphragm. It is the interior mounting and impedance matching of a piezoelectric-driven diaphragm that reduces its overall transducing efficiency relative to that of a magnetostrictive transducer.

The ultrasonic generator converts a standard electrical frequency of 60 Hz into the high frequencies required in ultrasonic transmission, generally in the range of 20 to 80 kHz. Many of the better generators today use advanced technologies such as sweep frequency and autofollow circuitry. Frequency sweep circuitry drives the transducers between a bandwidth slightly greater and slightly less than the center frequency. For example, a transducer designed to run at 30 kHz will be driven by a generator that sweeps between 29 and 31 kHz. This technology eliminates the standing waves and hot spots in the tank that are characteristic of older, fixed-frequency generators. Autofollow circuitry is designed to maintain the center frequency when the ultrasonic tank is subject to varying load conditions. When parts are placed in the tank or when the water level changes, the load on the generator changes. With autofollow circuitry, the generator matches electrically with the mechanical load, providing optimum output at all times to the ultrasonic tank.

Ultrasonic tanks are generally rectangular and can be manufactured in just about any size. Transducers are usually placed in the bottom or on the sides, or sometimes both when watt density (watts per gallon) is a concern. The transducers can be welded directly into the tank, or watertight immersible units can be placed directly into the aqueous solution. In some instances the immersibles may be mounted at the top of the tank, facing down. For applications such as strip cleaning, one immersible is placed on top and one on the bottom, with minimal distance between them. The strip is then run through the very high energy field. A tank should be sturdy in construction, ranging from 11 to 14 gauge in thickness. Larger, heavy-duty industrial tanks should be 11 to 12 gauge and should contain the proper stiffeners for support due to the weight of the solution.

Solution

The solution used in ultrasonic cleaning is a very important consideration. Solvents such as 1,1,1-trichloroethane and freon have been used effectively for many years, with and without ultrasonics. However, with the advent of the Montreal protocol, which calls for elimination of key ozone-depleting substances by 1996, companies are searching for more environmentally friendly methods to clean their parts. Chemical formulators are developing products that meet the demands of cleaning operations, yet are compatible with the health and well-being of society.

Whenever possible, it is best to use a water-based detergent in the ultrasonic cleaning process. Water is an excellent solvent, nontoxic, nonflammable, and environmentally friendly. However, it can be difficult and expensive to dispose of soiled water. Rinsing and drying can also be difficult without detergents. High surface tension exists in solutions without detergents, thus making rinsing difficult in hard-to-reach areas. Detergents can therefore be added to lower the surface tension and provide the necessary wetting action to loosen the bond of a contaminant to a substrate. As an added bonus, the cavitation energy in a water-based solution is more intense than in an organic solvent.

Table 1 is a guide for selection of appropriate cleaning agents for use with ultrasonic cleaning. Additional information about many of these agents is available in the other articles in this Section of the Handbook.

Table 1 Solutions used with ultrasonic cleaning of various parts

Material of construction	**Types of parts**	**Contaminants**	**Suitable Cleaning agent**
Iron, steel, stainless steel	Castings, Stampings, machined parts, drawn wire, diesel fuel injectors	Chips, lubricants, light oxides	High caustic with chelating agents
	Oil-quenched, used automotive parts; fine-mesh and sinterd filters	Carbonized oil and grease, carbon smut, heavy grime deposits	High caustic, silicated
	Bearing rings, pump parts, knife blades, drill taps, valves	Chips; grinding, lapping, and honing compounds; oils; waxes and abrasives	Moderately alkaline
	Roller bearings, electronic components that are affected by water or pose drying problems, knife blades, sintered filters	Buffing and polishing compounds; miscellaneous machining, shop, and other soils	Chlorinated-solvent degreaser (inhibited trichloroethylene, for example)
Aluminum and zinc	Castings, open-mesh air filters, used automotive carburetor parts, valves, switch components, drawn wire	Chips, lubricants, and general grime	Moderately alkaline, specially inhibited to prevent etching of metal, or neutral synthetic (usually in liquid form)
Copper and brass (also silver, gold, tin, lead, and solder)	Printed circuit boards, waveguides, switch components, instrument connector pins, jewelry (before and after plating), ring bearings	Chips, shop dirt, lubricants, light oxides, fingerprints, flux residues, buffing and lapping compounds	Moderately alkaline, silicated, or neutral synthetic (possibly with ammonium hydroxide for copper oxide removal)
Magnesium	Castings, machined parts	Chips, lubricants, shop dirt	High caustic with chelating agents
Various metals	Heat-treated tools, used automotive parts, copper-clad printed circuit boards, used fine-mesh filters	Oxide coatings	Moderately to strongly inhibited proprietary acid mixtures specific for the oxide and base metal of the part to be cleaned (except magnesium)
Glass and ceramics	Television tubes, electronic tubes, laboratory apparatus, coated and uncoated photographic and optical lenses	Chips, fingerprints, lint, shop dirt	Moderately alkaline or neutral synthetic
Plastics	Lenses, tubing, plates, switch components	Chips, fingerprints, lint, lubricants, shop dirt	Moderately alkaline or neutral synthetic
Various metals, plastics (nylon,Teflon, epoxy, etc.), and organic coatings when	Precision gears, bearings, switches, painted housings, printed circuit boards,	Lint, other particulate matter, and light oils	Trichlorotrifluoroethane (fluorocarbon solvent), sonic-vapor degreaser

water solutions cannot be tolerated	miniature servomotors, computer components		

Source: Ref 1

Solution temperature has a profound effect on ultrasonic cleaning effectiveness. In general, higher temperatures will result in higher cavitation intensity and better cleaning. However, if the temperature too closely approaches the boiling point of the solution, the liquid will boil in the negative pressure areas of the sound waves, reducing or eliminating cavitation. Water cavitates most effectively at about 70 °C (160 °F); a caustic/water solution, on the other hand, cleans most effectively at about 82 °C (180 °F) because of the increased effectiveness of the chemicals at the higher temperature. Solvents should be used at temperatures at least 6 °C (10 °F) below their boiling points (Ref 2).

References cited in this section

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2. EJ. Fuchs, Ultrasonic Cleaning, *Metal Finishing Guidebook and Directory,* Elsevier Science, 1992, p 134-139

System Design

Considerations in the design of any cleaning system include the contaminants on the part(s), the required cleanliness level, the geometry and material of the part(s), the quantity to be processed, and the previous system design and layout (if applicable). The part geometry, production rate, and cleaning time required will determine the size of the cleaning system, once the overall process has been decided. Typical tanks range from 20 to 4000 L (5 to 1000 gal), and some are even larger.

Industrial, heavy-duty applications require industrial, heavy-duty ultrasonic equipment. Other factors that need to be considered are cleaning solutions and temperatures, rinsing (with or without ultrasonics), drying, automation, and load requirements. Most manufacturers of ultrasonic cleaning systems will assist in these decisions and will offer laboratory services and technical expertise. A typical system is shown in Fig. 2.

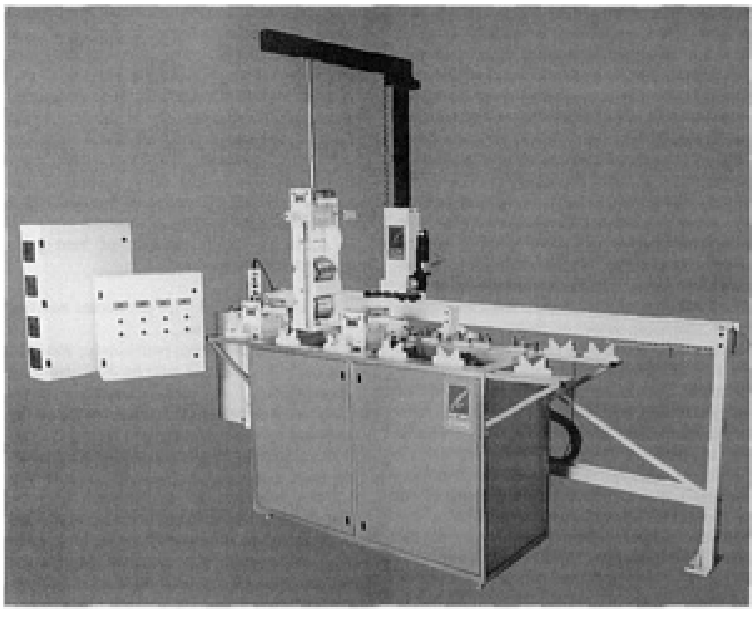

Fig. 2 Automated ultrasonic cleaning system. This system is designed to clean intricate metal hearing-aid components using a neutral-pH solution at 60 °C (140 °F) and three rinse stages at 70 °C (160 °F). Basket rotation (1 to 3 rpm) is used during each stage to ensure adequate cleaning and rinsing. The system computer

controls all functions, including the hoist, and allows for storage of different process parameters for different types of parts. Courtesy of Blue Wave Ultrasonics

Cleanliness Considerations. In a typical aqueous ultrasonic cleaning system, it is the cleaning stage(s) that will remove or loosen the contaminants. The following rinse stage(s) remove any remaining loosened soils and residual detergent, and a dryer removes any remaining rinse water. The overall process of the system is usually determined experimentally. Most reputable industrial cleaning equipment manufacturers have an applications lab where, through a process of experience, trial, and error, a properly designed cleaning process can be determined to meet the cleanliness levels specified.

There are a variety of ways to check for cleanliness. Some are as simple as a water break test on the part to see if most oil has been removed. Others are as elaborate as surface quality monitoring that uses optically stimulated electron emission technology to measure thin films of contaminants down to the Angstrom level.

Changing Existing Systems. If a current system exists, such as a vapor degreaser or soak tank, several things need to be considered. It may be practical, and possibly most economical, to retrofit the existing unit from one that uses solvent an organic solvent to one that uses an aqueous cleaner. Ultrasonic transducers can be added to an existing tank by cutting a hole in the tank and welding the transducer(s) in, or by simply dropping a watertight immersible unit into the tank. The latter method will take up some room in the tank, but it requires less labor. Additional work may have to be done to the tank, such as removing the cooling coils from the vapor degreaser, adding additional fittings for a filtration system, and so on.

In some existing systems, there is a large inventory of stainless steel baskets for handling the parts throughout the cleaning system. If possible, it is best to use these baskets due to the relatively high cost of replacement. In ultrasonic cleaning, the mesh size or hole configuration of the basket is very important. Some mesh sizes will inhibit the cavitation process inside the basket, thereby affecting the overall cleaning capability. Mesh sizes greater than 200 mesh or less than 10 mesh work best. An interesting note is that ultrasonic activity will pass through a variety of media. For example, solution A placed in a Pyrex beaker will cavitate if placed in solution B, which is cavitating in an ultrasonic tank.

Additional information on adapting vapor degreasing systems for ultrasonic immersion cleaning is provided in the article "Vapor Degreasing Alternatives" in this Volume.

Part Handling. The geometry of the parts must be carefully analyzed to determine how they will be placed in the cleaning tank. Large parts, such as engine blocks, can be suspended directly from a hoist, whereas smaller parts will usually be placed in a basket. The most important factor in parts placement is to be sure that air is not trapped anywhere inside the part. If an air pocket is allowed to form, such as in a blind hole that would be facing downward toward the bottom of the tank, the cleaning solution and effects of cavitation will not be able to reach this particular area. The part will have to be rotated somehow in the tank during the cleaning process to allow the cleaning solution to reach the area where air was previously trapped. This can be accomplished either manually, by the attending operator, or by a rotating arm on an automated lift mechanism.

It is best if small parts can be physically separated when placed in a basket. An example would be to place machined valve bodies in a basket with some type of divider or locator for each one. Many times, however, in high output lines it is not possible to separate parts physically, such as in the manufacture of electrical connector pins where thousands of parts may need to be cleaned at one time because of the high production output and the small size. Ultrasonic agitation will be able to reach between these parts and allow the solution's scrubbing power to remove the contaminants, even if the parts are stacked on top of one another. On the other hand, rinse water may not remove all of the residual detergent, and a dryer has a very hard time removing moisture from embedded parts. The problem is easily solved by having an automated hoist with a constant rotating fixture on the arm that allows the basket to tumble at 1 to 2 rpm. This rotation allows the parts to tumble slowly and exposes the embedded pieces for proper rinsing and drying.

Acid Cleaning

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Introduction

ACID CLEANING is a process in which a solution of a mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, oil, grease, and other contaminants from metal surfaces, with or without the application of heat. The distinction between acid cleaning and acid pickling is a matter of degree, and some overlapping in the use of these terms occurs. Acid pickling is a more severe treatment for the removal of scale from semifinished mill products, forgings, or castings, whereas acid cleaning generally refers to the use of acid solutions for final or near-final preparation of metal surfaces before plating, painting, or storage. Acid pickling is discussed in the article "Pickling and Descaling" in this Volume.

The focus of this article is on acid cleaning of iron and steel. Some limited information on acid cleaning of nonferrous metals is included at the end of this article; additional information is available in the Section "Surface Engineering of Non-ferrous Metals" in this Volume.

Mineral Acid Cleaning of Iron and Steel

Cleaner Composition

A variety of mineral acids and solutions of acid salts can be used, either with or without surfactants (wetting agents), inhibitors, and solvents. The large number of compositions that are used may be classified as:

- Inorganic (mineral) acid solutions
- Acid-solvent mixtures
- Solutions of acid salts

Many acid cleaners are available as proprietary compounds, either as a liquid concentrate or a powder to be mixed with water. Compositions of several solutions used for cleaning ferrous metals are given in Table 1. Table 2 contains some possible operating conditions when cleaning ferrous metals.

Table 1 Typical composition of acid cleaners for cleaning ferrous metals

Composition of each constituent is given in percent by weight.

Constituent	**Immersion**		**Spray**		**Barrel**	**Wipe**	**Electrolytic**
Phosphoric acid	70	. . .	70	. . .	. . .	15-25	. . .
Sodium acid pyrophosphate	. . .	16.5	. . .	16.5	16.5	. . .	. . .
Sodium bisulfate	. . .	80	. . .	80	80	. . .	. . .
Sulfuric acid	. . .	. . .	. . .	. . .	. . .	. . .	55-70
Nonionic wetting agent(a)	5	. . .	5	. . .	. . .	7-20	. . .
Anionic wetting agent	. . .	3	. . .	3	3	. . .	. . .
Other additives	(b)	(b)	(b)(c)	(b)(c)	(b)(c)	(b)(d)	(b)
Water	25(e)	. . .	25(e)	. . .	. . .	bal	bal

(a) Ethylene glycol monobutyl ether is used.

(b) Inhibitors up to 1 % concentration may be used to miminize attack on metal.

(c) An anti-foaming agent is usually required when the cleaner is used in a spray or barrel system.

(d) Small additions of sodium nitrate are often used as an accelerator in cleaning rolled steel; nickel nitrate is used in cleaning galvanized steel.

(e) Before dilution

Table 2 Operating conditions for acid cleaners for ferrous metals

Type of acid cleaner	Concentration		Temperature	
	g/L	oz/gal	°C	°F
Immersion	120 60-120	16 8-16	71 60	160 140
Spray	60 15-30	8 2-4	60 60	140 140
Barrel	15-60	2-8	Room	Room
Wipe	. . .	. . .	Room	Room

(a) Current density, 10 A/dM^2 (100 A/ft^2)

Sulfuric and especially hydrochloric acids are the most commonly used for cleaning operations. They are relatively economical to use and in some cases can be reclaimed by ion exchange or chilling methods whereby the dissolved iron is removed. Reclamation can have a significant positive impact on disposal and operating costs where large quantities of acid are consumed.

Typical operating concentrations are 20 to 60 vol% for hydrochloric acid and 4 to 12 vol% for sulfuric acid. Normally both are highly inhibited to minimize the attack of the base metal and process equipment.

Organic acids such as citric, tartaric, acetic, oxalic, and gluconic, and acid salts such as sodium phosphates, ammonium persulfate, sodium acid sulfate, and bifluoride salts, are used in various combinations. Solvents such as ethylene glycol monobutyl ether and other glycol ethers, wetting agents and detergents such as alkyl aryl, polyether alcohols, antifoam agents, and inhibitors may be included to enhance the removal of soil, oil, and grease.

Strength of the acid solutions varies from as weak as 5.5 pH for acid-salt mixtures to the equivalent of the strong acids used for pickling.

The phosphoric acid and ethylene glycol monobutyl ether mixtures (Table 1) are used for removing grease, oil, drawing compounds, and light rust from iron and steel. In various concentrations, these mixtures are adaptable to immersion, spray, or wiping methods and leave a light phosphate coating (110 to 320 mg/m^2, or 10 to 30 mg/ft^2) that provides a paint base or temporary resistance to rusting if the parts are to be sorted.

Chromic acid solutions are used occasionally to clean cast iron and stainless steel. A chromic acid formula used for cleaning stainless steel is 60 g/L (8 oz/gal) chromium trioxide, 60 g/L (8 oz/gal) sulfuric acid, and 60 g/L (8 oz/gal) hydro-fluoric acid in water, used at room temperature in an immersion system. Another solution used frequently for cleaning stainless steel is a solution of nitric acid (10 to 50 vol%) and hydrofluoric acid (1 to 3 vol%) in water. The steel is immersed in the solution at room temperature for 3 to 30 min.

Chromic acid solutions and mixtures containing chromic acid are often used as final rinses in acid cleaning-phosphating systems. The acid enhances the corrosion resistance of the coated surface. Paint applied following such a treatment gives greater protection against corrosion by salt and humid environments. Chromic acid is used in solutions of low pH when a strong oxidant is required. Nitric acid is also a strong oxidant, and a 10 to 20% nitric acid solution is used to brighten stainless steel.

For electrolytic cleaning applications, very high concentrations of sulfuric acid (Table 1) are recommended although hydrochloric acid may also be used. Phosphoric acid, however, is unsuitable due to its high gassing characteristic.

Various soils, including light rust, are removed by combining acid cleaning with mechanical action. Acid salts such as sodium acid pyrophosphate, sodium bisulfate, and mixtures of the two are sometimes used to clean ferrous metal parts in rotating barrels. (A formula is given in Table 1.) A solution with this formula may also be used for parts that are immersed or sprayed.

Additives such as oxalic acid occasionally are used with the acid salts when ferrous metal parts are being cleaned in rotating barrels. Oxalic acid attacks steel, but seldom to an objectionable degree. Thiourea is a good inhibitor, if inhibited oxalic acid solutions are required. The addition of fluoride salts to acid salts, such as 8 to 15 g/L (1 to 2 oz/gal) sodium fluoride or ammonium bifluoride, improves efficiency in the removal of silica sand from castings when parts are cleaned in a barrel or tank.

A formula used for wipe cleaning is also given in Table 1. Other cleaners used for wiping are 6 to 8 vol% sulfuric acid in water; 70% phosphoric acid, 5% wetting agent, and 25% water; and a paste made of 85 to 95% ammonium dihydrogen phosphate and the remainder wetting agent, used on a wet cloth or sponge.

Inhibitors are often included in cleaners used on ferrous metals to minimize attack on metal and lower acid consumption. Composition of inhibitors varies widely. Numerous byproducts, such as sludge acid from oil refineries, waste animal materials, waste sulfite cellulose liquor, offgrade wheat flour, and sulfonation products of such materials as wood tar, coal tar, and asphaltum, have been successfully used. These materials cost less than synthetic inhibitors but can vary widely in uniformity and effectiveness and may contain toxic or carcinogenic substances. For these reasons, synthetic inhibitors now dominate the market.

Synthetic inhibitors are usually complex organic compounds. One of the most common inhibitors for hydrochloric-acid-based cleaners was propargyl alcohol, which is poisonous and has been removed from most acid cleaners. Most often, a given compound or class of compounds will function most effectively with only one type of acid, so choosing the proper inhibitor should not be a haphazard process. Many proprietary compositions of these chemicals are available for use in various acid systems.

The amount of inhibitor used depends on the workpiece composition, acid cleaner formulation, temperature of operation, and nature of soil being removed. From $\frac{1}{2}$ to 1% inhibitor before dilution with water is used. Higher percentages of inhibitor may be used for higher acid concentrations and operating temperatures. Once the optimum concentration is established for a particular operation, higher concentrations have no positive effect and result in increased cost.

Antifoaming agents may be required in acid spray cleaners to prevent excessive foaming. Sometimes foaming can be reduced by using naturally hard water or by adding small amounts of calcium chloride, up to 30 grains hardness. Addition of a plasticizer such as triethylhexylphosphate or one of the high-molecular-weight polyols (organic alcohols) reduces foaming. Because of variation in water and other conditions in a specific installation, several additives may need to be tried before foaming is brought under control. Silicones are usually effective as antifoaming agents, but they should not be used if parts are to be painted or plated, because of residual contamination. Paint or plating does not adhere to the silicone contaminated areas, resulting in a fisheye appearance at the contaminated spots.

Foaming agents may be desirable in certain immersion applications, to reduce acid fume evolution to the atmosphere and to provide an insulating blanket on the surface of the tank to decrease heat loss from evaporation. Proprietary inhibitors having controlled foaming properties are available.

Methods of Application

Wipe on/wipe off, spray, immersion, flooding, and rotating barrel methods are all used extensively for acid cleaning. Although heating greatly increases efficiency, cleaning is frequently done at room temperature for superior process control and economy of operation. When heat is used, the temperature range of the cleaner is usually 60 to 82 °C (140 to 180 °F) with temperatures up to 93 °C (200 °F) used occasionally. Time cycles for acid cleaning are short compared to acid pickling, especially when stronger acids are being used. Selection of method depends on the nature of soil being removed, the size and shape of the workpiece, quantity of similar pieces to be cleaned, and type of acid cleaner used.

Wipe on/wipe off is the simplest method of acid cleaning; virtually no equipment is required. Using a formula such as that shown in Table 1, an operator suitably protected by rubber gloves, eye protection, and apron wipes the soiled workpieces with an acid-impregnated cloth or sponge. After the cleaner is allowed to react (2 or 3 min is usually sufficient), work is rinsed with water.

The wiping method is practical only for cleaning a few parts at a time or for large, bulky parts that cannot be immersed conveniently in a cleaning bath. Labor cost becomes excessive if many parts are cleaned. Cleaner concentrations are stronger than in dip and spray solutions, and the cleaner is not usually recovered for further use.

Spray cleaning is more practical than wiping when larger quantities of bulky parts are acid cleaned. Multistage spray washers have been designed to accommodate a variety of work that can be racked or suspended from hooks. Large components, such as truck cabs and furniture, are usually cleaned by this method. Cost of labor is lower than for hand wiping. Also, consumption of cleaner ingredients is considerably less because concentrations are lower, and cleaner is recirculated for reuse. The capital investment for spray cleaning equipment is high, and large production quantities are usually needed to justify the expense. Steady or high production quantities are not always necessary to warrant the installation of spray equipment. It is sometimes feasible to accumulate parts for about 2 days and then operate the washer for part of a day.

In one automotive plant, a spray system replaced a hand wiping system with the following results. A wipe on/wipe off system using phosphoric acid-ethylene glycol monobutyl ether was used to prepare large steel stampings for painting. A total of 46 supervisory and production employees were required. Installation of an automatic spray system decreased cleaner consumption and provided the same productivity with only six employees. In addition, a heavier phosphate coat was obtained, 5400 to 6500 mg/m^2 (500 to 600 mg/ft^2) by spraying, compared to 1100 to 2200 mg/m^2 (100 to 200 mg/ft^2) by wiping in subsequent zinc phosphating stages.

Immersion is the most versatile of the acid cleaning methods, particularly for cleaning irregular shapes, box sections, tube, and cylindrical configurations that cannot be penetrated using spray systems. The operation may vary from hand dipping a single part or agitating a basket containing several parts in an earthenware crock at room temperature to a highly automated installation operating at elevated temperature and using controlled agitation. The types of cleaner used in immersion systems are often chemically similar to spray cleaners but due to lack of impingement are generally run at higher concentrations (Table 1). Efficient cleaning by immersion depends on placing workpieces in baskets or on racks to avoid entrapment of air or nesting of parts.

Barrel cleaning is often used for large quantities of small parts. Perforated barrels containing 225 to 900 kg (500 to 2000 lb) of parts are immersed and rotated in tanks of cleaning solution. Solutions of acid salts (Table 1) are used for this method, although other cleaning solutions may be applicable. In some instances, a medium such as stones is added to the charge, frequently comprising up to two-thirds of the total load. The medium aids in cleaning by providing an abrading action. It also prevents workpieces from damaging each other. Acid cleaning in barrels is usually performed at room temperature. Heated solutions can be used if required by the nature of the soil being removed.

Barrel methods can be used for cleaning in continuous high production. Several barrels can be arranged so that some can be loaded while others are in the cleaning tank. The chief limitation of the barrel method is the size and shape of workpieces. Parts such as bolts are ideal for barrel cleaning, while delicate stampings are not.

Electrolytic cleaning is effective because of the mechanical scrubbing that results from evolution of gas and the chemical reduction of surface oxide films when used anodically. Sulfuric acid baths are most commonly electrolyzed (Table 1) and are usually used as a final cleaner before plating. All grease and oil should be removed before electrolytic cleaning, to reduce contaminating of the electrolytic bath. If alkaline cleaners are used as precleaners, the rinse must be thorough or the acid bath can be neutralized by the alkali. Time cycles in electrolyzed acid solutions must be short, usually less than 2 min, or excessive etching can occur. Current distribution must be uniform, or localized etching may damage the workpiece.

Selection Factors

In any acid cleaning operation, etching usually occurs. In many instances, this light etching is advantageous for final finishing operations. However, if etching is not permissible, some other cleaning process should be used.

Limitations of acid cleaning include:

- Inability to remove heavy deposits of oil or grease without large additions of expensive material such as surfactants and detergents
- Attack on the metal to some degree, even when inhibitors are used
- Requirement of acid-resistant equipment

If parts are soiled with heavy deposits of oil or grease, as well as rust, preliminary alkaline cleaning preceding acid cleaning is most often a necessity. Multiple rinses should be used to prevent carryover of alkali.

Selection of Process

Reasons for selecting acid cleaning and specific acids are illustrated in the following examples. Parts deep drawn from low-carbon sheet steel as received from the supplier were covered with pigmented drawing compound and other shop soil and frequently became rusty during transit. Alkaline cleaning, even with hand scrubbing, did not consistently remove the drawing compound and allowed most of the rust to remain. Acid cleaning in a multistage spray washer completely removed all soil and rust without hand scrubbing. A phosphoric acid and ethylene glycol monobutyl ether mixture (Table 1) was spray applied using a concentration of about 60 g/L (8 oz/gal) at 66 °C (150 °F). In addition to thorough cleaning, the process deposited the light phosphate coating that was desired as a base for subsequent painting.

Finish-machined surfaces on large castings showed a light blushing rust after a weekend in high humidity. Abrasive cleaning could not be used because of possible damage to finished surfaces. The rust was removed without etching by hand wiping with a pastelike compound of about 90% ammonium dihydrogen phosphate and 10% wetting agent, followed by wipe rinsing.

Combinations of alkaline and acid cleaning methods are often used advantageously. Machined parts having heavy deposits of oil, grease, and light blushing rust were being acid cleaned using phosphoric acid and ethylene glycol monobutyl ether in an immersion system at 60 °C (140 °F). Results were satisfactory, but the cleaner became contaminated from the oil and grease so rapidly that the replacement cost of cleaner became excessive. Adding a preliminary alkaline cleaning operation removed most of the soil. Parts were then rinsed, first in unheated water, then in an unheated neutralizing rinse containing 2% chromic acid. Immersion in the phosphoric acid and ethylene glycol monobutyl ether mixture removed the rust and provided a surface ready for painting. This practice prolonged the life of the acid cleaner by a factor of five or more.

In other instances, combining alkaline and acid cleaning does not prove economically feasible. In one plant, small steel Stampings were being prepared for painting by removing light oil and some rust in a five-stage spray washer. The first stage was alkaline, followed by water rinsing, then two stages of phosphoric acid cleaning, followed by water rinsing and a rinse in chromic acid solution. Alkaline contamination of the first acid stage was excessive, necessitating weekly dumping of the acid cleaner. A change to three successive stages of acid cleaning followed by one plain water rinse and one rinse with chromic acid in water proved more economical and satisfactory. The practice was then to dump the cleaner periodically from the first stage and decant the second stage cleaner to the first stage, recharging the second stage while maintaining the third stage.

For small parts that are not easily bent or otherwise damaged, barrel methods often are the most satisfactory. Small miscellaneous parts having no deep recesses required removal of light oil and minor rust. They were placed in a horizontal barrel and rotated in a solution of acid salt cleaner (similar to the composition shown in Table 1) at room temperature using a concentration of 45 to 60 g/L (6 to 8 oz/gal). After tumbling for 10 to 20 min, the barrel was removed from the cleaner tank, drained, rinsed, drained, and tumbled for 30 to 60 min at room temperature in a tank containing 45 to 60 g/L (6 to 8 oz/gal) of alkaline cleaner. The charge was then rinsed in water, unloaded, and dried. Tumbling in the alkaline solution neutralized residual acid and produced a shine on the workpieces.

If optimum equipment is not readily available, requirements may sometimes be met with available equipment. Box-shape cast iron parts, 200 by 150 by 100 mm (8 by 6 by 4 in.) deep, open on one end and having several drilled holes, were covered with light mineral oil. Parts needed to be cleaned and provided with a phosphate coating suitable for painting. Available equipment was a two-stage alkaline spray washer. Parts were washed in this equipment and then dipped in a phosphating tank. Because the workpieces were heavy and bulky, this procedure was inadequate to meet the production demand of 2500 to 3000 parts in 8 h. The problem was solved by changing the alkaline solution in the spray washer to an acid phosphate cleaner that contained low-foaming surfactants (wetting agents). Parts were sprayed for 1 min with a solution containing 110 g (4 oz) of acid phosphate cleaner per 4 L (1 gal) of solution, operated at 71 °C (160 °F). They were then sprayed with unheated water for 30 s, dipped in water-based inhibitor, air dried, and painted.

For parts that are to be electroplated, electrolytic acid cleaning is often used. After precleaning small parts to remove most of the oil, the following cycle was established for small carbon steel parts before electroplating:

1. Water rinse at 82 °C (180 °F)
2. Immerse for $\frac{3}{4}$ to 2 min in 55 to 70% sulfuric acid at 21 °C (70 °F), using a current density of 10 A/dm^2 (100 A/ft^2)
3. Flowing water rinse for 15 to 30 s at room temperature
4. Repeat step 3 in a second tank
5. Dip in 20% hydrochloric acid for 15 s at room temperature
6. Flowing water rinse for 15 to 30 s at room temperature

Electrolytic cleaning was successfully used in this application. Auto bumpers were cold formed from phosphated and lubricated sheet steel. Alkaline cleaning was used to remove mill dirt and soap-type lubricant. Electrolytic acid cleaning followed the alkaline treatment to ensure removal of the phosphate coating and residual lubricant. Because of scrubbing action by the gas evolved at the work surface, the electrolytic bath assisted in removing adherent solid particles that were the residue of a polishing compound. Slight metal removal occurred that removed metal slivers and produced a microetch suitable for plating. The ability of this bath to remove tenacious oxide coatings permitted the electroplating of nickel with good adhesion. While this cleaning could have been done by other means, the electrolytic acid system proved to be the most satisfactory method for this application.

Equipment

Wipe on/wipe off cleaning requires only the simplest equipment. Acid-resistant pails and protective clothing, and common mops, brushes, and wiping cloths are all that is needed.

Immersion systems require equipment varying from earthen crocks for hand dipping at room temperature to fully automated systems using heat and ultrasonic or electrolytic assistance. The construction for an acid tank is shown in Fig. 1. Tanks for sulfuric acid may be lined with natural rubber and acid-resistant red shale or carbon brick joined with silica-filled hot poured sulfur cement. Liners or freestanding fabricated tanks of polypropylene are also used. Tanks intended to contain nitric or hydrofluoric acids may be lined with polyvinyl chloride and carbon brick joined with carbon-filled hot poured sulfur cement. Carbon brick liners are not needed for nitric acid, but they are usually used to contain hydrofluoric acid.

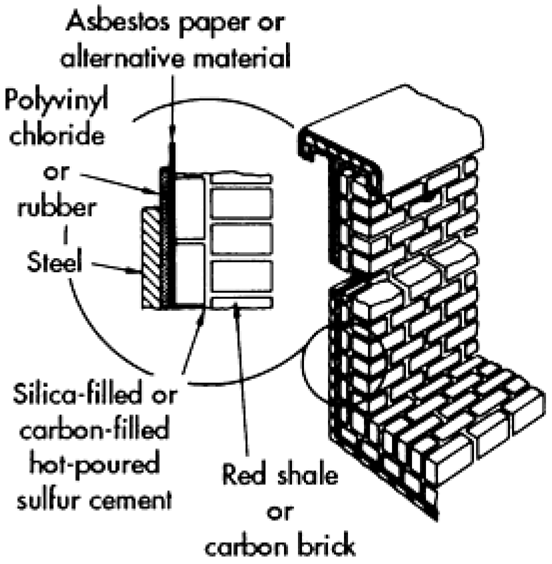

Fig. 1 Section of an acid cleaning tank. Inner lining of brick acts only as a thermal shield and as a protection against mechanical damage to the corrosion-resistant polyvinyl chloride or rubber membrane.

If the cleaning operation uses only acid solutions, an immersion installation would consist of an immersion tank for the acid solution, capable of being heated to 82 °C (180 °F), two rinse tanks for flowing cold water, and drying facilities, either convection or infrared.

Various modifications can be made for specific conditions. If parts are precleaned in alkaline solutions, two water rinse tanks should precede the acid cleaning tank. One of these two rinses may be a still tank containing dilute chromic acid. The final may be a heated still tank containing dilute chromic acid or a hot water tank (up to 82 °C, or 180 °F). One advantage in using heat in the final rinse is that subsequent drying is accelerated.

Various degrees of automation are feasible with immersion systems. Automated cleaning of racked parts can be applied to immersion systems by using an overhead monorail that raises and lowers racks according to a predetermined cycle.

Electrolytic acid cleaning tanks must be constructed to resist acids. Venting is recommended and usually required; otherwise, these tanks are no different from tanks used for electrolytic alkaline cleaning. A typical electrolytic cleaning tank is shown in the article on alkaline cleaning. Various types of auxiliary equipment may be used for removing fumes from an electrolytic tank. Electrodes are preferably made of lead.

Rinse tanks should be as small as is compatible with easy handling of the largest load to be rinsed, yet allow for adequate overflow to minimize contamination. For a given overflow rate, smaller tanks allow better mixing and faster rinsing of impurities. If a series of rinse tanks is used, all should be uniform in size for simple flow rate control.

Polyvinyl chloride is a proven material for rinse tanks. Polypropylene, which can withstand higher temperatures than polyvinyl chloride, has also been used, as well as polyester, rubber, brick, lead, and plain carbon steel coated with protective paint. Stainless steel can be used in rinse tanks where chloride solutions are not used. Chlorides cause pitting of stainless steel, especially if tanks are used intermittently.

Rinse tanks can be equipped with automatic controls that flush tanks when impurities reach an established level, as monitored by continuous measurement of the electrical conductivity.

Spray systems are designed with special features for high-production acid cleaning. The number of stations varies, but a five-stage system is usually used for cleaning and phosphating parts such as large stampings. The first stage is acid cleaning (usually phosphoric and ethylene glycol monobutyl ether) and is followed by a spray rinse followed by a phosphating stage. The process is completed by using either two successive stages of unheated water rinsing or one stage of unheated water and one of unheated or heated mild chromic acid solution. Parts are conveyed from stage to stage singly on a belt or by using an overhead monorail system with parts hanging singly or on racks.

Heating Equipment. Acid cleaners are rarely heated above 82 °C (180 °F). Improved detergent systems in recent years have permitted a much wider range of work to be acid cleaned at room temperature with consequent energy savings, but removal of rust or stubborn soils such as buffing compounds usually benefits from the application of heat. The temperature range most frequently used when acid cleaners are heated is 60 to 71 °C (140 to 160 °F).

Drying is usually accomplished by heated forced air. However, temperatures higher than about 100 °C (212 °F) are generally not used, for economic reasons. Infrared dryers may be used if controlled to proper operating temperature.

Acid Attack and Sludge Formation. In phosphoric acid cleaning and coating systems, acid attack on work is minor, although some metal is dissolved. Iron phosphate sludge is a natural byproduct of cleaning and coating with phosphoric acid-based chemicals. The amount of phosphate compounds in the sludge, as well as the severity of acid attack on the work, depends on the temperature and acid concentration.

Acid attack on the major items of equipment is almost negligible. For example, tanks and pipes used in one high-production installation have not been replaced during the first 16 years of operation and are still in serviceable condition. The tanks and pipes for this installation were made of low-carbon steel; pumps and nozzles were made of stainless steel. Most equipment deterioration is caused by erosion on parts such as pump impellers, riser pipe elbows, tees, and nipples. Some attack occurs initially, but once the steel surface has become coated with phosphate, attack is substantially reduced. Also, deposits of scale serve as inhibitors of acid attack and further protect the metal from the acid. The major cause for replacing parts such as risers and nozzles is clogging by sludge and scale.

In a spray system, sludge is usually removed by filters. In immersion systems, the sludge accumulated at the bottom of the tank is usually shoveled out after most of the still-usable solution has been removed (decanted). A sludge pan is often helpful. Such a pan covers the entire bottom of the tank except for small areas at the edges. This permits easy removal. The pan is usually 75 to 125 mm (3 to 5 in.) deep. Rods with hooks extending above the solution level allow the pan to be lifted to remove sludge. Thus, the solution need not be decanted, downtime is minimized, and labor is saved.

Handling and Conveying. Parts such as nuts and bolts are most commonly cleaned in rotating barrels. However, if barrel equipment is not available, such parts can be cleaned in baskets. Conveyance may be by hand, by lift systems, by belt when a spray is used, or by a combination of these systems. Small parts that cannot be tumbled in barrels may be placed in wire baskets, racked for immersing or spraying, or placed singly on belts in a spray system.

Racks, hooks, and baskets are usually made of a metal that will resist acids. Types 304, 316, 316L, and 347 stainless steel are successful for these components. Where racks or hooks travel through a series of cleaning, phosphating, and painting systems, the racks are continually recoated, making low-carbon steel an acceptable rack material. A rack used for cleaning and phosphating of small Stampings, such as doors for automobile glove compartments, is illustrated in Fig. 2. Large components are usually hung singly on hooks and transported by an overhead monorail. Figure 3 illustrates an arrangement for carrying truck cabs through a five-stage spray cleaning installation.

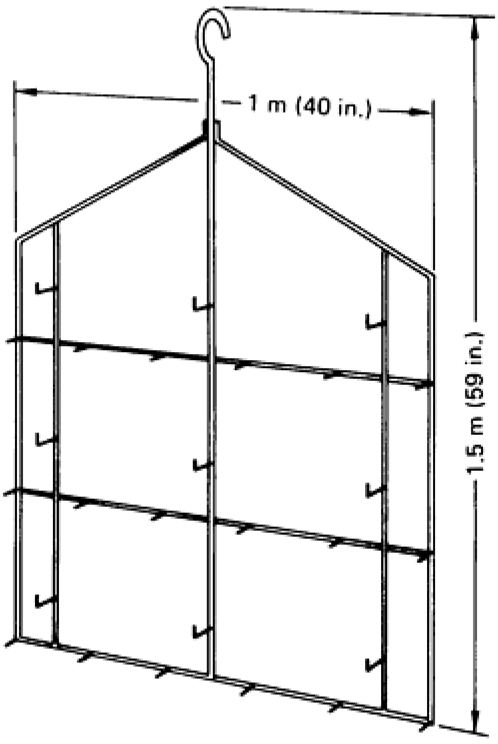

Fig. 2 Rack used for cleaning and phosphate coating small stampings

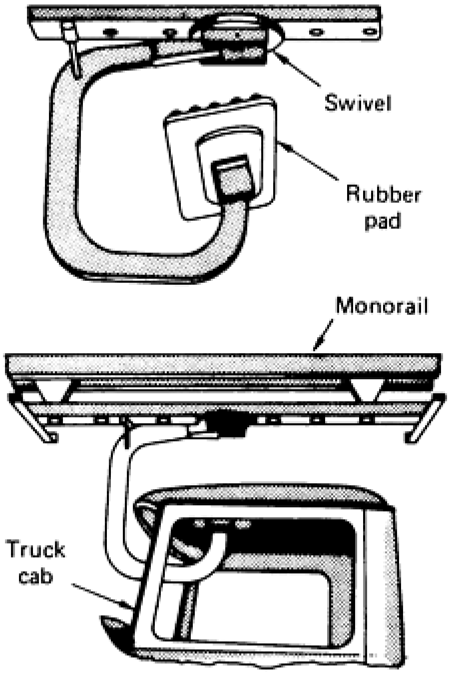

Fig. 3 Arrangement for conveying truck cabs through a five-stage spray cleaning installation

Control of Process Variables

Agitation, operating temperature, acid concentration, solution contamination, and rinsing are the principal variables that affect efficiency and quality in acid cleaning.

Agitation, either of the solution or the work-pieces, is usually necessary in all systems. In wipe on/wipe off methods, agitation is under direct control of an operator. In spray systems, agitation is provided by the impingement of the solution on the workpieces, and the impingement is basically controlled by the pressure. Pressures used in spray systems are commonly 100 to 170 kPa (15 to 25 psi), measured at the pump. Pressures up to 280 kPa (40 psi) are sometimes used for removing tenacious soils. For cleaning complex parts, some experimentation is usually required in adjusting the nozzles to achieve a spray pattern that reaches cavities and crevices.

Immersion systems use a variety of methods for agitation. In smaller production quantities, parts contained in baskets are hand agitated by raising, lowering, and turning. Underwater air jets or mechanical propellers are also effective for agitation in cleaning tanks, and they can decrease the soaking period. In automated immersion systems, the forward motion of parts often provides sufficient agitation. However, this can be enhanced if necessary by simultaneously agitating the solution. In barrel cleaning, agitation of both work and solution is provided by the rotation of the barrel.

Ultrasonic cleaning methods can be applied to acid cleaners in the same manner as is done with other cleaning methods. Because initial cost and maintenance of ultrasonic equipment is high, this form of energy is used only when simpler methods fail to achieve satisfactory cleaning, either because the soil is extremely difficult to remove or because the shape of the workpiece is complex.

Electrolytic cleaning provides agitation from gas evolution, which produces a scrubbing action.

Operating Temperature. Although the efficiency of soil removal increases as temperature increases, a significant amount of acid cleaning is done in unheated solutions, because heated solutions may present the following disadvantages:

- Attack on workpieces increases with temperature Cleaners deteriorate or are used up more rapidly, in part because of dissolved metal
- Surfaces emerging from hot acid solutions are likely to dry and become streaked before they are rinsed
- The life of the tanks and other equipment decreases as operating temperature is increased

As mentioned previously, when acid solutions are heated, temperatures ranging from 60 to 70 °C (140 to 160 °F) are most frequently used. Higher temperatures (up to 80 °C, or 180 °F) are sometimes required to remove soils such as drawing compounds that contain high-melting waxes or greases. In barrel cleaning with solutions of acid salt, temperatures up to 95 °C (200 °F) are sometimes used, but these cleaners are relatively mild so that problems of attack on workpieces and equipment are not great. Maintenance of temperature within ±3 °C (±5 °F) usually provides adequate reproducibility.

Control of cleaner composition is necessary for consistently satisfactory results. Depletion of cleaner by its reaction with workpieces or equipment, dragout, drag-in of alkali or other contaiminants, and decomposition of the cleaner constituents are factors that affect cleaner life.

Chemical analysis using simple titrations for acid and metal content permit control of solution composition. Visual inspection of processed workpieces also indicates condition of the cleaner. In a new installation, when a new solution is being used, or when a different soil is being removed, the solution should be checked every hour until the required frequency of testing is established.

Control of rinsing is necessary for consistently good results. Cold water is adequate for most purposes except when high-melting waxes and greases are being removed. Residues of such soils may set from cold water rinsing. An initial rinse with demineralized water at 70 to 82 °C (160 to 180 °F) is often used when removing these soils. Rinsing qualities of water can be greatly improved by adding a wetting agent at a low concentration. Agitation during rinsing is important and is achieved by the same means used with cleaning solutions.

Rinsing is expensive, but cost can be minimized by using tanks as small as possible, tanks of uniform size if in a series, automatic flush control of contamination limit, and using counterflow rinse tanks.

Sludge buildup is proportional to the amount and type of soils entering the system. Even though sludge buildup does not directly impair the efficiency of an immersion system, a large amount of sludge should not be allowed to accumulate because it may foul heating or control equipment. In spray systems, good filtration and screening are required to prevent fouling of nozzles and related equipment.

Maintenance

For obtaining consistently good results, a regular schedule of maintenance is recommended for any immersion or spray cleaning installation. The required frequency of maintenance varies considerably with the specific operation. Experience with a particular installation soon indicates the items that need close attention to prevent costly shutdowns or inadequate cleaning. The following list suggests a program for maintaining immersion and spray systems:

Daily

- Check temperature
- Check solution concentration
- Check and adjust spray nozzles
- Clean screens in spray systems

Weekly

- Decant or dump solutions and recharge
- Remove sludge from tanks, heating coils, and temperature regulators
- Flush risers in spray systems
- Remove and clean spray nozzles

Monthly

- Inspect exhaust hoods
- Clean tank exteriors
- Check temperature control systems
- Inspect pumps in spray systems
- Inspect spray nozzles, and replace if necessary

Semiannually

- Clean heating coils and exhaust hoods
- Clean and paint exterior components
- Clean riser scale
- Dismantle and repair pumps

Waste Disposal

Disposal of waste acid cleaners is a problem, regardless of whether the location is urban or rural. Several federal, state, and local groups regulate waste disposal. Laws and regulations, such as the Federal Resource Conservation and Recovery Act of 1976, as amended, are subject to change. Therefore, local authorities should be consulted about proposed and current operations.

Safety Precautions

Acids, even in dilute form, can cause serious injuries to the eyes and other portions of the body. Acids are destructive to clothing as well. Therefore operators should be protected with face shields and rubber boots and aprons. Eye fountains and showers adjacent to acid cleaning operations should be provided for use in case of accidents. Nonslip floor coverings in the vicinity of tanks or spray operations are also advised.

Precautions must be taken against cyanides entering the acid cleaning system to avoid formation of deadly hydrogen cyanide (HCN) gas.

Electrolytic cleaning systems are potentially dangerous because of splashing; therefore, rubber shoes and gloves are necessary to protect operators working near these installations. Electric power at 5 to 15 V is not hazardous to operators.

Mist from spray systems or from gassing can be a health hazard. Mist formation increases with the amount of work in process, the temperature, the acidity of the solution, and the current density in electrolytic cleaning. This mist contains all the ingredients of the acid solution. Adequate ventilation is important. Additional information concerning hazards in the use and disposal of acids is given in the article on pickling of iron and steel in this Volume.

Health and safety regulations are made and enforced by several groups within the federal, state, and local governments. Since the regulations vary and are subject to change, the several sets of regulations should be considered when planning an installation or major changes in operations.

Organic Acid Cleaning of Irons and Steels

Organic acids are presently used in a variety of metal cleaning applications. Primary organic acids used in metal cleaning include acetic acid, citric acid, ethylenediamine tetraacetic acid (EDTA), formic acid, gluconic acid, and hydroxyacetic acid. Depending on the application, acids may be used alone, but often are formulated with bases and other additives. Organic acids often replace mineral acids, such as hydrochloric and sulfuric acid, in many metal cleaning applications. Advantages in using organic acids include:

- Efficiency in removing certain metal oxides
- Low corrosivity to base metal
- Safety and ease of handling
- Ease of disposal

Disadvantages of organic acids include longer cleaning times, higher temperature requirements, and higher costs compared to other cleaning operations.

Advantages of Organic Acids

Although organic acids are relatively weak, they remove metal oxides through the following mechanisms. As the organic acid reacts with the metal to produce citrates, acetates and other byproducts, hydrogen gas is released. The hydrogen builds up under the scale and can often lift the remaining oxides off the metal. In addition, organic acids act as sequesterants by tying up the dissolved metal ions and carrying them away from the surface being cleaned. With the use of heated solutions and proper circulation of cleaning solution, organic acids efficiently remove metal oxides.

Low corrosivity to the cleaned metal surface is another important reason for choosing an organic acid over a mineral acid. Mineral acids have high corrosion rates, and repeated cleanings with these solvents can significantly corrode fabricated metal parts. The low corrosion rates of organic acids can be reduced further with the use of corrosion inhibitors. In addition, the sequestering ability of the organic acids allows cleaning at a higher pH, reducing corrosion rates even further. The weak acidic nature of most organic acids and the use of a higher pH than that in mineral acid-based processes provide for safe, easy-to-handle compositions. The cleaning solutions can be used with handheld steam and high-pressure spray equipment. Proper safety equipment should be used when using formic and acetic acids at high concentrations. Most of the organic acids are nonvolatile; therefore, harmful vapors are not released during the cleaning operation.

Spent organic acid cleaning solutions can be disposed of with relative ease. A variety of methods, such as biodegradation, chemical treatment, and incineration, are being used for disposal of organic acid-based cleaning solutions. Spent solutions can be regenerated with techniques such as ion exchange, electrodialysis, and reduction of metal ions with reducing agents.

Applications

Boiler Cleaning

A patented process (Ref 1) removes boiler deposits containing iron oxides, copper oxides, and copper metal with a single filling solution. For iron and copper oxide removal, a 3 to 5% citric acid solution is treated with sufficient ammonia to achieve a pH of 3.5. The boiler to be cleaned is filled with this solution, heated to 93 °C (200 °F), and the solution is circulated until iron oxide removal is complete. The progress of the iron removal operation is monitored analytically until the iron removal rate levels off. Any copper oxides present are rapidly dissolved in the low-pH citric acid solution; however, dissolved copper ions tend to plate out on the cleansed steel.

This plated copper is removed during the second stage of the cleaning process, which also results in a passive metal surface. The second-stage cleaning solution is prepared by ammoniating the same filling solution to pH 9.5 and allowing the temperature to drop to 49 °C (120 °F). An oxidant, such as sodium nitrite at a level of 0.25 to 0.5% of the solution weight, is added to oxidize ferrous ions to ferric ions, which are responsible for dissolving the plated copper according to the following equation:

$$2\mathrm{Fe}^{+3} + \mathrm{Cu}^{0} \rightarrow 2\mathrm{Fe}^{+2} + \mathrm{Cu}^{+2}$$

The dissolved copper is stabilized as the copper-ammonium complex, $Cu(NH_3)_4^{+2}$. The high-pH solution is also responsible for producing a film of hydrated iron oxide, which results in a passivated surface that remains rust-free while the citrate solution is removed and the boiler is rinsed with water. The unit is then ready to be placed back into service. To further protect the boiler components during the cleaning cycle, acid inhibitors designed for use with citric acid are available.

Stainless Steel Cleaning

Some of the uses for organic acids in the cleaning and finishing of stainless steels are presented below.

Acid Cleaning. Organic acid solutions are used to remove rust and mill scale from newly fabricated stainless steel stock. By removing embedded iron and scale from the stainless steel surface, the appearance and corrosion resistance of the alloy are restored. A typical formulation for this application consists of 5% dibasic ammonium citrate containing 0.1% wetting agent at a temperature of 80 °C (180 °F). This solution finds particular use in cleaning equipment for storage and manufacture of foods, beverages, fine chemicals, and pharmaceuticals.

Steam Cleaning. A particularly useful technique for cleaning these types of fabricated stainless steel tanks, as well as stainless steel machinery, trucks, and railroad cars, involves steam cleaning. A concentrated organic acid solution is injected into a high-pressure jet of steam at a rate that yields 1 to 5% concentration by weight in the superheated solutions. A low-foaming nonionic wetting agent added to the acid solution removes oil and grease from the steel surfaces.

Alkaline Cleaning. Caustic gluconate solutions, prepared by dissolving gluconic acid or sodium gluconate in caustic soda, are useful for removing both organic soils and metal oxides with one solution. Also, because the solution is on the alkaline side, the cleaned metal surface has little tendency to rerust (Ref 2).

Nuclear Power Plant Decontamination. Oxidation products of alloys used in nuclear power plant construction must be dissolved and flushed out of the unit. Because these oxidation products often contain radioactive materials, solvent and rinse waters require care in disposal. The following considerations are important for proper disposal of waste material: solvent volumes should be as slow as possible; the solvent should be compatible with different waste disposal methods, and quantitative stabilization of the radioactive materials in solutions should be maintained throughout solvent transfer and sampling. Among the cleaning methods employed, most involve an oxidizing pretreatment with alkaline permanganate (AP) followed by a chelant removal of the deposit. Among the chelant treatments are the following:

- Alkaline permanganate-ammoniated citric acid (APAC) -- citric acid, 5 to 10%, ammoniated to pH 5 to 7
- Alkaline permanganate-ammoniated citric acid-EDTA (APACE) -- citric acid, 2%; dibasic ammonium citrate, 5%; disodium EDTA, 0.5%

Additional benefits of using organic acids in stainless steel cleaning solutions are that they are chloride-free, which eliminates the problem of chloride-stress cracking, and their weakly acidic nature reduces the chances of hydrogen embrittlement (Ref 3). Additional applications include cleaning lube oil systems, heat exchanger surfaces, pendant superheaters and reheaters, and startup and operational cleaning of once-through boilers (Ref 4). Two new applications for organic acids have been developed.

Removal of Iron- and Copper-Bearing Deposits

A citric acid-based cleaning method is used to derust the steel shells of heat exchangers containing a high ratio of copper to iron, such as is found in marine air conditioning units. When the fluorocarbon refrigerant becomes contaminated with small amounts of water, corrosive hydrochloric and hydrofluoric acids are formed, causing significant corrosion of the steel shells. These corrosion products must be removed to restore the unit to its proper functioning.

Standard organic acid cleaning techniques are inadequate in this application due to the large amounts of copper oxides present, which are more easily dissolved than the iron oxide and tend to consume the organic acid before the iron oxides can be removed. To overcome this problem, a citrate-based cleaning formulation is modified to contain a reducing agent, which reduces the dissolved copper oxides to precipitated copper metal, which is filtered from the solution. This precipitated copper removal restores the citric acid content of the solution, making it available to dissolve the iron oxides. Any copper metal residue remaining in the system from the first solution is removed in a second step, which is also a citric acid-based solution. The second step also passivates the steel surfaces. The specific formulas for step one and step two are:

- **Step 1: Iron and copper oxide removal** 3% citric acid, 3% erythorbic acid, pH adjusted to 3.5 with triethanolamine (replaces ammonia, which is corrosive to copper).
- **Step 2: Copper metal removal and passivation** A second solution is prepared as follows: 3% trisodium citrate, 1.2% triethanolamine, 1% sodium nitrite (Ref 5). It is important that the order of additions be followed precisely to avoid toxic nitrogen oxide gas generation.

Another new application is the use of an EDTA-based solution to dissolve iron- and copper-bearing deposits from pressurized water reactor nuclear power plants. In pressurized water reactor nuclear power plant steam generators, the accumulation of secondary side corrosion deposits and impurities forms sludges that are composed primarily of metal oxides and metallic copper deposits. To remove these deposits, the following solution has been found effective:

Iron solvent

- 10% EDTA
- 1% hydrazine
- Ammonium hydroxide to pH 7
- 0.5% inhibitor CCI-80/1 applied at 90 to 120 °C (195 to 250 °F)

Copper solvent

- 5% EDTA
- Ammonium hydroxide to pH 7
- EDA (ethylenediamine) to pH 9.5 to 10.0
- 2 to 3% hydrogen peroxide applied at 32 to 43 °C (90 to 110 °F) (Ref 6)

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Acid Cleaning of Nonferrous Alloys

Aluminum Alloys. Acid cleaning of aluminum may be used alone or in conjunction with other acid, alkaline, or solvent cleaning systems. Vapor degreasing and alkaline cleaning may be required for removal of heavy oils and grease from workpieces before they are immersed in an acid bath. One of the main functions of an acid cleaner is the removal of surface oxides prior to resistance welding, painting, conversion coating, bright dipping, etching, or anodizing.

A mixture of chromic and sulfuric acids is commonly used to remove surface oxides, burntin oil,water stains or other films, such as the iridescent or colored films formed during heat treating. This acid mixture cleans and imparts a slightly etched appearance to the surface, preparing it for painting, caustic etching, conversion coating, or anodizing. Nonpolluting, proprietary products free of chromic acid are available for acid cleaning and deoxidizing.

When tungsten and molybdenum are slightly oxidized on the surface or after the heavily oxidized workpiece is cleaned with molten caustic, acid cleaning is used. The acid solution consists of 50 to 70 vol% concentrated nitric acid, 10 to 20% concentrated hydrofluoric acid, remainder water. The cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F).

Tantalum and Niobium. After mechanical grinding, abrasive blasting, or alkaline cleaning, tantalum and niobium are cleaned further with an acid solution. This consists of 40 to 60 vol% concentrated nitric acid, 10 to 30% concentrated hydrofluoric acid, remainder water. This cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F). After acid cleaning, the workpiece should be washed with water or rinsed thoroughly with a jet of water to remove any traces of acids.

Good ventilation and drainage systems should be installed in the acid cleaning or pickling room. A recycling system to remove the residues and to refresh the acid is preferred for both economical and ecological reasons.

Mechanical Cleaning Systems

Revised by Ted Kostilnik, Wheelabrator Corporation

Introduction

MECHANICAL CLEANING SYSTEMS are available for most industrial production applications to remove contaminants and prepare the work surface for subsequent finishing or coating operations. Typical uses include:

- Removing rust, scale, dry solids, mold sand, ceramic shell coatings, or dried paint
- Roughening surfaces in preparation for bonding, painting, enameling, or other coating substances
- Removing large burrs or weld spatter
- Developing a uniform surface finish, even when slightly dissimilar surfaces are present
- Removing flash from rubber or plastic molding operations
- Carving or decorative etching of glass, porcelain, wood, or natural stone such as granite or marble

The types of workpieces that can be mechanically cleaned include:

- Ferrous and nonferrous castings
- Forgings or stampings
- Steel plate, strip, or structural shapes

- Weldments and fabrications of ferrous and nonferrous materials
- Aluminum, magnesium, or zinc permanent mold or diecast items
- Thermoplastic or thermoset plastics
- Steel bar stock and wire rod
- Precision molded rubber parts
- High-alloy dies and molds for rubber, plastic, glass, or metal parts
- Miscellaneous exotic parts

Mechanical cleaning systems use various types of abrasive materials that are energized or propelled against the work surface of the part through one of three principal methods: airless centrifugal blast blade- or vane-type wheels; compressed air, direct-pressure dry blast nozzle systems; or compressed-air, indirect-suction (induction) wet or dry blast nozzle systems. Other available methods, not discussed in this article, include aggressive vibratory systems, media tumbling systems, and part-on-part tumbling systems.

Propelling Abrasive Media

Abrasive blast cleaning began commercially with air or steam directed through a conduit of pipe or hose with a final nozzle to direct the impacting abrasive stream. Both pressure blast and suction blast nozzle systems require high power to generate the compressed air or pressurized steam that is used to accelerate and propel the abrasive. This requirement is due to aerodynamic inefficiencies in accelerating the spherical and angular abrasive particles, especially the higher-density ferrous abrasives.

Wheels. Airless abrasive propelling wheels that use blades or vanes require about 10% of the horsepower required by air blast systems to throw equal volumes of abrasive at the same velocities. The power losses in an airless system are the friction between the abrasive and vanes, the impeller-control cage interference, and the wheel-drive system.

Airless abrasive blast wheels are generally of the blade type, as shown in Fig. 1. These wheels may have one or two side plates, one of which is attached to a hub, shaft bearings, and belt drive, or the side plate may be attached directly to the shaft of a suitable motor. The side plate holds four to twelve throwing blades, depending on the size of the wheel. Blade tip diameters range from 205 to 660 mm (8 to 26 in.) and blade widths range from 40 to 125 mm (1.5 to 5 in.). Rotational speeds range from 500 to 4000 rev/min or more. Usable abrasive velocities range from 15 m/s (50 ft/s) to 122 m/s (400 ft/s), with 75 m/s (245 ft/s) the most widely used velocity. Abrasive flow rates with steel shot range from 23 kg/min (50 lb/min) up to 1040 kg/min (2300 lb/min) with a 100 hp motor.

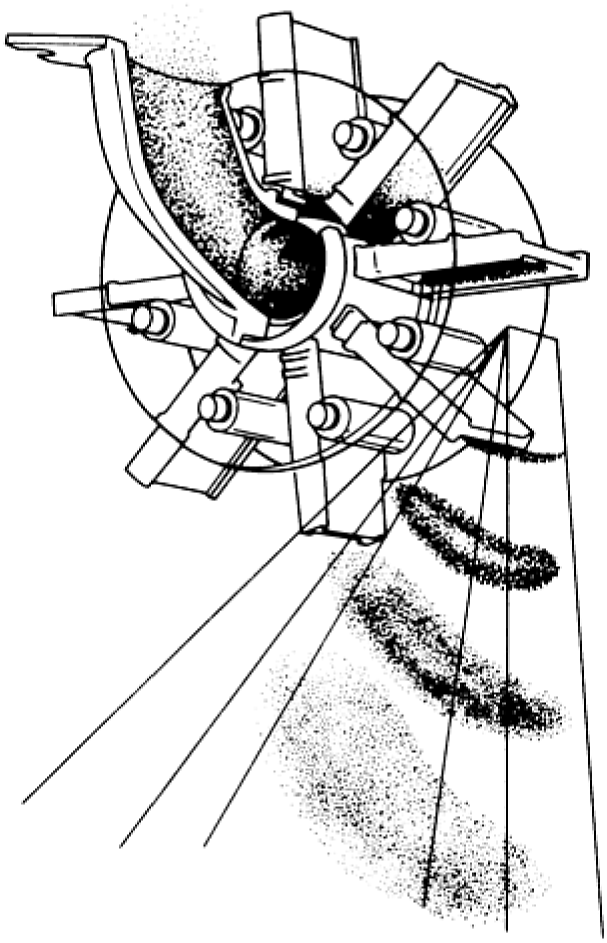


Fig. 1 Blade-type airless centrifugal abrasive blast wheel

Figure 1 also shows the operation of a blade-type wheel. A controlled flow of abrasive (through a valve not shown) is fed by gravity into an abrasive feed spout from which it flows into a rotating vaned impeller. The impeller rotates at the same speed as the bladed wheel, and the number of vanes is equal to the number of wheel blades. The impeller rotates in a stationary cylinder (referred to as a control cage or impeller case) that is equipped with an opening that may be rotated and locked in a preferred position. As the impeller forces the abrasive out of the control cage opening, each of the blades picks up a metered amount of abrasive at the inner end of the blade and accelerates the abrasive to produce a tent blast pattern, as shown.

Centrifugal blast wheel units are enclosed in housings to prevent the discharge of stray abrasive. The principal wearing parts of the blast wheel assembly are the impeller, control cage, wheel blades, and housing liners. These parts are most economically made of high-alloy cast iron, and each can be individually replaced. Unalloyed cast iron parts, although less expensive, have a very short life under normal operating conditions.

The life of these parts is influenced primarily by the type and condition of the abrasive medium and contaminants picked up in the cleaning process. Abrasive materials are discussed in depth later in this section. Clean steel shot provides the longest useful life of wheel and guard housing liners. Much greater wear results from the use of nonmetallic abrasives such as sand, aluminum oxide, and silicon carbide. Table 1 shows the effects of abrasive in various conditions on the life of the components of a centrifugal blast wheel unit. Relatively little wear on wheel parts and housing liners is caused by glass beads, nonferrous shot, or the agricultural abrasives frequently used in deburring and special finishing applications.

Table 1 Effect of abrasives on life of components of a centrifugal blast wheel unit

Abrasive	**Life of components**[(a)], **h**

	Blades	**Impeller**	**Control cage/case**	**Alloy housing liners**
100% steel shot (few fines)	600	600	600	3000
Steel shot, 1% sand	100-200	100	100	2000
Steel shot, 3% sand	15-50	50	50	1500
100% steel grit(b)	125-150	150	150	1000-1500
100% sand	4-6	4-8	4-8	500

(a) Life based on running time of centrifugal blast wheel 495 mm ($19\frac{1}{2}$ in.) diam and 65 mm ($2\frac{1}{2}$ in.) wide, 30 hp drive and flow rate of 375 kg/min (830 lb/min).

(b) G25 grit; hardness, 55 to 60 HRC

Centrifugal wheel-type blast machines may be relatively simple, having a single blast wheel, a simpler work conveyor, an abrasive recycling system, and a dust collection device.

Pressure blast nozzle systems generally rely on a 685 kPa (100 psig) air supply to propel the abrasive through a special nozzle. A typical intermittent pressure tank (Fig. 2) has dimensions of 610 by 610 mm (24 by 24 in.) and an abrasive discharge capacity of 0.12 m^3 (4.2 ft^3). This capacity is adequate to operate one 6 mm ($\frac{1}{4}$ in.) diameter blast nozzle for 30 to 60 min. This type of tank is refilled through the filling valve by gravity when the air supply is shut off. Without air pressure in the tank, the filling valve is pushed down and open by the weight of the abrasive. When the air pressure is turned on again, the valve rises and stops the flow of abrasive into the tank. The abrasive in the now-pressurized tank moves into a mixing chamber. Mixing chambers usually are equipped with an adjustable control to regulate the flow rate of abrasive into the mixing chamber and on through the hose and nozzle assembly. The pressure tank and filling valve may be vertically doubled with a timer and proper valving to provide a continuous automatic pressure tank.

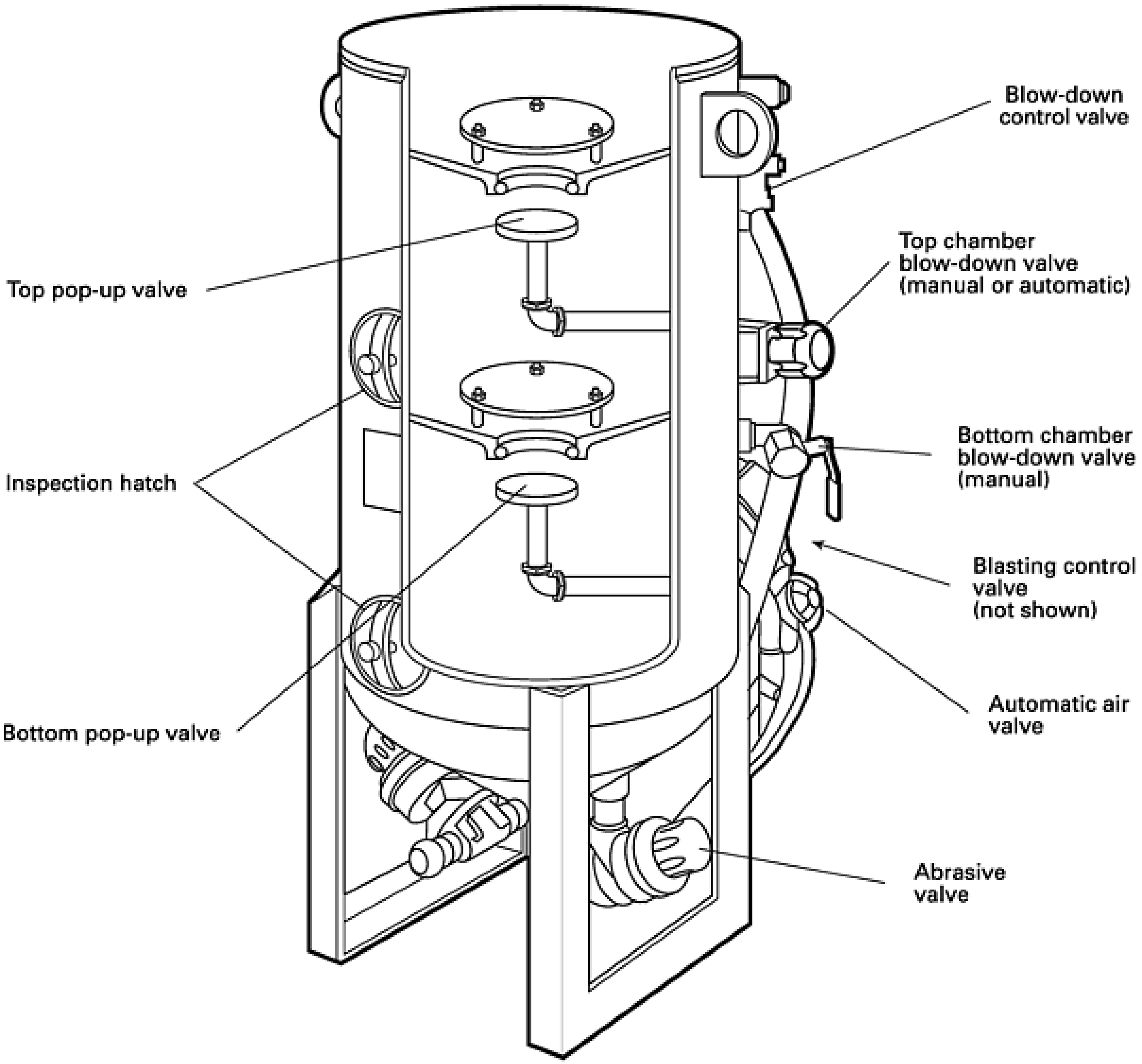


Fig. 2 Double-chamber abrasive blast pressure tank. Courtesy of Bob Thompson, Schmidt Manufacturing Inc.

Airblast nozzles are used in a variety of shapes, some as simple as a piece of pipe. Most systems are replaceable nozzles of metal alloys or nozzles with wear-resistant ceramic inserts. The latter nozzles may be of straight bore or venturi cross section. All types of abrasive may be handled with the pressure blast system in a variety of environments. In exceptional cases, air pressure blasting is performed in an open field with sand as the abrasive. Protective clothing and a helmet with air supply are the only health precautions taken. Quite often the sand is not recovered after use.

Suction blast cabinets are generally considered the simplest form of abrasive blast equipment. They may be used manually or have fixed or oscillating nozzles. Figure 3(a) illustrates a 1220 by 915 by 840 mm (48 by 36 by 33 in.) suction blast cabinet.

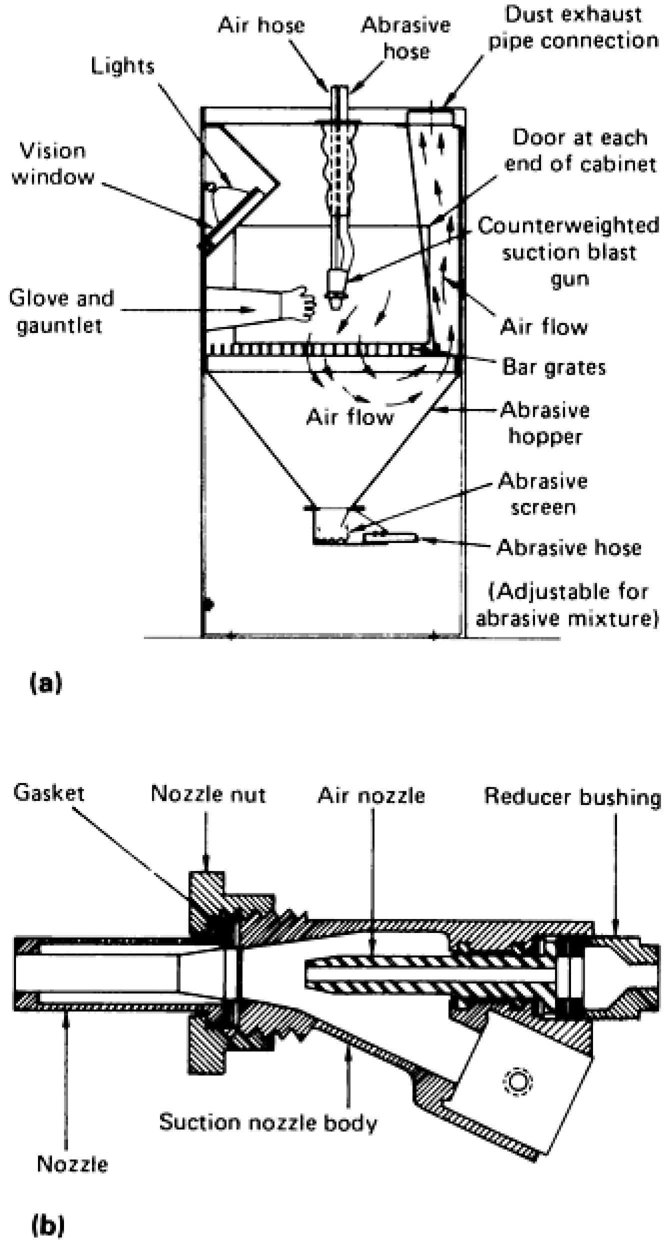


Fig. 3 Suction blast equipment (a) cabinet. (b) Nozzle assembly

Figure 3(b) illustrates a suction blast nozzle assembly. The nozzle in the suction cabinet is an induction nozzle that creates a blasting mixture by the siphon effect of the air discharged through the nozzle body. This effect pulls abrasive through the abrasive hose from the cabinet hopper, and the blast mixture is formed within the nozzle body. Because only compressed air flows through the air nozzle, the air consumption remains constant. The air nozzle is cast of a wear-resistant alloy. The nozzle can be used until considerably enlarged without affecting the efficiency of the blast. This cannot be done in a direct-pressure blast nozzle without seriously affecting air consumption. The amount of abrasive or the mixture of air and abrasive can be controlled in the suction cabinet by changing the relative position of the end of the abrasive hose to the abrasive flowing from the cabinet hopper.

Equipment for Dry Blast Cleaning

Dry blast cleaning is probably the most efficient and environmentally effective method for abrasive cleaning and finishing. Proper ventilation helps maintain a clean work area. No settling ponds or chemical treatment are required. Dust collectors provide dust disposal that is clean and simple, using sealed containers. Dry-blast systems need only be kept dry and can be started and stopped with minimum startup or shutdown operations. Several types of equipment are available for dry blast cleaning, and equipment selection is primarily based on the type of parts to be blasted and the relative throughput required.

Cabinet Machines. A high percentage of dry blast cleaning is performed using cabinet machines. A cabinet houses the abrasive-propelling mechanism, such as a centrifugal wheel or compressed air nozzle(s), holds the work in position, and confines flying abrasive particles and dust. Cabinets are available in a wide range of sizes, shapes, and types to meet various cleaning, production, and materials handling requirements. Cabinet machines may be designed for manual, semiautomatic, or completely automated operation to provide single-piece, batch, or continuous-flow blast cleaning.

The table-type machine (Fig. 4) contains a power-driven rotating worktable. Within the cabinet, the blast stream is confined to approximately half the table area. The unit shown is self-contained and mounted on the floor. The work is positioned on the slowly rotating table, and the abrasive particles are propelled by an overhead centrifugal wheel. When the doors are closed, blast cleaning continues for a predetermined time. Some table-type machines are designed with one or more openings in the cabinet. These openings are shielded by curtains and permit continuous loading and unloading or movement of parts during the blast cycle.

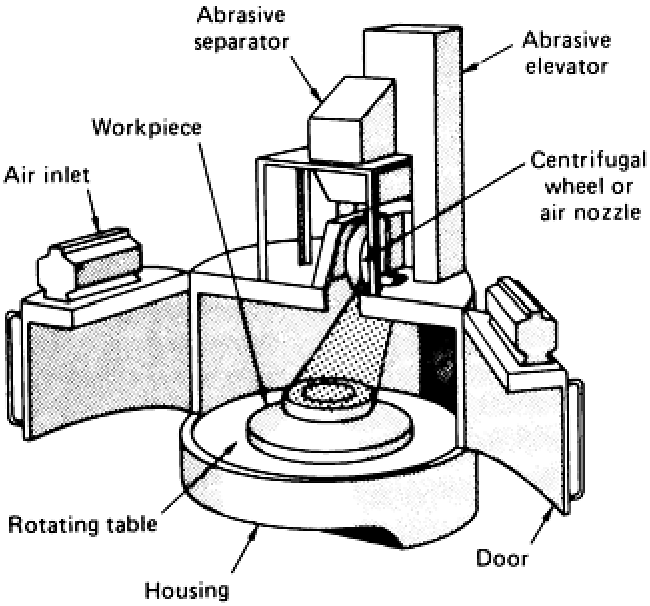


Fig. 4 Table-type blast cleaning machine. The centrifugal wheel propels the abrasive particles.

Removal of the contaminants and fines is performed with an airwash separator, as shown in Fig. 5. Spent abrasive and contaminants are fed by a belt and bucket elevator to the helicoid conveyor. The abrasive is screened in the rotary screen, falls in a vertical curtain, and passes under a swinging baffle. The abrasive is then subjected to a controlled cross-flow of air, which cleans it and removes foreign contaminants and fines. Finally, the abrasive gravitates to a storage hopper and is ready for reuse, while contaminants are routed to disposal.

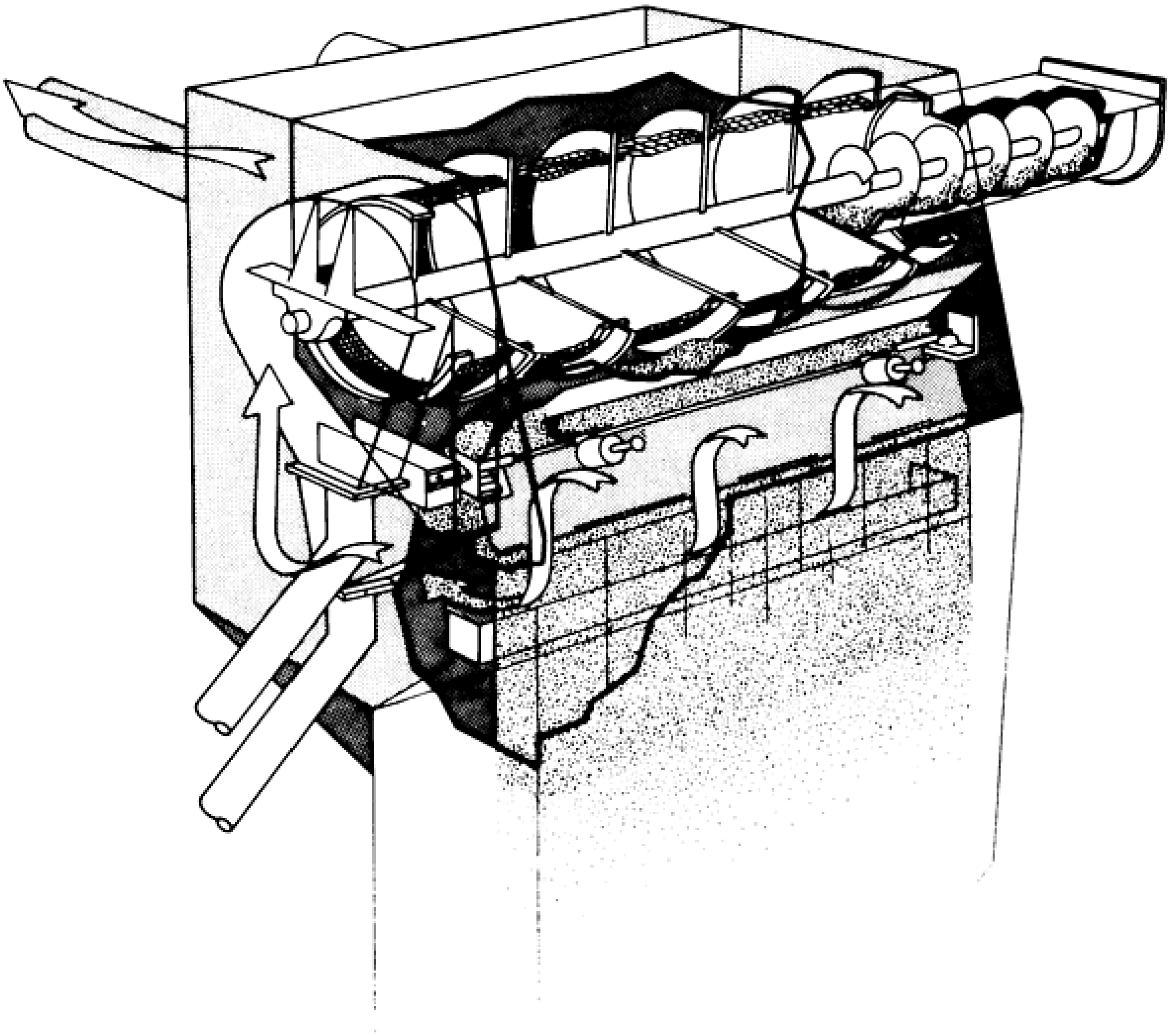


Fig. 5 Airwash separator

Continuous-flow machines equipped with proper supporting and conveying devices are used for continuous blast cleaning of steel strip, coil, and wire. These machines are also used to clean castings and forgings at a high production rate, making use of flat face or skew rolls, monorails, and other continuous work-handling mechanisms.

A continuous centrifugal blast cleaning machine, equipped with a monorail, is shown in Fig. 6. In operation, the work is loaded outside the blast cabinet and is conveyed into it through a curtained vestibule, which can be designed with 90° turns to reduce the escape of flying abrasive particles. The conveyor indexes the work to the center of each blast station and rotates it for complete blast coverage. If the workpiece contains intricate pockets, it may be indexed to an off-center position and be slowly conveyed past the blast in a manner that most effectively exposes the pockets to the abrasive stream. To minimize cycle time, the work is moved at an accelerated rate between blast stations. As it is conveyed and rotated on a return passageway that follows along the back of the cabinet, the work is exposed to additional cleaning and acts as a barrier to protect the cabinet walls from wear. Continuous-flow machines incorporate abrasive recycling facilities and an exhaust system for removing dust and fines.

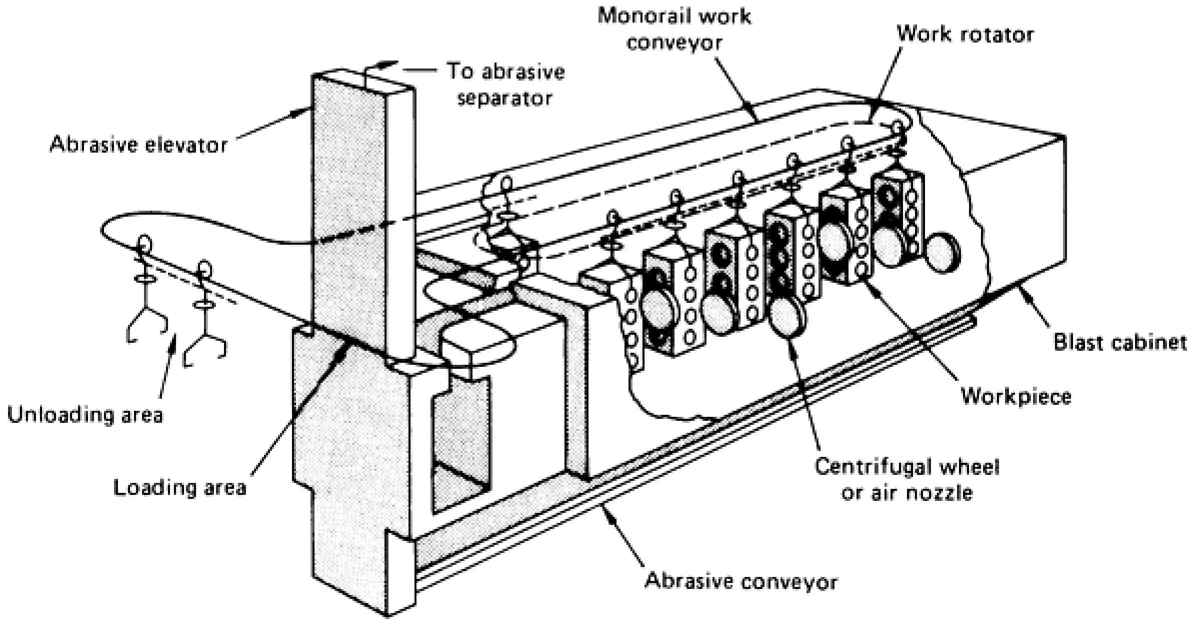


Fig. 6 Continuous centrifugal blast cleaning machine

Blasting-tumbling machines (Fig. 7) consist of an enclosed endless conveyor, a blast-propelling device or devices, and an abrasive recycling system. These machines simultaneously tumble and blast the work. They are made in various sizes to accommodate work loads from 0.03 to 2.8 m^3 (1 to 100 ft^3). The work usually is loaded into the conveyor by means of a skip-bucket loader. As the conveyor moves, it gently tumbles the work and exposes all workpiece surfaces to the abrasive blast. At the end of the cleaning cycle, the conveyor is reversed and the work is automatically discharged from the machine.

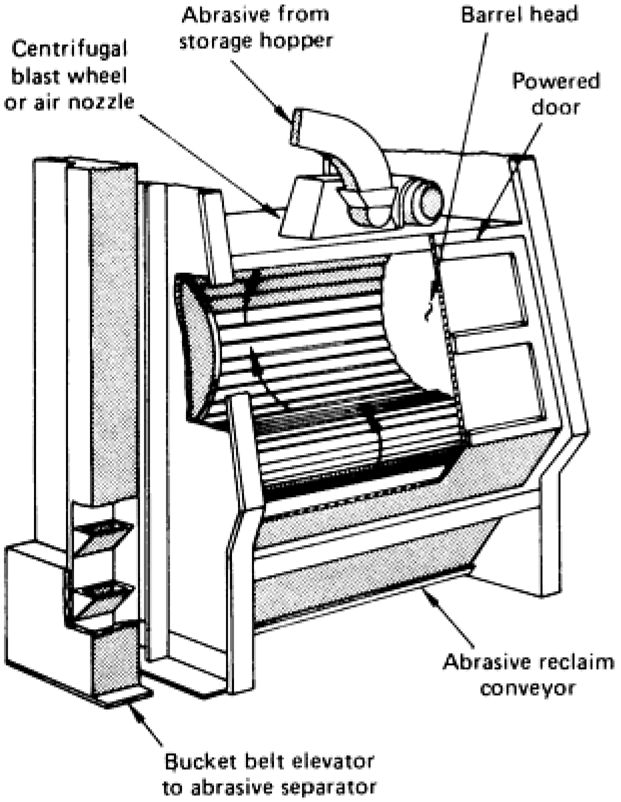


Fig. 7 Blasting-tumbling machine

Blasting-tumbling machines are used for cleaning unmachined castings, forgings, and weldments whose size, shape, and material permit them to be tumbled without damage. This equipment is not used for cleaning parts after machining, because tumbling damages machined surfaces. Blasting-tumbling machines remove dry contaminants such as sand, rust, scale, and welding flux, and they provide surface preparation for enameling, rubber bonding, electroplating, or etching before galvanizing. Blasting-tumbling machines can be integrated into automatic systems for high production rates. An example is the presort and tote box loader work-handling system shown in Fig. 8. Automatic vibrating feeder conveyors are also available to feed single or multiple machines in lieu of skip-bucket loaders.

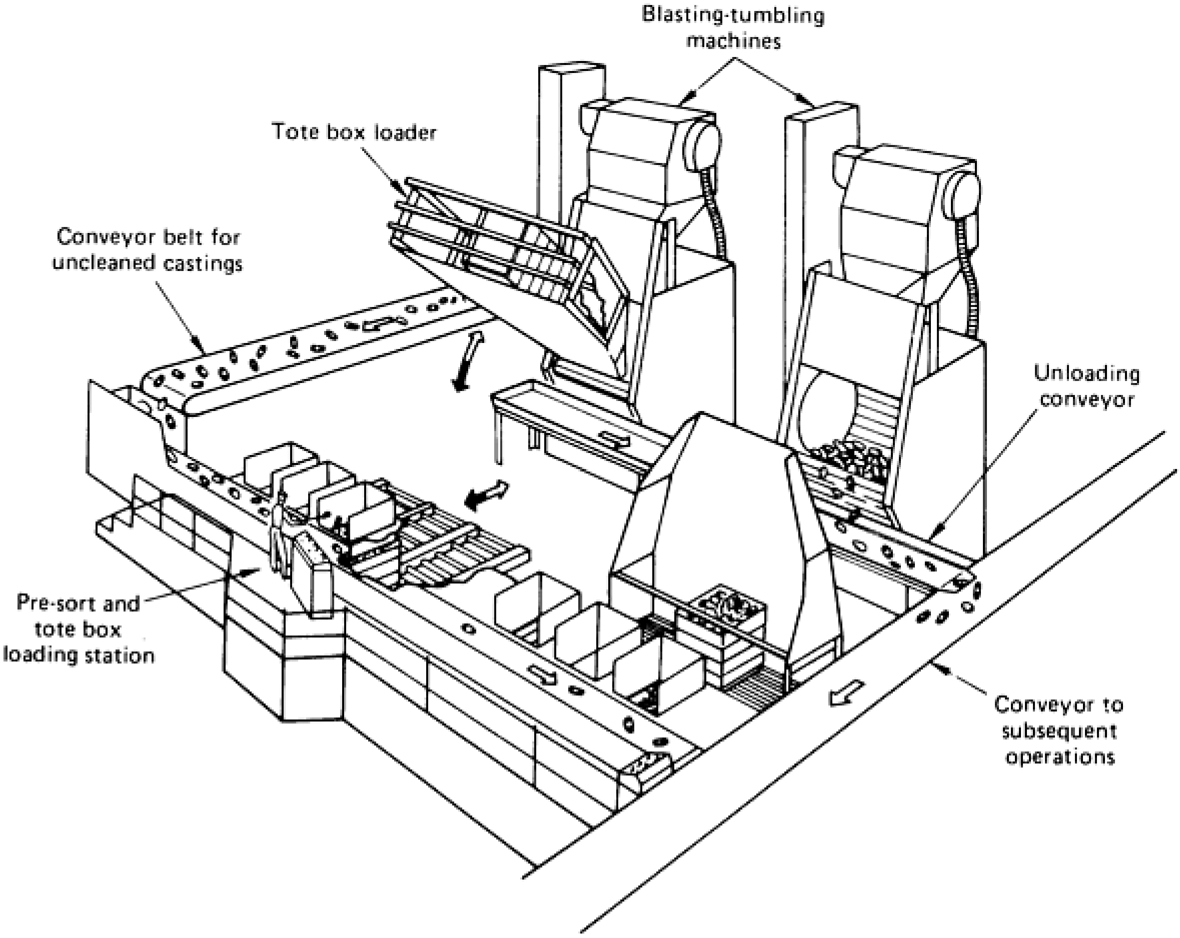


Fig. 8 Presort and tote box loader work-handling system. The sorter operates the tote box shuttle to and from the blasting-tumbling machine.

Portable Equipment. When parts to be cleaned are too large to be placed in blasting machines, portable equipment, such as air blast equipment, can be brought to the workpiece. A low-cost sand usually is used, because it is difficult to reclaim or recirculate the abrasive with portable equipment. Also, it is necessary to prevent random scatter of flying particles.

Portable recycling equipment is a new development in air pressure blasting. This equipment uses a pressurized media hose contained within a larger, evacuated hose. After impact, the media are returned through the outer hose to the central unit for reclaiming and recycling. A brush baffle prevents escape of media at the part surface. With this equipment, large external jobs may be done with specialized media without environmental problems.

Microabrasive blasting is another portable air blasting method. Both the abrasive particle size and nozzle opening are very small. Particle sizes are normally 10 to 100 μm (0.4 to 4 mils) and nozzle openings are 0.4 to 1.2 mm (0.015 to 0.045 in.) in diameter. The tungsten carbide nozzle tips are usually screwed into a pencil-shaped handpiece. Microabrasive blasting is normally a handheld operation for precision deburring, cleaning, or surface preparation. The design of the handpiece and the size of the abrasive particle allow a large degree of control in pointing the blast at the work surface. This is advantageous in deburring or cleaning blind orifices, intersecting slots, or internal bores with irregular surfaces. Microabrasive blasting is not effective for gross material removal or for covering large areas. Dryness and uniformity of particle classification are very critical, and abrasives cannot be reused. Because of the small nozzle size and the types of applications, abrasive usage is not excessive and nonreclamation is reasonable. In continuous-duty operation, 0.2 to 0.5 kg ($\frac{1}{2}$ to 1 lb) of abrasive is consumed per hour.

Ventilation. To ensure adequate ventilation of abrasive blast cabinets, a fabric filter dust collector is generally used with properly designed duct work. The fabric filters are generally equipped with exhaust fans on the clean-air side of the dust collector. This location is preferred because it eliminates erosion of the exhaust fan parts.

Two primary styles of fabric filter collectors are used. The first and oldest is the mechanical shaker type, in which an eccentric style drive activates pivoting racks from which the filters are suspended, providing periodic filter cleaning. A second type is the pulse jet, which uses tubular filter bags made of natural fibers or synthetic felt with an internal support cage of heavy wire and a venturi. Dust and foreign material accumulate on the outer surfaces of the bag and are removed by a short-time, high-pressure pulse of compressed air into the top opening of the venturi. Both types of fabric filters can be designed for light or heavy dust loadings and have throughput capacities from 2.83 m^3/s (100 ft^3/min) to several thousand cubic meters per second. The newest type of filter system uses a cartridge in lieu of a fabric tube. The cartridge is either paper- or fabric-based and is also cleaned by compressed-air pulsing.

Maintenance. Abrasive blasting machines are essentially self-destructive, and every effort must be made to protect components from the violent action of the abrasive. Machine interiors should be protected with wear-resistant cast or alloy metal liners or with heavy rubber mats or sheets to prevent erosion of metallic surfaces. High-velocity particles usually bounce from the rubber without damage to either the rubber or the abrasive. If the rubber receives the full impact of the blast, it will require periodic replacement.

Following are typical maintenance schedules that have proved satisfactory for the principal types of abrasive blasting machines:

Centrifugal wheel machines: weekly

- Check blades and wheel for wear. An unbalanced wheel can cause bearing wear and shaft bending. Install new blades if needed, check wheel balance, and test for cleaning pattern.
- Check for loose buckets on elevator belt; loose buckets may catch on the elevator shaft.
- Check sprocket at top and bottom of elevator shaft for wear and broken teeth.
- Check for wear on top plates of machine, rubber table tops, and table rings.
- Check for leaks in ventilation ducts.
- Check entire machine for possible wear holes through which abrasive might escape.
- Check rubber flaps at opening of machine for wear and escaping abrasives.

Automatic air blast machines: daily

- Check all nozzles and air jets for wear and proper flow.
- Check media and air hoses for leaks.
- Check table plates and rubber table tops for wear.
- Check suction lines for leaks.
- Check belts and chain for wear or slippage.
- Check shear pin; replace if necessary.

Hand air blast machines: daily

- Check nozzles and air jets for wear and proper flow.
- Check the following for leaks: media and air hoses, door gaskets, roof bellows and gauntlets, suction lines.
- Check gun bodies for uneven wear.
- Check suction lines for leaks.

Cycle Times for Dry Blast Cleaning

The amount of abrasive blasting required for a specific application depends on the workpiece material, the surface finish requirements, and the performance characteristics of the blast equipment. No dependable formula exists for establishing minimum blasting cycles; the amount of blasting time required to produce a given result in a given machine is established by trial. Table 2 lists abrasives, equipment, and cycles that have been used for dry blasting a number of materials or products for specific purposes.

Table 2 Abrasives, equipment, and cycles used for dry blasting

Material or product	**Reason for blasting**	**Abrasive**		**Equipment**				
				Type	**Horse-power**	**Nozzle diameter**		**Blasting cycle**
		Type	**Size No.**			**mm**	**in.**	
Ferrous metals								
Cast iron	Prepare for zinc impregnation	Iron grit	G80	Air, table(a)	. . .	6	$\frac{1}{4}$	1 h
	Remove molding sand	Steel shot	S230	Wheel, barrel	15	. . .	. . .	10 min
Cold rolled steel	Remove graphite for painting	Iron grit	G80	Wheel, barrel	15	. . .	. . .	10 min
				Air, table(a)	. . .	6	$\frac{1}{4}$	40 min
Gray iron exhaust manifolds, bearing caps	Clean for machining	Malleable iron shot	S460	Wheel, tumble(b)	80	. . .	. . .	1500 pieces/h
Gray iron motor blocks and heads	Remove sand and scale after heat treatment	Steel shot	S460	Wheel, blast cabinet(c)	500	. . .	. . .	6 s
Hardened steel screws	Remove heat treat scale	Iron grit	G80	Wheel, barrel	10	. . .	. . .	5 min

Material or product	Reason for blasting	Abrasive		Equipment				
				Type	Horse-power	Nozzle diameter		Blasting cycle
		Type	Size No.			mm	in.	
Hot rolled steel	Prepare for painting	Iron grit	G80	Air, table[(a)]	. . .	6	$\frac{1}{4}$	1 h
Malleable iron castings	Prepare for galvanizing	Steel grit	G50	Wheel, barrel	40	. . .	. . .	15 min
Pole-line hardware	Prepare for galvanizing	Steel grit	G50	Wheel, barrel	40	. . .	. . .	15-20 min
Round steel bar	Etch for adhesive coating	Iron grit	G80	Air, blast room	. . .	6	$\frac{1}{4}$	2 min
Soil pipe fittings	Remove molding sand	Steel shot	S330	Wheel, barrel	30	. . .	. . .	181 kg (400 lb) in 5 min
Steel drums	Prepare for painting	Iron grit	G80	Air, blast room	. . .	6	$\frac{1}{4}$	4 min
Steel rod	Clean for wiredrawing	Steel grit	G40	Wheel, continuous[(d)]	80	. . .	. . .	0.2-1.5 m/s (40-300 ft/min)
Steel screws	Prepare for plating	Iron grit	G80	Air, barrel[(a)]	. . .	8	$\frac{5}{16}$	2 min
Structural steel	Prepare for painting	Steel grit	G40	Wheel, continuous[(d)]	80	. . .	. . .	0.02 m/s (30 ft/min)
Weldments (steel)	Remove scale, welding flux, and splatter for painting	Steel grit	G25	Wheel, barrel	30	. . .	. . .	136-272 kg (300-600 lb) in 7 min
Engine parts for rebuilding	Remove paint, scale, and carbon deposits	Glass beads	60-100 mesh	Air	. . .	6	$\frac{1}{4}$	5-20 min
Nonferrous metals								

Material or product	**Reason for blasting**	**Abrasive**		**Equipment**				
				Type	**Horse-power**	**Nozzle diameter**		**Blasting cycle**
		Type	**Size No.**			**mm**	**in.**	
Aluminum	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min
	Prepare for painting	Iron grit	G80	Wheel, barrel	15	. . .	. . .	5 min
Bronze	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min
Aluminum and bronze	Prepare and condition surface	Glass beads	20-400	Air	. . .	6	$\frac{1}{4}$	5-20 min
Nonmetallic materials								
Clear plastic parts	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	15 min
Hard rubber	Improve appearance	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min
Molded plastic parts	Remove flash	Walnut shells	. . .	Wheel, barrel	10	. . .	. . .	8 min
Phenolic fiber	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	30 min
	Prepare for painting	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min

(a) Four air nozzles.

(b) Two wheels, 40 hp each.

(c) Ten wheels, 50 hp each.

(d) 4 wheels, 20 hp each

Applications and Limitations of Dry Blast Cleaning

Virtually all metals can be cleaned by at least one of the available abrasive blasting processes, but the abrasive medium must be carefully selected for soft, fragile metals and their alloys, such as aluminum, magnesium, copper, zinc, and beryllium. Otherwise, abrasive blasting may result in severe surface damage.

In some instances, abrasive blast cleaning induces residual compressive stresses in the surface of the workpiece. This is especially true with steel shot or glass beads. Although these stresses are highly desirable in terms of fatigue strength, they are detrimental to electrical components, such as motor laminations, because they alter electrical and magnetic characteristics.

Blasting at high pressures with a large particle size may produce warping in thin sections of steel and other metals as a result of induced stresses.

The blasting of extremely hard and brittle materials may result in chipping and excessive media consumption.

The corrosion resistance of stainless steels may be adversely affected by the adherence of dissimilar metals on the matte surface that is produced by abrasive blasting with metallic media. If this is a concern, grit blasting should be followed by chemical cleaning, or a stainless steel medium should be used.

Abrasive blasting usually roughens highly finished surfaces, particularly those of low hardness, so it is unsuitable for cleaning parts for which dimensional or surface finish requirements are critical.

The peening effect of abrasive particles may distort flat parts, particularly those with a high ratio of surface area to volume, such as clutch disks, long thin shafts, and control bars.

Even when the application of abrasive blast cleaning is known to be advantageous for a specific part, the particular abrasives and process selected should be entirely compatible with part requirements. For example, because small fragile parts may break in a tumbling operation, they should be processed in a stationary position on a rotating table or in conveyor equipment.

Shields or caps made of abrasion-resistant rubber compounds, sheet metal, or plastics are used to protect threaded sections from the abrasive blast. The tooth profiles of gear teeth may be protected from excessive blasting by positioning them in a way that controls their exposure to the blast.

Baffles and reflectors may be used to direct abrasive particles to certain areas, such as undercuts, that should not be exposed to the severity of direct impingement.

Because it is usually difficult to adjust velocities of mechanical cleaners, a finer shot or grit size may be selected to modify cleaning characteristics.

Type of Soil. Mechanical dry blasting does not readily lend itself to the removal of viscous or resilient soils such as grease, oil, or tar. These materials not only resist the blast action but also cling to, or coat, the abrasive material and components of the abrasive-recycling system. In time, such soils disrupt proper recycling, reclamation, and airwash separation of the reusable abrasive. Therefore, parts coated with oil or other viscous soils must be thoroughly degreased, or scrubbed and dried, before the mechanical dry blast operation.

Dry surface soils, such as sand, scale, rust, paint, weld spatter, and carbon, are readily removed by the dry blast action. These friable contaminants are compatible with airwash separation for reclamation of usable abrasive. Dry contaminants can be present on a surface in any quantity. Sand cores and molding sand are removed by the centrifugal blast method during core-knockout operations. Large castings are processed with portable equipment, and small castings are processed in batch-type machines.

On a limited or intermittent production basis, air or wet blast methods can be used to remove soils that are not removable by wheel blasting. (Wet blasting is described later in this article.) For example, an air blast nozzle may be used with soft agricultural abrasives, which absorb viscous soils, to clean oily or greasy surfaces. Because the initial cost of the abrasive is relatively low, the material can be discarded when it becomes contaminated or saturated. This method is often used by maintenance personnel for cleaning motors and gear reducers. New technology involving the use of baking soda aggregate is being developed as an additional potential cleaning solution.

Workpiece Shape. Parts of virtually any shape can be cleaned by some method of abrasive blasting, although complex parts with deep recesses or shielded areas present special problems. For example, it is often difficult for the abrasive to make contact with all surfaces of deep blind pockets with a velocity sufficient to loosen the soil to be removed. When direct impingement is impossible, deflection of the abrasive particles by means of baffles sometimes solves the problem. For effective cleaning of the inside surfaces of pipe, special air blast nozzles and lance air blast equipment must be used to deliver the abrasive with adequate velocity. Even these techniques have practical limitations, depending on the diameter and length of the pipe.

A second problem encountered in the cleaning of pockets or recessed areas is the buildup of abrasive in these areas. An accumulation of abrasive shields the surface from further blast action and interferes with cleaning. This problem is usually solved by positioning the work in a manner that permits the abrasive particles to drain by means of gravity. This positioning change may necessitate a corresponding change in the positioning of blast equipment. Cylinder blocks and valve bodies are typical examples of parts with recesses that catch and retain accumulations of abrasive.

Workpiece Size. The size of parts that can be cleaned by the centrifugal blast wheel method is limited principally by the size of the enclosure and the number of wheel units that can be applied economically. Wheel units are maneuverable to only a limited extent. Therefore, as part size increases, it is necessary to rotate or convey the part in a manner that properly exposes it to the available blast units. Castings and weldments 6 m (20 ft) in diameter, 5 m (16 ft) high, and weighing up to 136 tonnes (150 tons) have been cleaned in mechanical blast rooms. These rooms are equipped with a rotary table and several centrifugal wheel units operating simultaneously. During cleaning, such extremely large parts frequently require repositioning to expose all surfaces to the blast. Intricately shaped large parts may also require auxiliary air blast touch-up cleaning.

Various types of continuous blast machines are used for the cleaning of repetitive work. These machines vary in size and design in accordance with the application and type of work-handling equipment required. Rolled steel products, such as sheet, strip, wire, rod, and structural shapes, lend themselves to continuous mechanical blasting at moderate production rates. For example, rolled strip up to 1830 mm (72 in.) is mechanically blasted on a continual basis, to reduce the time required for acid pickling.

Structural shapes, including the largest sections rolled commercially, can be cleaned on continuous-roll conveyor machines equipped with multiple wheel units for coverage of all surfaces. The equipment is used for the removal of mill scale and rust before welding and painting. Hot-rolled rod and bar shapes are cleaned on single- or multiple-nozzle or wheel machines to remove surface scale and prepare the surface for drawing or cold heading.

By virtue of the flexibility provided by operator manipulation of blast hose nozzles, air blast equipment is widely used for cleaning extremely large parts and assemblies. Railroad cars, for example, can be reconditioned inside and outside by this method. Large storage tanks and vessels also are cleaned with air blast equipment, using inexpensive abrasives such as sand, slags, and natural minerals that need not be reclaimed or in conjunction with the reclaiming equipment previously described in this article.

In contrast, parts as small as 10 to 13 mm ($\frac{3}{8}$ to $\frac{1}{2}$ in.) in diameter can be satisfactorily cleaned by abrasive blasting. Usually, these small parts are most efficiently handled in mechanical or air blasting equipment, either barrel machines or combination blasting-tumbling units. Auxiliary devices, such as wire cages or baskets, may be used to prevent very small parts from being lost in the abrasive.

Mixed Work Loads. In blasting with either fixed nozzles or centrifugal wheels, it is always more economical to process loads made up of parts of about the same size. Mixing large and small parts in the same load is basically inefficient, because it wastes abrasive, wastes power, and frequently results in overblasting some parts and underblasting others, although parts can be mixed within reasonable limits. In job shop operations, especially, a varied production mix can be cleaned in a single tumbling and blasting operation. However, parts with thin sections that may bend or seriously distort should not be processed with parts that are relatively compact.

Quantity and Flow of Work. Continuous airless blast cleaning equipment is generally used for medium- to high-production cleaning applications. However, there are no actual quantity limitations. For the most economical use of continuous blast equipment, the work being cleaned must be repetitive and similar in size and shape, and the quantity of work flowing through the blast cleaning machines must be uniform and constant.

Monorail conveyor equipment should be operated with all work hangers fully loaded and few gaps in the production flow. This type of equipment usually is designed so that conveyor speeds can be regulated or index times varied to match work flow requirements, and so that the feeding of abrasive into the blast wheels can be regulated to suit work flow conditions. Automated conveyor equipment for cleaning gray iron motor blocks and similar parts is capable of cleaning from 400 to 600 workpieces per hour.

Continuous blasting-tumbling barrel machines also require a steady flow of work of relatively uniform size and shape. A constant level of work in the blast chamber makes the operation more economical and promotes uniform cleaning. In cleaning medium-size gray iron castings, these barrels have a capacity of over 23 tonnes (25 tons) per hour. If a steady flow of work cannot be maintained, it is economical to stockpile work until a sufficient accumulation is available. Barrel blasting machines, some table machines, and spinner hanger machines are suited to this type of operation.

Newer continuous process machines have been introduced that convey product via wire mesh belt or vibrating tracks. They are generally better suited for lower-volume or lower-tonnage applications. Die cast aluminum and zinc products represent ideal opportunities for use of these types of machines.

Miscellaneous Applications. Dry abrasive blasting has proven useful in applications in which cleaning is of only secondary importance. One automotive manufacturer blasts induction hardened transmission pins with chilled iron grit to permit rapid visual inspection and segregation of improperly hardened pins. After blasting, hardened surfaces have a markedly shiny appearance and unhardened surfaces appear dull. The same inspection technique is used by a manufacturer of rolling-mill rolls to determine uniformity of heat treatment of the roll surface. A manufacturer of carburized gears uses the technique to detect areas of decarburization and case leakage.

In some applications, dry abrasive blasting supplements other inspection techniques. Aircraft quality investment and sand castings are blasted before magnetic-particle inspection to reduce or eliminate glare caused by polishing or machining. Defects are more readily detected on the dull blasted surface.

Abrasives for Dry Blast Cleaning

The materials used in dry abrasive blast cleaning can be categorized as metallic grit, metallic shot, sand, glass, and miscellaneous. Hardness, density, size, and shape are important considerations in choosing an abrasive for a specific application. The selection of the type and size of the blast cleaning material will depend on the size and shape of the parts to be cleaned, the finish desired, and the treatment or operation that may follow blast cleaning. The success of blast cleaning operations depends primarily on judicious selection of method and abrasive medium. The surfaces, especially ferrous surfaces, tend to be very active following abrasive cleaning, and any subsequent operation such as plating or painting should be performed as soon as possible after abrasive cleaning.

Metallic abrasive media consist of grit, shot, and cut wire.

Grit consists of angular metallic particles with high cutting power. Grit is usually made of crushed, hardened cast steel shot, which may be tempered, or of chilled white cast iron shot, which may be malleabilized. Size specifications for cast grit are shown in Table 3. In general, three hardnesses are offered in steel grit: 45, 56, and 65 HRC. The screen distribution and the velocity of the grit impacting on the part surfaces control the finish. Usually, grit blast produces a brighter finish than shot blast. Applications for grit include removal of heavy forging and heat-treat scale, removal of rust, and controlled profiling of workpieces before bonding or coating. Hard grit is also used to provide a gripping surface on steel mill rolls.

Table 3 Size specifications for cast grit (SAE J444)

Size No.	Screen tolerances[(a)]	Screen opening	
		mm	in.
G10	All pass No. 7	2.82	0.1110
	80% min on No. 10	2.00	0.0787
	90% min on No. 12	1.68	0.0661
G12	All pass No. 8	2.38	0.0937
	80% min on No. 12	1.68	0.0661
	90% min on No. 14	1.41	0.0555
G14	All pass No. 10	2.00	0.787
	80% min on No. 14	1.41	0.0555
	90% min on No. 16	1.19	0.0469
G16	All pass No. 12	1.68	0.0661
	75% min on No. 16	1.19	0.0469
	85% min on No. 18	1.00	0.0394
G18	All pass No. 14	1.41	0.0555
	75% min on No. 18	1.00	0.0394
	85% min on No. 25	0.711	0.0280
G25	All pass No. 16	1.19	0.0469
	70% min on No. 25	0.711	0.0280
	80% min on No. 40	0.419	0.0165
G40	All pass No. 18	1.00	0.0394

	70% min on No. 40	0.419	0.0165
	80% min on No. 50	0.297	0.0117
G50	All pass No. 25	0.711	0.0280
	65% min on No. 50	0.297	0.0117
	75% min on No. 80	0.18	0.0070
G80	All pass No. 40	0.419	0.0165
	65% min on No. 80	0.18	0.0070
	75% min on No. 120	0.12	0.0049
G120	All pass No. 50	0.297	0.0117
	60% min on No. 120	0.12	0.0049
	70% min on No. 200	0.074	0.0029
G200	All pass No. 80	0.18	0.0070
	55% min on No. 200	0.074	0.0029
	65% min on No. 325	0.043	0.0017
G325	All pass No. 120	0.12	0.0049
	20% min on No. 325	0.043	0.0017

(a) Minimum cumulative percentages (by weight) allowed on screens of numbers and opening sizes as indicated

Shot, normally made of the same materials as grit, is usually in the form of spherical particles. Shot removes scale, sand, and other surface contaminants by impact. Size specifications for cast shot are indicated in Table 4. Steel shot is the most widely used metallic abrasive medium and is least destructive to the components of the abrasive blast system. The matte finish produced by steel shot on metal surfaces can be controlled by the screen distribution of the operating mix and the velocity of shot impacting on part surfaces.

Table 4 Cast shot size specifications for shot peening or blast cleaning (SAE)

Screen No.	**Screen size**		**Screen opening**[(a)]	**Passing**[(a)]**, %**
	mm	**in.**		
7	2.82	0.111	780	All pass
8	2.38	0.0937	660	All pass
10	2.00	0.0787	780	85 min
			550	All pass
			460	All pass
12	1.67	0.0661	780	97 min
			660	85 min
			460	5 max
			390	All pass
14	1.41	0.0555	660	97 min
			550	85 min
			390	5 max
			330	All pass
16	1.19	0.0469	550	97 min
			460	85 min
			330	5 max
			280	All pass
18	1.00	0.0394	460	96 min
			390	85 min

			280	5 max
			230	All pass
20	0.841	0.0331	390	96 min
			330	85 min
			230	10 min
			170	All pass
25	0.711	0.0280	330	96 min
			280	85 min
			170	All pass
30	0.590	0.232	280	96 min
			230	85 min
			110	All pass
35	0.500	0.0197	230	97 min
			110	10 max
40	0.419	0.0165	170	85 min
			70	All pass
45	0.351	0.0138	170	97 min
			70	10 max
50	0.297	0.0117	110	80 min
80	0.18	0.007	110	90 min
			70	80 min

120	0.124	0.0049	70	90 min

(a) Screen opening sizes and screen numbers with maximum and minimum cumulative percentages allowed on corresponding screens

Cut wire is available from aluminum, zinc, steel, or stainless steel primary metal. Cut wire deforms into rounded particles during usage or conditioning processes prior to sale; it is used frequently in the same manner as cast shot. Table 5 shows the specifications relating standard size numbers for cut steel wire shot to diameter and minimum hardness.

Table 5 Specifications for cut steel wire shot (SAE J441)

Size No.	Diameter of wire		Minimum hardness, HRC
	mm	in.	
CW-62	1.59±0.05	0.0625±0.002	36
CW-54	1.4±0.05	0.054±0.002	39
CW-47	1.2±0.05	0.047±0.002	41
CW-41	1.0±0.05	0.041±0.002	42
CW-35	0.89±0.03	0.035±0.001	44
CW-32	0.81±0.03	0.032±0.001	45
CW-28	0.71±0.03	0.028±0.001	46
CW-23	0.58±0.03	0.023±0.001	48

Nonmetallic abrasive media include sand, glass, agricultural products, and plastic and nylon. Table 6 lists physical properties and comparative characteristics of a variety of nonmetallic abrasives.

Table 6 Physical properties and comparative characteristics of nonmetallic abrasives

Description	Glass beads[(a)]	Coarse mineral abrasives[(b)]	Fine angular mineral abrasives[(c)]	Organic soft grit abrasives[(d)]	Plastic abrasives
Physical properties					

Shape	Spherical	Granular	Angular	Irregular	Cylindrical (diameter/length = 1)
Color	Clear	Tan	Brown/white	Brown/tan	Nylon: white, polycarbonate: orange
Specific gravity	2.45-2.50	2.4-2.7	2.4-4.0	1.3-1.4	Nylon: 1.15-1.17, polycarbonate: 1.2-1.65
Free silica content	None	100%	<1%	None	None
Free iron content	<1%	<1%	<1%	None	None
Hardness (Mohs)	5.5	7.5	9.0	1.0	R-110 to R-120
Media comparisons					
Toxicity	None	High	Low	Low/none	None
Metal removal	Low/none	High	High	None	Deburring only
Cleaning speed	Medium/high	High	High	Low	Low
Peening ability	High	None	None	None	None
Finish achieved	Range (various matte)	Rough anchor	Various matte	Smooth	Smooth
Surface contamination	None	Medium	Medium	Medium/high	Low to none
Suitability for wet blasting	High	Low	Low	Low	Low
Suitability for dry blasting	High	High	High	High	High
Standard size ranges	20-325	8-200	80-325	60-325	0.76 by 0.76 mm (0.030 by 0.030 in.)
	U.S. mesh	U.S. mesh	U.S. mesh	U.S. mesh	1.1 by 1.1 mm (0.045 by 0.045 in.) 1.5 by 1.5 mm (0.060 by 0.060 in.)
Consumption rate	Low	High	Medium	High	Very low
Cost comparison	Medium	Low	High/medium	High/medium	High/medium

(a) Glass beads are used for cleaning, finishing, light-to-medium peening, and deburring.

(b) Coarse mineral abrasives such as sand are used where metal removal and surface contamination are not considered.

(c) Fine angular mineral abrasives such as aluminum oxide are used in cleaning when smooth finish and surface contamination are not important.

(d) Organic soft grit abrasives, for example, walnut shells, are used in light deburring and cleaning of fragile items.

(e) (e)Plastic abrasives such as nylon and polycarbonate are used to deflash thermoset plastic parts and deburr finished machine parts.

Sand. This term is applied to diverse nonmetallic abrasives, in addition to ordinary silica sand. These materials are used when it is necessary to protect the surface of the workpiece from metallic contamination. They may be either natural materials, such as garnet, novaculite, dolomite, pumice, and flint quartz, or manufactured materials such as aluminum oxide, silicon carbide, and slag. The natural materials are lowest in initial cost; the manufactured materials, although somewhat more expensive than natural sands, cost less than metallic abrasives.

Glass is available as angular particles (ground glass) or spherical particles (glass beads) ranging in size from approximately 1 mm (0.039 in.) to less than 40 μm (0.0016 in.). The particles are usually made from soda-lime-silica glass with a hardness of about 500 HK (100 g load), equivalent to 46 to 50 HRC. Ground glass is effective for deburring and relatively aggressive finishing. Glass beads produce a fine matte appearance and clean without removing base metal. Size and roundness specifications for glass beads are given in Table 7.

Table 7 Standard size and roundness specifications for glass beads (MIL-G-9954A)

U.S. standard screen	Bead size	Roundness, minimum, %	Passing, %
10	1	60	100
12	1	60	95-100
	2	60	100
14	1	60	0-15
	2	60	95-100
	3	65	100
20	1	60	0-5
	2	60	0-15

	3	65	95-100
	4	70	100
30	2	60	0-5
	3	65	0-15
	4	70	95-100
	5	70	100
40	3	65	0-5
	4	70	0-15
	5	70	95-100
	6	80	100
50	4	70	0-5
	5	70	0-15
	6	80	95-100
	7	80	100
60	5	70	0-5
	7	80	95-100
	8	80	100
70	6	80	0-15
	8	80	95-100
	9	80	100
80	6	80	0-5

	7	80	0-15
	9	80	95-100
	10	90	100
100	7	80	0-5
	8	80	0-15
	10	90	95-100
	11	90	100
120	8	80	0-5
	9	80	0-15
	11	90	95-100
	12	90	100
140	9	80	0-5
	12	90	95-100
	13	95	100
170	10	90	0-15
	13	95	95-100
200	10	90	0-5
	11	90	0-15
230	11	90	0-5
	12	90	0-15
325	12	90	0-5

	13	95	0-15
400	13	95	0-5

Miscellaneous Materials. Mild abrasive action is provided by the use of such agricultural products as crushed walnut or pecan shells, rice hulls, rye husks, corncobs, and sawdust. Plastic and nylon media are also widely used for special purposes. Recent developments include the use of more environmentally attractive media such as CO_2 pellets and wheat starch.

Selection of abrasive for a specific application is influenced by the type of surface contamination to be removed, size and shape of the workpiece, surface finish specified, type and efficiency of cleaning equipment, and required production rate. Type, size, and hardness of metallic abrasives recommended for some typical applications are given in Table 8. In addition to the recommendations in this table, the following general observations relating to the performance of abrasive particles may be helpful:

- The smaller the abrasive particle, the finer the surface finish and the faster the surface coverage.
- The larger the abrasive particle, the greater the impact.
- In general, the harder the abrasive particle, the faster its cleaning action.
- The larger or harder the abrasive, the greater the wear on the equipment.

Table 8 Selection of abrasive

Application	Recommended abrasive[(a)]			
	Type	Nominal diameter		Hardness HRC
		mm	in.	
Blasting of ferrous metals				
Removal of light scale[(b)]	Shot or grit	0.2-0.71	0.007-0.028	30-66[(c)]
Removal of heavy scale[(b)]	Shot or grit	0.71-2.0	0.028-0.078	45-66
Cleaning of castings	Shot or grit	0.43-2.0	0.017-0.078	30-66[(c)]
Blasting of nonferrous metals				
Frosted appearance only	Grit	0.1-0.43	0.005-0.017	50-66
Preparation for other surface finishes	Shot or grit	0.2-0.71	0.007-0.028	30-66[(c)]

(a) Cast iron or cast steel.

(b) For phosphating or painting.

(c) Cast steel abrasive usually is not available in a hardness of less than 40 HRC.

Replacement of Abrasive. Production of a uniformly abraded surface depends on maintaining a uniform working mix of abrasive in the machine at all times. Metal surfaces treated with hard grit are more sensitive to a change in working mix than those treated with a soft grit or with shot. A program that includes testing and continuous gradual replacement of the abrasive is recommended. The working mix contains more abrasive fines than new abrasive. Examples of screen analyses of new and used abrasives are given in Table 9.

Table 9 Screen analysis of three metal abrasives

Screen No.	Screen size		Abrasive remaining on screen, %	
	mm	in.	New abrasive	Working mix
G25 cast steel grit				
16	1.19	0.0469	Trace	None
20	0.841	0.0331	82	23
30	0.589	0.0232	16	33
40	0.419	0.0165	1	19
50	0.297	0.0117	Trace	17
70	0.21	0.0083	Trace	6
Pan	. . .	. . .	Trace	2
G40 cast steel grit				
16	1.19	0.0469	None	None
20	0.841	0.0331	19	None
30	0.589	0.0232	76	18

40	0.419	0.0165	4	51
50	0.297	0.0117	Trace	26
70	0.21	0.0083	Trace	5
Pan	. . .	. . .	Trace	Trace
S280 cast steel shot				
16	1.19	0.0469	None	None
20	0.841	0.0331	40	27
30	0.589	0.0232	58	56
40	0.419	0.0165	1	11
50	0.297	0.0117	1	5
70	0.21	0.0083	None	1
Pan	. . .	. . .	None	None

A practical method of maintaining a reasonable degree of consistency of the working mix is to keep a uniform level of abrasive in the supply tank, bin, or hopper. This is accomplished by adding new abrasive periodically, usually at least once every 2 h. If surface finish requirements are more critical, hourly additions of new abrasive may be needed. The total tonnage of abrasive required to fill the machine to operating capacity also may affect the frequency of additions. When surface finish requirements are critical, the use of an automatic abrasive replenisher is indicated. This device maintains the abrasive level in the blasting machine by automatically feeding abrasive from a supply hopper. Consumption is gradual; therefore, replenishment should be equally gradual.

For control purposes, a representative sample of the abrasive used in the machine should be analyzed periodically. The frequency of these tests depends largely on surface finish and production requirements. Dust fines should be removed from the mix by an air separating system; proper performance of a separating device depends on a uniform flow of air through the separator and on maintenance of uniform abrasive sizes and quantities.

Control of Contaminants. After the abrasive medium makes contact with the workpiece, it is returned to a storage hopper for reuse. Coarse and fine contaminants picked up in the process are removed as the medium is returned to the hopper. Coarse contaminants include tramp metal, fins, core wire, core nails, slag, sand lumps, large flakes of rust and scale, and flash. These are usually removed by screening the abrasive mix through wire mesh, perforated plate, or expanded metal. Automatic rotary screens are preferred over stationary tray-type screens.

Fine contaminants include sand, fine mill scale and rust particles, metallic dusts, and disintegrated abrasive particles. Buildup of fine contaminants reduces blast efficiency, and a high sand content results in excessive wear of centrifugal blast wheel parts. Fine contaminants are removed from the mix by a current of air. In an expansion chamber, the heavier fine particles resist an upward turn of the air current and drop into the settling area to be discharged as refuse. Lighter particles remain suspended in the air current and are carried out through the ventilating lines to the dust collector or exhaust.

In many blast cleaning operations, small metallic particles resulting from the wearing or breaking down of abrasives assist in scouring small crevices or valleys. If such fines are to be retained, separators must be adjusted accordingly.

Wet Blasting

Wet blasting differs from dry blasting in that the abrasive particles used are usually much finer and are suspended in chemically treated water to form a slurry. The slurry, pumped and continually agitated to prevent settling, is forced by compressed air through one or more nozzles, which are directed at the work.

Applications

In further contrast to dry blasting, wet blasting is not intended for the gross removal of heavy scale, coarse burrs, or soil, but is intended to produce only relatively slight effects on the workpiece surface. Wet blasting is most commonly used for:

- Removing minute burrs on precision parts
- Producing satin or matte finishes
- Inspection finish ground, hardened parts
- Removing fine tool marks from hard parts
- Removing light mill scale or machining marks in preparation for plating
- Removing surface oxide in preparation for soldering of electronic components and printed circuits
- Removing welding scale

Many small parts, including hypodermic needles and electronic components, are deburred by wet blasting. The application of wet blasting to large parts is limited to the cleaning and finishing of forging dies from which a minimum of metal removal is desired; dies weighing up to 90 tonnes (100 tons) have been wet blasted. Many cutting tools are wet blasted after final grinding.

Precleaning. In most instances, precleaning must precede wet blasting to prevent contamination of the recirculating slurry. Grease, protective coatings, and heavy oils may be removed by conventional degreasing methods. Heavy rust and dry soils may be removed by dry blasting. A very light layer of rust may be removed from machined parts by wet blasting without precleaning. However, in general, the finer the abrasive used in the wet blast slurry, the greater is the need for precleaning to prevent contamination of the slurry.

Abrasives for Wet Blasting. Many different kinds and sizes of abrasives can be used in wet blasting. Sizes range from 20-mesh (very coarse) to 5000-mesh (much finer than face powder). Among the types of abrasives used are organic or agricultural materials such as walnut shells, baking soda, and peach pits; novaculite, silica, quartz, garnet, and aluminum oxide; other refractory abrasives; and glass beads.

The organic or agricultural materials are used for mild blasting only. Novaculite, a soft type of silicon dioxide (99.46% silica; Mohs hardness, 6 to 6.5), is used to remove very light burrs and produces a fine matte finish. The silicas are slightly more aggressive than novaculite and are used to remove larger burrs and scale. Quartz is still more aggressive than silica and lasts longer; it is used for the rapid removal of tenacious burrs and scale.

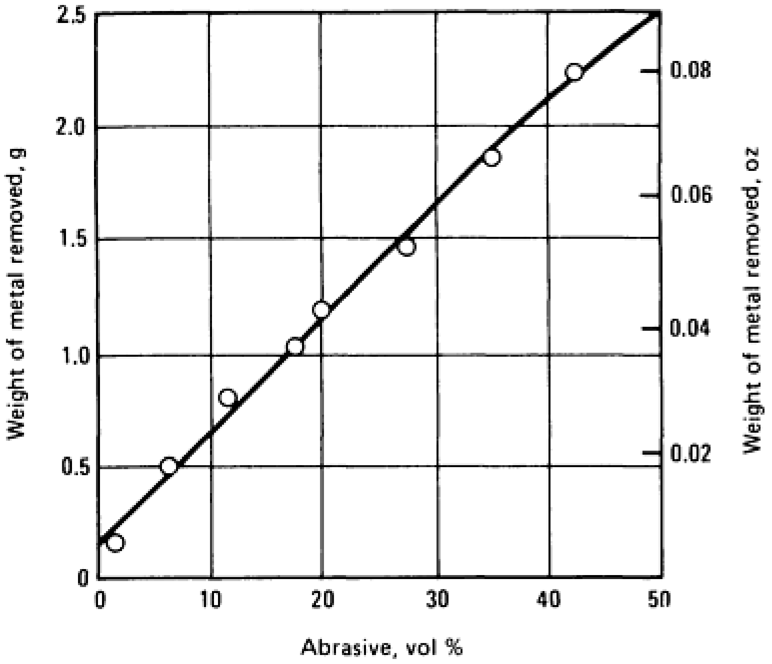
Garnet abrasives are highly aggressive and have long life; for a comparable mesh size, garnet will produce a rougher surface finish than will silicon dioxide. Aluminum oxide, silicon carbide, and other artificial abrasives are the most aggressive and erosive. Round glass shot (beads) composed of 72% silicon dioxide, 15% sodium monoxide, 9% calcium oxide, and 1% alumina produce a brighter finish and provide the most peening action. The high ricocheting property of glass beads is of value in blasting areas that are hard to reach. Table 10 describes various abrasives used in wet blasting and lists typical applications.

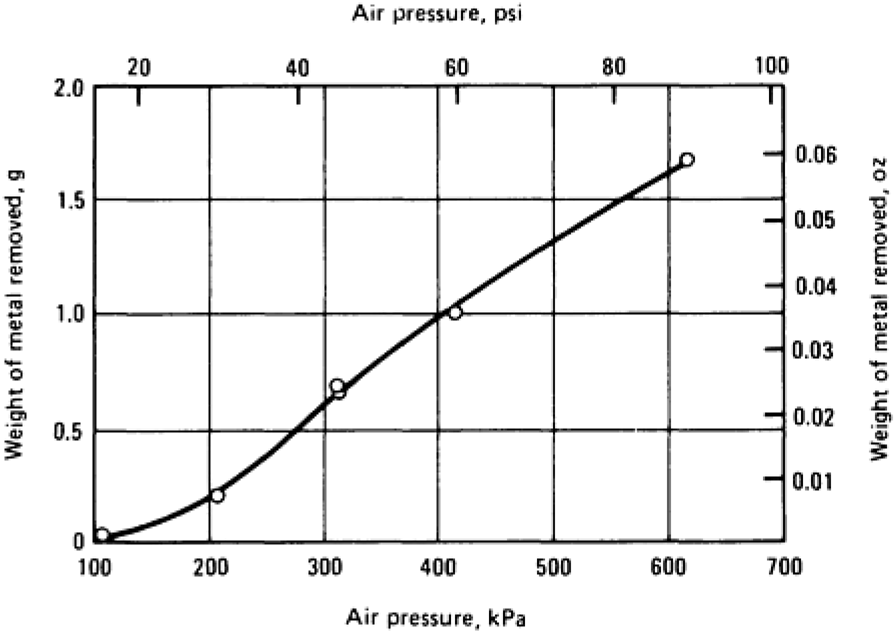
Table 10 Characteristics and typical applications of abrasives used in wet blasting

Abrasive	Mesh size	Characteristics and applications
Silica	40-80	Fast-cutting. Used for deburring steel and cast iron, removing oxides from steel. Close tolerances cannot be held
Silica	80	Fast-cutting. Used for deburring steel and cast iron, roughening surfaces for plastic bonding or rough plating. Has peening action. Tolerances cannot be held
Quartz (ground)	80	Very fast-cutting. Used for removing heavy burrs, light or medium scale, excessive rust. Can be used on nickel alloy steels. Tolerances cannot be held
Novaculite	100	Fast-cutting. Used for cleaning carbon from piston and valve heads: deburring brass, bronze, and copper. Can be used on crankshafts. Tolerances cannot be held
Quartz (ground)	100, 140	Fast-cutting. Used for blending-in preliminary grind lines on steel, brass and die castings; removing medium-hard carbon deposits; blasting radii of 0.1 to 0.3 mm (0.005 to 0.010 in.)
Silica	140	Used for removing small burrs from steel, copper, aluminum, and die castings; rough cleaning of dies and tools, removing metal. Tolerances cannot be held
Novaculite	325	Slow-cutting. Used in first stage for cleaning master rods and glass, and in second stage for cleaning aluminum pistons, crankshafts, impellers, valves. Holds tolerances to 0.06 mm (0.0025 in.)
Aluminum oxide	400	Fast-cutting. Used on stainless steel and on zinc and aluminum die castings. Excellent for oil-contaminated surfaces
Novaculite	1250	Used in second stage for cleaning crankshafts, impellers, rods, pistons, valves, gears and bearings. Also for polishing metals, tools, dies and die castings. Tolerances can be held
Novaculite	5000	Used for obtaining extra-fine surfaces on parts
Glass beads	20-400	Used for removing scale or discoloration after heat treating, removing oxide from jet-engine and electronic components. Produces peening effect

Liquid Carriers. The liquids most commonly used to carry the abrasive particles are water-containing additives such as rust inhibitors, wetting agents, and anticlogging and antisettling compounds. In a few applications, such as in the manufacture of spark plugs, petroleum distillates have been used as abrasive carriers for the removal of oil residues and fine chips and burrs. In these instances, the use of water would create difficulties. Petroleum distillates, however, can be used only with specially designed wet blasting units because of the fire hazard.

The proportion of abrasive to liquid in the wet abrasive slurry can be varied over a wide range, although certain limitations apply. The use of a very small percentage of abrasive results in slight cleaning action, while too large a percentage of abrasive might result in the formation of a paste that could not be properly circulated. Proportions should be fixed at a predetermined level for each application, to ensure uniform cleaning action and production of a uniform finish. A range of 20 to 35% volume abrasive is satisfactory for most applications but may be modified because of particle size, surface tension, specific gravity, agitation, or the desired effect on the workpiece. Figure 9 illustrates the effects of three variables on metal removal during wet blasting of 1010 steel. Reclamation of wet abrasive is usually impractical. The mixture generally is used until its cleaning action becomes unsatisfactory and is then discarded.


Weight of metal removed, g
2.5
2.0
1.5
1.0
0.5
0
0.08
0.06
0.04
0.02
Weight of metal removed, oz
0
10
20
30
40
50
Abrasive, vol %


Air pressure, psi
20
40
60
80
100
Weight of metal removed, g
2.0
1.5
1.0
0.5
0
0.06
0.05
0.04
0.03
0.02
0.01
Weight of metal removed, oz
100
200
300
400
500
600
700
Air pressure, kPa

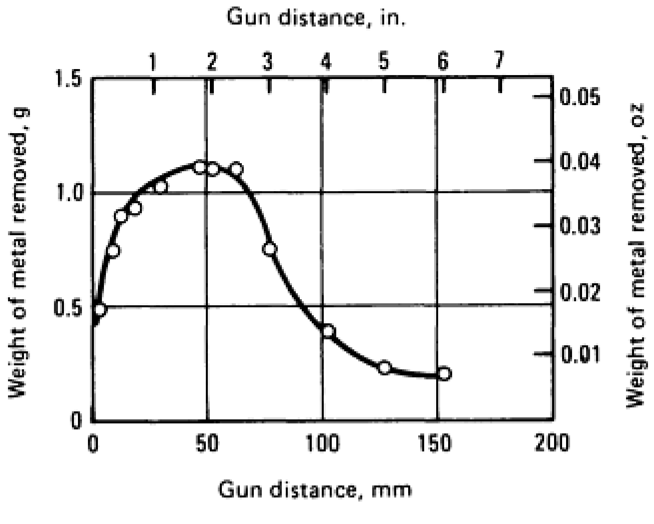

Gun distance, in.
1
2
3
4
5
6
7
Weight of metal removed, g
1.5
1.0
0.5
0
0.05
0.04
0.03
0.02
0.01
Weight of metal removed, oz
0
50
100
150
200
Gun distance, mm

Fig. 9 Effect of variables on amount of metal removed during wet blasting of 1010 steel

Equipment. Although equipment for wet blasting is often of special design for a particular application, several basic types of machines (Fig. 10) have been developed for general use, including:

- Cabinet-type machines
- Horizontal-plane turntable machines with tables of various diameters
- Vertical wheel-type machines
- Chain or belt conveyor machines
- Shuttle-type cabinets with cars and rail extensions
- Car-mounted, self-contained turning mechanisms for shafts or tubular parts

These basic types may be equipped with strippers, takeoff conveyors, and wash-rinse-dry stations. The blast guns may be mounted in a stationary position or be made to oscillate, depending on the application.

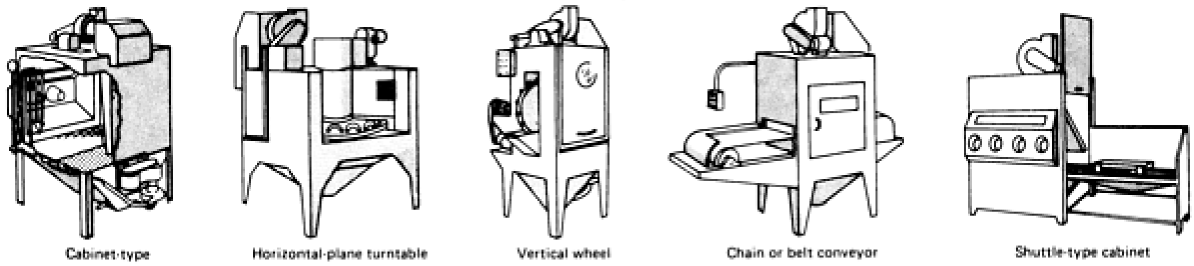

Cabinet-type
Horizontal-plane turntable
Vertical wheel
Chain or belt conveyor
Shuttle-type cabinet

Fig. 10 Wet blasting machines

Combination blasting-tumbling cabinet-type machines also are available. These machines are made with an extension stand provided with rails so that a car-mounted tumbling barrel can be moved into the cabinet. The barrel, a self-contained unit, is provided with a driving mechanism for turning the barrel and oscillating the blast gun or guns inside the barrel. Barrels range in diameter from 305 to 660 mm (12 to 26 in.) and are perforated to allow the slurry to escape and recirculate.

Nozzles for wet blasting vary in form, shape, length, and diameter according to the type of abrasive used and the size of the parts to be blasted. The most common form is a cylindrical nozzle about 25 mm (1 in.) long, 13 mm ($\frac{1}{2}$ in.) inside diameter, and 19 mm ($\frac{3}{4}$ in.) outside diameter. It is made of low-carbon steel and is used in hand-operated cabinets for general cleaning purposes. This nozzle uses silicates or quartz in mesh sizes ranging from 100 to 300 and at blasting pressures of 550 to 620 kPa (80 to 90 psi), and it has an average life of about 40 h.

Special nozzles, such as fan-shaped types, usually are made of an alloy cast iron chilled to a high hardness, although some special nozzles are made of rubber.

Carbide nozzles are used in mechanized units that provide surface preparation for processes such as anodizing and phosphating. The higher cost of cylindrical carbide nozzles is justifiable in terms of long life and low maintenance. For special shapes, however, the cost of carbide is likely to be prohibitive. When used with fine abrasives, a cylindrical carbide nozzle has a life of several thousand hours. In one application, a carbide nozzle exhibited no measurable wear after 1000 h of service with 140-mesh quartz at a pressure of 620 kPa (90 psi).

A nozzle for wet blasting is considered to be worn out when its wall thickness has been so reduced as to be potentially damaging to the gun, or the blast pattern provides inadequate coverage of the workpieces.

The amount of air required for wet blasting depends on the diameter of the air-jet nozzle and the operating pressure. Figure 11 illustrates the cubic feet of air needed to operate air-jet nozzles 2.4 to 8 mm ($\frac{3}{32}$ to $\frac{5}{16}$ in.) in diameter at pressures from 70 to 690 kPa (10 to 100 psi). The data are based on operating a wet blasting gun with a slurry containing 40 vol% abrasive of 140-mesh.

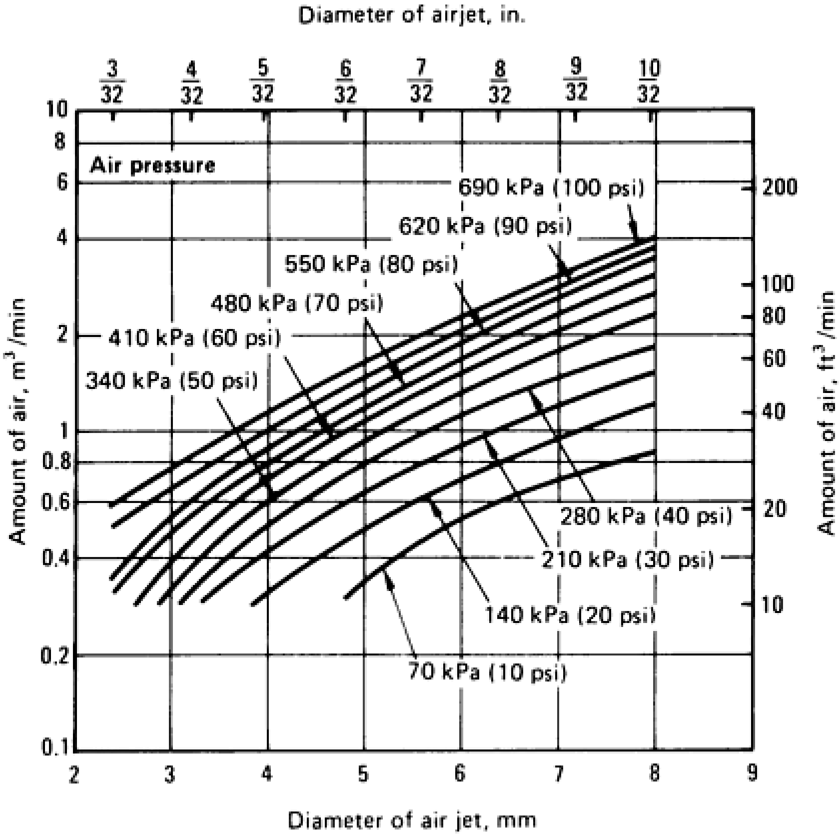


Fig. 11 Amount of air required for various sizes of air-jet nozzles at different operating pressures

Maintenance. Typical maintenance schedules for hand-operated wet blasting cabinets are as follows:

- *Weekly:* Wash filter and pump-intake strainer, making sure all foreign particles are removed; grease the pump follower.
- *Monthly:* Check pump packing gland for leaks and tighten if necessary.
- *Semiannually:* Remove wear plate from pump and inspect impeller and housing for wear; grease fan pillow-block bearings.

Health Hazards and Safety

Blast cleaning operations can be performed without risk to the health or safety of personnel if precautionary measures are followed rigorously. The health hazard that accompanies blast cleaning is silicosis, a disease of the lungs that results from the prolonged breathing of very fine particles of silica sand. In past years, improperly done sandblasting has been the cause of many cases of silicosis, which can be permanently disabling and even fatal. No matter how good the equipment, the operator should be examined by an accredited physician prior to employment and at least once a year thereafter.

Health Precautions. Air blasting of sand-free steel or iron castings and shot blasting of sandy castings produces enough fine silica to make the air dangerous to breathe. The blaster must be protected by a helmet supplied with air, special gauntlets, an apron, and often special leg protection. The blast room enclosure should be well lit (80 footcandles minimum illumination) and should provide ample clear space for walking and maneuvering by the operator. To meet current environmental standards, it should include ventilation and dust collection equipment to clean the air that is drawn through. The air supplied to the worker (about 0.17 m^3/s, or 6 ft^3/min) should be clean, odorless, dry, and free from gaseous contaminants. If taken directly from the compressed-air receiver, it is likely to be wet and malodorous. Use of a carbon monoxide monitoring device with an audible alarm is a mandatory requirement in any application in which breathing air is produced for the operator.

Pickling and Descaling

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Introduction

OXIDE SCALE must be completely removed from hot-worked or hot-rolled steel before subsequent processing is initiated, in order to prevent wear on dies and rolls and avoid surface defects in the final product. This oxide scale originates during the hot working or hot rolling of steel, when the surface of the metal reacts with oxygen in the air to form oxides of iron, or mill scale. The scale actually consists of three iron oxides with different proportions of iron and oxygen. Hematite, Fe_2O_3, which contains 30.1% oxygen, is the outermost oxide in the scale layer, whereas wustite, FeO, with 22.3% oxygen, is the innermost oxide. Magnetite, Fe_3O_4, contains 27.6% oxygen; when all oxides are present, the middle layer in the scale is magnetic. At temperatures above 566 °C (1050 °F), wustite is the predominant oxide, but during cooling below 566 °C (1050 °F), a portion of it is transformed to iron and magnetite ($4FeO = Fe_3O_4 + Fe$). In cases of rapid cooling, which can occur with rod and bar, substantial amounts of wustite are retained in the cooled product. When cooling after hot rolling is relatively slow, as it is with coiled strip, magnetite is the main oxide constituent of the scale in the cooled product.

Pickling is the most common of several processes used to remove the scale from steel surfaces. The term *pickling* refers to the chemical removal of scale by immersion in an aqueous acid solution. The process originated in the late 1700s, when sheets of steel were descaled by immersion in vats of vinegar. Wide variations are possible in the type, strength, and temperature of the acid solutions used, depending on time constraints (batch vs. continuous operations), as well as the thickness, composition, and physical nature (cracks) of the scale. Pickling is applicable for many types of forgings and castings, for merchant bar, blooms, billets, sheet, strip, wire, and for tubing.

Pickling Solutions

For carbon steel, sulfuric acid (H_2SO_4) is used in most batch pickling operations, whereas hydrochloric acid has become the pickling agent of choice, as of 1994, for continuous operations with wire and strip. Hydrochloric acid (HCl) is also used for special purposes, such as etching before galvanizing or tinning. Nitric-hydrofluoric acid mixtures are used to pickle stainless steel. Hydrofluoric acid is sometimes used when pickling castings to remove sand.

Mixtures of hydrochloric and sulfuric acids have been used in batch pickling, often by adding rock salt (NaCl) to a sulfuric acid pickling bath. Such practices might be expected to give the bright, pickled steel surface characteristics associated with hydrochloric acid and to increase pickling rates, but not without some drawbacks. The proportion of HCl to H_2SO_4 that is required to achieve the rapid scale removal rate that is possible with HCl alone is too high to be economical, and the mixed acids cannot be properly handled by many of the spent pickle liquor disposal methods now in use (Ref 1).

Acids other than HCl or H_2SO_4 have been used to remove rust and scale from carbon steel. Citric acid, oxalic acid, formic acid, hydrofluoric acid, fluoboric acid, and phosphoric acid are all capable of removing mill scale from steel, but the rates of removal are generally not regarded as useful or economical for most commercial applications, especially continuous operations.

The mechanism of scale removal, or pickling, by mineral acids involves the penetration of acid through cracks in the scale, followed by the reaction of the acid with the innermost scale layer and base metal. The presence of hydrogen gas, which forms when acid reacts with the base metal, and the dissolution of FeO help detach the outer scale layer from the metal surface. This classical concept of pickling with H_2SO_4 is supported by experimental work and commercial practices that demonstrate substantial increases in scale removal rates when scale cracking is initiated by flexing, temper-rolling (of strip), or tension leveling (Ref 2).

The reaction of H_2SO_4 with FeO or with scale that is substantially Fe_3O_4 mixed with iron will form ferrous sulfate and water:

$$FeO + H_2SO_4 = FeSO_4 + H_2O \quad \textbf{(Eq 1)}$$

$$Fe_3O_4 + Fe + 4H_2SO_4 = 4FeSO_4 + 4H_2O \quad \textbf{(Eq 2)}$$

The reaction of sulfuric acid with base metal forms ferrous sulfate and hydrogen gas:

$$Fe + H_2SO_4 = FeSO_4 + H_2(g) \quad \textbf{(Eq 3)}$$

With hydrochloric acid, descaling primarily involves direct attack on the oxides. However, the penetration of acid through cracks in the scale does contribute to the scale removal process, although the magnitude of the effect resulting from enhanced scale cracking is somewhat less than it is with sulfuric acid (Ref 3). The reaction of HCl with FeO or with scale that is substantially Fe_3O_4 mixed with iron will form ferrous chloride and water:

$$FeO + 2HCl = FeCl_2 + H_2O \quad \textbf{(Eq 4)}$$

$$Fe_3O_4 + Fe + 8HCl = 4FeCl_2 + 4H_2O \quad \textbf{(Eq 5)}$$

The reaction of hydrochloric acid with base metal forms ferrous chloride and hydrogen gas:

$$Fe + 2HCl = FeCl_2 + H_2(g) \quad \textbf{(Eq 6)}$$

Sulfuric Acid Pickling. Sulfuric acid produces satisfactory results when used for batch pickling of carbon steel rod and wire (up to 0.60% C) and for continuous cleaning, if the iron concentration in the bath is less than 8 g/100mL. Table 1 lists the types of carbon and alloy steel products that are pickled in sulfuric acid and the ranges of acid concentrations and temperatures used.

Table 1 Solution concentrations and operating temperatures used for pickling carbon and alloy steel products

Product	Sulfuric acid concentration, wt%		Bath temperature			
			Minimum		Maximum	
	Minimum	Maximum	°C	°F	°C	°F
Bar, low-carbon	7	18	68	155	85	185
Bar, alloy	9	12	66	150	77	170
Billet, low-carbon	7	12	74	165	82	180
Billet, alloy	9	12	82	180	93	200
Pipe for galvanizing	7	15	71	160	88	190

Sheet for galvanizing	4	12	66	150	77	170
Sheet, tin plate (white pickle)	9	12	66	150	85	185
Strip, soft	6	12	77	170	88	190
Strip, alloy and high-carbon	7	12	66	150	77	170
Strip, continuous pickling	23	38	77	170	100	212
Tubing, low-carbon seamless	7	18	77	170	88	190
Tubing, high-carbon and alloy structural	9	18	71	160	93	200
Tubing (over 0.40% carbon)	9	18	60	140	71	160
Wire, soft	4	18	77	170	88	190
Wire, alloy and high-carbon	3	18	55	130	74	165
Fabricated parts (for tinning):						
Initial pickle	5	10	66	150	88	190
Final dip	[a]	[a]	. . .	. . .	38	100

(a) Concentrated hydrochloric acid, 1.14 to 1.16 sp gr

Commercial sulfuric acid is usually supplied at a concentration of 93 wt%, whereas hydrochloric acid is supplied at concentrations of 31 or 35 wt%. Prices for tank car lots of sulfuric and hydrochloric acids vary geographically within the United States. During 1993, costs were similar for 93 wt% sulfuric acid and 35 wt% hydrochloric acid. An advantage of using sulfuric acid is less fuming over pickling solutions. Disadvantages include darker surfaces and the production of smut, particularly on high-carbon steel, as well as a greater inhibiting effect on the sulfuric acid of iron salts in the bath.

Emissions from sulfuric acid pickling may include a spray (droplets of pickling solution resulting from acid attack on base metal that generates hydrogen gas); adequate ventilation must be provided to prevent localized corrosion of equipment and unsatisfactory working conditions.

Hydrochloric Acid Pickling. Hydrochloric acid is preferred for the batch pickling of hot-rolled or heat-treated high-carbon steel rod and wire. Continuous pickling operations also use hydrochloric acid to produce the very uniform surface characteristics required for both low- and high-carbon steel. The possibility of overpickling is minimized in these short-time operations. The acid also dissolves lead oxides that adhere to steel previously heat treated in molten lead baths.

Operating conditions for batch pickling in hydrochloric acid solutions typically involve acid concentrations of 8 to 12 g/100 mL, temperatures of 38 to 40 °C (10 to 105 °F), and immersion times of 5 to 15 min, with a maximum allowable iron concentration of 13 g/100 mL. Operating conditions for continuous pickling in hydrochloric acid solutions typically involve acid concentrations of 2 to 20 g/100 mL, temperatures of 66 to 93 °C (150 to 200 °F), and immersion times of 1 to 20 s.

Hydrochloric acid offers a number of advantages, when compared with sulfuric and other acids. It consistently produces a uniform light-gray surface on high-carbon steel. The possibility of overpickling is less than it is with other acids. Effective pickling can be obtained with iron concentrations as high as 13 g/100 mL. Rinsing is facilitated because of the high solubility of chlorides. The cost of heating the bath for batch-type operations is less than it is with sulfuric acid because of lower operating temperatures. The chief disadvantage of hydrochloric acid is the necessity for a good fume-control system.

Emissions from hydrochloric acid pickling include hydrogen chloride gas and must be adequately vented to prevent localized corrosion of equipment and unsatisfactory working conditions.

Other Acid Mixtures. Excessive contamination of the pickling bath by oiled steel results in nonuniform descaling and staining of the steel. To avoid this problem, oiled steel should be degreased before pickling. When pickling either oiled or degreased steel, the use of a wetting agent in the acid solution increases the effectiveness and efficiency of the bath, thereby reducing immersion time. Many commercial pickling inhibitors are formulated with a wetting agent.

Annealing smut and heavy-metal ions can be removed from the surface of steel to be cold drawn, porcelain enameled, or tin plated by adding sodium ferrocyanide to the acid pickling solution. A solution of sulfuric and hydrofluoric acids can be used to pickle castings that have burned sand embedded in the surface. The relative concentration of each acid is determined by whether the primary objective is sand removal or scale removal.

Determination of Acid and Iron Concentrations in Pickling Baths. Plants frequently report acid and iron-salt concentrations in weight/volume (w/v) units of grams per 100 milliliters (g/100 mL). Although these units are sometimes loosely referred to as "percent," concentrations in g/100 mL must be divided by the density of the solution in grams per milliliter (g/mL) to convert to true weight percent (weight/weight, or w/w, units). For this purpose, approximate equations for calculating densities have been developed from published data on sulfuric acid-ferrous sulfate solutions (Ref 4, 5, 6, 7) and on hydrochloric acid-ferrous chloride solutions (Ref 8, 9):

$$D = 0.9971 + (6.33 \times 10^{-3})\, C_{H_2SO_4} + (9.90 \times 10^{-3})\, C_{FeSO_4} \qquad \textbf{(Eq 7)}$$

$$D = 0.9971 + (4.46 \times 10^{-3})\, C_{\mathrm{HCl}} + (8.15 \times 10^{-3})\, C_{FeCl_2} \qquad \textbf{(Eq 8)}$$

where D is expressed in g/mL at 25 °C (77 °F) and the concentrations, C, of H_2SO_4, ferrous sulfate ($FeSO_4$), HCl, and ferrous chloride ($FeCl_2$) are expressed in g/100 mL.

Equipment for the analysis of pickling solutions should be installed near the pickling operation to monitor acid concentration and to test the solutions at regular intervals. Testing after each acid addition and once or twice during an 8 h shift might be sufficient for batch operations. For continuous operations, which often involve continuous additions of acid, more frequent testing is required, at least once every 2 h. Titration methods for acid and iron concentrations in solutions are widely used. The calculations follow from the stoichiometric relationships between the reactants and products.

With sulfuric acid solutions, add 75 to 100 mL of distilled water and two or three drops of methyl orange indicator to a 5 mL sample. A burette containing a 1.02 *N* sodium hydroxide solution is used to titrate until the red color changes to yellow. The sample solution should be agitated during the titration. Each milliliter of sodium hydroxide solution is equivalent to 1 g H_2SO_4 per 100 mL of pickling solution. The concentration of H_2SO_4 in g/100 mL is determined by:

$$C_{H_2SO_4} = (\text{mL NaOH} \times N \times 0.0490 \times 100)/\text{mL sample} \qquad \textbf{(Eq 9)}$$

where N is the normality of the NaOH solution. With hydrochloric acid solutions, an analogous procedure is used. If a 1.37 N sodium hydroxide solution is used to titrate, each milliliter of this solution is equivalent to 1 g HCl per 100 mL of pickling solution. The concentration of HCl in g/100 mL is determined by:

$$C_{HCl} = (\text{mL NaOH} \times N \times 0.0365 \times 100)/\text{mL sample} \qquad \textbf{(Eq 10)}$$

To determine the concentration of iron in either sulfuric acid or hydrochloric acid pickling solutions, add 25 mL of distilled water and approximately 5 mL of concentrated sulfuric acid to a 5 mL sample and titrate with 0.895 N potassium permanganate to a purple end point. Potassium permanganate, an oxidizing agent, converts ferrous iron to ferric iron. Each milliliter of the potassium permanganate solution is equivalent to 1 g Fe/100 mL of pickling solution. The concentration of iron in g/100 mL is determined by:

$$C_{Fe} = (\text{mL } KMnO_4 \times N \times 0.0558 \times 100)/\text{mL sample} \qquad \textbf{(Eq 11)}$$

where N is the normality of the $KMnO_4$ solution. To calculate the concentration of ferrous sulfate in a sulfuric acid solution and the concentration of ferrous chloride in a hydrochloric acid solution, the calculated concentration of iron is multiplied by the factors 2.72 and 2.27, respectively.

The determination of acid and iron concentrations in hydrochloric and sulfuric acid pickling solutions is often carried out with automatic titration equipment. Concentrations of acid and iron can also be estimated from conductivity and density measurements made on pickling solutions (Ref 10).

Mixtures of nitric and hydrofluoric acids are used to pickle stainless steel. Fluoride-selective electrodes are used to control hydrofluoric acid additions on some lines (Ref 11). If the nitric acid concentration is known, it can be subtracted from total acid to estimate hydrofluoric acid. The complexing ability of hydrofluoric acid in nitric-hydrofluoric acid solutions has been determined using an automatic process titrator in a technique that involves a known addition of ferric nitrate to a sample of pickling solution, followed by titrations to determine uncomplexed iron (Ref 12).

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Inhibitors

Inhibitors are added to acid pickling solutions in order to:

- Minimize acid attack on the base metal with excessive loss of iron
- Avoid pitting associated with overpickling, which contributes to poor surface quality
- Reduce acid solution spray resulting from hydrogen that forms when acid attacks steel
- Lower acid consumption
- Minimize the risk of hydrogen embrittlement

When used at appropriate concentrations, inhibitors should not appreciably affect the rate of scale or rust removal.

A number of additives have been used in pickling solutions to inhibit acid attack on metals. Natural products, such as bran, gelatin, glue, byproducts from petroleum refining and coal coking, and wood tars were initially used. Modern inhibitors are largely formulations of wetting agents with mixtures of active synthetic materials, including nitrogen-base compounds (pyridine, quinidine, hexamethylene tetramine, and other amines or polyamines), aldehydes and thioaldehydes, acetylenic alcohols, and sulfur-containing compounds such as thiourea and thiourea derivatives (Ref 13). Frequently, two or more active ingredients provide a synergistic effect, whereby the mixture is more effective than the additive effect of the individual components. A good inhibitor should not exhibit "breakout," which is sludge that deposits on the work, a characteristic of many of the natural products formerly used. It should be stable at the temperature of the pickling bath and should not emit offensive odors. Modern inhibitors used with sulfuric acid often contain thiourea or a substituted thiourea with an amine. Most of the newer inhibitors developed for use with hydrochloric acid contain amines or heterocyclic nitrogen compounds as active ingredients.

In sulfuric acid pickling, the ferrous sulfate buildup in a worked pickling bath also inhibits the activity of the acid and reduces the effectiveness of the solution for cleaning and brightening the steel. Most steels are reactive with acid and require inhibited solutions. Steels with high phosphorus contents (0.03% or above) are particularly prone to overpickling. Inhibited acid solutions are generally used in continuous strip lines and in oil well drilling operations to clean the internal surfaces of pipes. Although the immersion times during continuous strip pickling are substantially shorter than in batch operations, an excessive loss of base metal would occur during a line stop if inhibitors were not used. This would not only be objectionable because of the roughened overpickled surface, but also because of the effect on critical final-gage requirements of the product.

In commercial practice, inhibitor concentrations are usually expressed in terms of percent by volume of the makeup acid used, because most inhibitors are liquids. For example, if an addition of 0.9 L (0.25 gal) of inhibitor is made with 380 L (100 gal) of concentrated acid, then the concentration of inhibitor is said to be 0.25 vol% of the acid. Additions are best made proportional to the acid additions to pickling tanks or to the acid volume in large storage tanks or truckload shipments of acid. A poor method of introducing inhibitor to pickling solutions is by adding inhibitor to the bath at certain time intervals that are not related to actual acid additions. Before inhibitor additions are made, the bath may be underinhibited, and just after additions are made, the bath might be overinhibited.

It is generally agreed that the primary step in the action of inhibitors in acid solutions is adsorption onto the metal surface. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical processes of the corrosion. When inhibitor concentrations are much below recommended levels, the adsorbed layer of inhibitor on the steel surface may be incomplete, which can result in preferential attack on unprotected areas.

To help control inhibitor concentrations in pickling solutions, inhibitor manufacturers have proposed the inclusion in their formulations of various materials that can be used as tracers in determining inhibitor concentration. One scheme involved the use of fluorescent dyes and colorimetric analyses. However, because of color changes in the dye with time, this approach has not proven satisfactory. Another possibility is the inclusion of phosphates or phosphoric acid, which can be detected in either sulfuric or hydrochloric acid pickling solutions by colorimetric procedures. Inclusion of lithium salts with subsequent analyses by neutron activation or atomic absorption spectrometry also has been tried. For amine-based inhibitors, concentrations in pickling solutions can be estimated by determining the nitrogen concentration in the solution and comparing it with the known nitrogen concentration in the neat inhibitor. Analyses can be made by the Kjeldahl method, or if the inhibitor contains simple amines rather than heterocyclic amines, by using an ammonia selective ion electrode with suitable standards.

Before a new inhibitor is introduced in a plant, some laboratory tests should be made to identify concentration dependence of inhibition under conditions appropriate for a particular operation. The degree of acid attack on the base metal can be measured by determining the weight loss or hydrogen evolution from a steel specimen of known size and weight that is immersed for a specified time in a solution containing known amounts of acid, iron salts, and inhibitor at a temperature typical of use. Results of inhibitor testing are often expressed as percent inhibition, defined as: 100 × [(weight loss, uninhibited) -- (weight loss, inhibited)] divided by (weight loss, uninhibited). This relationship is useful when a number of inhibitors are being compared under a selected set of conditions. A value of 90% inhibition, associated with proper usage of an effective inhibitor, implies that the corrosion rate is only 10% of the rate when no inhibitor is used.

For plain carbon steels containing less than 0.40% C, and for batch pickling baths that contain 10 to 14 wt% sulfuric acid (1.82 sp gr) and operate at 71 °C (160 °F) or higher, strong inhibitors are used at concentrations of 0.25 to 0.50 vol% raw acid in the tank. When the concentration of ferrous sulfate reaches 30 wt%, the solution should be discarded, because this level of iron salt slows down the pickling process and may cause smut to form on the surface of the product. When iron levels approach this concentration in batch pickling with sulfuric acid, further additions of inhibitor may not be required.

Plain carbon steels containing 0.40% C or more are pickled in similar baths with somewhat lower temperatures (60 to 66 °C, or 140 to 150 °F) and with ferrous sulfate concentrations of less than 20 wt%. With hydrochloric acid, strong inhibitors are used at concentrations of 0.125 to 0.25 vol% of raw acid. Because pickling rates in both sulfuric acid and hydrochloric acid tend to decrease when the pickling solution contains high levels of iron (higher levels are tolerable with HCl), especially when coupled with low acid concentration, commercial pickling bath additives, or accelerators, are sometimes used to enhance pickling rates. These proprietary materials are usually formulated with inhibitors to prevent excessive base-metal attack by the acid during scale dissolution.

Uninhibited acid solutions are often used for pickling high-alloy steels, because more chemical action is required to remove the oxide. Alloy or plain carbon steels used in forming flat and shaped sections are sometimes etched by uninhibited acid solutions to produce a surface that retains the die lubricant during cold working. These solutions are used also for conditioning steel with slivers and sharp corners, as well as steel that is ground before coating for additional cold working. If an inhibitor is used when pickling alloy steels, concentrations that are somewhat less than those recommended for plain carbon steels are suggested.

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Precleaning

Alkaline precleaning before acid pickling is beneficial for removing soils that do not readily react with acid, such as grease, oil, soaps, lubricants, and carrier coatings. A buildup of such materials in a pickling bath interferes with the pickling action, especially when the pickling time is short (20 s or less). A typical alkaline cleaning solution contains 20% sodium hydroxide, 30% organic chelating agents, 45% complex phosphates, and 5% surface-activating agents. The concentration of the cleaner in the precleaning solution is 30 to 45 g/L (4 to 6 oz/gal), and the operating temperature of the solution ranges from 82 °C (180 °F) to boiling. After immersion in the cleaning solution, the work is rinsed in water at room temperature.

Chelating Agents. Lubricants used in cold-drawing operations contain compounds of calcium, zinc, magnesium, iron, or some other metal. Removal is facilitated when alkaline cleaners containing chelating agents are used. Chelates react with the metal ion to form a soluble metal chelate. Chelates include citric acid, ethylene diamine tetraacetic acid, gluconic acid, and nitrilotriacetic acid. Although all chelating agents react in a similar manner, certain chelates have a greater affinity for specific metal ions. The solution must contain an adequate amount of chelate and be of the proper pH (usually, basic) for effective cleaning. Chelates must be stable with respect to the particular environment (oxidizing or reducing, acid or alkaline).

A procedure for determining the chelating power of the alkaline cleaning formula consists of mixing 10 mL of filtered cleaning solution with 10 mL of distilled water and 10 drops of saturated 5% ammonium oxalate solution. This mixture is then titrated carefully with a 2% solution of calcium chloride until one drop of the latter produces a faint, permanent turbidity. The number of milliliters of 2% calcium chloride required is equivalent to the chelating power.

Equipment

Storage Tanks for Acid. Hydrochloric acid can be stored in rubber-lined steel tanks or glass-fiber-reinforced polyester-resin tanks. Polyester-glass linings in steel tanks are not recommended, because permeation of acid through pinholes in the lining could result in attack on the steel. Hydrofluoric acid (70%) is usually stored in plastic-lined tanks, although low-carbon steel can be used at temperatures up to 38 °C (100 °F) if properly passivated. Concentrated nitric acid (94.2% or higher) is best stored in tanks made of 3003 aluminum. For less concentrated nitric acid, tanks should be of type 304L stainless steel (type 304 annealed stainless for nonwelded construction) or 15 to 16% high-chromium iron. Dilute sulfuric acid is more corrosive to iron and steel than more concentrated acid. A 93.2% sulfuric acid can be stored in iron tanks over a wide range of temperatures, but a 77.7% sulfuric acid must be stored below 38 °C (100 °F). A ≤74.4% sulfuric acid cannot be stored in unlined iron tanks or carried through unlined iron pipes. A glass or phenolic lining, among others, can be used.

Batch Pickling Tanks and Auxiliary Equipment. Construction materials for pickling tanks include wood, concrete, brick, plastic, and steel. Acid-resistant linings provide protection for the outer shell of the tank and are commonly made from natural, pure gum, or synthetic rubber. Acid-resistant brick is used to line the sides and floor of the tank. Bricks are mortared with poured sulfur cement or an acid-resistant resinous cement. Drainage lines should be made of vitrified tile caulked with an acid-resistant cement. Figure 1 shows the materials used in constructing a 3.5 to 4.4 Mg (3.9 to 4.9 ton) capacity tank for the pickling of coiled steel. In a batch pickling operation, bar product to be pickled is placed in tiers on crates and racks made of an acid-resistant material, such as Monel metal. Coils of strip, rod, or wire are pickled by passing a C-hook or chain through the open center. The holders are raised and lowered by an overhead crane.

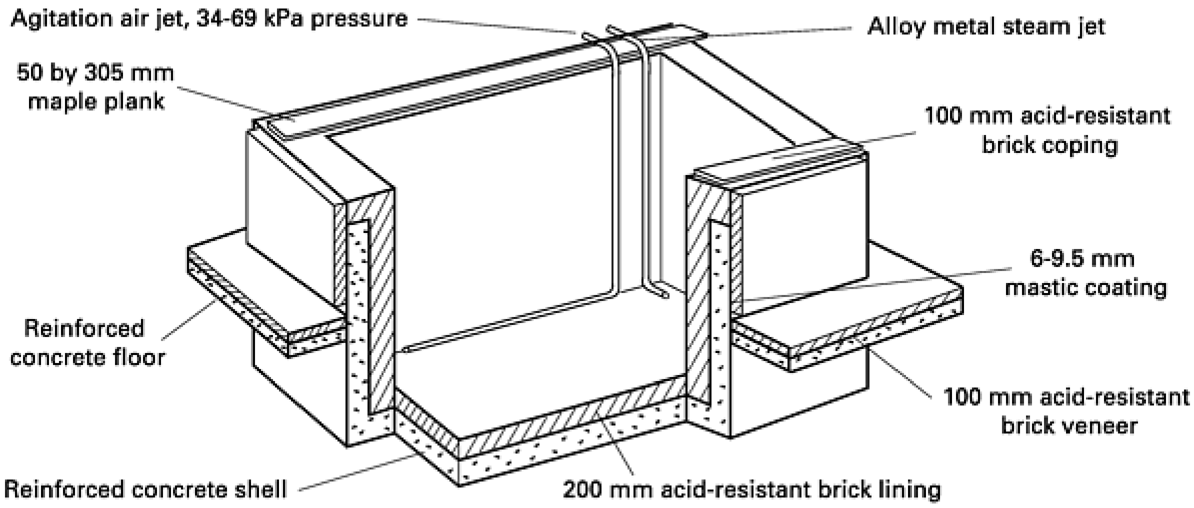

Fig. 1 Materials used in construction of 3.5 to 4.4 Mg (3.9 to 4.9 ton) capacity tanks for pickling coils of steel

After pickling, the product should be rinsed with high-pressure cold-water sprays to remove excess acid solution. It should then be placed in a hot-water rinse tank with sufficient overflow to ensure that the pH is not less than 5 or 6.

Heating Methods and Temperature Control. In the past, the most widely used method of heating pickling solutions was the direct injection of live steam through steam jets. Although steam so introduced does provide some agitation of the solution, the steam condensate dilutes the pickling solution, requiring higher amounts of acid to be added to maintain concentration. Steam sparging also increases the volume of spent pickle liquor. Better heating methods include coil steam heat, heat interchangers, and, for small installations, electric immersion heaters. Heating equipment must be made of acid-resistant materials, such as carbon, lead alloy, stainless steel, or zirconium for use with sulfuric acid. Carbon and polytetrafluoroethylene-covered heat exchangers should be used with hydrochloric acid. Acid-resistant indicating and regulating temperature-control instruments are available for pickling solutions. Heaters can be centrally located or, in the case of continuous pickling, placed at strategic intervals along the tank.

Continuous-Strip Pickling Lines. A few pickling lines make use of vertical towers in which one or two hydrochloric acid spray columns are used (Ref 14, 15). The acid spray columns are assembled and sealed in sections made of fiberglass-reinforced polyester, with a tower height of 21.3 to 45.7 m (70 to 150 ft). The tank sections are made from rubber-lined steel. After use, acid flows into a sump and is returned to the circulating tank. The composition of the acid in the recirculation tank is typically maintained at 11 g/100 mL HCl and 13% $FeCl_2$. It is passed through a carbon-block heat exchanger and delivered to the sprays at 77 °C (170 °F). Most lines of this type have acid-regenerating facilities. Entry and exit coil handling are similar to the more common horizontal lines.

Continuous-strip pickling lines with horizontal pickling tanks are capable of handling coils that are welded head to tail. The entry section comprises a coil conveyer, one or two uncoilers, one or two processors, one or two shears, and a welder. Processors are integral with the uncoiling equipment and consist of a mandrel, hold-down roll, and a series of smaller-diameter rolls. As the strip is flexed through the processor, some cracking occurs in the scale layer, although not nearly as much as that imparted by a temper mill. Proper welding and weld trimming is essential to avoid strip breaks in the line. The section prior to the pickling tanks uses bridles for tensioning the strip; a strip accumulator, either in the form of wet looping pits or, for more modern lines, a coil-car accumulator; and, for many lines, a temper mill to crack the scale on the surface of the strip. A stretch leveler can replace the temper mill and not only effectively cracks the scale, but also contributes to superior strip shape.

The pickling section usually contains three or more tanks. So-called "deep tanks" are typically 1.22 m (4 ft) in depth and up to 31.3 m (90 ft) in length. Acid tanks are steel shells with layers of rubber bonded to the steel. The rubber is protected from abrasion by a lining of silica-base acid-proof brick. Most lines have a cascade flow of pickling solutions countercurrent to the direction of strip movement. When fresh acid is added to the last tank, it will contain the highest concentration of acid. Acid concentrations will decrease from the last tank to the first tank, from which the spent pickle liquor is discharged. A rinse section follows the pickling section.

An especially effective rinsing method used on many continuous lines is the cascade rinse system (Ref 16). Several rinse compartments are used, and fresh water is added to the last compartment. The solution in that compartment cascades over weirs into the preceding compartments. The excess overflows from the first compartment and is sent to the waste-water treatment plant (a portion can be used for makeup water in the pickle tanks). Each compartment contains less acid than the previous compartment. At the exit end of the line, there are usually an exit strip accumulator, steering rolls, a strip inspection station, dual side trimmers, an oiler, and two coilers. Pickling lines must have fume scrubbers to capture emissions/spray from the pickle tanks.

In some modern lines, the pickling solution is contained in shallow tanks with liquid depths of approximately 0.41 m (16 in.) and lengths up to approximately 36 m (118 ft). Although they involve a cascade system, the solution in each tank is recirculated through a heat exchanger. During a line stop, the pickling solution can be rapidly drained from shallow tanks into individual storage tanks and then pumped back when the line starts up. Lines with deep tanks usually have strip lifters provided to remove the strip from the acid solution during an extended line stop. Tank covers may be made from fiberglass or polypropylene. Some lines have squeegee rolls, covered with acid-resistant rubber, located above and below the strip at each tank exit to minimize acid carryover from one tank to another.

Maximum speeds in modern lines in the pickling section can be as high as 305 to 457 m/min (1000 to 1500 ft/min). Although sustained operation at such speeds is limited by other aspects of coil handling, the selection of pickling tank acid concentrations and temperatures must be such that complete scale removal is achieved during periods of high-speed operation. The combination of a pickling line and a cold reduction mill in tandem represents a new state of the art in continuous processing facilities (Ref 17). Another type of strip pickling line suitable for plants with moderate production requirements is the push-pull type, which has many of the features of the continuous-type lines, but no welder (Ref 18). Turbulent-flow, shallow-tank, continuous-strip lines that claim to provide more effective pickling action than conventional lines have been developed (Ref 19).

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Effect of Process Variables on Scale Removal in Sulfuric Acid

The composition of scale on hot-rolled strip is primarily influenced by the cooling rate after coiling. When pickling with sulfuric acid, this is important because conditions that increase the amount of FeO in the scale (rapid cooling) render it more easily pickled (Ref 20, 21). With hydrochloric acid, the solubility of Fe_3O_4 is significantly greater than it is in sulfuric acid (Ref 22). Therefore, the relative amounts of FeO versus Fe_3O_4 in the scale layer are of less importance with hydrochloric acid. As the coiling temperature after hot rolling is increased, the scale thickness increases and pickling rates decrease (Ref 23).

The degree to which pickling rates are affected by concentrations of sulfuric acid and ferrous sulfate, as well as by temperature, is illustrated in Fig. 2 and 3. These bench-scale tests were made with specimens cut from the center and tail end of a hot-rolled coil (2.0 mm, or 0.080 in., thickness) of low-carbon drawing-quality steel. The respective scale thicknesses were 2.6 mg/cm^2 (0.00475 mm, or 0.000187 in.) and 5.2 mg/cm^2 (0.00953 mm, or 0.000375 in.). As might be expected, specimens with thicker scale required longer immersion times for scale removal than specimens with thinner scale under the same bath conditions. The time to remove scale decreased with increases in temperature from 80 to 100 °C (175 to 212 °F) and with increases in acid concentration from 5 to 25 g/100 mL. With sulfuric acid, increases in the concentration of ferrous sulfate exert an inhibiting action that increases the time for scale removal. The effect is greater when acid concentrations are 10 g/100 mL or lower. Pickling efficiency in a bath decreases with time, unless fresh acid additions are made, because the acid concentration drops while the ferrous sulfate concentration increases. Increased agitation in the bath increases the pickling rate. When specimens with thick scale are pickled in acid solutions of 10 g/100 mL or lower, increases in inhibitor concentration tend to slow down the pickling action.

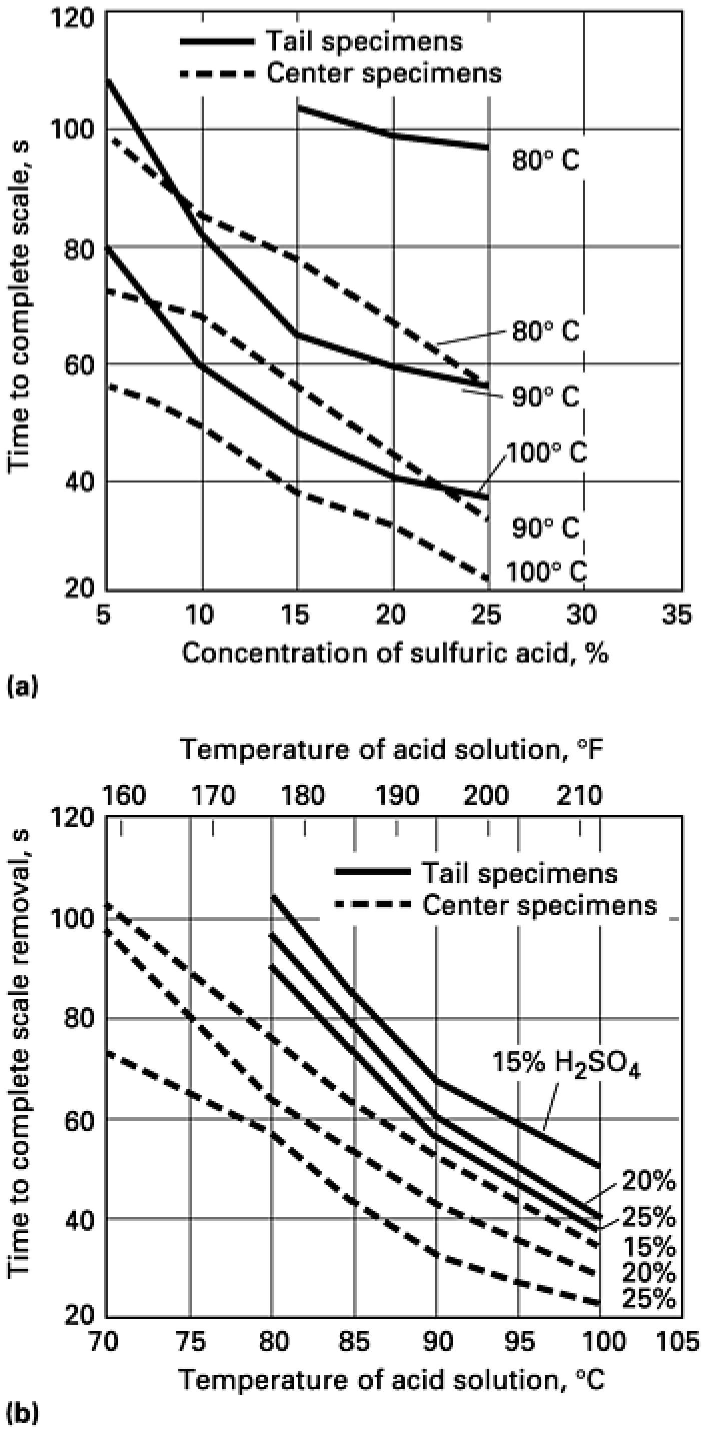

Fig. 2 Effect of acid concentration (a) and temperature of acid solution (b) on pickling time required to remove scale from sheet steel, 2 mm (0.080 in.) thick

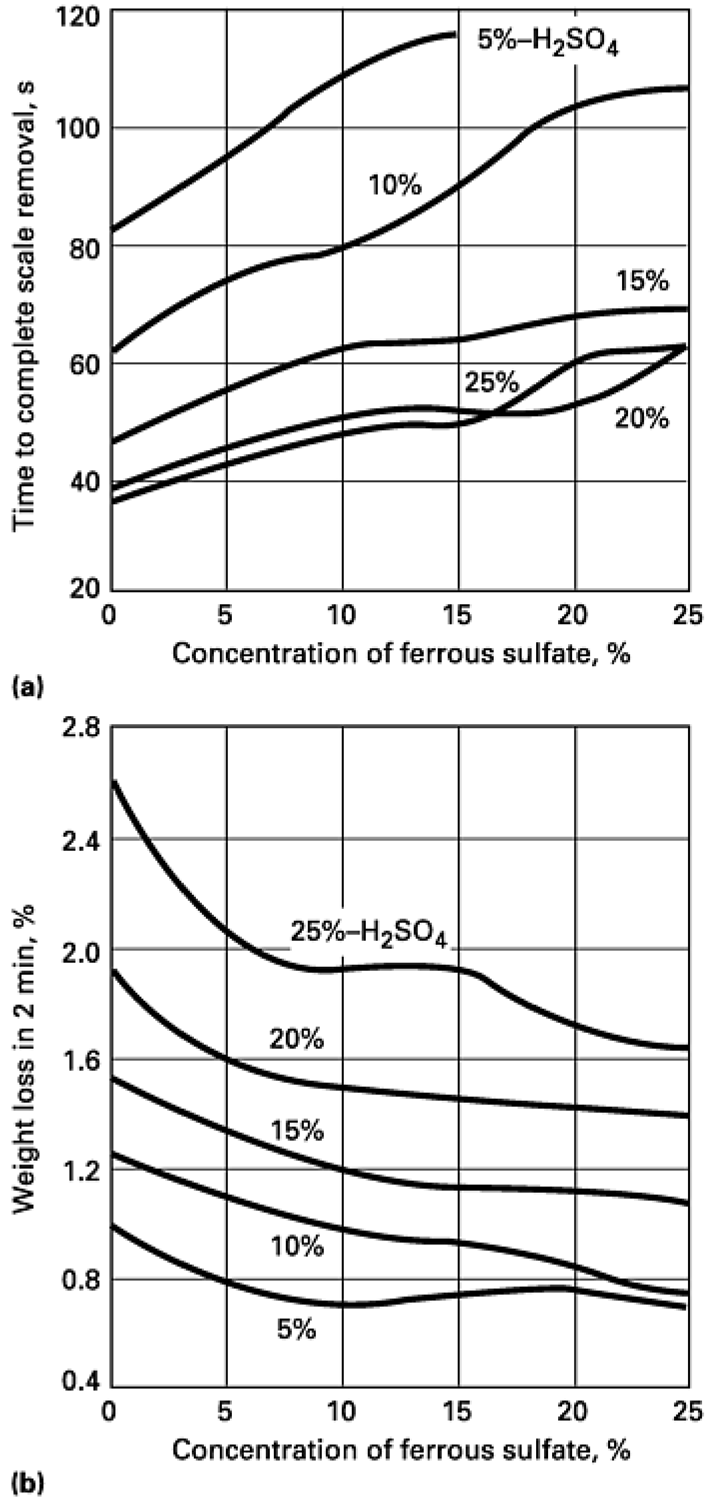

Fig. 3 Inhibiting action of ferrous sulfate on low-carbon drawing-quality sheet pickled for 2 min in sulfuric acid solutions of concentrations indicated. (a) Pickling time for complete scale removal. (b) Weight loss

In a separate bench-scale study (Ref 24), it was found that the influence of temper mill scale breaking (cracking the scale by imposing moderate room-temperature deformation to the workpiece) on the descaling time of hot-rolled strip in sulfuric acid solutions is pronounced. Descaling time is frequently half or less the amount required in a given solution without temper mill scale breaking, as illustrated in Fig. 4. The results of bench-scale experiments (unstirred solutions) with a commercial hot-rolled low-carbon steel with a scale weight of 3.4 mg/cm^2 (0.0062 mm, or 0.00024 in.) are also shown in Fig. 4. For nontemper-rolled material, descaling times were decreased as the temperature increased from 82 to 105 °C (180 to 220 °F). The pickling times achieved by increasing the temperature from 93 to 105 °C (200 to 220 °F) were about the same as those that resulted from maintaining the temperature at 93 °C (200 °F) and using temper mill scale breaking (3%) before pickling.

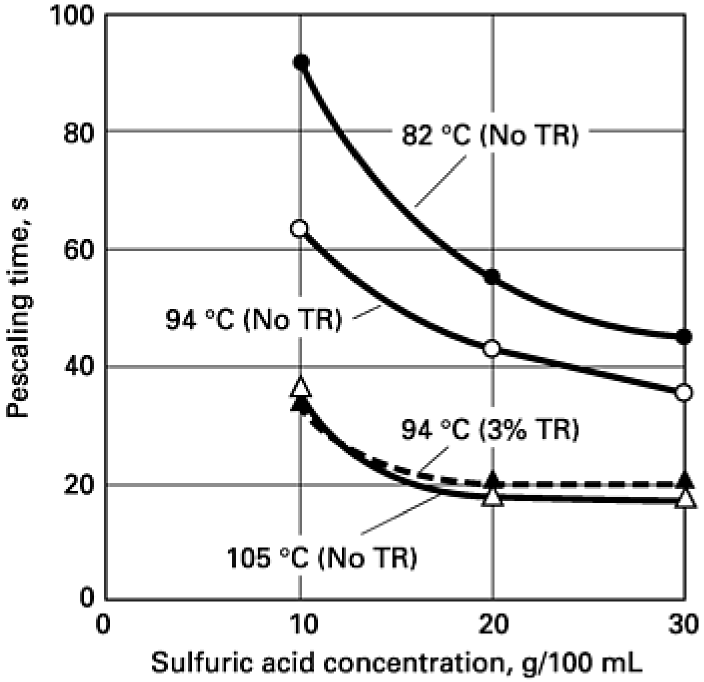

Fig. 4 Effect of solution temperature on pickling time for hot-rolled low-carbon steel; comparison with temper mill scale breaking. All solutions contained 15 g $FeSO_4$/100 mL. TR, temper rolled

Because the reductions in strip thickness introduced by temper rolling are relatively small, the effect of strip thickness profiles must be considered when used on pickling lines. *Crown* is an increase in thickness of the rolled center of strip as compared with the edges. For strip with some crown and feather edges, if the amount of reduction used for temper mill scale breaking is based on the center area with crown, then the thinner edge areas may not receive enough reduction to effectively crack the scale and enhance pickling. Commercial experience indicates that stretch leveling is at least as effective in cracking the scale as the use of a temper mill.

Decreases in pickling rates caused by increases in ferrous sulfate concentration were found to be less pronounced for more concentrated acid solutions. The time required for scale removal in tests at 93 °C (200 °F) was not affected by inhibitor usages up to 0.25 vol%, based on concentrated acid, but did increase when usages exceeded 0.50 vol% (0.25 or 0.50 gal inhibitor, respectively, per 100 gal concentrated acid).

The effect of strip speed, as well as the combined effects of acid and iron concentration, temperature, inhibitor usage, and degree of scale breaking on the pickling process was determined by using an apparatus constructed to simulate the motion of strip through a continuous-strip pickling line. Steel specimens were mounted on a cylindrical holder that could be rotated through a pickling solution. The solution was contained in a holder that had baffles to minimize bulk movement of the solution (Ref 2). Over the range of acid concentrations from 10 to 30 g/100 mL, descaling times were lowered by increases in strip speed from 0 to 30.5 m/min (0 to 100 ft/min), but the magnitude of the effect was not as great as that associated with hydrochloric acid solutions (which will be discussed below.) Only small decreases in descaling time were observed from 30.5 to 122 m/min (100 to 400 ft/min). Data obtained at a strip velocity of 122 m/min (400 ft/min), summarized in Table 2, should be pertinent to commercial continuous pickling in which line speeds can range from 1.5 to 6 m/s (300 to 1200 ft/min) or higher. Laboratory tests made with a well-stirred solution (mechanical stirring of 500 rev/min or greater) should give similar results to those in Table 2.

Table 2 Laboratory pickling tests using sulfuric acid solutions to remove scale from hot-rolled ingot cast steel

Temperature		**Sulfuric acid concentration, g/100 mL**	**Ferrous sulfate concentration, g/100 mL**	**Time to remove scale, s**			
°C	**°F**			**0%(a)**	**1.5%(a)**	**3%(a)**	**4.5%(a)**
82	180	10	15	90	. . .	. . .	. . .
82	180	20	15	55	. . .	. . .	. . .
82	180	30	15	45	. . .	. . .	. . .
93	200	10	10	55	. . .	. . .	. . .
93	200	20	10	30	. . .	. . .	. . .
93	200	30	10	30	. . .	. . .	. . .
93	200	5	15	. . .	. . .	15	. . .
93	200	10	15	70	20	10	10
93	200	20	15	50	15	10	5
93	200	30	15	40	15	10	5
93	200	10	20	70	. . .	. . .	. . .
93	200	20	20	40	. . .	. . .	. . .
101	214(b)	10	15	40	. . .	. . .	. . .
103	217(b)	20	15	30	. . .	. . .	. . .
106	222(b)	30	15	20	. . .	. . .	. . .

(a) Degree of temper mill scale breaking in percent temper rolled.

(b) Solutions were at the boiling point during the test.

The time required to remove scale from hot-rolled strip in stirred sulfuric acid solutions is significantly decreased by temper mill scale breaking. For nontemper-rolled material, pickling at temperatures near the solution boiling point (as high as 105 °C, or 222 °F) resulted in scale removal times that were about half those found at 82 °C (180 °F). At 93 °C

(200 °F), a typical solution temperature on commercial continuous-strip lines that use sulfuric acid, the benefit to be derived by temper mill scale breaking is much greater than would be achieved if the steel were pickled at higher temperatures without temper rolling. Without temper mill scale breaking, the time required to remove the scale was lowered by increasing the acid concentration from 10 to 30 g/100 mL and decreasing the ferrous sulfate concentration from the 15 to 20 g/100 mL range to 10 g/100 mL. An effective commercial inhibitor, even when used at twice the recommended concentration (0.25 vol% based on the makeup H_2SO_4), did not affect descaling rates. However, an effective accelerator does increase scale removal by as much as 30%.

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Effect of Process Variables on Scale Removal in Hydrochloric Acid

The effect of hydrochloric acid and ferrous chloride concentrations, solution temperature, and scale breaking on pickling rates was studied in a series of laboratory tests with nonstirred solutions (Ref 24). It was found that the time required for scale removal decreases with increases in acid concentration and with increases in temperature. For an ingot-cast low-carbon steel with a scale thickness of 3.6 mg/cm^2 (0.0066 mm, or 0.00026 in.), test data for nontemper-rolled specimens in solutions that contain from 1 to 14 g HCl/100 mL and up to about 30 g $FeCl_2$/100 mL at temperatures of 66 to 93 °C (150 to 200 °F) can be summarized by an empirical equation:

$$\log t = A + B \log C_{\mathrm{HCl}} + D\,(T_{\mathrm{F}} + 459)^{-1} \qquad \textbf{(Eq 12)}$$

where t is time in seconds for scale removal, C_{HCl} is acid concentration in g/100 mL, and T_{F} is the solution temperature in degrees Fahrenheit. For this steel, A = -2.22, B = -0.87, and D = 2824. From a limited number of tests made with specimens subjected to temper mill scale breaking, it was concluded that the times calculated by this equation are lower by approximately 10%. Inhibitor usages up to 0.50 vol% based on free acid did not affect time for descaling. The influence of iron buildup in hydrochloric acid solutions on pickling rate was not nearly as pronounced as the effect of iron buildup in sulfuric acid solutions.

In a subsequent study (Ref 3), the effect of strip speed on pickling time in hydrochloric acid was investigated. It was found that the time for scale removal decreased with an increase in strip velocity from 0 to ~1.3 m/s (0 to ~250 ft/min) (Fig. 5). As strip speeds were increased from 1.3 to 4 m/s (250 to 800 ft/min), there was no further decrease in descaling time. As expected, times were lowered by temperature increases from 66 to 93 °C (150 to 200 °F). The observed velocity effects for hydrochloric acid were greater than those observed for pickling in sulfuric acid, probably because of the depletion of acid that occurs near the steel surface during pickling in an unstirred bath and the higher acid concentrations usually used with sulfuric acid. Because descaling time in hydrochloric acid does not change for strip velocities above 1.3 m/s (250 ft/min), a number of tests carried out at 2 m/s (400 ft/min) are believed pertinent to continuous operations in which speeds can range from 1.5 to 6 m/s (300 to 1200 ft/min) or higher. These results were summarized by an empirical equation of the same form as that developed from still-bath data, except that A = -4.46, B = -0.56, and D = 3916. Similar equations have been obtained for other steels where coefficients A and B are negative and D is positive. For slow-pickling steels, A becomes less negative, whereas for fast-pickling steels, A becomes more negative. Equations of this type are useful for predicting the effect of changes in hydrochloric acid concentration and temperature on pickling time.

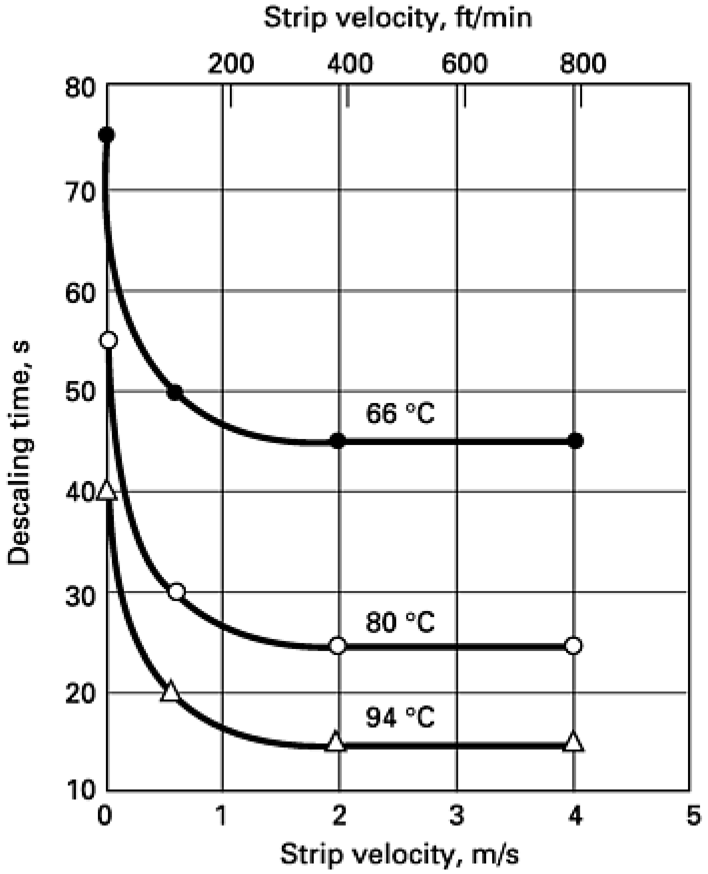

Fig. 5 Effect of strip velocity on descaling time of hot-rolled low-carbon steel in 4 g hydrochloric acid/100 mL, 22.7 g $FeCl_2$/100 mL

The effect of solution concentration and temperature on pickling has been studied in well-stirred hydrochloric acid solutions for aluminum-killed continuous-cast hot-rolled steels subjected to low coiling temperatures (LCT) of 566 to 593 °C (1050 to 1100 °F) and high coiling temperatures (HCT) (721 °C, or 1330 °F) after various degrees (up to 5%) of temper mill scale breaking (Ref 1). The average scale thickness on these steels was, respectively, 3.5 mg/cm^2 (0.0063 mm, or 0.00025 in.) and 5.0 mg/cm^2 (0.0090 mm, or 0.00036 in.). Pickling tests were made on temper-rolled and nontemper-rolled material at temperatures of 66 and 88 °C (150 and 190 °F) in uninhibited solutions that contained from 2 to 16 g HCl/100 mL and with 16 to 18 g $FeCl_2$/100 mL. The time required for complete removal of scale during pickling of nontemper-rolled LCT and HCT steels is shown in Fig. 6. The time required for complete removal of scale during pickling of these steels after 3% temper rolling is shown in Fig. 7. The data can be summarized using equations of the type mentioned above. Decreases in time for scale removal, going from 0 to 3% temper mill reduction, are much greater than the decrease in time associated with an increase in temper mill reduction from 3 to 5% (Table 3).

Table 3 Comparison of pickling times required for scale removal from hot-rolled AK-CC steels, as influenced by HCl concentration, solution temperature, degree of temper mill scale reaking and hot strip mill coiling temperature

Calculated from prediction equations developed for these steels. Solutions contained from 16 to 18 g $FeCl_2$/100 mL.

Temperature		**Hydrochloric acid concentration, g/100 mL**	**Steel**[(a)]	**Time to remove scale, s**		
°C	**°F**			**0%**[(b)]	**3%**[(b)]	**5%**[(b)]
65	150	2	LCT	52	34	25

65	150	6	LCT	28	18	13
65	150	10	LCT	20	13	10
65	150	16	LCT	16	10	7
65	150	2	HCT	114	43	22
65	150	6	HCT	61	23	12
65	150	10	HCT	46	17	9
88	190	2	LCT	25	19	16
88	190	6	LCT	13	10	8
88	190	10	LCT	10	8	6
88	190	2	HCT	42	27	20
88	190	6	HCT	22	14	11
88	190	10	HCT	17	11	8

(a) Based on hot strip mill coiling temperature. LCT, low coiling temperature; HCT, high coiling temperature.

(b) Degree of temper mill scale breaking in percent temper rolled

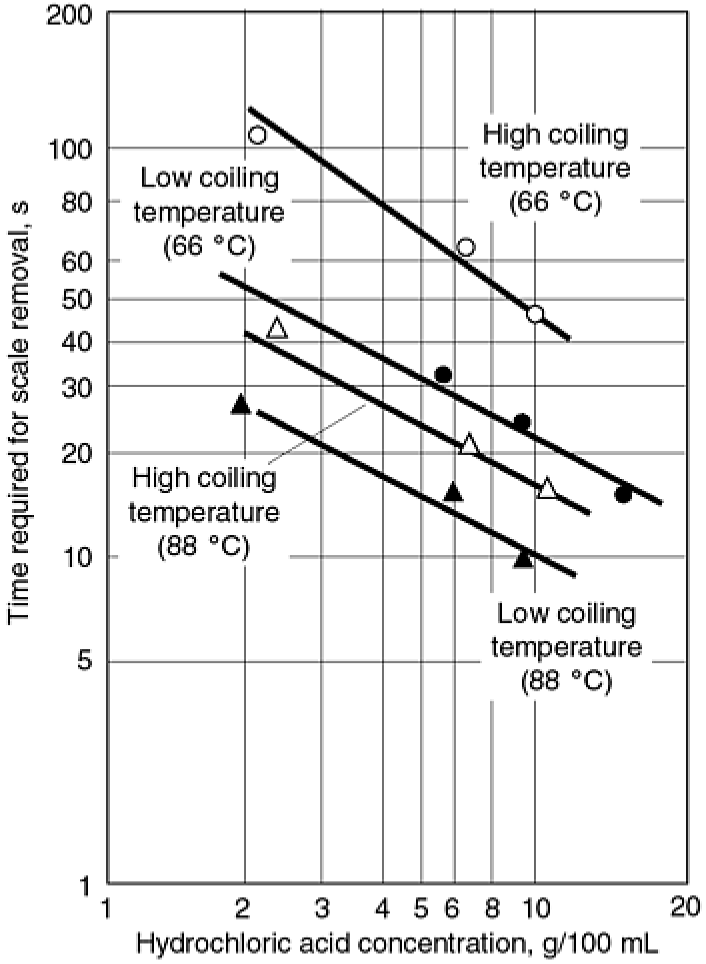

Fig. 6 Influence of acid concentration and solution temperature on time required for scale removal from hot-rolled strip, where strip was not subjected to temper mill scale breaking

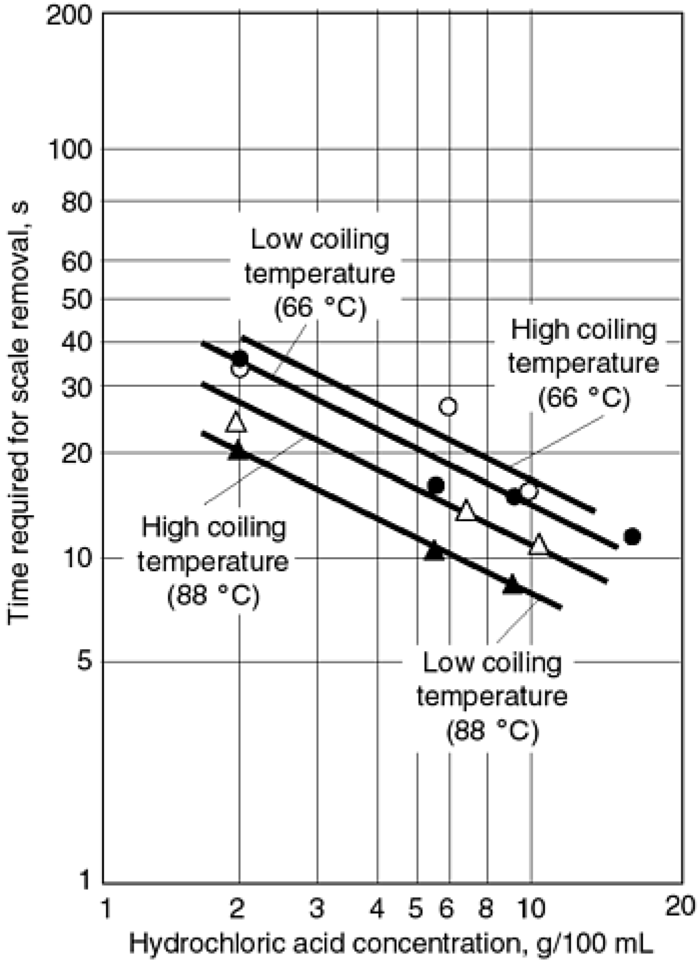

Fig. 7 Influence of acid concentration and solution temperature on time required for scale removal from hot-rolled strip, where strip was subjected to temper mill scale breaking (3% reduction)

For both LCT and HCT steels, the relative importance of degree of temper mill scale breaking is much greater for a solution temperature of 66 °C (150 °F) than it is for 88 °C (190 °F). Without scale breaking, the time required for scale removal under the same conditions of acid concentration and solution temperature is substantially longer for the HCT steel than for the LCT steel. With adequate scale breaking (3% or more reduction), and when using acid concentrations and temperatures that are favorable for pickling LCT material, commercially useful pickling rates can be achieved for HCT material.

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Batch Pickling

Carbon steel rod, wire, and pipe are usually batch pickled in sulfuric acid solutions. Rod ranging from 5 mm (0.200 in.) to over 17 mm (0.675 in.) in diameter in coils weighing from 136 kg (300 lb) to more than 454 kg (1000 lb) can be pickled using one to ten coils at a time. With wire, especially for diameters below 3 mm (0.100 in.) the packing effect makes it difficult for the acid solution to penetrate and contact all wraps uniformly. To promote better cleaning of wire, the coil sizes can be restricted and the coils bounced during the pickling operation. Bar flats are held apart with separators to improve solution contact. The heavy scale on patented rod (0.40% C, or higher) can also be removed by pickling for a sufficient time in sulfuric acid.

In one plant that batch pickles bar stock, the makeup solution contains 14 to 15 g/100 mL sulfuric acid and is operated at 60 °C (140 °F) until the concentration of acid drops to about 7 g/100 mL. Fresh acid is added to increase the concentration to about 12 g/100 mL, and the bath is operated until the concentration decreases to about 6 g/100 mL. The temperature is gradually increased during this period to about 68 °C (155 °F). Inhibitors are used at concentrations up to 0.5 vol% of the free acid present. When the iron content in solution reaches about 8 g/100 mL, the solution is no longer used.

Most iron and steel castings are cleaned by mechanical methods, such as shot blasting, sand blasting, and tumbling. When pickling is used, the castings are cleaned in solutions containing sulfuric and hydrofluoric acids. The concentration of each acid depends on whether the primary purpose is to remove sand or scale. Increased hydrofluoric acid is needed to remove embedded sand from the casting surface, whereas sulfuric or hydrochloric acids are sufficient for simple scale removal. Table 4 gives the operating conditions for pickling iron and steel castings. Before being pickled, castings must be free of oil, grease, and other contamination. After being removed from the pickling solution, castings are rinsed thoroughly in hot water. Residual heat permits self-drying, but drying can be accelerated by using a fan. If the shape of the castings hinders drying, then the process can be completed in a baking oven.

Table 4 Operating conditions and solution compositions for pickling iron and steel castings

Operating variable[(a)]	**Sand removal**	**Scale removal**
Sulfuric acid, %	5	7
Hydrofluoric acid, %	5	3
Water, %	90	90
Temperature[(b)], °C (°F)	66-85 (150-185)	49 to over 85 (120 to over 185)
Average immersion time, h	4	4

(a) Percentages by volume.

(b) 49 °C (120 °F) is for slow pickling, 66 to 85 °C (150 to 185 °F) is for average pickling speed, and over 85 °C (185 °F) is for fast pickling.

Stainless steel products should be free of oil, grease, or other soils that can contaminate the pickling solution. Heating the steel to a temperature under 540 °C (1005 °F) to burn off contaminants such as light oils is sometimes used as a cleaning method before pickling. However, some austenitic stainless steels are sensitized when heated at 400 to 900 °C (750 to 1650 °F) and may undergo intergranular corrosion. If alkaline precleaning is used, then adequate rinsing is required before pickling. Precleaning is not required if oxide or scale is the only soil on the surface. Forgings and castings usually are not pickled, but forgings can be pickled as an inspection procedure to determine the presence of surface defects. If pickling is necessary, then castings and forgings are pickled by the procedures used for rolled forms of stainless steel.

Pickling cycles for the 300-series austenitic stainless steels are given in Table 5. The lower immersion time values are for pickling the lower-alloy steels, whereas the upper values are for the more highly alloyed steels, such as types 309, 310, 316, 317, and 318. The immersion time in the acid solutions can be reduced substantially by prior treatment of the material in a salt descaling bath. Electrolytic pickling in sodium sulfate is also used as a pretreatment. Pickling cycles for the low-carbon 400-series stainless steels are given in Table 6. As with 300-series steels, immersion time can be reduced by pretreatment. The higher-carbon grades of 400-series stainless steels are pickled as indicated in Table 6, except that the immersion time in the sulfuric and nitric acid solutions is reduced to 5 to 20 min and 5 to 10 min, respectively.

Table 5 Sequence of procedures for pickling 300-series stainless steels

Cycle	**Solution composition(a), vol%**	**Operating temperature**		**Immersion time(b), min**
		°C	**°F**	
Sulfuric acid dip	15-25 H_2SO_4(c)	71-82	160-180	30-60
Water rinse(d)	. . .	Ambient	Ambient	. . .
Nitric-hydrofluoric acid dip	5-12 HNO_3, 2-4 HF	49 max	120 max	2-20
Water rinse(d)	. . .	Ambient	Ambient	. . .
Caustic permanganate dip(e)	18-20 NaOH, 4-6 $KMnO_4$(f)	71-93	160-200	15-60
Water rinse(d)	. . .	Ambient	Ambient	. . .
Sulfuric acid dip	15-25 H_2SO_4(c)	71-82	160-180	2-5
Water rinse(d)	. . .	Ambient	Ambient	. . .
Nitric acid dip	10-30 HNO_3	60-82	140-180	5-15

(a) Acid solutions are not inhibited.

(b) Shorter times are for lower-alloy steels; longer times are for more highly alloyed types, such as 309, 310, 316, 317, and 318.

(c) Sodium chloride (up to 5 wt%) may be added.

(d) Dip or pressure spray.

(e) Sometimes used to loosen scale.

(f) Percent by weight.

(g) Boiling water may be used to facilitate drying.

Table 6 Sequence for pickling low-carbon 400-series stainless steels

Cycle	**Solution composition**[(a)], **vol%**	**Operating temperature**		**Immersion time**
		°C	**°F**	
Sulfuric acid dip	15-25 H_2SO_4(b)	71-82	160-180	5-30 min
Water rinse(c)	. . .	Ambient	Ambient	. . .
Caustic permanganate dip(d)	18-20 NaOH, 4-6 $KMnO_4$(e)	71-93	160-200	20 min to 8 h(f)
Water rinse(c)	. . .	Ambient	Ambient	. . .
Sulfuric acid dip	15-25 H_2SO_4(b)	71-82	160-180	2-3 min
Nitric acid dip	30 HNO_3	Ambient	Ambient	10-30 min

(a) Acid solutions are not inhibited.

(b) Sodium chloride (up to 5 wt%) may be added.

(c) Dip, pressure hose, or spray. High-pressure spray or jets are more effective for removing scale and smut.

(d) Sometimes used to loosen scale.

(e) Percent by weight.

(f) Immersion time may exceed this range.

(g) Boiling water may be used to facilitate drying.

Precipitation-hardenable stainless steels, such as 17-7 PH, AM-350, and AM-355, can be pickled in the annealed condition in a manner similar to that for the 300-series grades. In the precipitation-hardened condition, the high hardness and the nature of the structure make the steel susceptible to strain cracking during pickling. Therefore, the immersion times during pickling should be as short as possible. For precipitation-hardenable steels in the fully hardened condition, grit blasting to remove scale, followed by passivation in a 30 to 50% nitric acid solution, is recommended.

Control of Process Variables. The immersion time required to pickle a particular product can best be determined by trial. The influence of temperature on pickling time and iron buildup in pickling solutions is pronounced and therefore temperature control is important. Because the rate of pickling also increases in proportion to the concentration of the acid, periodic testing of the solution is important. Rinse tanks of the overflowing variety should have a sufficient flow of fresh water, so that acid buildup indicated by low pH readings does not occur. If rinse tanks are not of the overflowing variety, then they should be frequently monitored to determine how often they should be dumped.

Solutions containing sulfuric acid and iron can either be diverted to the pickling of other material or discarded when the iron content reaches 5 to 7 wt%. Nitric-hydrofluoric acid solutions are discarded when the iron content reaches 5 wt%, whereas nitric acid solutions are discarded when iron reaches 2 wt%. The caustic permanganate solution (Tables 5 and 6) is desludged every 3 to 5 mo, and makeup materials are added to it. Analytical procedures and sampling of these solutions are described in many texts on chemical analysis.

Continuous Pickling

Carbon Sheet and Strip. In a continuous-strip pickling line with three or more tanks, the concentration of acid is generally highest in the final tank and lowest in the initial tank from which the spent pickle liquor is discharged. Iron-salt concentrations are lowest in the final tank and highest in the initial tank. In one commercial line using sulfuric acid with four tanks and steam sparging for heating, typical acid concentrations in the tanks are 12, 15, 17, and 20 g/100 mL. Typical ferrous sulfate concentrations in these tanks are 20, 17, 14, and 12 g/100 mL. Tank temperatures are maintained at 93 to 99 °C (200 to 210 °F). If indirect heating had been used instead of steam sparging, then ferrous sulfate concentrations would have been higher.

In another commercial line using hydrochloric acid with four tanks and steam sparging for heating (tank temperatures of 82 to 88 °C, or 180 to 190 °F), typical acid concentrations in the tanks are 2, 3, 5, and 7 g/100 mL, and typical ferrous chloride concentrations are 21, 19, 16, and 14 g/100 mL. When indirect heating is introduced on this line, the acid concentrations are maintained at nearly the same levels, but the ferrous chloride concentrations become 34, 32, 26, and 20 g/100 mL. In another line using hydrochloric acid with three tanks and indirect heating (tank temperatures at 79 °C, or 175 °F), typical acid concentrations are 4, 12, and 16 g/100 mL, with ferrous chloride concentrations of 31, 16, and 6 g/100 mL.

To estimate the maximum line speed consistent with complete descaling under various tank conditions, the fact that there are different pickling rates for each tank must be considered. In a continuous-strip pickling line with four tanks, the effective immersed strip lengths are L_1, L_2, L_3, and L_4 (these lengths, measured in feet, are somewhat less than the tank lengths, especially for the initial and final tanks). If S is the line speed in feet per minute, then the time in seconds that strip is immersed in each tank is equal to each of these distances multiplied by $(60/S)$. If the temperature and solution composition are known for each tank, then the times required for complete descaling, *if carried out completely in a tank,* can be estimated from bench-scale test data that relates pickling time to tank concentration and temperature. These required pickling times can be designated as t_1, t_2, t_3, and t_4. For complete descaling to occur in a continuous-strip pickling line, the fractions of scale removed in each tank should total 1.00 or greater. These individual fractions are $(60L_1/S)/t_1$, $(60L_2/S)/t_2$, $(60L_3/S)/t_3$, and $(60L_4/S)/t_4$ for tanks 1, 2, 3, and 4, respectively. Imposing the condition that:

$$(60/S)\,[(L_1/t_1) + (L_2/t_2) + (L_3/t_3) + (L_4/t_4)] = 1 \qquad \textbf{(Eq 13)}$$

and multiplying both sides by S gives an expression for the line speed that is the *maximum* consistent with complete descaling under a particular set of conditions.

$$S_{\max} = 60\,[(L_1/t_1) + (L_2/t_2) + (L_3/t_3) + (L_4/t_4)] \qquad \textbf{(Eq 14)}$$

If the calculation predicts a maximum line speed that is less than desired, then more aggressive tank conditions (higher acid concentration and/or temperature) should be adopted. If the calculation predicts a maximum line speed that is appreciably higher than that required or that can be mechanically sustained, then consideration should be given to adopting less aggressive tank conditions (lower acid concentration and/or temperature).

In one plant, strip from a continuous normalizing furnace exits into the air and the oxides formed are removed by pickling in two tanks that contain from 19 to 21 g H_2SO_4/100 mL with about 12 g $FeSO_4$/100 mL at 91 °C (195 °F). At the usual line speed of 0.61 m/s (120 ft/min), the total pickling time is about 60 s, and no difficulty is experienced in removing scale under these conditions. A specimen of strip sampled after normalizing and before pickling was examined, and the scale was found to be predominantly FeO, the oxide most readily attacked by sulfuric acid.

Carbon Steel Rod and Wire. In one plant, steel rod of 5.56 mm (0.22 in.) diameter with from 0.6 to 0.8% C is continuous pickled with hydrochloric acid. A reverse-bend scale breaking operation precedes immersion for about 80 s in a 54 °C (130 °F) solution that contains from 12 to 15 g HCl/100 mL and from 3 to 30 g $FeCl_2$/100 mL. Rod sampled before and after scale breaking, but before pickling, was found to have about 80% of the scale removed by scale breaking.

In another plant, continuous pickling is used in connection with the continuous galvanizing of steel wire. Wire containing from 0.4 to 0.8% C is pickled in a 10 to 15 vol% solution of sulfuric acid (1.83 sp gr) at 71 to 82 °C (160 to 180 °F), spray-rinsed with cold water, pickled in a 40 to 50 vol% solution of hydrochloric acid (1.16 sp gr) at 54 to 60 °C (130 to 140 °F), spray-rinsed with cold water, fluxed and dried, and then dipped in molten zinc. Immersion time in each of the pickling solutions ranges from 16 to 32 s. Wire may have patenting scale or a light scale of lead oxide that is obtained from a molten lead bath following drawing.

Stainless Steel (SS) Strip. [*]Continuous-anneal pickle lines necessitate pickling times of several minutes or less, depending on the capabilities of the line and the grade being processed. Whenever possible, production should not be limited by the ability to pickle. Pickling practices should be adjusted to allow for desired production rates. Generally, practices should be selected that produce complete scale removal, minimum yield loss, and an acceptable pickled surface for the specific application. Overall surface cleanliness and corrosion test performance may influence customer definition regarding acceptable pickled surfaces.

Scales that form on stainless steels are more difficult to remove than those formed on carbon steels. Therefore, a single reducing acid, such as sulfuric or hydrochloric, is usually not effective. Pickle liquors used for stainless strip include sulfuric, sulfuric-hydrofluoric, nitric-hydrofluoric, and nitric acids. A typical pickling scheme could consist of a tub of sulfuric acid, followed by nitric-hydrofluoric acid, followed by nitric acid only. The most aggressive liquor is nitric-hydrofluoric acid. The oxidizing ability of nitric acid, coupled with the formation of strong fluoride complexes with iron, chromium, titanium, aluminum, and silicon, makes nitric-hydrofluoric acid an effective scale remover for stainless steels. Its use should be controlled as well as possible, because hydrofluoric acid is the most expensive acid commonly used, and because overpickling can result in excessive groundwater and air pollution.

Hot-Rolled SS Strip (Hot Bands). Hot-band scale is generally thicker and more irregular than scale produced from annealing after cold rolling. If hot bands are annealed after hot rolling and are then pickled, then the additional scale produced by annealing makes scale removal even more difficult. In either case, a common practice is to assist scale removal by using a scale breaker or by shot blasting before pickling. If shot blasting is used, then its effectiveness will depend on processing line speed, the shot type, impingement density and energy, and inherent fracturability of the scale itself. Generally, pickling can be carried out in sulfuric acid with or without hydrofluoric acid, followed by nitric-hydrofluoric acid. The acid concentrations, times, and temperatures, which must be determined empirically, will depend on the grade being processed, the processing line speed, and incoming scale characteristics. General conditions for 400- and 300-series hot bands are given in Table 7.

Table 7 Pickling conditions for hot-rolled stainless steel strip following shot blasting

Grade	Concentration (g/100 mL) and acid type	Temperature		Time, s
		°C	°F	
Ferritic	10-15 sulfuric plus 0-4 hydrofluoric	50-65	120-150	20-60
	5-10 nitric plus 0.2-1 hydrofluoric	50-65	120-150	20-60
Austenitic	10-15 sulfuric plus 0-4 hydrofluoric	50-70	120-160	20-60

	5-15 nitric plus 1-4 hydrofluoric	50-70	120-160	20-60

It is important to note that 400-series grades do not normally passivate in mixtures of nitric-hydrofluoric acid. Therefore, considerable base-metal yield loss can occur if pickling conditions are not well controlled when using this acid mixture. In addition, an increasing base-metal yield loss will increase airborne nitrogen oxides and acid consumption. Hydrofluoric acid, in particular, should be added either slowly and continuously or in small-volume increments, rather than in large, bulk volumes, which would substantially increase the acid concentration and the pickling rate. Pickling of 300-series grades is easier to control, because of base-metal passivation (that is, pickling will eventually stop when the clean base-metal surface passivates). The higher hydrofluoric concentrations required by 300-series grades makes it possible to make less frequent acid additions and to maintain control of the pickling process.

Because of short immersion times, the mechanism of scale removal is a combination of scale dissolution, undercutting of scale by acid attack of base metal, and mechanical removal of loose scale or smut by sprays and brushes after pickling. Therefore, effective sprays and brushing after pickling can have a significant effect on surface cleanliness. Scale that is removed by undercutting and that remains in the pickle liquor will usually dissolve.

Cold-rolled SS strip is normally annealed and pickled before shipment. The cold-rolled strip should be free of contaminants that could cause it to have a nonuniform appearance or pattern after annealing and pickling. Small quantities of clean rolling emulsion will burn off during annealing and should not cause problems. Annealing conditions will affect pickling practices for annealed cold-rolled materials. A consistent annealing furnace atmosphere will help produce a consistent scale that can, in turn, be removed using a consistent pickling practice. Uncontrolled cycling of the annealing atmosphere between oxidizing and reducing conditions can produce scale that is difficult to remove, resulting in unexplained loss of pickling.

Scale Conditioning Before Pickling. Scale produced by annealing after cold rolling is usually thinner than hot-band scale. Shot blasting is not normally used to fracture scale before pickling, because the surface would be roughened by this treatment. An oxidizing alkaline molten salt bath is an effective scale-conditioning method to use before pickling. The strip should contact the molten salt for at least 5 s at 455 to 470 °C (850 to 875 °F). Salt-bath conditioning may cut pickling yield loss in half for some grades, because milder pickling conditions can be used, such as the lower acid concentrations and temperature ranges given in Table 8. Benefits of a molten salt plus mild-acid descaling scheme, when compared with a strong acid only scheme, include better control of strip cleanliness and brightness, lower base-metal yield loss, higher line speeds where pickle tub length is limited, lower nitrogen oxide emissions, lower acid consumption, and reduced waste-disposal requirements. In some cases, the cost of salt-bath conditioning can be more than offset by savings in raw-acid costs, yield loss, and waste-disposal costs.

Table 8 Pickling conditions for cold-rolled stainless steel strip after annealing

Grade	Concentration (g/100 mL) and acid type	Temperature		Time, s
		°C	°F	
Ferritic	5-15 sulfuric plus 0-4 hydrofluoric	50-65	120-150	15-60
	5-10 nitric plus 0.1-1 hydrofluoric	50-65	120-150	15-60
	10-15 nitric only	50-65	120-150	15-60
Austenitic	10-15 sulfuric plus 0-4 hydrofluoric	50-65	120-150	15-60
	5-15 nitric plus 1-4 hydrofluoric	50-65	120-150	15-60

	10-15 nitric only	50-65	120-150	15-60

Acid Pickling Schemes. If scale has been preconditioned or if it is inherently easy to remove, then use of electrolytic sodium sulfate or electrolytically assisted sulfuric and nitric acids may be sufficient. Use of these liquors should result in less base-metal yield loss than would result if nitric-hydrofluoric acid were used, especially with 400-series grades. In some cases, combining electrolytic tubs with a mild nitric-hydrofluoric acid is effective.

Scales that are more difficult to remove require progressively harsher treatment with acids. Use of sulfuric acid, followed by nitric-hydrofluoric acid, followed by nitric acid only can usually be made effective. A good general approach is to develop practices that begin with less aggressive pickling conditions (low temperature, low acid concentrations, and minimum immersion times) and work toward more aggressive conditions as necessary.

Effects of Process Variables. The pickling rate in nitric-hydrofluoric acid will increase with temperature, hydrofluoric acid concentration, and, to a lesser extent, nitric acid concentration. For 300-series grades, increasing the nitric acid concentration much above 8 g/100 mL (w/v) may actually result in lower pickling rates in nitric-hydrofluoric acid solutions. For the efficient use of acids, spent pickle liquors should be high in metals and low in free-acid content. The most consistent pickling will be obtained if pickle liquors are maintained at steady-state conditions. For example, a 409-type SS might be pickled in 7 w/v nitric acid plus 0.5 w/v hydrofluoric acid plus 5 w/v metals at 60 °C (140 °F). Maintaining constant pickle tub chemistry can be achieved by operating in a feed-and-bleed mode, whereby acids and water are added at one end of a tub and spent pickle liquor overflows or is drained from the other end of the tub. Failure to add appropriate amounts of water along with concentrated pickling acids will result in eventual precipitation of metal salts in the pickle tub. In a nitric-hydrofluoric acid solution, the product of the percent of metal times the percent of hydrofluoric acid should not exceed 15.

Accelerators can be added to the above-mentioned acids at concentrations as low as 0.5 w/v, based on the volume of raw acid needed to increase the pickling rate by as much as 40%. These accelerators lower the interfacial tension between the steel and the acid and reduce the acid consumption by as much as 60%.

Note cited in this section

* The sections on stainless steels were prepared by Ronald D. Rodabaugh, ARMCO Inc.

Electrolytic Pickling

Electrolytic pickling is widely used commercially to remove superficial oxides from light-gage strip that is to be electroplated in high-speed continuous processing lines. Such pickling is usually carried out at ambient or room temperature, using a solution that contains from 5 to 10 wt% sulfuric acid with less than 2 g Fe/100 mL, with a coulomb density of about 805 C/m^2 (75 C/ft^2). Coulomb density is the product of current density and the treatment time. Depending on line speed, electrolytic pickling times in commercial electrotinning lines range from about 1 to 1.5 s. Current densities consistent with the conditions cited are usually less than 1075 A/m^2 (100 A/ft^2). For most electrotinning applications, the strip is the cathode during electrolytic pickling and the steel does not dissolve, nor is hydrogen gas generated on the surface. When the strip is the anode, some steel does dissolve, forming iron salts in the pickling solution. Because anodic pickling can form some carbon smut on the surface, an anodic pickling pass is often followed by a cathodic pass to promote a cleaner surface.

Hot-mill scale can also be removed from carbon steels by electrolytic pickling in a fraction of the time that chemical pickling requires, but at much higher current densities and somewhat higher solution temperatures than are required in the electrotinning application. The production of hydrogen at a steel cathode aids in scale removal both mechanically and by reducing the oxide film. Economic analyses, however, indicate that the excessive power costs associated with electrolytic pickling of hot-rolled carbon steel strip would render the method unfeasible, compared with chemical pickling. Electrolytic pickling might be considered for abnormally thick hot-mill scale or for scale layers on alloy steels that are difficult to remove by chemical pickling. Stainless steel has oxides in the scale that are especially difficult to remove during chemical pickling (chromium sesquioxide, Cr_2O_3, and iron chromite, $FeCr_2O_4$). Therefore, electrolytic pickling at current densities in excess of 1075 A/m^2 (100 A/ft^2) has been applied commercially. The electrolyte solution can be sulfuric acid or sodium sulfate.

Although sulfuric acid is used for either chemical pickling or electrolytic pickling, hydrochloric acid should only be used for chemical pickling. During electrolysis with hydrochloric acid, the anode reaction produces chlorine gas.

Pickling Defects

Pickling is frequently blamed for certain defects that appear during the pickling operation, but actually originate elsewhere. Some defects are the result of earlier operations, such as rolling, heat treating, or forging. Scratches introduced during hot rolling or pickling, as well as pickle its, both result in line-type surface imperfections that persist through subsequent processing stages. The effect of such defects on the surface properties of steel has been extensively studied (Ref 25, 26).

Underpickling results when the steel has not had sufficient time in the pickling tanks to become free of adherent scale. It occurs when the solution composition and temperature are not properly controlled. Small patches of scale that are not removed by pickling may persist through subsequent operations. Annealing in a reducing atmosphere will convert such scale to a reduced sponge-iron type of surface defect.

Overpickling causes porosity of the transverse surfaces and a roughening of the whole surface, accompanied by discoloration and a decrease in size and weight. Overpickling can be avoided by removing the material from the bath promptly when scale removal is complete. Inhibitors aid in preventing overpickling. For strip product, the undercutting of surface grains can result in pickup at hold-down boards at a cold mill and can lead to cold-mill scratches.

Pitting may be caused by overpickling, particularly when inhibitors are used, but in less-than-adequate amounts. Such pitting appears when material remains in the bath much longer than is necessary for complete scale removal. Pits caused by rolled-in scale, nonmetallic inclusions, or refractories in the rolling process are intensified during pickling. On heat-treated alloy steels and forgings, electrolytic pitting can occur, characterized by a patchwork of irregularly shaped pitted areas that are caused by an electrical potential between scaled areas and areas where scale has been removed from small areas before pickling. The use of inhibitors generally results in pitted areas of uniform depth. Without inhibitors, pitted areas are irregular in depth.

Hydrogen embrittlement occurs when cold-working operations follow too soon after pickling, because nascent hydrogen diffuses into the steel during pickling. Embrittlement of this type can be avoided by aging. Baking cleaned parts at 200 to 240 °C (390 to 465 °F) for 3 to 4 h may be necessary for high-strength steel (>1380 MPa, or 200 ksi). Cracking may occur on such embrittled steel within 4 h after pickling. Inhibitors help minimize this effect, but some that contain organic sulfur compounds may actually promote hydrogen pickup, even though they are highly effective in limiting base-metal loss (Ref 13).

Blistering is a defect on sheet and strip steel that is related to flaws in the steel caused by formation of gas pockets just beneath the surface during rolling when gaseous inclusions are present. Hydrogen formed in the pickling operation can penetrate these pockets to lift the surface, causing a blister.

Rusting can result on pickled product if rinsing is not thorough enough to maintain pickle salt and acid concentrations on the surface below levels that promote in-plant rusting. Threshold concentrations of chlorides (0.4 mg/m^2, or 0.04 mg/ft^2) and sulfates (0.6 mg/m^2, or 0.06 mg/ft^2) are associated with rusting on bare steel when relative humidities exceed 30% for chlorides or 50% for sulfates (Ref 27). Somewhat higher surface-concentration levels of chlorides or sulfates can be tolerated on material that is oiled after pickling, particularly if rust preventative inhibitors are present in the oil. Rinse additives are helpful in preventing stains on pickled product that is shipped or further processed without oiling.

Another source of contamination of pickled product is improper storage in areas subjected to acid spray from pickle tanks or to air-borne hydrogen chloride emissions. The vapor pressure of hydrogen chloride above solutions that contain hydrochloric acid and ferrous chloride increases with temperature. It also increases with increases in both acid and salt concentration. Water vapor losses above pickling baths are far greater than hydrogen chloride vapor losses. The vapor pressure of water over pickling solutions increases with temperature and decreases with increases of acid and iron-salt concentration. This last statement is true for both hydrochloric and sulfuric acid solutions.

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Disposal of Spent Pickle Liquor

Spent pickle liquor (SPL) from sulfuric acid pickling may contain from 2 to 15 wt% H_2SO_4 and 5 to 20 wt% $FeSO_4$. Neutralization with a lime slurry produces a mixture of sparingly soluble gypsum ($CaSO_4$) and iron hydroxide that can be pumped to lagoons for settling and, eventually, disposed of as landfill. In a modification of this process, aeration is used to convert iron hydroxide to Fe_3O_4, forming a dense sludge and avoiding slimes or colloids that are difficult to handle. Hydrochloric acid SPL from continuous pickling lines typically contains from 1 to 4 g HCl/100 mL and from 20 to 30 g $FeCl_2$/100 mL. Neutralization of HCl SPL with lime produces highly soluble calcium chloride, which cannot be discharged to inland water systems. A process has been developed in which the calcium chloride solution is further treated with H_2SO_4 to precipitate gypsum and regenerate HCl, but this process is not in commercial use. In some areas of the United States, the underground rock formations are such that H_2SO_4 or HCl SPL can be injected into a deep well without affecting existing ground-water supplies. This method is no longer in wide use, because of concern that contamination of ground waters would eventually occur.

Because ferrous sulfate becomes less soluble as the temperature of the solution decreases or as the acid concentration increases, it can be recovered as crystals by cooling or concentrating H_2SO_4 SPL by evaporation. Recovery of the monohydrate $FeSO_4 \cdot H_2O$ from hot solutions is generally avoided. If it is produced, then the monohydrate can be roasted to produce sulfuric acid and iron oxide, but this process is generally not considered economically attractive. Recovery of the heptahydrate (copperas), $FeSO_4 \cdot 7H_2O$, utilizes a cold solution (-1 °C, or 30 °F) that is removed by centrifuging or by using a crystallizer from which solids can be removed. The solution contains sulfuric acid and lowered amounts of iron and water than exist in the SPL. The solution is then returned to the pickling tanks, thus effecting a recovery of the unreacted acid. Fresh acid additions must be made to the pickle tanks to maintain desired operating conditions. Use of this recovery method lowers overall acid consumption for pickling, compared with the amount required if no recovery system is used. The heptahydrate crystals are used in fertilizers and for water treatment.

Many commercial installations use this recovery method. Systems of this type can be operated on a batch or continuous basis. For a continuous basis, the amount of SPL withdrawn for treatment must be adjusted to the volume of the pickling solution. In addition, the recovery unit is sized so that the removal rate of iron from SPL equals the rate of iron entering the pickling solution from the pickling operation. A fairly constant iron content is maintained in the SPL.

An analogous process for removing iron from HCl SPL has been developed (Ref 28), and requires that either higher-than-conventional HCl concentrations be used in the pickling operation (probably coupled with lower solution temperatures) or that additions of concentrated HCl be made to the HCl SPL that is to be treated, so that ferrous chloride tetrahydrate crystals ($FeCl_2 \cdot 4H_2O$) form when the liquor is cooled below about -8 to -7 °C (18 to 20 °F) and to about -23 °C (-10 °F). Recovered crystals can be dissolved in water to prepare a solution suitable for use in water treatment.

A widely used process for complete regeneration (as high as 99% recovery) of HCl SPL involves spray roasting. The SPL is first concentrated by water evaporation. The concentrated SPL enters the roaster at a temperature ranging from 600 to 750 °C (1112 to 1382 °F). Free HCl and most of the water is evaporated and leaves the reactor with the combustion gases. Ferrous chloride reacts with the balance of water and oxygen to form hydrogen chloride and hematite:

$$2FeCl_2 + 1/2\ O_2 + 2H_2O = Fe_2O_3 + 4HCl \qquad \textbf{(Eq 15)}$$

Gases containing hydrogen chloride are washed with water to form an 18 to 20 wt% HCl solution. By-product Fe_2O_3 can be used as a pigment or, depending on purity, for magnetic tapes.

Ion exchange can be used to regenerate either H_2SO_4 or HCl from SPL. The SPL is pumped through an acidic ion-exchange bed, where the iron is stripped from the SPL and replaced by hydrogen ions. The iron-rich ion-exchange resin is then regenerated with another acid. Although ion-exchange procedures are not being used for H_2SO_4 or HCl SPL, they are in commercial use for treating hydrofluoric-nitric acid SPL from the pickling of stainless steels (Ref 29).

At some plants, HCl SPL is treated on site with chlorine gas to convert ferrous chloride to ferric chloride, which is used in sewage and water-treatment plants. Other plants pay to have their SPL hauled to an authorized treatment site. This method is becoming increasingly expensive. Drawbacks include possible closings of some disposal sites and the continuing responsibility of the source for environmental damage associated with hauling SPL and its final disposal.

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Safety

A number of safety practices should be followed during alkaline precleaning and acid-pickling operations. Employees handling chemicals should wash their hands and faces, both before eating and before leaving at the end of a shift. Only authorized employees familiar with chemical handling safety rules should be permitted to add the chemicals to pickling tanks. Face shields, chemical safety goggles, rubber gloves, and rubber aprons should be worn by employees who clean or repair tanks or make additions of chemicals. Hard hats and safety shoes also should be worn. If splashed or spilled chemicals contact body parts, then employees should wash immediately and thoroughly with cool water and report promptly to an emergency facility for treatment. An emergency shower with quick-opening valves that stay open should be available, as should eye-wash fountains. Any changes in working procedures or any unusual occurrences relating to the use of chemicals should be brought to the attention of supervisory personnel.

Safe practices in the use of alkaline and acid solutions should be followed. Alkalis should be added to water slowly, using a hopper or shovel. Adequate agitation should be provided after an alkali has been added, to ensure that the chemicals dissolve. To prevent eruption of the solution caused by rapid dissolving of the alkali, the temperature of the solution should not exceed 66 °C (150 °F) during additions. Acids should always be added to water, rather than water added to concentrated acid. When preparing a new solution, acid should be added to cold water, and the solution should not be heated until the acid has been added. Additions of acid to hot pickling solutions should be made with extreme caution. Materials should be carefully immersed in and withdrawn from acid solutions to avoid splashing. Adequate ventilation also should be provided in the vicinity of a pickling operation.

Classification and Selection of Finishing Processes

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Introduction

THE TERM *finishing* as used in this Section of the Handbook refers to a wide variety of processes used to generate surfaces with specific geometries, tolerances, and surface characteristics. The finishing methods described in the articles in this Section focus on material removal in one form or another to generate the desired surfaces. These surface generation methods are used usually to achieve certain functional or decorative characteristics of the surface. Other surface preparation processes such as cleaning, plating, coating, and surface modifications are covered in other sections in this Volume.

Most of the finishing methods described in this Section are carried out as the last operation in a series of industrial processes used to produce or manufacture parts or components. As an example, a cast product may need snagging or cutting off of gates and risers as the finishing operation before it is shipped for use or sent to the next component fabrication department. A forged shaft may be cut, machined, or otherwise finished before it becomes an industrial component for use in an assembly process. After heat treatment, bearing or gear components may be ground to desired tolerances and surface quality before they are assembled into finished bearings or a transmission, respectively. Computer parts such as microchips or magnetic heads may be ground, lapped, or polished before they are sent to assembly operations. Jet engine blades may have coolant holes drilled using electrical discharge machining or laser machining prior to their use in an assembly process to manufacture jet engines. The above are just a few of many applications in which finishing methods are used in a wide range of materials and industries. Thus, finishing methods play a key role in a number of engineering activities. It is beyond the scope of this Section to treat each process in detail, but the articles provide an overview of the various methods, their critical features, and the range of their application or use. This is supplemented by a large number of references that deal with each process in significant detail.

Technology Drivers for Finishing Methods

Engineering activity is usually driven by a few driving forces. These technology drivers are generally universal and are often found to be independent of geography. The scale or magnitude of these drivers may vary, depending on the local demands for quality, economic forces, and so on. Technology drivers for finishing methods are addressed briefly in the following paragraphs.

Tolerance in generic terms implies deviation from the nominal value. As it relates to finishing methods, tolerance refers to geometric dimensions and their deviation from the nominal. These may be used to measure linear dimensions such as thickness, length, and radius. They may also refer to surface features such as finish, form, flatness, and waviness. Extensive review of geometric dimensioning and tolerances may be found in a number of references (Ref 1, 2, 3).

Whichever tolerances are referred to, it is clear that one of the driving forces for finishing methods is to achieve improved or closer tolerances. As an example, finished parts of closer tolerances in a hydraulic pump help to achieve higher pump efficiency, which results in improved power steering performance and thus enhances the quality of an automobile. Closer tolerances in gears cause them to roll against other gears more readily while reducing sliding friction. This results in better gear efficiency, increased torque carrying ability, and lower noise level. These benefits have a wide range of applications in automotive components, jet engines, construction equipment, and so on. The trend for improvement in tolerances is constant, as shown in Fig. 1.

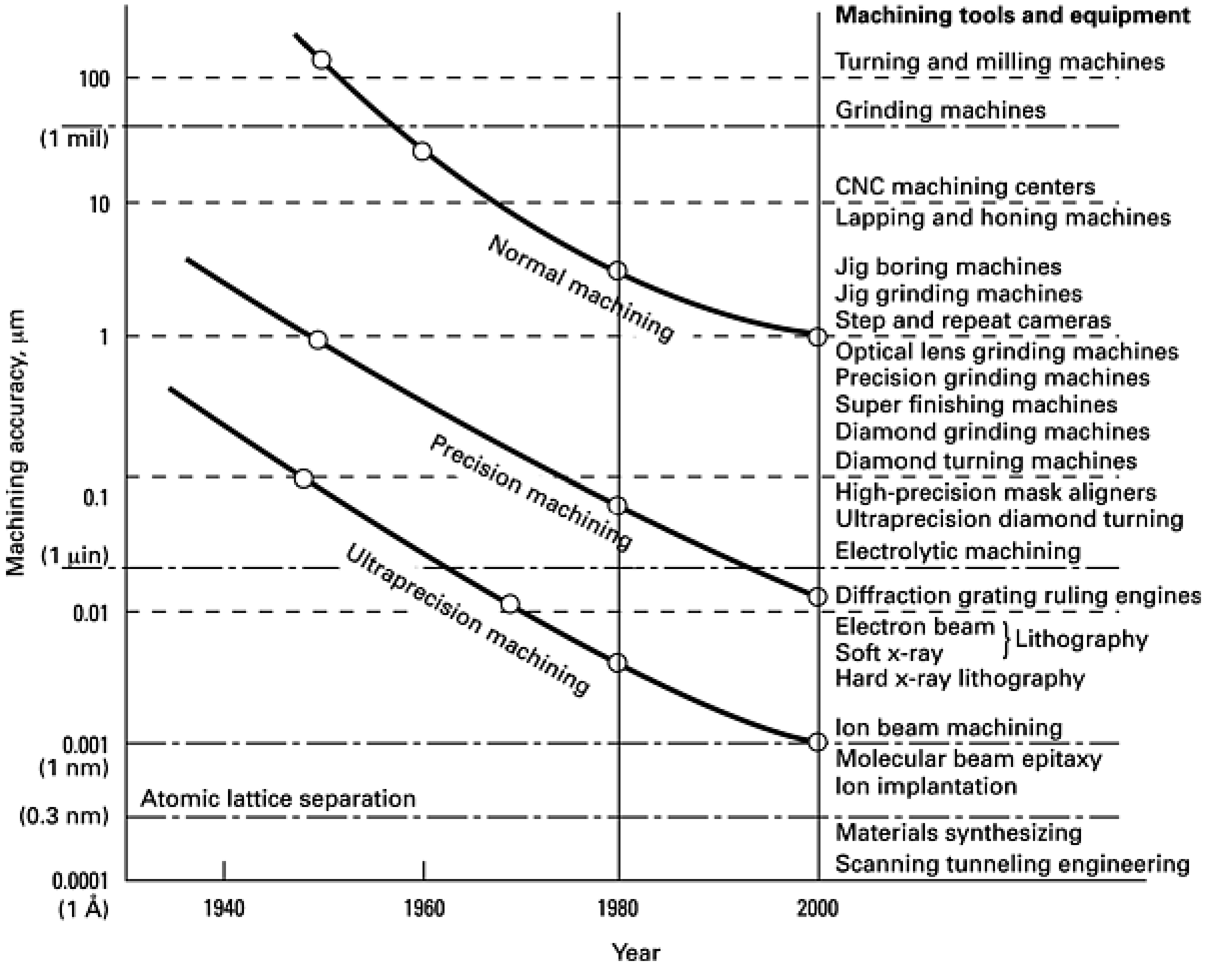

Fig. 1 Achievable machining accuracy. CNC, computer numerically controlled. Source: Ref 4, after Norio Taniguchi

Consistency. For a given tolerance of a finished part, it is critical to achieve them consistently over a batch of components. Consistency is established through the confidence limits arrived at through statistical process control. If a tolerance is viewed as a "set point" or location in geometric space, consistency defines the ability to stay close to the set point. Detailed discussions of statistical process control and methods of achieving consistency can be found in Ref 5, 6, and 7.

Finishing methods constantly strive to improve the consistency of their output (i.e., generated surfaces of required geometry and surface characteristics). Imagine that an improvement in the form accuracy or tolerances of a gear surface is achieved through a new or improved finishing method. This could result in significant improvement in the performance of the transmission in which the gear is used. The new process will become successful only when two conditions are met: the new process delivers the improved tolerances consistently and all other components in the transmission are manufactured consistently. If one of the consistency requirements is not met, the new transmission will not meet the higher performance levels and the new finishing method developed may not see the light of the day. Conversely, constant improvement in consistency is a key technology driver that closely follows improvement in tolerances of the finished components.

Surface Quality. Finishing methods result in generation of surfaces, which alters the surface layers of the work material. This alteration may change surface characteristics such as:

- Surface finish
- Fatigue strength
- Residual stress

- Retained strength

All finishing methods constantly strive to improve on these and other surface characteristics. Many of these topics are addressed in various articles in this Section. It is sufficient here to say that surface quality and its improvement is a key technology driver for finishing methods.

New materials such as high-silicon aluminum alloys, fiber-reinforced composites, metal matrix composites, ceramics, ceramic coatings, particle boards, and metallic glass constantly pose challenges for both innovation and improvements in finishing methods. Such new work materials are constantly introduced to achieve lower weight, higher strength-weight ratio, high-temperature resistance, or better operation under severe environments, or to achieve other unique performance improvements. These in turn influence the choice and improvements necessary in the finishing methods.

Productivity. Although this article has discussed technology drivers that relate to technical aspects of finishing methods, it is obvious that the results must be achieved at lower cost, to compete in the global marketplace. This requirement simply translates into improved productivity. All finishing methods seek to achieve higher productivity through incremental or small improvements in productivity or quantum improvements in new processes.

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Systems Approach for Finishing Methods

Every finishing method may be viewed as a manufacturing system consisting of four input categories: machine tool, processing tool, work material, and operational factors. These inputs result in microscopic or intrinsic process interactions that can be measured or monitored through macroscopic process variables. The interactions result in certain technical outputs or, when economic aspects are included, certain system outputs. The finishing method is shown as a system in Fig. 2.

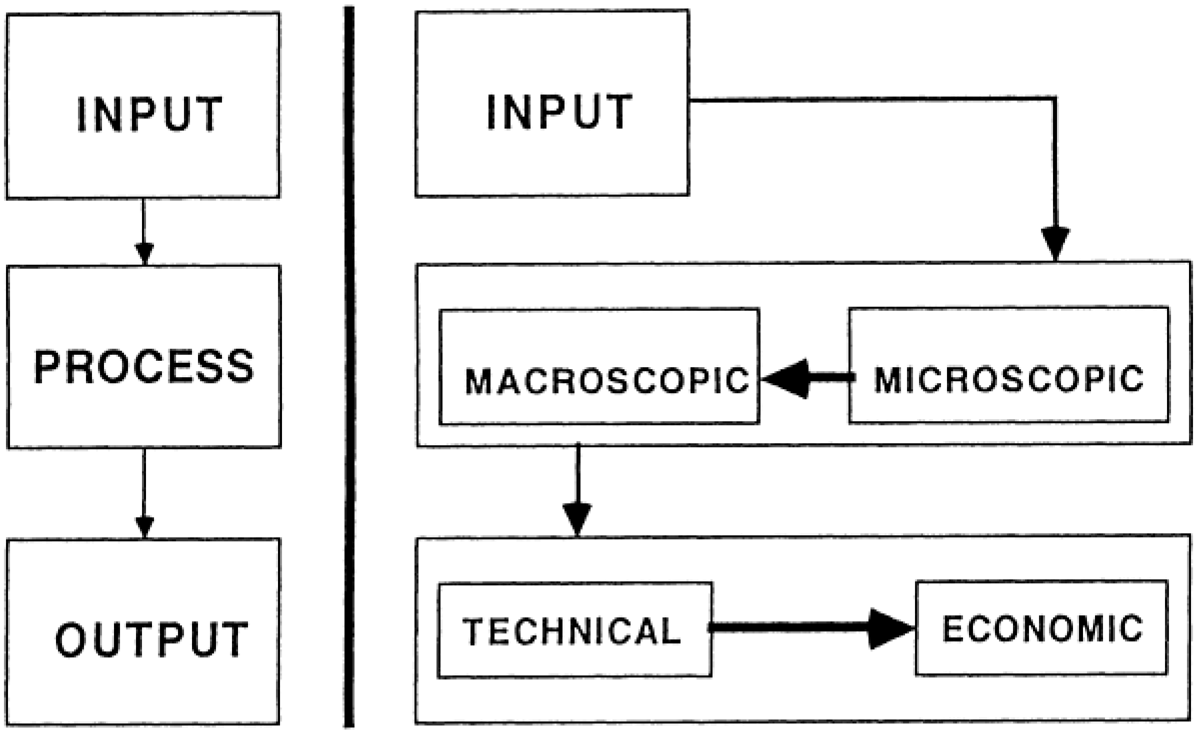

Fig. 2 Systems approach for the manufacturing process

When the microscopic process interactions are understood, the finishing method may be managed efficiently through casual relationships. Efficient achievement or quantum improvements of the technology drivers described above result when the four input elements are managed simultaneously to optimize the microscopic process interactions (Ref 8, 9). Whenever possible, the finishing methods outlined in this chapter are described in terms of the four input elements, key or governing microscopic interactions, characteristic macroscopic variables, and technical and economic outputs.

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Outline of Finishing Methods

In this Section, finishing as a surface generation process is broadly classified as follows.

"Finishing Methods Using Defined Cutting Edges." Many finishing processes use tools of well-defined geometry. Typical examples are turning, milling, and drilling.

"Finishing Methods Using Multipoint or Random Cutting Edges." As described in this title, many finishing processes use processing tools such as grinding wheels, abrasive belts, and abrasive slurries such that the surface generation process takes place between the work material and a number of cutting edges whose geometry is not precisely defined in each case.

"Nonabrasive Finishing Methods" are those in which surface generation takes place without any mechanical interaction between the processing tool and the work materials. These are generally described as nontraditional machining methods. Typical examples are electrochemical machining, electrical discharge machining, and laser machining.

"Mass Finishing Methods."The methods described in the articles mentioned above usually deal with only one or a few work materials or components at a time. However, a number of processes deal with surface modification of a large number of parts at the same time. Typical examples are tumbling and barrel finishing. Shot peening can be classified as a mass finishing method; however, because of its importance and unique characteristics, it is described in a separate article in this Section.

Every finishing method may be characterized as ultraprecision, precision, or rough, depending on the nature or scale of the output of the process, as shown in Fig. 3. The technology drivers described earlier push the advancements in all these methods, and the directions for such advancements are also shown in Fig. 3. The articles mentioned above describe these precision aspects and the trends for advancement in finishing methods.

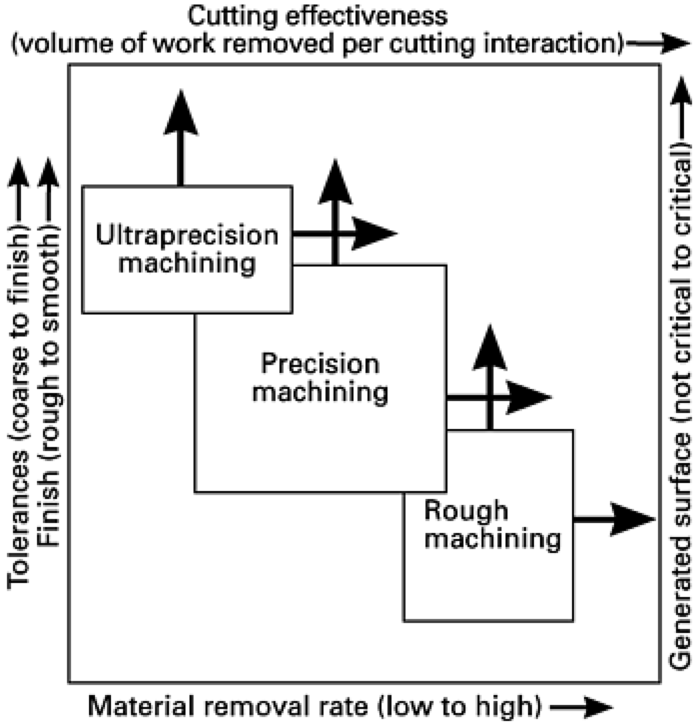

Fig. 3 Classification of finishing methods based on surface generation process and surface characteristics

Characteristics of Finished Surfaces

Surface generation is the primary output of all the methods described in this Section. It is natural, then, to address the characteristics of the generated surfaces and the methods used to measure them.

"Topography of Surface."One of the key characteristics of generated surfaces is the topography. Many contact and noncontact methods are used to measure surfaces, and a number of parameters are used to describe surface features, such as roughness, waviness, and bearing ratio.

"Microstructural Analysis of Finished Surfaces." Because finishing methods generate surfaces by material removal processes, they modify the microstructure of the work material through thermal and mechanical interactions. These results on the generated surfaces are measured and monitored through a number of methods.

"Residual Effects of Finishing Methods." Surface generation processes alter the geometry, topography, and microstructural aspects of finished surfaces. These in turn influence the behavior of the surface under various loads or forces (e.g., mechanical, optical, electrical, and magnetic properties).

Special Topics Related to Finishing Methods

In most finishing processes, thermomechanical interactions occur between the processing tool (cutting tool, grinding wheel, polishing pad, electron beam, etc.) and the work material in the presence of machine tool and operational factors.

Most of these interactions and their results are addressed in the articles mentioned above. However, a few topics common for all finishing methods deserve special attention.

"Thermal Aspects of Finishing Methods." Thermal interactions are one of the key types of microscopic interactions in all finishing methods. They are maximized in some applications and minimized in others. These interactions are strongly dependent on the process selected and the four input elements (machine tool, process tool, operational factors, and work material). General consideration of thermal interactions and their control is critical for any successful use of finishing methods.

"Selection, Application, and Disposal of Finishing Fluids." All finishing methods are carried out in the presence of an environment. Air or ambient conditions may be most common in dry finishing methods. All finishing methods that are carried out "wet" involve the use of a fluid whose function may be intrinsic to the process interactions, such as cooling effects and lubricating effects, or extrinsic, such as removal of the swarf and the thermal stability of the system. Environmental elements such as dielectric fluid play a critical role in electrical discharge machining. Whatever the role of the fluid used in the finishing methods, increasing attention will be paid to their use, maintenance, and proper disposal, and all these aspects of the fluids require special consideration.

"Influence of Work Material Properties on Finishing Methods." The microstructure, properties, and performance requirements of the work drive the selection of suitable finishing methods. Conversely, finishing methods influence the microstructure, properties, and performance of the surfaces generated on work materials. The final article in this Section describes these relationships and presents some guidelines relative to advanced materials.

Finishing Methods Using Defined Cutting Edges

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Introduction

THIS ARTICLE covers precision and ultraprecision finish machining techniques that make use of defined cutting edges, such as polycrystalline diamond (PCD) and cubic boron nitride (CBN) compacts. Grinding techniques are discussed in the article "Finishing Methods Using Multipoint or Random Cutting Edges" in this Volume. The turning, broaching, milling, drilling, and reaming processes discussed in this article are also covered extensively in *Machining,* Volume 16 of the *ASM Handbook* (Ref 1). The same volume provides in-depth information on machining fundamentals and cutting tool materials.

Reference

1. *Machining,* Vol 16, 9th ed., *Metals Handbook,* ASM International, 1989

Finish Turning

Much of the recent progress in turning has been made in precision and ultraprecision machining, and it is generally true that today's precision engineering will be tomorrow's general engineering. At present, the highest spindle speeds in conventional lathes are 2200 to 2400 rpm. For precision finishing cuts on steel and materials with similar properties, the highest spindle speeds should range from 3000 to 5000 rpm to give cutting speeds of 120 to 915 m/min (400 to 3000 ft/min). Fine stepless feeds are desirable to provide gradual entry of the tool into the workpiece, especially at high speeds. Inserts with chip control are essential, and it is not unusual for lathes to have slant beds and screw conveyors for continuous chip disposal. Machine tools must have high rigidity for finish turning that is carried out at high speeds (Ref 2).

The cutting tool materials widely used for finishing cuts are:

- Chemical vapor deposition ceramic (aluminum oxide) coated carbides
- Chemical vapor deposition triphase (TiC/TiCN/TiN) coated carbides
- Physical vapor deposition TiN (titanium nitride) coated carbides

- Cermets
- Ceramics (alumina-based and silicon nitride-based)
- PCD
- Polycrystalline CBN

These tool materials need to be used with specific work materials. Table 1 gives the cutting speeds, feeds, and depths of cut that correspond to some typical work materials.

Table 1 Depth of cut, feed rate, and cutting speed for finish turning of selected materials

Work material	**Depth of cut**		**Feed rate**		**Cutting speed using indicated tool materials, m/min (ft/min)**					
	mm	**in.**	**mm/rev**	**in./rev**	**Ceramic-coated carbides**	**TiN (CVD coated)**	**TiN (PVD coated)**	**Cermets**	**Ceramics**	**PCD/CBN**
Low-carbon and free-machining steel	0.5-2.5	0.02-0.1	0.15-0.28	0.006-0.011	185-455 (600-1500)	120-245 (400-800)	90-230 (300-375)	135-455 (450-1500)	245-915 (800-3000)	. . .
Medium-and high-carbon steel	0.25-2.5	0.01-0.1	0.15-0.3	0.006-0.012	150-410 (500-1350)	90-215 (300-700)	75-215 (250-700)	170-305 (450-850)	245-455 (800-1500)	. . .
Low-carbon alloy steel	0.25-2.5	0.01-0.1	0.15-0.3	0.006-0.012	135-335 (450-1100)	90-230 (300-750)	135-305 (450-1000)	75-185 (250-600)	230-425 (75-1400)	. . .
Medium-carbon alloy steel	0.4-2.5	0.015-0.1	0.08-0.2	0.003-0.008	150-275 (560-900)	60-120 (200-400)	55-130 (175-450)	325-750 (325-750)	230-410 (750-1350)	. . .
Hardened irons (400-525 HB)	0.08-1.5	0.003-0.6	0.08-0.3	0.003-0.012	. . .	. . .	. . .	. . .	60-185 (200-600)	CBN 25-120 (80-400)
Glasses and ceramics (200-250 HB)	0.12-1.2	0.005-0.050	0.12-0.25	0.005-0.1	. . .	. . .	. . .	. . .	. . .	PCD 230-1005 (750-3300)

For ultraprecision turning the lathes mentioned above are unsuitable. Among the tool materials indicated in Table 1 for finish machining, not even PCD or CBN compacts can be used for ultraprecision turning, only single-crystal diamonds and CBN. The machines need to have stiffness, which is provided by aerostatic bearings for the spindle and hydrostatic bearings for the bedway. The machine tool should be capable of giving feeds at the nanometer level for brittle materials, and this, combined with an equally fine depth of cut and moderately high speeds, enables the machining of brittle materials such as germanium and silicon. At such low feeds and depths of cut, brittle materials behave like ductile materials, and this mode of removal is known as ductile machining (Ref 3). Glass cannot be turned on these machines as yet, but this should be possible in the near future.

Pioneering work conducted at a number of institutions (Ref 3, 4, 5, 6, 7, 8, 9) has resulted in the development of ultraprecision lathes. Two typical machines are shown in Fig. 1. The cutting tools used are single-crystal diamonds. One mode of manufacture of these tools is chemical machining, in which the material removal rate ranges from 1 to 3000 μm^3/s (Ref 9). The cube face of the single-crystal diamond is selected as the cutting edge to avoid cleavage, which occurs easily on the octahedral face. The cutting edge should show no nicks or chips at magnifications of 10,000×. By way of comparison, PCDs used for finish turning are inspected at 50×.

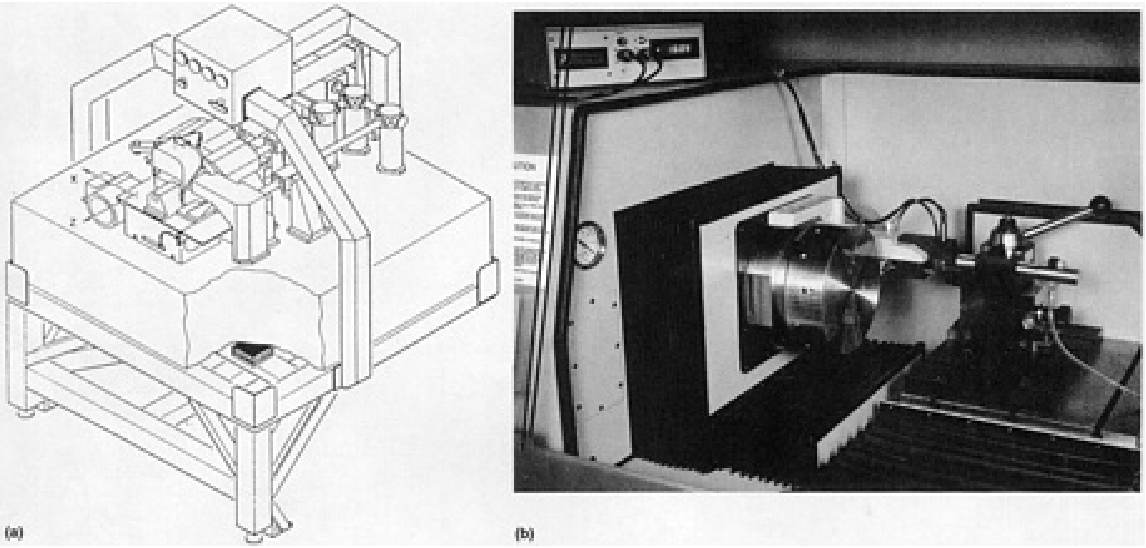

Fig. 1 Ultraprecision lathes. (a) Lawrence Livermore PAUL lathe. Source: Ref 3. (b) Rank Pneumo lathe. Source: Ref 5

Figure 2(a) shows a sketch of a single-crystal diamond/CBN tool. The cutting edge radius is around 50 nm; after wear it is about 350 nm (Fig. 2b). Brittle materials (such as silicon and its compounds, germanium used in aspheric lenses, and ceramics) and ductile materials (such as aluminum for computer hard disks and copper for laser printer mirrors) are easily machined with these tools. When they are used to finish germanium on an ultraprecision lathe, mirror-like surfaces with an average surface roughness (R_a) of 1 nm have been achieved. Even composites such as silicon-carbide-whisker-reinforced (SiC_w) aluminum have been successfully machined by single-crystal diamonds to R_a of 10 nm (Ref 9).

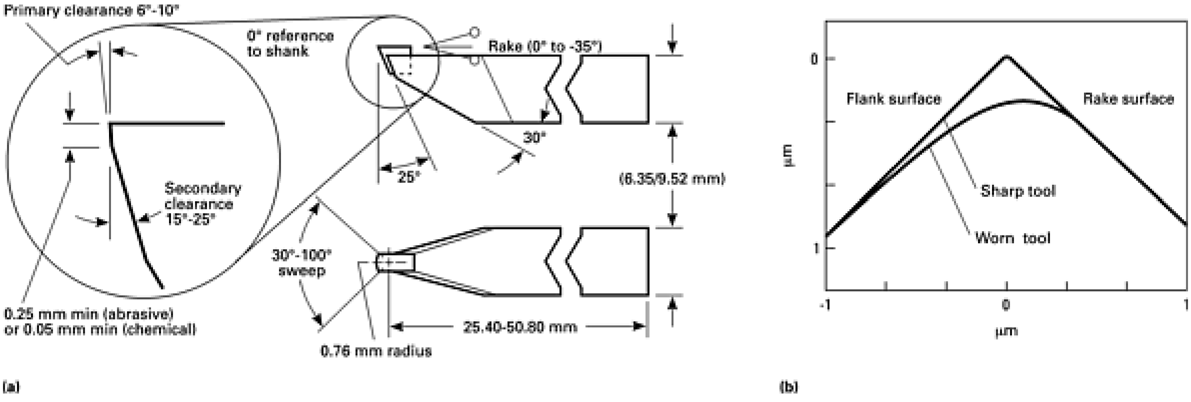

Fig. 2 Single-crystal diamond machining tools. (a) Schematic of a single-crystal diamond/cubic boron nitride tool (Ref 11). (b) Cutting edge radius on a single-crystal diamond before wear (50 nm) and after wear (350 nm). Source: Ref 8

Precision tolerances for silicon, germanium, aluminum, and copper are bilateral of the order of +20 nm for a linear dimension of 20 mm (0.8 in.). Ultraprecision tolerances are unilateral from +5 nm (lower) to +10 nm (upper) for a linear dimension of 20 mm (0.8 in.). A typical product where these tolerances are easily achieved is the polygon mirror. These tolerances are not as easily achieved with SiC_w aluminum alloys because of the orientation of whiskers and heavy tool wear.

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Finish Broaching

Broaching is a typical multipoint process that makes use of several transverse cutting edges, which are pushed or pulled through a hole or over a surface to remove metal by axial cutting. Because a broach has roughing, semifinishing, and finishing teeth, the holes or surfaces produced have close tolerances. The dimensional accuracies and surface finishes for various materials are given in Table 2.

Table 2 Commonly broached materials and typical results

Metal	Heat treatment[(a)]	Hardness HRC	Tolerance		Finish	
			mm	in.	μm	μin.
2618-T61 Al	G	70 HRB	0.05	0.002	0.80-1.15	32-45
2014-T6 Al	G	70 HRB	0.058	0.0023	0.80	32
Ti-6Al-4V	E	36-38	0.019	0.00075	0.61-0.80	24-32
Stellite 31	B	32	0.05	0.002	2.00	80
SAE 51410 (type 410 SS)	H	32-36	0.05	0.002	1.60	63
Greek Ascoloy	I	32-38	0.025	0.001	0.80-1.07	35-42

Inconel	A	85 HRB	0.13	0.005	2.00	80
Inconel X	H	29	0.025	0.001	0.80	32
Timken 16-25-6	F	20-28	0.025	0.001	0.80-1.60	32-63
A-286	G	28-30	0.060	0.0024	0.80	32
		30-35	0.025	0.001	0.89	35
		32-38	0.015	0.0006	0.80	32
S-816	G	23-30	0.025	0.001	0.80-1.00	32-40
SAE 3310	E	20	0.25	0.010	1.60	63
SAE 9310	I	36-38	0.05	0.002	1.60	63
17-22A(S)	H	29-34	0.025	0.001	1.50	60
17-22A	H	35-40	0.075	0.003	. . .	. . .
SAE 9840	I	32-36	0.025	0.001	1.25	50
SAE 4130	I	32	0.013	0.0005	1.60	63
SAE 4140	I	25-29	0.05	0.002	0.80-1.60	32-63
SAE 4340	I	38	0.05	0.002	1.14-1.60	45-63
M2 tool steel	A	24-28	0.02	0.0008	0.80	32
EMS 544	. . .	40-47	0.025	0.001	0.75	30
Inconel 901	I	32-36	0.038	0.0015	1.60	63
René 41	G	40-42	0.060	0.0024	0.80	32
WAD 7823A	. . .	28	0.0076	0.0003	1.0-1.5	40-60
D-979	I	38-40	0.013	0.0005	1.50	60

EMS 73030	. . .	32-36	0.071	0.0028	1.60	63
M-308	. . .	36-38	0.060	0.0024	0.80	32
Chromoloy	. . .	31-32	0.10	0.004	0.80	32
PWA-682 (Ti)	. . .	34-36	0.025	0.001	0.80	32
Lapelloy	J	30-37	0.20	0.008	0.80	32
Type 303 SS	A	85 HRB	0.025	0.001	1.60	63
Type 304 SS	A	80-85 HRB	0.05	0.002	1.60	63
Type 403 SS	I	37-40	0.015	0.006	1.60	63
SAE 1010	D	60	0.025	0.001	0.75	30
SAE 1020	D	3-12	0.05	0.002	1.55-2.05	60-80
SAE 1037	I	15-20	0.0076	0.0003	1.60	30
SAE 1045	I	24-31	0.013	0.0005	. . .	. . .
SAE 1063	E	12-18	0.10	0.004	0.63-1.5	25-60
SAE 1070	E	5-10	0.05	0.002	0.71-1.5	28-60
SAE 1112	. . .	87 HRB	0.025	0.001	1.0-1.15	40-45
SAE 1145	C	13-18	. . .	. . .	1.25-2.5	50-100
SAE 1340	C	15-20	0.075	0.003	. . .	. . .
SAE 4047	C	8-15	0.05	0.002	1.5-2.0	60-80
SAE 5140	C	8-15	0.05	0.002	1.5-2.0	60-80
SAE 52100	D	25	0.013	0.0005	0.75	30
Gray cast iron	B	90 HRB	0.075	0.003	2.0-2.5	80-100

KP-7 cast iron	B	. . .	0.013	0.0005	3.20	125

SS, stainless.

Source: *Metal Cutting: Today's Techniques for Engineers and Shop Personnel,* McGraw-Hill, 1979

(a) Treatment or condition. A, annealed; B, as-cast; C, as-forged; D, cold finished; E, hot finished; F, stress relieved; G, solution and precipitation treated; H, air quench, furnace temper; I, oil quench, furnace temper; J, salt quench, furnace temper.

Further accuracy can be obtained by providing burnishing teeth on the same broach, thus extending its size, or by having a separate broach with burnishing teeth to be used as a second operation only when needed (Fig. 3). A burnishing broach not only increases accuracy but also provides a smoother, more wear-resistant surface. A burnishing broach produces a glazed surface, particularly in steel, cast iron, and nonferrous materials. The total change in diameter produced by a burnishing operation may be no more than 0.013 to 0.025 mm (0.0005 to 0.001 in.). Burnishing teeth are rounded; they do not cut the surface but rather compress and cold work it, improving both the R_a and R_t (total roughness) surface finish values. Burnishing tools, used when surface finish and accuracy are critical, are relatively short and are generally designed as push broaches. Burnishing buttons are sometimes included behind the finishing tooth section of a conventional broaching tool (Fig. 3). The burnishing section can be added as a special attachment or an easily replaced shell. These shells are commonly used to reduce tooling costs when high wear or tool breakage is expected. Burnishing tolerances range from 13 nm (lower) to 25 nm (upper).

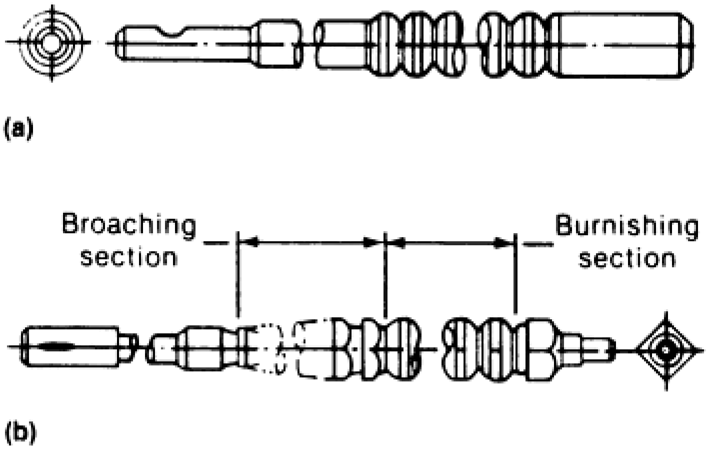

Fig. 3 Two types of broaches used for burnishing the walls of broached holes. (a) Broach for burnishing only. (b) Broach for cutting and burnishing. Source: Ref 10

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Finish Milling

Current practice is to use computer numerical control machining centers for milling, particularly finish milling. Milling is used primarily for machining surfaces and slots. Machining centers are divided into two types: vertical and horizontal. Both types are used for milling flat surfaces, contours, and slots. The workpiece is usually set on a portable pallet, and it is not unusual to find four to six pallets on a machining center. The spindle speed ranges from 40 to 6000 rpm with the possibility of using special spindles with speeds up to 8000 rpm. Spindle design has changed from the conventional add-on type to the current built-in type (Fig. 4). Machining centers are provided with automatic tool magazines (ATMs) capable of holding 20 to 30 tools. Special ATMs capable of holding 200 to 300 tools are available.

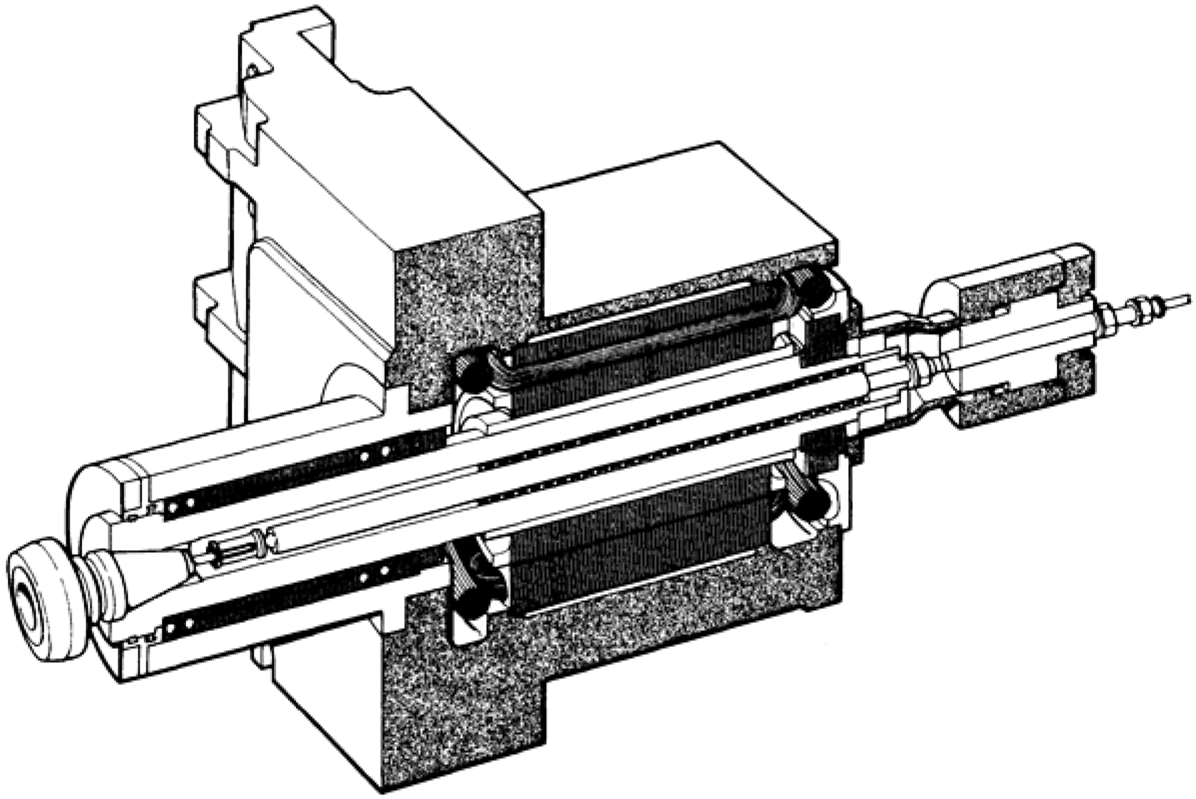

Fig. 4 Spindle head with built-in motor for high-speed (up to 12,000 rpm) finish milling

High-speed milling, which is usually associated with precision machining, involves the use of spindle speeds between 25,000 and 50,000 rpm, and in exceptional cases even as high as 100,000 rpm. A typical application on a horizontal machine is tool and die mold manufacture (Ref 12). High rake angles are used, typically 15° for carbon steels at 300 m/min (985 ft/min) and 25° for ductile materials such as copper and aluminum alloys at 500 m/min (1640 ft/min). Disposal of chips is very important, because they can envelope the tool and cause serious damage to the tool as well as the finished surface. Many machining centers therefore use a vacuum-type chip disposal system that collects the chips as soon as they are generated. However, to use this system, cutting tools must have chip breakers. Precision dies (made of high-carbon steel or chromium-molybdenum alloy steel) should be machined in the heat-treated condition (45 HRC), and in such cases CBN inserts can be used.

As with turning, ultraprecision milling is gaining ground, and a recent development is shown in Fig. 5(a). Single-crystal diamonds are used and mirror-like surfaces are obtained. With the development of diamond pseudo-end mills it is possible to manufacture sculptured surfaces such as toroids and paraboloids (Fig. 5b, c) with a typical feed and depth of cut of 2 and 75 μm, respectively, and with the spindle rotating at 23,000 rpm. Toroids and paraboloids can be generated by grinding (Ref 14), but small products are difficult.

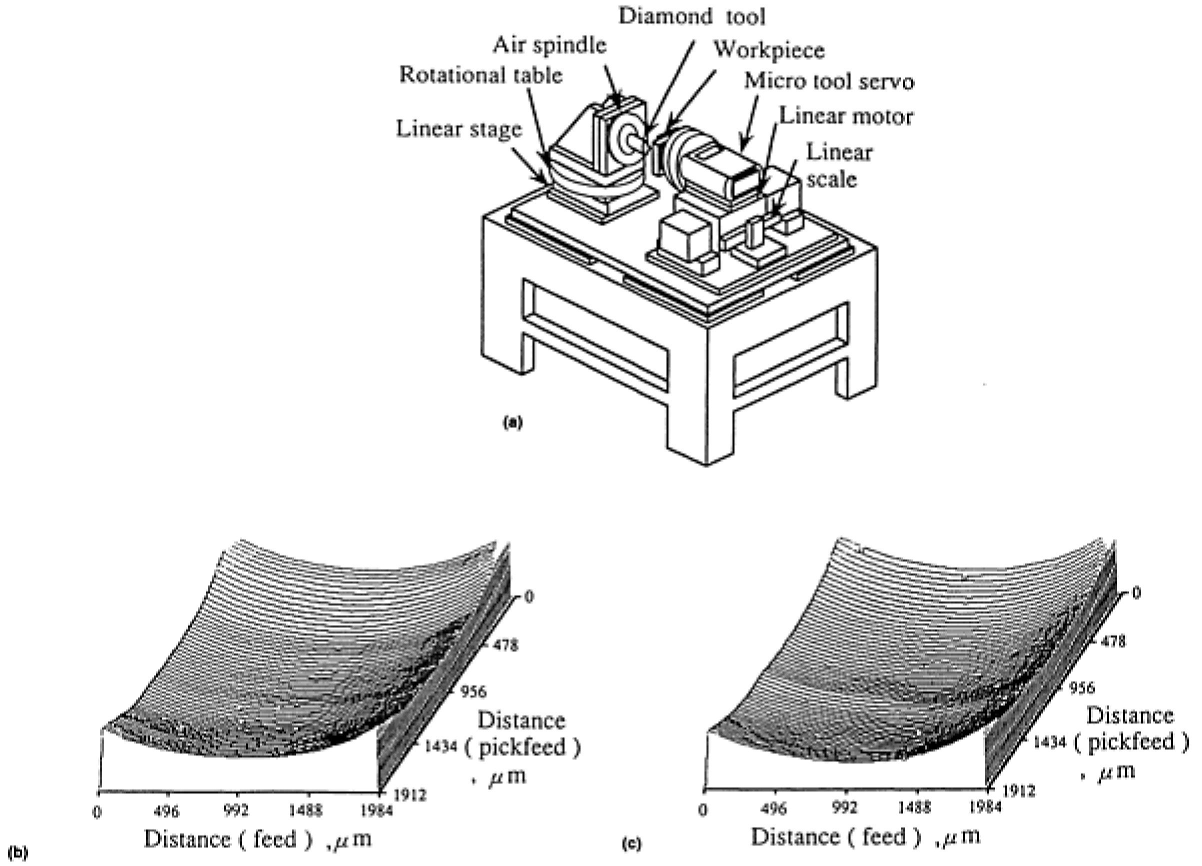

Fig. 5 Ultraprecision milling. (a) Ultraprecision machine for manufacturing sculptured surfaces. (b) Paraboloid surface. (c) Toroid surface. Source: Ref 13

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Finish Drilling

Next to turning, drilling is the most widely used machining process, accounting for about 25% of all machining operations, and as much as 60% in some small and medium industries. Despite this wide use, conventional drilling remains a rough process that generally needs to be finished by boring or reaming. The tool materials used for drills are high-speed steels, carbides, CBN, and diamonds. High-speed steel in the form of twist drills comes in all sizes and is used for rough machining. Carbide drills come in three forms: solid carbide drills of diameters of 8 mm (0.3 in.) and less, drills with brazed tips, and drills with indexable inserts for diameters of 14 mm (0.6 in.) and above. Carbide drills need to be used at much higher speeds than high-speed steel drills but result in higher productivity and better surfaces, often not requiring a secondary reaming or boring operation. Getting high speeds with small drills necessitates very high spindle speeds, and such spindles require air bearings.

Drilling of holes in printed circuit boards is done with carbide drills. As in milling, machining centers are popular for drilling. Hole fabrication by ultraprecision drilling has not gained ground, primarily because the width of cut, which is equal to the hole diameter, is very high. Using PCDs does not help because they are not good enough for ultraprecision turning and milling, let alone drilling. PCDs *are* used, however, for finish drilling of aluminum and copper. Precision hole fabrication can be done by techniques such as grinding (for small diameters) and boring (for large diameters where single-crystal diamonds can be used at low depths of cut and low feeds). Nontraditional machining techniques such as electrical discharge machining, electrochemical machining, and extrusion honing are other finishing techniques that are good for putting quality holes in difficult-to-machine materials.

The strategy for finish drilling is to modify twist drills to improve the hole quality, but not at the expense of productivity. A highly successful drill is the indexable drill, or endrill, where two indexable carbide inserts are used. The two inserts are positioned so as to get a negative (Fig. 6a) or a hybrid negative-positive (Fig. 6b) point angle. The negative point angle in drilling is equivalent to a negative side-cutting-edge angle in turning, and speeds of 70 to 120 m/min (230 to 395 ft/min) give excellent surface finish, cylindricity, and roundness. At speeds of 70 m/min (230 ft/min) a builtup edge is formed. Figure 7 shows a chip root obtained by using an explosive quick-stop device. Chip roots obtained in high-speed machining should show a secondary shear zone, and this has not been reported for indexable drilling (Ref 15).

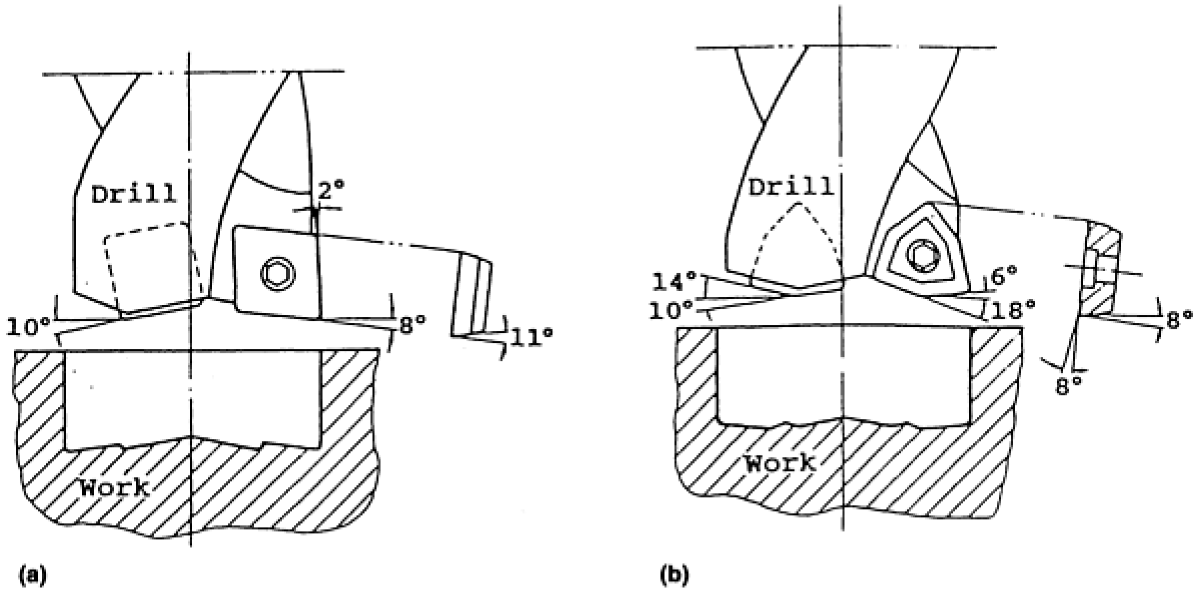

Fig. 6 Indexable drills using (a) square and rhomboid-shape inserts and (b) two trigon inserts to give (a) negative and (b) negative-positive point angles. Source: Ref 15

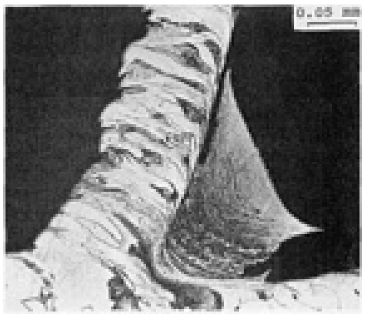

Fig. 7 A chip root obtained when machining 1018 steel with an indexable drill shows the presence of a builtup edge at a speed of 70 m/min (230 ft/min). Source: Ref 15

In a twist drill the two lips do the cutting while the chisel edge removes material by extrusion, which is less efficient than cutting and produces higher temperatures. This results in a lower removal rate and, hence, lower productivity. The chisel edge has a high negative rake angle equal to half the point angle (i.e., 59° in standard drills). By grinding a groove on both sides of the chisel edge (Fig. 8), the rake angle can be reduced from -59° to +5°, the thrust force can be reduced considerably, and extrusion action can be avoided. Surface roughness, roundness, and cylindricity can be improved by reducing vibration, which is often due to inefficient chip disposal. This can be achieved by providing nicks on the cutting edge of twist drills, as well as indexable drill inserts, to improve chip splitting and breaking (see Fig. 9).

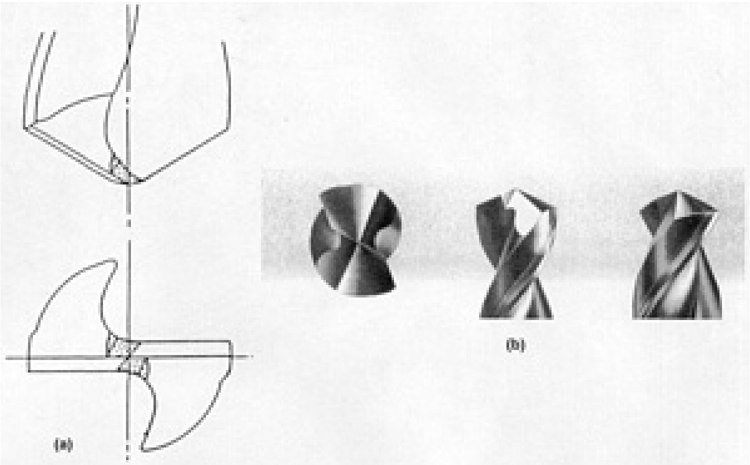

Fig. 8 Thrust force reduction achieved by eliminating the chisel edge by grinding grooves on either side. (a) Line diagram. (b) Three photographic views

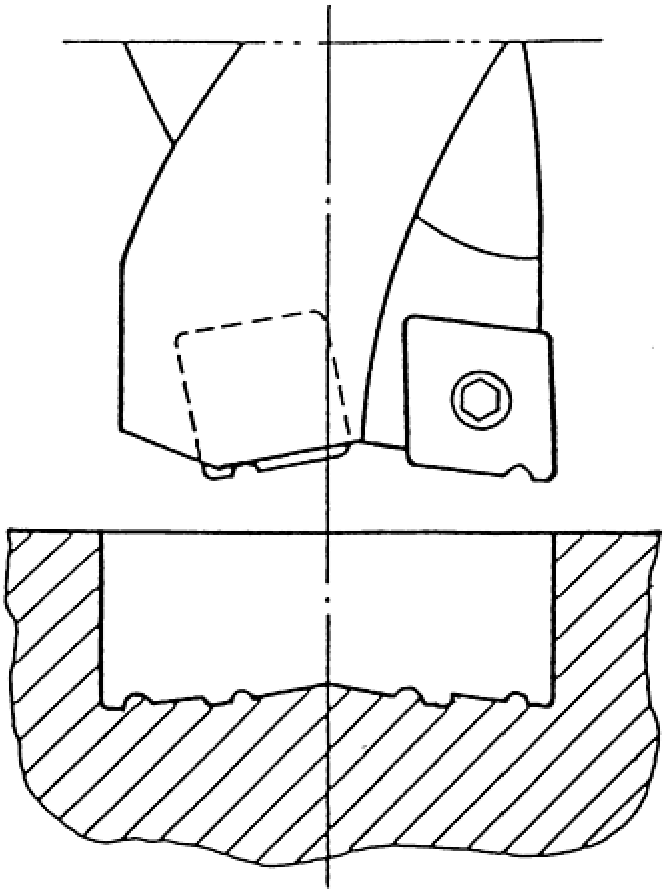

Fig. 9 Nicks or grooves on indexable inserts, used to reduce vibration by improving chip splitting and chip breaking. Source: Ref 15

Burr formation is undesirable, especially in fine finishing, and deburring can be a tedious and time-consuming operation. Burr height can be decreased by reducing the point angle from 118° to 90°, or by having a double cone with 118° and 90° for the two stages. A substantial decrease in burr height can be obtained by vibrating the drill in the feed direction at ultrasonic (Ref 17) or low (Ref 18) frequencies. In both cases, there is an optimum amplitude for each cutting condition.

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Finish Reaming

Reaming is traditionally a finishing process for a rough hole produced by a twist drill. With the modified drills discussed earlier, high-grade reamers corresponding to ISO Grade 4 or 5, instead of the traditional 6, give fine finished holes. Recent developments by a Japanese firm include the broach reamer, which rotates, and the carbide mill reamer, which can be used in a machining center or preferably a jig borer (Fig. 10). Broach reamers are available in sizes from 3 to 100 mm and carbide mill reamers are available in sizes from 5 to 100 mm. Both reamers give R_a of 1 μm and cylindricity and roundness of <2 μm.

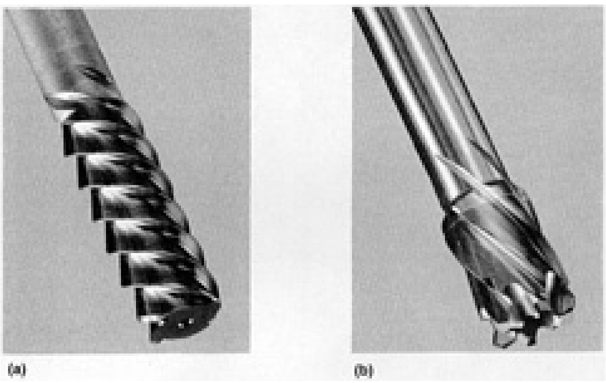

Fig. 10 Broach and carbide mill reamers. (a) Broach reamer, made of high-speed steel with a left-handed helix of 60° or more, that can cut at 20 m/min (65 ft/min) at a feed of 0.25 mm/rev (0.1 in./rev). (b) Carbide mill reamer that can cut at 30 m/min at a feed of 0.3 mm/rev (0.1 in./rev)

Introduction

ABRASIVE FINISHING includes many commercial processes, which can be generally classified as *rough grinding, precision grinding,* or *high-precision grinding.* The distinctions among these categories are based on the desired material removal rates and the acceptable tolerance or finish (Table 1). In rough grinding processes, material removal occurs at a rapid rate, with less emphasis on surface roughness/tolerances. In contrast, high-precision methods emphasize the attainment of fine surface finish and close tolerances at the expense of material removal rates. In precision grinding processes, removal rates are balanced with requirements of surface characteristics such as form, surface integrity, tolerances, and surface finish (roughness, waviness, roundness, etc.).

Table 1 Characteristics of abrasive finishing processes

Finishing processes	Cutting speed		Material removal rate		Tolerance		Finish	
	m/s	sfm	mm^3/mm/s	in.^{3}/in./min	mm	in.	µm	µin.
Rough grinding								
With grinding wheels	60-100	12,000-20,000	300-1000	30-100	±6-25	±0.250-1.0	2.5-25	100-1000
					±2.5	±0.100	2.5-25	100-1000
					±0.13	±0.005		
Belt grinding	15-25	3000-5000	6-3000	0.6-30	. . .	. . .	. . .	. . .
Precision grinding								
With grinding wheels								
Present	30-80	6000-16,000	0.1-50	0.01-5	±0.0025-0.125	±0.0001-0.005	0.75-1.25	30-50
Future	. . .	. . .	≤500	≤50	±0.25 µm	±10 µin.	0.0025	0.1
Belt grinding	15-37.5	3000-7500	. . .	. . .	. . .	. . .	. . .	. . .
High-precision abrasive finishing								
Lapping	<0.25	<50	. . .	. . .	<0.5 µm	<20 µin.	0.025-0.1	1-4
Honing	0.25-1	50-200	0.075	0.0075	0.5-1.25 µm	20-50 µin.	0.25-0.5	10-20
Polishing	Very slow	Very slow	(a)	(a)	. . .	. . .	. . .	. . .

(a) Surface finish altered; material removal rate is insignificant.

The basic idea of abrasive finishing is to use a large number of multipoint or random cutting edges for effective removal of material at smaller chip sizes than in the finishing methods that use cutting tools with defined edges. Machining at small chip sizes allows improved finish, closer tolerances, more localized control, and generation of more intricate surface features. Cutting tools with defined cutting edges are less feasible and less practical if small chip sizes are desired. An effective way of delivering small cutting edges to the machining zone is to use abrasive grains incorporated into a bond or matrix material.

Recent Developments. Abrasive finishing processes have seen a spurt in new developments in the past 20 years or so, thanks to a number of technology drivers as well as user needs.

Tolerances. Improvements in product performance can often be related to improvements in abrasive finishing processes and their ability to achieve closer tolerances. For example, transmission efficiency is improved when gears roll against each other with less sliding. This is made possible by grinding the gear to closer tolerances. Efficiency of magnetic recording is improved when the magnetic recording heads are finished to closer tolerances and improved surface by improvements in grinding and lapping.

Consistency. When components are finished to greater consistency, inspection costs are reduced and the process becomes more amenable to control. As an example, in a centerless grinding process for a bearing component, the operation consisted of rough, semifinish, and finishing steps involving three operations, three machines, a large in-process inventory, and inspection between each operation. By consistent finishing with cubic boron nitride (CBN) grinding wheels, the process was reduced to two steps, rough and finish, with minimal in-process inspection.

Surface Finish. Constant demand for improvements in surface finish has resulted in new processes (e.g., superfinishing, flat honing, and microgrinding). These requirements span a wide range of materials, from metals to nonmetals and from ferrous alloys to ceramics.

Material Removal Rate. With the advent of new abrasives (CBN, seeded gel, etc.) and new processes (high-efficiency deep grinding, creep-feed grinding, microgrinding, etc.), the material removal rates achievable using abrasive finishing processes exceed the previously known capabilities.

Productivity. The technical benefits described above often translate into faster production rates, shorter cycle timing, improved yields, and so on. All of these gains lead to lower total cost per part or higher productivity. Advancements of this kind have been noted in aerospace, automotive, tool production, bearings, and computer component manufacturing operations that use abrasive finishing processes.

New Products. The range of new abrasive finishing products, introduced worldwide, includes novel shapes and configurations, a wider range of sizes, an expanded range of grit sizes, and new bond types. For instance, abrasives are now available in extremely fine particle sizes with uniform size and shape control, which were not commonly available only a few years ago.

Machine Tool Improvements. Developments such as multiaxis computer numerical control (CNC), higher horsepower, greater rigidity and accuracy, automatic wheel changes, and on-machine truing and balancing systems make it possible to achieve faster production, better quality, or both.

New Grinding Methods. *Mirror-finish grinding*uses extremely fine abrasive particles to achieve extremely fine reflective surfaces of precise geometry. These methods are used to finish precision molds and dies, such as those used for making contact lenses and other optical products. *Grinding from solid* combines the high-material-removal capability of modern abrasive finishing methods with the closer tolerances and forms that can be achieved using grinding processes. As an example, end mills of large sizes are now routinely ground from solid blank, eliminating premilling operations and expensive in-process inventory. Such methods are also advocated for grinding ceramics, which improves the yield and reliability of ceramic components while reducing total fabrication cost.

Processing of New Materials. Ceramics and other materials, such as high-silicon aluminum alloys, powder metals, and cements, are increasingly being finished using abrasive methods. As the abrasion resistance of the work material increases due to included second-phase material or hard particles, multipoint finishing methods are often preferable to single-point machining methods. With the advent of processes such as high-efficiency deep grinding, it is likely that some soft and easy-to-machine materials will be finished using abrasive finishing methods.

Abrasive finishing is used in industrial practice for a wide range of materials. Typical examples are shown in Table 2. This article provides a broad overview of the various categories of abrasive products and materials, abrasive finishing processes, and the mechanisms of delivering the abrasives to the grinding or machining zone.

Table 2 Relative usage of abrasive machining for various work material types

Work material	Relative use			
	Conventional abrasives		Superabrasives	Powders slurries, and compounds
	Bonded	Coated/ impregnated		
Plastics	Low	Low	Low	None
Composites	Low	High	High	Low
Metals	High	High	High	High
Steel	High	High	High	High
Glass	Low	High	High	High
Carbides	High	Low	High	High
Ceramics	Low	Low	High	High
Wood	Low	High	High	None
Stone	None	Low	High	Low
Minerals	None	None	High	None

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Abrasive Products

Abrasive delivered in a bond or matrix is often called the *abrasive product* or *abrasive tool.* The products can be grouped under three broad categories: coated/impregnated abrasives, bonded abrasives, and powders, slurries, and compounds (Fig. 1). Each of these product types can be used in rough, precision, or high-precision applications (Table 3).

Table 3 Abrasive products and their typical application categories

Abrasive product type	Abrasive finishing process category

product type	Rough	Precision	High-precision
Bonded abrasives	Snagging surfacing cutoff grinding	Grinding (surface, creep feed, form, thread, contour, cylindrical, disc, tool, and cutter)	Honing, superfinishing, flat honing, microgrinding
Coated abrasives	Belt grinding, sanding	Belt grinding (surface, form or profile, flat stock finishing, polishing)	Belt polishing
Impregnated abrasives	. . .	Polishing, deburring, buffing	. . .
Powder, slurries, compounds, and jets	Abrasive jet machining	Polishing, buffing, liquid buffing, ultrasonic machining	Lapping, polishing, buffing

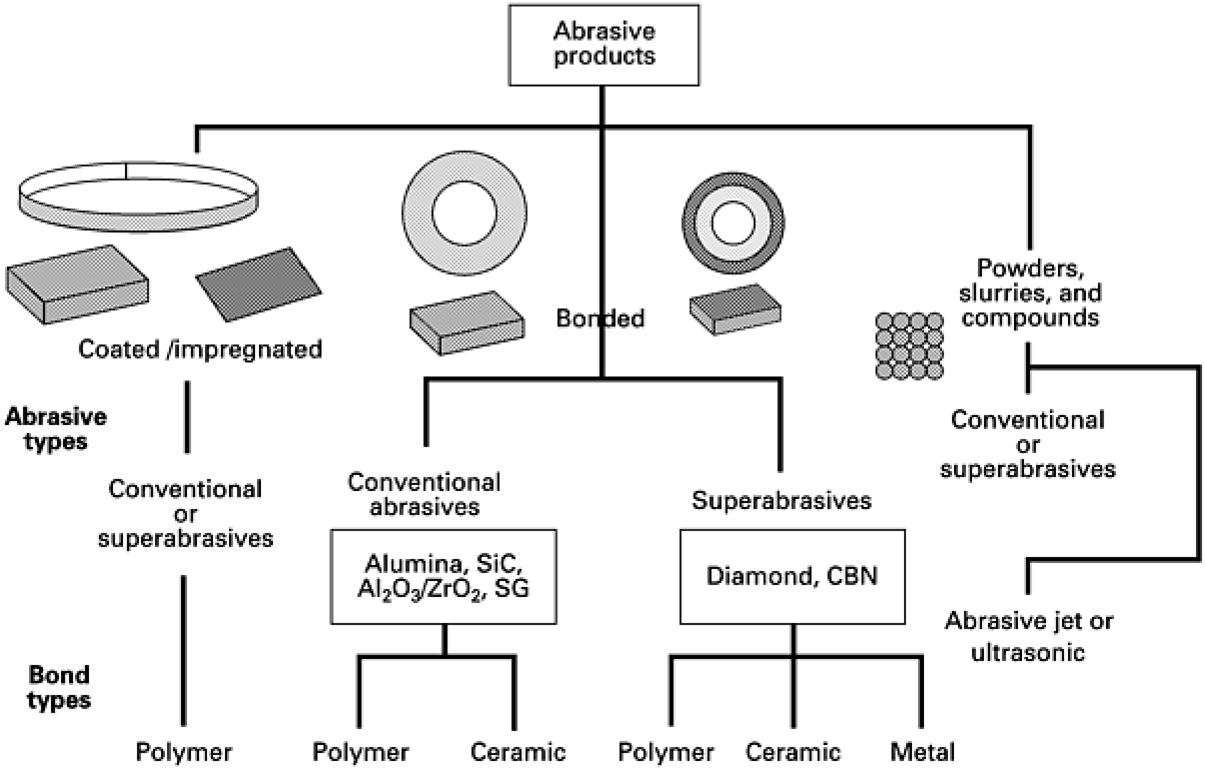


Fig. 1 Abrasive "machining" product categories

Bonded abrasives are so named because the abrasive is firmly retained in a matrix called the *bond.* They are available in discs or cylinders called *grinding wheels.* They are also available in segments of a cylinder, which are assembled into a wheel, and in rectangular blocks, nicknamed "stones," "sticks," or "hones," that are presented to the work material under various geometric configurations. The bond material can be made of phenolic resin, vitreous glass, or powder metal alloys, depending on the requirements. Every bonded abrasive product can be thought of as an engineered composite. This composite is usually of controlled pore size and structure, and its uniformity is critical for successful use of the abrasive product (Fig. 2). The size, shape, and configuration of bonded abrasives are constantly changing to meet growing needs. For example, grinding wheels are available in thicknesses from 0.02 to 500 mm (0.0008 to 20 in.). They are also available in a wide range of shapes.

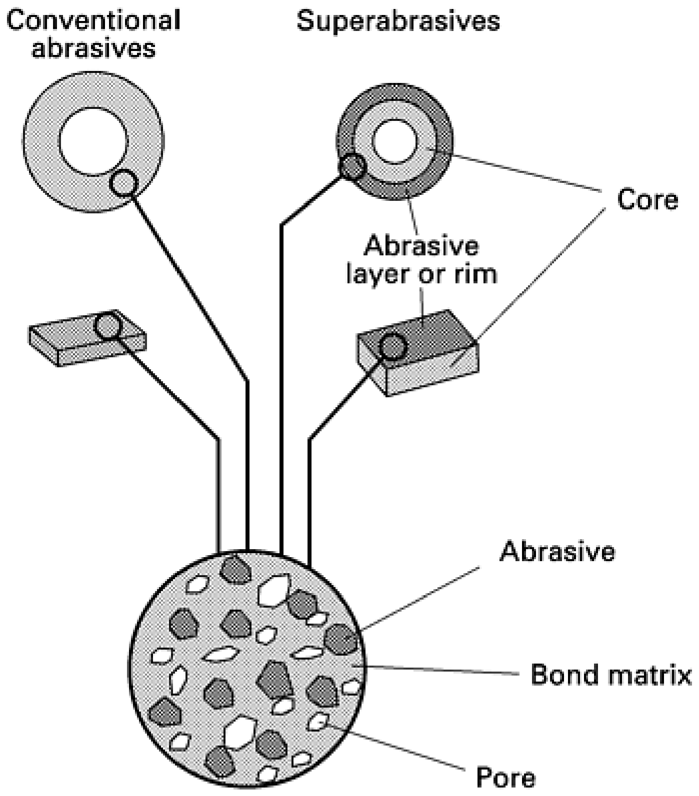


Fig. 2 Construction of typical bonded abrasive products

Coated/Impregnated Abrasives. *Coated abrasives* are single or multiple layers of abrasive products that adhere to a flexible sheet or belt. In *impregnated abrasives,* sold under various trade names, the abrasive is impregnated into flexible or woven material. Sometimes a layer of highly wear-resistant abrasives *(superabrasives)* are electroplated or brazed to a rigid steel core. Most coated and impregnated abrasives use a polymeric binder to retain the grains on the backing or the woven matrix. Most coated abrasives are available in flat sheets or belt loops of various lengths and widths.

Powders, slurries, and compounds are products in which the abrasive is delivered in a jet or in a liquid or paste configuration. When the abrasive is assisted by high-pressure water or air jet, the process is called *abrasive jet machining.* If the abrasive action is assisted by localized ultrasonic motion of a tool, it is called *ultrasonic machining.* Most abrasive powders, slurries, and compounds are delivered between the work and a wear-resistant plate called a *lapping plate,* flexible woven material called *polishing cloth,* or *buffing wheels.* (Lapping, polishing, and buffing are described in detail later in this article.) These products have extremely closely sized abrasive particles, often mixed in a liquid or carrier of controlled viscosity. Sometimes these abrasives remove the surface layer of work material through chemical action in addition to mechanical action.

Designations of Abrasive Products. A wide variety of products and their designations exist in industrial and consumer use. The common aspects of such designations are that:

- All abrasive products are identified by the abrasive type. The size of the abrasive used and its content are also frequently identified.
- In coated abrasives, the type of backing material (paper, cloth, etc.) and the features of the coating (open, closed, supersize, etc.) are also identified.
- In grinding wheels, the bond matrix used (resin, vitrified, metal, etc.) is designated along with its modifications, usually represented by a manufacturer code. The pore content is identified using the grade or hardness of the wheel.
- In the case of loose abrasives used in lapping or polishing, the particle size, shape, and distribution are critical and are identified in the specification. These products are also distinguished by the liquid

medium or carrier used and their flow properties, such as viscosity and temperature stability.

Abrasive Materials

Abrasive materials provide the cutting edges in abrasive finishing processes, so they are the essential element of any abrasive product. A variety of abrasives are used, selected for their hardness, thermal and chemical stability, and wear resistance. Figure 3 compares the hardnesses of abrasives to those of some common work materials. Figure 4 illustrates the range of abrasive sizes used and their applications.

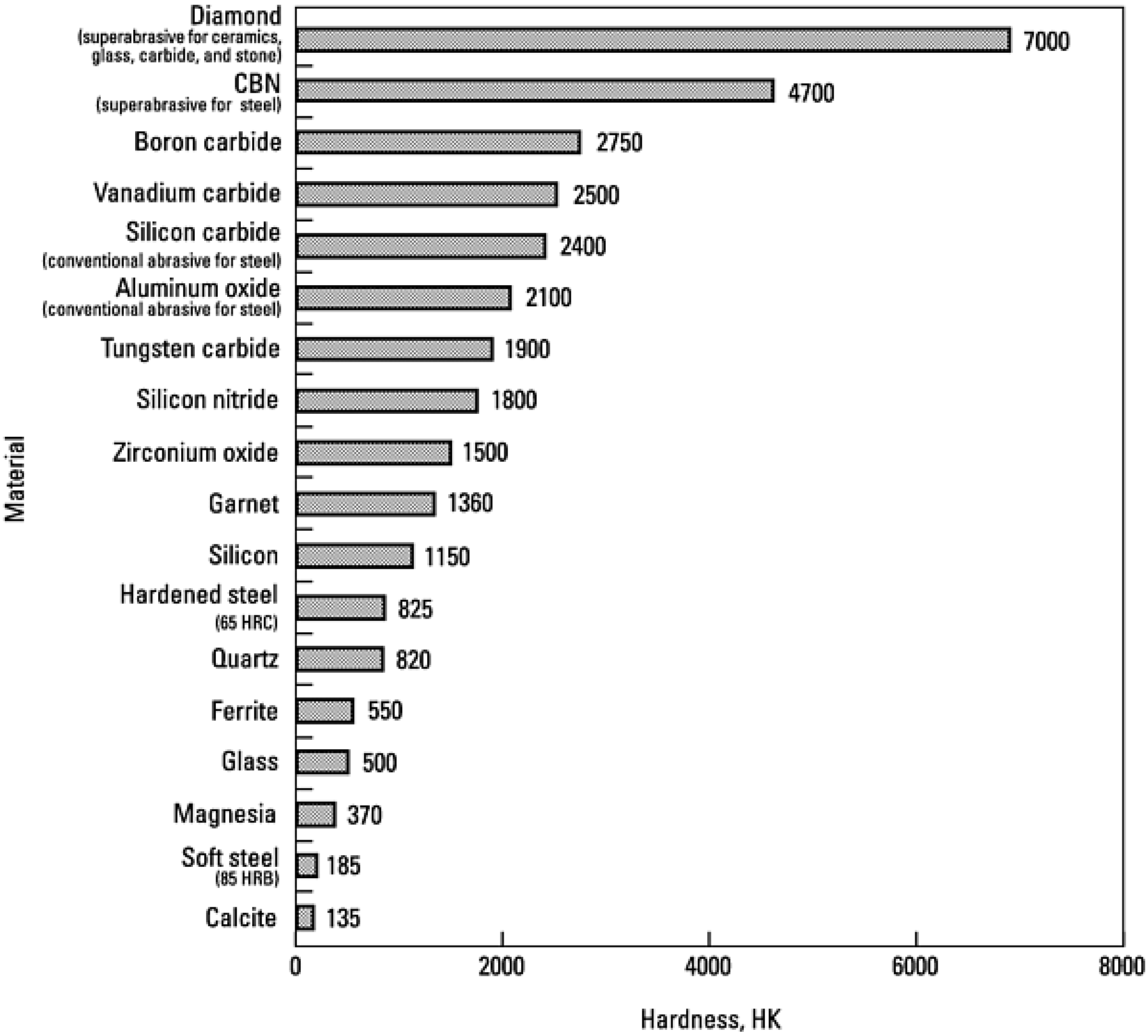


Fig. 3 Comparison of the hardnesses of work materials and the hardnesses of the abrasives used to machine them

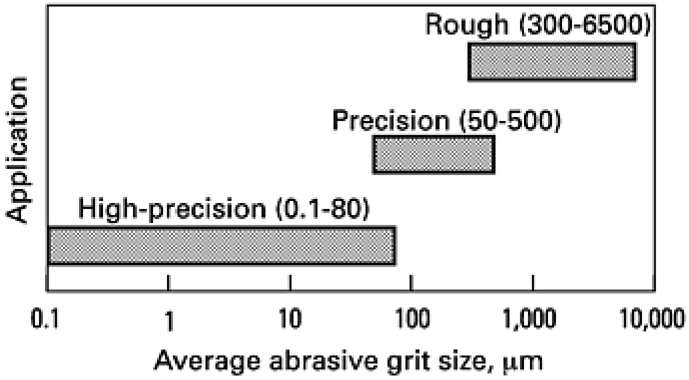


Fig. 4 Abrasive grain sizes vs. application type

The broad groupings of abrasives are identified in the following paragraphs, but in each category there are several versions that differ in shape, size, fracture strength, and so on. The reader is encouraged to obtain information about modifications from manufacturer literature and the references at the end of this article. This knowledge can be very useful in optimizing abrasive machining applications.

Conventional Abrasives. Emery and corundum are commonly used natural abrasives. Emery is a naturally occurring mixture containing between 57 and 75% aluminum oxide. The remainder is iron oxide and impurities. Corundum is a naturally occurring fused aluminum oxide that is tougher and harder than emery. Natural abrasives usually cost less than synthetic abrasives and are useful for polishing some softer metals. When applied to the harder metals, natural abrasives wear at a rapid rate, so they have been largely replaced by synthetic abrasives.

Synthetic Abrasives. Aluminum oxide and silicon carbide are the most widely used synthetic abrasives. They are harder, more uniform, longer lasting, and easier to control than natural abrasives. Because aluminum oxide grains are often very angular and have excellent bonding properties, they are particularly useful in finishing tougher metals, such as alloy steels, high-speed steels, and malleable and wrought iron.

Silicon carbide is harder and a better conductor of heat than aluminum oxide; it fractures easily, providing new cutting surfaces that extend the useful life of the abrasive. Silicon carbide is usually used in polishing low-strength metals, such as aluminum and copper. It is also applied in polishing hard, brittle materials, such as carbide tools, high-strength steels, and chilled and gray irons. Silicon carbide tends to decompose readily in the presence of iron and is not useful as an abrasive for grinding at high material removal rates involving ferrous work materials. However, it is used extensively in the grinding of titanium alloys.

Various types of alumina and silicon carbide are used as abrasives. The variations are derived from such factors as purity, crystal size, shape, and strength. Zirconia-alumina is a eutectic version with high impact strength and toughness, which are desirable characteristics for abrasives used in heavy or rough grinding conditions. A very pure form of aluminum oxide is produced using sol-gel techniques. In some cases, this microcrystalline alumina provides dramatic performance improvements compared to fused aluminum oxide.

Superabrasives. Diamond and CBN are the two superabrasive materials used in grinding applications. Diamond, available in both natural and synthetic forms, is the hardest known material. CBN, the second hardest material, is synthetic. Both of these superabrasive materials are synthesized at high pressures and temperatures in the presence of molten catalyst solvents.

Synthetic diamonds are available in a wide range of shapes and sizes. Weak, friable polycrystalline diamonds are generally used for grinding tough and brittle materials such as ceramics and carbides. Stronger abrasives find frequent application in the grinding of concrete, stone, and glass. The most popular form of CBN, used for grinding most steels and nonferrous high-strength alloys, is a monocrystalline variety. A tougher, polycrystalline form of CBN is also available.

Diamond and CBN are available with a coating of nickel metal. Metal-coated abrasives, predominantly used in resin-bonded wheels, increase grinding wheel life by a factor of 2 to 3. Diamond abrasives are also available with copper coatings, predominantly used in dry grinding applications.

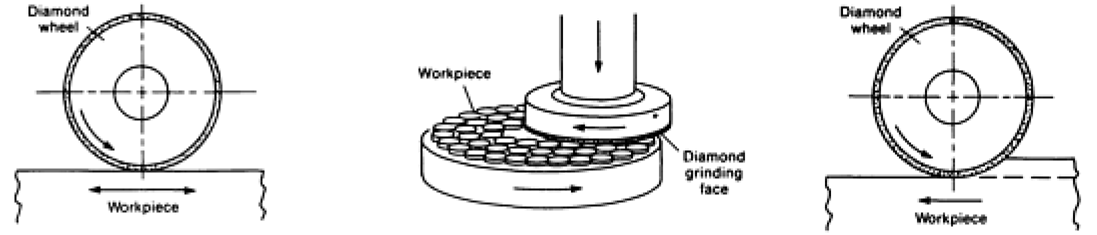
Combinations of abrasive types (combinations of superabrasives with conventional abrasives, combinations of conventional abrasives, and combinations of superabrasives) are sometimes made to take advantage of the best properties of each.

Grinding

A wide variety of abrasive finishing processes termed *grinding* are practiced in the finishing of industrial components. They offer the following advantages (compared to machining processes that use defined cutting edges):

- The range of surface geometries generated (e.g., contours, profiles, etc.) is frequently more complex than is economically possible in single-point machining processes.
- Grinding wheels can be used for high stock removal (i.e., rough grinding). The same wheel is often modified in situ to achieve an extremely fine finish or close tolerance during finish grinding processes. In situ modifications of cutting tools are not possible or practical.
- Grinding wheels can be designed so that the abrasive, bond, and pore distribution are carefully controlled to meet unique requirements of surface generation efficiency and quality of the generated surface.
- The material removal rate per cutting edge is often controlled by abrasive grain size and content, and the total volume of material removed per unit of time can be modified by the design of the wheel geometry and the kinematics of the wheel/work motions. The separation often allows for control of surface features somewhat independently of production economics. This separation is not possible in the processes described in the article "Finishing Methods Using Defined Cutting Edges" in this Volume.

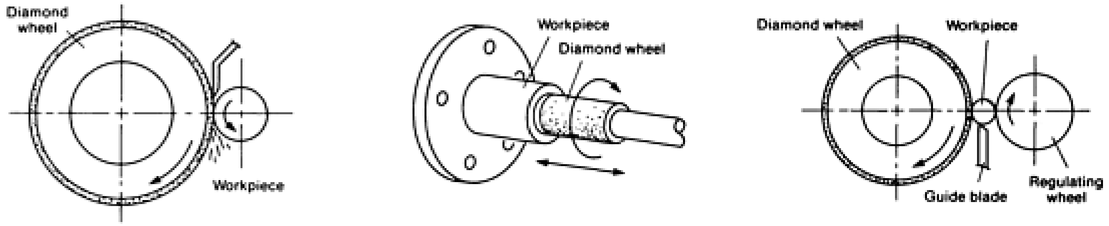
Typical grinding processes are shown in Fig. 5. Each of these applications can range from rough grinding to precision grinding to high-precision processes. Many of these operations in rough grinding are carried out using handheld grinders or manual effort. However, a large number of rough grinding processes and almost all precision grinding processes use automated equipment. They occasionally involve manual loading or unloading of parts and wheels. Large-volume production operations are often fully automated. Recent advancements in CNC grinding machines have extended the capability of conventional grinders by allowing for grinding of multiple surfaces in a single setup, using more than one wheel at a time as well as grinding multiple surfaces simultaneously.



(a) Horizontal-spindle surface grinding

(b) Verticle-spindle surface grinding

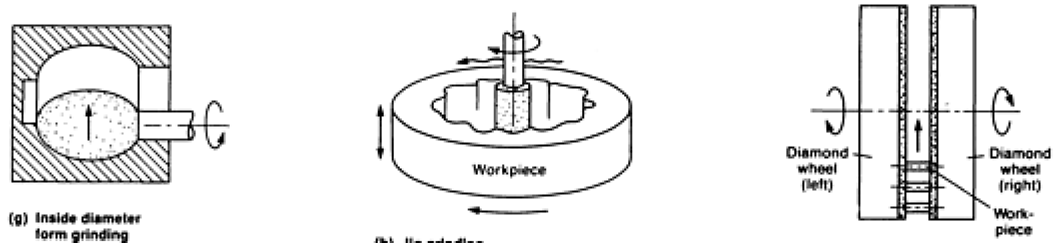
(c) Creep-feed grinding



(d) Outside diameter cylindrical grinding

(e) Internal grinding with a chucking machine

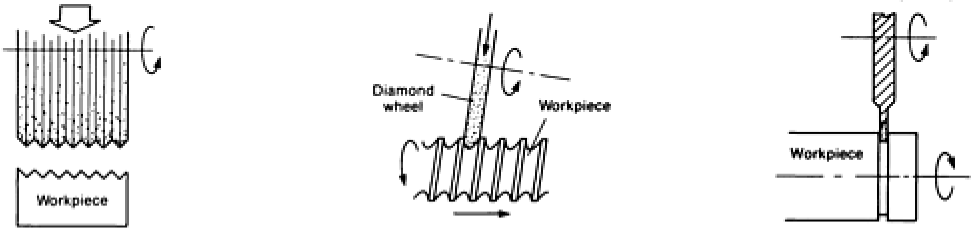
(f) Centerless grinding



(g) Inside diameter form grinding

(h) Jig grinding

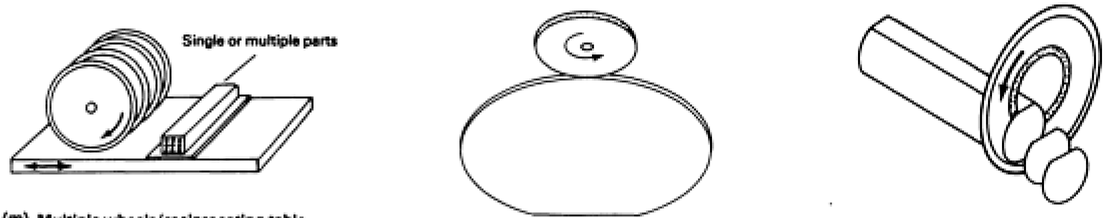
(i) Double-disk grinding



(j) Thread grinding

(k) Outside diameter form grinding

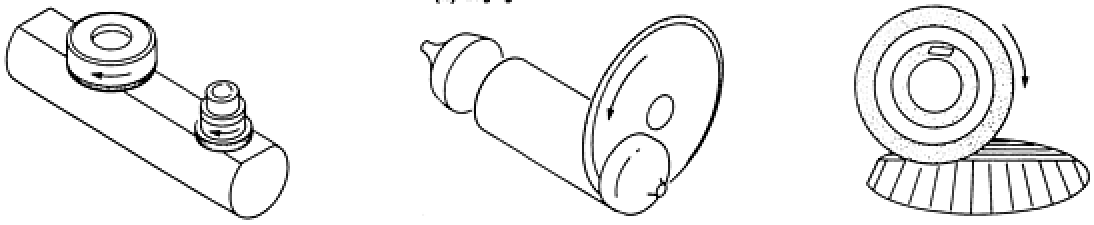
(l) Slot grinding



(m) Multiple wheels/reciprocating table

(n) Edging

(o) Slicing



(p) Flatting

(q) Cropping

(r) Dicing

Fig. 5 Grinding processes

The grinding machine features that frequently determine the production rate and/or part quality are:

- Rigidity/stiffness

- Vibration level
- Coolant systems
- Precision movements and positioning accuracy
- On-machine dynamic balancing capability
- Truing and dressing systems
- Multiaxis CNC capability
- Spindle horsepower
- Speed range and variability
- Torque/speed capability of the motor
- Materials handling systems
- Work space and its accessibility
- Grinding cycle design or capability

Grinding Cycle Design. One of the key elements in the grinding process is the design of the grinding cycle. This involves a programmed application of the grinding wheel against the work material. It can be measured or monitored in terms of the position of the slide in which the wheel or part is mounted with respect to the time.

Initially the slide is moved rapidly, thus removing a large volume of work material rapidly. This is the rough grinding portion of the cycle, as illustrated in Fig. 6(a). This is usually followed by a short dwell, during which the motion of the slide is sometimes stopped to allow the elastic deflections produced during rough grinding to be eliminated. The need for this dwell and its duration are often determined by the stiffness of the wheel, the work material, the work fixture, or the machine tool.

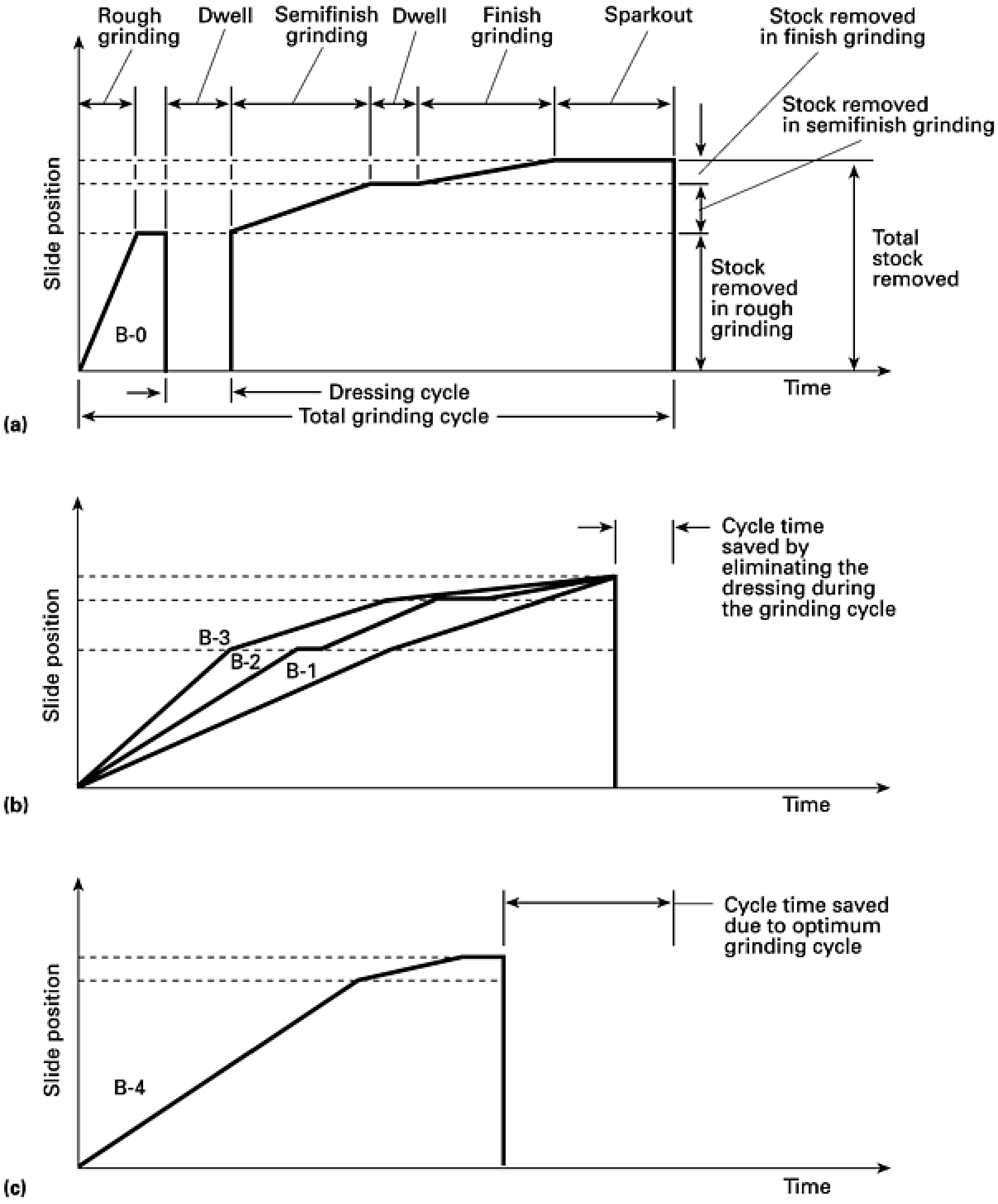


Fig. 6 Grinding cycle design. See text for details.

The rough grinding cycle has now affected the surface topography of the grinding wheel. This topography is modified by processes called *truing* and *dressing,* shown as "dressing cycle" in Fig. 6(a) and described in more detail later in this section. These processes are followed by a slower rate of grinding (judged by the smaller slope of the displacement/time curve), resulting in semifinish and finishing grinding cycles. The last portion of the cycle, akin to the dwell described earlier, is often called *sparkout.*

The suitable combination of rough, semifinish, and finishing grinding steps, with dwell, dress, and sparkout included as required, is called the *grinding cycle.* The design of the grinding cycle varies, depending on the machine tool characteristics and capabilities, grinding wheel characteristics and capabilities, work material properties and requirements, and operational conditions such as coolant applications, fixturing, and truing methods. Because of the range of variables that can influence the grinding cycle design, the process is often perceived to be an art. However, it is far from an art and can be managed as an engineered system with defined causal relations, as described in the section "Systems Approach" in this article.

The potential to alter the wheel face using the dress cycle is unique to precision grinding processes using grinding wheels. With coated abrasive belts containing a single layer of abrasives, this is often not possible. In those processes, individual coated abrasive product grades are assigned to rough, semifinish, and finish steps.

The rough grinding portion of the cycle can be modified by changing the rate of slide motion (and hence material removal rate), as shown in Fig. 6(b). This figure shows three alternative rough grinding paths, B-1, B-2, and B-3. These in turn require alterations in the semifinish and finish grinding steps, as shown. One reason for using an alternative path may be to reduce the amount of dressing or the number of dressing cycles during a grinding process. Paths B-1, B-2, and B-3 in Fig. 6(b) are less aggressive rough grinding paths that could ensure that wheel topography is not significantly affected during rough grinding, compared to path B-0 in Fig. 6(a). Hence, all these alternative paths can be accomplished and the part can be ground to final tolerances without the need for dwell in some cases and without the need for dress cycle in all cases, as shown in Fig. 6(b).

If the abrasive grain in the grinding wheel is an efficient cutting tool, then the forces or deflection induced during rough grinding may be small. This, combined with the efficient cutting action, may permit further reductions in the semifinish and finish operations and often eliminate the need for sparkout (Fig. 6c). Such optimizing of the cycle reduces the cycle time and hence improves productivity. This is one of the frequent objectives in using premium abrasive wheels, such as CBN grinding wheels for steel grinding.

The total force or power consumed during the rough grinding cycle is generally high, because the associated material removal rate is largest during the rough cycle. Thus, the deflection of the part under the applied forces of the machine tool is generally the limitation during the rough grinding cycle. Sometimes the work material or the coolant system is not able to dissipate the heat generated and the power input must be decreased, thus requiring alterations to the rough grinding cycle.

During the later portion of the grinding cycle (i.e., semifinish, finish, or sparkout), as the size of the chip generated decreases, the forces and power consumed also decrease. However, the chip generation efficiency decreases as the chip size decreases. (This is based on the mechanics of chip formation, described in the article "Finishing Methods Using Defined Cutting Edges" in this Volume.) The result is a large increase in specific energy, or the energy input per unit volume of the material removed. To avoid surface damage, this specific energy needs to be minimized in the later portions of the grinding cycle. The duration of the sparkout portion of the cycle is usually a balance between improved part geometry due to recovery from elastic deflections and the potential for surface damage due to the sliding of the abrasive wheel against the work material.

Truing and Dressing of Grinding Wheels. The tolerances and surface finishes produced on workpiece surfaces and the forces developed during grinding depend to a great extent on the manner in which the grinding wheel was prepared for operation. Preparation of the grinding wheel generally involves two operations: truing and dressing.

Truing refers to the process of generating a geometrically correct wheel surface in order to grind with minimal or no chatter. Successful use of grinding wheels requires that the wheel is concentric and free of lobes (Fig. 7). Conventional abrasives are most commonly trued by feeding a single-point or multipoint diamond dressing tool across the rotating wheel surface. Superabrasive wheels are trued with a vitrified silicon carbide truing wheel mounted on a brake-controlled truing device. Some of the other truing devices used are diamond truing rolls and cutters driven by hydraulic motors and diamond crush rollers.

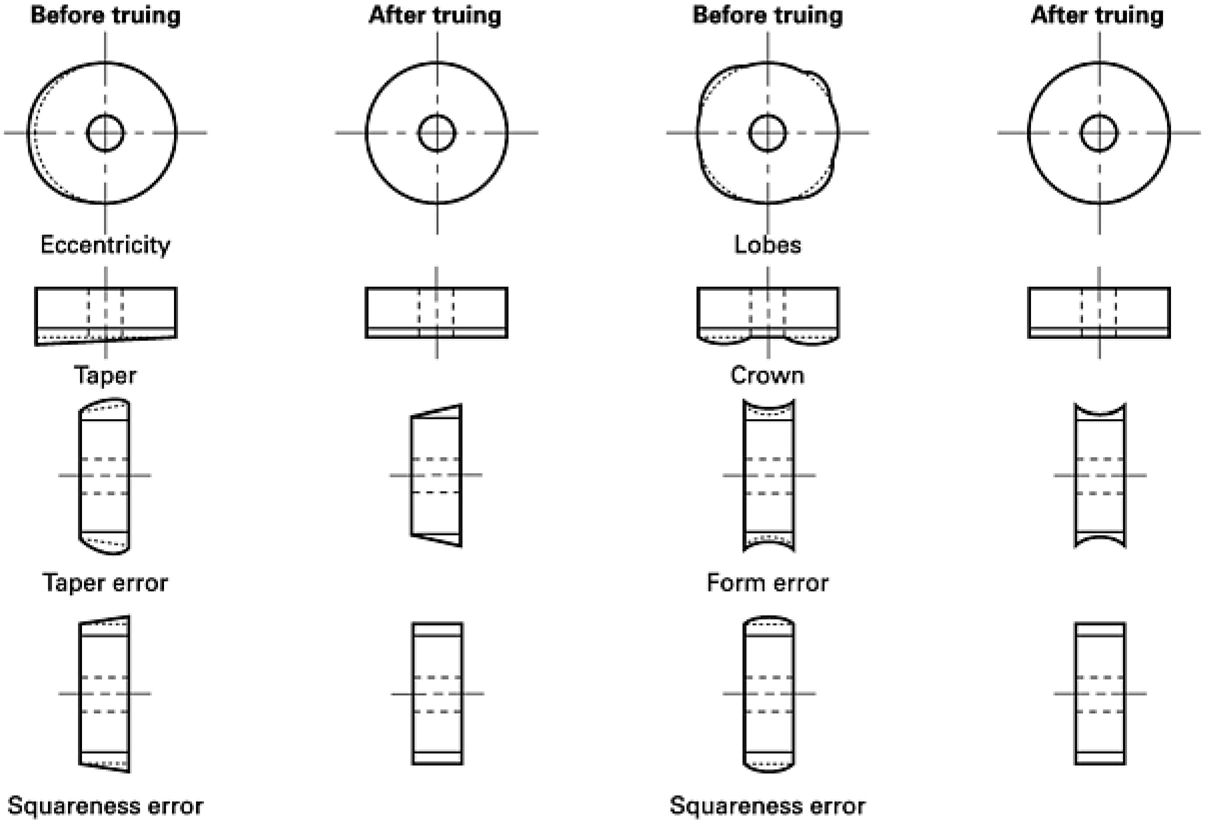


Fig. 7 Typical examples of conditions that require truing

Dressing is the process of eroding the bond matrix in the wheel surface after a truing operation or after grinding in order to expose the abrasive grains for efficient grinding. After truing, the wheel surface is generally very smooth; the bond adjacent to the grits has to be eroded in order to expose the grits. Occasionally, the chips fill up the pores and clog the wheel during grinding, resulting in an inefficient cutting action. The wheels then have to be dressed in order to remove the chips from the wheel surface. Dressing is usually accomplished by pressing or sliding an abrasive stick against the wheel surface. Recently, in-process dressing of metal bond diamond wheels using electrodischarge machining has been introduced. Electrolytic in-process dressing is another emerging technology for dressing fine abrasive metal bond diamond wheels. Abrasive slurries are also occasionally used for dressing operations.

Wheel Shapes. Grinding wheels are used in a variety of operations, as shown in Fig. 5. The different geometric configurations require that suitable grinding wheels also be available, so grinding wheels are made in several different shapes, including cylinders, cups, cones, and plugs (Fig. 8). In general, conventional abrasive wheels can be readily "machined" to the desired shape, but this is generally not true with superabrasive wheels, which are therefore available in a wider variety of shapes. Superabrasives are almost always made to near-net shape as required prior to their use. (See the article "Superabrasives" in Volume 16 of the *ASM Handbook.*)

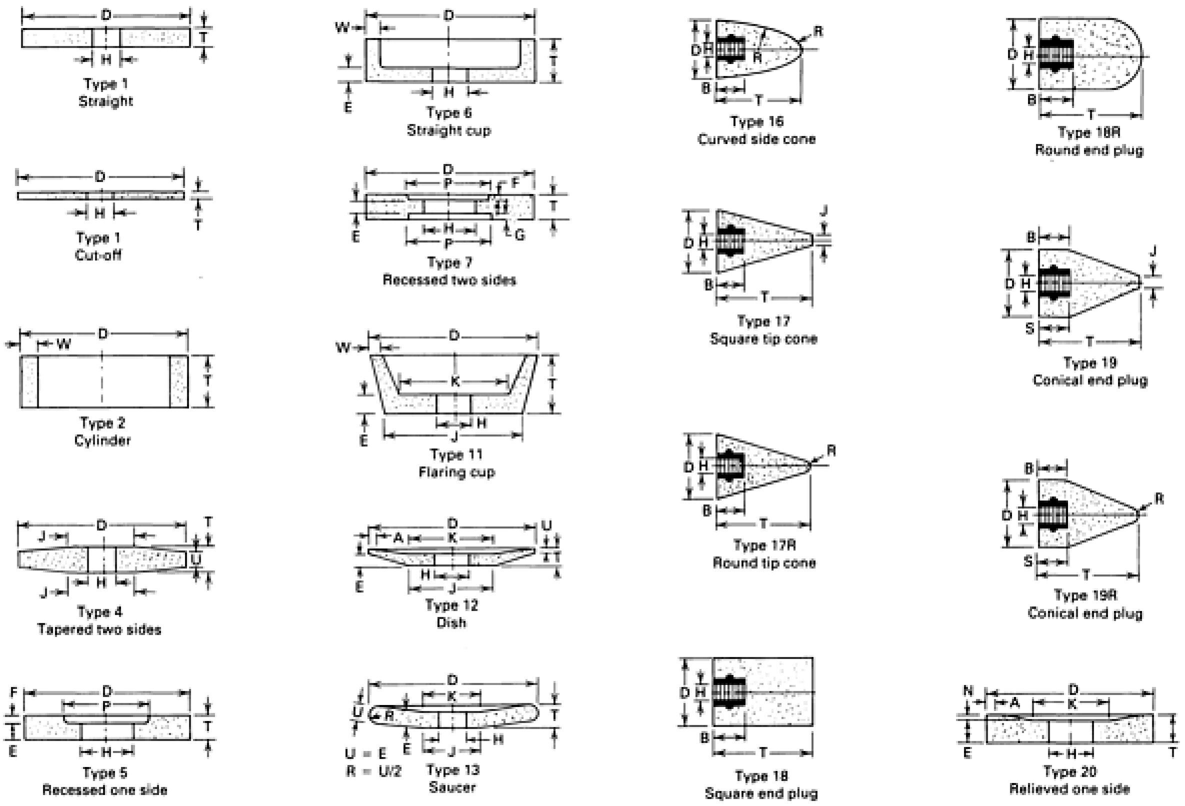


Fig. 8 Standard wheel configurations for conventional grinding wheels

Types of Bonds for Grinding Wheels. In order to effectively grind a large range of materials, a variety of bonding systems are available to hold the abrasives in the wheel. The most common bonding materials are resin (phenolic), ceramic (glass), and metal (bronze). Other bond types, such as shellac, oxychloride, rubber, and silicate are available but are not commonly used. The superabrasive wheels are also available in a metal-single-layer (MSL) specification that consists of a single layer of abrasives held together with the help of a metallic braze. Other superabrasive products, called *plated wheels* or *E-process wheels,* have a single layer of abrasives electroplated to the preform. Table 4 lists the characteristics of the four bond types available for grinding wheels.

Table 4 Characteristics of bond types used in abrasive products

Resin bonds
Readily available
Easy to true and dress
Moderate freeness of cut
Applicable for a range of operations
First selection for learning the use of superabrasive wheels

Generally used with coated abrasive product and rough grinding or operations with high material removal rates
Vitrified bonds
Free-cutting
Easy to true
Do not need dressing (if selected and trued properly)
Controlled porosity to enable coolant flow to the grinding zone and chip removal
Intricate forms can be crush formed on the wheels
Suitable for creep-feed or deep grinding, inside-diameter grinding, or high-conformity grinding
Potential for longer wheel life than resin bond
Excellent under oil as coolant
Metal bonds
(Available with superabrasives only)
Very durable
Excellent for thin-slot,groove,cutoff,simple form,or slot grinding
High stiffness
Good form holding
Good thermal conductivity
Potential for high-speed operation
Generally require high grinding forces and power
Difficult to true and dress

Layered products
Single abrasive layer plated on a premachined steel preform
Extremely free-cutting
High unit-width metal removal rates
Form wheels easily produced
Form accuracy dependent on preform and plating accuracy
Abrasive density is easily controlled
Generally not truable
Generally produce poorer surface finish than bonded abrasive wheels

Vitrified bonds made of clay, feldspar, and a glass frit are the most commonly used bonds for conventional abrasives and are becoming popular for use with superabrasives. They are rigid, free cutting, and have very good form retention. In addition, the porosity in these bonds can be controlled for more chip clearance and better coolant application at the grinding zone. These bonds do not have high impact resistance, however, and they are not used in heavy-pressure operations such as foundry snagging or steel conditioning.

Resin bonds are made of thermosetting polymers, usually phenol formaldehyde or epoxy resins. These bonds are resilient, have good impact resistance, and are very free cutting. Their rigidity can be varied by adding fillers such as glass fibers. Resin bonds are used in most rough grinding operations, such as snagging, weld grinding, and cutoff. Resin bonds are extremely popular for use with superabrasives and find extensive use in tool and cutter grinding, grinding of ceramics, carbide drill fluting, and glass beveling. The resilience of these bonds results in reduced chippage of brittle workpiece materials. Extremely fine-grit abrasives retained in flexible polyurethane bond material are commercially available and are used in extremely fine finishing processes.

Metal bonds are commonly used with superabrasives and are made from sintered bronze produced by powder metallurgy methods. Cast iron and aluminum bonds have been recently introduced. These bonds are very durable, have excellent form-holding characteristics, and have high stiffness. They require rigid machines, however, in order to withstand the high forces generated. Metal bonds are very popular in geological drilling, in asphalt and concrete cutting, and for cutoff wheels in precision electronic applications. Strong blocky diamonds are generally used as abrasives in metal bonds.

For more information on grinding wheels, see "Grinding Equipment and Processes" in Volume 16 of the *ASM Handbook*

Quantitative Aspects of Grinding Processes. When the work material is subjected to a grinding process, the interactions can be represented in terms such as equivalent diameter, chip size, specific energy, and grinding force. These parameters are described later in this section. A key parameter is the material removal rate (MRR), the volume of material removed in a unit of time. It is expressed as:

$$\text{MRR} = \text{Work speed } (v_w) \times \text{depth of cut } (d) \times \text{width of cut } (b_w)$$

When grinding takes place uniformly along the entire width of the wheel, the MRR can be normalized using the equation

$$\text{Unit width MRR}' = \text{MRR/width of cut}$$
$$(\text{in.}^3/\text{min/in.})$$

Equivalent Diameter. Figure 9 is a schematic representation of the concept of equivalent diameter. Grinding processes of various configurations can be normalized for ease of comparison using the following equations:

- *Outside diameter grinding:* $D_e = D_w \times D_s/(D_w + D_s)$
- *Inside diameter grinding:* $D_e = D_w \times D_s/(D_w - D_s)$
- *Surface grinding:* $D_e = D_s$

where D_e is equivalent diameter, D_w is the work diameter, and D_s is the wheel diameter. Large equivalent diameter represents longer arc of contact between the wheel and the work material. Hence, as D_e increases, the sliding interactions between wheel and the work material become dominant. This is usually observed as increased grinding power or force for the same grinding condition. In practice, this situation is overcome by using a "softer" grinding wheel as the D_e is increased.

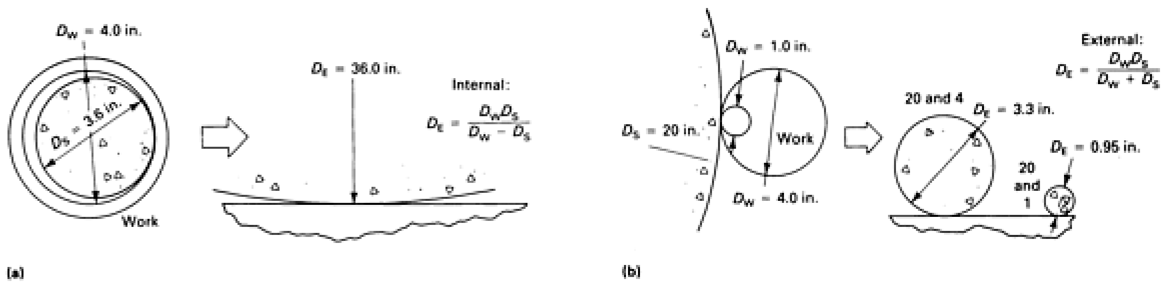


Fig. 9 Use of equivalent diameter to relate (a) internal and (b) external cylindrical grinding to surface grinding

There are unique situations, such as grinding a cam lobe profile, where D_e changes constantly from a small value, during outside diameter grinding of the nose or the base circle, to a large value, during surface grinding of the opening and closing ramps. The grinding wheel and the grinding system should be capable of accommodating such variations within one operation. Disc grinding or grinding of flat surfaces with cup wheels is another unique situation because the D_e can be perceived to be infinity. In such situations every attempt must be made to eliminate the frictional interactions. This is usually accomplished by using coolant slots in the grinding wheels, interruptions to the wheel face, and improved coolant applications.

Chip Size. The size of the chip produced by the abrasive grain during a grinding process (h) can be estimated as:

$$h = (v_w/v_s)^{1/2} \times (d/D_e)^{1/4} \times (KC)^{-1/2}$$

where v_s is wheel speed, K = 1 to 20, and C is the number of grains per square inch of grinding wheel surface. C is larger for fine abrasive grains and smaller for large abrasive grains. Like D_e, chip thickness can be used to compare grinding operations. In some cases, the larger the chip thickness, the higher the "cutting efficiency" as measured by a decrease in specific energy. However, as chip thickness increases, the force per cutting edge may increase, thus degrading the surface finish.

Grinding force is the force exerted between the grinding wheel and the work material. These forces can be normal to the work surface (F_n), tangential to the wheel (F_t), and occasionally in the transverse direction (F_z).

Specific energy is the ratio of grinding power to the material removal rate. It is a measure of the energy input per unit volume of material removed.

G-ratio is the ratio of the volume of work removed per unit volume of abrasive product consumed. It is a measure of the life or durability of abrasive product for a given application. In many applications, the wheel is trued or dressed frequently or even continuously. In those situations, the *G*-ratio may need to reflect the abrasive consumed during these nongrinding operations.

Grinding system performance index (GSPI), or "grindability," is one measure of the ease or difficulty in grinding. It is defined as:

$$\text{GSPI} = G\text{-ratio/specific energy}$$

Higher values of GSPI imply lower specific energy, greater performance economy (larger *G*-ratio), or both. More commonly, *G*-ratio is equated with grindability, although it is an incomplete description of grinding results.

Effect of Material Removal Rates on Force and Power. Figures 10(a) and (b) show the variation of normal force and power with material removal rate in a typical grinding operation. In general, the force and power increase with an increase in material removal rate, and a minimum force is required to initiate cutting. This minimum value of force or power is termed the *threshold force* or *threshold power*. Thus:

$$\text{Total power} = \text{Cutting power} + \text{threshold power}$$

which when divided by the MRR results in the relation:

$$\begin{aligned}&\text{Specific energy} = \text{Specific power}\\&+ \text{threshold power/MRR}\end{aligned}$$

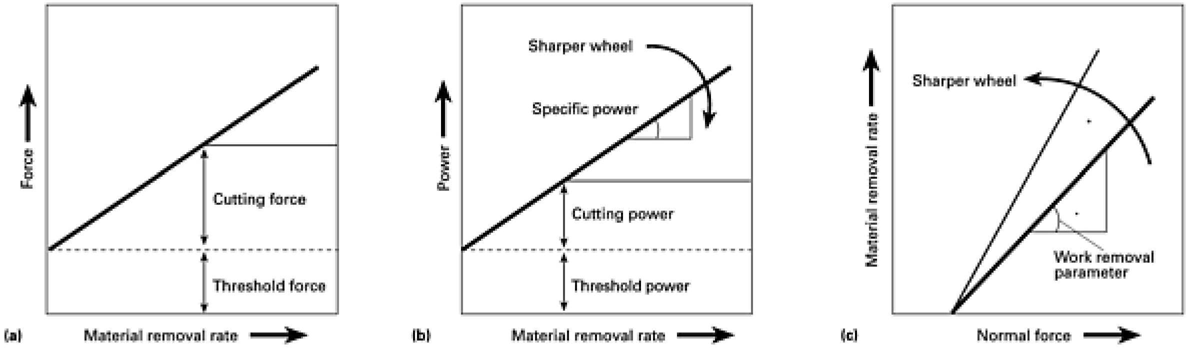


Fig. 10 (a, b) Effect of material removal rate on force and power. (c) Work removal parameter

Specific power is the slope of the power-versus-MRR curve (Fig. 10b) and is another important parameter used to analyze grinding results. It represents the cutting component of the specific energy and in physical units could be considered the specific cutting energy. The threshold power can be approximated as the power component required to overcome friction and material deformation effects. If these frictional effects are absent, specific energy is equivalent to specific power (or, more precisely, to specific cutting energy).

Figure 10(c) is a plot relating the material removal rate to the normal force. Such data can be obtained on a grinding machine using force-measuring equipment and can be effectively used to differentiate between the "sharpness" or cutting efficiency of grinding wheels. The slope of the MRR-versus-F_n curve is called the *work removal parameter* (*WRP*). A steep slope indicates a sharp wheel and low force, and a shallow slope indicates a dull wheel and high force. Like the power relation, force is modeled as follows:

$$\text{Total force} = \text{Cutting force} + \text{threshold force}$$

which when divided by the MRR results in the relation:

$$\text{Total force/MRR} = (\text{WRP})^{-1} + \text{threshold force/MRR}$$

where $(\text{WRP})^{-1}$ is the ratio of cutting force and MRR.

High-Precision, Fixed-Abrasive Finishing

A variety of high-precision processes have been in use, and new processes are constantly being developed to achieve extremely close geometric tolerances or to improve surface finish. The objective of all high-precision processes is to achieve geometrically precise components or surfaces of controlled texture or surface finish (Fig. 11). Table 5 compares the processes described in this section. A parallel set of processes using loose abrasives, called *lapping, buffing,* and *polishing,* are reviewed in later sections of this article.

Table 5 Comparison of high-precision finishing processes

Process features	**Process category**			
	Honing	**Superfinishing**	**Flat honing**	**Microgrinding**
Bonded abrasive tool used	Yes	Yes	Yes	Yes
Cutting speeds	<500 sfm	<500 sfm	<500 sfm	500 to 12,000 sfm
Oscillation of abrasive tool	Yes	Yes	No	No
Amplitude of oscillation of abrasive tool	Large	Small (about 1 to 6 mm)	. . .	. . .
Abrasive product size relative to the work size	Small to large	About equal	Large	Varies widely
Frequency of oscillation	Small (100-200 strokes/min)	Large (300-4000 strokes/min)	. . .	. . .
Abrasive tool motion	Linear or reciprocation	Angular, linear, or reciprocation	Rotation	Rotation
Work material motion during the abrading process	Fixed	Circumferential rotations	Epicyclic	Large range of motions and velocities are involved
Work surface	Generally straight cylindrical internal	External or internal surfaces, not limited to	Generally flat and parallel surfaces. Occasionally	Large range of surfaces and

configuration	surfaces	straight surfaces	cylindrical or sphere	contours
Amount of stock removed	Rough 0.010 to 0.015 in. Finish 0.002 to 0.006 in.	0.0001 to 0.0005 in.	Rough 0.010 to 0.015 in. Finish 0.002 to 0.006 in.	Similar to honing and superfinishing
Surface texture controlled	Yes	Yes (to a lesser degree than honing)	Maybe	Maybe
Abrasive tool bond type	Vitrified (also metal bond for superabrasives)	Vitrified	Vitrified (also metal bond for superabrasives)	Resin, metal or vitrified using conventional abrasives or superabrasives

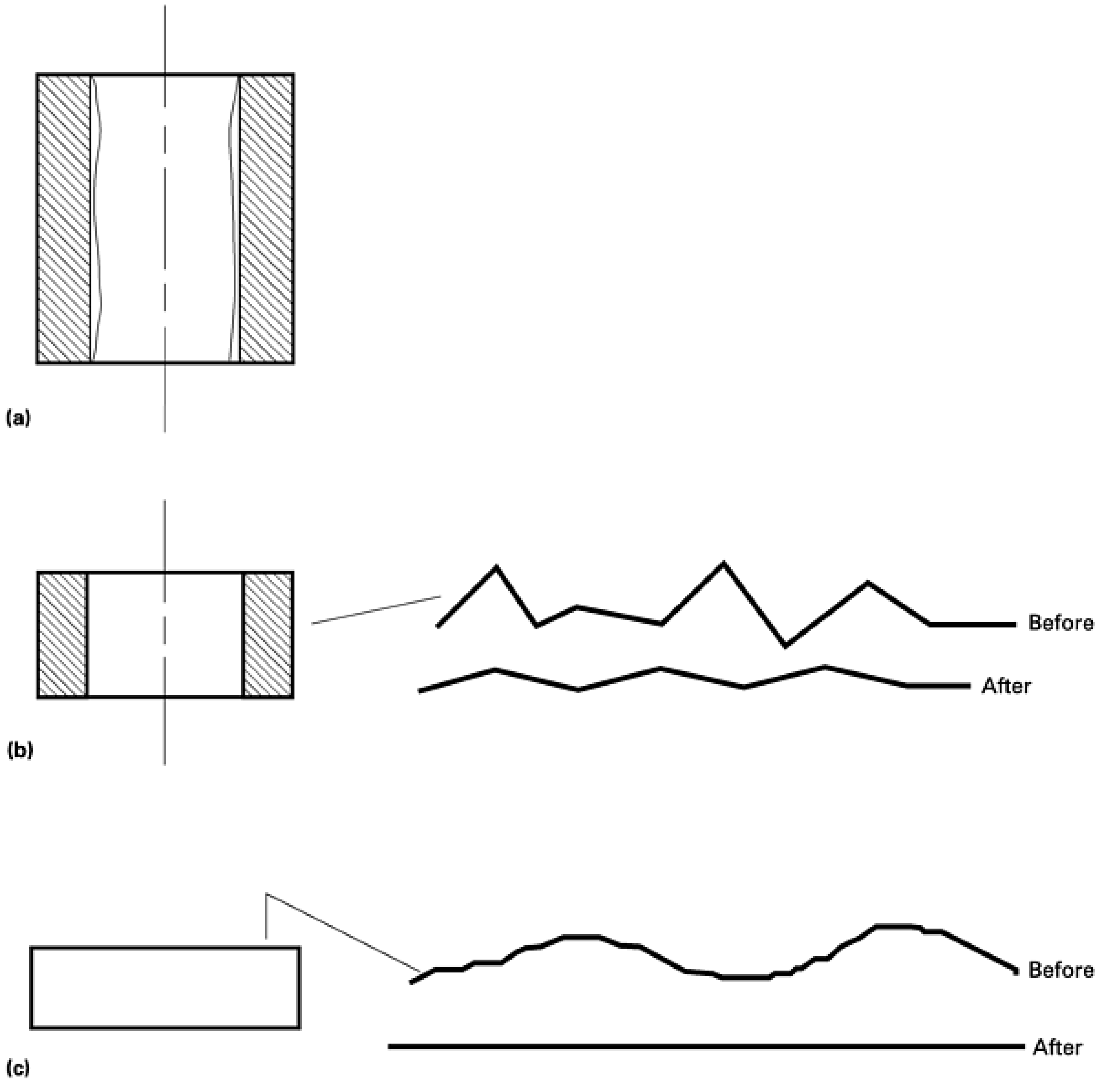


Fig. 11 Applications of high-precision processes using bonded abrasives. (a) Honing is most commonly used to correct the internal geometry of a bore hole. (b) Superfinishing is most commonly used to improve external

surface finish. (c) Flat honing is most commonly used to improve flatness and the parallelism between surfaces.

Honing is a low-velocity abrading process that uses bonded abrasive sticks to remove stock from metallic and nonmetallic surfaces. As one of the last operations performed on the surface of a part, honing generates functional characteristics specified for a surface, such as geometric accuracy, dimensional accuracy, and surface features (roughness, lay pattern, and integrity). It also reduces or corrects geometric errors resulting from previous operations.

The most common application of honing is on internal cylindrical surfaces (Fig. 12a). However, honing is also used to generate functional characteristics on external cylindrical surfaces, flat surfaces, truncated spherical surfaces, and toroidal surfaces (both internal and external). A characteristic common to all these shapes is that they can be generated by a simple combination of motions.

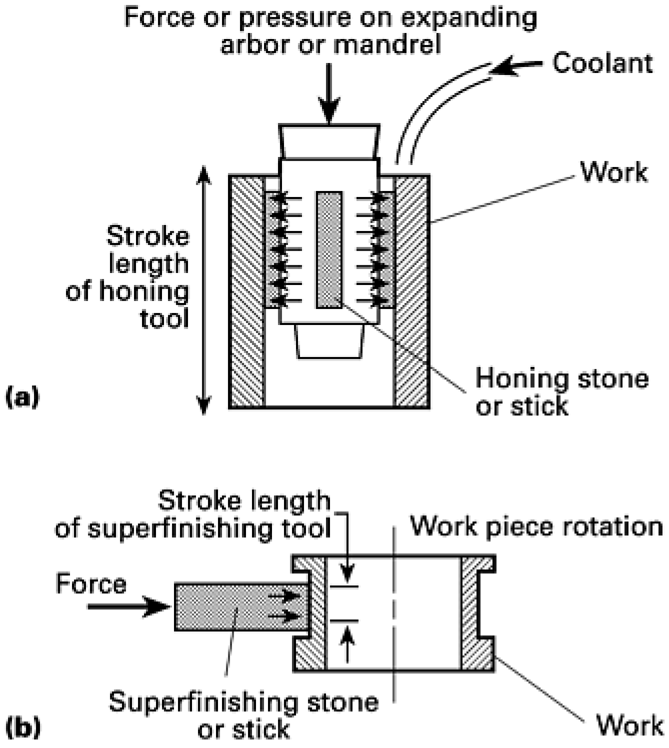


Fig. 12 (a) Schematic representation of honing. (b) Schematic representation of superfinishing

Superfinishing is a low-velocity abrading process very similar to honing. However, unlike honing, superfinishing processes focus primarily on the improvement of surface finish and much less on correction of geometric errors (Fig. 12b). As a result, the pressures and amplitude of oscillation applied during superfinishing are extremely small. This process is also referred to as *microhoning, microsurfacing,* and *microstoning.*

Flat honing is a low-velocity abrading process, similar to honing except that a large flat honing surface is used to simultaneously finish a large number of flat parts (Fig. 13). The predecessor to the flat honing process was *hyper lap,* in which the lapping plate was simply replaced by an abrasive product such as a grinding wheel. Modern flat honing machines "float" the abrasive product such that it can be applied under controlled pressure against the work surface. It is also critical to ensure that the flat honing tool wears uniformly and accepts uneven work surfaces that require correction during the honing process. These processes also true and dress the flat hone in a manner very similar to a grinding process. With suitable adaptation, flat honing equipment can be used for finishing cylindrical surfaces such as pins or rollers, as well as spherical surfaces such as balls.

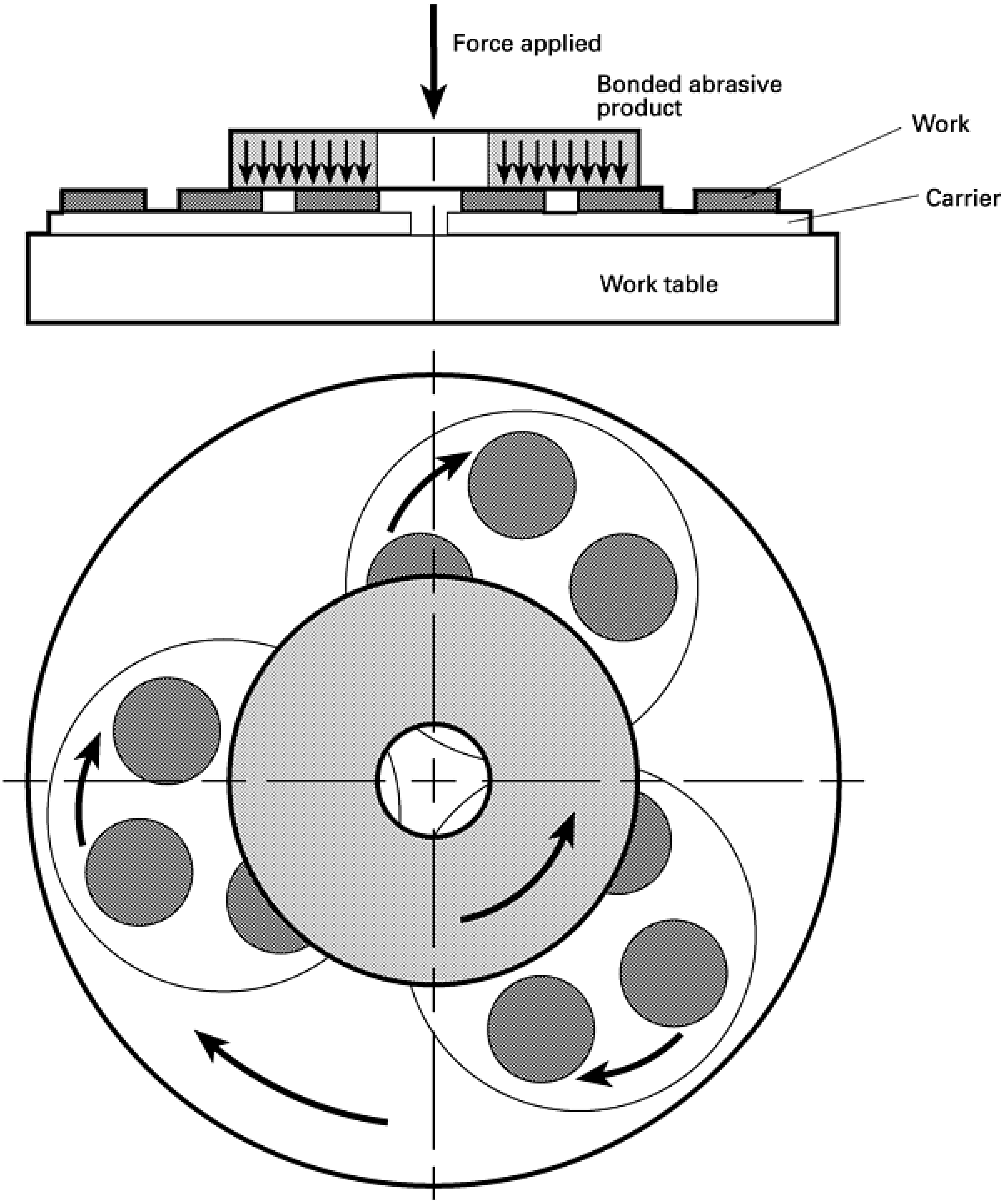


Fig. 13 Schematic representation of flat honing

Flat honing requires abrasive wheel(s) that will produce the required surface finish and accuracy of flatness and parallelism. To be efficient, the wheel(s) must continue to cut, load after load, without requiring frequent truing. The accuracy obtained depends on the flatness of the wheel surfaces. If the faces wear, then they must wear away evenly in order to keep the wheel surfaces flat.

At the time of this writing, the use of diamond or CBN wheels for flat honing is relatively new. Research is presently being done to flat hone hard ceramic materials with metal bond, fine-grit diamond wheels. The anticipated benefits of diamond wheel honing over conventional grinding are cost effectiveness, less surface damage, better accuracy and finishes, less chipping, and easier fixturing.

The coolant normally used in the flat honing process wets the small particles generated during the machining process and carries them away. In addition, it cools the workpiece and provides lubrication. Mineral oil or mineral seal oil are conventional fluids that meet these requirements and still have low enough odor and high enough flash point to be feasible and safe. Water-based coolants have specific applications, and some workpieces composed of carbon and other ceramics are often processed using water.

Microgrinding is akin to the precision grinding processes described above, except that extremely fine abrasives are used (50 μm and finer). The cutting velocities in microgrinding range from very low (500 sfm) to as large as those used for grinding (6000 to 12,000 sfm). This process is also called *fine grinding* or *microfinishing grinding.*

The Future. Each of these high-precision processes is an emerging technology, and many advancements can be expected, driven by functional or performance improvements of industrial components and their systems. For example:

- Honing and microgrinding are used to achieve closer-fitting cylinders and pistons that reduce leakage past the piston and improve performance efficiency in hydraulic cylinders and automotive engines.
- Flat honing and microgrinding improve the quality of flat and parallel surfaces that are used to align, join, or seal other surfaces.
- Microgrinding can be used to modify surfaces ground to a certain feature to improve the bearing area, which in turn improves load-bearing capacity (in the case of bearings) or signal processing capability (in the case of the magnetic heads used in computers).

Abrasive Belt Grinding and Polishing

Endless cloth belts precoated with abrasive are widely used in grinding and polishing operations. In comparison to grinding with bonded wheels, they offer the following advantages:

- Ability to finish large areas simultaneously
- Elimination of the need for costly wheel setup operations such as balancing, truing, and dressing
- Less heat generation in polishing because of the larger surface area of belts
- Ease of setup and ease of changing the abrasive belts
- Flexible or compliant abrasive tooling, not easily prone to chatter
- Smaller inventory of polishing accessories

Typical configurations of abrasive belt applications are shown in Fig. 14, 15, 16, and 17. In general, the abrasive belt is held between a drive roll and a contact roller. The belt tension determines its torque-carrying ability and hence the power delivered to the grinding zone. The work is usually applied against the belt under controlled force or pressure. Occasionally the work may be fed at a constant rate against the abrasive belt. The belt is replaced when it loses or sheds the abrasives or when the rate of material removal is decreased.

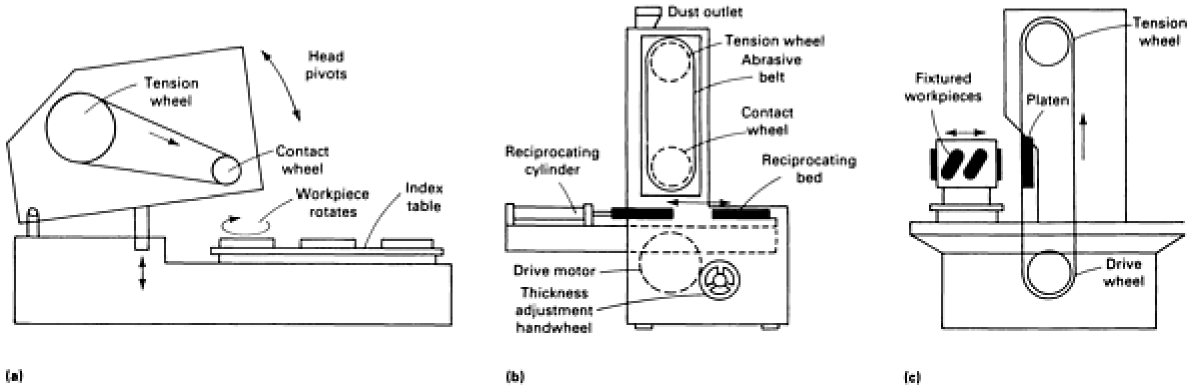


Fig. 14 Schematics illustrating the primary components of coated abrasive precision grinding machines. (a)

Rotary-table type. (b) Reciprocating (bed) table type. (c) Vertical-platen type (with hydraulic feed table)

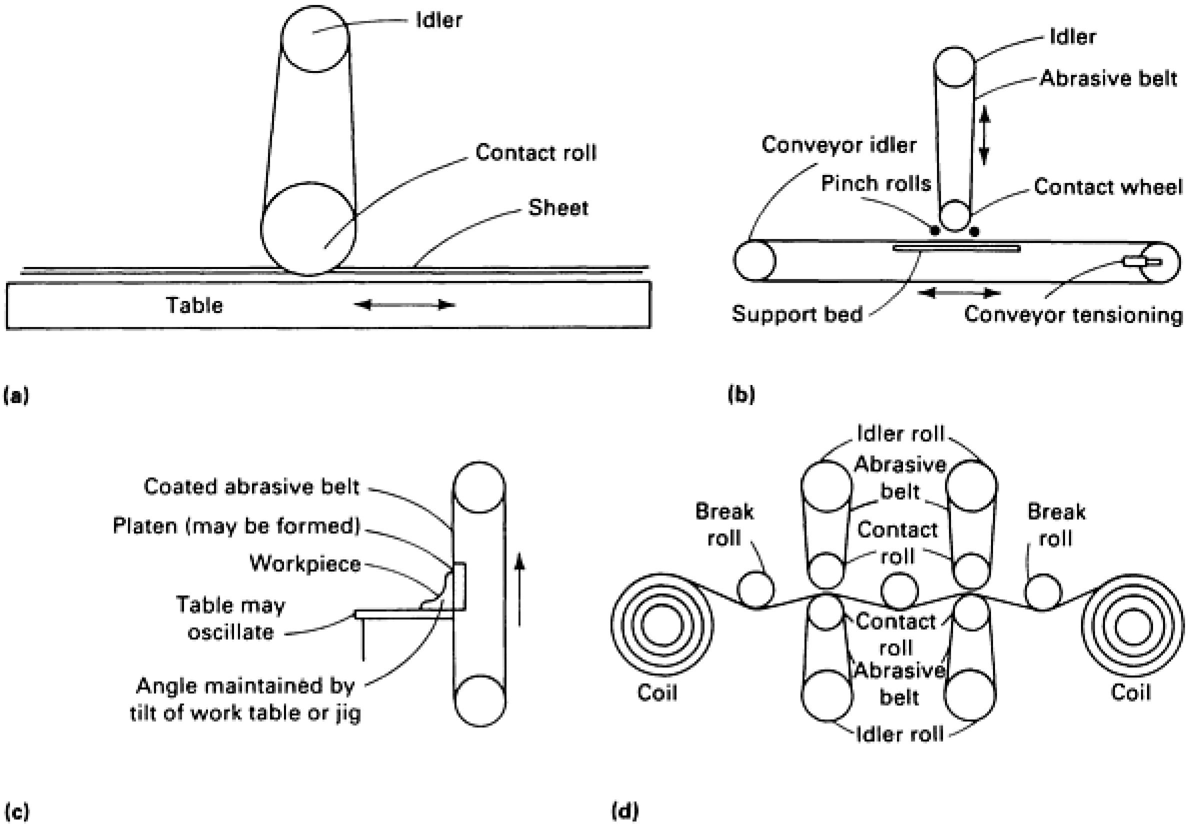


Fig. 15 Schematics illustrating the primary components of coated abrasive precision grinding operations. (a) Sheet dimensioning. (b) Conveyor grinding. (c) Vertical-platen sanding. (d) Coil

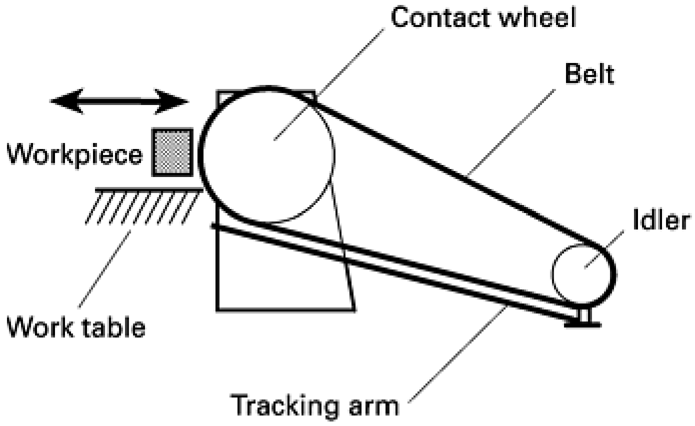


Fig. 16 Schematic of backstand grinder having coated abrasive belts for use in off-hand rough grinding operations

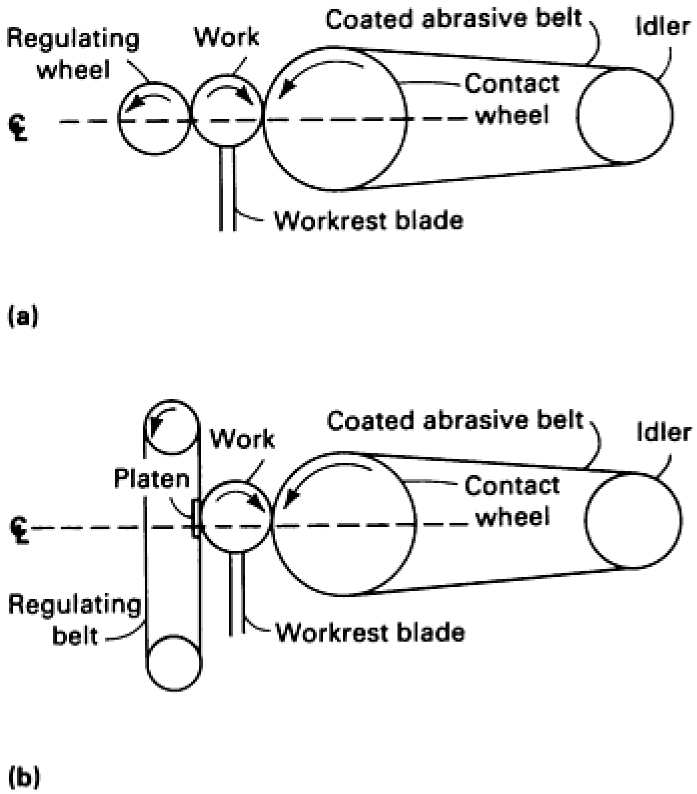


Fig. 17 Schematic of two different coated abrasive centerless grinding setups. (a) Abrasive belt centerless grinder with regulating wheel. (b) Abrasive belt centerless grinder with regulating belt

As in grinding wheel applications, the abrasive belt applications can be manual or make use of mechanical drives. In manual applications, the operator can vary the contact area during use to maximize the material removal rate and minimize the force or effort required. Mechanical means are adapted for large-volume production processes, usually involving components of constant geometry.

Coated abrasives are a composite of three components: backing, adhesive, and abrasive. In general, the backing for a belt is either paper or cloth. Different weights of paper and types of cloth are used, depending on requirements for strength, flexibility, and water resistance. The adhesive is usually resin or glue and is used to bond the abrasive to the backing. It is applied in two coats, with the first layer ("make coat") anchoring the abrasive in place on the backing. The second layer ("size coat") is applied over the abrasive to further strengthen its bond to the backing.

The abrasives most commonly used on coated abrasive belts are aluminum oxide and silicon carbide. Coated products containing CBN or diamond abrasives are beginning to be developed, with unique application for finishing steel components and glass or ceramics, respectively. The abrasive is applied to the backing by electrostatic deposition, then passed through an electric field where an electrostatic force propels it into the resin, while the orientation of each abrasive grain on the backing is controlled. This results in a sharp coated abrasive product containing many exposed, well-oriented cutting points.

An efficient belt grinding operation uses the coarsest grade that produces an acceptable finish. Depending on the objective of an operation, more than one abrasive grade may be needed. When both stock removal and finish are required, a sequence of abrasive grades is used. The coarsest grade is determined by the amount of stock removed and by the type of material. It should be the finest possible grade that still removes stock at an acceptable rate so that no excessively coarse scratches are produced. The finishing grade is determined by final finish requirements. If a number of grit sizes of intermediate grades are skipped, some deep scratches will remain that decrease buffability. In general, more grades can be skipped in the coarser grades and when finishing a softer material. Parts with small contact areas allow more grades to be skipped and require fewer finishing grades because of increased buffability. Table 6 shows the abrasive grades used for a given operation and the approximate number of grades that can be skipped.

Table 6 Abrasion grades for various operations

Operation	**Grade range**	**Condition**
Stripping	12-20	Removal of old finishes, rust, and other materials that tend to load belt
Heavy stock removal	24-30-36-40	Used for rapid stock removal and large depths of cut. Skip 1 to 3 grades.
Medium stock removal	50-60-80	Average stock removal and progression from rougher finishes. Skip 2 grades.
Light stock removal	100-120-150	Used in operations requiring minor dimensional changes. Skip 1 or 2 grades.
Finishing	180-220-240	Negligible stock removal. Produces the desired appearance or surface for plating. Skip 0 or 1 grade.
Polishing	(280-320)-(360-400)-(500-600)	Preparation for mirror or near-mirror finishes

In many operations, the surface finish specifications are determined by scratch depth, which is affected by factors such as abrasive grade and type, lubricant, material to be finished, and finishing conditions (e.g., contact wheel and abrasive speed). Figure 18 shows the typical range of surface finishes that can be obtained with a given abrasive grade. Finishes outside this range are used for some applications, so the graph should be used only as a general guideline.

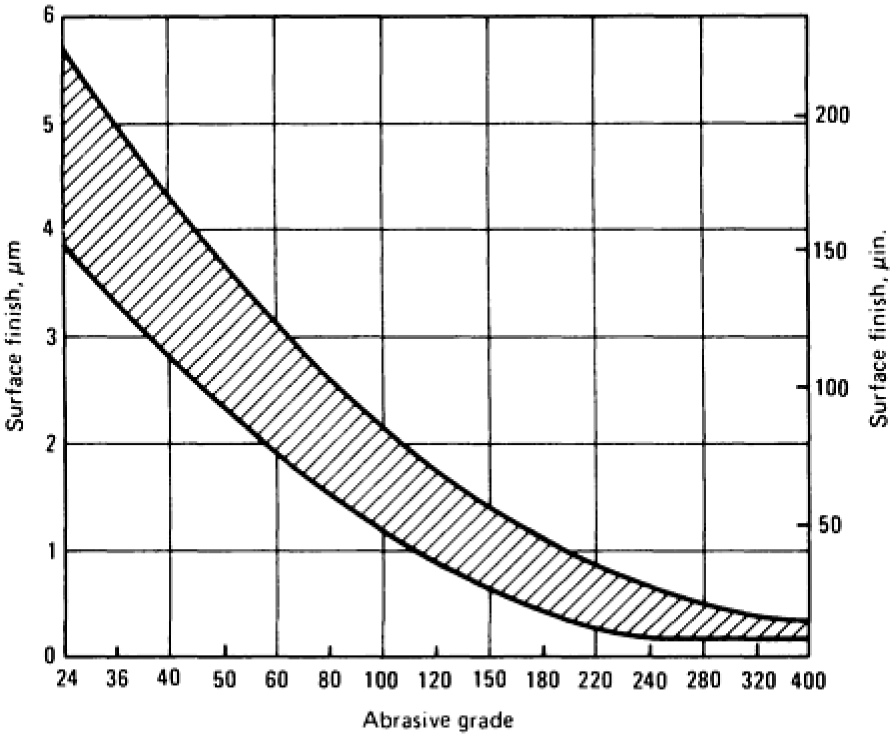


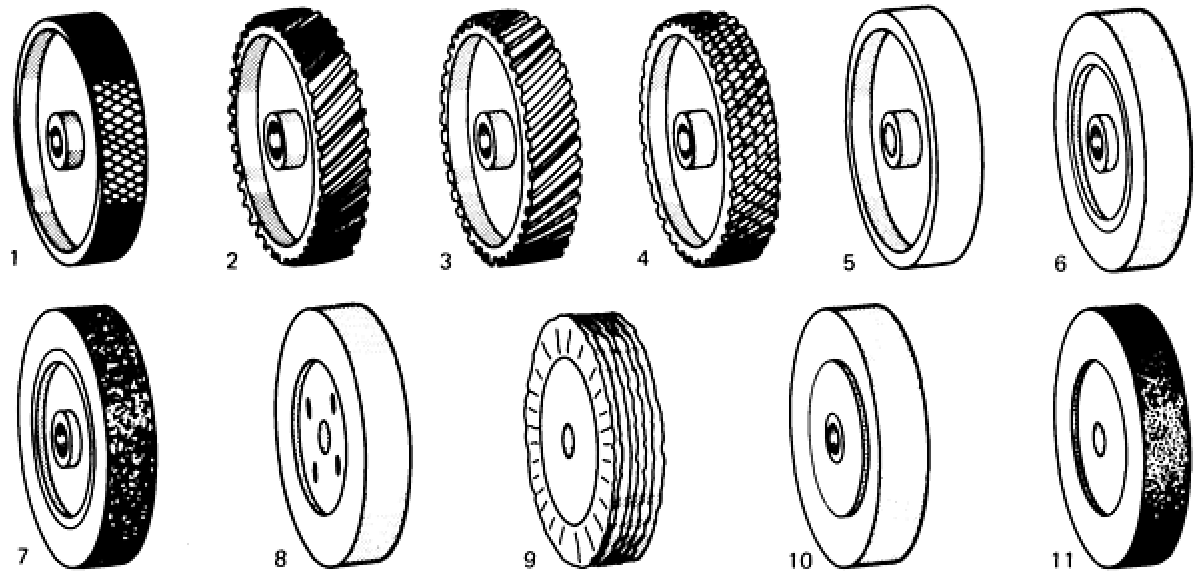
Fig. 18 Surface finishes obtained with varying grades of abrasive belts

Contact wheels over which the abrasive belt rides provide pressure of the belt against the workpiece. Depending on its hardness, the contact wheel can provide either high unit pressure, hard wheel, or low unit pressure, soft wheel. Selection of contact wheel directly affects the rate of stock removal, the ability to blend in polishing, the surface finish obtained, and the cost of the polishing operations.

Although it is possible to operate a contact wheel satisfactorily at speeds from 10 to 50 m/s (2000 to 10,000 sfm), normal operation speeds usually range from 18 to 38 m/s (3500 to 7500 sfm). Table 7 illustrates and describes the principal types of contact wheels and indicates their applicability to various grinding or polishing operations.

Table 7 Characteristics and uses of abrasive belt contact wheels

Wheel	Type	Material	Hardness	Purpose	Characteristics
1	Knurled or spiral grooved(a)	Steel	Rockwell C 52 to 55	Heavy grinding	Provides most aggressive action
2	Cog tooth(b)	Rubber	70 to 90 durometer	Grinding(c)	Fast-cutting, allows long belt life
3	Standard serrated(d)	Rubber	30 to 50 durometer(e)	Grinding(f)	Leaves rough-to-medium surface, excellent life
4	X-shaped serrations(g)	Rubber	30 to 60 durometer	Grinding, polishing(h)	Flexibility allows entry to contours
5	Plain face	Rubber	20 to 40 durometer(i)	Grinding, polishing(j)	Allows controlled penetration of abrasive grain
6	Flexible	Compressed canvas	(k)	Grinding, polishing(l)	Tough and durable
7	Flexible	Rubber-coated canvas	Medium	Contour polishing	Contours well, yet gives substantial stock removal
8	Flexible	Solid section canvas	Soft, medium, hard	Polishing(m)	A low-cost wheel with uniform face density
9	Flexible	Buff section canvas(n)	Soft	Contour polishing	For fine polishing and finishing, low-cost
10	Pneumatic drum	Inflated rubber	(o)	Grinding, polishing	Gives uniform finishes, adjusts to contours
11	Plastic foam	Polyurethane	Extremely soft	Fine polishing	Most flexible, for extreme contours



(a) No. 14 standard face; 4-pitch 2 by 2 mm ($\frac{1}{16}$ by $\frac{1}{16}$ in.).

(b) Land, 5 mm ($\frac{3}{16}$ in.); groove, 14 mm($\frac{9}{16}$ in.); depth, 1.5 mm ($\frac{1}{16}$ in.); cushion, 19 mm($\frac{3}{4}$ in.).

(c) For cutting down projections, such as weld beads, gates, risers, and sprues.

(d) Land, 10 mm ($\frac{3}{8}$ in.); groove, 10 mm($\frac{3}{8}$ in.); depth, 10 mm ($\frac{3}{8}$ in.);cushion, 22 mm($\frac{7}{8}$ in.).

(e) Wheel also may be of dual density, with hard rubber; 60 durometer, at hub, softer rubber, 20 to 40 durometer, at working surface.

(f) For smoothing or blending cutdown projections or surface defects.

(g) Land, 5 mm ($\frac{1}{16}$ in.); groove, 14 mm($\frac{1}{16}$ in.); depth, 8 mm ($\frac{5}{16}$ in.); slit, 13 mm ($\frac{1}{2}$ in.) spaced; cushion, 22 mm($\frac{7}{8}$ in.).

(h) For light stock removal and medium polishing; preferred to standard serrated wheel for softer nonferrous materials.

(i) Softer wheels give better finishes.

(j) For flat surfaces.

(k) Nine densities (very hard to very soft). Hard wheels can remove metal, but more slowly than wheel 2; softer wheels can polish to fine smoothness.

(l) Good for medium-range grinding and polishing. See footnote [k]

(m) Handles all types of polishing, giving uniform results without leaving abrasive pattern on work; adjusts to contours or can be preformed for contours.

(n) Can be widened or narrowed by addition or removal of sections.

(o) Hardness controlled by air pressure

Abrasive belt machines perform grinding, polishing, and deburring operations on bar, strip, coils, blanks, stampings, forgings, die castings, and sand castings. Parts made of metal, plastic, ceramic, wood, or rubber can be handled on this equipment. Any flat surface that requires finishing, sizing, deburring, and descaling can be processed. Parts can be fed against abrasive belt polishing heads by conveyor belts or feed rolls. Conveyor belts can be made from oil-resistant rubber, sponge rubber, or abrasive-coated cloth. Hold-down fingers and cleats are used to hold nonferrous materials for grinding or polishing operations and prevent slippage. Feed rolls are made of steel or rubber-covered steel.

Abrasive belts can be tensioned by mechanical or pneumatic means, and manual or automatic tracking devices are available. Automatic tracking devices are generally used for belts 300 mm (12 in.) or more in width. Manual or automatic adjustments for grinding pressure can be used to suit specific applications. Tandem arrangements of any of the machines mentioned can be made using as many polishing units as are necessary to produce the required successive grit finish in one pass through the machine. Conveyor belt machines can be furnished with an automatic turnover arrangement to polish or deburr both sides of parts. Abrasive belt heads or flap wheels can be mounted on the bottom side of the pass line to permit two-sided simultaneous polishing operations. Flat-surface polishing machines can be equipped for wet or dry finishing. A means for the application of oil spray, oil mist, or other wet polishing media may be provided.

A few of the applications for wide-sheet polishing mills include:

- Extrusion sizing, grinding, and deburring
- Prepolishing of stock before forming
- Polishing sheets to a high-quality satin finish
- Obtaining engineered finishes on stainless steel
- Upgrading finish of commercial cold-rolled stock
- Sizing operations on all types of sheet and coil stock

Sheet-polishing heads can be used as individual units or assembled in tandem arrays. Applications of these heads include prepolishing of carbon steel sheet for plating applications, conditioning of stainless steel coil stock, and polishing of sheet and plate to standard finishes. A broad (2 m, or 7 ft) wheel, angled to the sheet to be buffed, can achieve high degrees of microfinish and reflectivity by allowing the sheet to be transferred by the head or heads in a continuous mode or by having sheets placed individually on a reciprocating conveyor. The heads can be mounted at the top and bottom of the sheet in a pinch roll configuration. With some degree of oscillation, buffing streaks are avoided and uniform fine finish is achieved on both ferrous and nonferrous materials for finishing prior to the sheet's being blanked, stamped, or used full-dimensionally for other purposes.

Applications of Belts. Originally, the use of coated abrasive belts was limited to the finishing of flat surfaces, using straight-face contact wheels. Now that resin bonding of abrasives is practical, it is possible to produce belts with greater flexibility and improved joints. In addition, improvements in polishing machinery have made it possible use of coated abrasive belts for contour polishing operations. The selection of tough, flexible polyester backings also contributes to the ability of coated abrasives to contour polish. Extremely fine-grit abrasive belts are used for lapping and polishing applications. Use of superabrasive belts for ceramics finishing is also an emerging technology.

Polishing and Buffing

Polishing and buffing improve edge and surface conditions of a product for decorative or functional purposes. These techniques are abrading operations, although some plastic working of surfaces may occur, particularly in buffing. Buffing is the use of abrasives or abrasive compounds that adhere loosely to a flexible backing, such as a wheel. Polishing is the use of abrasives that are firmly attached to a flexible backing, such as a wheel or belt.

Polishing operations usually follow grinding and precede buffing. In general, polishing permits more aggressive abrading action than buffing. It has greater capability to modify the shape of a component and has greater definition of scratches. Buffing achieves finer finishes, has greater flexibility, and follows the contours of components.

Polishing and buffing processes are used on most metals and many nonmetals for refining edges and surfaces of castings, forgings, machined and stamped components, and molded and fabricated parts. Traditionally, these processes have been considered a means of developing attractive, decorative surfaces and generating suitable preplate and prepaint surfaces.

Polishing is used to remove or smooth grinding lines, scratches, pits, mold marks, parting lines, tool marks, stretcher strains, and surface defects that adversely affect the appearance or function of a part. Polishing is performed with either a wheel or belt to which an abrasive is bonded. The process causes some plastic working of the surface as metal is removed. The resulting polished surface usually has a finish of 0.4 μm (16 μin.) or less.

Polishing wheels are disks made of materials such as cloth and leather, sewed and/or glued together. The periphery is coated with alternating layers of adhesive and abrasive grain to the desired thickness. The type of material and construction determines the hardness and flexibility of the wheel. Muslin, canvas, leather, sheepskin, felt, and various weaves of cotton are among the materials used. Canvas is usually glued and pressed together, which makes it the hardest of these materials. The solid felt wheel is also hard, but its hardness depends on the density of the felt. Leather and sheepskin can be glued and pressed, machine sewn, or hand sewn to give the flexibility desired. Differences in types of leathers also determine the final effect. A leather strip can be glued to the periphery of a cloth or wooden wheel to combine the hardness of the underlying wheel with the flexibility of the leather.

The two main types of adhesives used are hide glue and silicate cements. Hide glue is the more resilient, but it melts under heavy pressure, must be soaked and made up daily, requires controlled heating between 60 and 65 °C (140 and 150 °F), and must be formulated to the size of the abrasive. Despite these disadvantages, hide glue is popular because it gives the softness, flexibility, or cushion required for certain applications. Silicate cement does not usually melt under heavy pressures when high heats are developed, and it can be used as received from the manufacturer; no heating is required. Silicate cements are formulated to give a range of effects.

The technique and care required to make the polishing or setup wheel can be eliminated by using polishing belts, but in certain applications, polishing wheels cannot be replaced. An obscure or confined area, such as an automobile wheel that is to be plated, is readily polished with a polishing wheel. The cutlery industry and the jewelry industry use polishing wheels and bobs for special effects, in some areas that are difficult to reach, and where the polished finish must be confined to certain areas.

During polishing with setup wheels, efficiency, the quality or results obtained, and cost are most significantly affected by the following operating variables:

- Type and density of the polishing wheel
- Preparation of the wheel before application of adhesive
- Wheel-curing (drying) procedures
- Wheel balancing
- Wheel abuse due to improper use
- Wheel speeds
- Type and grit size of abrasive

Limitations of polishing generally are associated either with part size and shape or with the ability of the process to attain a specific surface finish. A part with hooked edges or sharp projections can cut or snag the polishing belt or wheel. Limitations in terms of surface finishes obtainable are related primarily to the abrasive grit sizes available.

It is relatively simple to polish a part that is small enough to be manually manipulated against a stationary wheel, but it is exceedingly difficult to achieve a uniform finish over a large surface with a traveling wheel. As parts become too small to be manipulated manually, they must be held in jigs and fixtures. At this point, part configuration also becomes a controlling factor, because the complexity of the shape of a part frequently dictates the complexity of the jigs and fixtures required. A simple geometric shape, such as a ball, can be readily polished to a high finish in sizes down to 0.25 mm (0.010 in.) diameter by locating it in a circular groove of appropriate size and allowing it to move in contact with a firm wheel. Very small cylindrical parts can be polished in a similar manner. However, as part configuration becomes more complex, the polishing of small parts becomes increasingly difficult unless a mass finishing method can be used.

Large surfaces can be uniformly finished by affixing the part to a moving conveyor and having a polishing wheel exert even pressure against this component as it is drawn past the polishing head. Pneumatic controls allow automatic polishing equipment to be extremely exact in repeating finish generation or work to be accomplished.

Buffing produces smooth, reflective surfaces. It is the rearrangement and refinement of component scratch and has the ability to level surfaces where the scratch is visible only under high magnification. Buffing is accomplished by bringing a workpiece into direct contact with a revolving cloth or buffing wheel that is charged with a suitable compound. Depending on the type of wheel and compound, substantial stock can be removed, radii can be generated consistently, and smooth, bright, and lustrous surfaces can be produced with precision.

Hard buffing is used to cut down or smooth the surface of a material that may or may not have been polished previously. Buffs used for hard buffing are usually made of cloth with a high thread count (e.g., 86/80). The density of the thread count varies with the requirements of the job. Because hard buffing entails both a cutting action and a plowing action, an aggressive compound is generally used.

Color buffing refines a surface to a very low finish and produces a lustrous, scratch-free condition. Any marks or scratches left on a surface after hard buffing can be removed by color buffing. Color buffs are always softer than buffs used for hard buffing and are made of cloths with a lower thread count (e.g., 64/68). Color buffing compounds must produce a high finish and permit the buffing wheel to shed or throw off the small particles of metal and compound that build up during buffing. If a compound does not provide this shedding action, the buildup of particles forms a solid cutting head, requiring the buff to be raked or cleaned frequently.

Contact Buffing. Most conventional modern automatic buffing equipment is set up for contact buffing. A machine imitates the movement of a manual buffing operation, and densely packed wheels are used, rotating at shaft speeds that are usually higher than 1200 rpm. Because the wheel is very hard when rotating at high speeds, the area covered is relatively small. To increase the versatility of finishing equipment and to maintain more precise control, hydraulic drives for conveyors and for the buffing and polishing heads are readily available. Hydraulic drives facilitate precise control of speed, which can be readily changed when there is a change in the product to be finished. Other developments include high-speed and straight-line indexing conveyors, programmed controls, and three-dimensional fixture manipulation.

Mush buffing is a technique in which a broad wheel is used to cover much larger areas than is possible in contact buffing. Shafts can be up to 3.6 m (12 ft) long, with buffs mounted along the shafts, usually separated with 13 to 75 mm ($\frac{1}{2}$ to 3 in.) of space between each of the buff sections. The wheel itself flexes and envelops the contours of the components being finished. Parts travel across the face of the wheel without precise manipulation of the fixtures. In general, simple rotation or oscillation is all that is required to ensure a uniform finish on component faces. Shaft speeds for mush buffing are almost always much slower than for contact buffing. The slower speed of rotation keeps the working temperature of the buff sections lower, resulting in longer buff life. Productivity is generally considerably higher than with conventional methods. Uniformity and quality of finish are enhanced by the increased flexibility of the slower-speed buffs.

Refinement of the mush buffing process led to the development of modular construction of buffing equipment. Modular conveyors may be assembled from standard carriages mounted on a rigid framework. Modular design of equipment increases both short-term and long-term versatility. The suspended mush buffing heads can be placed inside or outside the conveyor and can be relocated for quick application changes. Hence, a single machine can finish a range of components simultaneously and can then be set up to handle a completely different range of parts, just by changing the positions of heads and component fixtures. When requirements change or production increases, the shape or size of the conveyor can be modified, and more heads of the same or a different type can be added.

Surface Finishes after Buffing. Following are descriptions of the typical surface quality achieved after various buffing operations:

- *Scratch brush finish* shows a combination of coarse lines with a slight underlying luster. This finish was used only on nonferrous metals and has been superseded in practically all cases by greaseless compound. Prior to the development of greaseless compound, the scratch brush finish was produced by a brass wire or nickel-silver wire wheel revolving over a tray. A mixture of water and bran meal was applied liberally over the work being finished and over the wheel. The bran meal provided a slight lubrication.
- *Butler finish* is composed of soft, fine parallel lines produced by a lubricated greaseless compound. This finish is generally found in the silver industry and is classified as dull butler, butler, or bright butler, according to the degree of brilliance achieved.
- *Satin finish* is the equivalent of scratch brush finish. It is a more economical finish to produce and has considerable luster. It is now widely accepted as an excellent finish for consumer products.
- *Colonial finish* is achieved by relieving an oxidized surface, emphasizing the lack of luster adjacent to the relieved area. The finished highlights are satin finished and create an attractive decorative effect against the oxidized background. Articles with raised or embossed designs are often given a colonial finish.
- *Matte finish* is produced by using a sand blast or acid dip, creating on the metal a frosted and nonreflective surface completely free of parallel lines. On metals such as aluminum, the greaseless compound method can produce a comparable finish by eliminating the lubricant and operating at high speeds.
- *Sanded finish* is applicable to wood and plastics and is produced in the same way as a satin finish would be produced on metal. In many cases, this method is used in place of belt sanders for finishing ornamental wood earrings, wood heels, and other irregularly shaped articles.

Nylon wheels are flexible, resilient, and made of abrasive-impregnated nonwoven nylon or another synthetic fiber. Abrasive is dispersed evenly throughout these materials, so that wheel performance remains substantially constant despite wheel wear. In many cases these wheels can be shaped to conform to curved, irregular surfaces. They are water resistant and range from 25 to 2000 mm (1 to 80 in.) in width and from 25 to 400 mm (1 to 16 in.) in diameter. A wide variety of densities and grit sizes are available. Nylon wheels may be used wet or dry or with grinding lubricants, such as waxes, oils, or greases.

These wheels are especially useful for imposing uniform scratch patterns or satin finishes on nonferrous metals, plastics, and wood. They are recommended for various types of blending, as well as for the removal of light surface stains, scale, rust, or old coatings. They are not suitable for the removal of large amounts of stock, deep defects, or surface irregularities, but they are effective in removing burrs and radiusing sharp edges. They operate with speeds ranging from 3 to 33 m/s (500 to 6500 sfm), depending on the specific wheel and application.

When nylon wheels are used to finish flat sheet stock, wheel oscillation is recommended to attain a uniform finish, free of streaks. An oscillation of about 200 cycles/min with 10 mm ($\frac{3}{8}$ in.) amplitude gives good results in a variety of applications. Greater amplitudes, up to 50 mm (2 in.), can be used on steel or other hard metals, but on softer metals, amplitudes greater that 13 mm ($\frac{1}{2}$ in.) are likely to create "snake marks."

Flap Wheels. There are basically two types of metal hub flap wheels: reloadable and throwaway. Either style can be used with coated abrasive materials for polishing and with various types of materials for buffing.

The basic construction of a flap wheel incorporates a metal hub that contains coated abrasive packs or buffing packs. Located around the outer perimeter of the wheel are a specific number of keyhole-shaped slots, and flap wheel packs are inserted into these slots. In polishing and buffing operations, the metal hub conveys the material to the workpiece, presenting a longer-lasting, stronger, and better-balanced tool that imparts a uniform finish from the time the wheel is put on until the packs are completely worn. This is accomplished by continually allowing new grain or buffing fabric to be exposed to the workpiece as the flap wheel packs wear.

Some features of modern flap wheels include contouring the face, slashing the packs, reversing the lead sheet, preoiling the packs, and combining the coated abrasive sheets with materials that cushion the cut. Although flap wheels are ideally used in automatic operations, they are quite effective in manual or off-hand polishing operations.

Abrasive Slurries and Compounds

Most compounds consist of an abrasive that is immersed in a binder carrier. The abrasive serves as the principal cutting medium; the binder provides lubrication, prevents overheating of the work, and firmly cements the abrasive to the wheel face or lapping plates. Binders must not chemically etch, corrode, or mar the metal surface. Abrasive slurries are similar to compounds, except that the percentage volume of the carrier fluid is large, providing fluid flow properties to the slurry.

Abrasive grains generally used with all finishing compounds include:

- Tripoli and/or silica for finishing of most nonferrous materials and plastics
- Fused aluminum oxide for finishing of ferrous products
- Calcined alumina for finishing of ferrous and nonferrous materials
- Red rouge for high coloring or finishing of brass products
- Green chromium oxide flours for high coloring or finishing of nonferrous materials and stainless steel, and for finishing of plastic products
- Silicon carbide or diamond for finishing of ceramics and hard materials such as carbides

All of these materials are used with fatty acids and wetting agents in liquid form and are made to suit all of the cleaning processes that are necessary prior to any plating or anodizing operation.

The action of any individual compound can be altered by increasing or decreasing the particle size of the abrasive or varying the amount and types of lubricant used in the binder. If a more intense cutting action is required of a given compound, the particle size of the same abrasive or the quantity of binder may be increased. Modern compounds use water-soluble binders. The lubricant used in the binder generally has a mineral, animal, or vegetable base.

Types of Compounds. The names of many buffing compounds are derived from the abrasives used in their formulas. The designations of other compounds reflect the type of metal on which they are most commonly used or the function they perform. Several of the more widely used buffing compounds are described in the following paragraphs.

Tripoli compound contains a form of silica, of which there is approximately 75% free or crystalline silica. It has the ability to cut sharply at first and then break down in size, resulting in a finer cut and a higher coloring action. It is used extensively for buffing nonferrous metals, particularly copper, zinc, aluminum, and brass.

Bobbing compounds usually contain some form of coarse silica, such as flint or quartz. These abrasives are considerably harder and sharper than tripoli compounds, and they are used for heavy cutting down and the removal of pits from extruded or cast aluminum and silver alloys.

Cut or cutdown compounds usually contain tripoli for buffing nonferrous metals and fused aluminum oxide abrasives for buffing carbon or stainless steel.

Cut and color compounds combine fast cutdown and coloring operations, sacrificing maximum cutting properties of cutdown buffing and the extra brilliance of separate color buffing. Abrasive mixtures are selected to suit the particular metal being buffed and the desired levels of cut and color.

Color or coloring compounds produce maximum brilliance and freedom from scratch on the buffed piece through the use of a very fine, soft abrasive. Choice of buff hardness, buffing compound, peripheral speed, rate of speed, contact pressure, and buffing time vary with the type of pieces being colored and the degree of luster required by the customer. Very fine, soft, white silica powder, very fine alumina powder with highly lubricated binders, or red rouge is usually used in compositions for coloring precious metals such as silver or gold. Fine alumina with lubricated binders and a minimum of buffing pressure is usually the choice for pewter, thermoplastic and thermosetting plastics, and magnesium and aluminum and their alloys. Fine calcined alumina, chromic oxide abrasives, and lime substitutes are combined with clean working binders to color nickel, chromium, and zinc. Fine fused or calcined alumina, or combinations of the two, are the abrasives generally used to color carbon and stainless steel.

Stainless steel buffing compounds generally contain fused or unfused aluminum oxide powder or a mixture of both. These abrasives are available in a wide range of particle sizes, hardnesses, and oil-absorbing qualities. The cutting and coloring action obtained depends on the type of aluminum oxide used and the amount of grease binder in the formulation.

Steel buffing compounds generally contain a mixture of fused and unfused aluminum oxides. They provide a sharp cutting action as well as a lustrous finish.

Chromium buffing compounds consist of fine unfused alumina. These abrasives are also used as secondary coloring compounds on stainless steel. They were developed to color buff chromium-plated parts that had been stained or frosted in the electroplating process.

Rouge compounds are prepared from almost pure red iron oxide powder and are intended for finishing the noble metals. Another form is made with green chromium oxide powder for buffing hard ferrous metals to produce an extremely high finish without stock removal.

Emery paste is a grease or tallow stick impregnated with emery. Although it can be used on setup polishing wheels during the breaking-in period, it is used most extensively on tampico brush wheels for producing a light satin or brush finish.

Greaseless compounds are a special variety of compounds that are entirely free of grease binders. The abrasive is blended with water and gelatin glue, then packaged in airtight containers. It should not be exposed to the air for an extended period of time as it becomes dry and too hard for efficient wheel transfer. When greaseless compounds are applied to cloth buffing wheels, a flexible, dry cutting abrasive head is formed. By varying the type of abrasive, a variety of finishes can be obtained, ranging from an almost bright luster to an almost totally nonreflective finish. Applied to loose buffs, greaseless compounds are effective in producing satin finishes or performing light polishing operations. Their cutting action is increased when they are applied to sewed cloth buffs or felt wheels. Because greaseless compounds are completely free of tallows, oils, or waxes, workpieces are left clean and dry and require no subsequent cleaning. The storage temperature of the product should be between 4 and 21 °C (40 and 70 °F) because it is perishable.

Liquid compounds or slurries contain abrasives that are suspended in a liquid binder carrier. The abrasives are identical to those used in solid bar compounds. Liquid compounds are applied to the buff or the work surface by means of gravity feed, spraying, brushing, or dipping. Liquid compounds are preferred for large-volume production on semiautomatic or automatic buffing equipment. Their advantages are that:

- They reduce direct labor costs, because less time is involved in applying or replacing compounds.
- They reduce waste of buffing compound, because they can be applied in small quantities with manual or automatic controls and leave no unusable waste.
- They provide a wider range of cutting and coloring characteristics because they can be formulated from a wider range of grease binders.
- They extend buff life by wetting and penetrating the buff to a greater depth, by maintaining an optimum amount of buffing compound on the surface of the buff at all times, and by permitting a cooler buff operating temperature.
- They saponify and emulsify faster than bar compounds and therefore are less likely to back-transfer on the workpiece or to set up solidly in crevices or recesses. Thus, they are easier to remove in subsequent cleaning operations.
- They are formulated precisely to meet the requirements of a specific application. Unlike bar compounds, they are not limited by the need to form a bar that is physically strong enough to survive application shock

Lapping

Lapping is the process of finishing work materials by applying a loose abrasive slurry between a work material and a closely fitting surface, called a *lapping plate.* When loose abrasive is used to machine the work material, it may slide, roll, become embedded, or do all three, depending on the shape of the abrasive grain and the composition of the backup surface.

Rolling Abrasives. Lapping takes place when abrasive grain entrained in a liquid vehicle, often known as *slurry,* is guided across the surface to be lapped and is backed up by a lapping plate. Because the abrasive grains used for lapping have sharp, irregular shapes and each grain is backed up by a lapping plate, when a relative motion is induced and pressure is applied, the sharp edges of the grains are forced into the workpiece material to be lapped and either make an indentation or cause the material to chip away microscopic particles. Even though the abrasive grains are irregular in size and shape, they are used in large quantities, so the cutting action takes place continuously over the entire surface of a workpiece. With regard to the movement of the abrasive grains, special importance has to be assigned to the liquid vehicle.

Sliding Abrasives. The initial conditions for lapping with sliding abrasives are similar to those for lapping with rolling abrasives. However, because the abrasive grains are flat or platelike in configuration, they simulate tiny scrapers. The exact movement of the abrasive grains has not been established; however, the platelike abrasive grains are believed to stack on top of each other, somewhat like tipped-over dominoes, providing many cutting edges to machine away the surface being lapped. The direction of cut is constantly shifted by the constantly changing direction of movement of the workpieces against the backup lapping plates, so that all edges of the abrasive grains are used.

With both rolling and sliding abrasive processes, the abrasive grit mixed with water vehicle is carefully metered and fed automatically to the work area to enable a uniform cutting action.

Charged Plate Abrasives. An early form of lapping, still used for some applications, utilizes embedding of abrasive in the lapping plate or tool. The abrasive grains that are doing most of the work become embedded and act as microscopic scraping tools. These abrasive grains eventually dull or break and are replaced by fresh grains, which are added periodically by hand or from an abrasive paste that works up from slots in the lap plate. The large abrasive grains that become embedded provide the most aggressive lapping action when a relative motion takes place between the workpiece and the lapping plate. As these larger grains are worn down or break down, the smaller grains start to embed and work. The cutting action of a charged plate abrasive is actually a combination of rolling, sliding, and embedding abrasive processes.

Most lapping plates used for this kind of processing have grooves in a waffle pattern and use a paste form of the lapping compound. The paste can be used as-purchased, or it can be mixed with an oil to the consistency of a heavy cream. The grooves hold the lapping compound, which works its way out to keep the lap plate lubricated and provide a recharging effect on the lapping surface. This type of lapping is more labor intensive than the two systems described above and requires the operator to manually apply the proper amount of compound. The cutting action changes as the abrasive grains are used up, thus requiring more operator attention.

Lap Plate Materials. The most commonly used material for making laps is cast iron, which has a special close-grain microstructure that has no porosity or other defects to affect the lapping action. Cast iron is very versatile and can be used for rolling abrasive, sliding abrasive, and embedding abrasive applications and for polishing with hard abrasives. The close-grain iron has the unique ability to grip the abrasive grains and make them roll or shave effectively (as in the case of the platelike aluminum oxide), giving them a foothold to work against the workpiece efficiently.

Another material sometimes used for the lapping plate (wheel) for one-wheel, single-sided flat lapping machines is made of a steel alloy hardened to 60 HRC. This plate is reported by the manufacturer to resist embedding of the rolling abrasive grains for the purpose of obtaining a deeper indentation of each working abrasive grain into the workpiece. A high pressure is applied to the workpiece, and a generous amount of abrasive slurry is fed to the lapping area to prevent the workpieces from making extremely close contact with the lapping plate.

Other materials, used less frequently, include nodular iron, aluminum, and nonmetallics such as granite.

Lapping Vehicle Fluids. Water-based vehicles are commonly used for lapping. Oil is also a good vehicle, but it is often objectionable because of its tendency to penetrate into the pores of some materials. In addition, oil is expensive to purchase, and its disposal is difficult and expensive because it is now classified as a hazardous waste.

The purpose of any vehicle is to carry the abrasive grains and position them to work most efficiently. The vehicle also lubricates the surfaces and carries away the abraded material removed from the workpieces. To prevent rust to the machine components, inhibitors are often added to water-based vehicles. Depending on the equipment, the vehicle is sometimes also depended on to carry away heat generated by the lapping process.

Suspension agents are occasionally added in order to prevent settling of the abrasive. These agents do not necessarily improve the actual lapping action. A variety of methods can be used to keep the abrasive in suspension with minimal negative effect at the area where the machining takes place.

Lapping Process. When lapping takes place on one side of the work material against a lapping plate, it is called *single-sided lapping.* If the work is held between two parallel lapping plates and the abrasive finishes both sides of the work simultaneously, the process is called *double-sided lapping.* Sometimes cylindrical components such as piston pins are finished between two parallel laps. Double-sided flat lapping offers the following advantages:

- Two sides of a workpiece can be machined in the time required to machine one side.
- A large number of workpieces can be produced simultaneously.
- Nonmagnetic material can be held, from plastic to diamond.
- It is the best available method to obtain close tolerances for flatness, parallelism, and size.
- Removing stock from both sides of a workpiece simultaneously helps to relieve the internal stress of the workpiece, thus making it easier to achieve flatness.
- The simple workholder design, with no need to clamp or rigidly hold the workpiece, eliminates stresses in the workpiece and thus improves tolerances for flatness, parallelism, and size.
- Accuracy with double-sided lapping is achieved by using flat lap faces and a freefloating top wheel. No critical machine alignment, precision high-speed spindle bearing, or accurately machined sliding ways are involved.
- The workpiece is exposed to minimal stress and surface damage, because lapping generates no heat.
- The cut rate is uniform and repeatable. No dulling of the abrasive takes place, because fresh sharp abrasive particles are fed to the lapping area continuously during the processing cycle.
- Operating costs are often lower because of less handling, higher efficiency, and the feasibility of combining machining operations.

Ultrasonic Machining

In ultrasonic machining, electrical energy is converted into mechanical motion. The linear motion is typically only 0.025 mm (0.001 in.), but at a rate of 20 kHz. The low-amplitude vibration is acoustically transmitted to a toolholder and specially designed tool. When combined with an abrasive slurry, the workpiece material is microscopically ground away, and the machined area becomes a mirror or counterpart of the vibrating tool. Ultrasonic machining is nonthermal, nonchemical, and nonelectrical. Therefore, no change takes place in the metallurgical, chemical, or microstructural properties of the workpiece. Although it can cut any material, ultrasonic machining is most effective on materials harder than 40 HRC.

The ultrasonic motion is produced by the combination of an electronic generator coupled to a transducer package (magnetostrictive or piezoelectric). The generator converts typical line voltage into the voltage and frequency required to energize the transducer coupled to the generator. The transducer is connected to a transmitting connecting body. The physical size is designed to resonate naturally at the same frequency as the electric current. A threaded stud is used on the end of the connecting body to connect the toolholder. Figure 19 shows an ultrasonic transducer and toolholder assembly.

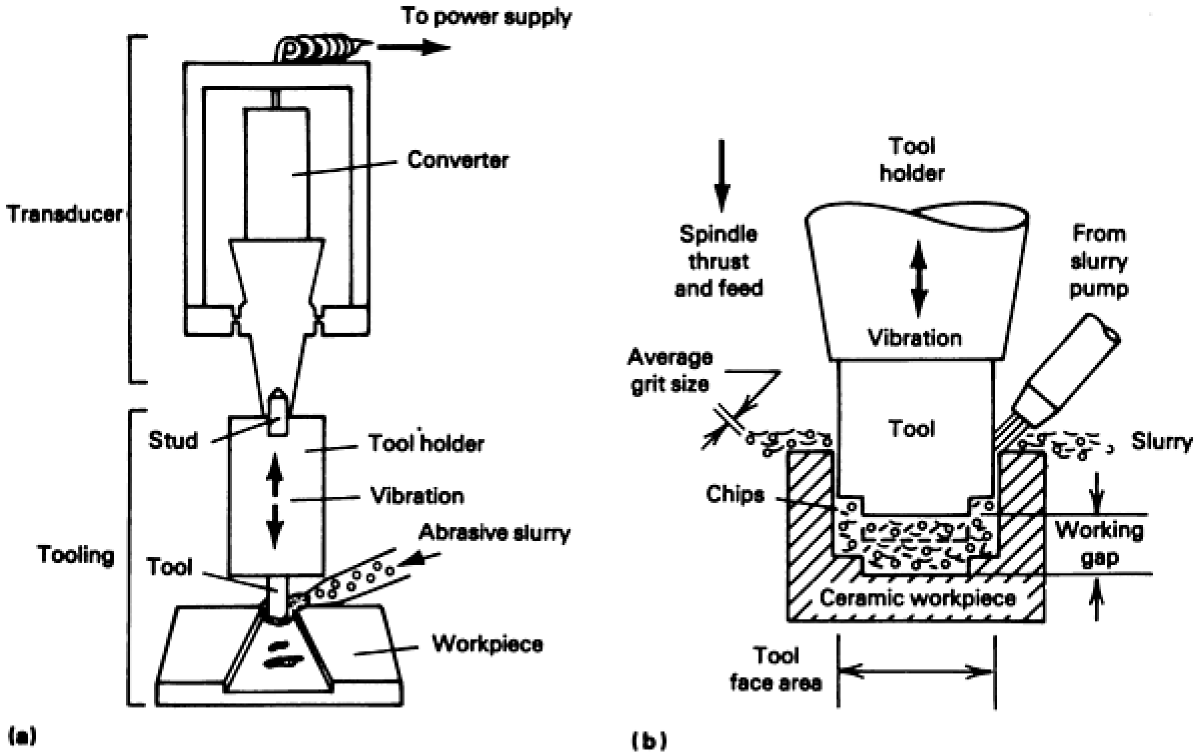


Fig. 19 Schematic showing primary components of a typical ultrasonic machining installation. (a) Transducer assembly coupled to tooling assembly of unit. (b) Closeup view of tooling assembly being used to machine a ceramic

Ultrasonic machining is frequently used to provide faster deliveries and to lower tooling costs for the machining of ceramics. When changes are required during the early design stages, alternatives can be made quickly and economically through the application of impact grinding.

Frequently, ultrasonic machining provides the only method that is capable of machining oddly shaped cuts or shapes in hard, brittle material. Sharper radii and tighter tolerances are also process advantages in some applications. Because of its nonthermal characteristics, ultrasonic machining produces virtually stress-free machined surfaces. An ultrasonic assist added to a rotating tool enhances material removal rates, finish capabilities, and overall drilling efficiency. Rotary ultrasonic machining uses a diamond-plated drill and is water cooled because the diamond-impregnated abrasive provides the cutting edge.

Rotary ultrasonic machining can be used for milling, drilling, threading, and grinding applications. However, its use is limited to round tool configurations.

Abrasive Jet Machining

Conventional abrasive jet machining is the use of abrasive-gas jets to propel particles against a surface and remove the material from that surface via particle impact and shear. Typically, abrasives in quantities up to 0.05 kg/min (0.1 lb/min) are propelled through a nozzle at inlet pressures ranging from 170 to 860 kPa (25 to 125 psi) in a gas (nitrogen or air) medium. Outlet velocities are generally supersonic, and the volume of material removed varies as particle velocity is raised to a power between 2 and 3. Sand blasting and deburring are the two most common applications for abrasive jet machining. Material removal rates can be enhanced by increasing the inlet pressure (experiments up to 12 MPa, or 1.8 ksi, have been carried out) and by optimizing nozzle design. However, difficulties in controlling shock-laden jet structure and particle distribution within the jet make this process impractical for precision machining. An extremely high noise level (>85 dB) is another problem.

Abrasive Waterjet Cutting. High-velocity water can be used to entrain and accelerate abrasive particles. Unlike gas jets, waterjets can be confined to a small diameter without spreading, and they can accelerate particles to desired velocities in a relatively short distance. In addition, relatively high abrasive mass flow rates (1.4 to 1.8 kg/min, or 3 to 4 lb/min) can be easily accommodated. The result is an extremely high-energy jet that can easily cut through a solid steel plate more than 102 mm (4 in.) thick.

In *abrasive slurry jets*, a thin slurry mixture of abrasive and water is directly pumped to a high pressure and then passed through a nozzle to form the jet. A slurry jet is more efficient because energy losses due to mixing and particle collision are much reduced. In addition, high abrasive loading can be readily achieved. However, other problems easily outweigh these advantages. Pump and component life is greatly reduced, and uniform mixing of the slurry is a problem. A continuous-batch, lower-pressure (20 to 105 MPa, or 3 to 15 ksi) system has recently been introduced that is designed primarily for portable applications.

Abrasive flow machining is a novel technique in which copious amounts of an abrasive compound (whose viscosity is between that of a compound and that of a slurry) is applied between the work material and a closely fitting mandrel. The abrasive "fluid" removes and sizes the work material as it is "extended" on the surface being finished. Some of the applications of abrasive flow machining are finishing of dies and molds, finishing of jet engine components, and cutting or trimming of sheet metals.

System Concepts

The key results of successful abrasive finishing or machining are improvements in:

- Surface quality
- Retained strength
- Tolerances/finish
- Production rate
- Cost per part
- Product performance

These results are affected by four categories of factors. Following is a list of these factors and some of the variables that influence them:

Machine tool factors

- *Design:* rigidity, precision, dynamic stability
- *Features:* controls, power/speed, slide movements/axes, truing and dressing equipment
- *Coolant:* type, pressure, flow, filtration system

Work material factors

- *Properties:* mechanical, thermal, chemical, abrasion resistance, microstructure
- *Geometry:* wheel-part conformity, access to coolant, shape/form required
- *Part quality:* geometry, tolerances, consistency

Wheel selection factors

- *Abrasive:* type, properties, particle size, distribution, content/concentration
- *Bond:* type, hardness/grade, stiffness, porosity, thermal conduction
- *Wheel design:* shape/size, core material, form or profile

Operational factors

- *Fixtures*

- *Wheel balancing*
- *Truing, dressing, and conditioning:* techniques, devices, parameters
- *Grinding cycle design*
- *Coolant application*
- *Inspection methods*

Regardless of the choice of variables in the four input categories, for every abrasive machining process it is possible to visualize four interactions between the abrasive product and the work material (Fig. 20):

- Abrasive/work interaction
- Chip/bond interaction
- Chip/work interaction
- Bond/work interaction

Of these, the abrasive/work interaction is the most critical, analogous in many respects to machining processes with cutting tools (Fig. 21). The interactions between the abrasive product and the work material may be categorized as *cutting* (material removal process), *plowing* (material displacement process), and *sliding* (surface modification process) (Fig. 20). Every abrasive machining process is an effort to balance cutting (surface generation) and plowing/sliding (which controls the characteristics of the generated surface).

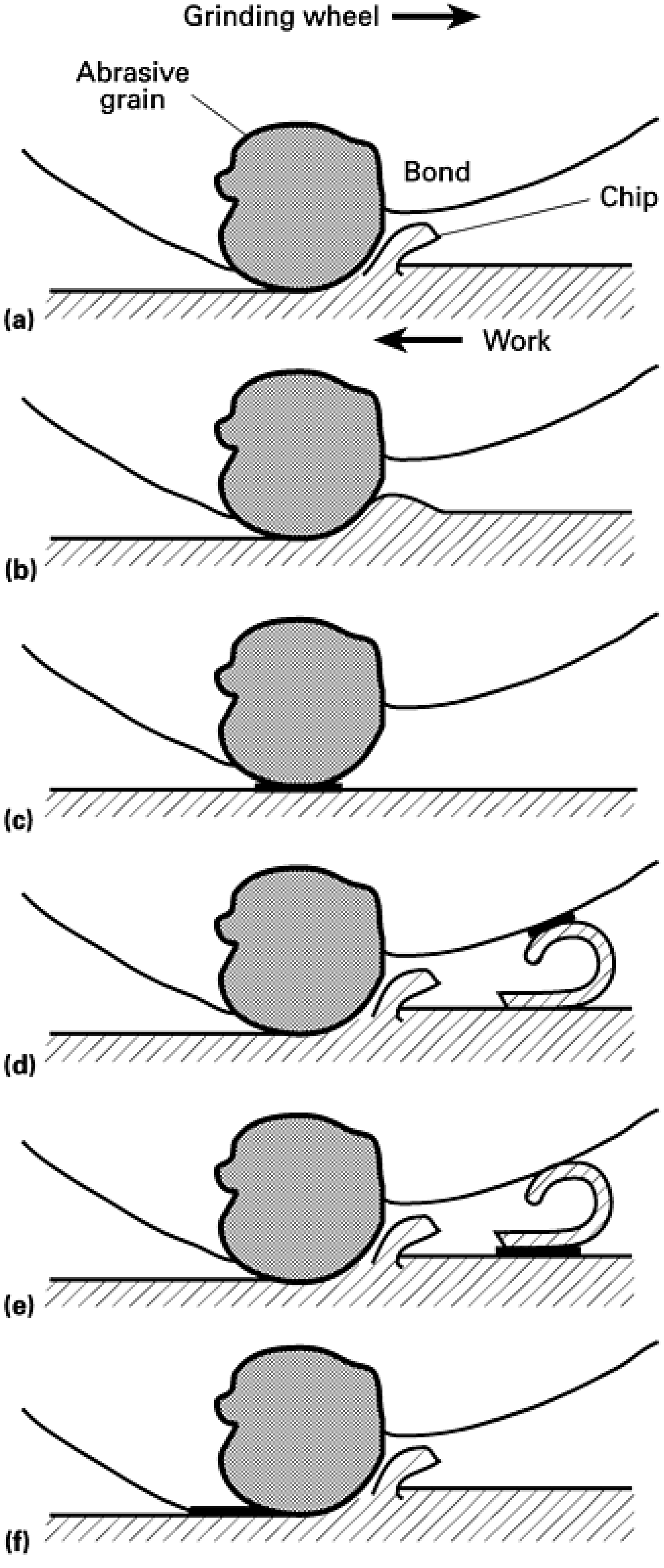


Fig. 20 Interactions in the grinding zone. (a) Abrasive/work cutting (material removal process). (b) Abrasive/work plowing (material displacement process). (c) Abrasive/work sliding (surface modification process). (d) Chip/bond sliding. (e) Chip/work sliding. (f) Bond/work sliding. See text for details.

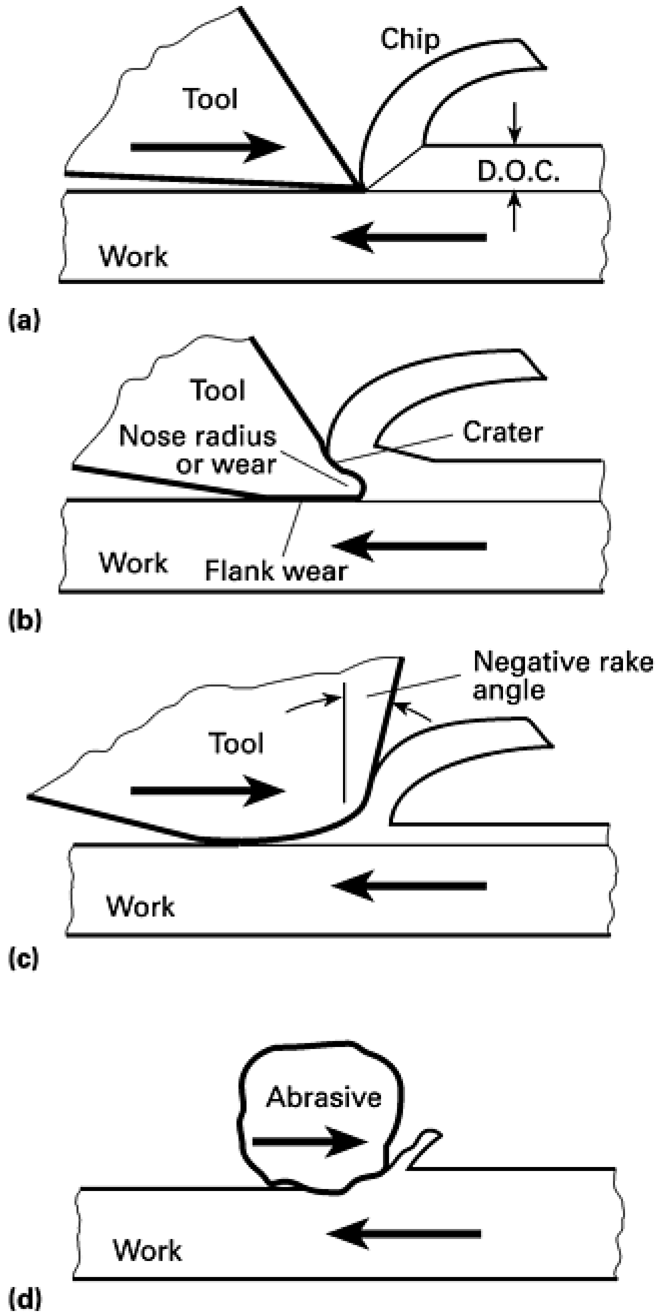


Fig. 21 Schematics of cutting and abrasive "machining" processes. (a) Ideal process. (b) Practical process. (c) Modified processes (diamond turning). (d) Abrasive process

Thus, every abrasive machining process can be thought of as an input/output process with defined microscopic interactions of cutting and tribological aspects of plowing and sliding. These interactions can be measured or monitored using macroscopic process variables such as force, power, and temperature. These result in certain technical outputs, and based on the rules of manufacturing economics, these in turn result in economic or system output. Figure 22 is a representation of the *systems approach* and illustrates the use of the principles of machining and tribology to manage and/or improve abrasive machining processes. Details of the systems approach can be obtained from the references to this article.

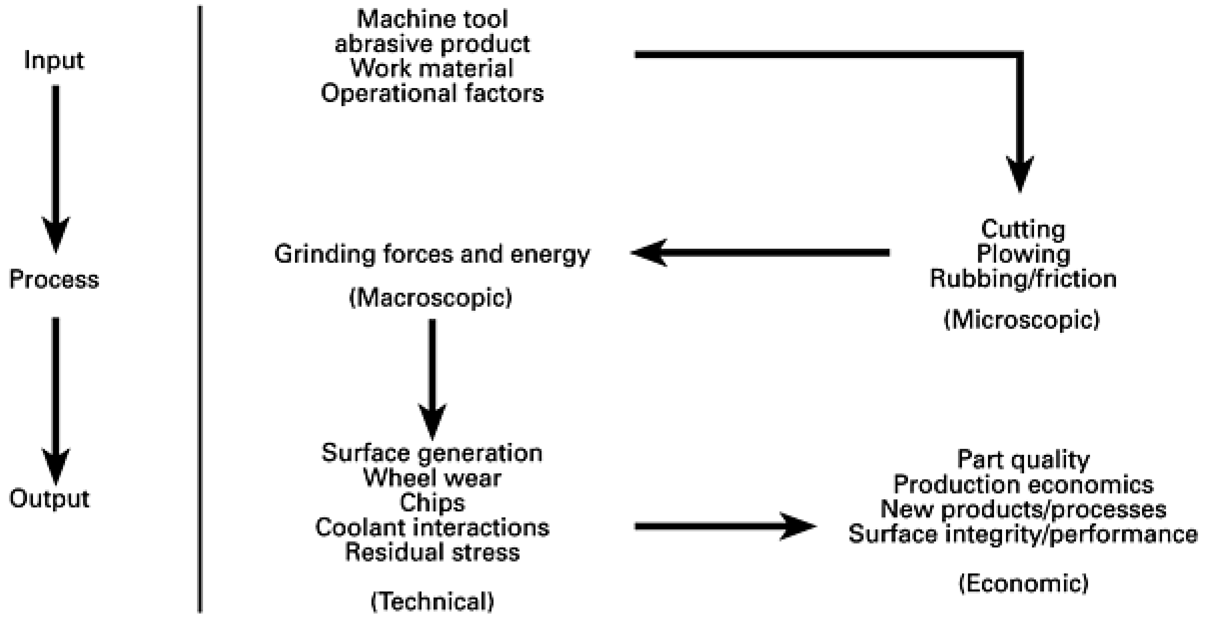


Fig. 22 A systems approach for abrasive finishing processes

The four interfaces in the grinding zone,listed above, may be elaborated as shown in Fig. 20. The presence of coolant or other liquids influences the nature of these sliding interactions. From this point of view, every abrasive finishing process becomes a situation of maximizing the cutting action of the abrasive (Fig. 20a) and minimizing all the sliding or tribological interactions (Fig. 20b to f):

- Minimizing abrasive/work plowing (Fig. 20b) implies proper choice of abrasive/work combination, appropriate size or shape of abrasives, and suitable chip thickness.
- Abrasive/work sliding (Fig. 20c) is minimized when the abrasive used is self-sharpening and wear flats are not generated in the abrasive during setup or truing.
- Chip/bond sliding (Fig. 20d) is minimized by suitable selection of bond/work combinations. Changing coolant, porosity in the bond, or lubricants in the bond matrix are other means of reducing this interaction.
- Minimizing chip/bond sliding has the complementary effect of simultaneously reducing chip/work sliding (Fig. 20e). From the principles of tribology, the sliding interaction between like materials has the highest coefficient of friction; hence, a poor combination must be avoided at all costs. In practice, this simple principle is often missed or ignored, resulting in high grinding forces, extensive abrasive product wear, or poor work surface quality.
- Bond/work sliding (Fig. 20f) is generally minimal when porous abrasive products are used or when vitrified or resin bond is used. However, they are very pronounced when metal bond abrasive products are used. This interaction becomes critical when fine abrasive grits are used or during finish grinding processes, when the abrasive exposure is deliberately small and the bond matrix is very close to the work surface.

The cutting action can be maximized using the principles of machining described in the article "Finishing Methods Using Defined Cutting Edges" in this Volume.

Managing sliding or tribological components while maximizing the cutting component determines whether finishing is rough, precision, or high-precision. For instance, rough finishing processes minimize the tribological components as much as possible. Precision finishing processes minimize the tribology during the rough grinding portion of the cycle and selectively use them during the semifinish and finish grinding portions of the cycle to achieve the desired surface finish or similar surface features. High-precision processes, such as lapping and polishing, depend entirely on the tribological components to achieve the desired results of surface finish, surface texture, luster, and so on.

The results of both cutting and tribological interactions are surface generation, surface deformation, or mechanical-to-thermal energy conversion. Maximizing the cutting component and minimizing tribological interactions are often associated with minimum use of forces or energy. Coolants dissipate the thermal energy to minimize the heat dissipation through the work material, if it affects the integrity of the parent material.

All of the above observations are true for a wide range of abrasive machining processes, independent of the work material type. Hence, the science of grinding may be expressed as simultaneous manipulation of four categories of inputs (i.e., machine tool factors, work material factors, wheel selection factors, and operational factors) to maximize the tribological components with the minimum force and at the minimum expenditure of energy. The balance between cutting and tribological components may depend on both technical and economic considerations. When all four categories of inputs are varied simultaneously, the benefits achieved are quantum improvements. If only one category is manipulated, the results generally are small or incremental in nature. When the microscopic interactions are not understood or considered, abrasive finishing processes are reduced to empirical and statistically managed operations, with extreme cost and quality penalties.

Nonabrasive Finishing Methods

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Introduction

NONABRASIVE FINISHING METHODS are processes in which the surface generation occurs with a very little or insignificant amount of mechanical interaction between the processing tool and the workpiece surfaces. These processes are classified in general as the nontraditional or unconventional machining processes. In these processes, chemical, electrical, or thermal actions, or a combination, are used for metal removal. Nontraditional processes include electrochemical machining (ECM), electrodischarge machining (EDM), and laser beam machining (LBM). The inherent nature of ECM and EDM makes them ideal for stock removal as well as finishing operations. The same is not true of LBM at the present time. Therefore, this article provides a brief review of ECM and EDM and their role in finishing operations. More detailed discussions of equipment and process characteristics appear in *Machining,* Volume 16 of the *ASM Handbook.*

Electrochemical Machining

ECM consists basically of the electrochemical dissolution of the surface metal of a workpiece by conversion of metal to its ions by means of an electric current. The whole process is accomplished in an electrolytic cell by applying a positive (anodic) potential to the workpiece and a negative (cathodic) potential to the tool used to shape the workpiece. ECM can be used for shaping, finishing for improving the quality of the surface, deburring, and radiusing. One kind of ECM is electropolishing. Figure 1 shows the various schematics for machining different geometries using ECM.

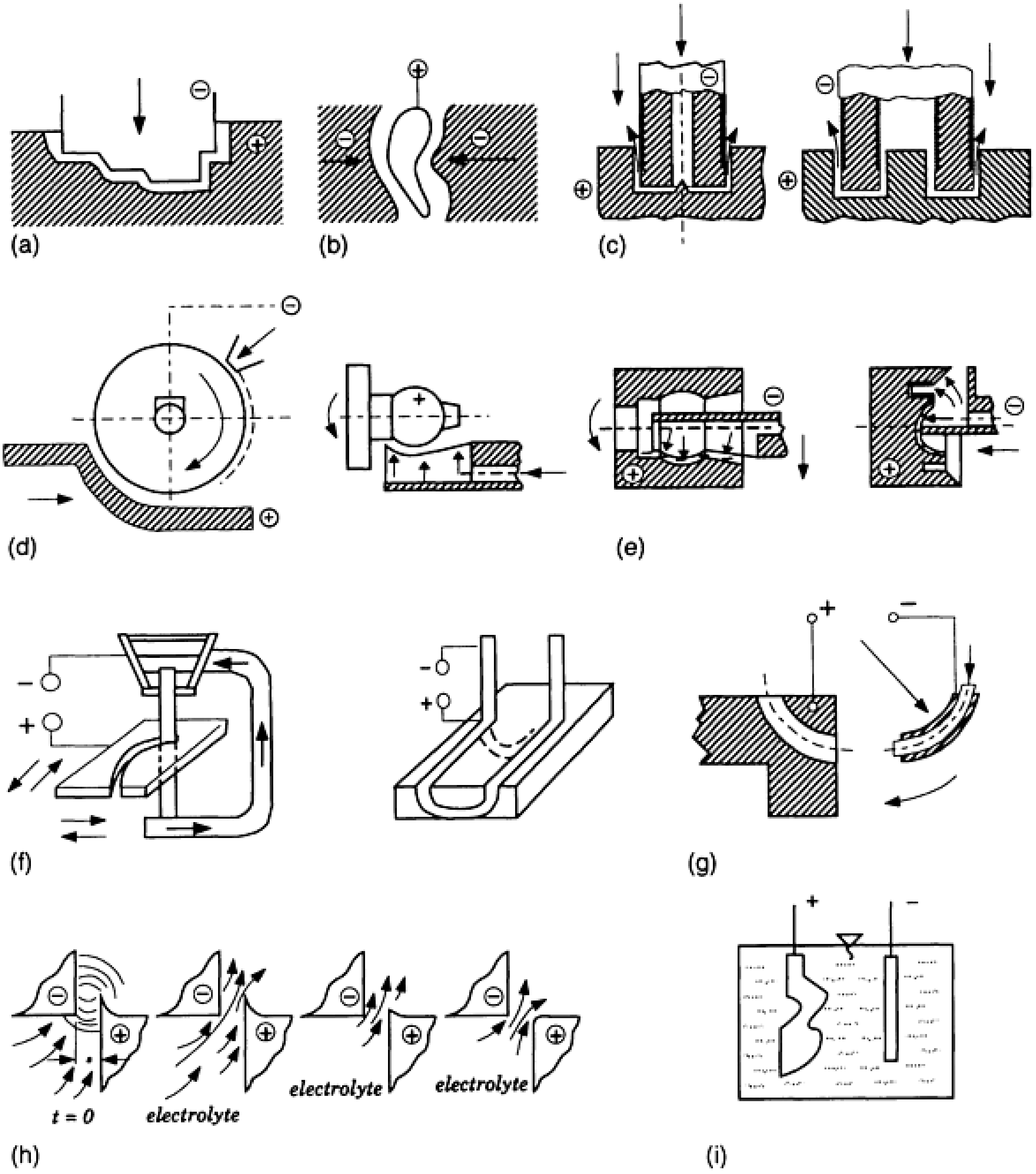

Fig. 1 Schematics of electrochemical machining (ECM) operations. (a) Die sinking. (b) Shaping of blades. (c) Drilling. (d) Milling. (e) Turning. (f) Wire ECM. (g) Drilling of curvilinear holes. (h) Deburring and radiusing. (i) Electropolishing

The rate of material removal in ECM is governed by Faraday's law, since it is a function of current. The primary variables that affect the current density and the material removal rate are:

- Voltage
- Feed rate
- Electrolyte conductivity
- Electrolyte composition
- Electrolyte flow
- Workpiece material

The voltage across the gap influences the current and the material removal rate and is controlled in most ECM operations. However, for a constant voltage, the current also depends on the electrical resistance of the cutting gap. Resistance is much more difficult to control because it depends on the conductivity of the electrolyte and the distance across the gap.

The feed rate, or penetration rate, is also controlled in most ECM operations. At a constant voltage, the gap is inversely proportional to the feed rate. The distance across the frontal gap is a function of feed rate because, as the cathode is fed into the workpiece at a higher rate, the gap closes, causing resistance to drop. As resistance drops, amperage increases; therefore, machining rate also increases until an equilibrium is reached. At slower feed rates, the material removal rate decreases as the gap increases because the cathode is not keeping up with the workpiece surface. As the gap increases, the resistance rises and amperage drops. Frontal gaps are usually between 0.1 to 0.8 mm (0.005 to 0.030 in.), and side gaps, in the case of drilling, are about 0.5 to 1.3 mm (0.020 to 0.050 in.).

The feed rate also varies directly with the current. For example, a hole machined at 2.5 mm/min (0.100 in./min) at 10 V and 1000 A would require 2000 A if the feed were increased to 5.0 mm/min (0.200 in./min). This would also require a potential of about 20 V and would increase power consumption ($V \cdot I$) from 10 to 40 kW.

The feed rate also depends on the application. Typical feed rates for different ECM operations on Inconel 718 are:

Operation	**Feed rate**	
	mm/min	**in./min**
Round holes (blind)	2.2	0.085
Simple cavities	2.2	0.085
19×10^3 mm^2 (30 in.^{2}) faces	1.3	0.050

Accurate estimates of feed rates usually require pilot testing in the desired ECM configuration.

Electrolyte conductivity also affects resistance across the gap. Increasing the concentration of an electrolyte causes conductivity to rise, which causes a decrease in resistance. Temperature increases of the electrolyte also increase conductivity. Therefore, electrolyte concentration and temperature must be controlled.

Electrolyte composition directly influences conductivity, material removal rates, and surface characteristics. The parameters used for a given application may not yield the same ECM results if a different type of electrolyte is used. The normal development of an operation usually begins with the selection of the correct electrolyte. The other parameters and the cathode are then adjusted to obtain the desired result.

Electrolyte flow rate is also a factor in ECM process control. The temperature increase of the electrolyte passing through the gap is dependent on the flow rate. In addition, the rate at which hydrogen bubbles are carried away is thought to influence conductivity. Pressure control is the method of controlling flow rate (especially when a centrifugal pump is used). The flow rate also affects the level of turbulence of the electrolyte as it passes through the gap, and this influences the surface finish. The flow rate must also be great enough to remove machining byproducts (sludge).

The workpiece material also affects the material removal rates. Theoretical removal rates for various metals are listed in Table 1. These removal rates are derived from Faraday's Second Law, which states that 1 Faraday (96,494 coulombs or ampere seconds) will liberate 1 g equivalent weight of a substance, or its atomic weight divided by the valence. For example, the gram equivalent weight of iron is the atomic weight divided by the valence of the dissolved iron, or 56 divided by 2 equals 28. Thus, 28 g of iron will dissolve during the passage of each Faraday of electricity. Table 1 lists the theoretical metal removal rates at 1000 A of current flow.

Table 1 Theoretical removal rates in electrochemical machining

Metal	Valence	Density		Removal rate (1000 A current, 100% efficiency[(a)])			
				Mass		Volume	
		g/cm^3	lb/in.^{3}	kg/h	lb/h	mm^3 × 10^3/min	in.^{3}/min
Aluminum	3	2.7	0.098	0.34	0.74	2.1	0.13
Beryllium	2	1.9	0.067	0.17	0.37	1.5	0.09
Copper	1	9.0	0.324	2.37	5.22	4.4	0.27
	2	9.0	0.324	1.18	2.61	2.1	0.13
Iron	2	7.9	0.284	1.04	2.30	2.3	0.14
	3	7.9	0.284	0.69	1.53	1.5	0.09
Magnesium	2	1.7	0.063	0.45	1.00	4.4	0.27
Molybdenum	3	10.2	0.369	1.19	2.63	2.0	0.12
	4	10.2	0.369	0.89	1.97	1.5	0.09
	6	10.2	0.369	0.60	1.32	1.0	0.06
Nickel	2	8.9	0.322	1.09	2.41	2.1	0.13
	3	8.9	0.322	0.73	1.61	1.3	0.08
Niobium	3	8.6	0.310	1.16	2.55	2.3	0.14
	4	8.6	0.310	0.87	1.92	1.6	0.10
	5	8.6	0.310	0.69	1.53	1.3	0.08

Tantalum	5	16.6	0.600	1.35	2.98	1.3	0.08
Titanium	3	4.5	0.163	0.59	1.31	2.1	0.13
	4	4.5	0.163	0.45	0.99	1.6	0.10
Tungsten	6	19.3	0.697	1.14	2.52	1.0	0.06
	8	19.3	0.697	0.86	1.89	0.8	0.05
Commercial alloys							
4340	. . .	. . .	. . .	. . .	. . .	2.18	0.133
17-4 PH	. . .	. . .	. . .	. . .	. . .	2.02	0.123
A-286	. . .	. . .	. . .	. . .	. . .	1.92	0.117
M-252	. . .	. . .	. . .	. . .	. . .	1.80	0.110
René 41	. . .	. . .	. . .	. . .	. . .	1.77	0.108
U-500	. . .	. . .	. . .	. . .	. . .	1.80	0.110
U-700	. . .	. . .	. . .	. . .	. . .	1.77	0.108
L-605	. . .	. . .	. . .	. . .	. . .	1.75	0.107

(a) It is not always possible to predict the valence at which some metals will dissolve nor how much current will flow through the gap. Also, practical factors, such as the shape of the electrode, can limit current flow.

Removal rates for a given current are, of course, less than the theoretical limit, and variations in temperature, metallurgy, and electrochemical reactivity of the electrolyte affect the metal removal rate. The most accurate method of determining removal rates is by empirical testing.

The electrical current in a particular application is determined by the current density and the area of the gap between the anode (wheel) and the cathode (workpiece). Current density most often depends on the material being processed, although it is also affected by gap distance and voltage. To obtain maximum removal rates, the area should be as large as possible so that it will draw greater current.

ECM Equipment

Figure 2 shows a schematic representation of the ECM system for finishing of a die or other complex shapes. The major components include the workpiece, cathode tool, electrolyte, power supply, and electrolyte circulating and purification system. A low voltage (8 to 30 V) is normally applied across the electrodes. A small gap (0.2 to 1 mm) is maintained between them, producing a current density of the order of 10 to 100 A/cm^2 (Ref 1, 2, 3). The electrolyte is forced through the small gap between the cathode tool and the anodic workpiece with velocities of 5 to 30 m/s (15 to 100 ft/s). The electrolyte movement flushes away the debris removed from the workpiece.

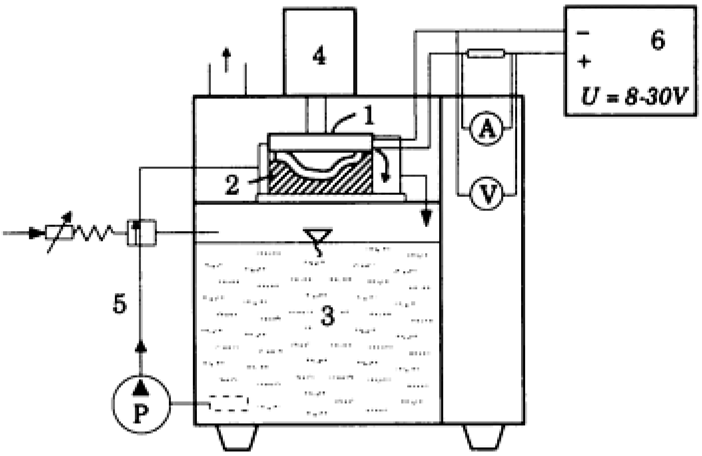

Fig. 2 Electrochemical machining equipment schematic. 1, tool electrode; 2, finishing workpiece; 3, tank of electrolyte; 4, clamping system; 5, electrolyte supply system; 6, power supply

A typical ECM machine consists of a table for mounting the workpiece and a platen mounted on a ram or quill for mounting the tool. The workpiece is mounted on the table and connected to the positive side of the power supply. The tool is mounted on the platen with electrical connection to the negative side of the power supply. The part to be machined is held on a fixed table and the tool is held on a ram that moves either horizontally or vertically onto the workpiece. During the finishing operations while ECM sinking, the tool is either stationary or is fed in the direction of the workpiece. During deburring and machining of contours, however, the tool usually does not move relative to the workpiece.

The corrosive nature of the electrolyte requires that any portion of the machine or tooling that comes in contact with it must be made of a corrosion-resistant material. Workholding fixtures for ECM are usually made from stainless steel, copper, or copper alloys.

Water-cooled power supplies are used on ECM equipment to convert alternating current (ac) electrical power to the direct current (dc) voltages required. ECM machines are available that can deliver currents from 50 to 10,000 amperes, with a voltage range of 4 to 30 V. Sufficient current must be available to maintain a current density of 10 to 500 A/cm^2 at the workpiece (Ref 1, 3).

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ECM Process Capabilities

There are numerous parameters that influence the ECM process in terms of machining rate, surface finish, and other end product physical characteristics. In particular, the metal removal rate and the surface finish depend on current density, machining gap, feed rate, electrolyte composition, temperature, and flow rate or pressure of the electrolyte. The design of an ECM system for a specific application should take into account the range of values for these parameters.

The only requirement of the workpiece material for ECM is that it should be electrically conductive. Because the physical properties (rather than the chemical properties) of the material determine the machining rate, alloys that contain more than one phase of the same material usually present no problem for ECM. However, alloys with inclusions of different materials may be difficult to machine by ECM , or the surface may be unacceptable because of the preferential erosion of one of the materials (e.g., some high-silicon aluminum alloys) (Ref 4). One of the benefits of ECM is the higher machining rates (0.2 to 10 mm/min) for difficult-to-machine materials such as heat-resistant alloys and titanium alloys. Table 1 lists some theoretical removal rates.

Surface Integrity. In addition to high machining rates, ECM produces smooth, damage-free surfaces. The surface finish produced by ECM depends on the workpiece metal or alloy, the electrolyte, and the operating conditions. In general, ECM of nickel-base, cobalt-base, and stainless steel alloys produces smoother surfaces (0.1 to 0.4 μm R_a) than the surfaces obtained with iron-base alloys and steels (0.6 to 1.5 μm R_a), where R_a is the surface roughness in terms of arithmetic average. Most of the ECM in industry, at present, is carried out with NaCl electrolyte because NaCl is inexpensive and gives surface finishes in the ranges mentioned above. However, $NaNO_3$ and KNO_3, which are more expensive electrolytes, are found to give smoother surfaces for many metals, including iron, copper, nickel, aluminum, and cobalt. Table 2 lists various electrolytes for common work metals.

Table 2 Electrolytes for the electrochemical machining of various metals

Work metal	Electrolyte		Removal rate, $mm^3 \times 10^3$/min ($in.^3$/min) per 1000 A
	Major constituent	Concentration (max), kg/L (lb/gal) of H_2O	
Steel; iron-, nickel-, and cobalt-base alloys	NaCl or KCl	0.30 ($2\frac{1}{2}$)	2.1 (0.13)
	$NaNO_3$	0.60 (5)	2.1 (0.13)
Steel; hardened tool steel	$NaClO_3$	0.78 ($6\frac{1}{2}$)	2.0 (0.12)
Gray iron	NaCl	0.30 ($2\frac{1}{2}$)	2.0 (0.12)(a)(b)
	$NaNO_3$	0.60 (5)	2.0 (0.12)(a)(b)
White cast iron	$NaNO_3$	0.60 (5)	1.6 (0.10)(c)
Aluminum and aluminum alloys(d)	$NaNO_3$	0.60 (5)	2.1 (0.13)
	NaCl or KCl	0.30 ($2\frac{1}{2}$)	2.1 (0.13)
Titanium alloys	NaCl or KCl(e)	0.12 (1)	1.6 (0.10)
Tungsten	NaOH(f)	0.18 ($1\frac{1}{2}$)(g)	1.0 (0.06)

Molybdenum	NaOH[h]	0.18 ($1\frac{1}{2}$)	1.0 (0.06)
	NaCl or KCl	0.30 ($2\frac{1}{2}$)	1.0 (0.06)
Copper and copper alloys[d]	NaCl or KCl	0.30 ($2\frac{1}{2}$)	4.4 (0.27)
	$NaNO_3$	0.60 (5)	3.3 (0.20)
Zirconium	NaCl or KCl	0.30 ($2\frac{1}{2}$)	2.1 (0.13)

(a) Feed rates limited by graphite particle size.

(b) Maximum; can vary widely.

(c) Rough surface finish.

(d) $NaNO_3$ electrolyte provides better surface finish.

(e) Voltage must be greater than 11.

(f) NaOH used up in process and must be replenished.

(g) Minimum of 0.09 kg/L ($\frac{3}{4}$ lb/gal).

(h) pH of electrolyte decreases with use; maintain pH by adding NaOH or KOH.

The main parameter affecting surface roughness of the workpieces is the current density (Fig. 3). Increasing the grain size of a material has also been found to increase the surface roughness, as shown in Fig. 4 (Ref 5). Under normal operating conditions, ECM produces stress-free, burr-free surfaces with no burning or thermal damage to workpiece surfaces or other detrimental effects on materials. ECM-produced surfaces frequently have better wear, friction, and corrosion-resistant characteristics than surfaces obtained with mechanical finishing. ECM also eliminates the need for subsequent operations such as polishing (Ref 4).

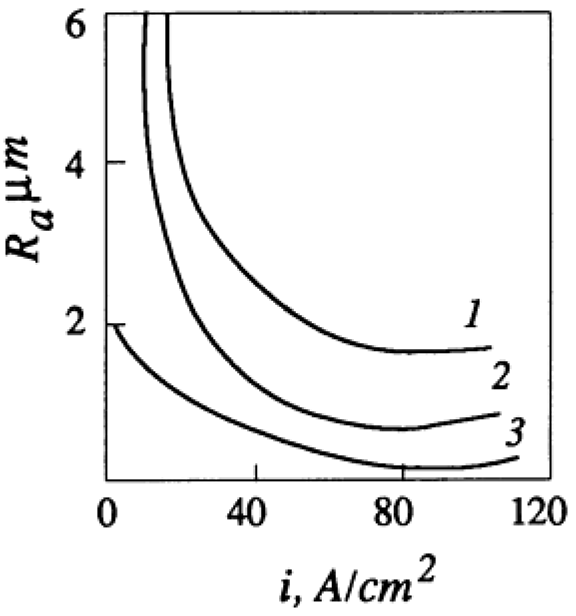

Fig. 3 The effect of electrochemical machining current density (*i*) on surface roughness (R_a) of three steels. 1, steel with Mo; 2, steel with Mo + W; 3, steel with Ni + Nb. Electrolyte: 150 g/L NaCl + H_2O

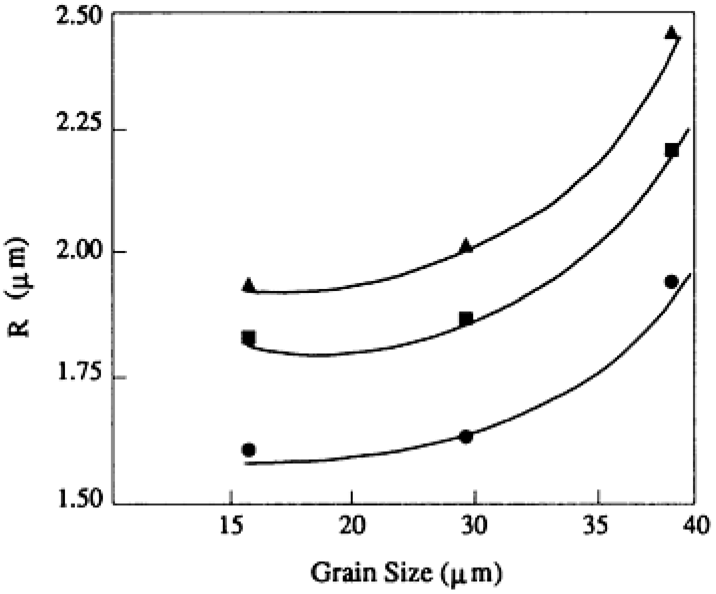

Fig. 4 Surface roughness (R_a) as a function of grain size (at 15 volts). Feed rate: (•), 2.54 mm/min; (■), 1.72 mm/min; (▲), 0.86 mm/min

However, the accuracy of the machining obtained by ECM is not very high, as ECM may not be able to produce clear cuts or sharp corners. The tolerances achieved by ECM are in the range of 0.02 to 0.2 mm. The positioning accuracy of ECM tools now reaches ±0.01 mm. ECM also requires special corrosion protection systems and waste (sludge) disposal techniques.

Electrochemical deburring (ECD) is used exclusively to deburr or radius workpieces (Fig. 5). ECD equipment is constructed with either single or multiple workstations. Some machines are designed with multiple workstations served from a single power supply. ECD equipment is extremely simple, with the electrolyte pump being the only moving part. The principle of ECD is to use a stationary tool, thus eliminating the need for feed mechanisms and control.

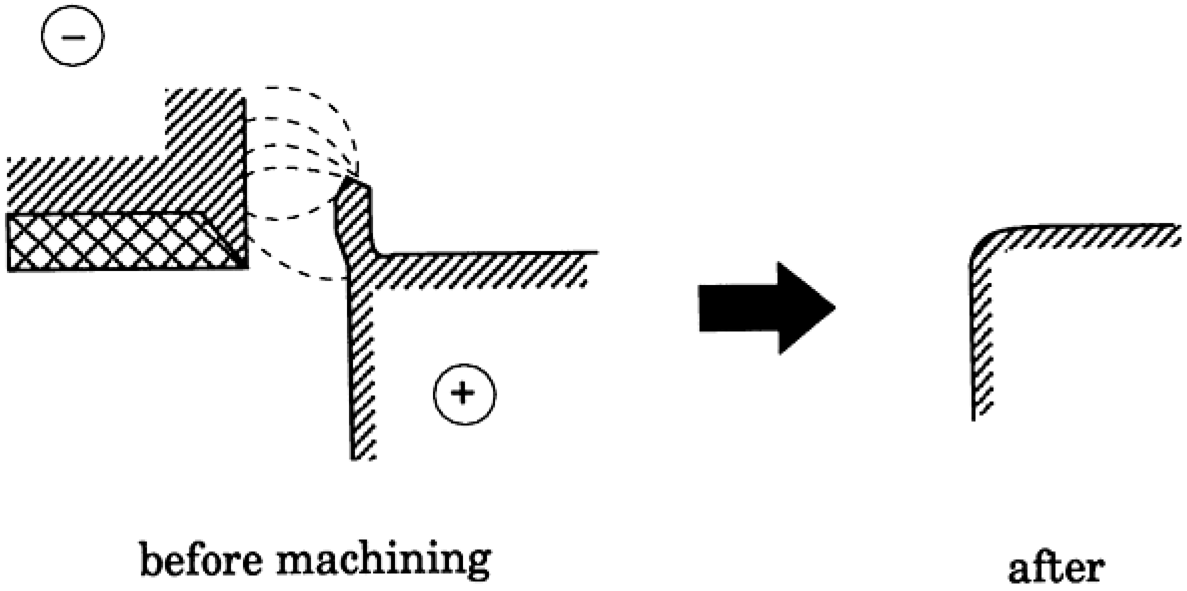

Fig. 5 Schematic of deburring and radiusing process

ECD systems have current ratings from 100 to 2000 A at a dc voltage of 7 to 25 V. Typical outputs are 100 to 1000 A and 0 to 30 V. The high power requirements result in heating of the equipment and thus it requires cooling. The units are normally air- or water-cooled. Depending on the thickness of the material and the current density, there are various methods of supplying the electric current. With thick materials, the current can be supplied directly to the workpiece by means of sliding contacts or pressure contacts. With thin material, the current can be conducted through a conductor beneath it, such as platinum. If higher current densities are required, a system can be used in which the workpiece floats with respect to the electrodes and the current is supplied through the electrolyte.

In an ECD system, the electrolyte pressure ranges from 0.15 to 0.5 MPa (15 to 70 psi), at a flow rate of 3 to 15 L/min (0.8 to 4 gal/min) for each 100 A. The electrolyte used is usually a neutral pH salt solution, such as sodium nitrate or sodium chloride.

The gap between the tool and the burr ranges from 0.2 to 1.2 mm (0.008 to 0.05 in.). ECD systems can handle workpieces manually as well as on completely automated transfer lines. ECD tools are usually made from brass, copper, or stainless steel and are insulated on all surfaces except the surface adjacent to the burr. The insulations range from acrylic and polyvinyl chloride to Delrin and epoxy coatings.

Applications and Limitations. Examples of tooling for ECD are shown in Fig. 6 and 7. ECD is used in industries ranging from consumer appliances and automobiles to biomedical and aerospace products. ECD is used to deburr a variety of parts including gears, gear plates, and fuel injector nozzles.

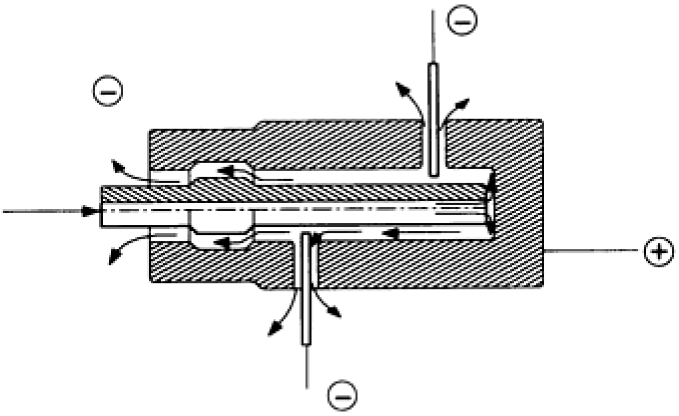

Fig. 6 Schematic of electrochemical machining: smoothing, deburring, and radiusing of piston pin. Machining parameters: *U* (in Fig. 2) = 17 V; electrolyte pressure, 0.3 MPa; electrolyte, 15% NaCl; time of machining, 75 s; maximum current per piece, 180 A

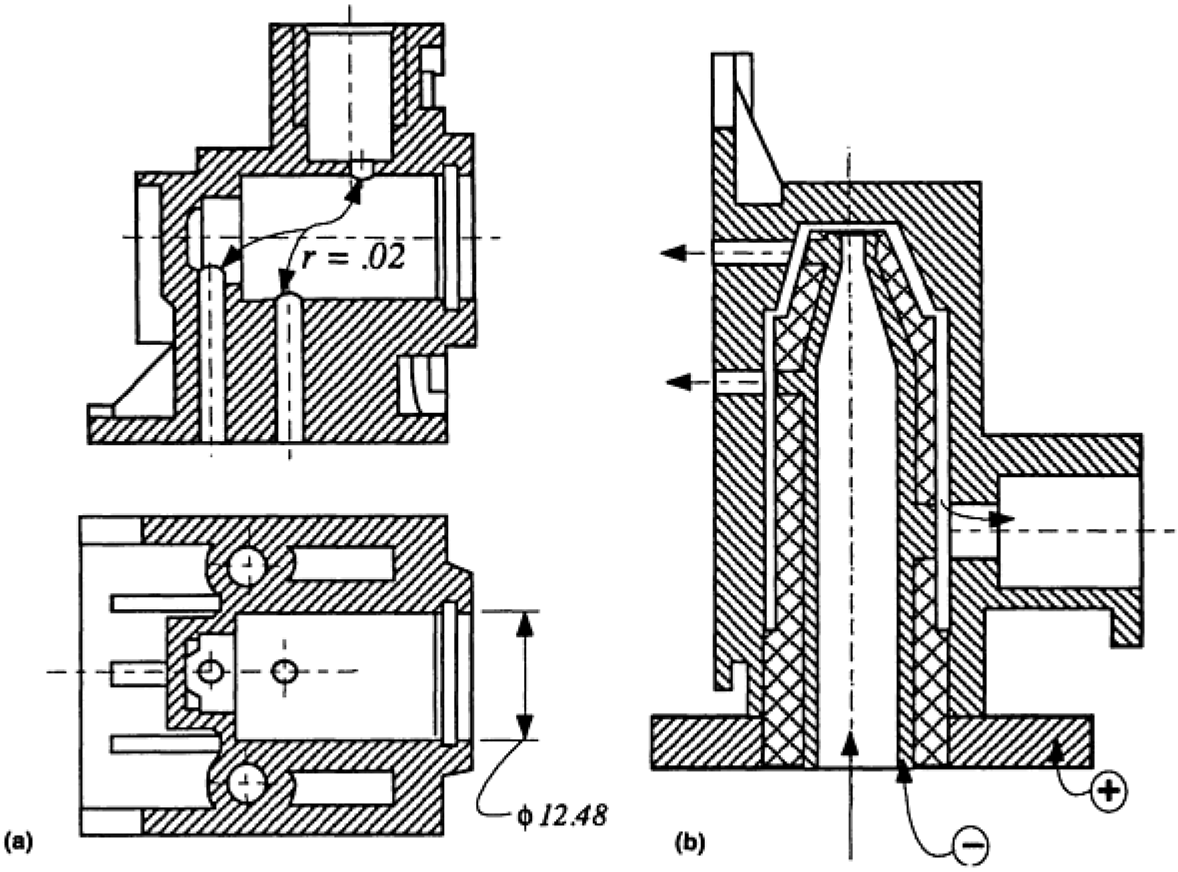

Fig. 7 Tooling for electrochemical machining deburring. (a) Valve casing. (b) A fragmentary schematic of the production jig. Machining parameters: 15% water solution of $NaNO_3$; *U* (in Fig. 2) = 15 V; machining time, 8 s; electrolyte pressure, 1 MPa; maximum current per piece, 20 A

Limitations. One of the major limitations of the ECM and ECD processes is their inability to machine electrically nonconductive materials. Usually, sharp corners or clear cuts cannot be obtained by ECM. The complexity of the shape to be machined, the workpiece material, and the electrolyte put a limit on the dimensional accuracy and the surface finish that can be achieved by ECM. Etching of the constituents, grain-boundary attack, and pitting due to electrochemical action may have drastic effects on the mechanical properties of the material, particularly the fatigue strength.

Recent Advances in ECM as a Surface Finishing Process. As mentioned earlier, different anodic reactions take place at high current densities during ECM, depending on the metal-electrolyte combination and operating conditions. Electropolishing is another finishing process (discussed in the next section) that involves anodic reactions. The rate of these reactions depends to a great extent on the ability of the system to remove the reaction products as soon as they are formed. All of these factors influence the machining performance (i.e., the dissolution rate, shape control, and the surface finish of the workpiece). An understanding of the kinetics and stoichiometry of anodic reactions and their dependence on mass transport conditions is therefore essential in order to optimize relevant ECM and electropolishing parameters. The high rate of anodic dissolution of metals that is applicable to ECM and electropolishing has been reviewed recently (Ref 6). Electrochemical and hydrodynamic parameters influence the nature of the anodic reactions and their rates. These in turn influence the performance of metal shaping and finishing operations. Surface finish during high-rate anodic dissolution depends on the mass transport conditions at the anode. At potentials below the limiting current range, rough surfaces are obtained as a result of crystallographic etching and grain boundary attack. The limiting current, which appears at higher potentials, is mass transport controlled. This corresponds to the formation of a salt layer at the anode that suppresses the influence of the metallurgical phenomena on the dissolution process (Ref 6). Dissolution at or above the limiting current therefore yields smooth surfaces (0.12 to 0.2 μm R_a). Pulsed dissolution is considered most suitable for electrochemical micromachining of thin films and foils when low dissolution rates are desirable for better control over the machining process (Ref 7).

In another recent development, "maskless" and "throughmask" electrochemical micromachining (EMM) techniques have been developed for the processing of thin films and foils of materials that are difficult to machine by other methods (Ref 7). In these processes at higher potentials, a layer of salt forms at the anode. The presence of this salt film also influences the current dissolution, hence the uniformity of metal dissolution and the shape profiles during throughmask EMM.

A new finishing method has been developed using an electrochemical finishing machine (Ref 8). This method enables the operator to set the timing of a switchover to pulses having a high current density, to provide an optimum working condition and thereby improve working efficiency. This method permits the removal of an oxide layer generated on a three-dimensional surface of an object, so that a highly accurate surface can be obtained in a short period of time.

Recently, ECM with an ac source was used for machining of some special alloys such as tungsten carbide. The pulse train used for the ac was asymmetric. This type of ECM is also known as alternate polarity ECM. Alternate polarity ECM has been found to be good for obtaining a uniform dissolution of tungsten carbide and for suppressing the dissolution of the tool electrode (Ref 9). A smooth surface (3.5 to 8 μm R_{max}) without any heat-affected layer or cracks was obtained by this method, where R_{max} is the maximum peak-to-valley roughness height.

The quality of surfaces produced by ECM has been investigated recently, based on how changing process variables affects the resulting plasticity index, which is an indication of surface capacity to bear plastic deformation during service of electrochemically machined surfaces (Ref 10).

Another variation of the ECM process is the use of pulsed current during ECM. This is known as pulse electrochemical machining (PECM). The electrochemical principles of PECM are identical to those of ECM with continuous current. In the PECM process, discrete machining pulses are applied, and the system is allowed to relax between these pulses. It is this alternating pulse on-time and off-time that fundamentally distinguishes PECM from continuous current ECM. Recent studies have shown that PECM results in higher anodic dissolution localization, smaller gap sizes, higher peak current densities and better surface finish (0.16 to 0.63 μm R_a) (Ref 11). Experimental results with pulse EMM indicate that good surface finish can be obtained even at low average current densities. In PECM, shorter pulse on-times (0.2 to 4 ms) are preferable for achieving better surface finishes.

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Electropolishing

Electropolishing is used for polishing of metal parts. The principle is just the reverse of that of electroplating. The workpiece is made the anode in an electrolyte, with a cathode added to complete the electrical circuit. In the resulting deplating, material is removed most rapidly from raised, rough spots, producing a very smooth, polished surface (Ref 12). During the process, products of anodic metal dissolution react with the electrolyte to form a film at the metal surface. Two types of films have been observed: a viscous liquid and an anodically discharged gas, usually oxygen (Ref 13). Neither film adheres closely to the microroughness of a metal surface, and both types conform to the macrocontour. Therefore, the film is essentially thinner over microprojections and thicker at microdepressions. Resistance to electric current flow over the microprojections is less, so more current can flow over the microprojections than in the microdepressions. The result is a more rapid dissolution process at the projections, causing microleveling of the surface. This gives a metal surface with so little scattering of incident light that a mirror-like glossy appearance is obtained.

This process is primarily used for obtaining mirror-like surfaces from highly smooth initial surfaces. A final finish of less than 0.05 μm can be obtained if the initial surface roughness (root mean square) does not exceed 0.18 to 0.20 μm. Electropolishing was primarily developed for polishing metallurgical specimens and for polishing of irregular shapes that were difficult to buff. Now electropolishing is used for polishing stainless steel sheets and parts.

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Electrodischarge Machining

Electrodischarge machining (EDM) is a thermoelectric process that removes material from the workpiece by a series of discrete sparks between a work and tool electrode immersed in a liquid dielectric medium. The method of removal of material from the workpiece is by melting and vaporizing minute amounts of electrode material, which are then ejected and flushed away by the dielectric (Ref 1, 14).

The two major types of EDM are die sinking EDM and wire EDM (WEDM). Die sinking EDM is traditionally performed vertically, but it may also be conducted horizontally. WEDM is a special form in which the electrode is a continuously moving conductive wire. In the WEDM process, spark discharges are generated between a small wire electrode (usually smaller than 0.5 mm diameter) and a workpiece with deionized water as the dielectric medium. The electroerosion process is used to produce complex two- and three-dimensional shapes, even in harder materials. According to the most agreed-on process mechanism, when a voltage is applied through a dielectric medium across the gap between the tool and the workpiece, an electric field builds along the path of least resistance. This causes a breakdown of the dielectric and initiates the flow of current. In the second stage, electrons and ions migrate toward the anode and cathode at high current density, forming a column of plasma and initiating the melting of the workpiece. When the application of voltage is stopped, the column collapses, a portion of the molten metal is ejected from the workpiece, and a crater is formed. The debris remaining on the workpiece is flushed away by the dielectric.

In EDM the erosion rate and tool wear, and the resulting surface integrity and geometry, depend on the current, voltage, on-time, off-time, polarity, pulse shape, work and tool material properties, dielectric flushing conditions, dielectric properties, electrode geometry, and machine characteristics. A general overview of the EDM process is given in Volume 16 of the *ASM Handbook.*

EDM Equipment

All EDM systems include the machine (including the frame, ram, worktable, tool and workpiece holders, and clamping devices), pulse-power supply, tool electrode, dielectric system, and servo control system. Figure 8 is a schematic of an integrated die sinking EDM system. The EDM power system transforms the utility ac power into pulsed dc power with 30 to 300 V and from several milliamperes to 100 A of peak current. Various types of power supply systems exist today. Among those that are suitable for EDM are the relaxation power system, which consists of a charge loop and a discharge loop, and the independent power system, which consists of a dc power source, pulse controller, and a power controller. The pulse controller in this type of power supply sets a time basis and controls the "on" and "off" states of the power controller. The power controller delivers the pulse to the gap with the required power. Some EDM machines are equipped with power supplies that combine the relaxation and independent power supplies in order to improve surface roughness.

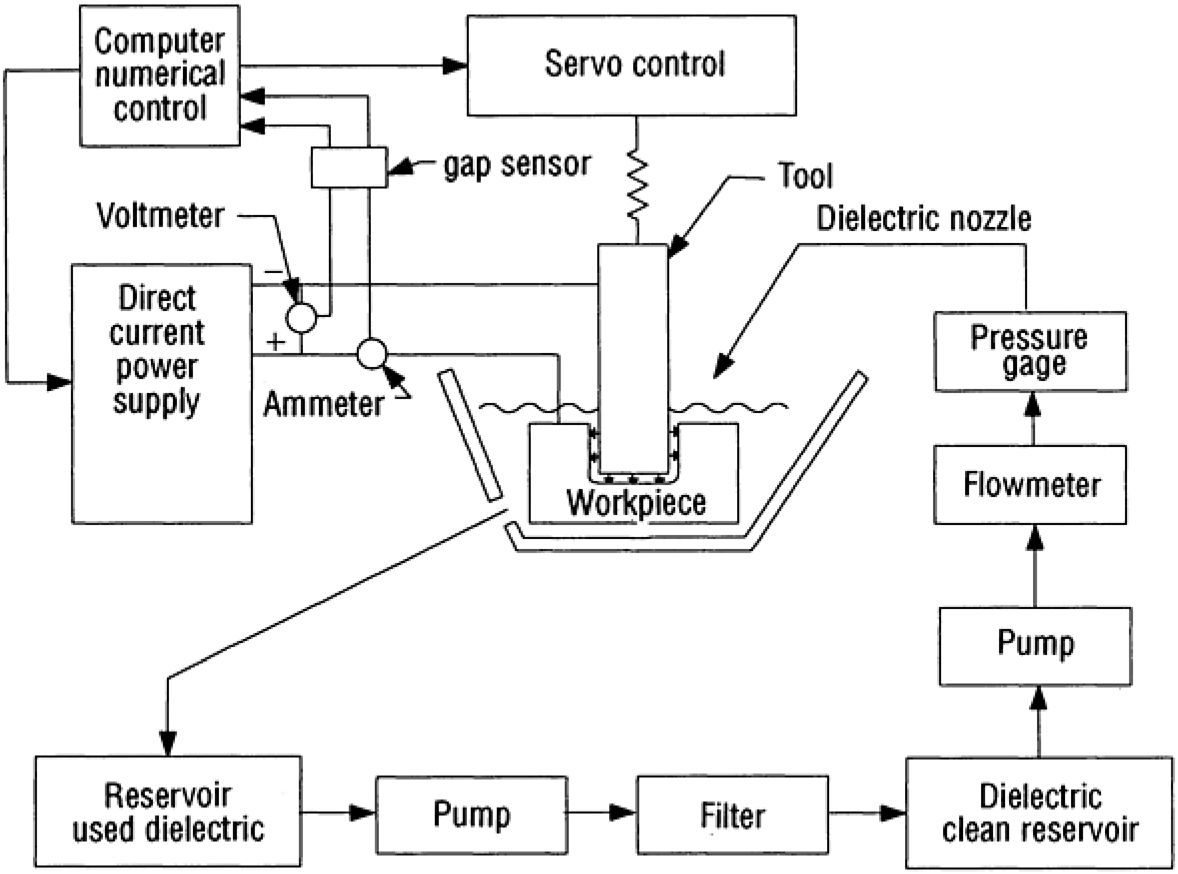

Fig. 8 Schematic of die-sinking electrodischarge machining system

Five-axis computer numerical control WEDM is now routinely employed in complex three-dimensional contour machining jobs (Ref 1). Another application of EDM is electrical discharge grinding, which is used for precision machining of electrically conductive workpieces. Electrical discharge grinding uses a rotating electrically conductive grinding wheel as the "electrode" or cutting tool. (See Volume 16 of the *ASM Handbook.*)

Tool Material. The basic requirements for a tool material are high electrical conductivity, high melting point, and high thermal conductivity. The tool materials should be easy to machine and inexpensive. Some of the most frequently used tool materials include graphite and bronze for machining steels and copper-tungsten for machining carbides. Bronze and copper tungsten are often used for producing smooth surfaces and for high-precision EDM.

Dielectric Fluid. The main functions of the dielectric fluid are to insulate the gap between the tool and the workpiece before high energy is accumulated, to concentrate the discharge energy to a tiny area, to recover the gap condition after the discharge, and to flush away the discharge products. The two most commonly used dielectric fluids are petroleum-based hydrocarbon mineral oils and deionized water. Dielectric flushing is very important in EDM operations. The commonly used flushing methods are immersion, spray, or jet.

Controls. A servo control is used to keep the interelectrode gap within a small range of variations around a desired setting during machining. Typical values of the gap that are used during EDM are 0.010 to 0.050 mm, though gaps as small as a few microns or as large as several hundred microns can be used, depending on the voltage, current, dielectric media, and surface finish requirements. In order to maintain a constant gap size, the tool feed rate should equal the material removal rate in the feed direction. However, because the removal rate is often not constant, a servo control is used that takes the gap signals (the average voltage) as the measure of the gap size and compares them with the servo reference voltage. Action as to whether to retract the tool or to move it faster toward the workpiece is taken, depending on this comparison.

EDM Process Characteristics

In the case of EDM, the metal removal rate and the surface roughness depend on the peak current, pulse on-time, peak voltage, frequency of pulses, and the flow rate of the dielectric. The surface roughness obtained by EDM can range from 2.5 to 30 μm R_a for rough machining. The metal removal rate achieved by EDM can range from 50 to 200 cm^3/hr for rough cuts. As the removal rates increase, the surface finish deteriorates.

Electrodischarge polishing (EDP) uses exactly the same principle as that of EDM; however, the objective is to produce smooth, lustrous surfaces. Hence EDP is carried out with very low discharge energy. EDP can be used to produce smooth surfaces (0.2 μm R_a) that exhibit extremely thin, homogeneous, crack-free surface layers of uniform width (Ref 15). In this process, the high metal removal rate associated with deep craters is undesirable. The aim is to achieve melting of roughness peaks with ensuing resolidification, while avoiding molten metal spinoff. It has been found that EDP with a positive workpiece electrode produces flat craters with a smooth surface and a crater rim raised only slightly above the surrounding workpiece surface (Ref 15). EDP makes use of a gradual reduction of the discharge energy of the individual pulses of less than 3 μJ and a simultaneous increase of the frequency to around 100 kHz. It has been found that the surface roughness rises sharply with increasing discharge current and is found to decrease with increasing polishing depth. The higher smoothing of the surface achieved as a result of the increased polishing depth increases the processing time drastically, however. Because gap widths in EDP are extremely small and difficult to control, flushing is another significant factor influencing the variables for physical conditions in the working gap. With continuous flushing, the workpiece roughness decreases with a decreasing flow rate. In EDP, planetary motion is necessary to avoid undulating workpiece surfaces, because this technique entails relative movement of the electrodes, producing a surface that is microscopically as well as macroscopically smooth.

Applications, Process Capabilities, and Limitations. EDM is capable of machining difficult-to-cut materials such as hardened steels, carbides, high-strength alloys, and even ultrahard conductive materials such as polycrystalline diamond and some ceramics. The process is particularly well suited to sinking cavities and drilling irregularly shaped holes. The only limit in machinability is the electrical conductivity of the workpiece material. The other problems in EDM include tool wear and the irregularity of the tool wear, and limitations of EDM to machine very sharp corners because of the existence of the gap between the tool and the workpiece. A recently developed EDM process called micro-EDM expands the capabilities of EDM with respect to fine part fabrication. This process can achieve a surface roughness of 0.1 μm R_{max} and a high accuracy (roundness of 0.1 μm, and the straightness of some fine parts as small as 0.5 μm).

Recent Advances in EDM as a Surface Finishing Process. As described earlier, EDM and WEDM are performed by passing a dc pulse anywhere between several tens to several hundreds of volts between the tool (the negative wire in case of WEDM) and the positive workpiece. In the case of WEDM, water is generally used as the machining fluid. During WEDM, there is some electrolysis during machining. Consequently, besides being affected by the heat at the time of electric discharge, the electrolysis results in a drop in the machined surface quality. In a recent development, engineers at Mitsubishi Electric have developed a WEDM with an antielectrolysis (AE) power source (Ref 16). Experiments using AE power supply show that the corrosion of the workpiece surface is totally preventable. One of the problems of EDM is the formation of microcracks, which must be avoided, and the use of AE power supply with uniform pulses has also been found to reduce the number of microcracks in EDM surfaces (Ref 16).

In an attempt to achieve extremely fine surface finishes by EDM, different kinds of powders such as silicon, aluminum, and graphite have been suspended in the working fluid (Ref 17). In the case of conventional EDM, during finishing operations, the gap distance between the electrode and the work is very small, resulting in frequent abnormal discharges. Use of a suspended powder in the working fluid results in an increase in the working gap distance. The effective working gap distance depends on the concentration of the powder and the type of the powder (Ref 17, 18). In fact, experiments show that the working gap distance increases ten times compared to that of the conventional working fluid. The powder suspension is also found to disperse the electrical discharge very well. A good dispersion of the electrical discharge is extremely important for a fine surface finish. The work surface machined using a fluid with suspended powder also has strong corrosion resistance. The surface finish achieved by the use of a fluid with suspended powder was in the range of 0.6 to 1.8 μm $R_{\max}$.

Because EDM is becoming a key process for die manufacturing, it has also become necessary to realize full automation of the EDM process. Engineers at the Toyota Technological Institute have developed a technique to eliminate manual polishing after EDM. During die manufacturing, cusps are left on the workpiece after milling, and in this research, the cusps were removed by EDM under high-wear conditions with planetary motion of the electrode (Ref 19). In order to realize a mirror-like surface on the workpiece, electrically resistive material such as silicon was used as an electrode. This improved the surface finish remarkably; surface roughnesses in the range of 2 to 3 μm were achieved. However, because silicon is hard and brittle, forming an electrode in a complicated shape was extremely difficult. Hence silicon powder was suspended in the working fluid and EDM was carried out. EDM carried out by suspended powders also helps improve the surface finish rapidly.

All of the above methods have been demonstrated in the laboratory to result in mirror-like finishes. However, in most of these cases, large areas (i.e., greater than 300 mm^2) cannot be successfully machined by EDM for a good surface finish. A new method of achieving mirror-like finishes with EDM has recently been attempted (Ref 20). In this method, narrow spark duration and small discharge current (i.e., with the smallest of discharge energies) have been used. In order to reduce the dependence of surface roughness on the working area, a partially induced electric field is used during machining. The concept is to reduce the space in which the electric energy is stored before breakdown.

It has also been demonstrated that surface roughness achieved after EDM can be improved by the use of a radio-frequency (RF) controller (Ref 21). In the presence of bad flushing conditions, the occurrence of stable arcs results in thermal damage to the workpiece surface. Hence it is important to detect the occurrence of stable arcs. Research shows that normal spark discharges generate intense high-frequency (HF) noise signals that are a component of the discharge voltages and are emitted as RF signals. The intensity of the HF or RF signal drops as the gap conditions change from normal sparking to harmful arcing (Ref 21). The RF controller has been modified to include an isoenergetic function, and the sensing gain of the RF detecting circuit has been improved. The EDM operations carried out with the RF controller have been shown to improve the surface finish by 40%.

As mentioned earlier, a uniform surface finish on large areas is difficult to achieve by EDM. However, an electrical discharge texturing system has been developed to obtain improved machining performance and precise control of the surface roughness (Ref 22). The electrical discharge texturing system incorporates an RF monitoring and controlling unit, a unique gap voltage measuring circuitry, and MOSFET (metal oxide semiconductor field-effect transistors) for power switching.

In another attempt to achieve good surface finish by EDM, surface modification by the use of composite electrodes has been performed (Ref 23). In this new technique, the electrode used for EDM is made from fine powder or green compact and shows higher wear than a conventional solid electrode. The machined surface shows the presence of components of the electrode, and there are fewer microcracks in the machined surface layer.

EDM has recently become an important method for machining advanced ceramic materials for many applications, due to the fine finishes that it provides. It has been found that the grain size of the dispersed phase plays the dominant role in affecting the surface roughness (Ref 24).

New developments in the field of materials science have led to new engineering methods for metallic materials, composite materials, and high-tech ceramics. EDM (both rough and finishing) of ceramics turns out to be a very good alternative to traditional machining techniques such as grinding, milling, turning, and sawing. Because EDM is a thermal machining process, it provides a means of machining ceramic materials, irrespective of their hardness and strength. Recorded machining speeds when EDM is applied on those ceramics are much better than those obtained with traditional machining techniques. This, combined with the extremely good surface finishes obtained makes EDM a viable alternative to traditional finishing techniques for ceramic materials (Ref 25).

However, because ceramic materials have higher melting points compared to metals, in general the metal removal rate of ceramics is lower. The removal mechanism during EDM of metals is based on melting and vaporization phenomena. In the case of ceramics, metal removal is due to two types of mechanisms, depending on melting point. The lower-melting-point ceramics exhibit metal removal due to failure by thermal shock (spalling). Spalling occurs when high internal stresses created by steep temperature gradients cause the material to flake. Ceramics that are machined by spalling exhibit very smooth surfaces (1.11 to 1.67 μm). It has been observed that EDM of ceramics results in higher machining speeds compared to the traditional machining techniques for the same surface roughnesses (Ref 25).

In other recent research into the machining of new materials, polycrystalline diamond (PCD) has been machined by WEDM (Ref 26). PCD is challenging to shape due to its hardness, high strength, and high toughness. Diamond grinding is one of the most commonly used techniques for shaping of PCD. However, diamond grinding results in rapid tool wear during machining of PCD, and WEDM has been found to be a much more cost-effective method. The surface quality of workpieces machined by WEDM is very good, and there is not much difference in the surface roughness with a change in the diamond grain size.

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Mass Finishing

Revised by Edward H. Tulinski, Harper Surface Finishing Systems, Inc.

Introduction

MASS FINISHING normally involves loading components to be finished into a container together with some abrasive media, water, and compound. Action is applied to the container to cause the media to rub against the surfaces, edges, and corners of the components, or for components to rub against each other, or both. This action may deburr, generate edge and corner radii, clean the parts by removing rust and scale, and modify the surface stress. The basic mass finishing processes include:

- Barrel finishing
- Vibratory finishing
- Centrifugal disc finishing
- Centrifugal barrel finishing
- Spindle finishing
- Drag finishing

Mass finishing is a simple and low-cost means of deburring and surface conditioning components. Consistent results from part to part and batch to batch are generally ensured. All metals and many nonmetals in a variety of sizes and shapes can be handled. Processes range from heavy radiusing and grinding operations to very fine finishing.

A basic advantage of mass finishing is that the action is effective on all the surface edges and corners of the part. Normally, preferential treatment to one area is impossible. Action is greater on corners than other similarly exposed surfaces. Action in holes and recesses is less than on exposed areas.

The mass finishing processes are used to:

- Clean, descale, and degrease
- Deburr
- Radius edges and corners
- Change surface condition
- Remove surface roughness
- Brighten
- Inhibit corrosion
- Dry
- Stress relieve
- Impart compressive stress

Barrel Finishing

The rotary barrel, or tumbling barrel, utilizes the sliding movement of an upper layer of workload in the tumbling barrel, as shown in Fig. 1. The barrel is normally loaded about 60% full with a mixture of parts, media, compound, and water. As the barrel rotates, the load moves upward to a turnover point; then the force of gravity overcomes the tendency of the mass to stick together, and the top layer slides toward the lower area of the barrel.

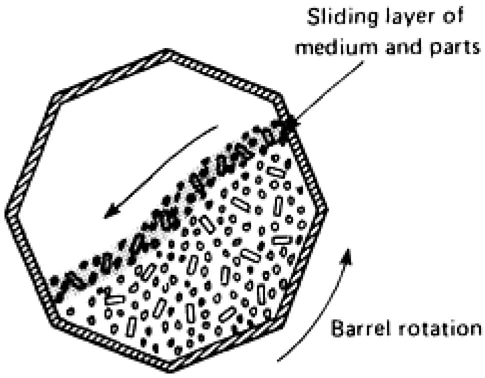


Fig. 1 Action of media and parts within a rotating barrel

Although abrading action may occur as the work load rises, about 90% of the rubbing action occurs during the slide. In the case of a horizontal barrel that is just over half full, the most effective action occurs to produce the longest slide. As may be judged from Fig. 1, the faster the rotation of the barrel, the steeper the angle of the slide. With all but the shallowest of angles of slide, there is invariably more tendency for tumbling of the load, as well as sliding. The faster the rotation of the barrel, the faster the action will take place. However, the faster the action, the poorer the surface and edge condition will be, and the greater the likelihood of parts being damaged.

Typical equipment for barrel tumbling is shown in Fig. 2 and includes:

- Open-ended, tilted-type barrel (concrete mixer)
- An adaptation known as the bottle-neck barrel
- Horizontal barrel
- Submerged barrel
- Fixtured barrel

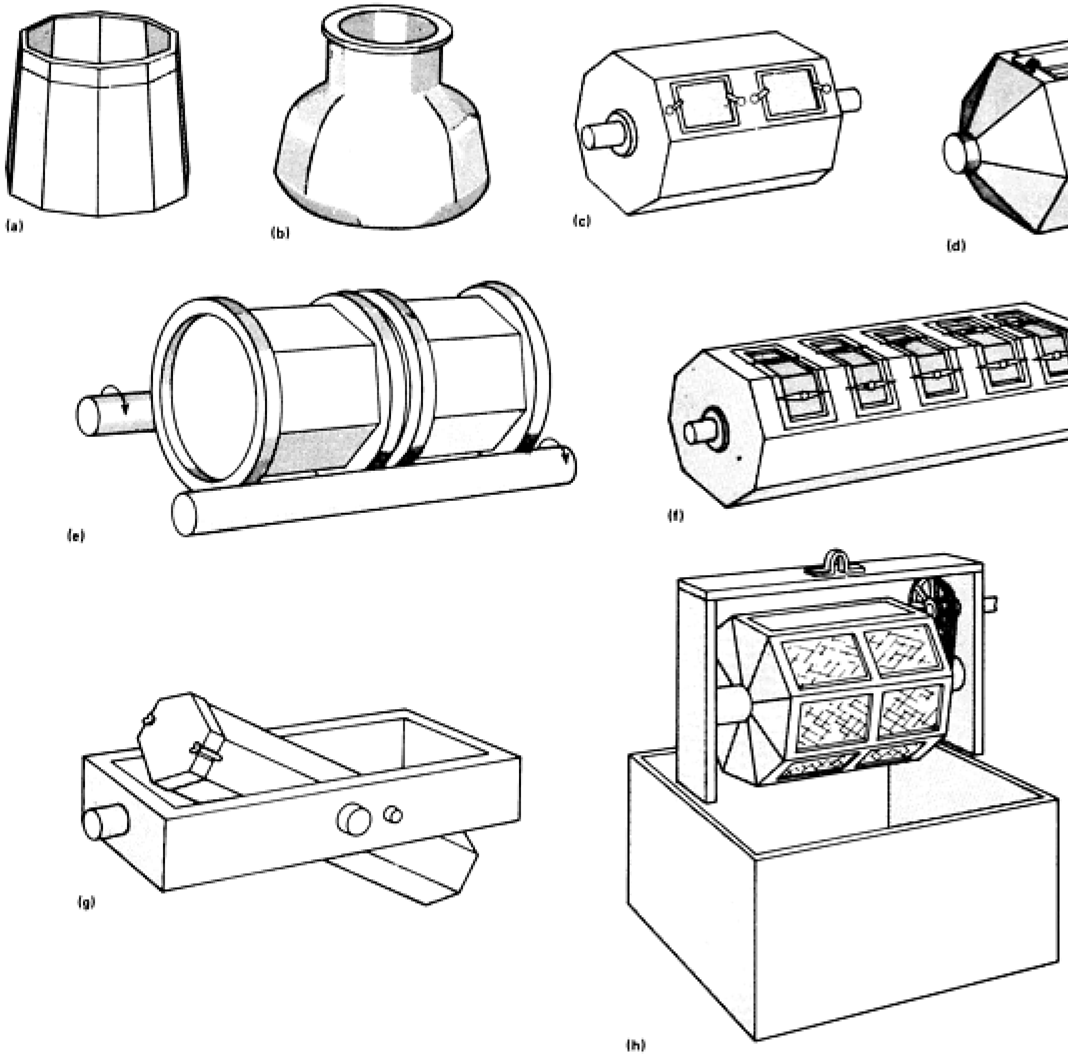


Fig. 2 Barrels available in a variety of sizes. (a) Standard open-end, tilting. (b) Bottlenecked. (c) Horizontal octagonal. (d) Triple-action, polygonal. (e) Multiple drums. (f) Multicompartment. (g) End loading. (h) Submerged

The open-ended, tilting barrel is used for light finishing and also for drying. The bottle-neck shape provides essentially the same action, but more effectively, because parts and media remain better mixed. The horizontal barrel, usually of octagonal cross section, is the standard or most used tumbling barrel, capable of achieving a variety of results and maintaining real consistency. Rotational speeds of these barrels range from as low as 4 rpm for large barrels to 60 rpm for small barrels; surface speeds range from about 6 to 60 m/min (20 to 200 sfm); the higher speeds are used for cutting, the slower speeds for burnishing and fine finishing.

Ratio of media to parts ranges from about 3-to-1 to 15-to-1 by volume. Rough work can be loaded only with parts, so that parts self-tumble against each other. Some of the factors to be considered in determining the media to parts ratio are:

- Size and complexity of the workpiece
- Possibility of media lodging in the parts
- Possibility of the parts nesting
- Required quality of final finish

Automation of barrel tumbling equipment is possible. The barrel can rotate in a clockwise direction to deburr and finish the parts. At the end of the process, the barrel rotation is reversed and parts feed out through a scroll, then through a screener into a material handling unit.

The capital cost of barrel tumbling equipment is low and generally maintenance costs are also low. Because barrel tumbling is a very well-established process, the basic conditions are well understood and guidance on best process techniques is readily available. Barrel tumbling is, however, a slow process, almost invariably involving several hours and on occasion several days. The process is space consuming with a high level of work in progress. More modern mass finishing processes offer greater versatility and convenience, with better use of labor and consistency of quality in production. For these reasons, and because higher operator skills are needed, barrel tumbling has been replaced in most modern production facilities.

Vibratory Finishing

A vibratory finishing machine is an open-topped tub or bowl mounted on springs, usually lined with polyurethane. Parts and media are loaded in a fashion similar to that of a tumbling barrel. With a vibratory machine, the container can be almost completely filled. Vibratory action is created either by a vibratory motor attached to the bottom of the container, by a shaft or shafts with eccentric loads driven by a standard motor, or by a system of electromagnets operating at 50 or 60 Hz. The action of media against components takes place throughout the load, so that process cycles are substantially shorter than conventional tumbling in barrels. Components can be inspected and checked during the process cycle. This process is faster, more convenient, and more versatile than tumbling barrels. The vibratory machine is able to handle larger parts and is more readily automated. The process achieves more abrasive action in the recessed areas of components, is easier to operate, and is cleaner.

Two important variables for operation of vibratory equipment are frequency and amplitude of vibration. Frequency may range from 900 to 3000 cycles/min. Amplitude can range from 2 to 10 mm ($\frac{1}{16}$ to $\frac{3}{8}$ in.). Most equipment operates in the range of 1200 to 1800 cycles/min and 3 to 6 mm ($\frac{1}{8}$ to $\frac{1}{4}$ in.) amplitude.

The tub vibrator consists of an open container where the cross section is either U-shaped, a round inverted keyhole shape, or a modification of these. Figure 3 shows three types of tub vibrators. The modifications from the U-shaped cross section are constructed to develop more uniform flow of the mass, because the U-shaped cross section has a tendency for some back flow against one of the walls. The means of creating the vibratory action is with a single shaft mounted directly underneath the tub. At each end of the shaft, or along its length, are eccentric weights and a facility to add or reduce some of the weights. The greater the weight, the more amplitude. The faster the action, the rougher the surface finish and the greater the media wear. The shaft may be driven from a motor coupled to the shaft through a flexible coupling or by belts. Variable speed of rotation of the shaft is fairly easily obtained and gives variable frequency of vibration. The higher the frequency, the faster the cut, but the rougher the surface. Modifications of the drive system include:

- Use of double shaft, as shown in both Fig. 3(b) and 3(c), to maintain greater uniformity of the parts and media mix and offer somewhat faster action
- Use of eccentric shaft, rather than eccentric weights at the ends of a shaft, to give greater consistency of action throughout the load
- Location of eccentric weights or shaft on one side, at top of tub wall, or at both sides

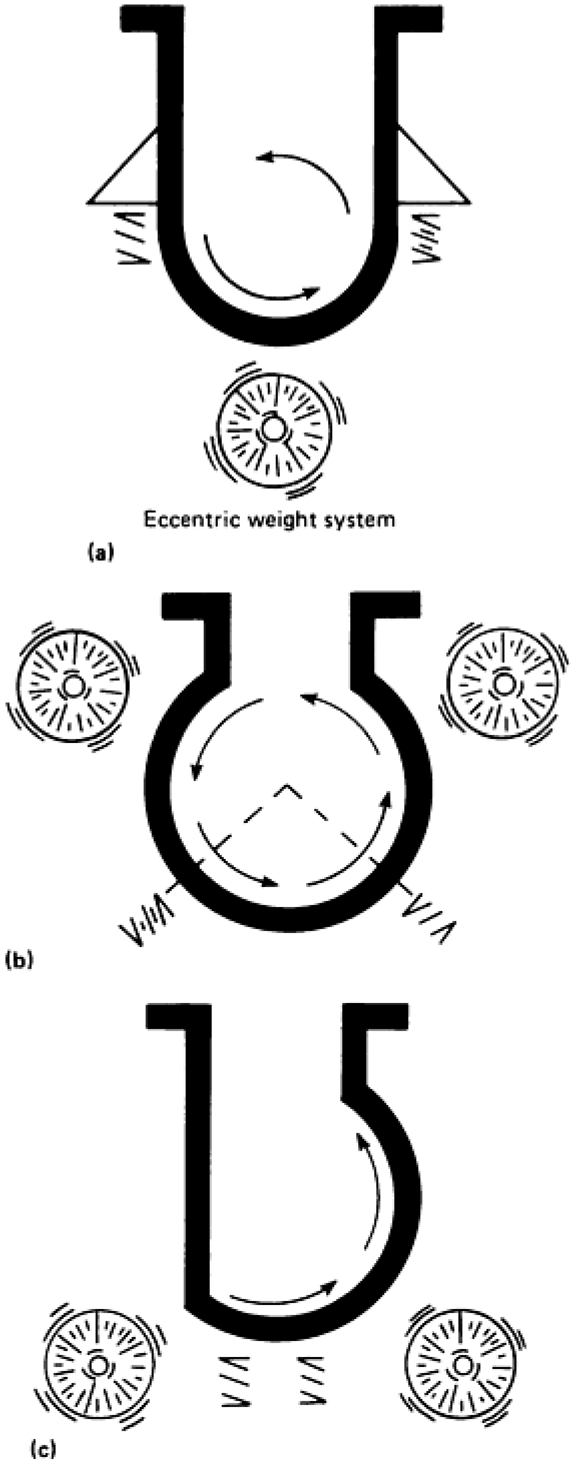


Fig. 3 Tub vibrators

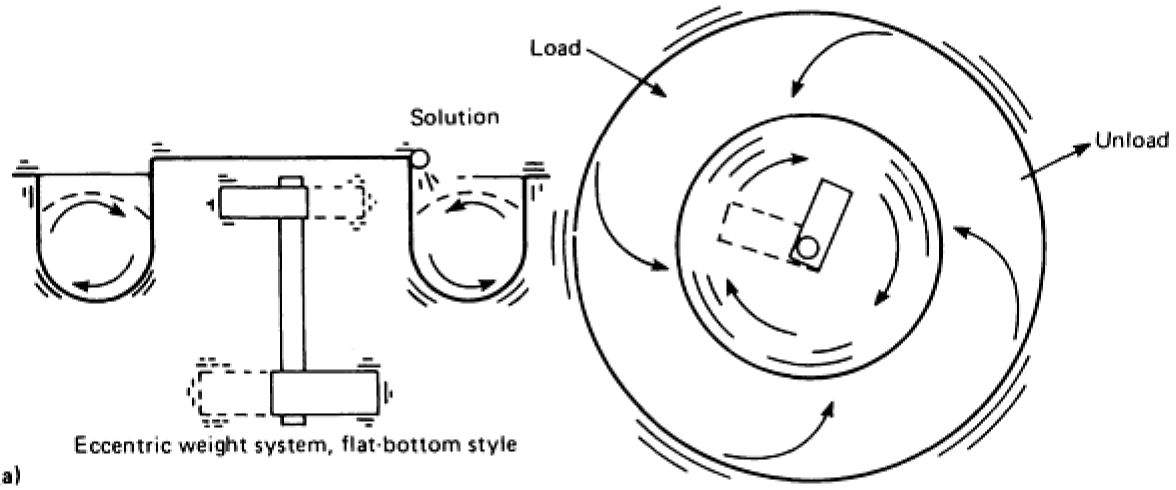
Tub vibratory equipment can be sized to suit the largest components. Units are in production to handle parts as long as 12 m (40 ft), and other equipment has been built to handle parts of cross section as much as 2 m (6 ft) by 2 m (6 ft).

Separation of parts and media is sometimes accomplished by dumping the total contents of the vibratory tub into a material handling system. Most tub vibrators have unload doors at one end, which may be opened manually or automatically and through which the total load is fed. Some units have a system for emptying by inverting the complete tub.

Tub vibratory equipment is readily automated for continuous production. A long tub vibrator may have parts and media fed in at one end of the container. These proceed along the tub until finished parts and media exit at the other end. The discharge end is lower than the parts' entry end, causing the media and parts to move to the discharge end. Parts are then screened out from the media. The media is returned with a simple belt conveyor directly or through a storage unit. Such systems are suitable for processes where satisfactory results are achieved with process cycles of up to 30 min.

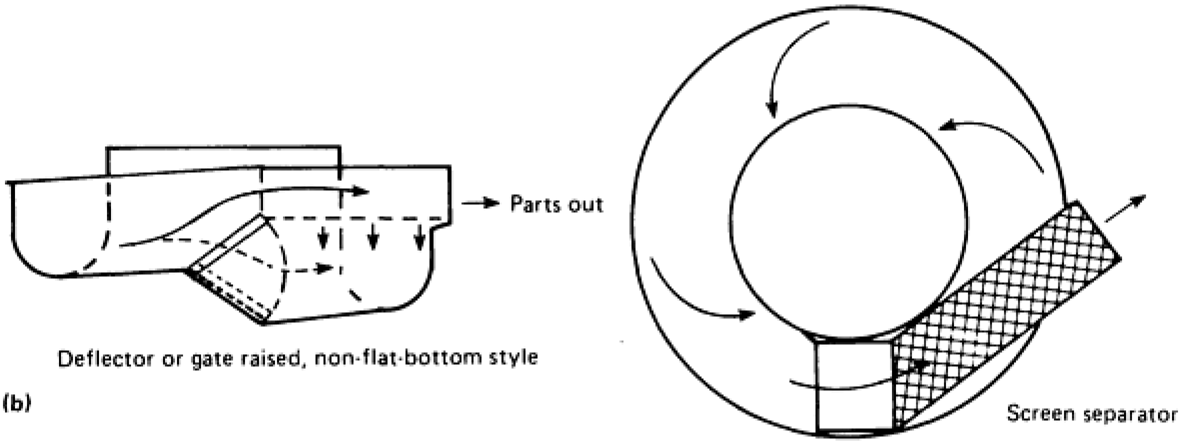
Other automated tub vibratory systems include storage for different media that may be automatically selected for different processing tasks. Tub vibratory machines can be highly versatile and permit process cycles normally $\frac{1}{5}$ to $\frac{1}{10}$ of those achieved with tumbling barrels. They are capable of handling all sizes of workpieces, including complex shapes. Materials handling is usually accomplished by units added onto the vibrator itself, designed and built to meet specific applications.

Bowl vibrators are round bowl- or toroidal (doughnut)-shaped and, like the tub vibrator, have a container mounted on springs. The principle of this type of equipment is shown in Fig. 4. Vibratory action is imparted to the bowl by eccentric weights mounted on a vertical shaft at the center of the bowl. Eccentric weights at either end of the shaft are adjustable in their relationship to one another. This is referred to as the lead angle. When set within the normal range established by the manufacturer, a spiral motion is imparted to the mass of parts and media. Changing the relationship of the weights alters the spiral path, the speed at which the load moves around the bowl, and the amplitude of vibration. The bowl vibrator is capable of more gentle action than tub equipment because parts hold their relationship to one another as they proceed around the bowl; consequently there is less chance of part-on-part impingement. Another advantage of bowl vibrators is that they require less floor space than most tub units of similar capacity.



Eccentric weight system, flat-bottom style

(a)



Deflector or gate raised, non-flat-bottom style

(b)

Fig. 4 Bowl vibrators

The major advantage of bowl vibrators is that an integral separation system can be incorporated, such as that shown in Fig. 4(b). To separate parts from media, a dam is placed in the channel so that parts and media are forced up and over. At the top of the dam is a screen over which parts and media pass. Media fall through the screen back into the vibrator bowl. Parts are deflected off the screen into a collection hopper or conveyor. Bowl vibrators with integral separation may have a non-flat-bottom base, so the dam has a shorter distance to travel. Parts and media do not have to lift as high to reach the screen, excellent separation is achieved, and there is less likelihood of parts piling up at the dam with danger of impingement. Action of the dam may be automatic; some equipment has automatic reversal of the action and increased vibration to promote faster and more complete separation. Therefore, the round vibrators can be fully automated. For short process cycles up to about 30 min, flow-through automation can be achieved with the dam permanently in place.

Bowl vibratory equipment is preferred if integral separation meets all requirements, and if there is no need for frequent media change. Bowl vibrators are somewhat slower than the tub units. They cannot handle very large parts, but they are gentle and can handle parts in individual compartments.

Causes of Problems. Some causes of sluggish, ineffective vibratory action include:

- Water flow rate that is too high or drains that are clogged, resulting in excessive dampening
- Use of wrong type of compound, little or too much compound
- Frequency of vibratory action that is not best for the partsAmplitude that is too great
- Equipment that is underpowered and therefore does not develop enough vibratory action for effective performance

Unacceptable finishes may be the result of:

- Insufficient cutdown of surface
- Improper media for amount of cut needed on workpieces
- Dirt, oil, or metal fragments in the solution that work back into the surface of parts
- Insufficient flushing and cleaning of media from processing tub
- Use of wrong type of finishing compound and/or wrong concentration
- Vibratory action that is too harsh
- Incorrect ratio of parts to media
- Careless handling in auxiliary operations

Spindle Finishing Machines

Spindle finishing is categorized as a mass finishing process, although parts to be deburred or finished are mounted on fixtures. The process uses fine abrasive media for finishing. The spindle machine is a circular rotating tub that holds the abrasive media, and a rotating or oscillating spindle to which the part is fixed. The workpiece mounted on the spindle is immersed into the rapidly moving abrasive slurry, causing the abrasive to flow swiftly over rough edges and over the surfaces of components. In some designs, the media container is stationary, and the fixtures move the parts rapidly through the media. Figure 5 shows a layout of a spindle machine.

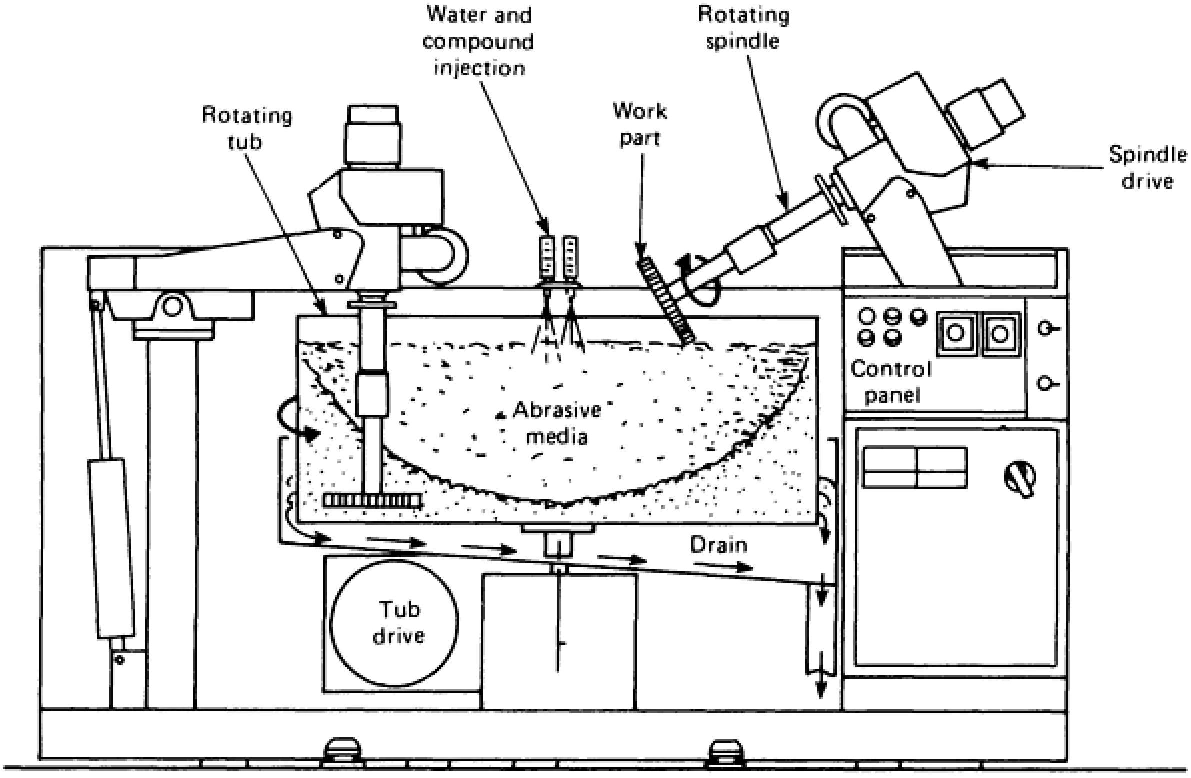


Fig. 5 Two-spindle mass finishing machine

The media used are usually small aluminum oxide nuggets, although all forms of small finishing media are applicable. Most operations are carried out in a water solution, although very fine finishing of some components can be achieved by dry operation using media composed of fine abrasives and corncob or walnut shells.

Process cycles in spindle equipment rarely exceed 20 min and are frequently less than 30 s. The equipment is well suited for parts such as gears, sprockets, and bearing cages where parts cannot be allowed to contact one another. Equipment can deburr, edge radius, and produce very fine surface finishes. Because parts are fixtured, part-on-part impingement does not occur during the process or at reload time. The limitations of this process result primarily from the need to fixture the workpieces. Where parts can be handled entirely satisfactorily in bulk in vibratory equipment, centrifugal barrel machines, or centrifugal disc equipment, the operation will be more economical, convenient, and versatile.

Centrifugal Disc Finishing

The centrifugal disc process is a high-energy mass finishing process. The basic design is a vertical cylinder with side walls that are stationary. The top of the cylinder is open. The bottom of the cylinder is formed by a disc that is driven to rotate at a high speed. Media, compound, and parts are contained in the cylinder. As the disc rotates with peripheral speeds of up to 10.2 m/s (2000 ft/min), the mass within the container is accelerated outward and then upward against the stationary side walls of the container, which act as a brake. The media and parts rise to the top of the load and then flow in toward the center and back down to the disc.

The action achieved in the centrifugal disc machine, shown in Fig. 6, is substantially faster than in vibratory equipment because of the centrifugal forces of as much as ten times gravity pressing abrasive media against components. Process cycle times are up to $\frac{1}{20}$ those of vibratory processing. The short process cycles result in reduced floor space requirements in the finishing department, increased versatility, and less work in progress. As with vibratory equipment, parts can be readily inspected during the process cycle and variable speed can occasionally combine deburring with a final, more gentle surface refinement operation. The faster process speeds create a much greater rate of media wear and increase demands on the compound solution and its flow rate.

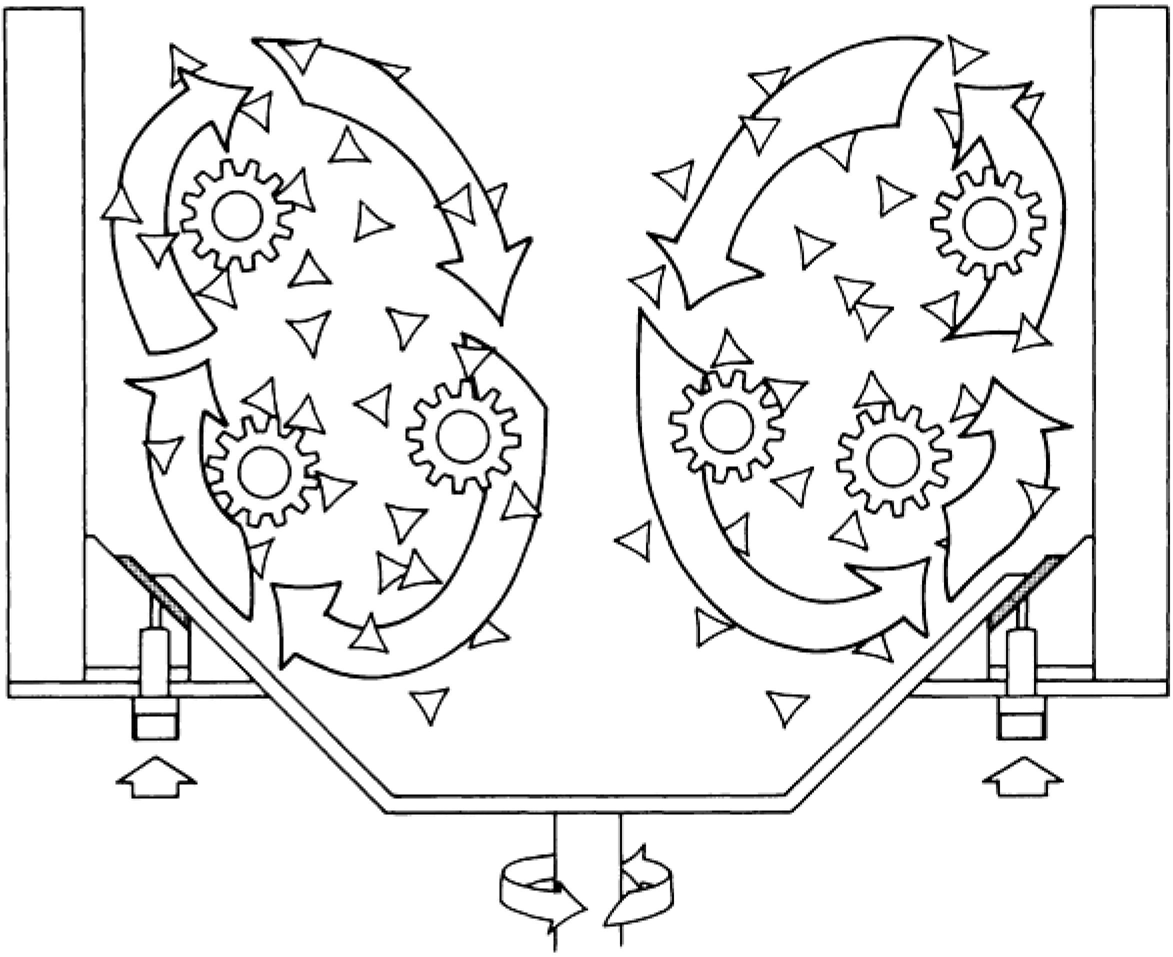


Fig. 6 Centrifugal disc machine

Centrifugal disc equipment is available with capacities ranging from 0.04 to 0.6 m^3 (1.5 to 20 ft^3). This equipment is easily automated. The load is emptied through a door in the side of the container through which parts and media can be fed, or by tilting the whole bowl through 180° to dump the load. Subsequent separation, classification, washing systems, and the return of media to the container for the next operation are similar to those techniques used with tub vibratory machines.

Centrifugal Barrel Finishing

Centrifugal barrel equipment is comprised of containers mounted on the periphery of a turret. The turret rotates at a high speed in one direction while the drums rotate at a slower speed in the opposite direction. The drums are loaded in a manner similar to normal tumbling or vibratory operations with parts, media, water, and some form of compound. Turret rotation creates a high centrifugal force, up to 100 times gravity. This force compacts the load within the drums into a tight mass. Rotation of the drums causes the media to slide against the work load, to remove burrs and to refine surfaces. The action of a centrifugal barrel machine is shown in Fig. 7.

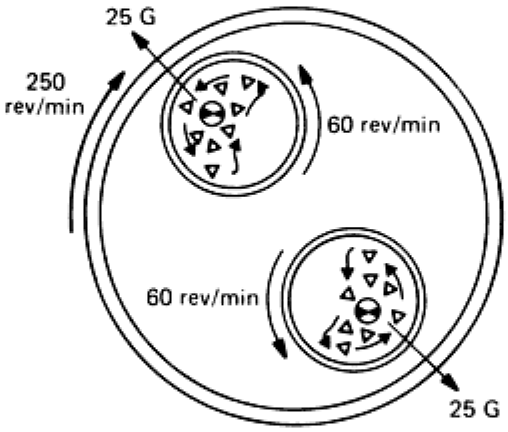


Fig. 7 Action of turret and drums within a centrifugal barrel finishing machine

The abrading action, under high centrifugal force, results in short process cycles, generally less than $\frac{1}{50}$ of the time taken in vibratory equipment. Because of the counter rotation of drums to turrets, a completely smooth sliding action of media against components is generated, with little possibility of one part falling or impinging against another. This completely smooth action achieves consistent and reproducible results. Very high tolerances are maintained even with fragile parts, and very high surface finishes are achieved.

Process variables are similar to those of other mass finishing processes, but an advantage of centrifugal barrel finishing is the ability to control the force with which media are pressed against components. This gives greater latitude in choice of media. For example, hard and low-abrasion media may be used to deburr by running at high speed. Then the same media refine surfaces when the machine is switched to a low speed. Therefore, two operations can be combined into a single cycle. Particle size of media is selected to meet requirements of uniformity and to ease separation without increasing the time of the process cycle.

One important application of centrifugal barrel equipment is to impart a high compressive stress to the surface layer of components and to increase resistance to fatigue failure. The capability of imparting improved fatigue strength is used in bearings, aircraft engine parts, springs, and compressor and pump components. The improved fatigue strength is generally greater than that of the other finishing processes combined with shot peening. It is almost always significantly lower in cost.

Economic considerations frequently dictate the choice between centrifugal barrel equipment and the other mass finishing processes. If satisfactory results are achieved with a process cycle of less than 1 h, a vibratory process is the more economical method. If the process cycle is much longer, if there is a wide variety of components to be handled, or if there are special finishing requirements or parts of very high precision, centrifugal barrel machines are usually better suited.

Centrifugal barrel equipment is available in sizes ranging from less than 0.01 m^3 ($\frac{1}{4}$ ft^3) capacity to 1.4 m^3 (50 ft^3) capacity. The process is fully batch automated but not subject to continuous flow-through of workpieces.

Other Types of Mass Finishing Equipment

The mass finishing processes discussed so far are the well-established mechanical finishing techniques throughout industry. Equipment comes in a variety of shapes and sizes to meet special requirements. Equipment has been developed to suit changing requirements and is frequently built to meet special purposes. Other mass finishing machines offered with slightly different actions from those that have been discussed include the following:

- *Vibratory rotary barrel machines* are conventional tumbling barrels that are vibrated as they rotate. They were originally developed to avoid some of the problems of parts migrating out of the media in tub vibratory equipment. These machines do not appear to have any substantial merit for modern general-purpose deburring and finishing.

- *Reciprocal finishing:* As in spindle finishing systems, parts are attached to a holding device and placed into a tub of media, water, and compound. The component is moved through the mass of media in a reciprocating motion. This process permits the handling of parts too large for spindle finishing machines. Action is concentrated on just one side of the component for specialized finishing. Process cycles are generally much longer than with spin finishing machines, and equipment is special and of limited purpose.
- *Chemically accelerated centrifugal barrel finishing:* A combination of chemical polishing with centrifugal barrel finishing has found many worthwhile applications, particularly with high-precision, complex-shaped ferrous components. The process is substantially more costly than normal centrifugal barrel finishing and is only suited to very special purposes.
- *Electrochemically accelerated mass finishing equipment:* For special purposes, a combination of electropolish and vibratory or tumbling barrel action achieves very fast stock removal. The process is expensive and inconvenient and is not commercially used in the United States.
- *Orboresonant cleaning and finishing:* Parts clamped on fixtures are oscillated at very high frequency in a bed of fluidized media, with some capability for removing internal burrs and cleaning internal surfaces.

Selecting Mass Finishing Equipment

Factors to be considered when selecting the most suitable mass finishing process include:

Production requirements

- Size and configuration of parts
- Batch size
- Part material
- Variety of parts
- Hourly production
- Annual production

Quality requirements

- Consistency of quality entering department
- Consistency of quality leaving department
- Surface finish
- Edge condition required
- Cleanliness of parts
- Uniformity over edges and surfaces
- Uniformity part to part

Process variables

- Relationship to other manufacturing processes
- Automation requirements
- Process time
- Total investment
- Operation and maintenance costs
- Consumable materials
- Energy
- Water and effluent removal and treatment

- Preventive maintenance and repairs
- Available floor space
- Inventory requirements
- EPA and OSHA considerations
- Labor, direct, supervisory, and quality control
- Future and current needs

Traditionally, mechanical finishing has been a centralized service operation for all manufacturing operations within an organization. Although the centralized finishing department is still suitable in many organizations, deburring and mechanical finishing is frequently incorporated in the production line. In reviewing mechanical finishing requirements, as in buying any metal-forming equipment, one should consider that equipment as part of a system with all controls between the system and all ancillary and handling equipment.

Some of the advantages and disadvantages of mass finishing processes that should be considered are included in Table 1.

Table 1 Advantages and disadvantages of mass finishing processes

Process	**Advantage**	**Disadvantage**
Industry standard		
Tumble barrel	Low initial cost Low operating cost for supplies Very low equipment maintenance cost	Slow process Skillful operator essential Automation impractical Wet working area No in-process inspection
Vibratory tub	Fast operation Handles all part sizes Open for in-process inspection Practical full batch automation Practical in-line automation	Slower than high-energy process External material handling required
Vibratory bowl	Open for in-process inspection Practical full batch and continuous operations Requires no auxiliary equipment to automate Internal separation Space saving Lowest cost for general purpose work Simple selection and operation with little operator skill required Can produce cleanest parts and excellent surface finish	Somewhat slower than vibratory tub
High-energy		
Spindle	Fast processing Possible automation, robot load and unload No part-on-part impingement	Limited part geometry Parts must be fixtured High labor cost
Centrifugal disc	Fast processing Open for in-process inspection Practical automated batch process Compact operation	Part size limitation High initial investment

Centrifugal barrel	Fast processing Fragile part handling High precision part handling Potential automated batch processing Automatic change from grind to super finish Produces finest finish Improves fatigue strength	No in-process inspection High initial investment

Mass Finishing Consumable Materials

For the vast majority of mass finishing processes, equipment is loaded with components to be finished, media, compound, and water. Media are solid stones or chips. Compounds are the materials that dissolve in water to form solutions to facilitate or modify the action of media against components.

There are very few occasions when media can be used with no water and, therefore, no compound. There are some occasions when the parts themselves act as the media; this is a self-tumbling process.

Clearly, the selection of media and compounds for the mass finishing operation is as important as the selection of the correct tooling for any forming operation, and an understanding of the materials available is essential for effective use of equipment.

Mass Finishing Compounds. The correct use of compound-water solutions is vital to good and consistent mass finishing processing in any equipment. The compound solution is used to:

- Develop and maintain cleanliness of parts and media during the process
- Control pH, foam, and water hardness
- Wet surfaces
- Emulsify oily soils
- Remove tarnish or scale
- Control part color
- Suspend soils
- Control lubricity
- Prevent corrosion
- Provide cooling
- Ensure effluent meets EPA, OSHA, and plant standards

Compounds may be liquid or powder. Addition of compound to the mass finishing equipment may be made in three ways:

- *Batch:* This is the simplest technique, used in closed machines, barrels, small centrifugal barrels, and vibrators with no drains. The machine is charged with compound and water, which is flushed away at the end of the process cycle.
- *Recirculation:* The solution is mixed in a tank and pumped into the process, allowing it to drain back into the tank for reuse. This process is simple and has the basic benefit that there is no continuous drainage, and the effluent can be treated on a batch basis. The major disadvantage of this system is that the solution deteriorates during its life and, therefore, results vary. For this reason, recirculation should be avoided if at all possible.
- *Flow-through:* This system pumps fresh solution into the machine, allows it to act, and then drains it out. Modern compound solutions can be very dilute and economical. For example, a 0.3 m^3 (10 ft^3) machine normally uses less than 4 L (1 gal) of compound per shift. When using flow-through systems with liquid compounds, automatic addition through a compound metering pump is possible, further reducing waste and improving consistency of the process.

Because the use of a flow-through compound solution system permits close control and is readily automated, liquid compounds are normally preferred for consistent results. When mass finishing in closed-batch systems, powdered compounds can be economical. Powdered compounds can include loose abrasives that enhance cutting capabilities of media. Abrasives are seldom recommended in vibratory systems.

Finishing Media. The media in the mass finishing operation are equivalent to the tooling used in any machining operation. The functions of media are to abrade or burnish edges and surfaces of components to be finished and to keep parts separate from one another to avoid or limit any part-on-part impingement. Media may be selected from any of the following materials:

- *Natural media:* Stones that have been quarried, crushed, and graded were the original media for mass finishing operations. Natural media have been largely replaced by synthetic materials that are harder with longer life; greater consistency of cut, wear, and dimension; and greater variety of capabilities.
- *Agricultural materials:* Sawdust, corncob, and walnut shells are frequently used in mass finishing machines for drying. Mixed with fine abrasives, these materials are suited for some fine polishing operations, particularly in the jewelry industry. Wood pegs may be coated with fine abrasives or waxes for edge radiusing and finishing of some wooden and plastic components.
- *Synthetic random media:* Fused and sintered aluminum-oxide media, crushed and graded, are available in a number of grades, both heavy cutting and fine finishing. Generally they are much tougher than natural media and more consistent.
- *Preformed ceramic media:* Porcelain or other vitreous material is mixed with abrasives and formed into shapes, then fired to vitrify. These media are available in a large range of shapes, sizes, grades of abrasive, proportions of abrasive to binder, and types of binder to enable selection of material to suit virtually every application. The consistency of quality can be ensured. This type of material is the present standard for the mass finishing industry.
- *Preformed resin-bonded media* are abrasives bonded into polyester or urea-formaldehyde resins. Like the ceramic materials, these are available in a broad range of shapes and sizes with different types, grades, and quantities of abrasive to meet a range of applications. Plastic media are somewhat softer than ceramic, and for a given degree of abrasion they usually have shorter life, but they also have somewhat lower cost and lower density. These softer materials achieve better preplate finish than other media and are better suited for handling soft metals.
- *Steel:* Hardened steel preformed shapes are available in a variety of shapes and sizes and are well suited for burnishing. Steel applications also include cleaning and light deburring. The basic benefit is that these media wear very little. Although there is a high initial investment, they are not consumable and do not need reclassification. Steel pins and tacks used with abrasive compounds can be useful means of removing somewhat inaccessible burrs.

Final selection of the best media must be made on a trial and error basis, but the following factors affecting selection should be understood and considered before any form of testing is started:

Shape and size of media

- To remove burrs
- To achieve uniform edge and surface finishes
- To avoid jamming in holes and recesses
- To achieve ease of separation
- To achieve shortest cycle time

Availability and cost of media

- From consistent supplier
- For economical cost per pound or unit volume

- For consistent quality

Ability and versatility of media

- For minimum wear and reclassification
- For handling a range of products within a given machine
- For minimum break-in requirements
- For cushioning action between parts

Optimum media-to-part ratio is another consideration for choosing the best media (Table 2).

Table 2 Typical media-to-part ratios for vibratory and tumbling mass finishing processes

Media to part ratio, by volume	Commercial application
0:1	No media, part-on-part, used for beating off burrs, no media for cutting, sometimes suitable for burnishing
1:1	Equal volumes of media and parts, forgings, and castings; crude, very rough surfaces
2:1	More gentle, more separation, still severe part-on-part damage is possible
3:1	About minimum for nonferrous parts, considerable part-on-part contact, fair to good for ferrous metals
4:1	Probably average conditions for nonferrous parts, fair to good surfaces, good for ferrous metals
5:1	Good for nonferrous metals, minimal part-to-part contact
6:1	Very good for nonferrous parts, common for preplate work on zinc with plastic media
8:1	For higher-quality preplate finishes
10:1 to 15:1 or more	Better, used for very irregularly shaped parts or parts that tangle or bend
No contact	Absolutely no part-on-part contact, one part per machine or compartment, part fixturing

Mass Finishing Process Considerations

The mechanical finishing department in virtually every metal-working plant is used as a general rectification shop. This is inevitable because metal forming machinery does not produce consistent burrs or truly consistent surface and edge finish conditions. Equipment in the mechanical finishing department should be sufficiently versatile to meet the changing quality of parts.

Cleanliness. Most mass finishing processes tolerate some oil, scale, and dirt on components. In fact, mass finishing is frequently used as a highly effective means of cleaning components, having both mechanical and chemical action; however, some operations, particularly super finishing on very high-precision parts, demand cleanliness or at least consistency of any surface contamination. The finishing department should be notified of any changes in prior operations, such as change of machining lubricants or heat treatment methods.

Ancillary Equipment. Most mass finishing processes are wet operations. After parts are unloaded from the mass finishing equipment, parts are rinsed, corrosion protection is applied, and the parts are dried. A decision must be made whether these processes are separate from the mass finishing machine or if combination compounds could incorporate these steps in the finishing machine.

There is a requirement to separate parts from media by screening or magnetic separation. Media reclassification is also frequently incorporated into a screening separator.

Automation. Opportunities to automate mass finishing should be investigated. Mass finishing operation requires measured quantities of parts and media to be placed into the equipment; controlled addition of compound solution with change of solution at some point during the process cycle; unloading of the equipment; separation of parts from media; washing, drying, and conveying parts; and classification, conveying, and storage of media. Such a sequence may represent a substantial labor involvement and many opportunities for errors that are difficult to control. The cost of automation is repaid by improved work flow, improved quality, and lower labor costs.

Process Instructions and Control. Process instructions should cover all variables, which include:

- Machine cycle, including process times, barrel speeds, or vibratory frequency and amplitude, or G force and speed, depending on type of equipment
- Load levels, total load, and proportion of parts to media
- Compound and water flow rates
- Media and compound variables
- Pretreatment and post-treatment variables

Masking and Fixturing. Holes in components with rubber or plastic are plugged to keep media from being jammed into those holes during processing. Corners and edges that must be left sharp can also be masked. Some components are processed on fixtures in the mass finishing equipment. This is essential for spindle finishing. In some mass finishing equipment, large components are better processed in individual compartments within the machine. Occasionally, threads are masked that might get damaged or abraded too much during processing.

Causes of Difficulties Commonly Encountered in Mass Finishing. The following is a list of difficulties encountered during mass finishing processes:

Excessive impingement on part surface

- Insufficient amount of media in chamber
- Parts in work load too large for the machine
- Excessive equipment speed or amplitude
- Low solution level or flow rate
- Insufficient or wrong compounds
- Undesirable handling methods
- Media too large for part size
- Wrong type of media

Rollover of edges, corners, and burrs

- Abrasive action too slow
- Wrong type of media
- Media particles too large for part size
- Excessive equipment speed or amplitude
- Excessive work load for volume of media
- Incorrect water level

- Processing time too long

Persistent lodging of media in holes, slots, or recessed areas

- Wrong size of media
- Wrong shape of media
- Excessive wear or depreciation of media
- Media fracturing during operation
- Failure to classify media as required

Poor surface finish

- Insufficient cutdown in process
- Inadequate flushing and cleaning of equipment
- Incorrect compound
- In-process corrosion
- Water flow not correct
- Media too aggressive or too hard
- Part-on-part impingement

Safety Precautions

In addition to the normal hazards with rotating machinery, other hazards in finishing are generation of gas, usually flammable, in a closed barrel, and handling of acid or alkaline compounds. Accidents caused by a buildup of gas pressure within a closed barrel have ranged from the blowing off of a cover during its removal to the fracture and fragmentation of portions of a barrel during operation. All closed barrels should have a cover-locking device that permits loosening of the cover but restrains it so that it cannot be blown off. Ventilation of the barrel, preferably automatic, is also highly recommended.

Hazards connected with the use of acids and alkalis are generally recognized. The use of rubber gloves and face masks is recommended.

Waste Disposal

Some compounds used in barrel finishing are harmful and their disposal may pose problems. In all instances, local regulations should be checked before establishing any procedure for waste disposal.

Most compounds are alkaline when mixed with water, although some are acid. Compounds containing cyanides or chromates are toxic and are not recommended.

Methods of waste treatment include:

- Neutralizing acid or alkaline waste before disposal
- Removing oils by running the solution under a skimming bar
- Settling out solid wastes in a basin, preferably after neutralization

Shot Peening

Revised by Ted Kostilnik, Wheelabrator Corporation

Introduction

SHOT PEENING is a method of cold working in which compressive stresses are induced in the exposed surface layers of metallic parts by the impingement of a stream of shot, directed at the metal surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Although shot peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength. The process has other useful applications, such as relieving tensile stresses that contribute to stress-corrosion cracking, forming and straightening of metal parts, and testing the adhesion of silver plate on steel.

Peening Action

When individual particles of shot in a high-velocity stream contact a metal surface, they produce slight, rounded depressions in the surface, stretching it radially and causing plastic flow of surface metal at the instant of contact. The effect usually extends to about 0.13 to 0.25 mm (0.005 to 0.010 in.) but may extend as much as 0.50 mm (0.02 in.) below the surface. The metal beneath this layer is not plastically deformed. In the stress distribution that results, the surface metal has induced or residual compressive stress parallel to the surface, while metal beneath has reaction-induced tensile stress. The surface compressive stress may be several times greater than the subsurface tensile stress. This compressive stress offsets any service-imposed tensile stress, such as that encountered in bending, and improves fatigue life of parts in service markedly.

Peening action improves the distribution of stresses in surfaces that have been disturbed by grinding, machining, or heat treating. It is particularly effective on ground or machined surfaces, because it changes the undesirable residual tensile stress condition that these processes usually impose in a metal surface to a beneficial compressive stress condition. Shot peening is especially effective in reducing the harmful stress concentration effects of notches, fillets, forging pits, surface defects, and the low-strength effects of decarburization, and the heat-affected zones of weldments.

Strain Peening. The magnitude of residual stress that can be induced by shot peening is limited. In hard metals, it is slightly more than half the yield strength. A higher residual stress, approaching the full yield strength, can be obtained by strain peening, which consists of peening the surface as it is being strained in tension. The effectiveness of strain peening is limited to parts such as springs, gears, and shafts, that are subjected to unidirectional service loads.

Surface Coverage and Peening Intensity

The workpiece surface being peened is affected by the amount of the target surface peened and the effectiveness of the peening action on that target surface.

Surface coverage is a measure of how completely an area has been hit by the myriad of impinging shot particles. Without 100% coverage or saturation, the improvement in fatigue characteristics conventionally produced by shot peening is not obtained.

As stated in SAE Recommended Practice J443, "Procedure for Using Shot Peening Test Strip," a definite and quantitative relationship between coverage and exposure time exists, which may be expressed as follows:

$$C_n = 1 - (1 - C_1)^n$$

where C_1 is the percentage of coverage (decimal) after 1 cycle, C_n is the percentage of coverage (decimal) after n cycles, and n is the number of cycles.

This relationship indicates that coverage approaches 100% as a limit. Accurate measurements above 98% coverage are difficult to obtain, but a measurement at a lower degree of coverage serves as a means of determining the exposure time or equivalent time required to obtain any desired coverage. Because accurate measurement can be made up to 98%

coverage, this value is arbitrarily chosen to represent full coverage or saturation. Peening at less than saturation is ineffective because of the amount of unpeened surface. Beyond this value, the coverage is expressed as a multiple of the exposure time require to produce saturation. For example, 1.5 coverage represents a condition in which the specimen or workpiece has been exposed to the blast 1.5 times the exposure required to obtain saturation. Figure 1 shows the relationship between exposure time and coverage and indicates that after a measurement of a low percentage of coverage has been established, the correct exposure time for any percentage of coverage can be readily determined.

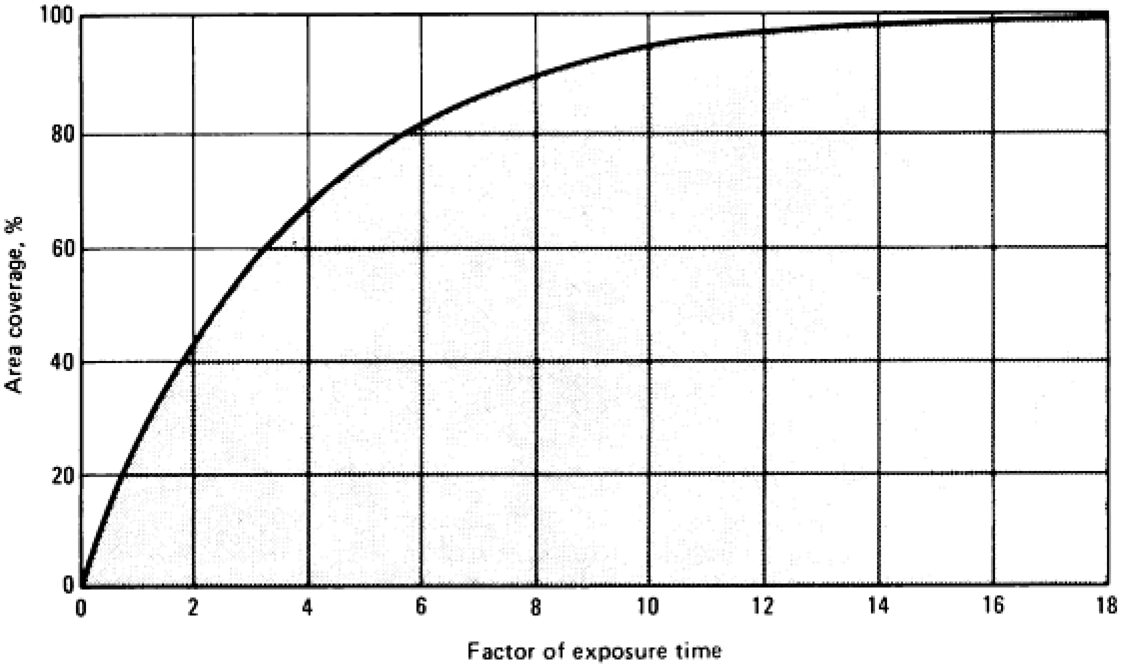


Fig. 1 Area coverage as a function of exposure time in shot peening

Measurement of Coverage. Direct methods for measuring coverage include visual methods and the Straub method. One of the indirect methods is the Valentine method, which involves layer removal.

Visual methods, although not quantitative, are almost universally used. The simplest of these consists of visual inspection, with or without the aid of optical (10×) magnification of the surface of the peened part. This method may be supplemented by a series of reference photographs illustrating various percentages of coverage.

Another visual method consists of preparing a transparent plastic replica of the peened surface and comparing it, by means of photographic projection, with reference replicas having various percentages of coverage.

The Straub method consists of exposing a polished surface to the shot stream, projecting the surface at a magnification of 50 diameters on the ground glass of a metallographic camera, tracing the images of the indented areas on translucent paper, and measuring the total area and the indented area with a planimeter. Percentage of coverage is expressed as the ratio of indented area to total area multiplied by 100. About 15 min is required to make one measurement.

The Peenscan method is offered in lieu of visual inspection in MIL-S-13165 and consists of painting a part before peening with a dye sensitive to ultraviolet light, shot peening the part, inspecting the part under the ultraviolet light for any missed areas, shot peening the part, and reinspecting the part under ultraviolet light. Complete removal of the dye indicates 100% coverage of the part.

The Valentine method consists of making a duplicate of the part from low-carbon steel, peening the part, annealing it for several hours to promote recrystallization and grain growth, and relating peening coverage to the amount and continuity of grain growth by metallographic examination of cross-sectional areas.

Because of the difficulty in quantitatively measuring coverage by these methods, percent coverage is usually estimated from the curve of Almen arc height against the duration of shot exposure. The Almen test is described in the section "Peening Test Strips, Holder, and Gage" in this article. The graph in Fig. 2 shows the relation between shot coverage and doubling exposure time. A change in arc height of 10% or less indicates saturation peening.

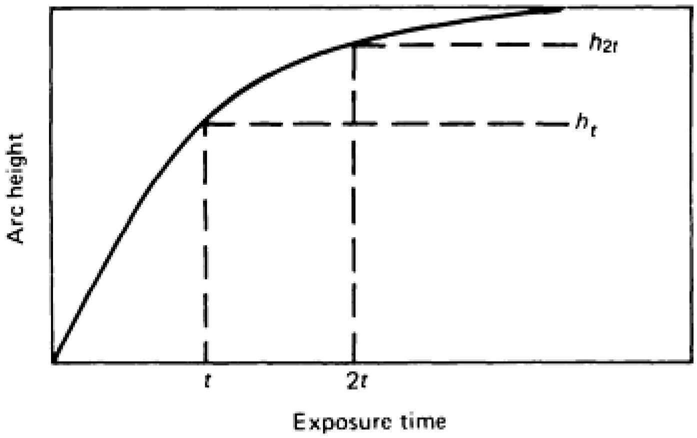


Fig. 2 Relation of measuring coverage to peening time. Coverage is considered full at time *t*, if doubling exposure to time 2*t* results in change in arc height less than 10%.

Peening intensity is governed by the velocity, hardness, size, and weight of the shot pellets, and by the angle at which the stream of shot impinges against the surface of the workpiece. Intensity is expressed as the arc height of an Almen test strip at or at more than saturation coverage. Arc height is the measure of the curvature of a test strip that has been peened on one side only. At or above saturation of the Almen strip, arc height is a measure of the effectiveness of the peening operation on a specific part. The Almen test is the primary standard of quality control and should be used at regular intervals, often on a day-to-day basis, and in the same location in the peening setup. Used correctly, a lower arc height indicates a reduction in peening intensity caused by a reduction in wheel speed or air pressure, excessive breakdown of shot, or other operational faults, such as undersized shot in the machine or clogged feed valves.

Selection of Intensity. The lowest peening intensity capable of producing the desired compressive stress is the most efficient and least costly, because the peening process can be achieved with the minimum shot size in the minimum exposure time. Conversely, an intensity may be considered excessive if, as with very thin parts, a condition is produced in which the tensile stresses of the core material outweigh the beneficial compressive stresses induced at the surface. Figure 3 presents data that indicate the relation of peening intensity to cross-sectional thickness.

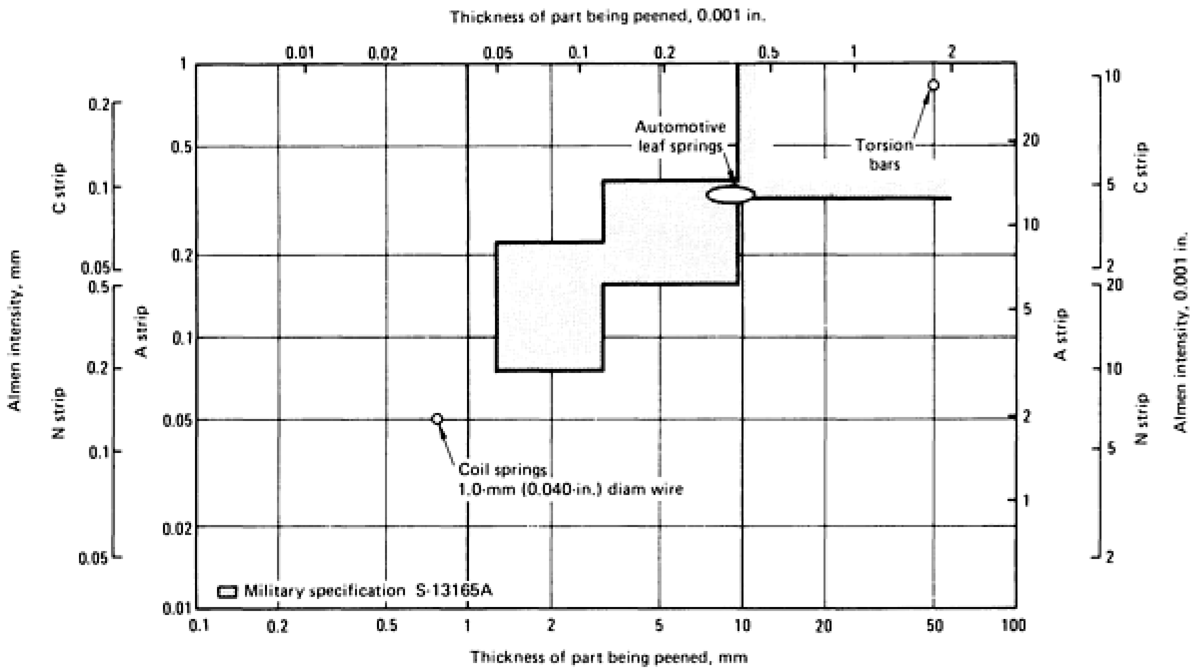


Fig. 3 Relation of peening intensity to cross-sectional thickness of parts peened

The depth of compressed layer to be produced by peening is a factor in selecting peening intensity. For instance, a heavy steel component with a partially decarburized skin requires a peening intensity high enough to induce a compressive stress beneath the decarburized layer. The relation between peening intensity and depth of compressed layer, for steel hardened to 31 and 52 HRC, is shown in Fig. 4.

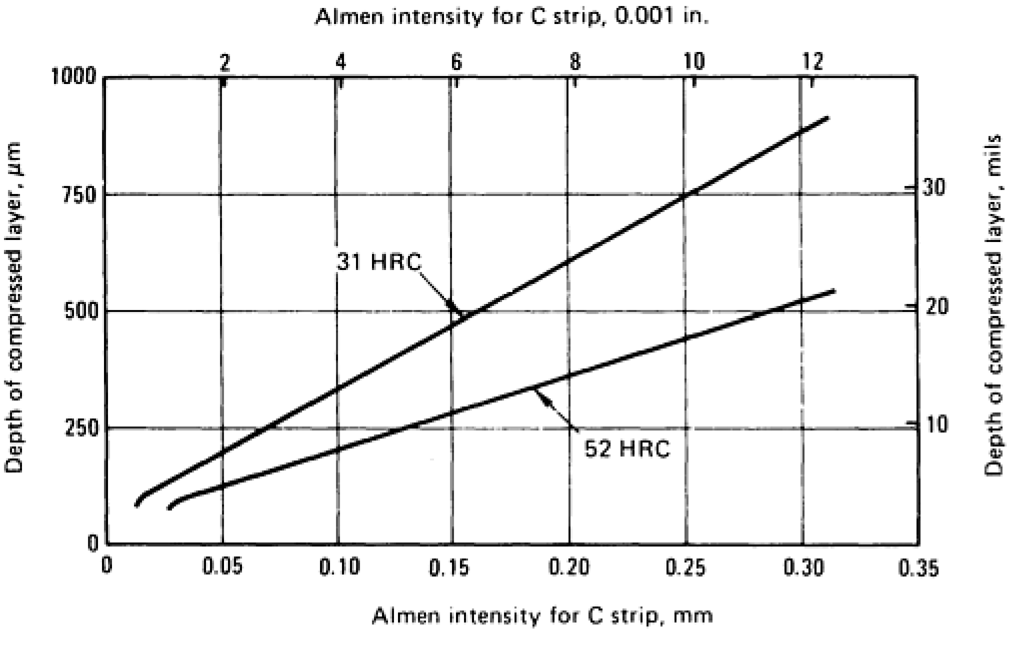


Fig. 4 Relation of depth of compressed layer to peening intensity for steel of two different hardnesses

Types and Sizes of Media

Media used for peening can be iron, steel, or glass shot, or cut steel or stainless steel wire. Metallic shot is designated by numbers according to size. Shot numbers, as standardized by MIL-S-13165, range from S70 to S930. The shot number is approximately the same as the nominal diameter of the individual pellets in ten thousandths of an inch. Standard size specifications for cast iron and steel shot are given in Table 1.

Table 1 Cast shot numbers and screening tolerances

Numbers in parentheses measured in inches

Peening shot size No.	All pass U.S. screen size	Maximum 2% on U.S. screen	Maximum 50% on U.S. screen	Cumulative minimum 90% on U.S. screen	Maximum 8% on U.S. screen	Maximum number of deformed shot acceptable
930	5 (0.157)	6 (0.1320)	7 (0.1110)	8 (0.0937)	10 (0.0787)	5(a)
780	6 (0.132)	7 (0.1110)	8 (0.0937)	10 (0.0787)	12 (0.0661)	5(a)
660	7 (0.111)	8 (0.0937)	10 (0.0787)	12 (0.0661)	14 (0.0555)	12(a)
550	8 (0.0937)	10 (0.0787)	12 (0.0661)	14 (0.0555)	16 (0.0469)	12(a)
460	10 (0.0787)	12 (0.0661)	14 (0.0555)	16 (0.0469)	18 (0.0394)	15(a)
390	12 (0.0661)	14 (0.0555)	16 (0.0469)	18 (0.0394)	20 (0.0331)	20(a)
330	14 (0.0555)	16 (0.0469)	18 (0.0394)	20 (0.0331)	25 (0.0280)	20(b)
280	16 (0.0469)	18 (0.0394)	20 (0.0331)	25 (0.0280)	30 (0.0232)	20(b)
230	18 (0.0394)	20 (0.0331)	25 (0.0280)	30 (0.0232)	35 (0.0197)	20(b)
190	20 (0.0331)	25 (0.0280)	30 (0.0232)	35 (0.0197)	40 (0.0165)	20(b)
170	25 (0.0280)	30 (0.0232)	35 (0.0197)	40 (0.0165)	45 (0.0138)	20(b)
130	30 (0.0232)	35 (0.0197)	40 (0.0165)	45 (0.0138)	50 (0.0117)	30(c)
110	35 (0.0197)	40 (0.0165)	45 (0.0138)	50 (0.0117)	80 (0.0070)	40(c)
70	40 (0.0165)	45 (0.0138)	50 (0.0117)	80 (0.0070)	120 (0.0049)	40(c)

(a) Per area, 1 in. square.

(b) Per area, $\frac{1}{2}$ in. square.

(c) Per area, $\frac{1}{4}$ in. square

Glass shot, used primarily for peening nonferrous material, is available in a wider range of basic diameters. Hardness of glass shot is equivalent to 46 to 50 HRC. For further information on glass beads, see the article "Mechanical Cleaning Systems" in this Volume. Table 2 shows the effect of shot size and peening intensity on fatigue life.

Table 2 Effect of shot peening on fatigue strength of aluminum alloys and carbon and low-alloy steels

Metal tested	**Type of specimen**	**Stress cycle**	**Surface condition as-received**
Aluminum alloys			
2014-T6	Plain, 38 mm (1.5 in.) diam	Reversed bending	Smooth turned(a)
2024-T4	Plain, 38 mm (1.5 in.) diam	Reversed bending	Turned(a)
7079-T6	Plain, 38 mm (1.5 in.) diam	Reversed bending	Turned(a)
7075-T6		Reversed bending	Turned(a)
Carbon and low-alloy steels			
5160 spring steel(c)	Flat leaf, 38 mm (1.5 in.) wide, 4.88 mm (0.192 in.) thick	Unidirectional bending	Machined before heat treatment(d)
1045 steel (165 HB)	Plain (R.R. Moore)	Rotating bending	Machined
1045 steel (285 HB)	Plain (R.R. Moore)	Rotating bending	Machined
9260 steel (526 HB)	Plain (R.R. Moore)	Rotating bending	Machined
Ingot iron (121 HB)	Plain (R.R. Moore)	Rotating bending	Machined
4340 steel (277 HB)	Plain (R.R. Moore)	Rotating bending	Machined

4118 steel (60 HRC)	Single gear tooth	Unidirectional bending	Machined
8620 steel (58 HRC)	Single gear tooth	Unidirectional bending	Machined
S-11 steel(n)	Grooved, 7 mm (0.3 in.) D(o)	Rotating bending	Machined
0.54% C steel(q)	Plain, 8 mm (0.315 in.) diam	Rotating bending	Decarburized
	Plain, 5.99 mm (0.236 in.) diam	Reversed torsion	Decarburized
	10.0 mm (0.394 in.) diam bars:		
	Smooth	Rotating bending	Polished
	Round-notched(r)	Rotating bending	Machined
	V-notched(s)	Rotating bending	Machined(t)
Music wire(u)	Coil spring	Not reversed	. . .
4340 steel(w)	14 mm (0.560 in.) diam(x)	Reversed torsion	Smooth turned
4340 steel(z)	6.4 mm (0.250 in.) diam(x)	Rotating bending	Highly polished
4340 steel(})	6.4 mm (0.250 in.) diam(x)	Rotating bending	Highly polished

Metal tested	**Peening conditions**				**Fatigue strength**						**Strength gain by peening, %**		**Ref**
	Shot		**Intensity**		**As-received**		**Polished**		**Peened**		**Over as-rec'd**	**Over polished**	
	Type	**Size No.**	**0.025 mm**	**0.001 in.**	**7 MPa**	**1 ksi**	**7 MPa**	**1 ksi**	**7 MPa**	**1 ksi**			
Aluminum alloys													
2014-T6	Cast steel	70	0.15	6 A	215	31(b)	. . .	. . .	260	38(b)	23	. . .	. . .
		230	0.76	30 A	215	31(b)	. . .	. . .	260	38(b)	23	. . .	. . .

		550	0.33	13 A	215	31(b)	. . .	. . .	260	38(b)	23	. . .	. . .
2024-T4	Cast steel	230	0.25	10 A	180	26(b)	. . .	. . .	240	35(b)	34	. . .	. . .
7079-T6	Cast steel	230	0.25	10 A	195	28(b)	. . .	. . .	250	36.5(b)	30	. . .	. . .
7075-T6		MIL-5	0.15	6 A	220	32(b)	. . .	. . .	275	40(b)	25	. . .	(~)
Carbon and low-alloy steels													
5160 spring steel(c)	Chilled iron	230(e)	0.15	6 C(f)	880	128(g)	. . .	. . .	1340	194(g)	51	. . .	(!)
		230(e)	0.15	6 C	880	128(g)	. . .	. . .	1215	176(g)	37	. . .	. . .
		230(e)	0.15	6 C(h)	880	128(g)	. . .	. . .	970	141(g)	10	. . .	. . .
1045 steel (165 HB)	Chilled iron	(i)	(j)	(j)	. . .	. . .	275	40(k)	305	43.8(k)	. . .	10	(?)
1045 steel (285 HB)	Chilled iron	(i)	(j)	(j)	. . .	. . .	560	81(k)	515	75(k)	. . .	-7	(?)
9260 steel (526 HB)	Chilled iron	(i)	(j)(l)	(j)(l)	. . .	. . .	750	109(k)	730	106(k)	. . .	-2	(?)
Ingot iron (121 HB)	Chilled iron	(i)	(j)(l)	(j)(l)	. . .	. . .	185	27(k)	185	27(k)	. . .	0.7	(?)
4340 steel (277 HB)	Chilled iron	(i)	(j)	(j)	. . .	. . .	455	66(k)	540	78(k)	. . .	18	(?)
4118 steel (60 HRC)	Cast steel	110	0.20-0.25	8-10 A	16,200	2,350(m)	. . .	. . .	20,900	3,025(m)	29	. . .	(>)
8620 steel (58 HRC)	Cast steel	230	0.41	16 A	86,185	12,500(m)	. . .	. . .	105,150	5,250(m)	22	. . .	(>)
S-11 steel(n)	. . .	280	(p)	(p)	260	38	. . .	. . .	420	61	62	. . .	(<)
0.54% C steel(q)	Chilled iron	460	0.48	19 A	310	45	. . .	. . .	475	69	54	. . .	(+)

	Chilled iron	460	0.48	19 A	225	33	. . .	. . .	325	47	43	. . .	. . .
	Chilled iron	460	0.48	19 A	585	85	. . .	. . .	600	87	3	. . .	(+)
	Chilled iron	460	0.48	19 A	285	43	. . .	. . .	395	57	33	. . .	. . .
	Chilled iron	460	0.48	19 A	185	27	. . .	. . .	325	47	73	. . .	. . .
Music wire(u)	. . .	110	. . .	. . .	825	120(v)	. . .	. . .	1310	190(v)	58	. . .	(++)
4340 steel(w)	Cast steel	170	0.20	8 A	275	40(g)	. . .	. . .	515	75(g)(y)	87	. . .	(*)
4340 steel(z)	. . .	. . .	0.25	10 A	570	83	270	39({)	675	98(|)	. . .	150	(**)
4340 steel(})	. . .	. . .	0.25	10 A	725	105	380	55({)	710	103(|)	. . .	87	(**)

(a) 0.50 µm (20 µin.).

(b) Values at 1,000,000 cycles.

(c) Oil quenched and tempered at 370 °C (700 °F), hardness is 46 to 50 HRC.

(d) 0.2 to 0.3 µm (7 to 12 µin.).

(e) Shot peened only on side subjected to tension in fatigue test.

(f) Peened under a strain +0.60, 1240 MPa (180 ksi).

(g) Fatigue limit based on 5,000,000 cycles.

(h) Peened under zero strain.

(i) Equal parts of 170 and 280.

(j) Depth of cold work, peening, 150 µm (6 mils).

(k) Fatigue limit based on 10,000,000 cycles.

(l) Stress relieved at 205 °C (400 °F) for 20 min after peening.

(m) Fatigue limit in kilograms (pounds) load based on 5,000,000 cycles.

(n) 3% nickel-chromium steel, oil quenched from 830 °C (1525 °F), tempered at 600 °C (1110 °F), tensile strength 930 MPa (135 ksi).

(o) 0.79 mm (0.031 in.) semicircular groove.

(p) Air pressure, 345 kPa (50 psi).

(q) Tensile strength, 1410 MPa (205 ksi).

(r) Notch depth 1.0 mm (0.040 in.), radius 0.051 mm (0.002 in.).

(s) Notch depth 1.0 mm (0.040 in.).

(t) Root of notch not hit by shot.

(u) 0.99 mm (0.039 in.) diam.

(v) For 400,000-cycle life.

(w) Tensile strength 1860 MPa (270 ksi).

(x) Chromium plated.

(y) Same value obtained for peened and chromium plated; not peened and plated is less than 275 MPa (40 ksi).

(z) Tensile strength 1520 MPa (220 ksi).

({) Fatigue limit for chromium plated and baked.

(|) Fatigue limit for peened, chromium plated, and baked.

(}) Tensile 1990 MPa (288 ksi).

(~) Fatigue Strength of 7075-T6 Aluminum Alloys When Peened with Steel Shot or Glass Beads, Potters Industries PII-I-74, 1974.

(!) R.L. Mattson and J.G. Roberts, The Effect of Residual Stresses Induced by Strain-Peening upon Fatigue Strength, *Internal Stresses and Fatigue in Metals*; Elsevier, Amsterdam, 1958.

(?) J.M. Lessells and W.M. Murray, *Proc. ASTM*, 41, 659 (1941).

(>) J.A. Halgren and D.J. Wulpi, *Trans. SAE*, 65, 452 (1957).

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(+) S. Takeuchi and M. Honma, Effect of Shot Peening on Fatigue Strength of Metals, *Reports of the Research Institute for Iron, Steel and Other Metals*, Tohoku University, Sendai, Japan, 1959.

(++) H.C. Burnett, *Proc. ASTM,* 58, 515 (1958).

(*) "Effect of Chromium Plate on Torsion Fatigue Life of Shot Peened 4340 Steel," Douglas Aircraft Co. Report No. MP 20.005 (Sept. 13, 1960); available through SAE.

(**) B. Cohen, "Effect of Shot Peening Prior to Chromium Plate on the Fatigue Strength of High Strength Steel," WADC Technical Note 57-178, U.S. Air Force, June 1957

Cast steel shot is made by blasting a stream of molten steel with water and forming globules that rapidly solidify into nearly spherical pellets. This process is also called atomizing. The pellets are screened for sizing, reheated for hardening, quenched, and tempered to the desired hardness. According to SAE Recommended Practice J827, "Cast Steel Shot," 90% of the hardness measurements made on the representative sample should fall within the range equivalent to 40 to 50 HRC. To maximize the peened effect, shot should always be at least as hard as the workpiece. For hard metals, special hard-cast steel shot, 57 to 62 HRC, should be used.

Cast steel shot is the most widely used peening medium. With suitable heat treatment, it has a useful life many times that of cast iron shot. Its improved impact and fatigue properties markedly lower the rate of shot breakage, increase peening quality, and extend the life of components of peening machines.

Cast iron shot or chilled iron is brittle, with an as-cast hardness of 58 to 65 HRC. It breaks down rapidly; however, its inherently high hardness yields higher peening intensities for a given shot size, in comparison to softer materials. A high rate of shot breakage complicates the control of peening quality and increases the cost of equipment maintenance and cost of shot, because broken shot must be eliminated for best results.

Glass beads are used for peening stainless steel, titanium, aluminum, magnesium, and other metals that might be contaminated by iron or steel shot. They are also used for peening thin sections. Relatively low Almen A shot peening intensities, seldom exceeding 0.15 to 0.25 mm (0.006 to 0.010 in.), are used. Glass beads can be used in either wet or dry peening processes.

Cut wire is generally manufactured from carbon steel or stainless steel. The cut wire is mechanically manufactured and as a result is more uniform than cast steel or iron shot in size distribution. For peening applications, it is "conditioned" or blasted into a spherical shape. This conditioning process also hardens the cut wire media. For information about sizing and related subjects, see the article "Mechanical Cleaning Systems" in this Volume.

Control of Process Variables

Major variables in the shot peening process are shot size and hardness, shot velocity, surface coverage, angle of impingement, the resulting peening intensity, and shot breakdown. The quality and effectiveness of shot peening depend on the control of each of these interdependent variables.

Size of Shot. When other factors, such as shot velocity and exposure time, are constant, an increase in shot size results in an increase in peening intensity and depth of the compressed layer, plus a decrease in coverage. Selecting the minimum shot size capable of producing the required intensity is preferable to take advantage of the more rapid rate of coverage obtained with smaller shot.

The selection of a particular shot size may be dictated by the shape of the part to be peened. In shot peening of the fir-tree serrations of steel compressor blades, complete coverage can be obtained only if the radius of the shot does not exceed the radius of the serrations. The same principle applies to the selection of shot size for peening the root radius of threads. When peening fillets, the diameter of the shot used should not exceed one half the radius of the fillet.

Hardness of Shot. Variations in the hardness of shot do not affect peening intensity, provided the shot is harder than the workpiece. If the shot is softer than the workpiece, a decrease in intensity occurs.

Velocity of Shot. Peening intensity increases with shot velocity; however, when velocity is increased, shot must be inspected for breakdown more frequently for purging the system of broken shot.

Angle of Impingement. By definition, the angle of impingement is the angle, 90° or less, between the surface of the workpiece and the direction of the blast. As this angle is decreased from 90°, peening intensity is reduced. Peening intensity varies directly as the sine of the angle of impingement. When a low impingement angle is unavoidable, increases in shot size and velocity may be required to attain a desired intensity.

Breakdown of Shot. To maintain the required intensity and to provide consistent peening results, a production peening unit must be equipped with a separator that continuously removes broken or undersized shot from the system. The rate of removal should approximate the rate of wear and breakdown. The percentage of full-size and rounded shot in the system should never fall below 85%. Higher percentages are preferred. Sharp-edged broken media can scratch a part, generating a stress raiser; therefore, rounded shot, like minuscule peening hammers, is mandatory. Integral shot conditioners on peening machines consist of screens of air wash systems, neither of which can fully discriminate whether shot is broken because these devices are designed to handle only the specific weight of the shot. The only practical method of maintaining 85% good shot in the machine is to remove the entire shot load and reclassify it in a separate machine that distinguishes both size and shape.

Equipment

The equipment used in shot peening is essentially the same as that used in abrasive blast cleaning, except for certain auxiliary equipment made necessary by the more stringent controls imposed in the shot peening process. For a description of basic equipment, such as cabinets, wheels, nozzles, and conveyors, see the article "Mechanical Cleaning Systems" in this Volume.

The principal components of shot peening equipment are a shot-propelling device, shot recycling and classification arrangements, and a work handling conveyor. All portions of equipment that are exposed to the stream of shot are enclosed to confine the shot and permit it to be recycled.

Propulsion of Shot. Two methods of propelling the shot are used widely in shot peening. One uses a motor-driven bladed wheel, rotating at high speed. The other uses a continuous stream of compressed air.

In the wheel method, shot is propelled by a bladed wheel that uses a combination of radial and tangential forces to impart the necessary peening velocity to the shot. The position on the wheel from which the spot is projected is controlled to concentrate the peening blast in the desired direction. Among the advantages of the wheel method of propulsion are easy control of shot velocity when equipped with a variable-speed drive, high production capacity, lower power consumption, and freedom from the moisture problem encountered with compressed air.

The air blast method introduces the shot, either by gravity or by direct pressure, into a stream of compressed air directed through a nozzle onto the work to be peened. Aside from being more economical for limited production quantities, the air blast method can develop higher intensities with small shot sizes, permits the peening of deep holes and cavities by using a long nozzle, consumes less shot in peening small areas on intricate parts, and has lower initial cost, especially when a source of compressed air is already available.

In the late 1970s, another peening method was developed that uses gravitational force to propel the shot. Kinetic energy of the peening media is closely controlled by requiring the media to pass through a labyrinth before falling on the substrate from specified heights. Utilizing 1 to 2 mm (0.04 to 0.08 in.) hardened and polished steel balls as a peening media, surface finishes of less than 0.38 μm (15 μin.) are obtained while peening in the range of 0.23 to 0.38 mm (0.009 to 0.010 in.) Almen N shot peening intensities. Gravity peening has the drawback of requiring much more time for saturation, due to much lower impact velocities and greater shot diameter.

Cycling of Shot. Equipment for shot recycling consists of devices for the separation and removal of dust and undersize shot from the used shot mix. An air current or air wash, adjusted to the size of shot being processed, passes through a thin curtain of used shot as it falls through the separator. The air draws the dust and undersized shot from the mix, allowing the reusable shot to fall into a hopper for storage until needed at the peening machine. The major differences between the low-volume and the high-volume separators, illustrated in Fig. 5 and 6, are the use of trash removal screen in the low-volume separator (Fig. 5) prior to the air wash and the direct dumping of used shot from the elevator buckets into the separator (not shown), in contrast to the hopper and screw conveyor feed of used shot into the high-volume separator (Fig. 6). The effectiveness of the separator depends on careful control of the velocity of the air.

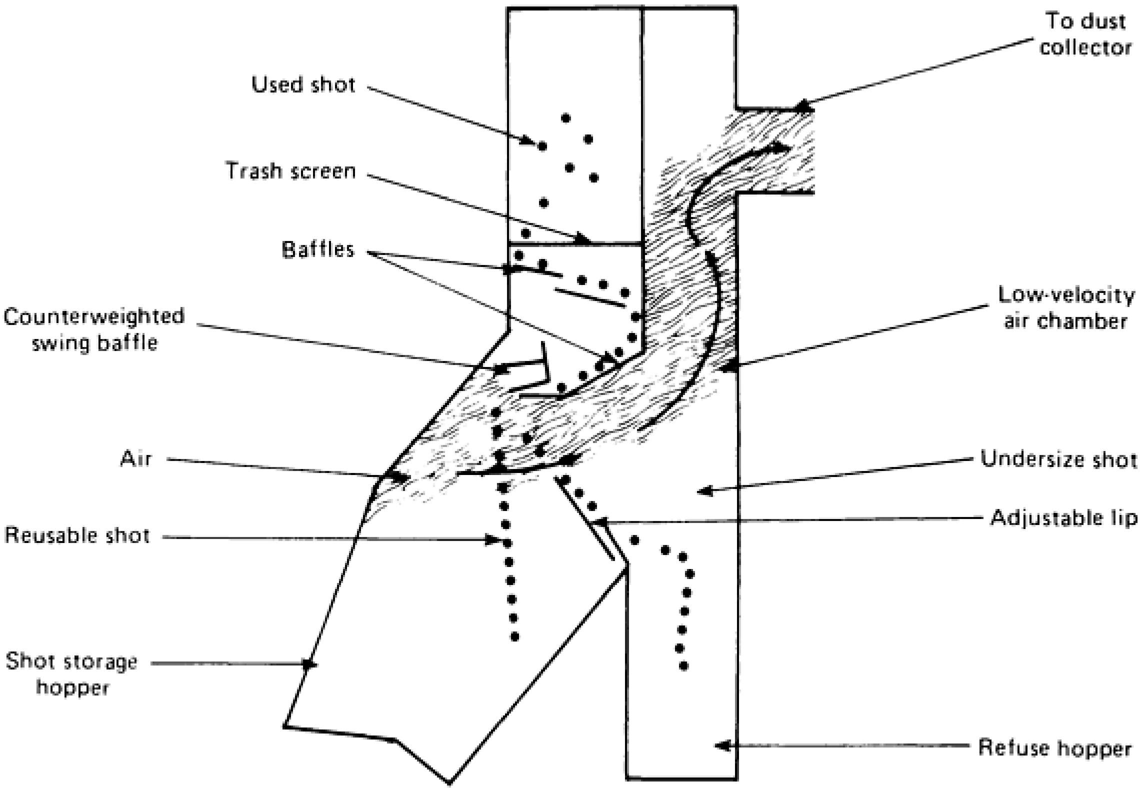


Fig. 5 Shot separator for use with a low-volume shot peening machine. Shot elevator not shown

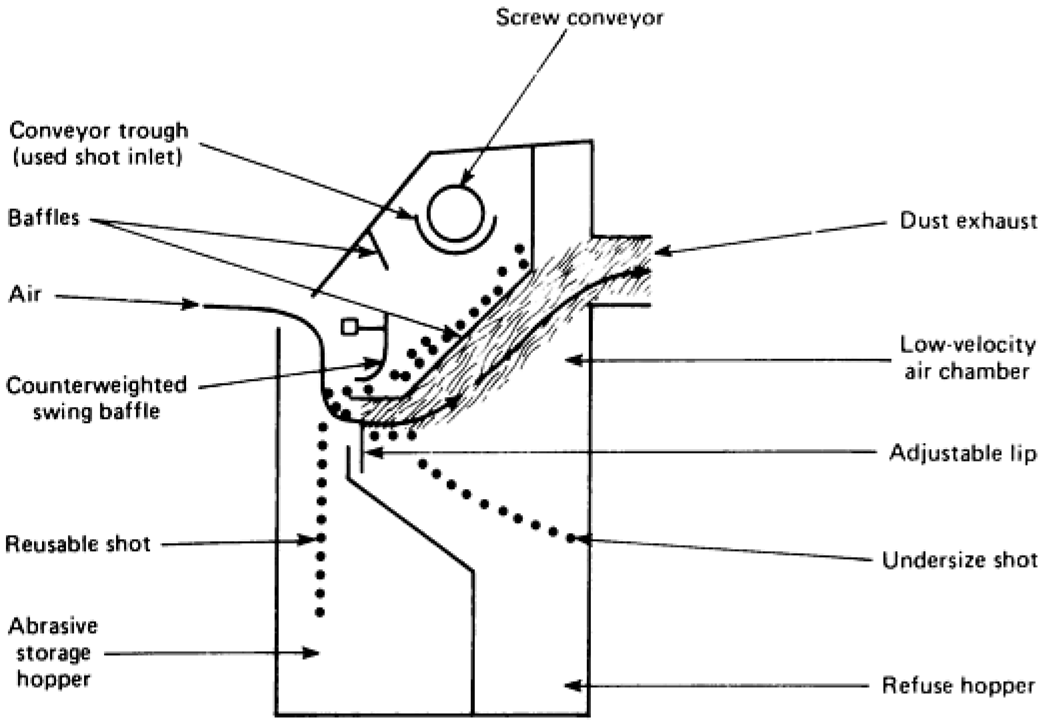


Fig. 6 Shot separator for use with a high-volume shot peening machine. Shot elevator and overflow not shown

Shot-adding devices automatically replenish the machine to maintain an adequate quantity of shot at all times. They are equipped with a capacitance switch or similar device to control the level of shot in the storage hopper and to add shot, as required, from a supply hopper.

Work Handling. The effectiveness of shot peening depends largely on peening intensity and adequate exposure of the workpiece to the blast stream. Proper exposure is facilitated by using efficient work-handling fixtures, conveyors, and mechanisms. Figure 7 shows six types of work-handling mechanisms, which incorporate several basic motions for effective exposure of parts with a variety of shapes.

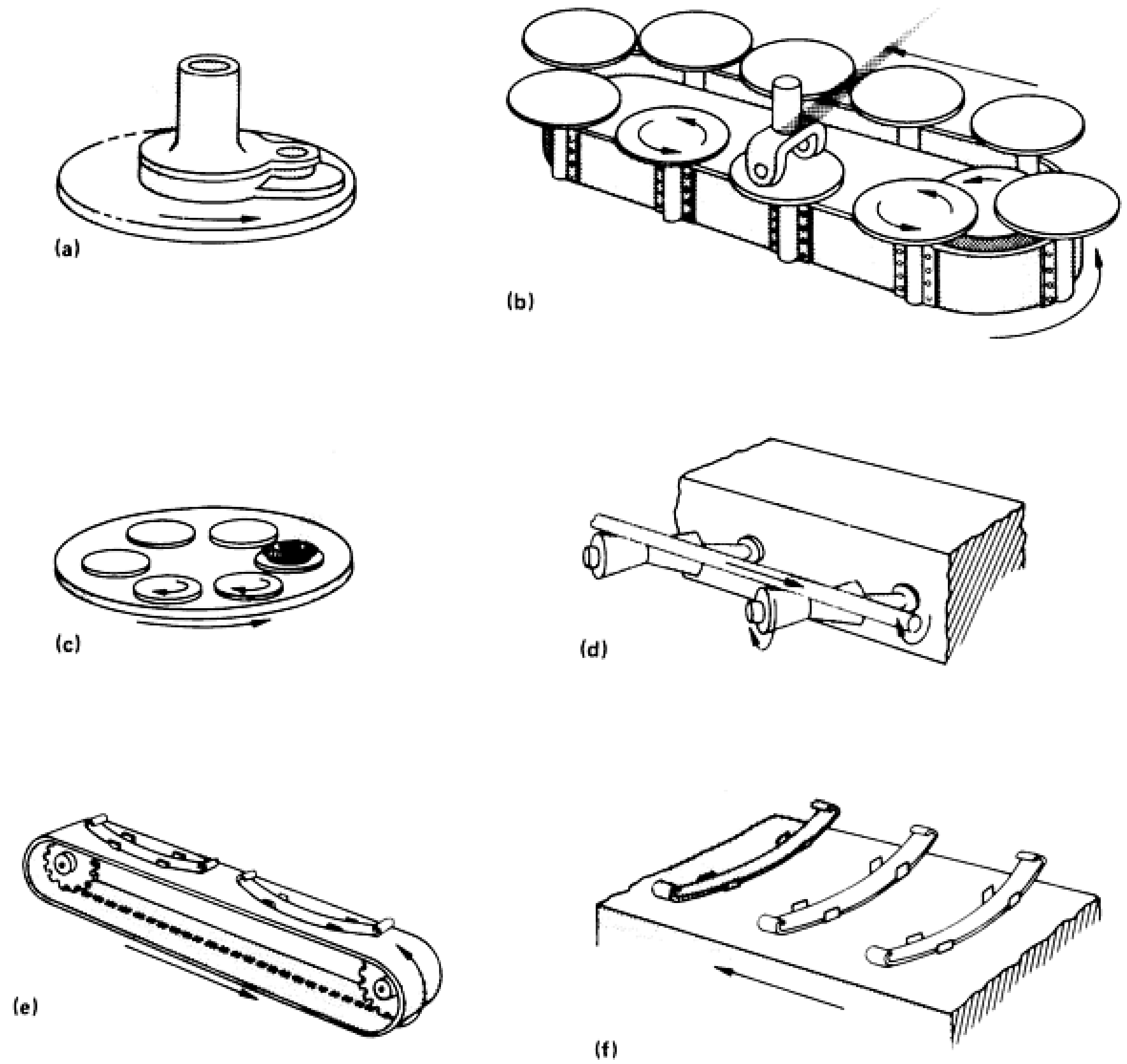


Fig. 7 Motion and fixturing used in work-handling equipment. (a) Rotation of work around a vertical axis in indexed position. (b) Rotation of work around a vertical axis, with straight-line travel. (c) Rotation of work around a vertical axis, with circular travel. (d) Rotation of work around a horizontal axis, with straight-line travel parallel to the axis of rotation. (e) Straight-line travel of work with no rotation. (f) Straight-line travel of work in a transverse direction

Stopoffs. Various methods and materials have been developed for masking parts that require shot peening on localized areas. Masking with tape is economical when low production quantities are involved, but its cost is prohibitive on a large-scale basis.

When fabrication of special masks is warranted, masks usually are designed to serve as holding fixtures as well as stopoffs. Ordinarily, masks of this type are made of molded urethane or rubber, as shown in Fig. 8. Large parts sometimes are protected with masks made of steel, carbide, polypropylene, or urethane.

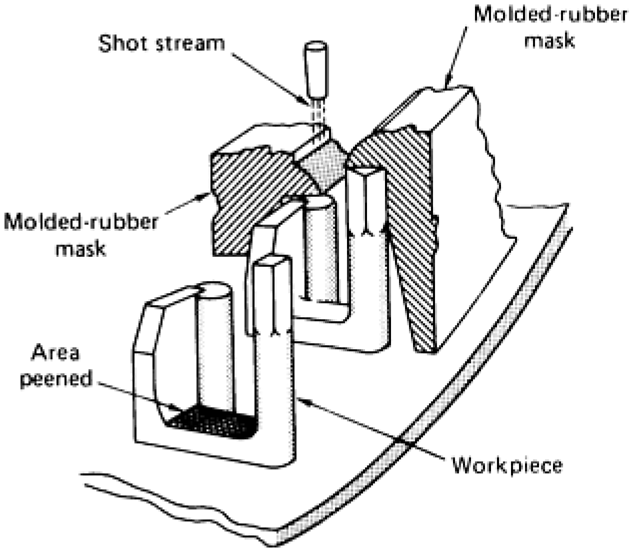


Fig. 8 Special mask made of molded rubber for shot peening a selected area and for holding the work during peening

Testing. Control of the shot peening process depends on systematic, periodic testing to determine intensity, coverage, and other important control factors. Standardized equipment for measuring peening intensity is illustrated and described in SAE Standard J442, "Holder and Gage for Shot Peening." A digest for measuring intensity is given in the section "Peening Test Strips, Holder, and Gage" in this article.

Dry Peening with Glass Beads. The methods used for dry peening with glass beads are comparable to the methods that use dry metallic shot. Separation of broken or damaged beads, as well as dust and other contamination, is accomplished by a centrifugal cyclone air separator, with final classification performed by a vibrating screen.

Wet Peening with Glass Beads. Wet glass peening is performed with glass beads, usually mixed in water and contained in a suitable hopper. In the automatic machine shown in Fig. 9, a mixer pump maintains a slurry of beads in water, and a feed pump forces the flow of slurry to the nozzle. The movement of slurry through the nozzle is accelerated by compressed air. The nozzles are attached to an oscillating bar that directs the flow of slurry at the workpiece. After making contact with the workpiece, the slurry is fed back to the hopper and recycled.

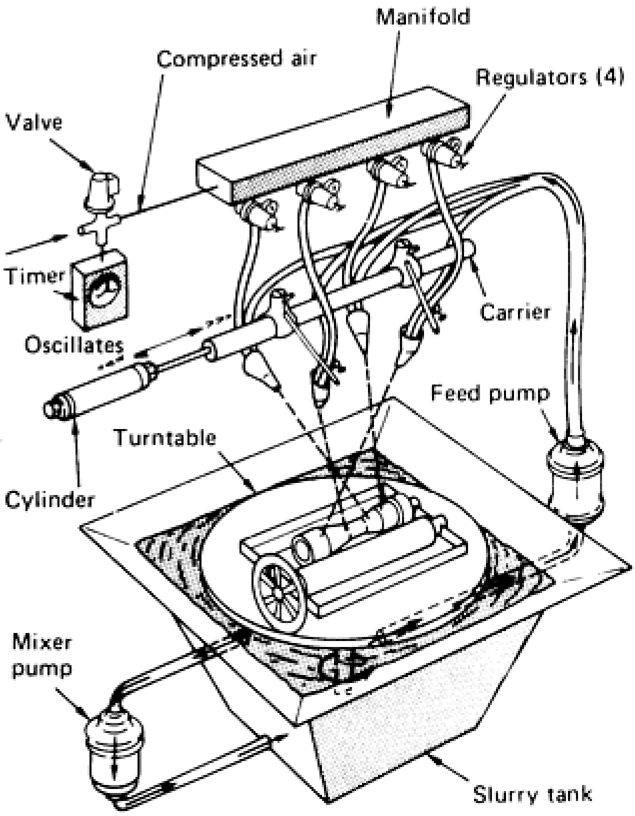


Fig. 9 Automatic machine for wet peening with glass beads

The principal controls in wet peening with glass are similar to those used in conventional shot peening. The peening pattern of the slurry is controlled by the oscillating nozzles. Air pressure is controlled at each nozzle by separate regulators. Exposure time for the peening cycle is controlled by automatic timing devices. Intensity of peening must be carefully matched to bead size, both to sustain maximum fatigue life of the peened part and to minimize bead breakage.

Applications

Although the major application of shot peening is related to improvement of fatigue characteristics, other useful applications have been developed, such as metal forming, straightening, improving resistance to stress corrosion, and testing the adhesion of plated deposits of silver on steel.

Improving Fatigue Properties. The improvement in fatigue strength obtained on several aluminum alloys and carbon and low-alloy steels is indicated in Table 2, which lists the type and size of shot, the peening intensity used on most of the materials, and data on the fatigue test specimens, the type of fatigue test, and the surface condition of specimens.

Forming. Shot peening is well suited for certain operations in the forming of thin sections. It has been used to form, as well as to strengthen, structural components of aircraft. An example is integrally stiffened aircraft wing panels. These were machined from slabs of aluminum alloy 2024-T6, 7075-T6, or others, which had to be curved for aerodynamic reasons. The large size of these panels, 10 m (32 ft) by 1.2 m (46 in.), precluded the use of hot forming. Cold forming produced surface tensile stresses of 140 MPa (20 ksi) or more, which were alleviated by shot peening the panels on the tension side. Proper curvature of the panels could be obtained by shot peening alone, with careful control of intensity. The need for conventional cold forming methods was avoided, and the high compressive stresses induced by peening reduced the probability of early fatigue failure.

Other parts that have been successfully formed by peening techniques include precision collets and large aluminum tubes that were preformed in halves in a press brake and peened to the desired diameter.

Straightening and correcting of distortion by peening have been used in salvaging parts. For example, large ring gears, 915 mm (36 in.) outside diameter by 19 mm ($\frac{3}{4}$ in.) thick, developed 3 mm ($\frac{1}{8}$ in.) out-of-roundness as a result of heat treating. Shot peening restored the gears to within 0.13 mm (0.005 in.) of perfect roundness. In another instance, shafts 50 mm (2 in.) outside diameter by 2 m (80 in.) long developed a 19 mm ($\frac{3}{4}$ in.) bow, which was straightened to within 0.8 mm ($\frac{1}{32}$ in.) by shot peening.

Improving Resistance to Stress Corrosion. Stress corrosion is a complex interaction of sustained tensile stress at a surface and corrosive attack that can result in brittle failure of a ductile material. Cracking due to stress corrosion has been associated with several metals, including brass, steel, stainless steel, aluminum, zinc, titanium, and magnesium. The surface tensile stresses that cause stress corrosion can be effectively overcome by the compressive stresses induced by shot peening, with either steel shot or glass beads.

In one case, test bars, 11.1 mm (0.437 in.) in diameter were cut in the short transverse direction from a 7075-T6 aluminum alloy hand forging and stressed to 75% of the yield strength. During alternate immersion tests in $3\frac{1}{2}$% sodium chloride solution, unpeened specimens failed in 1, 5, 17, and 28 days, respectively. Specimens peened in the unstressed condition with S230 cast steel shot lasted 365 and 730 days, when failure occurred in the unpeened grip outside the test area. During exposure to an industrial atmosphere, similar unpeened test bars failed in 20, 37, 120, and 161 days, respectively, whereas a peened specimen under the same conditions as above was uncracked when it was removed from testing after an exposure of $8\frac{1}{2}$ years.

Salt-fog tests on axial tension-test specimens of martensitic stainless steel showed that failure could be expected in a few days at stresses between 275 MPa (40 ksi) and 965 MPa (140 ksi). Shot peened specimens stressed at 690 MPa (100 ksi) lasted 14 to 21 days, as compared to 2 to 4 days for unpeened specimens. At a stress of 415 MPa (60 ksi), no failure of a peened specimen had occurred in 75 days, at which point the test was discontinued. Peening was beneficial, but it could not prevent stress corrosion at high stress levels. Table 3 presents stress-corrosion data indicating the life of peened and unpeened specimens of magnesium alloys, brass, and stainless steel in various corrosive mediums. All of these materials showed a high degree of improvement in resistance to stress corrosion as a result of shot peening.

Table 3 Effects of shot peening on stress-corrosion life of alloys

Material	Solution to which exposed	Time to failure	
		Unpeened	Peened
Magnesium, AZ31B-H	Potassium chromate and sodium chromate	110 s	>10 days
Magnesium, AZ61A-H	Potassium chromate and sodium chloride	$9\frac{1}{4}$ min	430 h
Brass cups, cold drawn	Ammonia	$2\frac{1}{2}$ h	19 and 47 h

Testing Adhesion of Silver Plate. The successful use of silver as a heavy-duty bearing material depends on a uniform high-strength bond between the silver plate and the steel substrate. Evaluating the integrity of the bond by peening has been accomplished with a high degree of reliability. Use of this technique on other electrodeposits is unknown. In the poorly bonded areas, the silver deforms plastically under the peening action of the shot and forms wrinkles or blisters.

Shot peening intensities required for revealing defectively bonded areas may be determined experimentally, using the data in Fig. 10 as a guide. Figure 10(a) shows the minimum shot peening intensity required to blister poorly bonded silver plate in relation to the thickness of the plate. Silver is plated at least 60% thicker than the finished dimensions require. The plate is then machined to a uniform extra thickness for peen testing. The intensity is adjusted to +0.004, -0 of that indicated in Fig. 10(a). Uniform coverage and exposure time should be maintained. Masking is applied to the unplated areas. After peening, the surface is machined again to final dimensions. Data in Fig. 10(b) show the relation between the minimum thickness of silver for peen testing and the maximum finished thickness of silver.

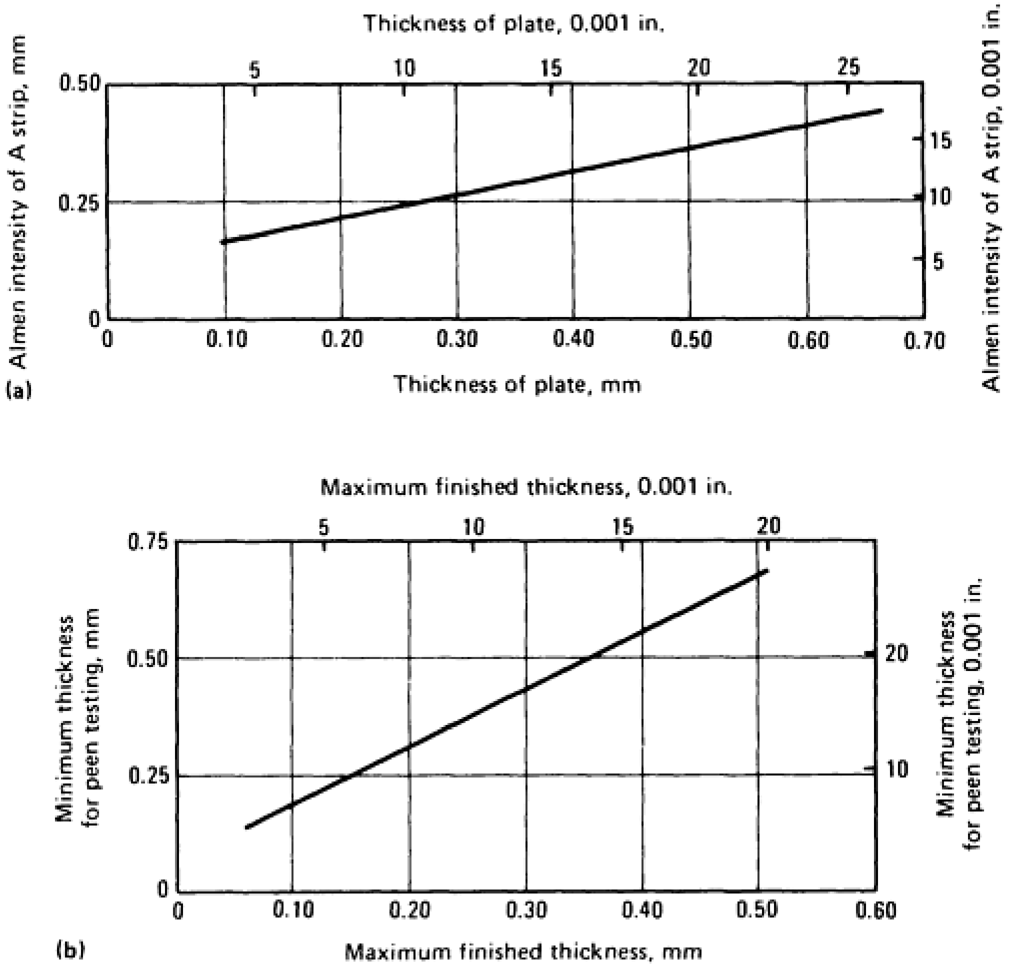


Fig. 10 Peen testing of silver plate on steel. (a) Minimum shot peening intensity required to blister poorly bonded silver plate, shown as related to plate thickness. (b) Relation between minimum thickness of silver plate for peen testing and maximum finished thickness of plate.

Limitations

Shot peening has few practical limitations in terms of the materials or the size, shape, quantity, surface condition, and surface hardness of parts that can be peened. Major limitations are not related to the mechanical aspects of the peening process, but to subsequent processing, such as the effects of machining and post-peening elevated temperature, that can nullify the beneficial results of shot peening.

Size and Shape of Workpiece. The size of the peening cabinet is usually the only limitation on the size of workpiece that can be peened. To some extent, even this limitation can be overcome by the use of portable mechanized peening equipment. Provided the surface to be peened is accessible to the blast, the shape of a workpiece is seldom a limitation. The peening of small radii in fillets and thread roots is limited by the smallest available media size, currently 0.0200 mm (0.001 in.) diameter glass beads. Sharp edges that must retain their sharpness should not be peened.

Surface condition, provided the workpiece surface is free of gross contaminants, is seldom a limitation in shot peening. Water, oil, and grease seriously contaminate the shot and interfere with peening quality and effectiveness. An as-forged surface usually shows greater improvement in fatigue strength than a polished surface as a result of peening. Cast surfaces respond as well to peening as wrought surfaces. Peened aluminum parts may be bright-dipped before being anodized.

Temperature Limitations. Low tempering temperatures, such as those conventionally used for carburized parts, have no adverse effect on peening stresses. Low-alloy steels can be heated to about 175 to 230 °C (350 to 450 °F) for about a half hour before significant decrease in the compressive stresses occurs. Steels intended for elevated-temperature application usually withstand temperatures of 260 to 290 °C (500 to 550 °F) without undergoing a significant stress-relieving effect; however, exposure at 540 °C (1000 °F) or above relieves induced stresses in all high-temperature alloys. Exposure to temperatures above 175 °C (350 °F) can eliminate the induced compressive stresses in some alloys of aluminum.

Problems in Production Peening

Problems in the shot peening of production parts have been corrected by a variety of solutions. A small forging, as shown in Fig. 11(a), contained two holes with thin-wall sections. The inner bearing surfaces had to be held to a tolerance of 0.013 mm (0.0005 in.). In shot peening a hole with a heavy walled section, the size of the hole is reduced by the peening action. With the thin-wall section here, the size of the hole was not reduced, but the hole became oval shaped. The solution to this problem required the establishment of new dimensions before shot peening that permitted a light honing operation after shot peening to bring the hole size to within dimensional requirements.

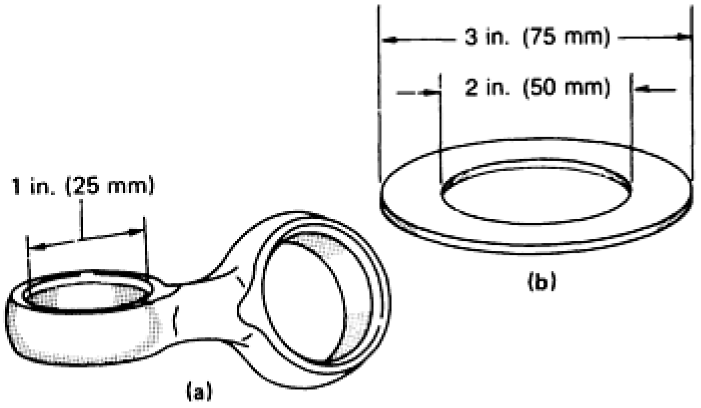


Fig. 11 Production parts that presented problems in shot peening

In another instance, a flat ring, as shown in Fig. 11(b), failed in fatigue either by cracking from the inside diameter to the outside diameter or by flaking. Shot peening eliminated the fatigue failures but caused the parts to dish as well as to warp. These parts were required to retain flatness to within a tolerance of 0.013 mm (0.0005 in.). After various intensities were tried, the distortion problem was solved by peening one side of the ring at a higher intensity than that used on the other side, depending on warpage direction.

In shot peening the fir-tree serrations of type 410 stainless steel compressor blades used in a jet aircraft engine, as shown in Fig. 12, it was determined that a maximum improvement of 26% in the fatigue life of serrated blade roots could be obtained only if a closely controlled peening procedure was followed. Certain variations from this procedure actually proved harmful to blade life. An alteration in peening intensity had a marked effect on fatigue characteristics. Variations in blast intensity that could be obtained by changing nozzle size, aspirator size, or the distance from the nozzle to the work are given in Table 4.

Table 4 Peening intensity as affected by nozzle and aspirator sizes and distance from nozzle to work

Test	Nozzle size	Aspirator size	Almen intensity, A strip, 0.025 mm (0.001 in.),

No.[a]					at given distance from nozzle to work, mm (in.)				
	mm	in.	mm	in.	200 (8)	180 (7)	150 (5)	120 (5)	100 (4)
1	9.5	$\frac{3}{8}$	4	$\frac{5}{32}$	5.5	4	5	5.5	5
2	9.5	$\frac{3}{8}$	5.5	$\frac{7}{32}$	4	5.5	5	5.5	5
3	13	$\frac{1}{2}$	4	$\frac{5}{32}$	3	2.5	3	3	3.5
4	13	$\frac{1}{2}$	5.5	$\frac{7}{32}$	5	6	7	7	7
5	16	$\frac{5}{8}$	4	$\frac{5}{32}$	7	6	5.5	7	7-8
6	16	$\frac{5}{8}$	7	$\frac{9}{32}$	6	6.5	7	7	7.5

(a) Tests made using suction shot peening test cabinet, 70 steel shot; pressure 635 kPa (92 psi); flow of shot to nozzle 3.3 kg/min ($7\frac{1}{4}$ lb/min)

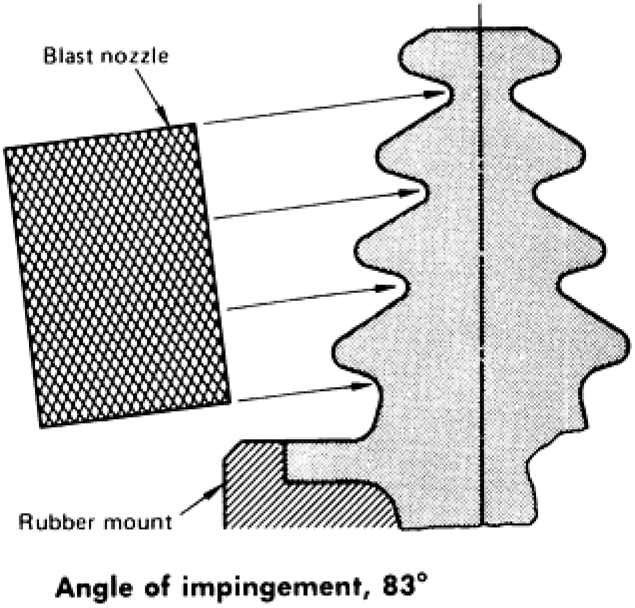


Fig. 12 Relation of nozzle angle, angle of load face, and resulting angle of impingement in peening root serrations of compressor blades. Angle of impingement, 83°

The procedure adopted consisted of peening the root serrations with S70 steel shot at an intensity of 0.007 to 0.008 A at an impingement angle of 83°. The intensity indicated was measured at an impingement angle of 90°. The true intensity on various portions of the root serrations was considerably less, depending on impingement angle; however, maximum intensity was obtained at the critical root radius, using the 83° impingement angle calculated to have this effect. The relation between impingement angle and intensity is shown in Fig. 13.

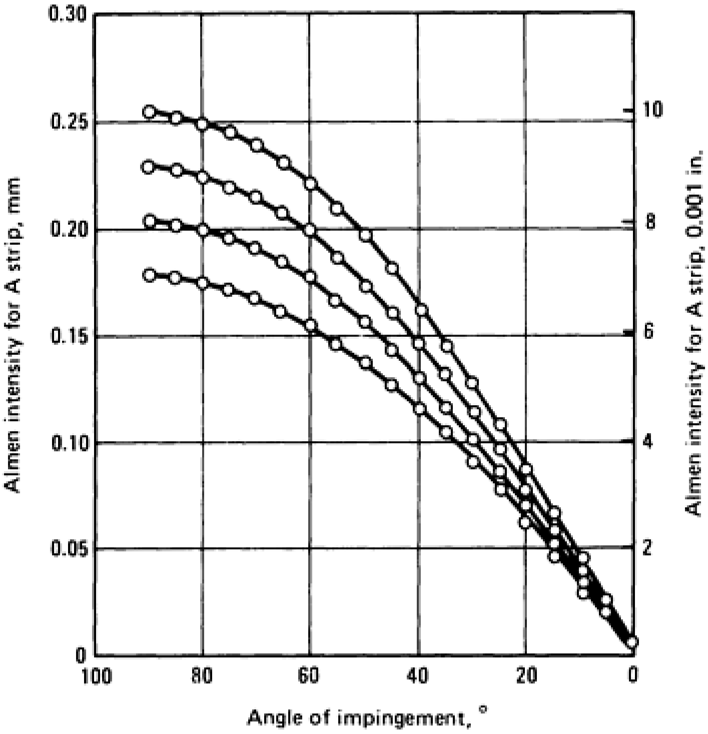


Fig. 13 Peening intensity as a function of angle of impingement

Peening was performed in a gravity-feed, continuous-conveyor production cabinet, using a 16 mm ($\frac{5}{8}$ in.) bore diameter nozzle, a 4 mm ($\frac{5}{32}$ in.) aspirator, 635 kPa (92 psi) air line pressure, and a shot flow of 3.4 kg/min (7.5 lb/min). The distance from the nozzle to the work was set at 100 mm (4 in.). The cabinet conveyor moved at a fixed speed that exposed the work to the blast for a period of 5 s. The peening operation required two passes under the nozzle, one for each side of the blade root. The airfoil sections of the blade were protected from the blast by a sheet rubber covering.

Costs

The cost of shot peening on a production basis depends on several factors, including the size, shape, and hardness of parts, the total area to be peened, and the required intensity and coverage. Shot type, size, and velocity also influence costs, because they affect peening intensity, rate of shot breakdown, and the rate at which the desired coverage is obtained.

With an increase in shot velocity, the rate of shot breakdown increases far more rapidly than the intensity of the peening blast; however, the weight of a shot pellet varies directly, while the number of pellets per kilogram (pound) of shot varies inversely, with the cube of the diameter of the pellet. Consequently, for a given Almen intensity, coverage is obtained much more rapidly with smaller shot and higher velocity. Because of these opposing factors, the number of kilograms (pounds) of shot used per part is virtually the same for various shot sizes, assuming similar intensity, coverage, and control of uniform shot size. The use of small shot at high velocity increases production rate and reduces labor costs.

Processing after Peening

Shot peening itself is a finishing treatment, and usually no further processing of peened work is required, except for the application of a rust preventive on low-alloy steels. The as-peened surfaces of these steels are clean and chemically active and are highly susceptible to corrosion from fingerprints and other contaminants. Such surfaces are also highly receptive to oils for rust prevention and lubrication, and they provide an excellent base for organic or inorganic coatings that do not require thermal treatment other than low-temperature baking. Temperatures high enough to relieve the beneficial compressive stresses imposed by peening must be avoided.

Stainless steel that has been peened with iron or steel shot should be passivated to counteract contamination by iron particles, which causes rusting. Passivation is not required for use at elevated temperature. Secondary peening with glass beads, after peening with steel shot, removes contaminating ferrous residue and increases the fatigue life of the peened part.

Because the compressive layer induced by peening is relatively thin, subsequent grinding or machining of peened surfaces should be avoided, except for aluminum and magnesium alloys that have been peened to a greater depth. As much as 0.13 mm (0.005 in.) may be removed from the surface of these alloys without harmful effect to the peened layer, and the improved surface finish may prove beneficial to fatigue properties; however, a knowledge of stress gradients must be available before stock removal.

Steels may be lightly honed or lapped after peening. There is limited evidence that these operations for fine-particle abrasive blasting have a beneficial effect where maximum fatigue resistance is desired. After peening, straightening or cold forming by conventional methods should be avoided. These operations may result in a complete reversal of the stress pattern. Peen straightening and peen forming, however, are permissible, because these processes do not introduce harmful residual tensile stresses.

Peening Test Strips, Holder, and Gage

SAE standard J442 describes the test strips, strip holder, and gage used in measuring shot peening intensity.

If a thin flat piece of steel is clamped to a solid block and exposed to a blast of shot, it will be curved after removal from the block. The curvature is convex on the peened side. The extent of this curvature on a standard sample serves as a means of measurement of the intensity of the peening.

Standard test strips of three thicknesses used are shown in Fig. 14. Made of 1070 cold-rolled spring steel, these strips have a specified hardness of 44 to 50 HRC. Strip A is recommended for testing intensities that produce curvatures having arc heights ranging from 0.15 to 0.60 mm (0.006 to 0.024 in.). For lesser intensities, the N strip is recommended. For greater intensities, the C strip is used. The relationship between strips A, C, and N is shown in Fig. 15. The data represent readings for conditions of identical blast and exposure.

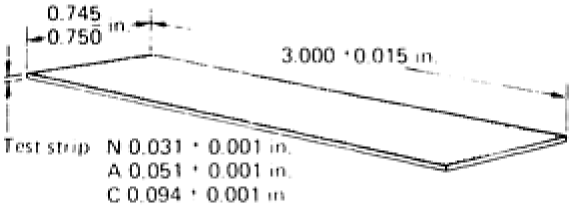
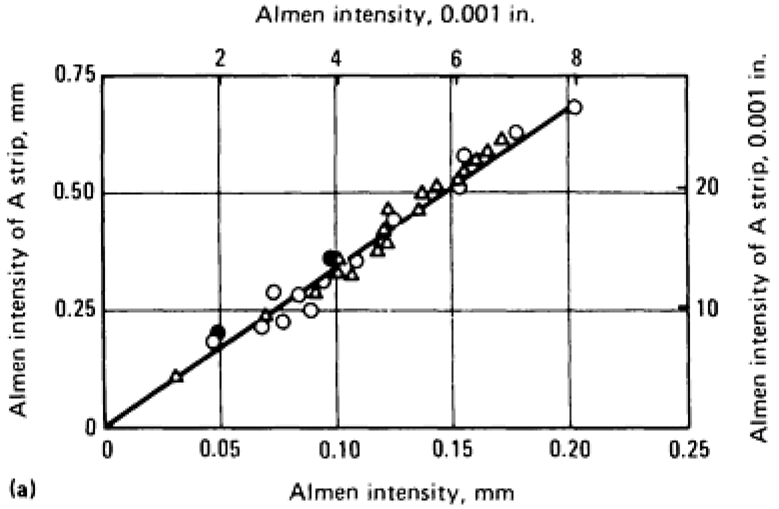


Fig. 14 Designations and dimensions of standard Almen test strips used in measuring shot peening intensity



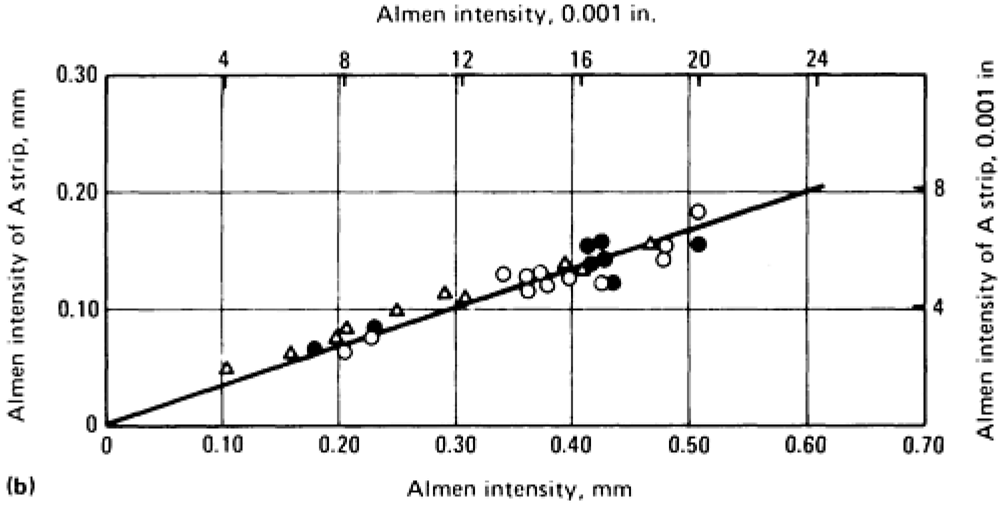


Fig. 15 Correlation of intensities as indicated by arc heights of A, C, and N strips peened under identical blast and exposure conditions. (a) C strip. (b) N strip (SAE J442)

During peening, the test strip is mounted on a holder as shown in Fig. 16. After being peened, the strip is removed and placed in an Almen gage (Fig. 17), located so that the dial indicator stem bears against the unpeened surface. The curvature of the strip is determined by a measurement of the height of the combined longitudinal and transverse arcs across standard chords. This arc height is obtained by measuring the displacement of a central point on the unpeened surface from the plane of four balls forming the corners of a rectangle. Almen gages are available with either analog or digital readout. In digital units, accuracy can be posted to four decimal places.

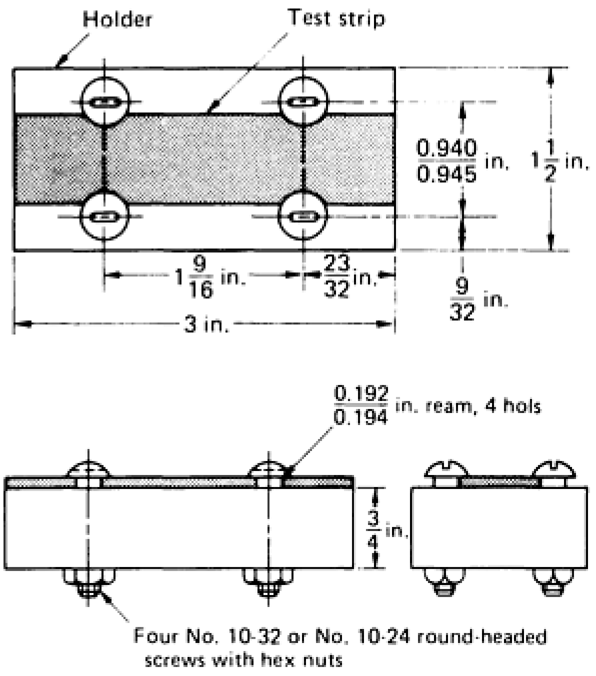


Fig. 16 Assembled Almen test strip and holder

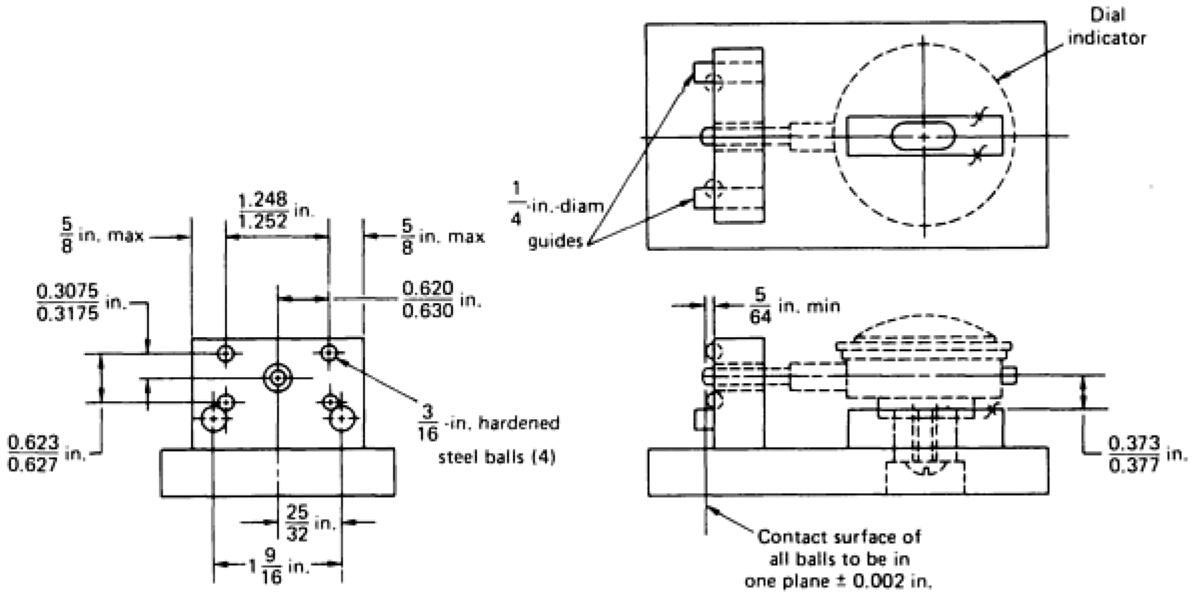


Fig. 17 Almen gage for measuring arc height for test strip

The standard designation of intensity includes the gage reading or arc height and the test strip used. For example, 0.013 A signifies that the arc height of the peened test strip is 0.33 mm (0.013 in.) and that the test strip used was of the A thickness. Uniform procedures for using the standard test strips described in the above digest of SAE J442 are provided in SAE Recommended Practice J443.

Topography of Surfaces

R.K. Morton, Rank Taylor Hobson Inc.

Introduction

MOST SURFACES have regular and irregular spacings that tend to form a pattern or texture on the surface. This surface texture is generated by a combination of various factors that are due either to the manufacturing process or the material being finished. Of the factors due to the material, the most fundamental is the microstructure of the material. For example, cast aluminum surfaces generally produce a granular surface when machined, while wrought aluminum alloys can be machined to produce a highly reflective, flat, and smooth topography. Internal stress in the material, released after machining, can also contribute to surface deformation.

The machining or finishing process itself has the greatest impact on the geometry of the surface. A major factor is the action of the cutting tool on the material. Elements such as tool shape, speed, feed, and cutting fluid can be varied to affect the surface topography. Other factors affecting the surface are the instability of the cutting tool due to chatter or imbalance in the grinding wheel, and errors in the machine tool guideway.

General Background

Reasons to Measure Surface Topography. The primary reason to measure a surface is to try to predict the performance of the component. As an example, a bearing surface requires a level of surface texture that allows lubricant to be retained in small pockets and at the same time allows the bearing to roll with a minimum of friction. If the surface is too rough, wear can quickly develop; however, if the surface is too smooth, inadequate lubrication and seizure might occur.

The other principal reason to measure a surface is to control the manufacturing process. By measuring the surface topography during processing, an operator can detect changes in the surface finish and adjust the manufacturing process to ensure that the process remains in limit.

The Components of a Surface. The topography of a surface is made up of a combination of three features (Fig. 1).

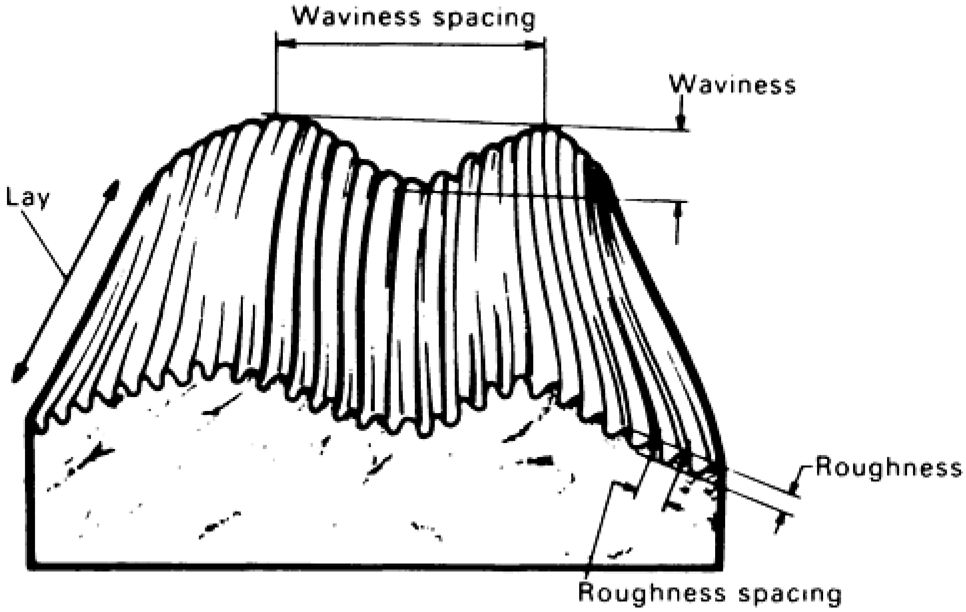


Fig. 1 Illustration of the roughness, waviness, and general form of a surface

Surface roughness refers to the high-frequency irregularities on the surface caused by the interaction of the material microstructure and the cutting tool action.

Surface waviness refers to the medium-frequency irregularities on the surface on which the surface roughness is superimposed. These forms can be caused by the instability of the cutting tool and errors in the machine tool guideway.

Surface form is the general shape of the surface, neglecting roughness and waviness, which are caused principally by errors in the machine tool guideway, and deformations due to stress patterns in the component.

Lay is another important feature of a surface. This is a machining pattern that has a distinctly directional characteristic, such as a parallel, circular, radial, or multidirectional pattern. The lay is an important consideration because surface topography measurements will differ depending on the direction from which they are taken. Measurement should be made perpendicular to the lay of the surface.

Measuring Surface Topography

Because the basic types of surface geometry are caused by different factors and tend to have different relationships to the performance of the component, it is conventional to consider them separately during analysis. In general, if control of aspects of component performance related to surface topography is required (e.g., wear characteristics, friction, reflectivity, resistance to stress failure, or lubrication properties), roughness is analyzed. If control of some aspect of machine tool performance or component performance (e.g., noise or vibration generation) is required, waviness is analyzed.

Surface Texture Recorder. The most common type of contact method for measuring surface topography is the surface texture recorder, the principle of which is shown in Fig. 2. The stylus of the instrument is moved across the surface via a guiding mechanism to produce the "traced profile," which is defined by the interaction of the stylus with the component. The transducer produces a signal that is the difference between the traced profile and a "reference profile" or "datum profile" provided by the guideway. The transducer signal is then converted into a digital signal via an analog-to-digital converter. At this point the transducer contains only the vertical or Z-component of the profile. The horizontal or X-component generated by the traversing mechanism is combined with the Z-component to produce the "total profile." The total profile is then filtered to remove unnecessary information, which produces a "primary profile." This profile can then be subjected to filtering techniques that can separate the roughness, waviness, and form features of the surface.

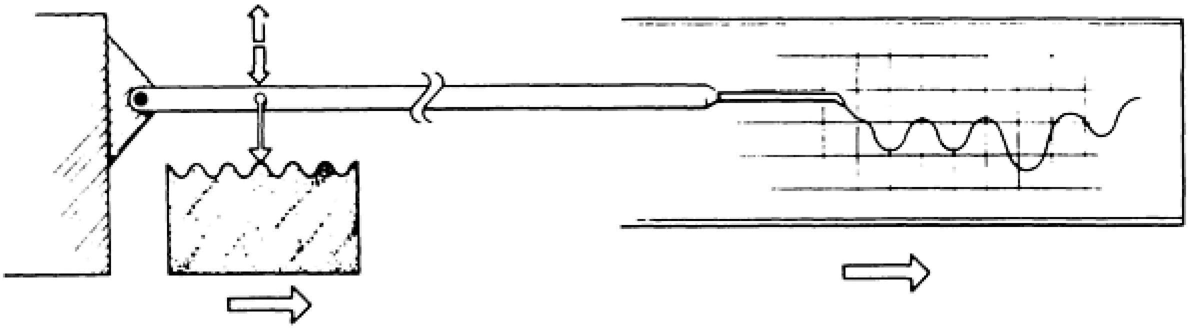


Fig. 2 Basic principle of a surface texture recorder

Noncontact techniques are becoming increasingly popular in the measurement of surface topography, especially for surfaces that may be subject to damage using contact techniques. The results obtained are very similar to those of stylus methods and can use the same parameter definitions. Some noncontact methods, such as diffraction measurement, can measure surfaces quickly and easily and can potentially be used on machine tools at the point of manufacture.

Some noncontact methods do have limitations in measuring certain surfaces. For instance, in surfaces with high slope, an insufficient intensity of light is reflected back to the detector and the focus lens begins to follow inaccurately. Another example is that on contaminated surfaces, the contamination is measured because there is no force to remove it, and this distorts the results. Oxide layers on surfaces such as aluminum can also present problems, because the focusing lens will oscillate between the top and bottom of the oxide layer, giving the false impression of a very rough surface.

The focus-follow method (Fig. 3) involves the use of a moving lens to try to keep a spot of light focused on the surface. The lens movement correlates to the profile of the surface and its vertical movement is controlled by an electric motor. The analog electrical signal generated to drive the motor is digitized and processed in the same manner as a contact stylus. A variation of this method involves the use of a separate transducer to monitor the position of the lens; the electric signal from this transducer is used in the same manner as a contact stylus.

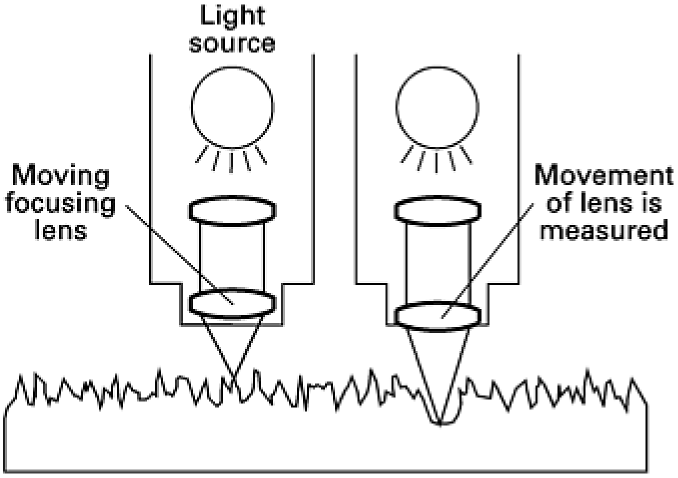


Fig. 3 Focus-follow method for noncontact measurement of roughness

Multiple-beam interferometers, such as the Fizeau interferometer, also have useful application in microtopography. They are used with a microscope to provide high resolution in three dimensions. The interference microscope divides the light from a single-point source into two or more waves. In multiple-beam interference microscopes, this is done by placing a partially transmitting and partially reflecting reference mirror near the surface of the specimen (Fig. 4).

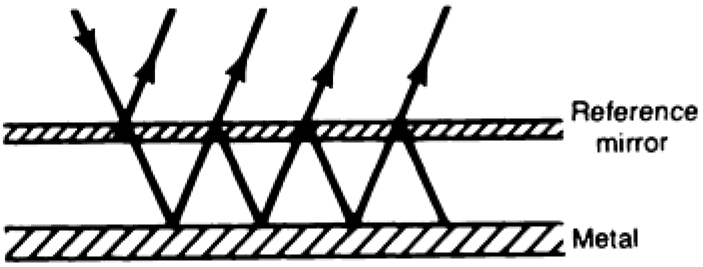


Fig. 4 General principle of a multiple-beam interferometer

The multiple beams illustrated in Fig. 4 are superimposed after traveling different lengths. This produces interference patterns, which are magnified by the microscope. The interference fringes having a perfectly flat surface appear as straight, parallel lines of equal width and spacing. Height variations cause the fringes to appear curved or jagged, depending on the unit used. With multiple-beam interferometers, height differences as small as $\lambda/200$ can be measured, where λ is the wavelength of the light source.

Lasers can provide a monochromatic light source, which is required in interference microscopes. Typical systems can provide displays of isometric plots, contour plots, and qualitative parameters, such as surface roughness, camber, crown, radius of curvature, cylindrical sag, and spherical sag.

The Profile. Before surface topography assessment can be understood clearly, an important factor needs to be explained concerning the measured profile generated from the surface. To obtain a reasonably clear display of the height and spacing of the surface profile, the vertical stylus deviation typically needs to be magnified by at least 5,000×, whereas the horizontal measurement length is magnified by about 100×. So it is important to note that the resultant display is not a magnified cross section of the surface. Figure 5 provides an illustration of this principle.

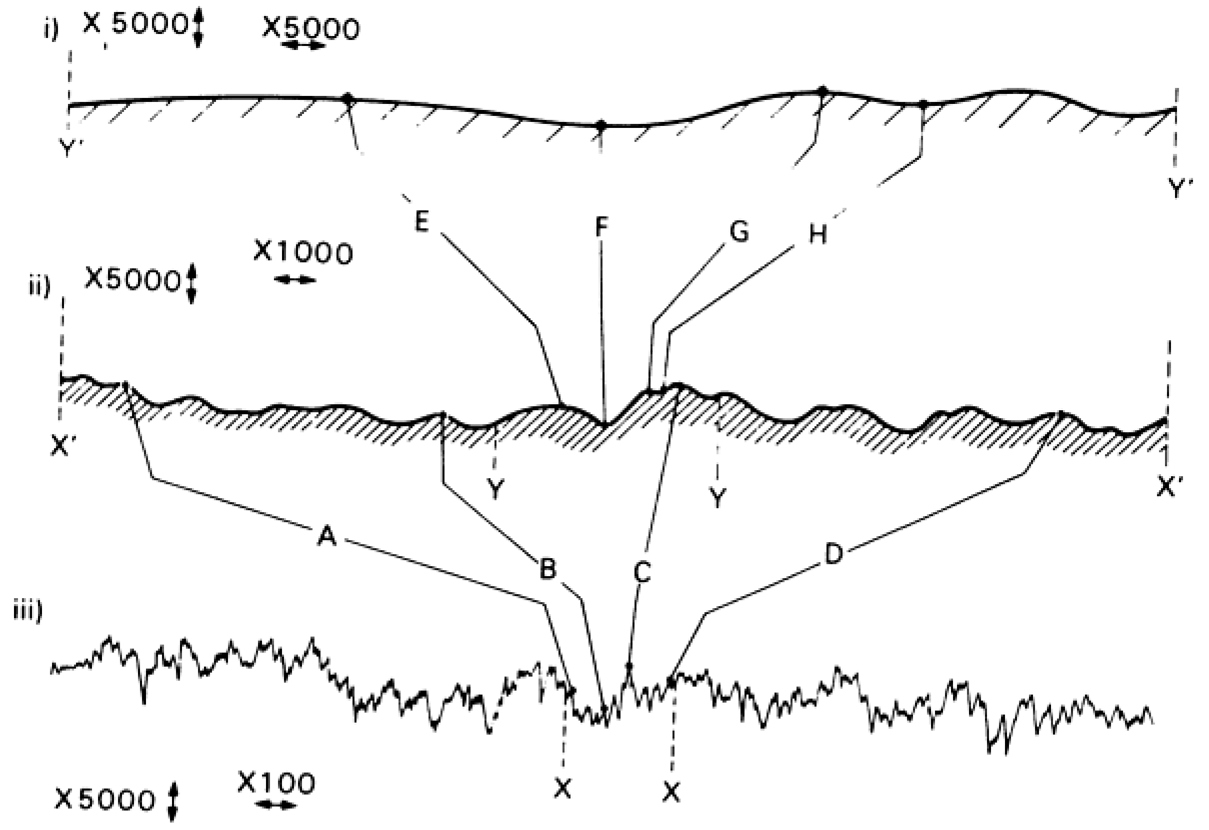


Fig. 5 Diagram illustrating how the profile shape varies as V_h, horizontal magnification, is reduced relative to V_v, vertical magnification. (i) Surface profile magnified 5000× equally in all directions. (ii) Profile with V_v:V_h ratio of 5:1. (iii) Profile graph recorded with a V_v:V_h ratio of 50:1. As the horizontal magnification of the profile is increased, the length X-X is expanded to X'-X' and the peaks A, B, C, and D appear flatter. Increasing the horizontal magnification still further until it equals the vertical magnification expands the length Y-Y to Y'-Y'. Peaks E and G and valleys F and H now appear much flatter, but the actual difference in heights of the corresponding peaks and valleys in (i), (ii), and (iii) are exactly the same.

Parameters

For effective analysis of surface roughness or waviness, the profile generated by the measuring instrument needs to be evaluated according to internationally recognized mathematical formulas, called parameters. The purpose of using a parameter is to apply a number that can characterize a certain aspect of the surface and hence remove the need for subjective operator assessment. It is not possible to characterize a surface completely with a single parameter, so a combination of parameters is normally used.

Parameters can be separated into four basic types:

- *Amplitude parameters* are measures of the vertical characteristics of the surface deviations.
- *Spacing parameters* are measures of irregularity spacings along the surface, regardless of the amplitude of these irregularities.
- *Hybrid parameters* analyze a combination of the amplitude and spacing of the surface irregularities.
- *Extended parameters* are not simply defined by the profile data and require further inputs or attributes.

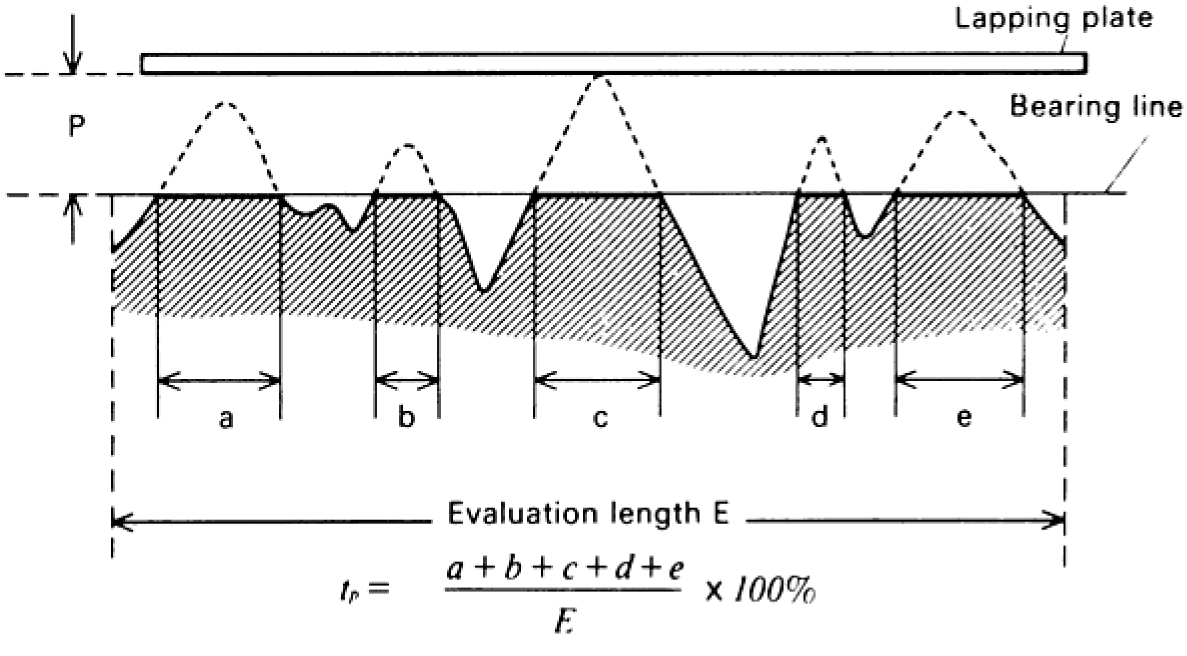
In order to characterize a surface using parameters, between three and six parameters must be chosen, including at least one of each of the types listed above. Examples of different types of parameters and how they are applied can best be described by discussing the various types of surfaces generated by finishing methods.

Ground, Turned, and Milled Machined Surfaces. One of the most commonly used roughness amplitude parameters is the roughness average (R_a), which is used to assess the coarseness of the surface such as those produced by grinding, turning, and milling operations. The parameter R_a is defined as the mean height of the roughness profile. It does have some significant drawbacks in that many differing profiles can have the same Ra and yet have very different performance characteristics. Another averaging parameter, R_q, takes the root mean square of the profile and is more sensitive to surface variations.

Surfaces Subject to Stress. For some surfaces it is sometimes desirable to specify the maximum roughness height, R_{max}, or the peak-to-valley height, R_z, rather than use the mean height given by R_a. The R_{max} parameter measures the highest and lowest points of the profile and is particularly valuable where components are subjected to high stresses. Any large peak-to-valley heights may be areas likely to suffer from crack propagation. However, because R_z is very susceptible to dirt or scratches, it is an unstable parameter. It is usual to take an average of the individual peak-to-valley heights, which can be done in slightly different ways with the parameters R_{tm} (R_z in DIN specifications) and R_z in ISO specifications.

Sheet Steel and Peak Counting. Although roughness amplitude is very important in most applications, the spacing of the roughness peaks can be equally important. Particularly in the manufacture and use of sheet steel, surface texture control is necessary to obtain consistent lubrication when forming the sheet, avoid scoring, and prevent the texture from showing through the paint on the finished product. Amplitude parameters such as R_a are not sufficient to specify the different types of texture that can be obtained from the rolling process. The peak count parameter, P_c, allows the operator to monitor and control the roughness peak spacing as well as the amplitude, thus producing a better bonding of finishes, a more uniform finish of plating and painting, and a reduced risk of cracking during drawing or forming operations. Peak spacing is also an important factor in the performance of friction surfaces such as brake drums. The high spot count is another spacing parameter; it is used frequently by the automotive industry on cylinder liners and other surfaces where the lubrication characteristics of the topography are important.

Bearing Surfaces. The most common use of engineering surfaces is to provide a bearing surface for another component moving relative to it, resulting in wear. The material ratio parameter, T_p (in %), is commonly used to simulate the effect of wear on a surface. Material ratio is defined as the ratio of the length of the surface to the evaluation length at a specified depth in the profile. A practical example is to imagine a surface plate resting on the highest peak of a profile as illustrated in Fig. 6. As the peaks wear and the material line (the top line of the remaining profile) descends, the length of the bearing surface (the length of the profile in contact with the lapping plate) increases. The parameter T_p can thus be used to control bearing surfaces as well as surfaces requiring lubrication.



$$t_p = \frac{a+b+c+d+e}{E} \times 100\%$$

Fig. 6 Illustration showing the derivation of material ratio, t_p

Plateau Honed and Lapped Surfaces. The R_k parameter uses the material ratio curve for analysis. It is commonly used to evaluate plateau honed surfaces, which are the result of multiple machining operations. Peaks are removed and large valleys are created to retain lubrication. The parameter has a wide application in the automotive field.

In using the R_k parameter five primary areas are analyzed. All measurements and parameters are scale dependent.

- *Core roughness depth* (R_k) is the working part of the surface that, after the initial running-in period, will carry the load and influence the life and performance of the surface.
- *Reduced peak height* (R_{pk}) is the top portion of the surface that will be worn away in the running-in period. Used in conjunction with this is the parameter M_{r1}, the associated percent length of the top portion of the profile that will be removed during the same process.
- *Reduced valley depth* (R_{vk}) is the lowest part of the surface that has the function of retaining the lubricant during its working life. Used in conjunction with this is the parameter M_{r2}, which is the associated percent length of the bottom part of the profile that will be used to retain lubricant.

Reflective, Painted, Elastic, and Wear-Resistant Surfaces. A useful hybrid parameter that has a close correlation to various surface properties is the average slope of the surface. The slope of the profile is the angle (in terms of the gradient) that it makes with a line parallel to the center line. It is defined as the mean of all the slopes at all points on the profile.

The parameter can be used to measure the actual profile length (i.e., the length that would be occupied if all the peaks and valleys were stretched out in a straight line). The steeper the average slope, the longer the actual length of the surface compared with its nominal length. The parameter is employed in painting and plating applications where the length of the surface available for keying is important. It is scale dependent.

Average slope is also useful in assessing other properties of engineering surfaces. It can be related to the hardness and elasticity of the surface, where the higher the slope, the greater the chance of surface deformation upon loading. In assessing surface reflectivity a high slope indicates a surface with low reflectivity. Also, the higher the level of average surface slope, the higher the level of friction and the greater the level of wear.

Microstructural Analysis of Finished Surfaces

Donald C. Zipperian, Buehler Ltd.

Introduction

MICROSTRUCTURAL ANALYSIS of a finished surface can provide important information regarding material properties and reliability. For example, surface cracks or other machining damage can act as stress risers in brittle materials. Additionally, improper machining techniques can create excessive heat that results in smearing or alteration of the microstructure. Microstructural analysis has been used extensively for characterizing ferrous and nonferrous metals, but it is also extremely useful for characterizing advanced materials such as composites and ceramics.

Traditional quantitative metallography or stereology relates two-dimensional features, as seen on photographs or images, to the actual three-dimensional microstructure. Common measurements include grain size, inclusion rating, phase determination, and density of dislocations. E.E. Underwood has described the basic measurement techniques and their relationships to traditional stereological analysis (Ref 1). Prior to the time when computers and image analysis software became accessible, feature counting methods were used (e.g., a grid is used to frame the object, or a line of known length is drawn on a photograph and the number of features or intersecting points are counted). Although these techniques were surprisingly accurate, they were time-consuming and subject to human bias.

Modern quantitative image analysis has expanded the capabilities of surface analysis significantly with the use of computer technology. For example, a typical computer-based image analysis system can measure and statistically analyze a variety of surface features over a number of fields of view very quickly and accurately. Table 1 provides a list of common image analysis features and field measurements.

Table 1 Quantitative image analysis

Field measurements (stereology)	**Object measurements (feature measurement)**
Area fraction	Area
Area percent	Length
ASTM E 112 grain size	Width
Count	Aspect ratio
Perimeter	Feret measurements
Mean intercept distance	Perimeter
Mean particle surface area	Sphericity
Density	Convex perimeter
	Roughness
	Breath
	Orientation

Reference

1. E.E. Underwood, Quantitative Metallography, *Metallography and Microstructure,* Vol 9, 9th ed., *Metals Handbook,* American Society for Metals, 1985, p 123-134

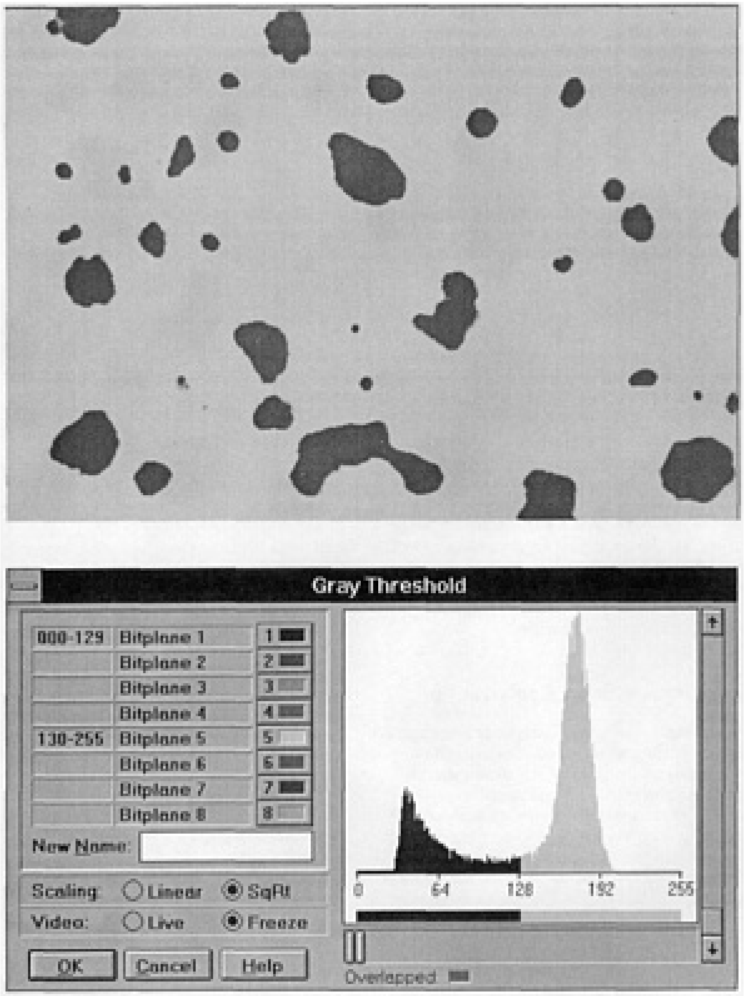
Quantitative Image Analysis

Computer-based image analysis is a contrast-based microstructural analysis tool that is finding widespread use because of significant improvements in computer speed and memory capabilities. The modern quantitative image analysis systems driven by personal computers can handle complex images quickly and accurately, with resolutions comparable to those of the human eye. The most economical image systems convert an analog camera signal to a digital signal through a hardware processor. Although digital cameras are available, they are significantly more expensive.

Image analysis consists of six basic steps (Ref 2):

1. *Image acquisition* for microstructural analysis is accomplished with a microscope and a video camera.
2. *Image enhancement* is required to correct for nonuniform illumination and to sharpen the digitized image. Image sharpening is required because the conversion from an analog signal to a digitized signal does not produce sharp edges. Delineation, the most commonly used image enhancement function, converts digitized signals to a square-wave function, thus producing sharper images.

3. *Feature detection* (also called *thresholding*) assigns specific contrast values to the image (0 to 255 gray levels). The most accurate and precise method for properly thresholding an image is to use a gray-level histogram. Figure 1 shows a porous steatite ceramic sample and the corresponding gray-level histogram. The darker phase (porosity) occurs at a lower value and is detected between gray levels of 0 to 129; the lighter phase (background matrix) is detected between gray levels of 130 to 255.
4. *Editing* is used to separate, delineate, or classify features based on their morphology or size. Examples of editing functions include dilation, erosion, grain-boundary reconstruction, filing, elimination, and chord sizing. These functions are used to add or remove pixels, rebuild missing or incomplete boundaries, fill in undetected features, or eliminate objects greater than a set pixel size. Another useful editing feature is the use of Boolean operators, such as AND, OR, XOR, NOR, NXOR, and NAND, to combine or separate features.
5. *Quantitative measurement and analysis* is performed for three categories of data. *Object measurements* analyze individual features such as area, length, width, aspect ratio, and sphericity (see Table 1). *Field measurements* analyze individual objects and report values over the entire field. Examples include area fraction, area percent, and density (see Table 1). *Total area measurements* analyze the cumulative values reported over multiple fields. Figure 2 shows the analysis of an etched steatite sample. Note that the phase percentages as well as the percent porosity have been measured.
6. *Report generation* presents the data in a clear and understandable fashion.



Gray Threshold

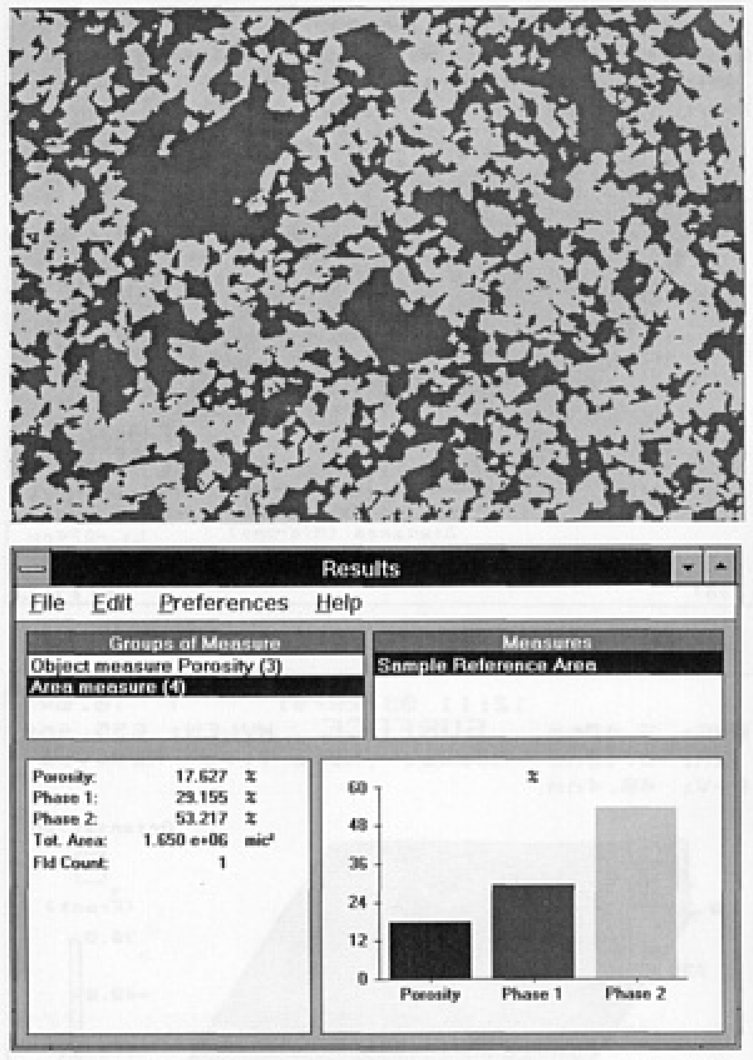
000-129	Bitplane 1	1
	Bitplane 2	2
	Bitplane 3	3
	Bitplane 4	4
130-255	Bitplane 5	5
	Bitplane 6	6
	Bitplane 7	7
	Bitplane 8	8

New Name:

Scaling: ○ Linear ● SqRt

Video: ○ Live ● Freeze

Fig. 1 Gray-level threshold for a porous steatite ceramic sample



```
Porosity:      17.627    %
Phase 1:       29.155    %
Phase 2:       53.217    %
Tot. Area:   1.650 e+06  mic²
Fld Count:          1
```

Fig. 2 Phase analysis of an etched steatite ceramic sample

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Sample Preparation

Microstructural analysis requires a deformation- and damage-free sample for correct characterization. A typical preparation procedure includes sectioning, mounting, planar grinding (coarse grinding), sample integrity (rough polishing), polishing, etching, and examination. Ideally a specimen is prepared in such a way as to minimize the amount of damage produced at each stage. For example, the correct cutting blade can significantly reduce the amount of damage to the material, thus reducing the aggressiveness of the subsequent coarse grinding step (Ref 3, 4, 5).

To achieve the required surface finishes, combinations of grinding, lapping, polishing, and mechanochemical polishing techniques are used. For metallic samples, hardness is the critical feature for determining the preparation sequence, whereas ceramic preparation procedures depend on both hardness and fracture toughness. For metal samples, mechanical abrasives such as SiC, diamond, and alumina are commonly used in the preparation sequence. For ceramics, initial sectioning and grinding are accomplished with diamond abrasives; however, for the fine grinding steps, either diamond or softer mechanochemical abrasives (colloidal silica) are used. Nearly all ceramic materials that are final polished with colloidal silica produce damage-free samples. In the final-polished condition, surface features such as porosity, cracks, inclusions, and other defects can be observed.

In most cases, however, an etching step is used to reveal microstructural features such as grain boundaries or phase features. Common etching techniques include chemical, electrolytic, thermal, and plasma techniques (Ref 6). The commonly used techniques for metals are the chemical and electrolytic etching methods. For ceramics, thermal and plasma etching methods are very effective; however, chemical etching with very aggressive acids is also common. Another approach for etching both ceramics and composites is to relief polish the specimen. This technique requires a high-nap cloth and an alkaline-based colloidal silica suspension.

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Optical Microscopy

For lower magnifications, 25× to 1000×, the optical microscope is the most important tool for the study of microstructure. For magnifications greater than 1000×, the scanning electron microscope is a useful tool. Today there are also other types of microscopes, including the scanning tunneling microscope and the confocal microscope.

The optical microscope offers a number of forms of illumination for revealing surface detail:

- *Bright-field illumination* is the most widely used. The incident light is reflected back through the objective, producing a bright background with dark features.
- *Dark-field illumination* is particularly useful for analyzing surface artifacts, such as surface scratches, and for studying grain structures. The incident light is supplied through the outside of the lens and is reflected back through the objective, producing a dark background with bright features.
- *Oblique illumination* is useful for low-magnification analysis that requires a three-dimensional appearance. It uses low-angle illumination, so higher magnifications are limited.
- *Polarized light* is especially useful for analyzing optically anisotropic metals, such as beryllium, α-titanium, and zirconium.
- *Differential interference contrast (DIC) illumination* is used to enhance topographic features in a surface. DIC illumination uses a Nomarski-modified Wollaston prism to split light into two wavefronts. Along with a polarizer, this enhances the relief effects on the surface.

Figures 3(a) to (c) show the same sample of machinable, reaction-bonded silicon-silicon carbide (SiSiC). In bright-field illumination, little information other than porosity is revealed, but in dark-field illumination, features such as grain boundaries and the porosity of the sample can be examined. In DIC illumination, the different phases of silicon and silicon carbide become very apparent.

Fig. 3 (a) Bright-field image of SiSiC. 200×. (b) Dark-field image of SiSiC. 200×. (c) Differential interference contrast illumination image of SiSiC. 200×

Abrasion Damage and Abrasion Artifacts

Machining ductile materials such as metals produces surface scratches as well as a plastically deformed surface layer. The depth of this deformed layer depends on the machining parameters as well as the metal type. For example, highly alloyed copper alloys such as 70-30 brass are among the most sensitive (Ref 7). To reveal the abrasion artifacts in 70-30 brass, etchants are used to remove the smeared layer. Figure 4 shows a polished 70-30 brass specimen along with its corresponding etched microstructure. Note that the artifacts have been highlighted by etching. To remove this abrasion damage, careful machining is required.

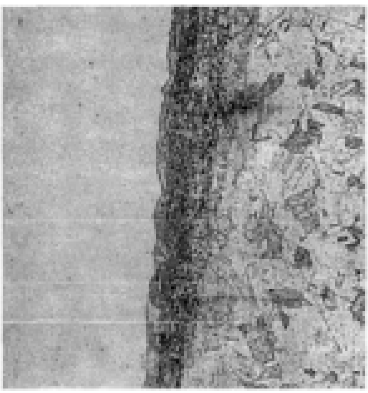


Fig. 4 Etching of 70-30 brass reveals smeared layer

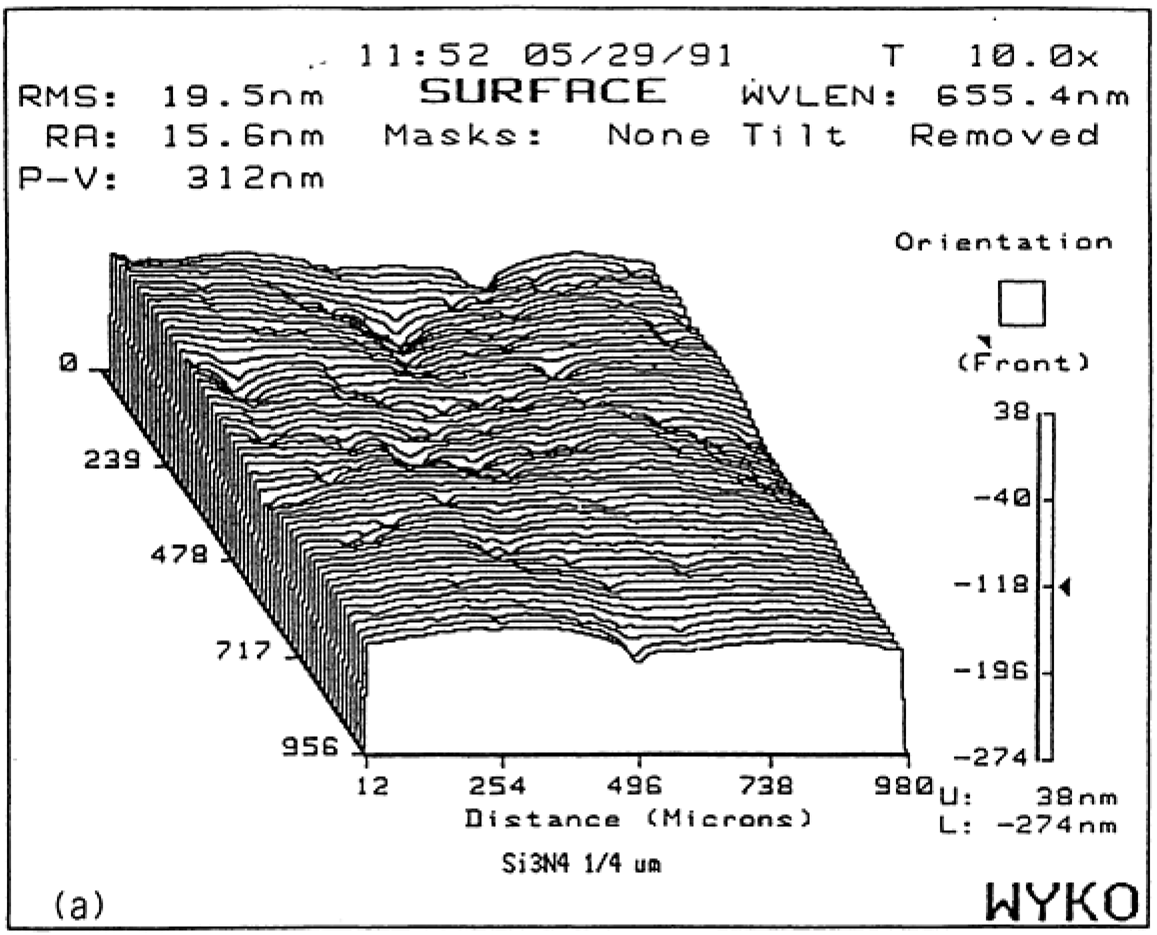
For ductile materials, the depth of the artifact-containing layer generally decreases with increasing specimen hardness. It also decreases with the use of finer abrasives. Additional examples of artifacts are given in Table 2. Other types of abrasion damage found in metals include hardening of the surface via cold working, embedded abrasives, and poor surface flatness.

Table 2 Common examples of abrasion artifacts for metals

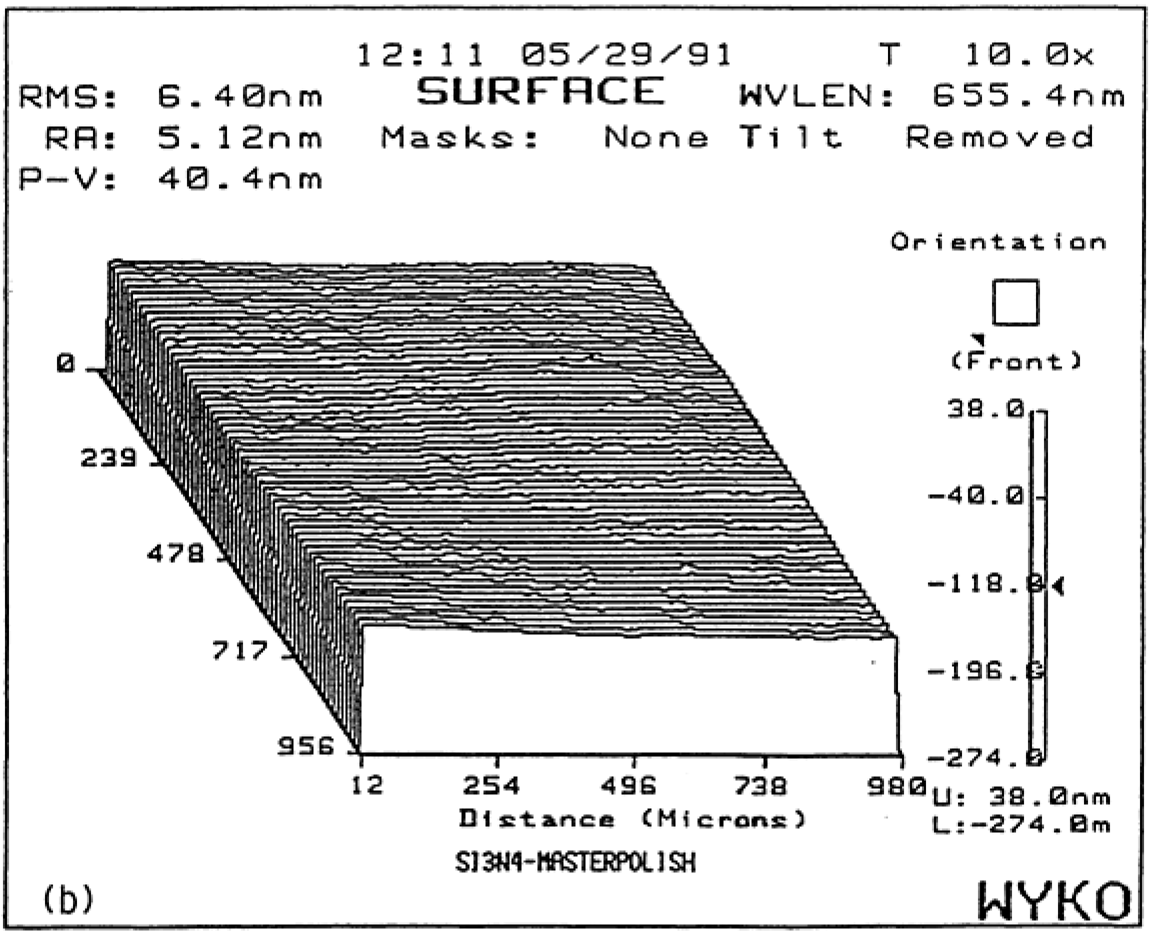
Metal	**Common artifacts**	**Solution**
Austenitic steels	Deep surface layer artifacts	Extended rough polishing
Zinc	Mechanical twinning; Recrystallization abrasion layer	Avoid production of deep damage by severe grinding
Ferritic steels	Outer fragmented layer	Continued polishing beyond the scratch depth
Pearlitic steels	Disturbance in outer fragmented layer	Continued polishing
Tempered steels	Rehardened martensite caused by excessive heat	Appropriate cooling

Source: Ref 7

For ceramic and composite materials, the most important abrasion artifacts are surface and subsurface damage. For brittle ceramics in particular, grain pullout is a common abrasion artifact. Removal of this type of damage is difficult when only hard abrasives are used, such as diamond. The damage may be several orders of magnitude deeper than can be reached by the abrasives used in the final machining (polishing) stages, so it may not be removed. In fact, the most effective way to remove this type of damage is to use mechanochemical abrasives such as colloidal silica. Figure 5 compares the effects of 0.25 μm diamond polish and a mechanochemical polish on Si_3N_4.


11:52 05/29/91
T 10.0x
RMS: 19.5nm
SURFACE
WVLEN: 655.4nm
RA: 15.6nm
Masks: None Tilt Removed
P-V: 312nm
Orientation
(Front)
0
239
478
717
956
38
-40
-118
-196
-274
12
254
496
738
980
Distance (Microns)
U: 38nm
L: -274nm
Si3N4 1/4 um
WYKO

(a)


12:11 05/29/91
T 10.0x
RMS: 6.40nm
SURFACE
WVLEN: 655.4nm
RA: 5.12nm
Masks: None Tilt Removed
P-V: 40.4nm
Orientation
(Front)
0
239
478
717
956
38.0
-40.0
-118.0
-196.0
-274.0
12
254
496
738
980
Distance (Microns)
U: 38.0nm
L:-274.0m
SI3N4-MASTERPOLISH
WYKO

(b)

Fig. 5 Surface roughness of Si_3N_4 after (a) 0.25 μm diamond polish and (b) mechanochemical polish

Another aspect of subsurface damage is that unlike ductile materials, brittle materials can fracture, forming subsurface cracks that can continue to propagate with less aggressive surface finishing operations. Unless this damage is removed, the integrity and mechanical properties of the material can be compromised. In this respect, it is critical to minimize damage at each individual machining step. Analysis of a finished surface can provide a statistical analysis of the machining process and identify any significant changes in the material microstructure.

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Microhardness Testing

Microhardness testing is a useful tool for the microstructural analysis of a finished surface. Information such as phase identification and fracture toughness data can be determined. Hardness is defined as the resistance to penetration by an indenter, and the Knoop and Vickers measurements are the most common.

A Knoop hardness number (HK) is obtained by:

$$\mathrm{HK} = P/A_\mathrm{p} = 14.229\ P/d^2$$

where P is the load in kilogram force, A_p is the projected area of indentation in millimeters, and d is the length of the longest diagonal in millimeters.

The Vickers hardness number (HV) is obtained by:

$$\mathrm{HV} = P/A_\mathrm{s} = 1.8544\ P/d^2$$

where P is the load in kilogram force, A_s is the surface area of indentation in millimeters, and d is the length of the longest diagonal in millimeters.

Surface preparation is typically required before hardness testing to ensure that accurate reproducible results can be obtained. The surface finish used depends on the load to be applied to the indenter. For microhardness testing (1 to 1000 gf), a final polish is recommended.

Microhardness testing is a useful technique in characterizing different phases, and it has also been used to determine the fracture toughness in brittle materials. Fracture toughness is determined by initiating a controlled crack, then breaking the specimen, or by measuring crack lengths and applying fracture toughness equations (Ref 8, 9, 10, 11).

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Residual Effects of Finishing Methods

Marc Tricard, Norton Company

Introduction

THE CONCEPT OF "SURFACE INTEGRITY," originally defined in 1964 (Ref 1) for grinding operations, applies to any finishing operation. It can be extended to encompass six different groups of key factors: visual, dimensional, residual stress, tribological, metallurgical, and other factors as described in Fig. 1. This article shows the importance of these factors in the performance and behavior of various manufactured parts. Special emphasis is given to residual stresses and their influence on the final mechanical properties of a part.

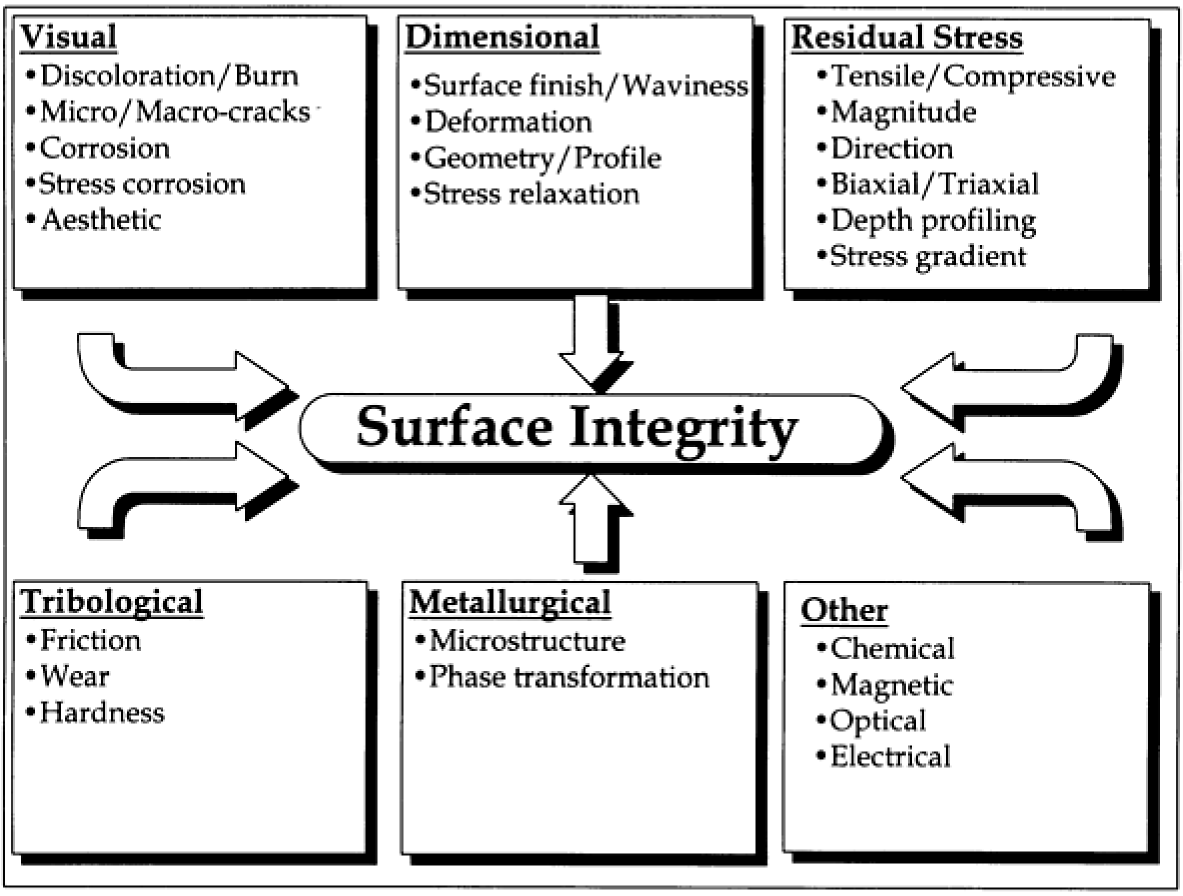

Fig. 1 The six different groups of key factors that define the surface integrity of a finished material

Acknowledgements

The author thanks K. Subramanian for his helpful comments on this manuscript, as well as Carol Cooper, Anna Durilin, Frank Esposito, Mary Silverberg, and Bruce Vigeant.

Reference

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Systems Approach to Finishing

Finishing methods, like any manufacturing operation, can be looked at efficiently using a systems approach (Ref 2). As can be seen from Fig. 2, a systems approach can also be used to consider a finishing operation and its resulting surface integrity:

- *Input:* Finishing processes involve a vast array of variables pertaining to four categories (i.e., the work material, the machine tool, the processing tool used, and the operational factors).
- *Process:* The four inputs define the microscopic aspects of a finishing operation, especially the thermal and mechanical interactions that condition the final surface integrity. These microscopic aspects can be measured macroscopically with forces, power, energy, or temperature transducers during the finishing operation.
- *Output:* The process leads to a finished part that has a given surface integrity and specific visual, dimensional, residual stress, tribological, metallurgical, and other factors (Fig. 1). The resulting surface integrity of the finished part conditions its operational performance.

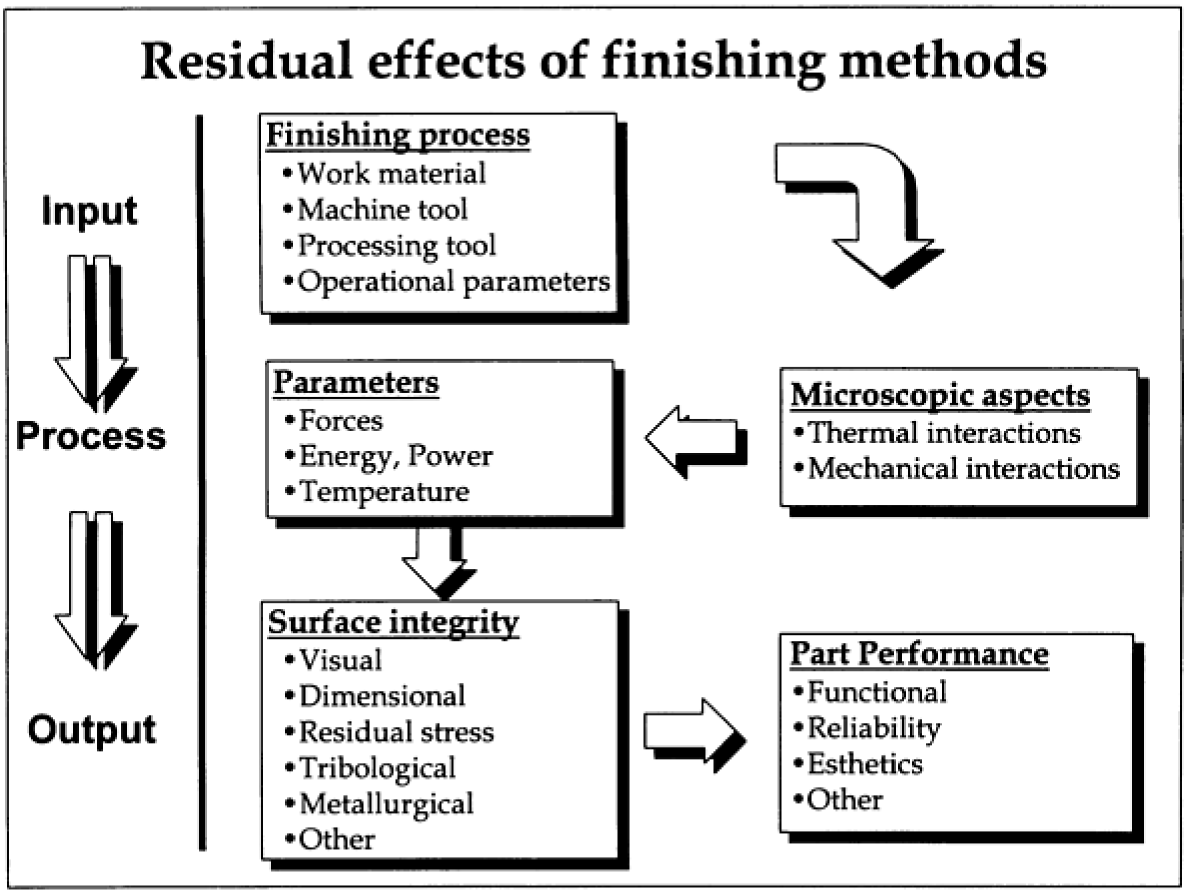


Fig. 2 Systems approach to the residual effects of finishing methods

As the name implies, finishing methods occur at the end of a manufacturing process, and thus the residual effects they leave on the part are of crucial importance. Manufactured components typically result from a succession of operations, but in most cases it is the last operation that governs the residual stress profile imparted to the component prior to its use or service. Exceptions occur when the final machining operation has a penetration depth smaller than the previous ones (Ref 3). In such situations, the superimposition of residual stress must be considered (Fig. 3). In more conventional cases, the final grinding operations determine the final state of residual stress rather than the turning operation(s) that preceded them.

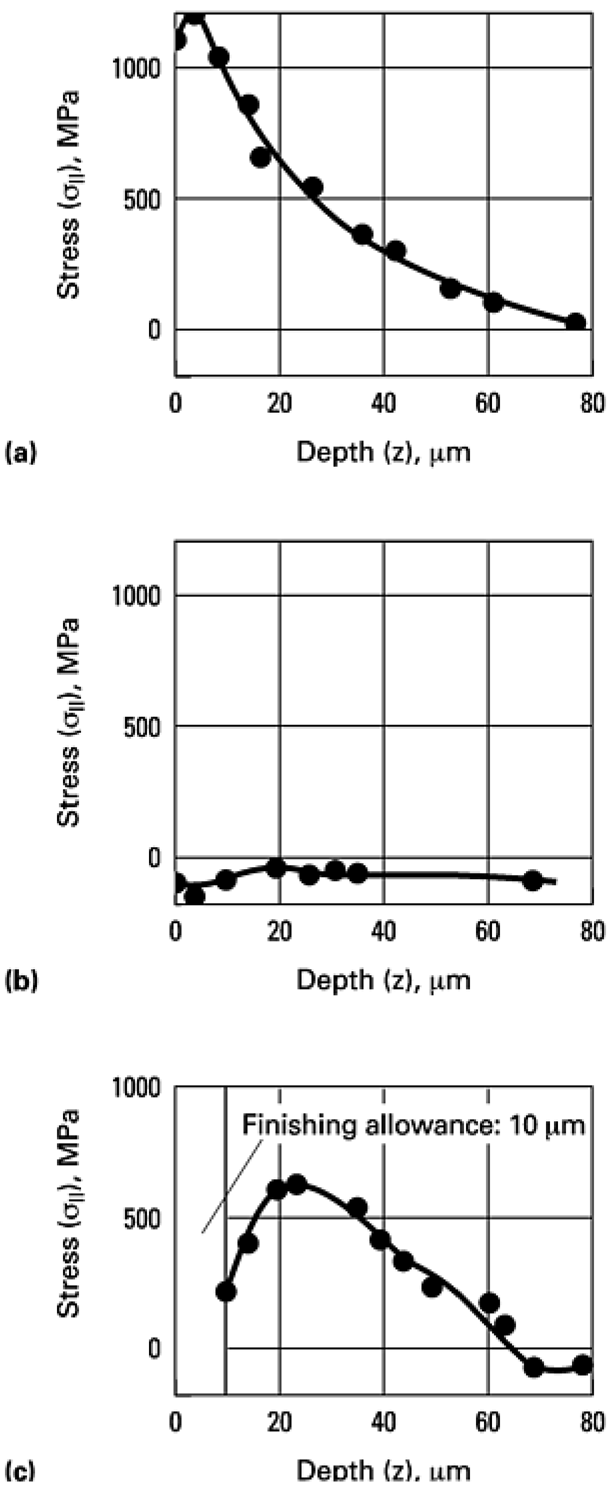


Fig. 3 Residual stress profiles in internal grinding cycles. Workpiece: 100Cr6; hardness, 62 HRC; diameter, 40 mm (1.6 in.). Table speed: 1 m/s. Corundum grinding wheel: A80K6V; diameter, 30 mm (1.2 in.); width, 8 mm (0.3 in.); speed, 40 m/s. Dressing: D 427 diamond cup wheel; speed ratio, 0.7; overlap, 40; infeed, 2 μm. Cooling: 4% emulsion. (a) Roughing. Relative metal removal rate (MRR), 6 $mm^3/mm \cdot s$; relative volume of material removed, 18.8 mm^3/mm. (b) Finishing. Relative MRR, 1 $mm^3/mm \cdot s$; relative volume of material removed, 1.6 mm^3/mm. (c) Roughing and finishing. Source: Ref 4

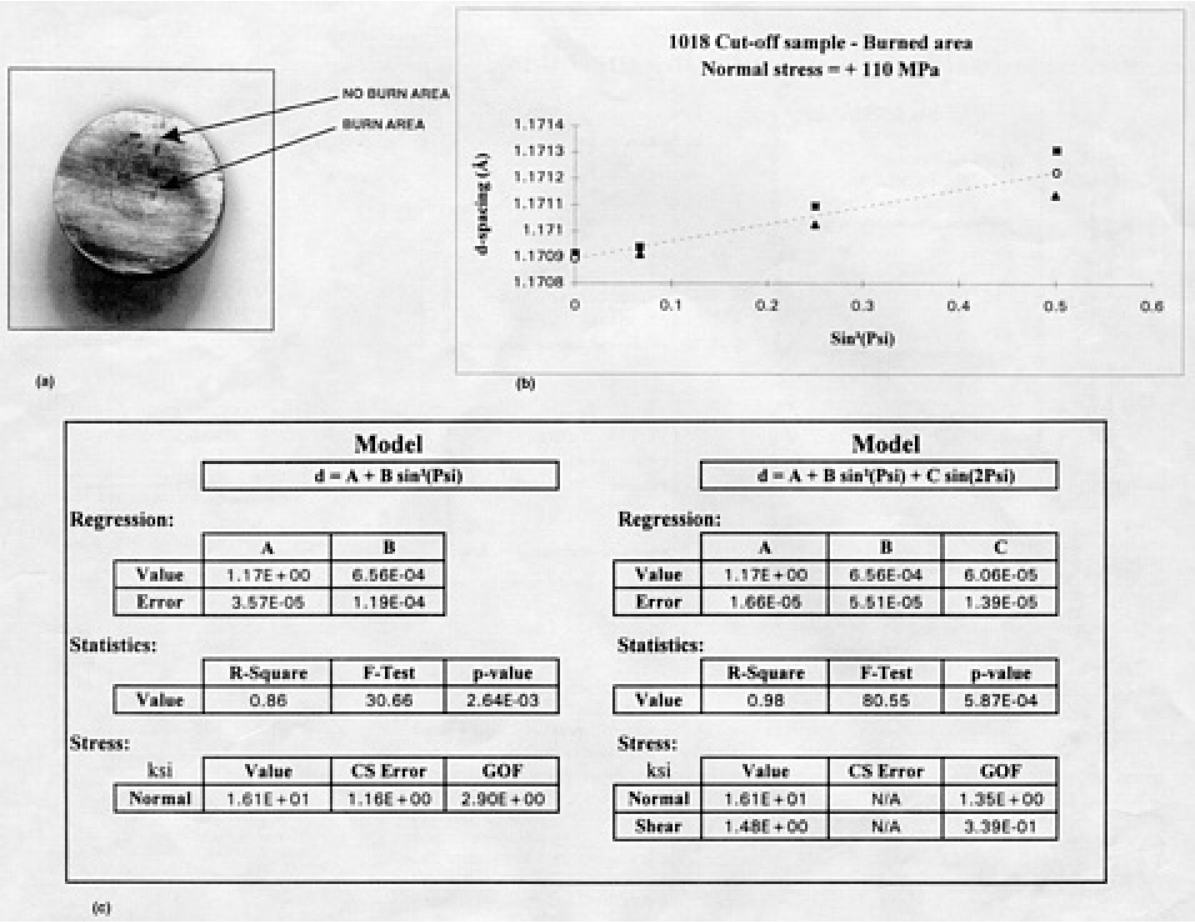
The residual stress effects of finishing processes can have a significant impact on the performance and viability of engineering components. Examples of possible negative effects are presented in Ref 5, which includes case histories of four finished parts that failed due to residual stresses.

Factors in Surface Integrity

When dealing with manufacturing issues, it is important to keep in mind that all the parameters involved in the finishing process have a direct influence on the surface integrity of the part. The six groups of key factors presented in Fig. 1 are not random, but are rather the deterministic outcome of the process chosen (Ref 2, 6). Basic understanding of the causal relationships between the mechanical, thermal, and chemical aspects of a finishing process and the six groups of key factors related to surface integrity is the key to successful improvement of a finishing process.

Visual Factors

Discoloration/Burn. In many manufacturing operations, surface damage can be detected with simple visual observations. See, for example, the 1018 steel cutoff sample shown in Fig. 4. Grinding burns are simply a discoloration due to the oxidation at high temperature. However, the absence of discoloration does not imply that the surface was not heated excessively. Work can be badly overheated in grinding without any trace of discoloration remaining on the finished surface if the conditions are such that the wheel cleans off the discoloration almost as soon as it appears. In cross-feed grinding, if the leading edge of the wheel takes a heavy cut so that the work is heated severely to a depth of several thousandths of an inch, the trailing portion subsequently may remove a layer a fraction of a thousandth inch deep, thus eliminating all evidence of the prior discoloration and leaving practically all of the heat-affected layer of metal (Ref 7).



Model

d = A + B sin²(Psi)

Regression:

	A	B
Value	1.17E+00	6.56E-04
Error	3.57E-05	1.19E-04

Statistics:

	R-Square	F-Test	p-value
Value	0.86	30.66	2.64E-03

Stress:

ksi	Value	CS Error	GOF
Normal	1.61E+01	1.16E+00	2.90E+00

Model

d = A + B sin²(Psi) + C sin(2Psi)

Regression:

	A	B	C
Value	1.17E+00	6.56E-04	6.06E-05
Error	1.66E-05	5.51E-05	1.39E-05

Statistics:

	R-Square	F-Test	p-value
Value	0.98	80.55	5.87E-04

Stress:

ksi	Value	CS Error	GOF
Normal	1.61E+01	N/A	1.35E+00
Shear	1.48E+00	N/A	3.39E-01

Fig. 4 Measurement and analysis of surface damage using x-ray diffraction. (a) 38 mm (1.5 in.) 1018 steel cutoff sample showing burn-related discoloration. Two residual stress measurements by x-ray diffraction were made on the sample at the locations marked by the four concentric markers. (b) Typical *d* versus sin ^{2} ψ curve (where *d* is the interatomic distance, which varies according to stress level, and ψ is the angle of the incoming x-ray beam relative to the surface) obtained from an x-ray diffractometer. Seven different ψ orientations (from -45° to +45°) were used. The *d*-spacing can be looked at as a natural strain gage in a material: a compressive stress tends to diminish the *d*-spacing value, whereas a tensile stress increases it by bringing two interatomic spaces farther apart. The x-ray diffractometer allows one to measure this value by providing a measurement for *d* from Bragg's law (2*d* sin Θ = *n*λ, where Θ is the angular distance between the incident and diffracted beams, *n* is the order of reflection, and λ is the wavelength of the x-rays). The slope of the curve, obtained by

linear regression, is directly proportional to the residual stress. (c) Two analyses of the curve shown in (b). The first is a simple linear regression that relates the lattice *d*-spacing to the $\sin^2\psi$ at various ψ angles, with the result σ_{11} = 110 MPa (16 ksi); it is assumed that $\sigma_{13} = 0$. The second model is a multiple linear regression with the result σ_{11} = 110 MPa (16 ksi) and σ_{13} = 10 MPa (1.5 ksi). Additional information about these measurement techniques is available in Ref 28.

As demonstrated in Fig. 4, measurement of residual stresses by x-ray diffraction now offers a practical way to quantify what used to be only a visual observation. A stress measurement in the burned area (darkest zone in Fig. 4a) indicated a tensile residual stress of 110 MPa (16 ksi), whereas the unburned area (clearest zone) indicated a compressive stress of -30 MPa (-4 ksi). The Eddy-current technique or careful microhardness measurements can also lead to meaningful information (Ref 8).

Micro- and Macrocracks. Cracks or even spalling may occur in finishing operations that have significant thermal and mechanical effects, such as grinding. For flat-surface grinding, cracks appear primarily perpendicular to the grinding direction, with typical depths from 0.010 to 0.020 in. (Ref 9). Interesting crack formations have been described (Ref 1) resulting from additional operations, including milling, reaming, drilling, electrodischarge machining, and laser beam machining.

Susceptibility to Corrosion / Stress-Corrosion Cracking. Finishing operations have a significant influence on the stress-corrosion resistance of a part, and it is well known that the introduction of some surface roughness may improve resistance in corrosive atmospheres. Crack propagation in a stressed material in a corrosive environment, termed *stress-corrosion cracking* (SCC), can occur in a finished part due only to residual stress, without any applied load.

Extensive research has been performed on the relationship between residual stress and SCC susceptibility for 304 and 316 austenitic stainless steel pipe weldments used in nuclear power plant boiling water reactors. In one study (Ref 10), intergranular SCC in a weld heat-affected zone (HAZ) was detected by ultrasonic testing long before any rupture occurred. Measurements of residual stress, by x-ray diffraction and stress relief techniques, were used in multipass gas-tungsten arc welding with reported accuracy of ±35 to 50 MPa (±5 to 7 ksi) and 135 MPa (15 ksi), respectively. It was found that the welding operations, along with the grinding operations used before and after welding, generated tensile stress. This stress contributed to the intergranular SCC in the weld microstructure, which was sensitized by the reactor water coolant containing small amounts of dissolved oxygen (200 to 300 ppb). A significant reduction in SCC was obtained by deliberately introducing compressive residual stress on the inside pipe surface. This was accomplished by creating a thermal gradient during the welding operation--the outside diameter of the pipe was maintained at a temperature between 500 and 550 °C (930 and 1020 °F), while the inner diameter was kept at 100 °C (212 °F) with circulating water.

Rough-turning operations studies have shown that tensile residual stresses at the surface of a part are quite detrimental to its corrosion resistance. Fluids used in finishing operations should also be considered when dealing with corrosion issues. For instance, based on hot-salt stress-corrosion tests (Ref 11), it has been shown that chemical milling can destroy the compressive stress layers that normally exist after machining, which gives a finished part reduced resistance to stress-corrosion cracking. Aluminum parts can show corrosion if they are machined for an extended period of time, due to galvanic action: current flow can occur between the machine tool base and the part if no special fluid is used (Ref 12). Even blowing off parts after machining can lead to rust if the compressed air used contains any moisture.

Aesthetic considerations are also important. When performance requirements are nearly equal, the finished component of choice is the one that has the better appearance. Cast iron sinks, brass plumbing equipment, hand levers, golf clubs, faucets, hammers, and silverware are examples of parts deburred, polished, or buffed by the thousands to improve their appearance. Even very large parts can be buffed to a bright finish. For example, Ref 13 describes the buffing of an entire aircraft fuselage (32.3 m, or 106 ft, long) using machines with 457 mm (18 in.) buffing wheels mounted on four computer numerically controlled floating heads on a movable gantry.

Dimensional Factors

Surface Finish / Waviness. Figure 5 indicates the surface finish (expressed as the roughness average, R_a) that can be achieved with a variety of manufacturing processes. Traditionally, the requirements for finishing processes have been compromises between achieving better surface finishes while at the same time reducing the total finishing time. Recent developments in microgrinding with fixed abrasives have enabled this process to compete with the slower lapping operation using loose abrasives (Ref 14).

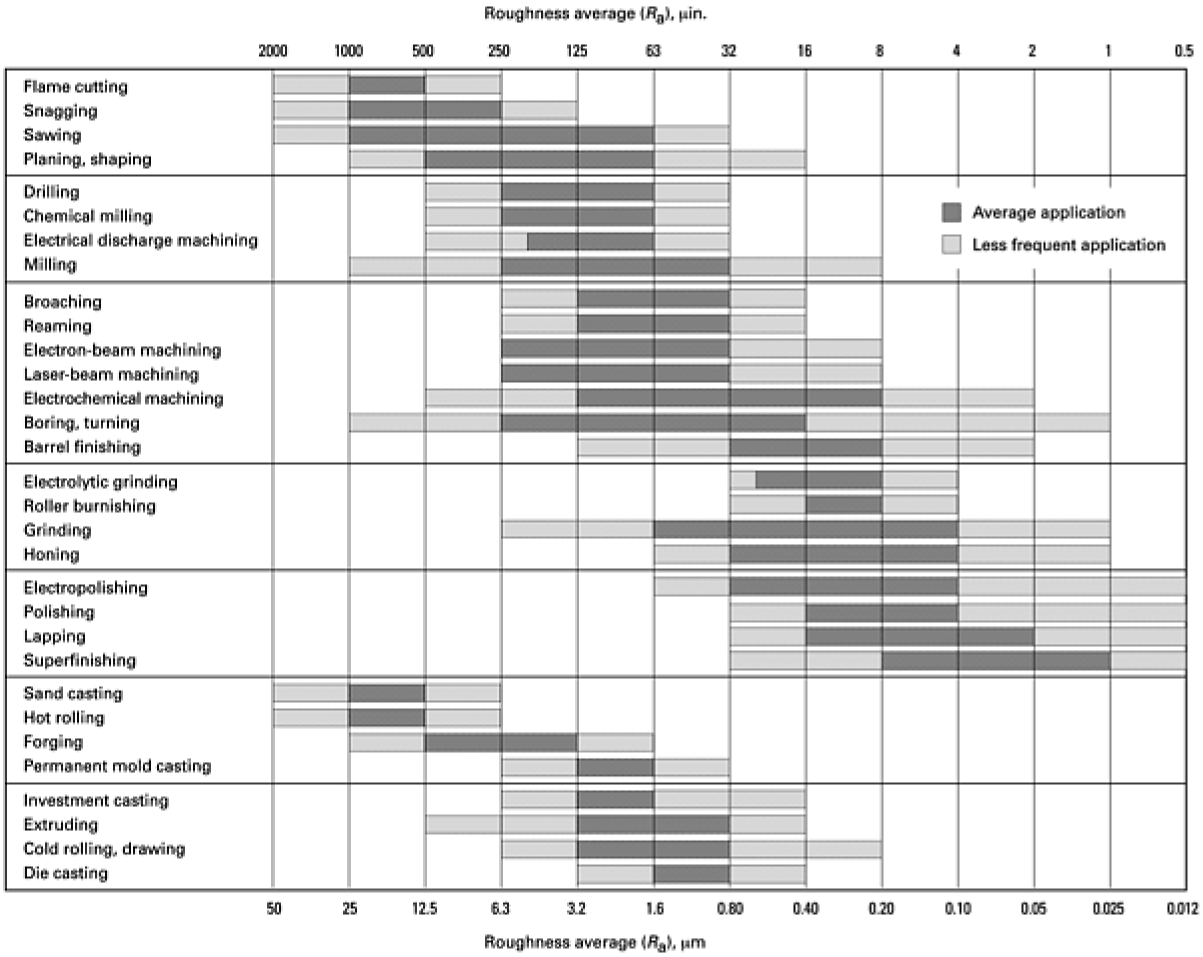


Fig. 5 Ranges of average surface roughness produced by various processing methods. Source: *Machinery's Handbook,* 24th ed., Industrial Press, 1992, p 672

Beyond their well-known importance for tribology (Ref 15, 16) and aesthetics, surface finish and waviness can have a significant impact on the surface integrity of a part, because wear behavior of surfaces is influenced by the surface roughness. Huang (Ref 17) has studied the fatigue life of turned and ground superalloys and has shown that the surface roughness, especially at high temperature, and residual stresses of the samples had more effect on fatigue resistance than surface hardening does.

Stress relaxation can be a finishing operation per se. Reference 18 describes a variety of thermal and/or mechanical operations can be applied for stress relieving. For example, 90 s in a salt bath at 345 °C (650 °F) relieved 80% of the residual stress of ground steel parts (Ref 19). Even if no stress relaxation technique is used, fatigue-related relaxation sometimes occurs due to microplastic deformation. The rate of relaxation is greatest when the finishing process produces the steepest residual stress gradient normal to the surface (Ref 20). Thus, sand-blasted or rolled parts could be expected to relieve their residual stress much faster than milled ones, for metallic components.

Residual Stress Factors

Sign of the Residual Stress. It has frequently been stated that a compressive state of residual stress enhances the fatigue behavior of a finished component. Crack initiation and propagation in ground components of aerospace or automotive engines are indeed slowed down tremendously when negative (compressive) residual stress values are present. In a few instances zero residual stress is the desired goal, as in the case of read/write heads of hard disks, because all residual stresses lead to magnetically inactive layers.

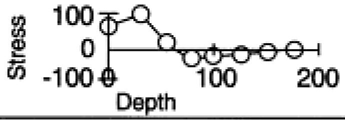
Magnitude and Direction of the Residual Stress. The loading conditions to which the finished part will be submitted are an important consideration. The total applied stress (mechanical, thermal, etc.) plus the residual stress determine the mechanical behavior of a finished part, such as its fatigue resistance. Quantitative analysis of residual stress with both destructive techniques (e.g., hole drilling, deflection technique, indentation, etching) and nondestructive techniques (e.g., x-ray or neutron diffraction, Eddy current, Barkhausen noise analysis) are being used more often to help characterize the magnitude and direction (Ref 21). Applications have been reported in gear grinding assessment (Ref 22), bearings manufacturing (Ref 23), camshaft grinding monitoring (Ref 24), rotor shaft examination (Ref 25), welding (Ref 26), and even production of rail components for the French fast speed TGV train (Ref 27).

Residual Stress Field. When considering the type of residual stress field present in the part, it is important to know about the specific stress tensor component concerned. Many studies focus only on the principle stress component, σ_{11}, when the shear component, σ_{13}, should also be considered. Indeed, many experimental techniques assume a perfectly biaxial stress when the various characteristics of the finishing method being considered can lead to a highly triaxial residual stress field. X-ray or neutron diffraction techniques can be valuable nondestructive tools in quantifying such biaxial and/or triaxial stress fields (Ref 28).

Stress Below the Surface. X-ray techniques emphasize *surface* measurement of residual stress, because x-ray penetration depths are typically less than 20 μm in steels. However, the critical areas often appear much deeper in the part (150 to 200 μm being typical), emphasizing the need for careful plotting of residual stress versus depth, possibly with the help of electropolishing techniques.

The four residual stress factors are summarized in Table 1. Examples of residual stress introduced by grinding, milling, turning, planing, shaping, electrical discharge machining (Ref 29), abrasive tumbling, rolling, and shot peening can be found in Ref 2 and 19, as well as in the very good survey paper by Brinksmeier et al. (Ref 30).

Table 1 Parameters that characterize a state of residual stress in a finished component

Parameter	Comments
Sign at the surface	Tensile or compressive
Magnitude/Direction	Applied stress + Residual stress = Total loading conditions
Stress field	Stress tensor components $\begin{bmatrix}\sigma_{11} & \sigma_{12} & \sigma_{13}\\ \sigma_{12} & \sigma_{22} & \sigma_{23}\\ \sigma_{13} & \sigma_{23} & \sigma_{33}\end{bmatrix}$
Stress below the surface	Stress profile — Stress gradient Typically with electropolishing 

Example 1: Residual Stresses in Grinding.

The existence of residual stresses in a ground specimen is due to the combined action of mechanical and thermal effects.

Mechanical Effect. Mechanical forces during grinding expand the surface of a sample, so that the plastically deformed surface experiences a compressive residual stress state while the elastically deformed near-surface layer is left in a state of residual tension. The elevation of temperature in the surface of the sample as a result of the cutting action causes a reduction in local yield strength and, therefore, more plastic deformation. This mechanical aspect of grinding is somewhat comparable to shot peening, in which small-diameter beads plastically deform the surface of a sample, leaving the finished surface in a compressive state of residual stress.

The thermal effect is probably the more important of the two effects. During the grinding operation, the temperature dramatically increases in a thin surface layer of the specimen, while the bulk inner parts remain cool. It has been shown (Ref 31) that the maximum value of the tensile stress in a machined surface obtained by grinding or any other cutting technique is directly related to the maximum surface temperature reached during the process. As the plastically deformed surface layer cools, its thermal contraction is aided by the part's interior, generating tensile residual stresses at the surface.

As shown in Fig. 6, the resulting value of the residual stress induced during the grinding operation is the superimposition of these two phenomena. If the thermal effect is the more important, as in high-metal-removal-rate grinding where considerable heat is generated, the first layers of the specimen's surface show tensile residual stresses. In "low-stress grinding" (that is, grinding operations with low metal-removal rates), the mechanical effect overtakes the thermal aspects, and the superimposition of the two results in a residual stress profile that is predominantly in the compressive zone. Of course, this distinction between mechanical and thermal aspects is a simplification--during grinding the two phenomena cannot be dissociated. The friction associated with the mechanical effect is the primary source of heat, while in turn the temperature generated can considerably reduce the yield strength of the material being ground. Consequently, if the material being ground has a higher thermal expansion coefficient, this will directly translate into higher stresses (Ref 32). A material with a low yield strength will experience the same effect.

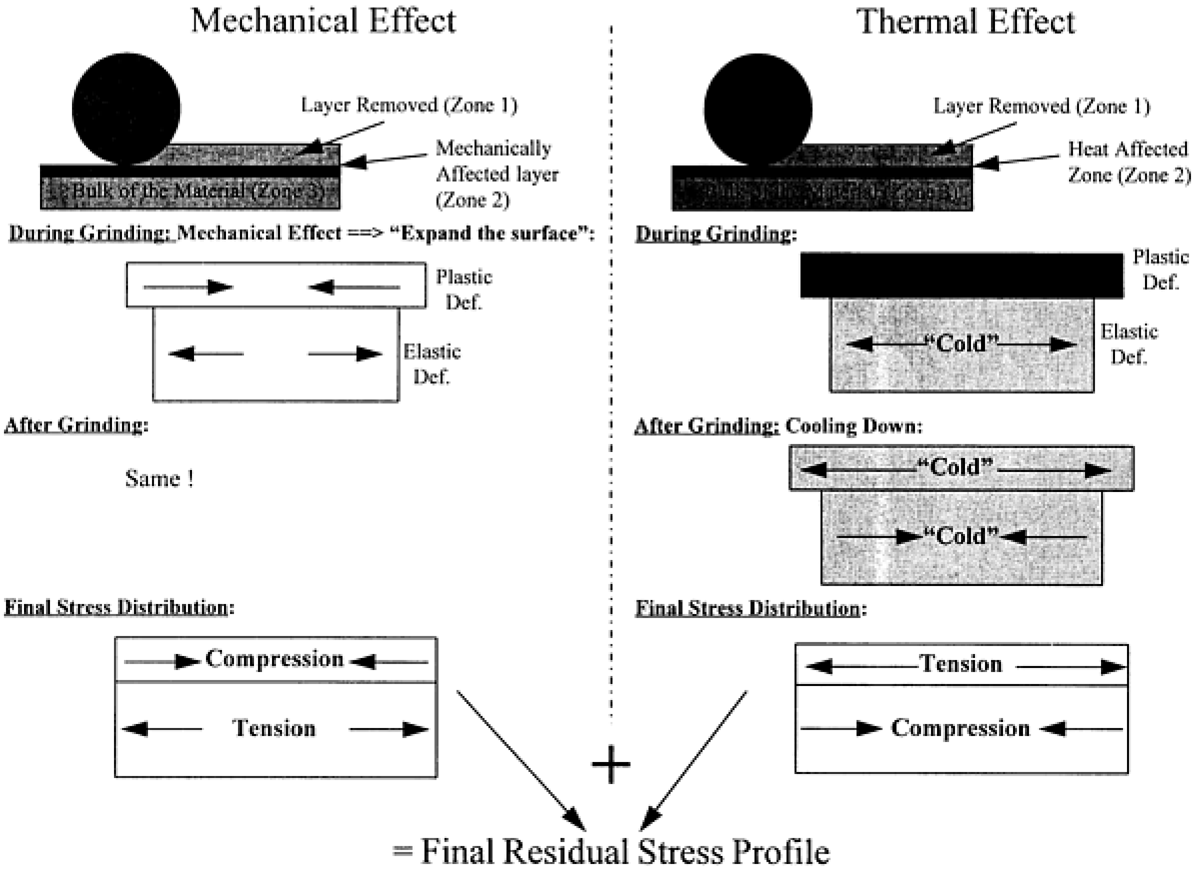


Fig. 6 Residual stress profile left in ground components by the superimposition of a mechanical (left) and a thermal (right) effect. For the process shown on the left, three distinct zones can be distinguished: zone 1 is the surface layer being ground, zone 2 is the "mechanically affected zone" immediately underneath zone 1, and zone 3 is the remaining bulk of the material. During grinding, zone 2 experiences an increase in length, which is constrained by the unaffected zone 3. The plastically deformed surface (zone 2) is therefore left in a state of compression, while the bulk of the material (zone 3) is in slight tension. For the process shown on the right, zone 2 is the "heat-affected zone" at the surface of the material. During grinding, the heated surface (zone 2) expands in length, but once again is constrained by the bulk of the material (zone 3), which remains at room temperature, leaving the surface in a state of compression. The workpiece begins to cool immediately after grinding, reversing the distribution and resulting in a surface layer in tension and the bulk of the part in slight compression. For most parts, the "real" stress distribution is the sum of these mechanical and thermal effects.

References 33 and 34 explain in depth how residual stresses are generated during a grinding operation. Reference 35 contains an interesting discussion of these mechanical and thermal effects and their influence on the fatigue life of a ground component. Numerous additional studies have been devoted to surface integrity in specific finishing operations, such as for grinding (Ref 30, 36, 37, 38), honing (Ref 39), and lapping (Ref 40). For all finishing operations, relative control of the residual stresses generated by the process can be achieved through a good understanding of the thermal and mechanical effects involved. Some operations, such as shot peening and rolling, are predominantly governed by the mechanical aspects, while others, such as electrical discharge machining, favor the thermal aspects. Most combine both aspects in a ratio that depends on the specific operating parameters of the process.

Example 2: Residual Stresses in Shot Peening.

Shot peening is a cold working process in which thousands of spherical shot (typically $\frac{1}{2}$ mm diam spheres of steel, glass, or ceramic) are propelled against the surface of a part. The overlap of the small craters formed by the impact of each sphere creates a compressive layer at the surface of the part. In this process, the intensity of the stresses generated typically exceeds half the yield strength of the material being peened. The depth of the residual stress layer obtained depends on the operating parameters of the process, including the intensity of the process as measured by Almen gages; the size, velocity, and impingement angle of the shot (Ref 41); and the characteristics of the material being shot peened.

Table 2 indicates the wide variation in fatigue life performance that can be obtained by varying the finishing process. These data clearly demonstrate the benefits of creating compressive residual stresses at the surface of a part by shot peening. In addition to improving the fatigue behavior of a part, controlled shot peening can also be used as a finishing process to generate three-dimensional surfaces such as those on aircraft wings and empennage skin. Additional examples of shot peening applications are listed in Ref 43. This process is described in detail in the article "Shot Peening" in this Volume.

Table 2 Fatigue life performance obtained by parts finished using various methods

Operation	**Endurance limit in bending (10^7 cycles), MPa (ksi)**	**Relative endurance limit**[(a)]
Surface grinding		
Gentle	414(60)	100
Conventional	165(24)	40
Turning		
Gentle	414(60)	100
Abusive	414(60)	100
Electrochemical machining		
Standard	269(39)	65
Off standard	269(39)	65
Standard plus peening	538(78)	130
Off standard plus peening	462(67)	112
Electrical discharge machining		
Finish	152(22)	37

Rough	152(22)	37
Finish plus peening	455(66)	110
Rough plus peening	517(75)	125
Electropolishing		
Standard	290(42)	110
Standard plus peening	538(78)	130

Note: Material for all parts was Inconel 718.

Source: Ref 42

(a) Expressed as a percentage of that obtained with gentle grinding.

Tribological Factors

A finished workpiece is often designed to be part of a moving mechanism where wear or friction might become an important issue. Finishing operations therefore should to be selected based on their consequences on the wear resistance of the parts, their friction coefficient, their hardness, and so on (Ref 15, 16).

Wear. The influence of finishing method on the run-in of AISI A10 and AISI 4140 steel cams has been demonstrated (Ref 44). The wear mechanisms involved were found to be strongly dependent on the surface finishing method used (milling, grinding, ion nitriding, or blasting) as well as the microstructure of the steel. Interestingly, this study also clearly demonstrated the advantage of computer-controlled finishing machines over their analog counterparts as far as wear is concerned.

Friction. A study of the break-in period of automotive components demonstrated that honing and lapping operations can reduce the initial friction of cylinder liners and cam shafts (Ref 45).

Hardness. As many studies have demonstrated (e.g., Ref 17), surface hardening resulting from a finishing operation can lead to significant improvement in the fatigue life of a component.

A good understanding of the micromechanisms associated with a finishing technique might bring some significant mechanical advantages. Of course, a tradeoff might have to be made. In Ref 44, for instance, the lower wear of nitrided and bead-blasted cams had to be judged against a decrease in their dynamic performance, compared with that of ground cams.

Metallurgical Factors

A wide variety of metallurgical effects can occur during a finishing process: formation of untempered or overtempered martensite, retained austenite, volume changes due to phase transformation, oxidation, and other effects can become important, depending on the mechanical and thermal aspects of the finishing operation. Reference 9 provides a good introduction to these phenomena in the case of grinding, while Ref 1 reviews various metallurgical alterations in the cases of milling, reaming, drilling, electrodischarge machining, and laser beam machining.

Most of these metallurgical characteristics can be qualitatively assessed through a wide variety of observation techniques, such as metallography, scanning electron microscopy, and chemical etching. New techniques have also been developed for better quantification. For example, the percentage of retained austenite present at the surface of material can be measured by x-ray diffraction on the same diffractometer used for residual stress measurements. Reference 47 describes measurements of both residual stress and percentage of retained austenite on various heat-treated steels ground with cubic boron nitride. Acoustic microscopy has also been used to evaluate the thickness of the metallurgically damaged layer on a ground surface (Ref 48). Table 3 lists various testing techniques and references that provide additional information. Some of these metallurgical factors that may restrict a finishing operation can also be turned to advantage. For example, significant toughening of ceramic materials can be obtained by forcing phase transformations to occur at the surface through a grinding operation. Reference 21 gives an example of a controlled stress-induced phase transformation from the tetragonal to monoclinic phase of ZrO_2. The 3 to 5% volume expansion associated with this phase transformation resulted in highly compressive residual stresses with values exceeding 1 GPa at the surface, which strengthened the ceramic.

Table 3 Testing techniques for surface integrity evaluation

Surface integrity factor considered	**Evaluation technique**	**References**
Cracks	Acoustic emission	57
	Acoustic microscope	48
	Eddy current	
	Etching	9, 46
	Magnetic particle	9
	Metallography	9
	Optical microscope	58
	Penetrant	9
	Scanning electron microscopy	
	Transmission electron microscopy	
	Ultrasonic signal	4
	Visual observation	
Metallurgy	Magnetic particle	
	Metallography	1, 9, 58
	Scanning electron microscopy with microprobe analysis	4

	X-ray diffraction	47, 56
Hardness	Microhardness	58
	Superficial hardness	4
	Ultrasonic signal	4
Residual stresses	Barkhausen noise analysis	4, 24
	Eddy current	
	Hole drilling	59, 60, 61
	Interferometry	62
	Layer removal	27, 30, 42
	Neutron diffraction	26, 63
	Ultrasonic signal	4
	X-ray diffraction (XRD)	27, 28, 30, 42
	XRD with electropolishing	4

This table, by no means exhaustive, provides references that describe various techniques one can use to qualify or quantify key surface integrity factors and that present practical examples of applications for various finishing methods. Volume 9 *Metallography and Microstructures,* and Volume 17, *Nondestructive Evaluation and Quality Control,* of the *ASM Handbook* also provide specifics on most of these techniques.

Other Surface Integrity Considerations

In some applications, additional specific properties of the surface layers have to be considered. The chemical, magnetic, optical, or electrical properties of a finished part can sometimes be dramatically affected by a finishing process. For instance:

- Chemical glass strengthening by ion exchange can result in high compressive residual stress when large sodium ions replace smaller lithium ions in a salt bath rich in sodium ions (Ref 49).
- For manganese-zinc and nickel-zinc surfaces, the deformation and residual stress induced during a lapping operation can generate magnetically dead layers detrimental to the performance of a magnetic recording head system (Ref 50).
- Optical properties of infrared materials may be influenced by various processing techniques (Ref 51).
- The surface condition, particularly the presence of cracks due to brittle fracture during the finishing process, can affect the electrical behaviors of insulators (Ref 52).

In other cases (Ref 53), the finish surface might require special consideration due to the risks of hydrogen embrittlement (cracking without corrosion) or liquid metal embrittlement (as in the case of aluminum alloys with mercury). The breakdown of machining fluid, especially sulfurized ones, can result in high levels of hydrogen in ground steel samples (Ref 54). Other examples include a sanding technique that influences the wettability and shear strength of wood (Ref 55) and abrasive jet machining finishing techniques that are used where there is risk of explosion.

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Thermal Aspects of Surface Finishing Processes

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Introduction

THE FINISH MACHINING of materials is commonly accomplished by surface finishing processes such as grinding, lapping, and polishing. All of these processes typically use abrasive particles to carry out material removal. In grinding, the abrasive particles are usually bonded to a wheel using a vitrified or resin bond, whereas in lapping and polishing, the particles are usually present in a slurry that is between the workpiece and a lapping block. The material removal action in grinding resembles two-body abrasion, whereas in lapping and polishing, this action is akin to three-body wear. The surface finish (roughness average, or R_a) on ground surfaces is typically in the range of 0.2 to 1 μm, whereas lapped and polished surfaces can have R_a values of less than 0.05 μm. The material removal rates in lapping and polishing are usually an order of magnitude less than in grinding. At the fundamental level, material removal takes place in all of these processes due to the localized action of an abrasive particle on the workpiece surface. The local pressures prevalent in the abrasive-workpiece contact region are of the order of the hardness of the workpiece material (Ref 1), and the relative sliding speeds between the particle and the workpiece are in the range of a few centimeters per second to 150 m/s, with the higher speeds occurring for modern high-speed grinders (Ref 2). At the local level, the action of the abrasive particle resembles that of a sliding indenter applied to the workpiece surface.

The localized abrasive-workpiece contact pressures and high sliding speed cause high temperatures to be generated at the interface between the abrasive particle and the work surface, as well as in the work subsurface, due to frictional heating (Ref 3, 4). This is especially so in grinding, where sliding speeds are high (30 to 150 m/s). The high temperatures are an important source of several forms of damage on the machined surface. First, the transient temperatures contribute to residual stresses and microcracking on ground surfaces (Ref 5, 6, 7). Second, the localized temperatures can cause warping of the component being finished, especially when it is of small size, having a relatively large surface-to-volume ratio. This is a serious problem in the finishing of small electronic devices such as recording heads (Ref 8). Third, they can induce phase transformations in the materials being finished. For example, during the grinding of hardened steels, if the surface temperature of the workpiece is sufficiently high, the surface reaustenitizes; a consequence of the transformation is the formation of brittle, untempered martensite. This type of thermal damage is commonly referred to as *workpiece burn* and is highly undesirable (Ref 9, 10, 11, 12). Another type of phase transformation occurs during the grinding of transformation-toughened zirconia. Here, the phase transformation is due to the transient mechanical and thermal stresses generated during grinding. These forms of thermal damage alter the mechanical, magnetic, and electrical properties of finished materials.

Thus far, thermally induced damage in work materials produced by finishing processes has been highlighted. The local temperatures also play an important role in the degradation of abrasive particles and their bonding material. The transient temperatures prevailing at the abrasive particle tip during grinding contribute significantly to wheel wear. For example, during grinding with diamond wheels, wheel wear can occur by thermally induced degradation of the bond holding the diamond abrasives together on the wheel, by graphitization of the diamond particles when heated above 1200 °C (2200 °F) in air, by microfracture of the abrasive grain as a consequence of repeated heating and cooling, or by diffusion wear of diamond at high temperatures when grinding ferrous metals (Ref 9).

Thermal phenomena thus play a key role in the mechanics of surface finishing processes. The analysis and measurement of temperatures and associated thermal damage generated by finishing processes are essential to the production of engineered components with controlled surface properties. A discussion of these topics constitutes the bulk of this article. Focus is placed on kinematically simple configurations of finishing processes such as surface grinding and flat surface polishing and lapping. The discussion will be applicable with some modifications to kinematically more complex finishing configurations such as form grinding and polishing as well as honing.

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Grinding

Figure 1 shows a schematic of a surface grinding process that will serve as the framework for the discussion of the thermal aspects of grinding. In this operation, the workpiece is moved back and forth across a grinding wheel that is rotated at surface speeds typically exceeding 30 m/s.

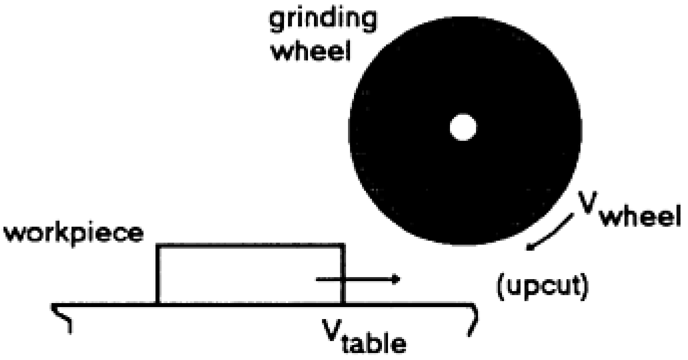

Fig. 1 Typical surface grinding configuration

The Moving Heat Source. In grinding, significant heat is generated at the localized contacts between the abrasive particle and the workpiece material. Moving heat source theory, with the heat generation being taken as the product of a frictional force (idealized to act tangentially at the particle-workpiece contact) and the relative sliding velocity between the abrasive and the workpiece, is applied to calculate the temperature field produced. The moving heat source model does not address the mechanism of heat generation, which is thought to be primarily due to plastic deformation of the workpiece very near the surface (Ref 13). However, this phrase *near the surface* begs the question of defining the workpiece-particle interface. This question is especially difficult in grinding, where material is being constantly removed from the workpiece.

The temperature field produced by a heat source moving over the surface of a semi-infinite solid (here, the workpiece) has been analyzed extensively (Ref 14, 15, 16, 17). One of the earliest analyses of such problems is that due to Blok (Ref 14); this was in the context of calculating sliding contact temperatures. He calculated the maximum surface temperature produced by frictional heating when a single asperity (attached to a semi-infinite solid) was slid against the surface of another semi-infinite solid. Blok's main contribution was in the estimation of the partition of the frictional heat between the two bodies, which was based on the assumption that the maximum temperature in the contact region was the same in either of the two bodies. Subsequently, Jaeger (Ref 15) provided a detailed analytical solution of the temperature field in a semi-infinite solid due to an infinitely wide strip heat source, having finite length in the direction of motion, moving over it. The calculations of Blok and Jaeger showed that the maximum surface temperature produced by the moving heat source in the solid was reached at the trailing edge of the contact region. Shaw (Ref 3) combined the work of Blok and Jaeger and applied it to estimate wheel and work temperatures in dry surface grinding. In this analysis the frictional heat generated at the wheel-work interface was applied as a moving heat source to the surface of a semi-infinite solid. Partition of the heat into the wheel and workpiece was carried out based on Blok's procedure. The mean work-surface temperatures thus calculated were found to be in good agreement with measured surface temperatures in dry grinding. The application of this analysis to calculate the maximum temperature of the abrasive particle and the workpiece during grinding is described below. More details can be found in Ref 1.

Calculation of Abrasive Grain Temperatures. Figure 2 shows a schematic of the moving heat source model used in the following calculations. The moving heat source model approximates the workpiece as a semi-infinite solid whose boundary is insulated away from the heat source. The heat source has length 2*a* in the sliding direction and is of infinite extent perpendicular to the sliding direction. It is moving across the solid with a velocity *V* and is assumed to generate heat at a rate of *q* per unit area per unit time. This solution of the temperature distribution for this problem involves modified Bessel functions. If the Peclet number

$$L \cong \frac{2Va}{a} > 20 \qquad \textbf{(Eq 1)}$$

where α= *k*/(*c*) is the thermal diffusivity of the solid, *k* is the thermal conductivity,   is the mass density, and *c* is the specific heat, then the flow of heat parallel to the surface can be neglected with respect to the velocity of the moving heat source. This approximation is appropriate for single-point (particle) grinding experiments where the abrasive particle is moving with a velocity of ≈ 30 m/s.

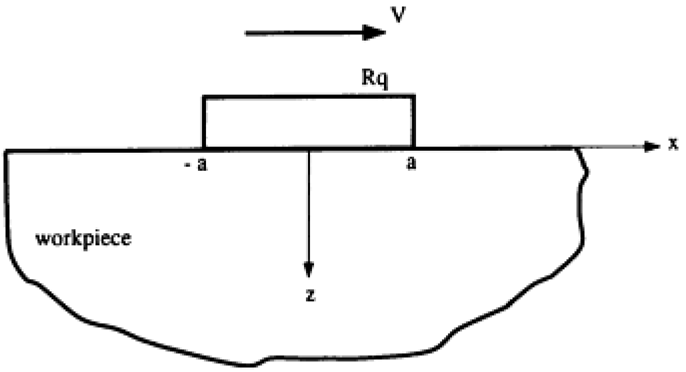

Fig. 2 Schematic of the moving heat source model used in the temperature calculations in text

The differential equation and the boundary conditions governing the one-dimensional transient temperature distribution are:

$$\begin{aligned} &\alpha\frac{\partial^2 T}{\partial z^2} = \frac{\partial T}{\partial t} \qquad z \geq 0, t \geq 0 \\ &k\frac{\partial T}{\partial z}\Big|_{z=0} = -Rq \\ &\lim_{z\to\infty} T \to 0 \\ &T(z, 0) = 0 \end{aligned} \qquad \textbf{(Eq 2)}$$

where $T \equiv T(z, t)$ is the temperature of the workpiece, t is time, and R is the fraction of the generated heat that flows into the workpiece. The solution to this boundary value problem is (Ref 17):

$$T(z, t) = \frac{Rq}{k}\left[2\sqrt{\frac{\alpha t}{\pi}} \exp\left(-\left[\frac{z}{2\sqrt{\alpha t}}\right]^2\right) - z \operatorname{erfc}\left(\frac{z}{2\sqrt{\alpha t}}\right)\right] \qquad \textbf{(Eq 3)}$$

where erfc is the complementary error function. On the surface:

$$T(0, t) = 2\frac{Rq}{k}\frac{\sqrt{\alpha t}}{\sqrt{\pi}} \qquad \textbf{(Eq 3a)}$$

Assuming that at a particular point on the surface the heat is applied beginning at $x = -a$, the time of heating for a point on the surface is $t = (a - x)/V$ and the temperature at a point on the surface is:

$$\bar{T}(x) = 2\frac{Rq}{k}\frac{\sqrt{\frac{\alpha(a-x)}{V}}}{\sqrt{\pi}}, \text{ for } -a < x < a \qquad \textbf{(Eq 4)}$$

The average surface temperature is:

$$\bar{T}_{\text{avg}} \equiv \frac{1}{2a}\int_{-a}^{a} \bar{T}(x)\mathrm{d}x = \frac{4}{3\sqrt{\pi}}\frac{Rq2a}{k}\frac{1}{\sqrt{L}} \qquad \textbf{(Eq 5)}$$

The form of this analysis is consistent with that of a similar analysis given by Ramanath and Shaw (Ref 18) for full wheel grinding.

Equations 2 and 5 can be written for the abrasive particle (or wheel) as well as the workpiece if R is replaced by $1 - R$ and the properties of the abrasive are used. Writing such an equation and setting the average temperature of the grain equal to the average temperature of the workpiece under conditions of thermal equilibrium gives (Ref 18):

$$R = \frac{1}{1 + \sqrt{\frac{(k\rho c)_{\text{A}}}{(k\rho c)_{\text{W}}}}} \qquad \textbf{(Eq 6)}$$

where the subscripts A and W refer to the abrasive and the workpiece, respectively.

The concentrated contact between the abrasive and the workpiece is very similar to that occurring in a microhardness test. If we assume that the contact is a circular patch of radius a, the radius of contact can be obtained as:

$$a = \sqrt{\frac{N}{\pi H}} \qquad \textbf{(Eq 7)}$$

where N is the normal grinding force and H is the Knoop hardness of the workpiece. (The workpiece generally has a smaller hardness than the abrasive.) The heat generated per unit area per unit time is:

$$q = \frac{FV}{\pi a^2} \qquad \textbf{(Eq 8)}$$

where F is the tangential grinding force. Note that this model of the moving heat source does not require any knowledge of the fundamental deformation mechanism (such as brittle fracture, plastic deformation, or plowing) leading to heat generation. Substituting Eq 1, 6, 7, and 8 in Eq 5, the average surface temperature ($\overline{T}_{\text{avg}}$) of the workpiece and the particle in single-point grinding is obtained as:

$$\overline{T}_{\text{avg}} = \frac{8\sqrt{V}}{3\pi^{3/2}\sqrt{2}} \frac{F}{a^{3/2}} \frac{1}{\sqrt{(k\rho c)_{\text{W}}}} \frac{1}{1 + \sqrt{\frac{(k\rho c)_{\text{A}}}{(k\rho c)_{\text{W}}}}} \qquad \textbf{(Eq 9)}$$

When $\frac{(k\rho c)_{\text{A}}}{(k\rho c)_{\text{W}}} >> 1$, Eq 9 becomes:

$$\overline{T}_{\text{avg}} = \frac{8\sqrt{V}}{3\pi^{3/2}\sqrt{2}} \frac{F}{a^{3/2}} \frac{1}{\sqrt{(k\rho c)_{\text{A}}}} \qquad \textbf{(Eq 10)}$$

and ($\overline{T}_{\text{avg}}$) is independent of the thermal properties of the work material. Equation 9 or 10, along with Eq 7 and 8, can now be used to calculate $\overline{T}_{\text{avg}}$ if the normal and tangential grinding forces acting on an abrasive particle are known.

The normal and tangential forces on a single abrasive particle can be directly measured during single-point grinding or in single-grain fly cutting (Ref 1, 9, 19). When grinding is done with a full wheel, the statistical distribution of forces on individual grits can be estimated from a statistical analysis of grit sizes on the wheel surface. Such a calculation has recently been carried out for lapping and polishing (Ref 20). There has, however, been no direct measurement of forces on individual grits during full wheel grinding of metals and ceramics.

There are two important points to be noted in Eq 8 and 9. First, the work-surface (or particle-surface) temperature (Eq 9) is a function of the grinding specific energy (i.e., the energy required for a unit volume of material removal) and the heat partition coefficient, R. This implies that to achieve lower grinding temperatures, a lower specific energy and a smaller value of R are needed. The specific energy depends on the physics of deformation processes leading to material removal, but R is dependent on the thermal properties of the abrasive and the workpiece (Eq 6). The second point is that the main thermal property influencing R is not just the conductivity (k), but the product (k c) of the abrasive and workpiece materials, respectively. This fact has been highlighted by Shaw (Ref 3). Table 1 gives physical properties of various abrasive and work materials, including values of k c. From Table 1, it can be seen that both cubic boron nitride (CBN), and diamond have significantly higher values of k c than alumina (sapphire). Thus, Eq 6 and 9 imply that all other factors remaining the same, grinding temperatures would be lower with a system using CBN or diamond wheels than with one using aluminum oxide wheels. This is consistent with both direct and indirect experimental measurements of temperatures and its derived variables. Quantitative comparisons between measured and predicted temperatures (using Eq 9) are made in the next section.

Table 1 Properties of work materials and diamond abrasive

Property	**Material**						
	Zirconia (YZ-110)[(a)]	**Si_3N_4**	**Sapphire**	**Ni-Zn ferrite**	**1070 steel**	**Diamond**	**CBN**
E, GPa	210	300	390	191	203	1000	660

v	0.24	0.26	0.23	0.2	0.26	0.2	0.15
k, W/m/°C	2.2	33	35	8.7	47	1000	300-600
c, J/gm/°C	0.63	0.72	0.95	0.71	0.432	0.525	0.51
, gm/cc	6.1	3.22	3.90	5.3	7.84	3.5	3.48
k c	8.45	76.5	129.7	32.7	159.2	1837.5	532-1065
HK, GPa	12	16.7	19.6	7.3	. . .	88	40-70

(a) YZ-110 is a tetragonal zirconia polycrystal manufactured by Norton Co.

Measurement of Grinding Temperatures. The abrasive-tip and work-surface temperatures in grinding are highly localized spatially (~100 μm or less in spot size) and decay rapidly with time (within microseconds). Measurement of these temperatures is therefore a challenging task.

Some of the early measurements of grinding temperatures were carried out with thermocouples embedded into the workpiece (Ref 9, 21). The relatively large time constant and poor spatial resolution of thermocouples enable only an estimate of the average temperature to be obtained. In the grinding of steels, such measurements have reported values of ~800 °C (1475 °F) for the work-surface temperature (Ref 9). This is in the neighborhood of the austenitizing temperature for many low-carbon steels.

Another technique for measuring grinding temperatures, which is much more sensitive both spatially and in time, involves monitoring and analysis of infrared radiation being emitted by the abrasive particle and/or the workpiece (Ref 1, 6, 22, 23). Using such a technique, the authors recently measured full-wheel, single-particle, and work-surface temperatures during the dry grinding of metals and ceramics (Ref 1, 23). For more details about the technique, see Ref 1; Table 2 and Fig. 3, 4, 5, and 6 show some of the results. In Table 2, the measured temperatures in single-particle (diamond) grinding of ceramics are compared with the analytical estimates (Eq 9) for this temperature at different wheel velocities. There is good agreement between the measured and predicted values. It must be noted here that the measured particle temperatures are high, ~600 to 1600 °C. When grinding is done with a full wheel, different abrasive particles on the wheel surface are exposed to different depths of cut due to their varying amounts of protrusion from the wheel surface. Therefore, each of these particles cuts out a different volume of material, and their tip temperatures are likely to differ. Indeed, this is seen to be the case in Fig. 3, 4, 5, and 6, where the particle temperatures are plotted as histograms. The mean of the particle-surface temperatures on the wheel (and consequently work-surface hot-spot temperatures) are found to vary between 592 °C for zirconia and 721 °C for 1070 steel.

Table 2 Single-point grinding temperatures

Material	***R***	**Temperature, °C, at wheel velocity of:**					
		25 m/sec		**32 m/sec**		**37 m/sec**	
		E	**A**	**E**	**A**	**E**	**A**

Zirconia	0.064	1260±51	1320	1601±74	1494	. . .	. . .
Si_3N_4	0.17	1133±60	1110	1452±49	1255	. . .	. . .
Ni-Zn ferrite	0.12	570±30	537	620±35	607	690±30	653
Sapphire	0.21	920±65	. . .	1060±45	. . .	1270±80	. . .

(a) *R*, fraction of the generated heat that flows into the workpiece, as defined in Eq 6; E, experimentally measured value (including standard deviation; A, analytically measured value (depth of cut 10 μm, table velocity 23.4 mm/s, diamond indenter tip radius 15 μm)

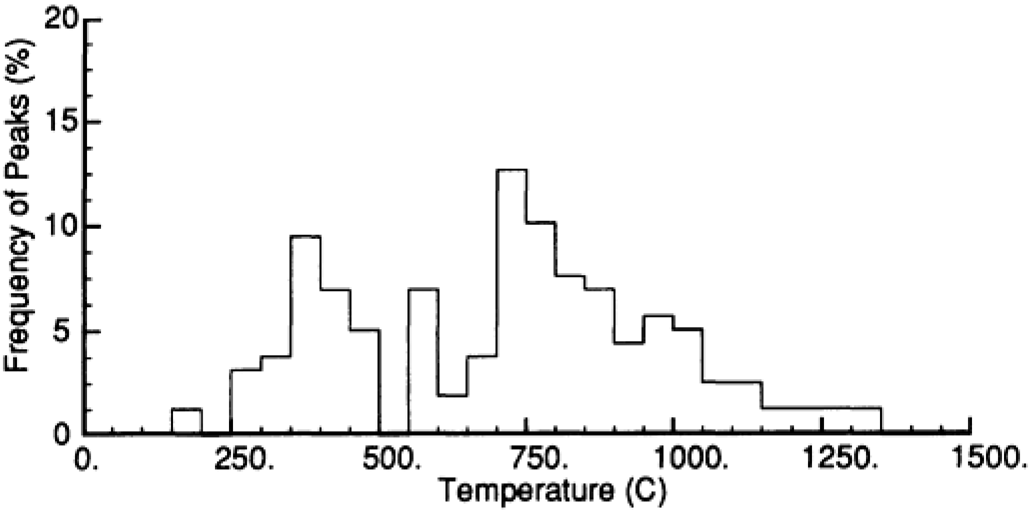

Fig. 3 Distribution of wheel temperatures in full wheel grinding of silicon nitride. Depth of cut, 12.5 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 220-grit

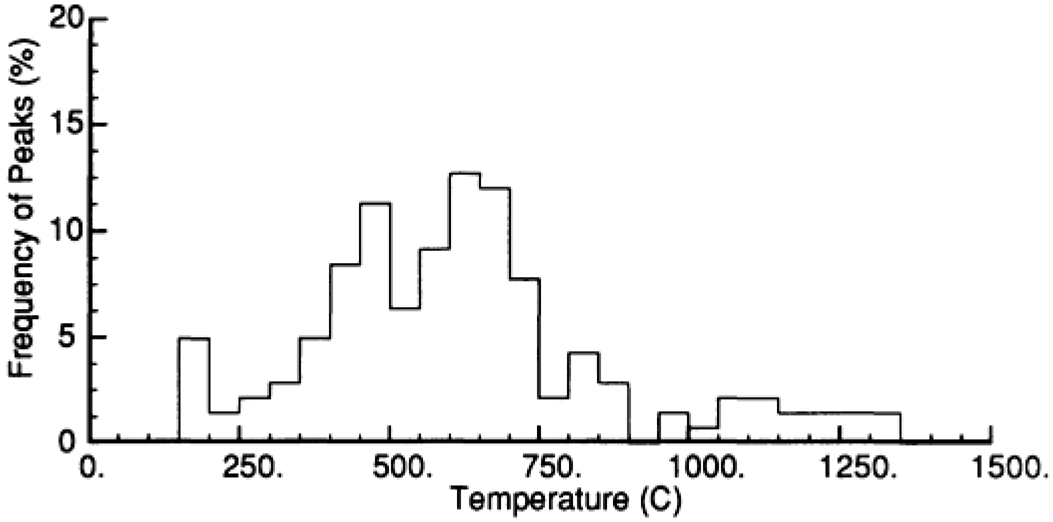

Fig. 4 Distribution of wheel temperatures in full wheel grinding of zirconia. Depth of cut, 12.5 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 220-grit

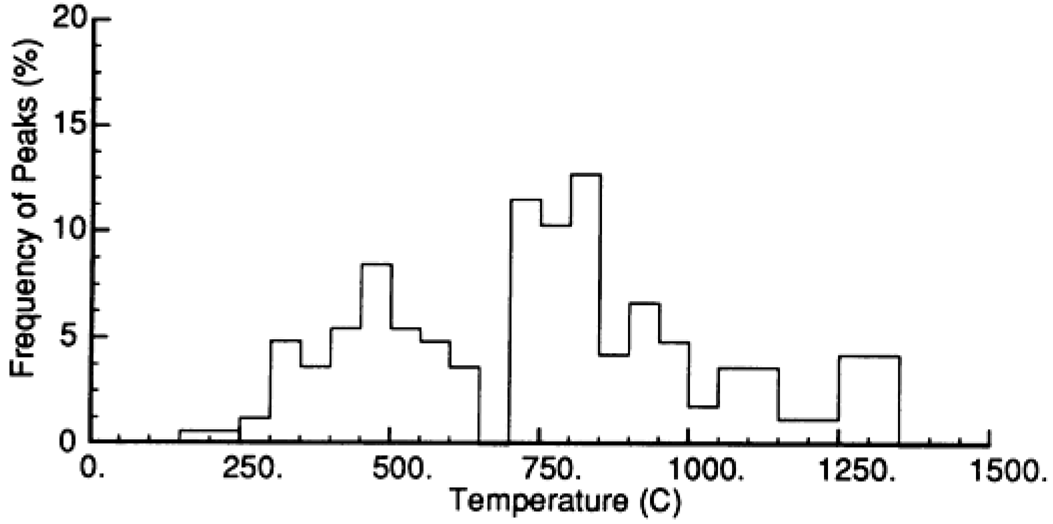

Fig. 5 Distribution of wheel temperatures in full wheel grinding of 1070 carbon steel. Depth of cut, 12.5 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 220-grit

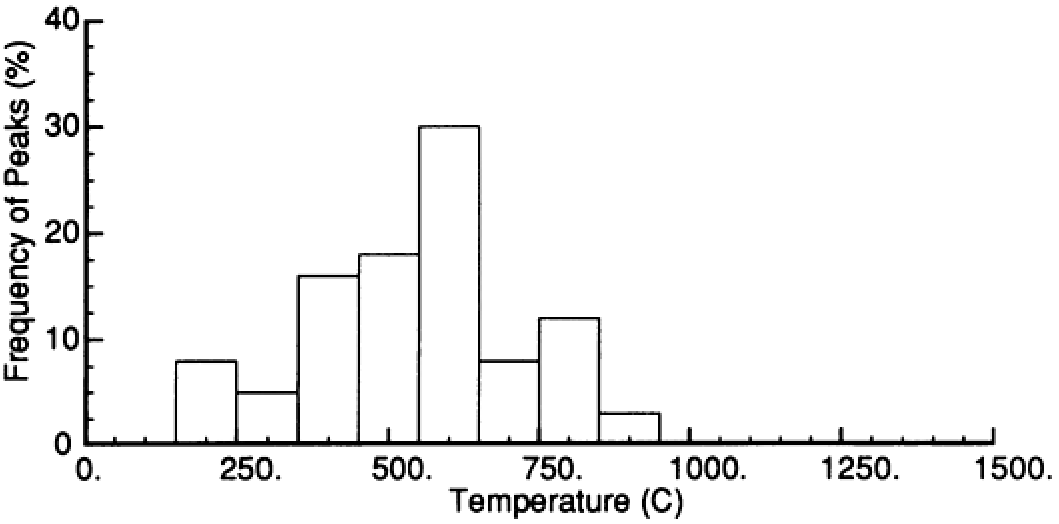

Fig. 6 Distribution of wheel temperatures in full wheel grinding of ferrite. Depth of cut, 20 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 320-grit

Sometimes, abrasive-particle temperatures are observed to reach the melting point of steel during the grinding of hardened steels. It is possible that under such conditions, there is actually melting of the steel at some regions along the wheel-work contact. Such melting could cause the spherical swarf particles shown in Fig. 7. Indeed, there is compelling evidence in support of this hypothesis (Ref 24). Many investigators (Ref 9, 25), however, have attributed the formation of such spherical particles only to melting during exothermic oxidation of the chips in air; this is, no doubt, a parallel mechanism. Infrared temperature measurements have also shown that the subsurface temperature in a workpiece decays rapidly with depth (Fig. 8). The high temperature gradients are the primary source of the tensile residual stresses, microcracking, and phase transformations sometimes observed on ground surfaces. Another observation from temperature measurements is that an abrasive grain on the wheel surface cools down rapidly after leaving the grinding zone and almost reaches room temperature in one revolution of the wheel before it begins its next cut (Ref 1).

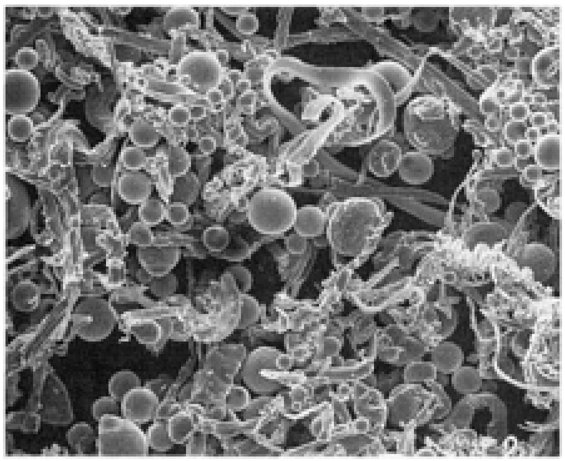

Fig. 7 Scanning electron micrograph of grinding swarf from 52100 steel showing spherical particles

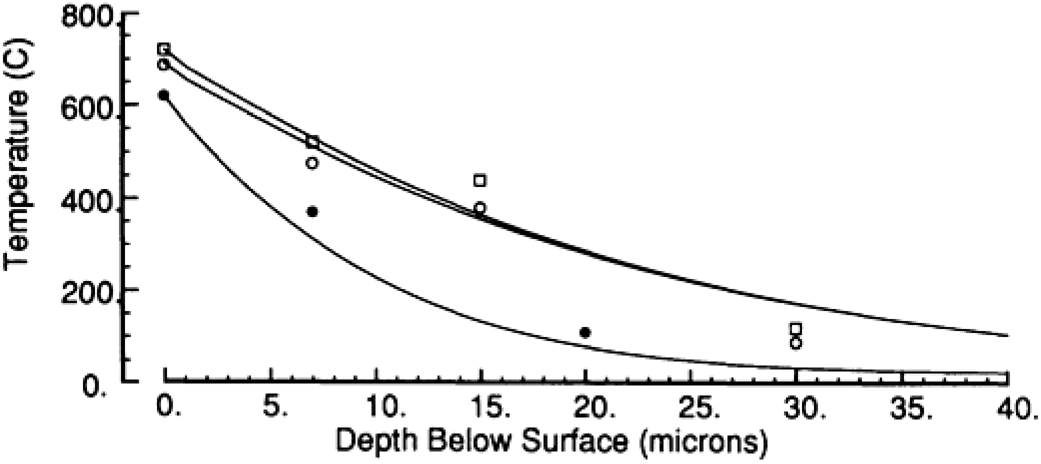

Fig. 8 Distribution of subsurface workpiece temperatures in full wheel grinding. Table velocity, 23.4 mm/s; wheel velocity, 32 m/s. d , silicon nitride (measured, 220-grit, 12.5 μm depth of cut); •, ferrite (measured, 320-grit, 20 μm depth of cut); □, 1070 steel (measured, 220-grit, 12.5 μm depth of cut). The solid lines are calculated values for the subsurface temperature obtained by matching the experimentally measured temperatures at the surface.

Coolant and Grinding Temperatures. Thus far, focus has been concentrated primarily on dry surface grinding. In practice, grinding operations on metals usually involve use of a coolant-lubricant fluid (Ref 4, 9). The purpose of this fluid is twofold: to provide lubrication and reduce frictional forces at the wheel-work interface and to cool the workpiece. No well-validated analysis of grinding temperatures takes into account heat transfer into the fluid, but the physical principles underlying such an analysis would not alter the broad nature of the temperature calculations given in Eq 9. It is generally accepted that the coolant has little influence on the peak abrasive tip temperature but does reduce the average bulk temperatures of the wheel and workpiece, thereby limiting thermally induced dimensional distortions. Although there is no experimental verification of the former hypothesis, the proper application of coolant is very beneficial in many grinding operations with metals due to its influence on the bulk temperature.

Surface Damage. The high surface temperatures and steep temperature gradients at the surface of the workpiece material during grinding are responsible for many forms of damage (Ref 26). During the grinding of ceramics, which are relatively brittle compared to metals, the high thermal stresses developed near the surface cause microcracking (Ref 27). Such microcracking is one of the main causes of strength degradation and strength anisotropy (with respect to grinding direction) commonly observed in ground ceramic components (Ref 28). Control of these thermal stresses is critical to the development of better grinding methods for ceramics. In electronic ceramic materials, the high temperatures and temperature gradients cause the near-surface electromagnetic properties to be changed, which affects the performance of these materials when they are fabricated into devices. Examples in this category are the ferrites (Ni-Zn, Mn-Zn, etc.) used in recording heads in magnetic storage systems. Grinding residual stresses or heating of the material during grinding to above the Curie temperature (typically between 800 and 900 °C, or 1470 to 1650 °F, for these materials) usually leads to the formation of magnetically damaged surface layers that have an adverse effect on recording head performance during the read/write process (Ref 8).

During the grinding of plain carbon or hardened alloy steels, one of the most common types of thermally induced damage is workpiece burn (Ref 29). The burn is characterized visually by bluish temper colors on the work surfaces, which are usually attributed to oxide-layer formation. The temper colors can be removed by sparkout at the end of the grinding cycle. However, this does not mean that the effects of burn are removed. Microhardness measurements on workpieces show that visible burn is accompanied by reaustenitization of the work surface during grinding. When hardened steels are ground without any burning, there is generally some softening due to tempering of the material close to the surface. This is seen in the "no burn" curve in Fig. 9 (Ref 29). Here, the material near the surface is seen to have a smaller microhardness value than the material in the bulk. However, under burn conditions in hardened steels, quite the opposite effect is seen at the surface; the "burn" curve in Fig. 9 shows that the surface layer has been hardened by grinding. This occurs as a consequence of reaustenitization of the work material near the surface during grinding, followed by the formation of hard, untempered martensite as a result of quenching. The martensitic layer can be identified upon etching of the surface as a white phase, usually occurring in patches (Ref 11, 12, 29). When grinding of soft steels is done, however, workpiece burn is not seen to cause any surface hardening. In such instances, burn is best detected by metallographic techniques (Ref 11, 12). The occurrence of workpiece burn in steels has been shown to be virtually coincident with the work-surface temperature exceeding the austenizing temperature (~800 °C, or 1470 °F, for low- to medium-carbon steels) during grinding. This observation has provided a basis for analytically deriving "burn limit" conditions for steels through calculations of grinding temperature from power or force measurements (Ref 29).

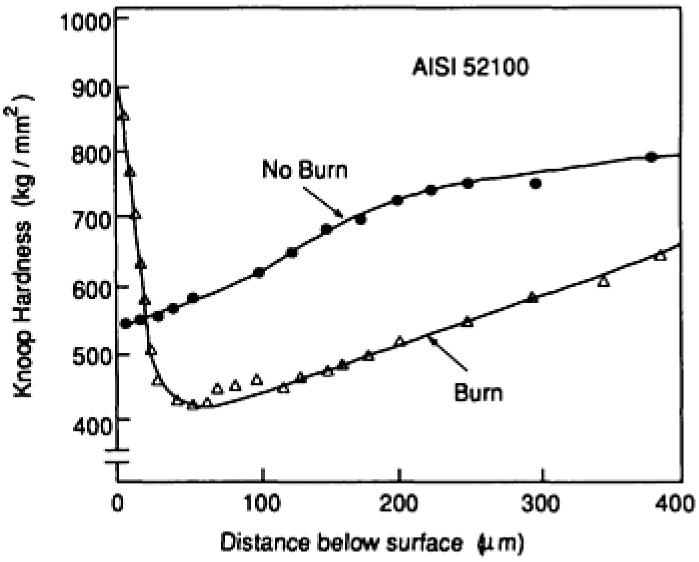

Fig. 9 Variation of microhardness with depth in a hardened bearing steel ground under "burn" and "no burn" conditions. Source: Ref 9

The avoidance of workpiece burn during the grinding of hardened steels is critical for better tribological performance. For example, workpiece burn in bearing steels is found to affect their fatigue life adversely (Ref 30). Figure 10 shows the L_{10} fatigue life of hardened bearing rings finished under various grinding conditions (L_{10} is the fatigue life exceeded by 90% of the specimens). The fatigue life decreases dramatically when the grinding specific energy, *u*, exceeds the threshold limit for burn, u^* (i.e., $u/u^* > 1$).

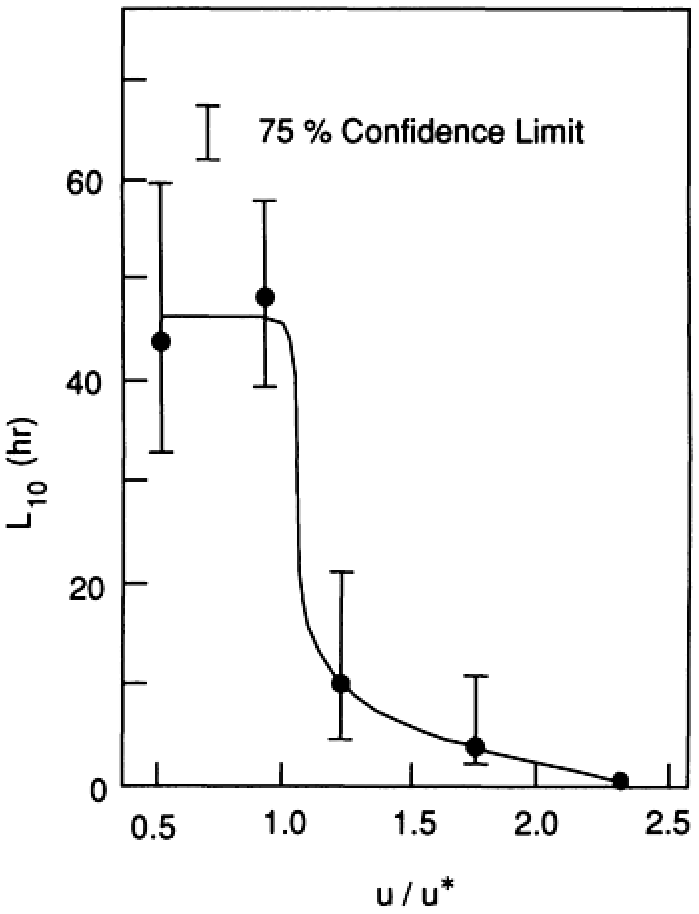

Fig. 10 Variation of L_{10} fatigue life with specific energy ratio (u/u^*) for a ground bearing steel. The critical value is $u/u^* = 1$, beyond which burn is observed to occur typically. Source: Ref 9

Besides workpiece burn in steels, the occurrence of high temperatures usually leads to tensile residual stresses on ground steel surfaces. This is again undesirable for enhanced tribological performance. However, control of the residual stress distribution on ground surfaces of steels is possible by ensuring that surface temperatures are kept low during grinding. Figure 11 shows the variation of measured surface residual stress with calculated grinding temperature for 52100 bearing steel ground with Al_2O_3 and CBN wheels. Under most conditions reported in Fig. 11, CBN grinding is found to produce compressive residual stresses on the surface, in contrast to Al_2O_3 grinding. This is due to the lower temperatures at the ground surface in CBN grinding. It has been suggested that lower grinding temperatures lead to reduced tensile stresses on ground surfaces, and Fig. 11 provides perhaps the most striking experimental illustration in support of this speculation.

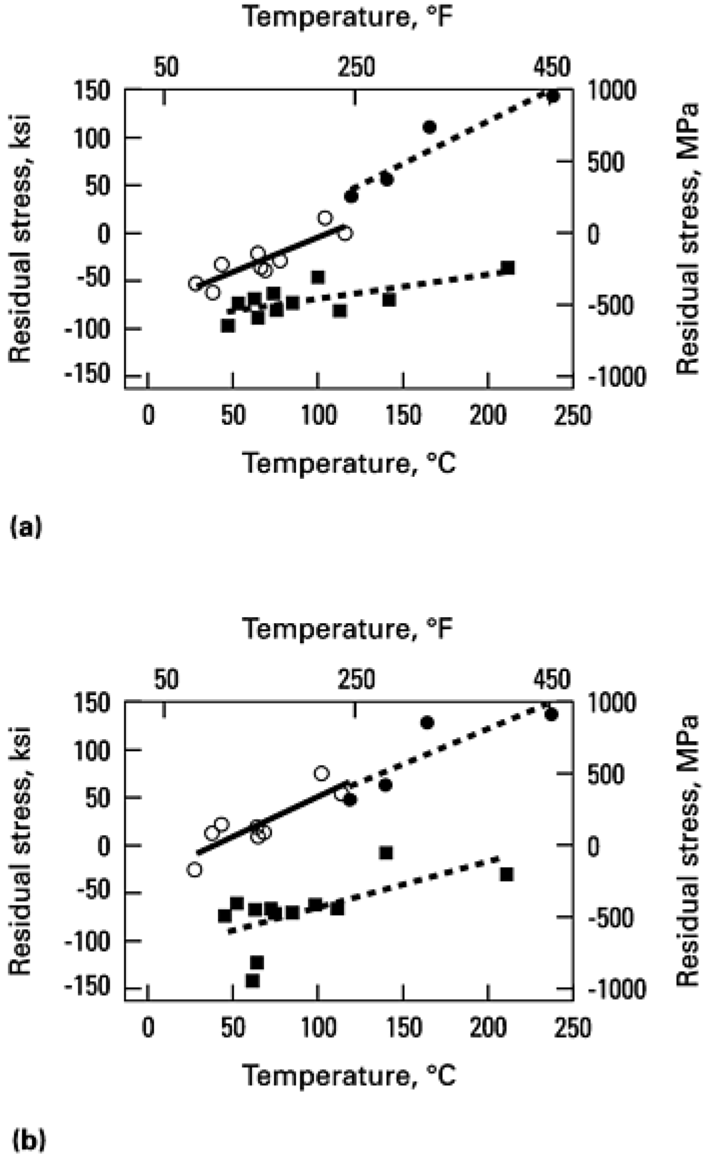

Fig. 11 Variation of surface residual stresses with grinding temperature in ground surfaces of 52100 steel. d , aluminum oxide 60 J6; •, aluminum oxide 100 H6; ■cubic boron nitride. (a) Residual stress perpendicular to grinding. (b) Residual stress parallel to grinding

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Lapping and Polishing

Lapping and polishing are used to produce smooth or ultrasmooth surfaces (i.e., surfaces with an R_a of a few nanometers). They are carried out by placing a slurry of abrasive particles in a liquid vehicle between the specimen and a hard metallic block (lapping) or a soft, flexible pad (polishing). While the block is loaded against the workpiece (specimen) either hydraulically or mechanically, the abrasive particles roll or slide across the specimen so that the wear process is one of three-body abrasion (Ref 20). As in grinding, the abrasive particles have a wide range of sizes, with an average value typically between of 0.05 to 70 μm. The mean sliding velocity between the abrasive and the specimen in lapping or polishing is typically no greater than 0.5 m/s, which is two orders of magnitude less than that in grinding.

At present there are no reliable calculations of lapping and polishing temperatures. The maximum temperature rise at the abrasive-work interface is thought to be small due to the relatively low sliding velocity between the contacting surfaces, and several arguments support this hypothesis. Recent calculations of the distribution of forces on diamond abrasive particles during the lapping and polishing of ceramics show that the average load applied to a particle is no greater than 1 N under typical conditions (Ref 20). If this load is assumed to act on a particle sliding at a velocity less than 0.5 m/s, a heat partition and heat-transfer analysis carried out along the lines of the grinding calculations described earlier shows that the maximum temperature rise at the work surface is no greater than 100 °C (212 °F) for a friction coefficient of μ= 0.1 between the abrasive and work surface. Even though such an analysis might not be completely rigorous for lapping and polishing, the error in the calculation of the temperature rise is not expected to be significant. Further evidence to support the low temperature rises comes from observations pertaining to residual stresses and microcracking. Lapped or polished surfaces of metals and ceramics are generally found to contain compressive residual stresses due to localized plastic deformation resulting from an indentation/microcutting action of the abrasive particles (Ref 6, 8). Thermally induced residual stresses, in contrast, are tensile in nature; see the previous discussion pertaining to grinding. Metallurgical studies of the structure of lapped or polished steel surfaces show little evidence of structural changes commonly associated with localized high temperatures (e.g., no indication of phase transformations or burn in lapped surfaces of hardened steels). Also, there is very little microcracking to be seen on lapped or polished surfaces of ceramics (Ref 6, 8). Such microcracking, if present, is usually a strong indicator of the occurrence of steep temperature gradients near the surface that cause high, transient stresses.

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Selection, Application, and Disposal of Finishing Fluids

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Introduction

FINISHING METHODS can include a wide variety of processes such as lapping, polishing, tumbling, and loose media. However, in keeping with metalworking tradition and for the purposes of this discussion, the term *finishing methods* will largely be confined to what are commonly called grinding operations. It should be kept in mind, however, that rapid advances in ceramic, cubic boron nitride, and diamond tools, machine rigidity, high-speed spindles, and machine control systems are providing metal workers with many alternatives traditional grinding operations in generating smooth, close-tolerance surfaces. By the same token, the creep-feed grinding process, especially the "continuous dress" version, can effect extremely high rates of stock removal while generating very close size control and good surface finish *without* causing thermal damage to the workpiece, and it is allowing a grinding process to be substituted for more traditional chipmaking material removal processes.

This article discusses environment issues and regulations related to surface finishing processes. Additional information is a available in the article "Environmental Regulation of Surface Engineering" in this Volume.

The Grinding Zone Environment

The grinding process is extremely complex, and a number of elements in it must be reviewed in order to make a reasonably adroit initial selection of a fluid or fluids for a manufacturing plant. At a minimum one must catalog the grinding operations, the work materials and their hardnesses, the wheels and/or belts in use and their bond systems, the amount of material to be removed and the finish desired in each operation, and the relative need for in-process corrosion protection. A number of these elements can impose conflicting requirements on fluids and force compromises in fluid selection. For example, lubricating and cooling ability are conflicting properties in grinding fluids, very much as hardness and toughness are conflicting properties in cutting tools.

Grinding fluids can be composed of petroleum oil, extreme-pressure lubricants, emulsifiers, soaps, wetting agents, coupling agents, corrosion inhibitors, biocides, antifoams, and water. Depending on composition, fluids are generally categorized as:

- *Synthetic or chemical fluids* contain no petroleum oil and generally have very high cooling but low lubricating properties.
- *Semisynthetic or semichemical fluids* contain a small to moderate amount of oil and generally have high cooling and moderate lubricating properties.
- *Emulsions or soluble oils* are largely composed of oil and emulsifiers and generally have good cooling an moderate to high lubricating properties.
- *Straight or "neat" oils* are used without dilution in water and generally have poor cooling but the highest lubricating properties.

In general, one will never be able to select a single fluid that will be optimum for all types of grinding operations, all types of work materials, and all types of abrasives. The object then becomes finding a reasonable number of fluids, perhaps two or three, that will work well for the vast majority of grinding operations in the plant and have the desirable characteristics of being safe for the machine operators, being "kind" to the machine tools, providing good in-process corrosion protection, and providing long sump life and the potential for recycling. With the proper selection of fluids, total manufacturing costs will decrease because of improved wheel life, decreased dressing, higher throughput, and decreased machine maintenance and fluid disposal.

Fluid Selection. The use of the metalworking fluid itself should be appropriate for the intended operation. However, one has to take into consideration the other operations in the shop, because to keep the management of the fluid easier it is sometimes best to use one fluid that can do the majority of the work. In a grinding operation it is important for the fluid to provide cooling and not foam, so synthetic fluids or soluble oils are generally recommended. The synthetic fluids are commonly used in surface grinders or when diamond wheels are involved, whereas the soluble oils are used in centerless or creep-feed grinding. Straight oils are used in thread grinding or crush grinding where more lubricity is required.

The semisynthetic fluids are somewhere in the middle where cooling is important but lubricity is required. In an electrical discharge machining operation, it is important that the dielectric oil provide good resistivity at the point of initial forming of the part and not smoke. Table 1 lists suggested fluids for a variety of metals on specific operations.

Table 1 Selection guide for metalworking fluids for finishing operations

Work materials	Thread gear, form	Centerless cylindrical	Internal	Surface	Abrasive cutoff
Free-machining steel (low-medium carbon)	MD oil, HD water	LD oil, MD-HD water (miscible)	GP water (miscible)	LD-GP water (miscible)	Water (miscible)
Low-alloy structural steel (martensitic)	HD oil, HD water (miscible)	HD oil, HD water (miscible)	LD oil, GP water (miscible)	GP water (miscible)	Water (miscible)
Hot-work die steels (martensitic), stainless steels (austenitic, martensitic, precipitation-hardened), maraging steels, nickel and cobalt alloys	HD oil, HD water (miscible)	HD water (miscible)	GP oil, GP water (miscible)	HD water (miscible)	Water (miscible)
Cast iron	HD water (miscible)	GP water (miscible)	GP water (miscible)	GP water (miscible)	Water (miscible)
Magnesium and alloys	LD oil, SP fluids	LD oil, SP fluids	LD oil, SP fluids	LD oil, SP fluids	LD oil, SP fluids
Aluminum and alloys	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)
Copper and alloys	HD water (miscible)	LD oil, HD water (miscible)	LD oil, HD water (miscible)	LD oil, HD water (miscible)	HD water (miscible)
Titanium and alloys	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)
Beryllium and alloys	HD water (miscible)	HD water (miscible), SP fluids	HD water (miscible), SP fluids	HD water (miscible), SP fluids	Water (miscible)
Refractories	HD oil	HD oil, HD water (miscible)	HD oil, HD water (miscible)	HD oil, HD water (miscible)	HD oil, HD water (miscible)

MD, medium duty; HD, heavy duty; LD, light duty; GP, general purpose; SP, special.

Source: Ref 1

The fluid recommendation and correct dilution should be supplied by the manufacturer. The proper dilution is important because a lean solution increases rust and bacteria growth, whereas a rich solution can produce residues and dermatitis. Another area of concern is the water used for the dilution, which may contain contaminants that can cause the concentrate to separate and produce residues and rust. The use of a deionizer will remove the minerals from hard water and form a better dilution.

Once the metalworking fluid is in the machine it needs to be maintained to ensure chemical stability and operator safety. The metalworking fluid can be contaminated with oils, rust preventives, cleaners, and solubilized metals that can degrade the fluid. The fluid manufacturer will be able to determine the problem and make the necessary corrections. All additives and biocides should be used only as recommended by the manufacturer.

Fluid Application. Proper fluid application (volume and pressure) is essential to make the grinding wheel run cooler, decrease its tendency to grab and hold particles of metal removed from the work, and reduce the cut and therefore create a smoother, finer finish. In a grinding operation, it is most important that chips not interfere with the operation, so the application of the selected fluid is vital to provide the appropriate amount of cooling at the point of cut and still flush the chips from the machining area.

To deliver cutting fluid efficiently into the arc of cut, the velocity of the cutting fluid must be at least equal to or 10 to 15% faster than the peripheral speed of the grinding wheel. The optimum flow rate and pressure need to be developed for each application; however, in creep-feed grinding it is recommended that the flow rate should be of the order of 60 to 80 gal/min (225 to 300 L/min) and the nozzle pressure around 80 to 100 psi (550 to 700 kPa). The nozzle should be adjusted to direct the fluid stream on the work at or above the point of cut, and the incorporation of a cutting fluid guideway behind the workpiece will maintain the flow of fluid through the arc of cut, eliminating the burn at the end of a cut. Specially designed nozzles or slotted and grooved wheels will help the metalworking fluid penetrate to the point of cut. Methods of applying the fluid range from flooding to misting, depending on the type of fluid selected, the operation itself, and the amount of heat being transferred to the tool and workpiece.

The effect of the fluid on the cutting temperature may be due either to direct cooling or the reduction of the energy required in performing the operation. At low speeds, the fluid has time to penetrate to reduce friction and decrease the temperature. At high speeds the fluid has little effect on the temperature at the point of cut, but it removes heat from the tool and workpiece, preventing heat accumulation and temperature buildup in the vicinity of the active cutting edge of the tool. Application of the correct fluid can also cut down the number of passes required to finish the part. Another way to shorten the cycle time is to increase the speeds and feeds.

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Disposal Issues

When the time comes to dispose of spent fluids, consideration must be given to the myriad of regulations that protect the environment and the people from improper dumping of hazardous materials. All municipalities and states have the authority to promulgate their own specific set of waste disposal regulations, and many have done so. It is important that before any waste is disposed of, the appropriate local, state, and federal regulations be consulted. This discussion, however, is limited to the federal Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) regulations. This federal law establishes the minimum requirements for waste disposal and is the basis for local regulation of wastes. All industrial waste, including spent metalworking fluids, must be evaluated against RCRA criteria to determine if it is hazardous or not.

Hazard Determination. RCRA gives the EPA the authority to regulate industrial waste from generation through transportation to treatment and ultimate disposal, the so-called "cradle-to-grave" approach. Currently the major thrust of RCRA is directed toward the management of hazardous waste. EPA has indicated in its regulatory agenda that designated waste oil (i.e., engine, hydraulic, lubricating, and cutting oils) is not classified as a hazardous waste. Although this designation does encompass all types of cutting and grinding fluids, the fact that they are not generically listed as a hazardous waste does not mean specific spent fluids are not hazardous or subject to regulation. For example, a spent fluid might be classified as a hazardous waste due to the presence of certain metals. Any fluid used in the machining process tends to dissolve some of the metals being machined. If the part being worked contains any metals considered to be hazardous by RCRA definition and the fluid solubilizes enough of that metal to exceed the regulatory limit, the fluid as a whole is considered to be a hazardous waste. For many possible metallic contaminants, a few parts per million is sufficient to exceed the regulatory limit. The only way to be certain is to run a toxicity characterization test to determine whether any of the contaminants on the list are present in the fluid at levels that would trigger treatment of the waste as hazardous. Table 2 is a listing of the contaminants and their trigger levels.

Table 2 Maximum concentration of contaminants for the toxicity characteristic

EPA HW No.[(a)]	Contaminant	CAS No.[(b)]	Regulatory level, mg/L
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon tetrachloride	56-23-5	0.5
D021	Chlorbenzene	108-90-7	100.0
D020	Chlordane	57-74-9	0.03
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D024	m-Cresol	108-39-4	200.0(c)
D023	o-Cresol	95-48-7	200.0(c)
D025	p-Cresol	106-44-5	200.0(c)
D026	Cresol	. . .	200.0(c)
D016	2,4-D	94-75-7	10.0
D027	1, 4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichloroethane	107-06-2	0.5
D029	1,1-Dichloroethylene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.13(d)
D012	Endrin	72-20-8	0.02

D031	Heptachlor (and its epoxide)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	0.13(d)
D033	Hexachlorobutadiene	87-68-3	0.5
D034	Hexachloroethane	67-72-1	3.0
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D009	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentrachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	5.0(d)
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	8001-35-2	0.5
D017	2, 4,5-TP (Silvex)	93-72-1	1.0
D040	Trichloroethylene	79-01-6	0.5
D041	2, 4,5-Trichlorophenol	95-95-4	400.0
D042	2, 4,6-Trichlorophenol	88-06-2	2.0
D043	Vinyl chloride	75-01-4	0.2

Source: Ref 2

(a) HW, hazardous waste.

(b) CAS, Chemical Abstracts Service.

(c) If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D0026) concentration is used. The regulatory level of total cresol is 200 mg/L.

(d) The quantitation limit is greater than the calculated regulatory level and therefore becomes the regulatory level.

Another factor in determining whether the spent fluid is hazardous is chlorine content. According to the federal regulations, if the waste contains over 1000 ppm Cl it is assumed to be hazardous. However, if the chlorine present is due to chlorinated paraffins, which are used in industry as an extreme-pressure additive, then the classification as "hazardous" can be rebutted. That is, if the generator of the waste can demonstrate that the only source of chlorine present in the spent fluid is from a nonhazardous and nonregulated component and/or contaminant, then the waste need not be handled as hazardous. An important point to note is that several states have promulgated their own state laws that define all waste oils that contain any chlorine or petroleum oil as hazardous.

Reducing Disposal Frequency. If a spent fluid is determined to be a hazardous waste, the effects include increases in disposal, administrative, labor, and insurance expenses. The amount of paperwork increases, due to requirements for use of a manifest system, labeling, reporting, and recordkeeping, and the liability exposure of the waste generator increases. One solution that helps minimize the impact of all these costs is to set up a recycling program that extends the life of the fluid, therefore decreasing the amount of environmental pollution and eliminating some of the cost, paperwork, and liability. The fluid is periodically removed from the machine, and the tramp oil and metal fines are removed from the dirty fluid. Fresh fluid is then added as makeup to the recycled fluid, and the clean mixture goes back into the machine. The recycling process reduces the frequency with which the fluid, which can be as much as 98% water, must be hauled away. This can save a substantial amount, as the costs for haulaway have increased considerably (Table 3). It is therefore very advantageous for the metalworking fluid user to consider some form of recycling to extend the life of the fluid.

Table 3 Trends in haulaway costs for spent coolant

Region	**Dollar cost per gallon**			
	1983	**1985**	**1988**	**1991**
Northeast	0.20-2.00	0.20-3.00	0.24-3.00	0.50-5.00
Southeast	0.20-1.00	0.20-1.25	0.30-2.00	0.20-2.75
Midwest	0.12-1.00	0.18-1.00	0.17-1.75	0.22-3.00
Northwest	0.30-1.00	0.50-1.75	0.70-2.25	2.00-4.00
Southwest	0.07-1.50	0.16-1.75	0.60-2.00	0.75-5.00

Note: These costs do not include transportation, lab fees, or surcharges for waste. Source: Ref 3

Disposal Methods. Eventually the fluid will reach a point where it can no longer be recycled and must be disposed of. Currently there are three methods: haul everything away; evaporate the water and haul the residual away; or perform chemical/mechanical pretreatment.

Hauling. When selecting a company that hauls away the spent fluid and treats it, it is important to ensure that it is licensed and reputable. If the fluid is disposed of illegally the law will hold the waste generator responsible.

Evaporating. The use of an evaporator to reduce the volume of water can eliminate some of the cost. A problem area can be created if oil floats to the top, where it has a tendency to cover the fluid and prevent the evaporation process from taking place. Some types of agitation, such as the introduction of small air bubbles to dissipate the oil layer, will aid the evaporation process. The use of heat to increase the evaporation rate is effective but needs to be controlled so that the fluid does not boil, creating a potential for air pollution and the need for air permits.

Pretreating involves breaking the fluid down by separating the water from the fluid concentrate and contaminants. The reduced volume of oil and organic material can then be hauled away at a lower cost. The waste generator treats the water phase so it can be released to the sanitary sewer for further treatment by the local wastewater treatment company. The water phase should not go into a waterway. The oil that is discarded of can be rerefined or used in the supplemental fuels program.

The disposal of grinding fines is another concern, so one needs to select the correct type of chip wringer to squeeze out as much fluid as possible. The drier the chip, the lower the cost. There are several methods to dry chips, including evaporators, filters, and wringers. As with fluid, the waste generator of the chips is responsible for them forever, making it very important to use a reputable chip hauler and disposal firm. Some of these chips can be remelted, although others will have to be scrapped.

References cited in this section

2. 40 CFR 261.24, Table 1, 1 July 1992

3. Survey by Master Chemical Corp., 1992

Regulatory Trends

The 1970s saw the passage of numerous legislative efforts to improve worker health and safety and protect the environment. The Occupational Safety and Health Act, National Environmental Protection Act, Clean Water Act, Clean Drinking Water Act, Clean Air Act, Toxic Substances Control Act, Comprehensive Environmental Response, Compensation and Liability Act ("Superfund"), and Resource Conservation and Recovery Act are just a few.

This regulatory trend has carried on into the 1990s, but with a slightly different emphasis. Initially, the greatest impact was felt by chemical producing companies. Now, chemical user industries, including the metalworking industry, are being more directly affected by the regulation of chemicals. Regulations such as the OSHA Hazard Communication Standard (worker right-to-know) and the EPA rules for the Emergency Response and Community Right-To-Know Act place considerable responsibilities on all manufacturing sectors that use chemicals in their processes, not just on the chemical makers. These responsibilities include education and training of workers, use of proper labels and material safety data sheets, written plans, maintenance of inventory records, and submission of inventory and release data. All metalworking fluids will be covered by many of the regulations to some degree or another, so users of cutting and grinding fluids will find themselves subjected to many of these regulations. To determine which regulations apply and to what degree takes a considerable amount of time, but the consequences of not complying can include fines and jail sentences.

Future regulations which the metalworking industry should carefully watch are OSHA reform, EPA management standards, the Great Lakes Initiative, the Clean Air Act, and the Oil Pollution Act.

Influence of Work Material Properties on Finishing Methods

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Introduction

FINISHING METHODS used to generate surfaces of work materials range from rough finishing to precision finishing to ultraprecision finishing, depending on the surface features or quality desired. For instance, stone is quarried by cutting processes, which are primarily rough finishing methods. The stone may then be precision finished to achieve the smooth surfaces used in tiles or furniture. If the stone is to be used for a machine tool bed or gaging plate, extreme control of tolerances and surface finish will be required, and an ultraprecision finishing method will probably be used to achieve the desired results. The ability to finish a work material through all these processes largely depends on the work material properties.

Work Material Properties and Their Role in Finishing

Hardness is the resistance to indentation. Because every surface finishing method involves creation of new surfaces, higher hardness always implies greater machining forces (e.g., it is more difficult to machine harder steel than softer steel). Higher hardness also implies greater wear of the cutting tool or abrasive product. This may be due to the wear caused by direct contact between the tool and the work, or it may be due to the wear caused by the hard and abrasive chip after it is released from the work material.

Toughness is the resistance to fracture. It is easier to propagate cracks or fracture through material of lower toughness. Hence, it is easier to machine high-hardness, low-toughness alloy steels than high-toughness stainless steel of equal hardness. However, extremely low toughness is not desirable, as is readily evident from the difficulty in machining glass or ceramics. In these materials it is desirable to use finishing methods or finishing process conditions that prevent the generation of cracks rather than minimizing or controlling crack propagation.

Stiffness is the resistance to deformation. It is often measured as the elastic modulus, or the slope of the stress-strain curve. Because most finishing methods require application of force for surface generation, it is desirable to have minimum deflection or distortion under the applied force to achieve close dimensional tolerances. In this regard, it is easier to achieve complex contours, closer geometry, and closer surface finish in higher-stiffness material. For instance, extremely thin sections can be machined in ceramics, and closer tolerances and surface finishes can be achieved in ceramics than in metals, because ceramics have about twice the stiffness (elastic modulus) of most metals or alloys.

Ductility is the ability of the material to deform plastically before fracture is initiated or propagated. This is generally measured in terms of percentage elongation. Ductile materials are generally more difficult to machine; they require considerably more energy to generate the chips. For instance, the specific energy required to machine soft steel is generally higher than that required to machine cast iron of equal hardness. This energy requirement is minimized by close control of the geometry of the cutting tool. Hence, positive-rake tools of small nose radius are required for machining aluminum, brass, and so forth.

The long, stringy chips produced in ductile materials often lead to extensive sliding that results in erosion or wear of the cutting tool or bond matrix (in the case of abrasive finishing methods). Hence, it is essential to have a means to control the shape (or curl) of the chip, as well as a means to dispose of the chip away from the cutting zone (chip clearance) in the finishing of ductile materials such as aluminum and copper and their alloys, as well as thermoplastic materials.

Ductility is also used to advantage in ultraprecision processes such as lapping or buffing, where mirror finish surfaces are achieved by extensive deformation of surface layers without affecting bulk material structure or properties. This is the technique used in the preparation of hard disks for computers and the machining of printing rolls.

Thermal Properties. Because most finishing methods are mechanical processes in the presence of a thermal front, the thermal properties of work materials play a key role in their response to finishing. For example, the conduction of heat away from the machining zone and the rate of heat buildup determine the maximum temperature at the surface, which influences tool life as well as the quality of the work surface after finishing. As a rule, poor thermal conductors are difficult to machine. Typical examples are polymers, stainless steel, and titanium. Any external effort to reduce surface sliding and heat conduction are very beneficial in the finishing of these materials.

Thermal cracks are generated when the thermal stress exceeds the strength of the material. Materials with high thermal conductivity, a low thermal expansion coefficient, and low stiffness (elastic modulus) are less susceptible to thermal cracks.

Thermal stability is resistance to decomposition. For example, in the presence of high temperatures, titanium readily reacts with carbon to form carbides. This is an inherent limitation for tool life in the finishing of titanium using diamond or silicon carbide tools.

The mechanical properties described earlier (hardness, toughness, ductility, and so on) need to be considered at room temperature as well as at elevated temperatures corresponding to the maximum "cutting" temperature. The conventional wisdom is that the strength of a work material decreases with temperature and increases with strain rate, and that these two opposing effects have a minimal net effect on machining processes. However, this may not always be the case.

Thermal properties are also of interest to the nonmechanical finishing processes such as electrical discharge machining and laser machining. These processes depend primarily on thermal energy and its use for material removal and surface generation.

Thermal effects are inherently unstable and should be carefully controlled in any finishing process. For instance, excessive heat buildup at the grinding zone increases the maximum temperature, which accelerates tool wear. This results in inefficient cutting action, which in turn leads to further increase in heat input to the grinding zone. These effects can proceed until severe damage is caused to the part, the abrasive tool, or both. Thermal effects also depend on the geometry of the work material and the nature of the applied forces. Thin cross sections of work materials are more susceptible to thermal damage than large cross sections, and heat distribution that minimizes thermal inputs to he cross section (e.g., up grinding vs. down grinding) also improves part quality and minimizes thermal damage.

Electrical and Magnetic Properties. Electrical conduction and resistivity are properties of importance, particularly in finishing methods such as electrical discharge machining. Magnetic materials such as ferrous alloys are readily clamped by electromagnetic chucks during their finishing, whereas paramagnetic and nonmagnetic materials require mechanical clamping.

Microstructure Effects. As a general rule, a uniform and predictable microstructure of the work material is preferable for reliable finishing processes and their automation. Inclusions, surface defects, and hard surface layers always impair performance. This is true for castings, forged components, rolled steels, densified ceramics, and so on.

The size, shape, content, and uniformity of hard second-phase material and second-phase particles also influence finishing results. As a general rule, the smaller the hard second-phase particles, the more efficient the finishing.

Grain size of the work material plays a key role in finishing results. Finer grain size is usually associated with higher strength and toughness and greater machining difficulty. Grain size modifications due to processing, such as by heat treatment and shot peening, yield results such as residual stresses, anisotropic properties, and work hardening, all of which pose difficulty in the finishing processes and hence should be carefully controlled or monitored. Changes in the morphology in one finishing process may influence the next finishing step. For example, brass is frequently work hardened during drawing or forming, which may contribute to a nonuniform finish. Polishing prior to buffing is desirable to reduce this nonuniformity.

Material Properties and Their Relationship to Grindability

This section addresses the relative response of work materials such as metals, ceramics, and composites to grinding.

Relative Grindability of Metals. Table 1 gives the relative grindability of seven metallic alloys. As used in the table, *grindability* is a calculated value that represents the efficiency of the grinding process. Grindability can be calculated using the the following relationships:

$$\text{Specific energy} = \frac{\text{Grinding power (W)}}{\text{Material removal rate}\,(\text{mm}^3/\text{s})}$$

$$\text{G-ratio} = \frac{\text{Volume of material removed}\,(\text{mm}^3)}{\text{Volume of wheel used}\,(\text{mm}^3)}$$

$$\text{Grindability} = \frac{\text{G-ratio (mm}^3\text{)}}{\text{Specific energy (J)}}$$

Grindability is then a measure of the volume of material removed per unit of energy consumed, normalized by the volume of wheel material consumed during the process. It takes into account the ease of difficulty of removing the material along with the process economics influenced by the rate of material removed and the breakdown of the grinding tool. Absolute values of grindability are useful specific situations. However, comparisons of grindability among work materials under identical conditions, as shown in Table 1, are more relevant for the purposes of the present discussion. Table 1 shows that grindability is dramatically affected by the type of work material and by the use of oil coolant.

Table 1 Relative grindability of work materials in wet outside diameter grinding

Work material	**Hardness HRC**	**Relative grindability**	
		Water-soluble coolant	**Oil coolant**
512100 bearing steel	60	60-80	500-1000
4340 structural steel	60	50-100	500-700
1020 low-carbon steel	23	10-40	100-150
M7, D2 tool steel	60	1-2	100-150
440 stainless steel	47	1-10	200-500
304 stainless steel	4	1-5	100-200
Inco 718 aerospace alloy	30	1	30-60

Notes: (1) A set of outside-diameter grinding tests were conducted using the same grinding wheel specifications and identical grinding process conditions. The tests were conducted using water-soluble coolant and oil coolant. From these tests, data were analyzed to compute grindability (defined in text). The individual grindability measures for each alloy and each coolant were normalized to the grindability of Inco 718 using water-soluble coolant to determine the relative grindability. (2) The above data are based on limited data sets and should be used only as a guideline.

Grindability of Ceramics versus Grindability of Metals. The strength of ceramic material varies widely, depending on the material chosen. Even for a given material such as silicon nitride, the strength depends on the sintering aids used and the sintering methods applied (pressureless sintering, hot pressing, hot isostatic pressing, etc.). Ceramic materials are analogous to metals in that their composition, microstructure, and strength influence grindability. Table 2 compares the typical properties of selected ceramic materials with those of metals and those of a typical polymer.

Table 2 Physical and mechanical properties of selected ceramics, metals, and a polymer

Material	**Physical properties**				**Mechanical properties**		
	Density	**Melting/ decomposition**	**Thermal**	**Coefficient of thermal**	**Tensile**	**Modulus of**	**Fracture**

			temperature		**conductivity, *k***		**expansion, 10^{-6}/K**	**strength**		**elasticity, *E***		**toughness**	
	g/cm^3	**lb/in.^{3}**	**°C**	**°F**	**W/m · K**	**Btu · in./ft^2 · h · °F**		**MPa**	**ksi**	**GPa**	**10^6 psi**	**MPa $\sqrt{m}$**	**ksi $\sqrt{in}$**
Ceramics													
Aluminum oxide	3.4-4.0	0.12-0.14	2050	3720	27	190	8	205-550	30-80	385	55	2.0-3.0	1.8-2.7
Silicon carbide	3.0-3.2	0.11-0.12	2500	4530	63-155	435-1075	4-5	415-550	60-80	420	60	2.5-3.5	2.3-3.2
Silicon nitride	3.2-3.5	0.12-0.13	1900	3450	9-30	60-210	3	620-1100	90-160	305	44	3.5-5.0	3.2-4.6
Zirconium oxide	5.8	0.21	2500	4530	2	14	9-10	965-1380	140-200	140	20	6.0-8.0	5.5-7.3
Ferrite	5.0-6.0	0.18-0.22	2000	3630	8	55	7.5	140-170	20-25	205	29	1.0-1.3	0.9-1.2
Fused quartz	2.2	0.079	1670	3040	1.4	9.7	0.55	110	16	77	11	1.0	0.9
Metals													
Inconel 718	8.1	0.29	1400	2550	12.4	86.0	7	1240-1405	180-204	215	31	24	22
Tool steel	7.84	0.283	1500	2730	52	360	7	1405-2000	180-290	210	30	98	89
52100 bearing steel	7.85	0.284	1500	2730	30-40	210-280	11	415-550	60-80	210	30	56	51
Aluminum	2.2	0.079	660	1220	204	1420	13	275-550	40-80	70	10	36	33
Polymer													
Polyethylene	1.1	0.040	120	250	0.32	2.2	167	7-20	1-3	3.5	0.5	0.25	0.23

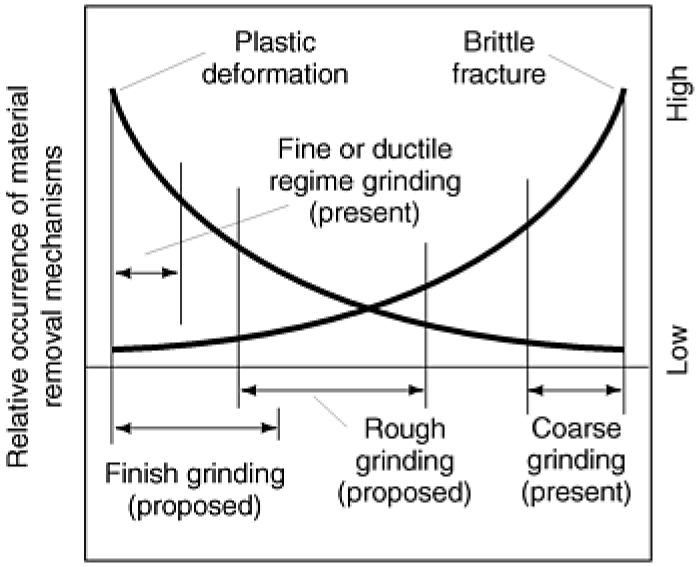
In general, ceramic materials have higher stiffness (Young's modulus) than metals. The elastic deformation of ceramic materials during grinding is therefore less than that for metals, given the same grinding forces, so ceramic materials can be machined to closer tolerances, more precise geometries, superior finishes, and better flatness and parallelism than is possible for metals. This is the basis for choosing ceramic materials over metals in precision-made instrument parts, machine tool beds or ways, and gage blocks.

Ceramic materials are generally more chemically stable than metals, so the burn sometimes observed on metals during grinding is rarely observed on ceramics. On the other hand, the hot hardness and recovery hardness of ceramics are much higher than those of metals, and the large-scale thermal softening that often aids in the grinding of metals can rarely be counted on in the grinding of ceramics.

Thermal conductivity (the property that determines the ability to conduct heat away from the grinding zone) varies widely in ceramic materials. Just as poor thermal conductivity in metals such as titanium and Inconel can lead to high temperatures and great difficulty in grinding, it is more difficult to grind ceramic materials that have poor thermal conductivity. The problem becomes worse when the ceramics are also poor in thermal shock resistance.

One characteristic that significantly distinguishes ceramics from metals is their low fracture toughness. Considering all the similarities between metals and ceramics, it should be possible to achieve successful grinding of ceramics if the generation and propagation of cracks during the grinding process can be minimized.

From Fig. 1, it appears that the mechanisms of material removal in the grinding of ceramic material are associated with both plastic deformation and brittle fracture. It may be nearly impossible to isolate one mechanism or the other unless extreme grinding conditions are chosen. These are identified as *coarse grinding* (where brittle fracture dominates) and *fine* or *ductile regime grinding* (where plastic deformation dominates). The consequences of such choices are low strength and poor reliability, in the case of coarse grinding, and an extremely small material removal rate, high forces, and high specific energy, in the case of fine or ductile regime grinding. Referring to the process interactions described in Fig. 1, it may be envisioned that plastic deformation is desirable in order to increase the cutting component. However, excessive deformation may produce an inefficient cutting process accompanied by excessive ploughing and rubbing and/or sliding. Although brittle fracture is a means of generating surfaces at the lowest forces and energy, it is certainly not desirable where highest strength and reliability are required.



Input		
Machine tool		
Low	Vibration	Large
Processing tool		
Small	Grain size	Large
Small	Grain tip radius	Large
Work material		
Small	Grain size	Large
High	Fracture toughness	Low
Operational factors		
Large	Cutting velocity	Small
Small	Depth of cut	Large
Small	Chip thickness	Large
Process variables		
Small	Force per grain	Large
Large	Specific energy	Small
Large	Grinding force	Small
Output		
High	Part strength	Low
Fine	Surface finish	Poor
Good	Edge chippage	Poor
Low	Material removal rate	High

Fig. 1 Governing mechanisms and control variables for grinding of ceramics

Thus, optimizing the ceramic grinding system becomes a process of maximizing the cutting component through plastic deformation while minimizing the grinding forces and energy input. This can be accomplished through a careful and simultaneous selection of the input parameters identified in Fig. 1 and Fig. 2. Although this approach is common with metals grinding, the additional factor in ceramics grinding is the control of force per grain. Under such process interactions, selection of a suitable grinding cycle, including rough and finish grinding steps, is a tradeoff between process economics and the surface characteristics desired.

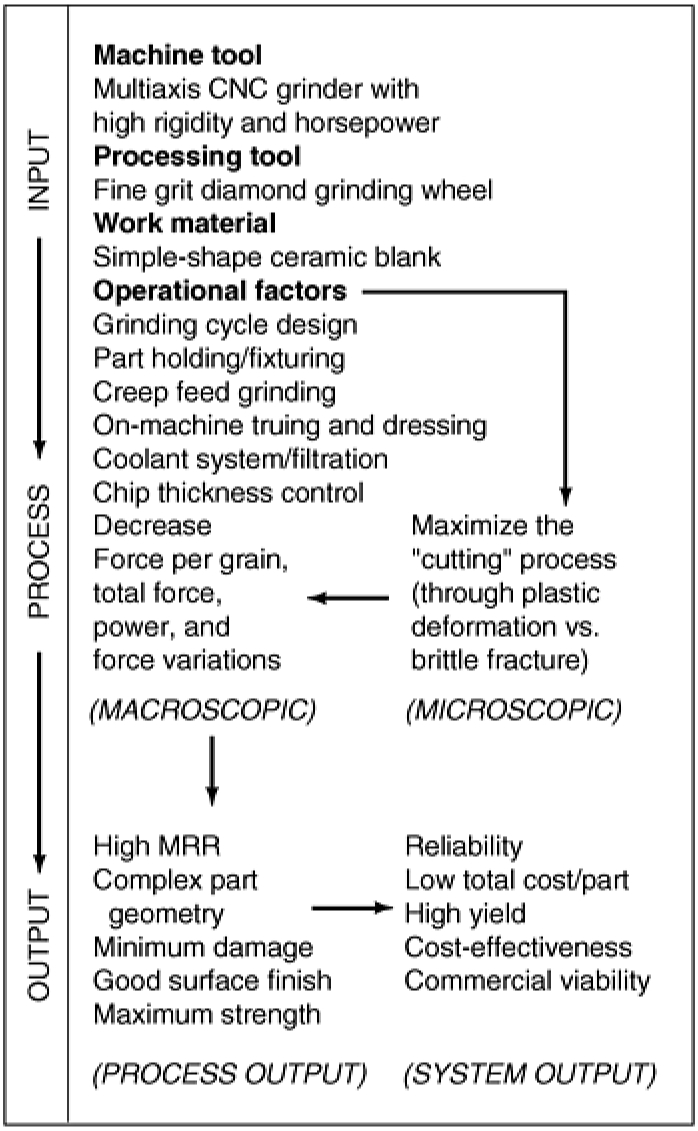


Fig. 2 Systems description of the precision grinding of ceramics. CNC, computer numerically controlled; MRR, material removal rate

Finishing of Composites. There are a wide variety of materials in which more than one family of materials has been brought together to achieve unique performance requirements. Typical examples are shown in Fig. 3. Successful finishing of such composites depends on understanding each of the components of the composite, its properties, and its response to finishing. It is also important to understand whether a composite is dominated by a "hard" or "soft" matrix, as outlined in Table 3. This distinction is crucial in developing rational and economical finishing methods.

Table 3 Matrix material that influences the finishing difficulty of typical composites

Composite	**"Hard" matrix**	**"Soft" matrix**
Castings	Sand	Cast iron
High-silicon aluminum alloys	Silicon	Aluminum
Polycrystalline diamond tools	Diamond	Carbide substrate

Reinforced concrete	Steel reinforcement	Concrete
Carbide-tipped tools	Carbide	Steel
Fiber-reinforced composites	Glass-carbon fiber	Polymer
Ceramic coatings for thermal barriers	Alloy steel	Ceramic coating

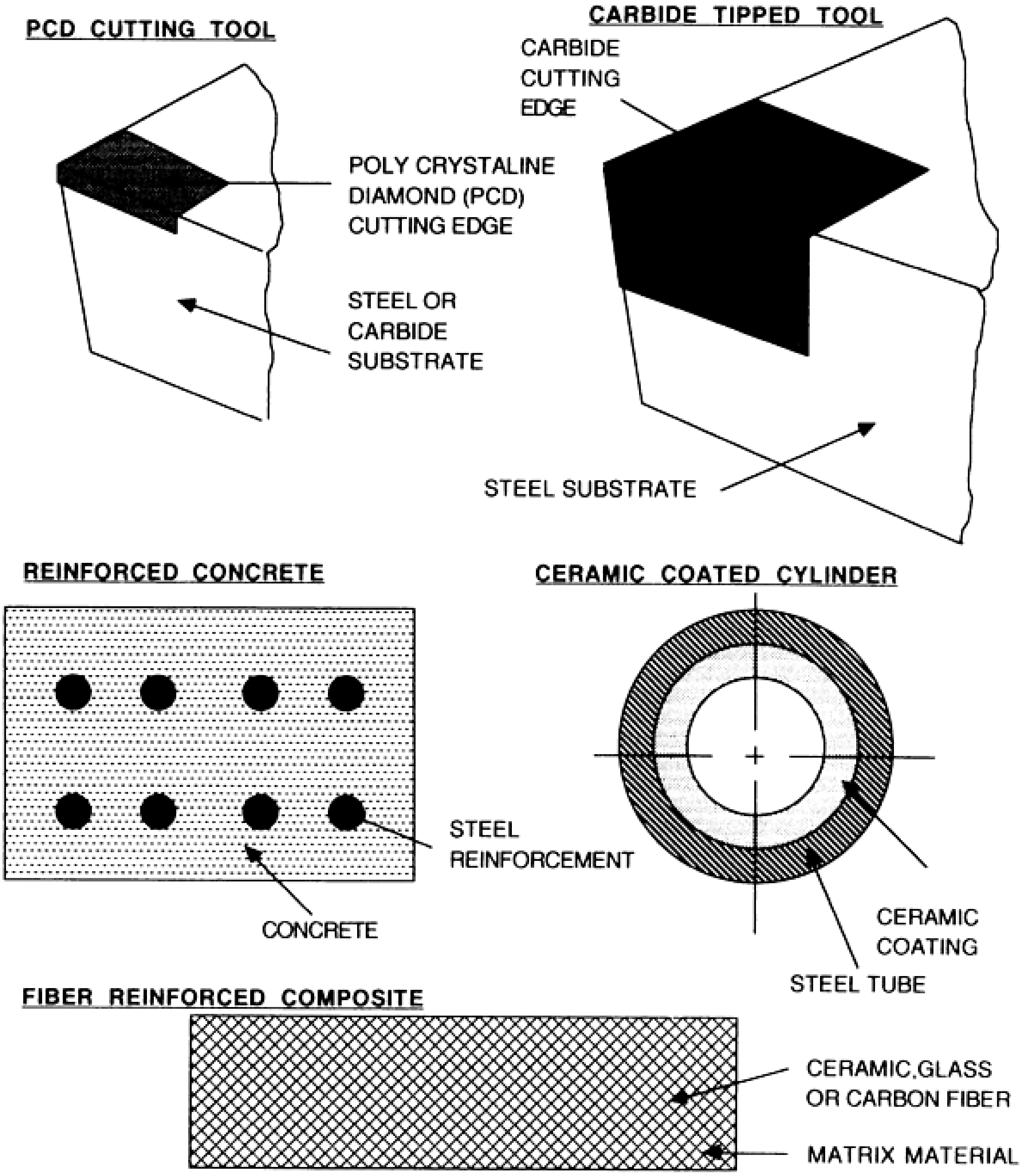


Fig. 3 Typical composites that require surface generation

Copper Plating

Revised by L.M. Weisenberger and B.J. Durkin, MacDermid, Inc.

Introduction

COPPER PLATING DEPOSITS are used for both functional and decorative applications. They are used widely as underplates in multiplate systems, as barrier coatings, as stopoffs in heat treatment, and for heat transfer (e.g., as heat sinks). They also find use in electroforming, in electromagnetic shielding, and in plating of electronic circuitry. The smoothness and brightness of copper deposits can be improved through buffing techniques because copper is a relatively soft metal. Copper deposits also act as thermal expansion barriers, especially in multiplate systems, due to their ability to absorb the stress produced when metals with different thermal expansion properties undergo temperature changes or if the deposit is thermally shocked. Similarly, corrosion failures from cracking caused by physical deformation of a part can be reduced by incorporation of a soft metal such as copper in the composite plate. Copper plating is also used as a final finish in some decorative applications and is sometimes used alone in applications where a durable and attractive surface is required. However, copper tarnishes and stains rapidly when exposed to the atmosphere and must be protected against this by an overcoating of clear lacquer or another suitable type of corrosion-resistant finish.

Copper can be deposited from both electrolytic and autocatalytic (electroless) electrolytes that are alkaline or acid.

Cyanide and noncyanide, pyrophosphate alkalines plus sulfate and fluoborate acid baths are the electrolytes used in the electrolytic deposition of copper deposits. For additional information, see the article "Electroless Copper Plating" in this Volume.

Alkaline Plating Baths

Alkaline cyanide copper solutions are used to plate the initial deposits (as a strike) on a variety of substrates. These baths can be easily controlled to produce thin deposits of relatively uniform thicknesses on all surfaces. They have the best macro throwing power, which describes the relative plating thickness distribution over all current densities. They also have traditionally been the most widely used strike and plating baths. However, with a greater emphasis on hazards and waste management, more recently developed alkaline, noncyanide systems are being examined and used as replacements for the copper cyanide systems in many applications. The deposits from the noncyanide copper processes compare favorably with those from the cyanide processes. These noncyanide processes require more precise control and more thorough cleaning and surface preparation compared to cyanide systems; however, their use does allow the elimination of cyanide in many plating facilities. Pyrophosphate alkaline copper solutions are seldom used because they are difficult to control and have limited operating ranges. They are used primarily to produce thick deposits because they exhibit good plating rates. They also find some use in through-hole printed wiring board applications.

Dilute cyanide and Rochelle cyanide baths are primarily used to deposit a strike coating of 1.0 to 3.0 μm (0.05 to 0.1 mil) of copper prior to further copper plating or electrodeposition of other metals. Often the coverage during this step is the most important in the overall performance and appearance of the final plated part. The high-concentration Rochelle cyanide bath can be used efficiently for plating up to about 8 μm (0.3 mil) thickness. With a modification in composition, the Rochelle electrolyte may be used for barrel plating. The Rochelle cyanide bath can be used for still-tank plating, with mechanical agitation, or more efficiently with air agitation. These baths can also be used with pulsed-current or periodic-reverse plating.

The cyanide copper plating baths listed in Table 1 are characterized by low-copper metal and high free-cyanide contents. This type of chemistry helps to clean the surface of parts during the plating operation. This results because of the tendency to produce gassing at the work due to the low cathode efficiencies. Although plating baths should not be used intentionally for cleaning purposes, the cleaning action of these cyanide baths can be an advantage, because difficult-to-clean parts can be given a copper strike in one of these baths with a high degree of success. Plating in other baths without the use of an alkaline cyanide copper strike could result in poor adhesion and incomplete coverage.

Table 1 Compositions and operating conditions of cyanide copper plating baths

Constituent or condition	Rochelle cyanide				High-efficiency	
	Dilute cyanide (strike)	Standard barrel	Low concentration[(a)]	High concentration[(a)]	Sodium cyanide[(b)]	Potassium cyanide[(b)]
Bath composition, g/L (oz/gal)						
Copper cyanide	22 (3)	45 (6)	26 (4)	60 (8)	80 (11)	80 (11)
Sodium cyanide	33 (4)	68 (9)	35 (5)	80 (11)	105 (14)	105 (14)
Sodium carbonate	15 (2)	. . .	30 (4)	30 (4)	. . .	. . .
Sodium hydroxide	To pH	. . .	To pH	To pH	30 (4)	. . .
Rochelle salt	15 (2)[(c)]	45-75 (6-10)	45 (6)	90 (12)	. . .	. . .
Potassium hydroxide	. . .	8-15 (1-2)	. . .	. . .	. . .	35 (5)
Bath analysis, g/L (oz/gal)						
Copper	16 (2)	32 (4)	18 (2)	43 (6)	56 (7)	56 (7)
Free cyanide	9 (1)	27 (3.6)	7 (0.8)	15 (2)	18 (2)	18 (2)
Operating conditions						
Temperature, °C (°F)	30-50 (86-120)	55-70 (130-160)	55-70 (130-160)[(d)]	60-75 (140-170)	60-75 (140-170)	60-75 (140-170)
Cathode current density, A/dm^2 (A/ft^2)	1.0-1.5 (10-15)	. . .	1.0-4.0 (10-40)	2.0-5.0 (20-50)	2.0-6.0 (20-60)	2.0-6.0 (20-60)
Cathode efficiency, %	30-50	. . .	40-60	60-90	70-100	70-100
Voltage, V	6	6[(e)]	6	6	6	6
pH	12.0-12.6	. . .	12.0-12.6[(d)]	13	>13	>13
Anodes	Copper, steel	Copper	Copper	Copper	Copper	Copper

(a) Low concentration typical for strike; high concentration typical for plating.

(b) Used with addition agents, as proprietary or patented processes.

(c) Optional

(d) For zinc-base die castings, maintain temperature at 60-71 °C (140-160 °F)and a pH between 11.6 and 12.3.

(e) At 6 V, the bath draws approximately 0.3 A/L (2 A/gal) through the solution. At 12 V, the bath draws 0.4 A/L (3 A/gal).

High-Efficiency Sodium and Potassium Cyanide Baths. With proprietary additives, the high-concentration baths are used to produce deposits of various degrees of brightness and leveling, in thicknesses ranging from 8 to 50 μm (0.3 to 2.0 mils). Thick deposits that are ductile and bright can be produced in routine operations. Under most plating conditions, the high throwing power of the electrolyte produces adequate coverage of sufficient thickness in recessed areas. Antipitting additives are generally used in these baths to promote pore-free (nonpitted) deposits.

Before being plated in the high-efficiency baths, parts must first receive a strike coating of copper, about 1.3 μm (0.05 mil) thick from a dilute cyanide copper electrolyte.

The high-efficiency baths are characterized by relatively high operating temperature, high copper content, and rapid operation. Deposition rates are three to five times faster than the rates for the dilute cyanide and Rochelle cyanide baths. Parts to be plated in the high-efficiency electrolytes must be cleaned thoroughly, or the plate will be of inferior quality and the bath will require frequent purification for the removal of organic contaminants.

The potassium complexes formed by the combination of potassium cyanide and copper cyanide are more soluble than those formed when sodium cyanide is used; therefore, a higher metal content and higher rates of deposition are possible than with the sodium cyanide high-concentration bath. The potassium bath has more operating flexibility than the sodium bath and is favored because it raises the resistance to deposit burning and accordingly permits the use of higher current densities (faster plating rates).

Pulsed-current techniques are used frequently for operating high-efficiency electrolytes to produce greater leveling and uniform distribution of copper on complex shapes and to reduce plating time and the amount of metal required for plating complex shapes to a specified minimum thickness. Periodic reversal may be used to provide even higher leveling and better metal distribution than can be obtained with current interruption. Periodic reversal also improves the pore-filling characteristics of the high-efficiency electrolytes. Compositions and operating conditions of cyanide copper plating baths are given in Table 1.

The operation of high-efficiency electrolytes can be improved by the use of proprietary additives, which improve anodic and cathodic bath efficiency and anode corrosion. These additives produce matte to full-bright, fine-grain deposits. Proprietary additives are also used to control the effects of organic and inorganic contaminants.

Alkaline noncyanide copper plating is the subject of recent interest due primarily to environmental pressures on the use and disposal of cyanide-containing processes. These systems are being used in many of the same applications where cyanide systems have traditionally found success. In applications where copper is plated as a heat-treat masking barrier prior to carburizing, nitriding, or through hardening, the noncyanide processes have been shown to perform equally well or better than cyanide systems (Ref 1). These systems produce fine-grain, smooth, dense deposits that are nonporous and exhibit good bonding properties that can be deposited in rack, barrel, and continuous operations. These systems have also found use as strikes prior to the additional plating of metals and in EMI shielding applications. Their proprietary formulations are based on a variety of chelating ligands, most commonly carboxylic acids, amines, and phosphonates (Ref 2). Metallurgical analysis of these deposits shows a crystalline structure and surface morphology comparable to that produced by copper cyanide plating baths, except that the cyanide-free deposit is more compact (Ref 3). Concentration limits and operating conditions of these baths are given in Table 2.

Table 2 Concentration limits and operating conditions of alkaline noncyanide copper plating baths

Constituent or condition	**Typical**
Copper metal (from copper sulfate) concentration limit, g/L (oz/gal)	6-13.5 (0.8-1.8)
pH, electrometric	9.0-10.5
Temperature, °C (°F)	38-65 (100-150)
Cathode current density, A/dm^2 (A/ft^2)	0.5-3.0 (5-30)
Tank voltage	2-12
Anode:cathode ratio	1.5:1
Copper anodes	OFHC or EPT 110 copper

Note: The systems currently commercially available are proprietary but typically contain an organic complexing agent, buffer salts, anode depolarizer, and proprietary addition agents.

Alkaline copper pyrophosphate baths are used for decorative multiplate applications including plating on plastic, plating through-holes of printed circuit boards, and as a stopoff in selective case hardening of steels. Concentration limits and operating conditions are given in Table 3.

Table 3 Concentration limits and operating conditions of copper pyrophosphate plating baths

Constituent or condition	**Strike**	**Typical**
Concentration limits, g/L (oz/gal)		
Copper metal	9-11 (1.2-1.5)	19-30 (2.5-4.0)
Potassium pyrophosphate	112-205 (15-27)	235-405 (31-54)
Copper pyrophosphate	25-30 (3.3-4.0)	52-84 (7.0-11.0)
Ammonium hydroxide (conc. mL/L)	0.5-1.0	3.75-11.0
Potassium nitrate	1.5-3.0 (0.2-0.4)	3.0-12.0 (0.4-1.6)
Weight ratio (pyrophosphate:copper)	7.0-8.0:1	7.0-7.5:1
Operating conditions		

Temperature, °C (°F)	22-30 (72-86)	43-60 (110-140)
Current density, A/dm^2 (A/ft^2)	1.0-3.0 (10-30)	1.0-7.0 (10-70)
Cathode efficiency	. . .	95-100%
Voltage at tank, V	2-5	2-6
pH, electrometric(a)	8.0-8.5	8.0-8.7
Anodes(b)	Copper	Copper
Anode:cathode ratio	2:1	2:1

(a) May be maintained with pyrophosphoric acid and potassium hydroxide.

(b) OFHC anodes

Copper pyrophosphate bath characteristics are intermediate between those of cyanide and acid baths and are very similar to those of the high-efficiency cyanide bath. Electrode efficiencies are 100%; throwing power and plating rates are good. The bath also operates at an almost neutral pH. Deposits from pyrophosphate baths are fine-grain and semibright. For pyrophosphate plating on steel, zinc die castings, magnesium, or aluminum, a preliminary strike should be used. For striking, a dilute cyanide or pyrophosphate copper, nickel, or other solution may be used.

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2. U.S. Patent No. 3,475,293, 1969
3. L.C. Tomaszewski and R.A. Tremmel, *Proc. of the 72nd AES Annual Tech. Conf.,* American Electroplating Society, 1985

Acid Plating Baths

Electrodeposition of copper from acid baths is used extensively for electroforming, electrorefining, and decorative electroplating. Acid copper plating baths contain copper in the bivalent form and are more tolerant of ionic impurities than alkaline baths. They also have less macro throwing power and poorer metal distribution. Acid baths have excellent micro throwing power, resulting in the ability to fill or level scratches, grooves, or other substrate conditions, and additionally they are effective in sealing porous substrates. In most instances the smooth deposits produced by these solutions reduce or eliminate the need for mechanical smoothing for various substrates. A cyanide, noncyanide copper, or nickel strike must be applied to steel or zinc-alloy die castings before they are plated in acid copper solutions. Acid copper solutions cannot be used directly over substrates that are attacked by the high acidity or those where the copper forms an immersion deposit. Immersion deposits usually have poor adhesion to the substrate. Concentration limits and operating conditions of acid copper plating baths are given in Table 4.

Table 4 Compositions and operating conditions of acid copper plating baths

Constituent or condition	**Copper sulfate bath**		**Copper fluoborate bath**	
	General	**Printed circuit through-hole**	**Low copper**	**High copper**
Bath composition, g/L (oz/gal)				
Copper sulfate, $CuSO_4 \cdot 5H_2O$	200-240 (27-32)	60-110 (8-15)	. . .	. . .
Sulfuric acid, H_2SO_4	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Copper fluoborate, $Cu(BF_4)_2$	. . .	. . .	225 (30)	450 (60)
Fluoboric acid, HBF_4	. . .	. . .	To pH	40 (5)
Bath analysis, g/L (oz/gal)				
Copper	50-60 (7-8)	15-28 (2-4)	8 (1)	16 (2)
Sulfuric acid	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Specific gravity at 25 °C (77 °F)	. . .	. . .	1.17-1.18	1.35-1.37
Operating conditions				
Temperature, °C (°F)	20-50 (68-120)	20-40 (68-105)	20-70 (68-160)	20-70 (68-160)
Current density, A/dm^2 (A/ft^2)	2.0-10.0 (20-100)	0.1-6.0 (1-6)	7.0-13.0 (70-130)	12-35 (120-350)
Cathode efficiency, %	95-100	95-100	95-100	95-100
Voltage, V	6	6	6	6-12
pH	. . .	. . .	0.8-1.7	<0.6
Anodes	Copper[a]	Copper[a]	Copper[b]	Copper[b]

(a) Phosphorized copper (0.02-0.08% P) is recommended.

(b) High-purity, oxygen-free, nonphosphorized copper is recommended.

The copper sulfate bath is the most frequently used of the acid copper electrolytes and has its primary use in electroforming. In this application, the advantages of acid copper lie in its strength and ductility. Acid copper sulfate is used to plate thick deposits over 150 μm (6 mils) on large nickel-plated rolls; it is then engraved to electroform textile printing screens. It is also used extensively for the application of copper as an undercoating for bright nickel-chromium plating, especially for automotive components. Plates and rolls have been plated with acid copper sulfate for graphic arts and rotogravure printing where thicknesses of 500 μm (20 mils) or more are not uncommon. Bright acid copper sulfate baths are used extensively as an underlayer in decorative plating of the plastic trim found on automobiles, appliances, and various housewares. By altering the composition of the copper sulfate bath, it can be used in through-hole plating of printed circuit boards where a deposit ratio of 1 to 1 in the hole-to-board surface is desired. In some applications, acid copper sulfate solutions are used to plate over electroless deposited copper or nickel. With additives, the bath produces a bright deposit with good leveling characteristics or a semibright deposit that is easily buffed. Where copper is used as an undercoating, deposit thicknesses will generally range up to about 50 μm (2 mils).

The copper fluoborate bath produces high-speed plating and dense deposits up to any required thickness, usually 500 μm (20 mils). This bath is simple to prepare, stable, and easy to control. Operating efficiency approaches 100%. Deposits are smooth and attractive. Deposits from the low-copper bath operated at 49 °C (120 °F) are soft and are easily buffed to a high luster. The addition of molasses to either the high copper or the low copper bath operated at 49 °C (120 °F) results in deposits that are harder and stronger. Good smoothness of coatings up to 500 μm (20 mils) thick can be obtained without addition agents. For greater thicknesses, addition agents must be used to avoid excessive porosity.

Surface Preparation Considerations

Careful cleaning and preparation of the substrate material being plated is required for the effective electrodeposition of copper. Surface oils and greases, buffing compounds, rust, scale, and oxides, especially around weld or solder areas must be thoroughly removed before copper plating to ensure adhesion and to minimize contamination of the plating bath. However, before considering any preparation, it is important to know the type of substrate being used as well as any substrate surface conditions that may be present. This information is important because the preparation cycles used prior to copper plating can vary considerably, depending on the alloy or type of substrate. Also, substrate heat treatment variations can contribute to complications in surface preparation. Because there are also variations in organic and inorganic soil conditions on the work to be plated, preparation cycles should include adequate cleaning, rinsing, and activation steps to ensure quality deposits. Some of the cleaning methods used to prepare substrate surfaces prior to copper plating include soak or electrolytic alkaline cleaning, alkaline derusting, vapor degreasing, and solvent cleaning.

Good rinsing between preparation steps is a very important and often-overlooked step in the preparation cycle. Time, temperature, and concentration considerations should be applied to rinsing techniques as well as to the cleaning processing solutions. Often, rinse times are too short, immersion temperatures are too cold, and the water flow rate is too low to adequately rinse cleaner films from the surfaces.

The activation step is usually carried out with the use of an acid to remove inorganic soils, oxides, or cleaner films from the surfaces. The acid used depends on the type of substrate to be plated. The most commonly used acids in preplate processes are hydrochloric acid and sulfuric acid. More information about the techniques used in these preparation processes is found in the Section "Surface Cleaning" in this Volume. Specifications and practices for copper electroplating are given in Table 5.

Table 5 Specifications and standards for copper electroplating

Specification	**Uses**
Copper plating	
AMS 2418	Copper plating
MIL-C-14550 (Ord)	Copper plating

ASTM B 503	Recommended practice for use of copper and nickel electroplating solution for electroforming
Copper plating in multiplate systems	
ASTM B 456	Specification for electrodeposited coatings of copper plus nickel plus chromium and nickel plus chromium
ASTM B 200	Specification for electrodeposited coatings of lead and lead-tin alloys on steel and ferrous alloys
AMS 2412	Plating silver, copper strike, low bake
AMS 2413	Silver and rhodium plating
AMS 2420	Plating, aluminum for solderability, zincate process
AMS 2421	Plating, magnesium for solderability, zincate process
QQ-N-290	Nickel plating (electrodeposited)
Surface preparation	
ASTM A 380	Practice for cleaning and descaling stainless steel parts, equipment, and systems
ASTM B 183	Practice for preparation of low-carbon steel for electroplating
ASTM B 242	Practice for preparation of high-carbon steel for electroplating
ASTM B 252	Recommended practice for preparation of zinc alloy die castings for electroplating
ASTM B 253	Practice for preparation of aluminum alloys for electroplating
ASTM B 254	Practice for preparation of and electroplating on stainless steel
ASTM B 281	Practice for preparation of copper and copper-base alloys for electroplating and conversion coatings
ASTM B 319	Guide for preparation of lead and lead alloys for electroplating
ASTM B 322	Practice for cleaning metals prior to electroplating
ASTM B 480	Practice for preparation of magnesium and magnesium alloys for electroplating
ASTM B 481	Practice for preparation of titanium and titanium alloys for electroplating

MIL-HDBK-132 (Ord)	Military handbook, protective finishes

Cyanide Baths. Although the dilute cyanide and Rochelle cyanide baths exert a significant cleaning action on the surface of the parts during the plating operation, thorough cleaning of parts to be plated in these baths is still necessary.

The high-efficiency sodium cyanide and potassium cyanide electrolytes have virtually no surface-cleaning ability during plating because of the absence of hydrogen evolution. Parts to be plated in these electrolytes must be thoroughly cleaned. Parts also must receive first a dilute cyanide copper strike about 1.3 μm (0.05 mil) thick.

Noncyanide Alkaline Baths. Unlike cyanide baths, noncyanide alkaline baths do not offer any cleaning, and parts plated in these electrolytes must first be thoroughly cleaned, rinsed, and activated. If being used as a strike prior to acid copper or other similar deposit, a minimum thickness of 5.2 μm (0.2 mil) is desired. These systems can be plated directly on properly prepared steel, brass, stainless steel, zincated aluminum, lead-tin, and most high-quality, properly prepared zinc-base die castings (Ref 4, 5). One advantage of the noncyanide electrolyte is the fact that accidental drag-in of acids poses no hazard of the evolution of poisonous cyanide gas, which could occur with cyanide copper electrolytes.

Pyrophosphate Baths. If pyrophosphate electrolytes are to be used, conventional cleaning cycles are generally satisfactory. A preliminary strike should be applied to steel, zinc-base die castings, magnesium, and aluminum. The strike solution may be a dilute cyanide copper, dilute pyrophosphate copper, or nickel. If a cyanide copper strike is used, adequate rinsing or, preferably, a mild acid dip following the strike is recommended before final pyrophosphate copper plating.

Acid Baths. When sulfate or fluoborate copper is to be deposited, steel or zinc must first receive a cyanide or noncyanide alkaline copper or nickel strike. With complete coverage, the strike may be as thin as 2 μm (0.08 mil). After the strike, the parts should be dipped in a dilute solution of sulfuric acid to neutralize solution retained from the alkaline strike bath. The parts should be rinsed thoroughly before acid copper plating. Nickel or nickel alloy parts, when surface activated by reverse-current etching in sulfuric acid, can be plated directly, provided contact is made to the work with the current or power on before immersion into the acid copper solution.

References cited in this section

4. "Cupral Alkaline Non-cyanide Copper," Operating Technical Data Sheet, Enthone/OMI, Warren, MI
5. "E-Brite 30/30 Alkaline Non-cyanide Copper," Operating Technical Data Sheet, Electrochemical Products, Inc., New Berlin, WI

Bath Composition and Operating Variables

The compositions and analyses given in Tables 1, 2, 3, and 4 for cyanide, noncyanide alkaline, pyrophosphate, and acid copper plating baths may be varied within the control limits to satisfy requirements for specific applications.

Current density can be altered to effect more efficient control and to increase the deposition rate of copper. The data in Table 6 can be used as a guide to the selection of current density.

Table 6 Estimated time required for plating copper (valence 1) to a given thickness at 100% cathode efficiency

Cyanide baths contain copper with a valence of 1. For baths containing copper with a valence of 2, such as noncyanide alkaline, sulfate, pyrophosphate, and fluoborate baths, double the time values given in this table. Values must be corrected for losses in cathode efficiency by adding the difference between the actual cathode efficiency and 100%; for example, for 70% cathode efficiency, add 30% to values in table to determine estimated time.

Thickness of plate	Plating time, min[(a)] at current density, A/dm^2 (A/ft^2)

µm	mils	1.0 (10)	1.5 (15)	2.0 (20)	2.5 (25)	3.0 (30)	3.5 (35)	4.0 (40)	4.5 (45)
2	0.08	4	3	2	2	2	1	1	1
5	0.2	11	8	6	5	4	3	3	2
10	0.4	23	15	11	9	8	6	6	5
20	0.8	45	30	23	18	15	13	11	9
30	1.2	68	45	34	27	23	19	17	14
40	1.6	90	60	45	36	30	26	23	18
50	2.0	113	75	57	45	38	32	28	23
60	2.4	136	90	68	54	45	39	34	27
70	2.8	158	106	79	63	53	45	40	32
80	3.1	181	120	90	72	60	52	45	36

(a) To nearest whole value

Impurities. The degree of control required to protect copper plating baths from impurities varies with the type of bath and the method of processing used. Known causes of roughness in copper deposits are:

- Dragover from cleaners, which results in the formation of insoluble silicates in the electrolyte
- Poor anode corrosion
- Insoluble metallic sulfides because of sulfide impurities
- Organic matter in the water used for composition, especially in rinse tanks
- Insoluble carbonates because of calcium and magnesium in hard water
- Oil from overhead conveyors
- Airborne dust or particles

If the level of impurities reaches a critical point, causing poor results, a batch carbon treatment or circulation through a carbon-packed filter may be required. For the noncyanide processes, a sulfur-free carbon pack must be maintained on the bath and changed weekly. Lead and cyanide are contaminants to these systems and tend to cause a black smutted deposit. When converting a plating line from a cyanide system to a noncyanide electrolyte, all associated equipment must be cleaned and thoroughly washed to ensure no cyanide contamination.

Caution: Cyanide remains in the system. Acids can be used only after all traces of cyanide have been eliminated.

Purity of Water Used in Composition. The purity of the water used in the composition of the baths is important for all plating operations. Iron in the water causes roughness in the deposit if the pH of the electrolyte is above 3.5 where iron can be precipitated. Chlorides in concentrations greater than about 0.44 g/L (0.05 oz/gal) promote the formation of nodular deposits. Calcium, magnesium, and iron precipitate in the bath. Organic matter may cause pitting of deposits.

When plating in sodium or potassium, high-efficiency electrolytes and distilled, deionized, softened, or good quality tap water may be used for solution composition and for replenishment. Tap water with high contents of calcium and/or iron should not be used, because it may cause roughness of the deposit. Softened water should be used with care, especially in plating baths where chloride contents are critical, such as bright copper sulfate baths.

Agitation during plating permits the use of higher current densities, which create rapid deposition of copper. The amount of increase permissible in current density varies for the different baths. Preferred methods of agitation for the types of baths are:

Cyanide baths	Cathode movement, air agitation, or both
Pyrophosphate baths	Air agitation
Acid baths	Cathode movement, air agitation, or both
Noncyanide baths	Vigorous air agitation

When air agitation is used, all airline pipes should be made of inert material or coated with an inert material to prevent attack by the electrolytes. The air used for agitation must be clean to avoid bath contamination. Filtered air from a low-pressure blower is required.

Ultrasonic vibration also has been used for the agitation of copper plating baths. This method does not largely improve the properties or appearance of electroplates, but it can improve plating speed by permitting an increase in the current density without the hazard of burning the parts. Increased plating speed does not necessarily justify the increased cost and complexity of ultrasonic operation, because the high-speed baths can usually be operated with a fairly high current density at nearly 100% efficiency.

Plating in Dilute Cyanide Baths

In the dilute cyanide bath, corrosion of the anodes increases with increasing concentration of free cyanide. Low free-cyanide content may cause rough deposits due to anode polarization; however, excessive free cyanide lowers cathode efficiency, resulting in thinner deposits per unit of time. Modifications of the pH, or alkalinity, of the strike compositions are used for striking various substrates. For use on steel, additional NaOH or KOH improves the conductivity of the solution and aids in protecting steel anode baskets, tanks, and other steel fixtures from corrosion. For use on zinc-base die castings, the hydroxide concentration is kept in the range of 1.3 to 3.8 g/L (0.2 to 0.5 oz/gal). For use on zincated aluminum alloys, the pH should be reduced to approximately 9.7 to 10.0 with sodium bicarbonate. The operator should keep adding tartaric acid or sodium bicarbonate to the solution to maintain the desired pH range (e.g., 10.0 to 10.5 for plating on aluminum alloys.

The dilute copper cyanide bath can be operated at room temperature, but the general practice is to operate the bath between 32 and 49 °C (90 and 120 °F) to increase the rate of deposition and to improve anode dissolution. This electrolyte is usually operated with a cathode current density of 1 to 1.5 A/dm^2 (10 to 15 A/ft^2). The tank voltage is normally between 4 and 6 V.

Agitation of the bath produces more uniform composition throughout the electrolyte, more uniform anode corrosion, and an increase in current densities where the brightest deposits are obtained. Current densities in excess of 5 A/dm^2 (50 A/ft^2) have been applied successfully by using air agitation of the solution and agitating the work.

Continuous filtration is preferred for dilute cyanide baths. Organic contamination or suspended matter in the strike is frequently responsible for roughness of copper plate subsequently deposited in the cyanide copper plating bath. Hexavalent chromium in the strike causes blistering of the deposit. Proprietary additives can be used to improve the bath operation, as well as aid in the control of organic and inorganic contaminants. These proprietary additives consist of organic complexing agents, such as tartrate salts. Organic reducing agents are used to control impurities such as hexavalent chromium. Wetting agents (surfactants) are used to control organic contaminants and to lower the surface tension of the plating solution, to allow better throwing power of copper over substrate irregularities, and to aid drainage and rinsing.

Plating in Rochelle Cyanide Baths

Rochelle electrolytes with lower metal concentrations can be used both for striking applications and, with higher metal concentrations, for plating applications. Rochelle salts produce some grain refinement, reduce the effects of some metallic contaminants, and aid in anode corrosion by increasing the anode current density range before anode polarization occurs. The Rochelle electrolyte can also be used for periodic-reverse plating with good results. Barrel plating with a Rochelle bath requires a variation in the chemistry. When plating parts that tend to nest or stick together during the barrel rotation, it is necessary to increase the free cyanide to 25 to 30 g/L (3 to 4 oz/gal) or slightly higher to obtain adequate coverage on the nested parts.

Rochelle baths usually are operated at a current density between 2 and 5 A/dm^2 (20 and 50 A/ft^2). Substituting potassium salts for sodium salts in the baths with higher metal concentration, up to 38 g/L (5 oz/gal) copper, can increase the allowable current density to 6 A/dm^2 (60 A/ft^2), with the penalty of lowering the cathode efficiency. The Rochelle baths are usually operated at between 54 and 71 °C (130 and 160 °F) for best efficiency. The rate of deposition is higher at the higher temperatures. A high-efficiency electrolyte having a higher metal concentration can be operated at up to 77 °C (170 °F). For copper plating zinc-base die castings, the electrolyte is best operated at 60 to 71 °C (140 to 160 °F), provided the pH of the bath is maintained between 11.6 and 12.3. An increase in the operating temperature of Rochelle cyanide baths increases the efficiency of the anode and cathode; however, free cyanide decomposes more rapidly, which increases carbonate formation. An increase in agitation causes an increase in anode efficiency, but this also increases carbonate formation. Carbonates are always present in cyanide copper solutions from oxidation of the cyanide and, also, from adsorption of carbon dioxide from the air that reacts with the alkali in solution. Carbonates from a sodium copper cyanide plating solution can be removed by cooling the solution, which precipitates the less soluble sodium carbonate. High carbonate concentrations lower the anode efficiency, which accelerates additional carbonate formation in addition to producing rough or porous plated deposits (Ref 6).

Rochelle copper baths should be maintained at a pH between 12.2 and 13.0. Anode efficiency may be prohibitively low if the pH is too high. Raising the pH also decreases the voltage drop across the anode film. Figure 1 shows a buffer curve for adjusting the pH of Rochelle electrolytes.

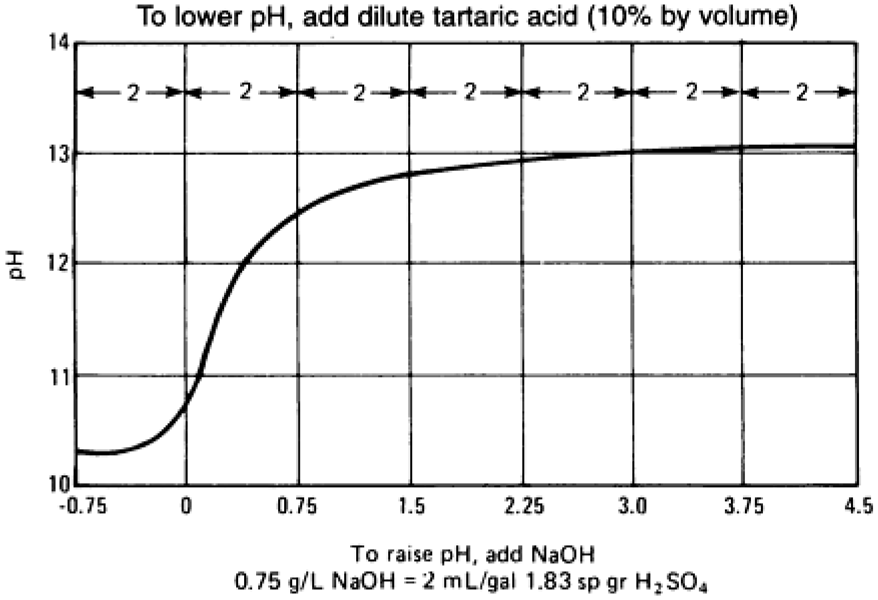

Fig. 1 Buffer curve for adjusting the pH of Rochelle electrolytes. Source: Ref 7

Conductivity of the bath is improved by raising the free alkali cyanide and the concentration of the copper complexes. When depositing copper directly on steel, brass, or copper, conductivity can be improved by the addition of 2 to 15 g/L ($\frac{1}{4}$ to 2 oz/gal) of sodium hydroxide. Sodium hydroxide concentrations should be reduced if the electrolyte is used to deposit copper onto zinc-base die castings, aluminum, or magnesium.

Rochelle baths can become contaminated during plating of zinc-base die castings. Zinc contamination can be removed by electrolysis of the bath at room temperature, at the current density that produces the most brassy or off-color deposit, usually 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2). Iron, which forms complexes with cyanide, cannot be removed readily from the bath and causes a reduction in current efficiency. Drag-in of chloride ion from acid dips must be kept very low to prevent iron buildup due to dissolution of steel equipment. Bipolarity of steel tanks or heat exchangers should be avoided.

The Rochelle bath is susceptible to organic contamination, which can be controlled by the use of wetting agents. Organic contaminants should be removed by periodic batch treatment of the electrolyte with activated carbon, followed by filtration. Organic contamination is especially high in barrel plating. A low-foaming, free-rinsing surfactant or a dispersion agent must be used in barrel plating baths to prevent organic contamination from adversely affecting the quality of the plated deposit. Organic contamination can be controlled with carbon treatment methods. Continuous filtration of cyanide electrolytes is recommended to eliminate particulate matter or salts, which can result in rough deposits.

Increase in the current density or the presence of lead in the Rochelle cyanide bath causes an increase in the stresses of copper plate. These stresses can be reduced by increasing the concentration of copper in Rochelle baths. The addition of 15 g/L (2 oz/gal) of potassium thiocyanate produces an expansion stress instead of the usual contraction stress. Figure 2 shows stress in thin copper electrodeposits plated from a cyanide solution onto stainless steel.

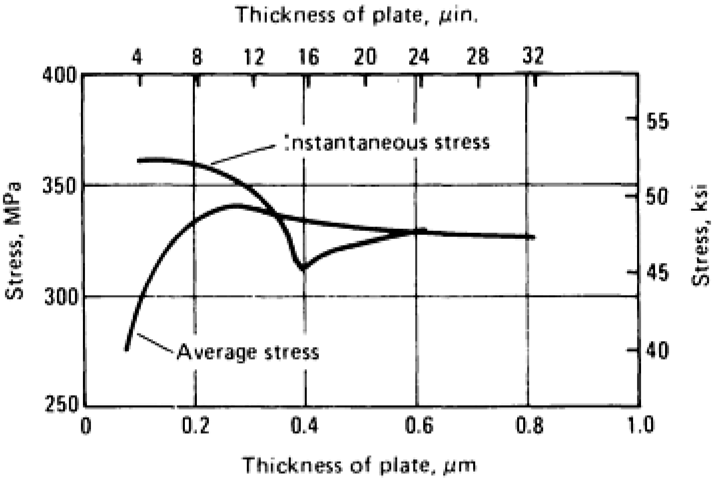

Fig. 2 Stress in thin copper plate deposited on stainless steel spirals. Stainless steel spirals are 0.127 mm (0.005 in.) thick. Source: Ref 8

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Plating in High-Efficiency Sodium and Potassium Cyanide Baths

High-efficiency sodium and potassium cyanide baths allow the use of higher current densities. Cyanide plating baths typically decrease in cathode efficiency, or speed of deposition, with increasing current, which accounts for the good plate distribution (throwing power). The cathode efficiency approaches 100% only at low current densities, often 10A/dm^2 or less. With more practical current densities of 2.0 to 3.0 A/dm^2, the cathode efficiency may drop 20%, especially with lower agitation rates. The sodium or potassium constituent improves the conductivity of the bath.

Operation of the sodium cyanide and potassium cyanide electrolytes at 66 to 74 °C (150 to 165 °F) produces quality deposits. Temperatures in excess of 74 °C (165 °F) allow the use of higher current densities, but breakdown of the cyanide becomes excessive at elevated temperatures. The anode current densities are limited by polarization, resulting in poor anode efficiency and higher voltage requirements. The cathode current densities are limited by burning of the deposit, resulting in reduced efficiency, loss of brightness, and roughness. These limits are higher in the potassium cyanide electrolyte.

Agitation of sodium cyanide and potassium cyanide high-efficiency baths is important for achieving maximum plating speed. Agitation can be accomplished by solution movement, cathode-rod movement, or use of air. Each type of agitation improves the maximum allowable current densities, with air agitation providing the greatest improvement. However, it should be noted that carbonate levels in air-agitated baths tend to increase at a greater rate than baths using mechanical agitation. All three types of agitation may be used within a single bath. Solution movement can be accomplished by mixing or by the flow of solution through filtration equipment. Cathode-rod movement of about 1 to 2 m/min (3 to 7 ft/min) allows increased plating rates. Gentle air agitation should be supplied by the use of a low-pressure blower that has a clean, filtered air source. Care must be taken to use clean, oil-free air for agitation to avoid contamination of the plating solution.

Filtration is also essential when operating high-efficiency cyanide copper electrolytes, especially for plating deposits thicker than 13 μm (0.5 mil). Filtration equipment should have the capability of one to two complete turnovers of the solution each hour while removing particulate matter from the electrolyte. Roughness of the copper deposits from particulate matter is often caused by faulty cleaning or by the formation of metallic copper or cuprous oxide particles at the anodes. Suspended dirt or solid matter in the cyanide copper electrolyte also causes surface roughness. Anode bags of proper size, material, weight, and weave are beneficial in retaining particulate matter formed at the anode. Other foreign particles introduced into the cyanide copper electrolyte are removed by the filtration equipment.

Carbonate buildup in high-efficiency copper cyanide baths can adversely affect the bath operation. High concentrations of carbonate reduce plating efficiency and speed. Excessive carbonates also affect the smoothness of the deposits. Carbonate contents of 120 to 150 g/L (16 to 20 oz/gal) or more may result in lower plating efficiency and plating speed. Excessive carbonates can also lower and reduce the acceptable plating range. These effects are more pronounced in a sodium cyanide bath than in a potassium cyanide bath.

The primary source of carbonate formation is the breakdown of cyanide as a result of poor anode efficiency. Operating cyanide electrolytes at temperatures above the recommended levels can also result in carbonate formation. Operating temperatures above about 74 °C (165 °F) cause decomposition of the cyanide ion. Air containing high levels of carbon dioxide should not be used in air-agitated systems, because the carbon dioxide is dissolved by the alkaline plating solution, also forming carbonate. The air source for air-agitated systems should be placed where it provides a clean, fresh supply.

Excessive carbonates can be removed by freezing or precipitation with lime or proprietary additives. Sodium cyanide baths can be treated either by precipitation or freezing. Potassium cyanide baths can only be treated by precipitation. Freezing is not effective for potassium cyanide baths because of the high solubility of the carbonate salts.

Current interruption cycles frequently improve the operating range of high-efficiency sodium or potassium copper cyanide plating solutions. Current interruption cycles generally allow the use of higher current densities while maintaining bath efficiency. Current interruption cycles also improve the brightness of the copper deposits, and in some cases they give excellent deposit brightness from bright plating baths that are so contaminated that acceptable deposits cannot be produced when using continuous direct current.

Current interruption cycles in the range of 8 to 15 s plating time followed by 1 to 3 s current interruption are generally used. Plating times of less than 8 s and current interruptions of more than 3 s lower the net plating rate. Plating times of more than 15 s and current interruption of less than 1 s reduce the benefits obtained by using a current interruption cycle.

The use of periodic current reversal can also be used to great advantage in high-efficiency copper cyanide plating solutions. This technique involves plating parts in the conventional manner for a selected time and then deplating for a shorter period by reversing the current. Shorter periodic reversal cycles, such as 2 to 40 s of plating followed by 1 to 10 s of deplating (reversal), result in improved deposit brightness similar to that obtained with current interruption. A major advantage in using periodic reversal is the degree of leveling that can be achieved, particularly when relatively long reversal cycles are used. These longer cycles, in excess of 45 s direct with reverse cycles in excess of 10 s, can provide leveling characteristics in excess of 50%. The use of periodic reversal permits the use of higher plating and deplating current densities.

The leveling characteristics of the deposit are improved by increasing the reversal current, whereas cycle efficiency is increased by lowering the reversal current. Figure 3 shows cycle efficiency for periodic-reverse plating. Figure 4 indicates thickness of deposit as a function of cycle efficiency.

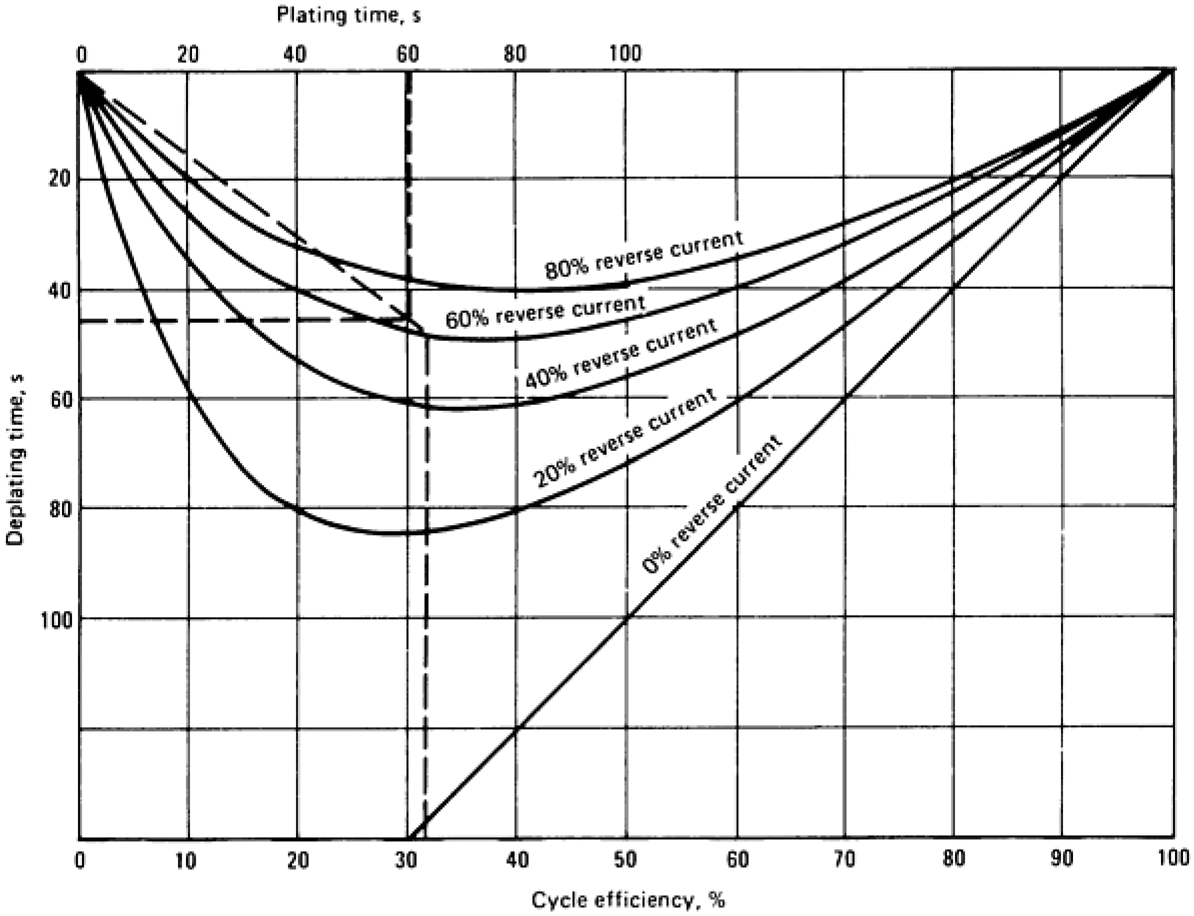

Fig. 3 Cycle efficiency during copper plating with periodic current reversal. Source: Ref 9

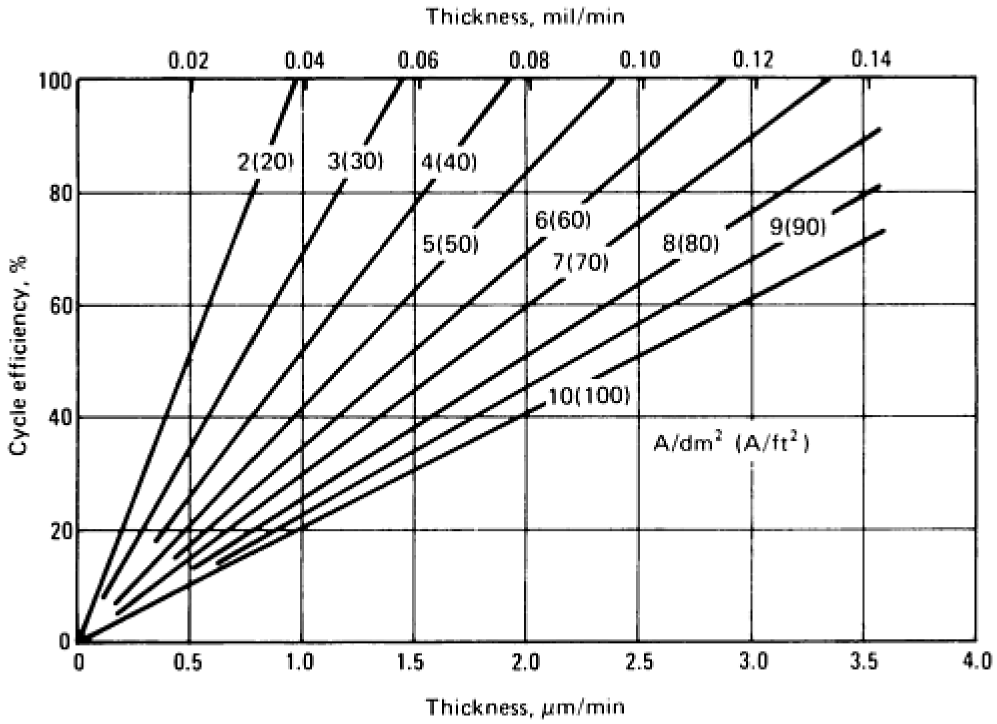

Fig. 4 Thickness of copper deposits as a function of cycle efficiency and current density during plating with periodic current reversal. Source: Ref 9

Another current-interrupting scheme being used for this and other copper plating systems is pulse plating. This normally involves a pulse power source (rectifier) that produces square-wave current pulses. *Square wave* conventionally suggests a pulse with a rise-and-fall time of approximately 10 to 85 μs and a standard frequency of 150 and 10,000 cycles. The periodic interruption of the current with proper time sequences allows much faster plating without surface burning, produces finer grain deposits, and increases throwing power and distribution.

Proprietary additives are used in high-efficiency copper cyanide baths to improve anode corrosion, increase both anode and cathode efficiencies, and control contamination. Organic and metallic additives are also used to improve deposit characteristics and brightness. These additives produce deposits ranging from matte to full-bright.

Reference cited in this section

9. *Electroplating Engineering Handbook,* Reinhold, 1971, p 748, 750

Plating in Noncyanide Copper Baths

The development and refinement of proprietary noncyanide copper baths continues today. The copper deposit from these systems is a fine-grain, dense deposit (Ref 3). The noncyanide copper systems exhibit excellent throwing and covering power, even in deeply recessed areas. In addition to eliminating the cyanide, these processes operate at much lower copper metal concentrations of 7.5 to 13.5 g/L (1 to 2 oz/gal). As a result, they offer additional savings in lowering waste treatment costs. Copper sulfate is the source of copper ions for these systems. The plating electrolytes producing these deposits are very stable compared to those of cyanide copper processes, because there is no decomposition of cyanide resulting in carbonate buildup.

Over the typical current density range of 0.5 to 3.5 A/dm^2 (5 to 35 A/ft^2), the cathode efficiency of noncyanide systems approaches 100%. The good efficiency tends to offset the lower deposition rate of divalent copper electrolysis compared to that of monovalent copper systems. Agitation has a dramatic effect on deposit appearance and cathode efficiency. To obtain a uniform, fine-grain deposit over a wide current density range, air agitation is required for these systems. Lack of agitation produces dull, burned deposits at average current densities of 1.5 to 2.0 A/dm^2 (15 to 20 A/ft^2).

Of the commercially available systems, one process is affected by the buildup of cuprous ions in the cupric phosphonate system, which results in rough, nonadherent copper deposits (Ref 10). To overcome this effect, the process uses continuous electrolysis carried out in an auxiliary tank with special ceramic or platinized anodes to oxidize the cuprous to cupric.

Because the operating pH of these systems is in the range of 9 to 10, these baths can be used as both strikes and plates. There are no special adjustments required for processing zinc diecast and zincated aluminum, as there are in cyanide copper plating. At pH values below 9, the deposits are brighter but adhesion is adversely affected. Values greater than 10 cause high-current-density dullness and can reduce the limiting current density.

These systems, unlike the cyanide systems, are more susceptible to metallic and organic contaminants. Iron, lead, and silver are critical impurities that should be removed by low-current-density electrolytic treatments. Organic impurities are treated using hydrogen peroxide and carbon treatments on a regular basis. Continuous filtration through a 10 μm retention-size cartridge is beneficial for the noncyanide systems. Occasional carbon filtration using a sulfur-free carbon can be used to control organic contamination. Noncyanide systems have very little tolerance to cyanide contamination. When converting cyanide plating lines to noncyanide processes, it is essential to clean and leach out all the cyanide from the tank linings, racks, filters, heaters, plating barrels, and any associated equipment.

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3. L.C. Tomaszewski and R.A. Tremmel, *Proc. of the 72nd AES Annual Tech. Conf.,* American Electroplating Society, 1985
10. D. Maule and B. Srinivasan, Alkaline Non-cyanide Plating, *Proc. of the 80th AESF Tech. Conf.,* American Electroplating and Surface Finishers, 1993

Plating in Pyrophosphate Baths

Copper pyrophosphate plating baths offer a number of desirable features. Copper pyrophosphate forms a highly soluble and conductive complex when dissolved in potassium pyrophosphate solution. Potassium salts are preferred because of their higher solubilities. Copper pyrophosphate plating baths operate at nearly 100% cathode efficiency and provide good throwing power. They are noncorrosive because the operating pH is near neutral. Concentration limits and operating conditions for copper pyrophosphate baths are given in Table 3.

Pyrophosphate forms a highly soluble complex with copper. Excess pyrophosphate is necessary to increase the conductivity of the bath and to effect proper corrosion of the anodes. Ammonia assists anode corrosion, helps enhance the luster of the deposit, and aids pH control. Nitrate allows the use of higher operating current densities by inhibiting the reduction of hydrogen at the upper end of the current density range. The pH of the pyrophosphate bath is maintained between 8.0 and 8.8. A high pH reduces anode efficiency, and a low pH reduces the throwing power of the solution and the stability of the complex compound in solution with the formation of orthophosphate. The pH of the bath can be lowered with pyrophosphoric acid and raised with potassium hydroxide. Good agitation is also essential for consistent operation. Air agitation provides for good performance of the anodes and cathodes and is preferred to cathode agitation.

Pyrophosphate electrolytes can be operated at current densities up to 7.0 A/dm^2 (70 A/ft^2) or higher. The operating current density can be increased by agitating the solution or by increasing the temperature of the bath. The anode current density should be maintained between 2 and 4 A/dm^2 (20 and 40 A/ft^2).

High bath temperatures should be avoided, because excessive formation of orthophosphate occurs. Orthophosphate formed by the hydrolysis of pyrophosphate is beneficial up to about 90 g/L (12 oz/gal), because it promotes anode corrosion and acts as a buffer. Above this concentration, conductivity and bright plating range are decreased and banded deposits are obtained. Orthophosphate cannot be removed chemically from the solution. The concentration can be reduced only by discarding the bath or diluting and rebuilding the pyrophosphate plating solution.

Copper pyrophosphate plating baths are susceptible to organic contamination, including oil and excess or decomposed addition agents. These are removed by treatment with activated carbon and filtration. Cyanide and lead also contaminate the bath. Cyanide is removed by treatment with hydrogen peroxide and lead by electrolysis. Precautionary methods, such as proper cleaning, adequate rinsing, and good solution control and maintenance, prevent these contaminants from entering or building up in the bath, avoiding the need for frequent purification. Copper pyrophosphate solutions are tolerant of other metallic contamination.

Proprietary brighteners are available that refine the grain structure, impart leveling characteristics, and act as brighteners. However, decomposition products from an excessive additive concentration cause stress and brittle deposits. Thus, for quality deposits, additives should be added to the bath on an as-consumed basis.

Plating in Acid Sulfate Baths

The chemical composition of acid sulfate baths is simple. Copper sulfate pentahydrate and sulfuric acid are the primary constituents of the copper sulfate electrolyte. The metal ions are furnished by the copper sulfate. Sulfuric acid increases solution conductivity and helps prevent the formation of basic cuprous or cupric crystals on the anodes and the tank, which causes poor anode corrosion and roughness. Low sulfuric acid contents produce more high-current-density burn, poorer leveling, more low-current-density dullness, and more nodular deposits. High sulfuric acid has less effect on the deposit but increases the anode dissolution. With cathode efficiencies of 95 to 100%, the copper sulfate bath is easy to operate and control.

Many copper sulfate plating solutions require the use of additives to produce smooth, fine-grain, bright, leveled, and ductile deposits. Most of the addition agents used in copper sulfate plating solutions are proprietary formulations. These proprietary additives are capable of producing the desired characteristics in the copper deposit, and deposit hardness can be increased where necessary.

In copper sulfate systems that produce bright deposits, a catalyst must be added in addition to the primary constituents to avoid streaky deposits. This catalyst is chloride, which is maintained between 0.02 to 0.1 g/L (0.003 to 0.01 oz/gal), or 20 to 100 ppm. The chloride, usually added as hydrochloric acid, inhibits rough nodular plate from forming. Low chloride can cause dark deposits on the edges and high-current-density areas of the work, loss of leveling, loss of brightness, pitting, and poor anode corrosion. High chloride causes streaks, increased brightener usage, and loss of leveling and brightness in the bright bath formulations. High chloride can be reduced with zinc dust treatments or precipitation with silver.

If solution agitation or work movement is minimal, current densities should not exceed about 4.5 A/dm^2 (45 A/ft^2), because excessive anode polarization may occur and the deposits can be spongy. Where higher current densities are desired, such as for electrotypes or wire plating, air agitation is used. Air agitation is necessary to accelerate ionic diffusion and produce high-quality, fine-grain deposits where current densities are in excess of 10 A/dm^2 (100 A/ft^2).

The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper sulfate bath is less significant than the effect of changes in cathode current densities. An increase in temperature results in higher conductivity and reduced anode and cathode polarization. Increased temperature also reduces the tensile strength of deposits and increases grain size. Excessive temperatures should be avoided in copper sulfate baths where proprietary brightener formulations are used, because reduced plating ranges, excessive additive use, and solution contamination from additive breakdown result.

Care must be taken to avoid accelerated buildup of copper metal, as in cases where dragout rates are low or improper anode-to-cathode ratios are maintained. An increase in the concentration of the copper sulfate increases the solution resistivity and slightly reduces the anode and cathode polarization. Copper sulfate concentrations in excess of 248 g/L (33 oz/gal) may result in salt crystallization in the plating solution. Normal bath composition is restored by discarding a portion of the bath and adding water and sulfuric acid.

To improve the throwing power of some bright copper sulfate baths used for plating printed circuit boards, a low copper sulfate and high sulfuric acid electrolyte is used. The use of this electrolyte allows a nearly equal deposit distribution when plating the through-holes of the printed circuit board.

In sulfate electrolytes, impurities such as silver, gold, arsenic, and antimony can codeposit with copper. Arsenic and antimony cause copper deposits to be brittle and rough, and silver may cause roughness. Nickel and iron impurities reduce the conductivity of the plating bath. Lead impurities do not codeposit with copper; however, they precipitate in the electrolyte. Soluble silicates may precipitate onto the work. Organic contamination from decomposition products of addition agents, tank linings, and anode bags can cause brittle or discolored deposits. These organics can be removed from the electrolyte by treating it with activated carbon.

Plating in Fluoborate Baths

Copper fluoborate and fluoboric acid are the primary constituents of the copper fluoborate electrolyte. The metal ions are furnished by the copper fluoborate, which is more soluble than copper sulfate used in the sulfate bath, and the anode current density is not critical. Therefore, the metal-ion concentration in the fluoborate bath can be more than twice that in the copper sulfate solution, and this permits higher cathode current densities. The cupric salts in the fluoborate bath are highly ionized, except for small amounts of less ionized complex salts formed with certain addition agents.

In the copper fluoborate bath, the anode current density can be as high as 40 A/dm^2 (400 A/ft^2) without excessive anode polarization. The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper fluoborate bath is less significant than the effect of changes in cathode current density.

Agitation is preferred for the fluoborate bath, although acceptable deposits 25 μm (1 mil) thick have been produced in a high-concentration bath without agitation and with current density maintained at 35 A/dm^2 (350 A/ft^2). When agitation is used, a low-concentration bath operated at a current density of 4 to 5 A/dm^2 (40 to 50 A/ft^2) is preferred.

Although fluoborate baths containing no additives can produce dense and smooth deposits up to 500 μm (20 mils) thick, additives may be used to aid in the deposition of brighter or more uniform coatings or to assist in control of plating conditions. Although deposits from fluoborate baths are easily buffed to a high luster, brighteners of acetyl thiourea can be added to the electrolyte to produce bright coatings. The addition of free acid to the bath increases solution conductivity, reduces anode and cathode polarization, and prevents the precipitation of basic salts. Hard deposits and minimum edge effects result when molasses (1 mL/L, or 0.1 fluid oz/gal) is added to the electrolyte. If the pH of these baths exceeds 1.7, deposits become dull, dark, and brittle.

The resistivity of fluoborate electrolytes is reduced if the concentration of fluoboric acid exceeds 15 g/L (2 oz/gal) or if the concentration of copper fluoborate exceeds 220 g/L (29 oz/gal). In the fluoborate bath, the metal-ion concentration can be more than double that in a copper sulfate solution containing 50 to 75 g/L (6.7 to 10 oz/gal) of sulfuric acid.

In the fluoborate electrolytes, silver, gold, arsenic, and antimony may co-deposit with copper, but the effects of such impurities in this electrolyte have not been reported. Lead is the only metallic impurity known to interfere with the deposition of ductile copper deposits. Additions of sulfuric acid precipitate the lead. As with the sulfate electrolytes, organic impurities sometimes cause deposits to be brittle or discolored. They can be removed by treating the bath with activated carbon

Wastewater Control and Treatment

Increasing regulations governing discharge water have led to improved techniques for reducing the quantities of wastes that must be treated. These techniques have not only reduced the quantity of wastewater to be treated, but have also reduced the quantity of chemicals used and have lowered water consumption. These methods can be applied to any plating operation. Many references are available, including Ref 11, that cover waste treatment technologies.

The use of counterflow rinses has reduced water consumption and wastewaters while maintaining adequate rinsing between plating operations. Reduced dragout of plating electrolytes can be accomplished by allowing processed parts leaving the plating solution to drain into the plating solution. Drip pans also reduce the amount of electrolyte dragout.

Closed-loop systems have dramatically reduced wastewater, lowered water consumption, and diminished chemical usage. Closed-loop systems allow recovery of rinse waters and chemicals by evaporative, reverse osmosis, or ion exchange recovery methods. Care must be exercised when using closed-loop systems, especially with copper plating, to keep impurities and contaminants from preplate operations out of the copper plating bath where they will be trapped by the closed-loop operation.

In any plating operation, wastewaters must be treated to reduce the hazardous materials to meet regulations. The general procedures for treating copper plating electrolytes and rinse waters resulting from copper plating systems are:

- Cyanide-bearing solutions require oxidation of the cyanide with an oxidizing agent such as chlorine or hypochlorite, followed by precipitation of the heavy metals.
- Noncyanide alkaline solutions are pH-adjusted and have calcium chloride added to precipitate the

copper.

- Pyrophosphate wastes require low pH hydrolysis to orthophosphate, followed by precipitation of the heavy metals.
- Acid sulfate and fluoborate wastes are pH-adjusted to precipitate the copper.

Reference cited in this section

11. J.W. Patterson, *Industrial Waste Water Treatment Technology,* 2nd ed., Butterworth Publishers, 1985

Copper Plating Equipment

Construction materials for equipment are indicated in Table 7. Construction materials for racks and anodes are given in Table 8.

Table 7 Materials of construction for equipment basic to copper plating

Tank linings are of rubber or plastic[(a)], or Koroseal.

Plating bath	**Heating coils**	**Filters**	**Filter aids**
Dilute cyanide	Low-carbon steel Teflon[(b)]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Rochelle cyanide	Low-carbon steel Teflon[(b)]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
High-efficiency cyanide	Low-carbon steel Teflon[(b)]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Pyrophosphate	Stainless steel Teflon[(b)]	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Noncyanide alkaline[(c)]	Stainless steel Titanium	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Acid copper sulfate	Titanium[(d)] Teflon[(b)]	Rubber- or vinyl-lined steel	Diatomite Cellulose
Fluoborate	Carbon[(d)] Teflon[(b)]	Rubber- or vinyl-lined steel	Diatomite Cellulose

(a) Of approved compositions; in the absence of data on bath contamination and effects on deposits, compatibility tests are required.

(b) Dupont trademark.

(c) Polypropylene filter cartridges may be used.

(d) Also for cooling coils, if bath is used below 32 °C (90 °F)

Table 8 Materials for anodes and racks for use in copper plating

Racks are made of copper(a).

Plating bath	**Anodes**
Dilute cyanide	Copper; steel
Rochelle cyanide	Copper(b)(c)(d)
High-efficiency cyanide	Copper(b)(c)(d)
Noncyanide alkaline	Copper(d)
Pyrophosphate	Copper(b)(c)(d)
Acid copper sulfate	Copper(e)
Fluoborate	Copper(d)

(a) Racks are generally coated with an inert plastic coating to prevent plating.

(b) Cast copper, high purity.

(c) Rolled copper, high purity.

(d) Oxygen-free high-purity copper.

(e) Phosphorized copper

Tanks. For cyanide copper solutions, low-carbon steel tanks are suitable. Polypropylene tanks with adequate reinforcing may also be used, provided that the operating temperature is not excessive. Low-carbon steel tanks should be lined with rubber, polyvinylchloride, or another synthetic material that is not susceptible to attack by the cyanide plating solution. This will prevent bipolar effects, which may rob current from significant areas of the work. Tanks for alkaline noncyanide copper, copper pyrophosphate, acid copper sulfate, and copper fluoborate solutions should be of similar construction. Low-carbon steel tanks used for these solutions must be lined with the above materials to prevent the solutions from attacking the low-carbon steel, resulting in short tank life and immersion deposits. New tanks, as well as all other equipment coming in contact with the plating solution, should be leached before use to remove any materials that may leach into the plating solution and cause poor quality deposits. Leaching solutions should be similar to the plating solution to be used, such as a 15 to 30 g/L (2 to 4 oz/gal) caustic solution for copper cyanide or noncyanide copper equipment, or a 5 to 10% sulfuric acid solution for acid copper sulfate. When converting a tank or line that contained cyanide to a noncyanide electrolyte, it is essential to leach out all residual cyanide from the tank lining and any associated equipment.

Barrels. High-speed copper plating solutions for barrel plating are being used in product operations. Polypropylene barrels have been used successfully for prolonged periods.

Anodes. The types of copper anodes used in each of the copper plating solutions are indicated in Table 8. High-purity copper anodes are recommended. Anodes with a lesser purity may form heavy sludges during electrolysis and contribute appreciably to roughness of the deposit. Anodes used for acid copper plating solutions should be phosphorized. These contain a small percentage of phosphorus, which helps to control chemical dissolution and limits the buildup rate of copper in the acid solution. These types should not be used in alkaline cyanide or noncyanide electrolytes, because anode polarization will develop and cause deposit roughness and more difficult copper metal control.

Copper anodes are available in many forms, such as bars, balls, or chips. Bars are suspended from the anode bar. Balls or chips are placed in titanium baskets.

The anode area in a copper plating solution should be controlled and maintained. If the anode area is not maintained, it decreases as the copper is dissolved and the anode current density rises, resulting in increased polarization and formation of undesirable films. These films can restrict current flow or sluff from the anode and cause roughness in the plating solution.

Anode Bags. Bags made of cotton, Dynel, or polypropylene are used in copper plating solutions. Cotton bags are preferred for cyanide copper solutions, and Dynel or polypropylene are used in the acid copper solutions. Bags are used to keep the fine particles formed at the anode from migrating to the cathode, resulting in roughness. The weave and weight of the anode bag are most important. The bag material must be capable of retaining the particles formed at the anode and at the same time allow the plating solution to flow freely around the anode. Anode bags are not generally used in pyrophosphate baths, because they interfere with dissolution of the anode by decreasing the circulation of the solution around the anode.

Characteristics of Copper Plate

Variations in processing during surface preparation or during plating have significant effects on the quality of the copper electrodeposit. Certain variations can adversely affect the adhesion of copper to the substrate metal. Variations also can affect brightness, porosity, blistering, roughness, hardness, solderability, and leveling.

Brightness. Bright copper coatings are generally obtained by the addition of brighteners to the electrolyte, although buffing of the electrodeposited coating provides a high luster. Plating from high-concentration cyanide baths with current interruption or periodic reversal of current also improves the luster of the copper coating.

Buffing or electropolishing the work before plating it in an electrolyte not containing a brightener results in the deposition of a smooth and sometimes semibright coating. If an electrolyte containing a brightener is used, the luster of the coating is enhanced. The high cost of labor is a primary concern when buffing is considered as the method of brightening the coatings. Plating from high-efficiency cyanide baths with current interruption or periodic reversal of current also improves the luster of the deposits. Improved casting techniques and mechanical finishing before plating can improve the quality of the copper deposit.

Adhesion. Careful selection of substrate surface and proper preparation of the surface before plating are important for good adhesion. In general, cast and other porous surfaces are less receptive to good-quality electrodeposited coatings than wrought surfaces.

The kind of material to be electroplated with copper is another important consideration. For magnesium-base or aluminum-base die castings, the zincate layer between the substrate and the copper deposit is a critical control factor. For a properly activated stainless steel surface, a controlling factor for ensured adhesion of copper is the speed with which the workpiece is immersed in the bath. Some brighteners, especially organic brighteners, may adversely affect adhesion of subsequent electrodeposited coatings. Adhesion of copper electrodeposits from acid baths can be ensured only if a strike from a cyanide copper bath precedes copper plating.

Porosity. The degree of porosity in a copper coating can be controlled by the kind of copper plating bath selected, the composition and control of the electrolyte, the basis material to be plated, and the condition of the surface to be plated. The degree of porosity on the surface of the metal to be plated also dictates the techniques needed to minimize porosity in the coating. A porous surface has high surface area and requires high current density for efficient plating.

Blistering of copper plate, particularly when the plated work is subjected to heat, occurs mostly on zinc-base die castings. Blistering can also occur on parts made of magnesium or aluminum in any form, as a result of poor quality of castings, poor surface preparation, or both. Blistering of copper plate on zinc-base die castings plated in a cyanide strike electrolyte and then subjected to heat can be reduced by lowering the pH of the cyanide strike bath from the range of 12.0 to 12.6 to about 10. Caution must be used because operation at a pH value this low may result in the release of poisonous hydrogen cyanide gas. It is imperative that the plating bath be thoroughly vented.

Blistering of copper-plated magnesium and aluminum, especially during subsequent soldering or heating in service, is caused by poor adhesion at the zincate-copper interface. Unfortunately, blistering often does not become evident until subsequent electrodeposits have been applied and the coating has been subjected to heat. Exposing all copper-plated magnesium and aluminum parts to controlled heat representative of that to be subsequently encountered is good practice. This causes blistering before deposition of subsequent metal coatings if there is poor adhesion at the interface.

Roughness in copper deposits is often caused by foreign particles present in the bath as the result of faulty cleaning, or by the migration to the cathode of metallic copper or cuprous oxide particles that form at the anode. Such roughness is especially likely to occur with the sodium cyanide high-concentration electrolytes and can be prevented by using anode bags.

Solderability of the coating is good when the copper surface is free of oxide, the coating is thick enough, and the adhesion of the copper plate is superior. Direct soldering of electrodeposited copper is not unusual for parts that are subsequently contained in hermetically sealed units.

Soldering is a routine operation for aluminum and magnesium electronic parts used in aerospace applications. A copper strike and copper plate frequently comprise the initial metal coating over the zincated surfaces of these parts, after which electrodeposits of other metals are applied before soldering. A top coat of tin, or of cadmium plate that has been chromate conversion coated, is a particularly effective means of producing a good combination of solderability and corrosion resistance for parts exposed to the atmosphere.

Hardness. Without the use of addition agents, cyanide electrolytes produce harder coatings than acid baths. With the use of addition agents, the hardness of copper deposits from any electrolyte can be increased. Hardness of the electrodeposit is generally associated with fine grain, but hardness can be increased by introducing preferred crystal orientation in the absence of grain refinement. Changes in the copper sulfate or sulfuric acid concentration of acid baths have little effect on the hardness of copper plate.

Leveling has a significant effect on the appearance of the copper coating, as well as on the appearance of the final product when other metals are subsequently plated over the copper. Often, the substrate metal does not have the degree of smoothness that is desired of the plated surface. Metal substrate surfaces can be mechanically or chemically worked to reduce surface roughness before electroplating; however, some copper electrolytes can produce substantial leveling in the deposited coating, thus reducing cost related to elaborate prepolishing or other means of smoothing the surface. The high-concentration potassium cyanide electrolytes produce excellent leveling when certain addition agents are added and interrupted current or periodic reversal is used during plating. Although somewhat less effective, high-concentration sodium cyanide baths, mixed sodium and potassium electrolytes, and Rochelle cyanide electrolytes also have good leveling characteristics with interrupted or periodically reversed current. Acid copper sulfate electrolytes also provide very good leveling characteristics.

Copper in Multiplate Systems

Electrodeposited copper is widely used as a basis for subsequent plated coatings in multiplate systems. The use of copper plate in copper-nickel-chromium systems is discussed in the article "Decorative Chromium Plating" in this Volume.

Cost

The cost of copper plating is influenced largely by the type of installation. In a modern, automated, multiple-phase shop, brighteners and wetting agents probably are the greatest cost factor. In a still-tank operation, the cost of labor is of major importance. An increase in current density reduces cost because of the reduction in time required to deposit a given thickness of coating.

For a routine plating operation, the cost of the copper deposited can be estimated with the aid of Fig. 5. For example, Fig. 5 shows that 120 g (4 oz) of copper is required for plating an area of 0.7 m^2 (7 ft^2) with a coating 20 μm (0.8 mil) thick. The cost of the copper coating is obtained by multiplying the weight of copper required by the cost of copper anodes. For areas larger than 2.4 m^2 (10 ft^2), multiply by the proper factor.

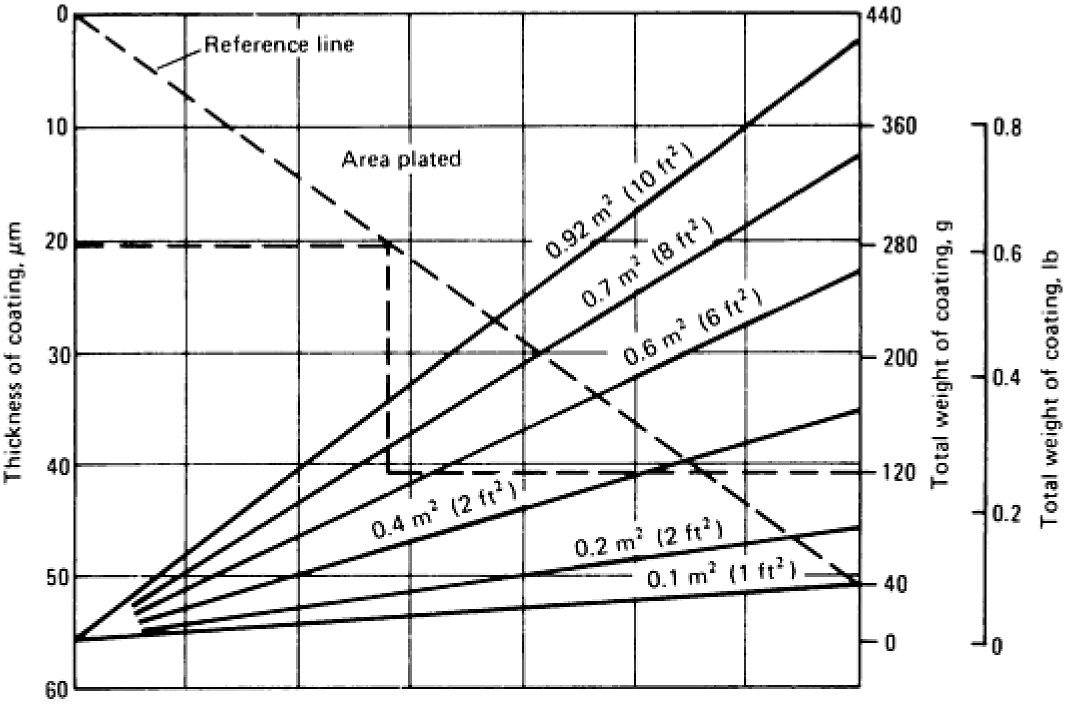

Fig. 5 Copper required for covering an area with a specific thickness

Industrial (Hard) Chromium Plating

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Introduction

HARD CHROMIUM PLATING is produced by electrodeposition from a solution containing chromic acid (CrO_3) and a catalytic anion in proper proportion. The metal so produced is extremely hard and corrosion resistant. The process is used for applications where excellent wear and/or corrosion resistance is required. This includes products such as piston rings, shock absorbers, struts, brake pistons, engine valve stems, cylinder liners, and hydraulic rods. Other applications are for aircraft landing gears, textile and gravure rolls, plastic rolls, and dies and molds. The rebuilding of mismachined or worn parts comprises large segments of the industry. One specialized application is a thin chromium layer used as a lacquer adhesive layer in the manufacture of "tin" cans.

Hard chromium plating is also known as industrial, functional, or engineering chromium plating. It differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase the service life of functional parts by providing a surface with a low coefficient of friction that resists galling, abrasive and lubricated wear, and corrosion. Another major purpose is to restore dimensions of undersized parts.
- Hard chromium normally is deposited to thicknesses ranging from 2.5 to 500 μm (0.1 to 20 mils) and for certain applications to considerably greater thicknesses, whereas decorative coatings seldom exceed 1.3 μm (0.05 mil).
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is

applied over undercoats of nickel or of copper and nickel.

Principal Uses

The major uses of hard chromium plating are for wear-resistance applications, improvement of tool performance and tool life, and part salvage. Table 1 lists parts to which hard chromium plate is applied and representative data regarding plate thickness and plating times. Plating times can be reduced by using high-efficiency or mixed-catalyst solutions.

Table 1 Typical thicknesses and plating times for selected applications of hard chromium plating

Part	**Base metal**	**Thickness of plate**		**Plating time**[(a)]
		μm	**mils**	
Computer printer type	Carbon steel	25	1	60 min
Face seals	Steel or copper	75-180	3-7	10 h
Aircraft engine parts	Nickel-based alloys, high strength steel	75-180	3-7	10 h
Plastic molds	Tool steel	5-13	0.2-0.5	30 min
Textile guides	Steel	5-100	0.2-4	20-240 min
Piston rings	Steel or cast iron	150-255	6-10	8 h
Balls for ball valves	Brass or steel	7.5-13	0.3-0.5	20 min
Micrometers	Steel	7.5-13	0.3-0.5	20 min
Golf ball molds	Brass or steel	7.5-25	0.3-1	20-60 min
Lock cases	Brass	5-7.5	0.2-0.3	20 min
Cylinder	Cast iron	255	10	300 min
Bushing	1018 carburized, 56 HRC	25	1	45 min
Crankshafts	Steel	255-3800	10-150	. . .
Cutting tools	Tool steel	1.3	0.05	5 min
Forming and drawing dies	Steel	25	1	60 min

Part	Base metal	Thickness of plate		Plating time[a]
		µm	mils	
Gage	Steel	125	5	150 min
Gun barrels, 30 caliber[b]	Steel	25	1	40 min
Hydraulic cylinder	1045 steel	13	0.5	40 min
Pin	Steel	13	0.5	30 min
Pin	1045 steel, 60 HRC	125	5	40 min
Plug gage	1040 steel, 55 HRC	125	5	150 min
Relief-valve plunger	1113 steel, soft	100	4	60 min
Ring gage	Steel	205	8	240 min
Rolls	Steel	13-255	0.5-10	20-300 min

(a) Times shown are for conventional plating solutions; plating times for the proprietary fluoride-free solution are half of those shown.

(b) M-16 rifle, barrel and chamber

Wear Resistance. Extensive performance data indicate the effectiveness of chromium plate in reducing the wear of piston rings caused by scuffing and abrasion. The average life of a chromium-plated ring is approximately five times that of an unplated ring made of the same base metal. Piston rings for most engines have a chromium plate thickness of 100 to 200 μm (4 to 8 mils) on the bearing face, although thicknesses up to 250 µm (10 mils) are specified for some heavy-duty engines.

In the automotive industry, hard chromium is also applied to shock absorber rods and struts to increase their resistance to wear and corrosion. Valve stems are plated with a flash coating (about 2.5 µm, or 0.1 mil) to reduce wear. Hydraulic shafts for all kinds of equipment are plated with 20 to 30 µm (0.8 to 1.2 mil) of hard chromium to increase service life.

Tooling Applications. Various types of tools are plated with chromium to minimize wear, prevent seizing and galling, reduce friction, and/or prevent or minimize corrosion. Steel or beryllium copper dies for molding of plastics are usually plated with chromium, especially when vinyl or other corrosive plastic materials are to be molded. Plating thicknesses of 2.5 to 125 µm (0.1 to 5 mils) usually are recommended for preventing wear in parts sticking in molds and for reducing frequency of polishing when plastics that attack steel or beryllium copper are being molded. Chromium-plated dies should not be used when plastics containing fire-retardant chlorides are molded.

The service life of plug gages and other types of gages may be prolonged by hard chromium plating. Most gage manufacturers provide chromium-plated gages. Records in one plant indicate that plug gages made from hardened O1 tool steel wore 0.0025 mm (0.0001 in.) after gaging 5000 cast iron parts. Hard chromium plating of these gages allowed the gaging of 40,000 parts per 0.0025 mm (0.0001 in.) of wear.

Worn gages can be salvaged by being built up with hard chromium plate. Also, chromium plate provides steel gages with good protection against rusting in normal exposure and handling. Chromium plating is not recommended, however, for gages that are subjected to impact at exposed edges during operation.

Deep drawing tools often are plated with chromium, in thicknesses up to 100 μm (4 mils), for improvement of tool performance and/or building up of worn areas. The life of draw rings and punches may be prolonged by plating. In addition, plating reduces frictional force on punches and facilitates removal of workpieces from punches in instances where sticking is encountered with plain steel surfaces. If deep drawing tools are chromium plated, the base metal should be harder than 50 HRC. Steel dies used for drawing bars and tubes are often plated with relatively heavy thicknesses (up to 250 μm, or 10 mils) of chromium to minimize die wear, reduce friction, and prevent seizing and galling.

The service life of cutting tools is often extended by chromium plate, in thicknesses ranging from less than 2.5 to 13 μm (0.1 to 0.5 mil). Taps and reamers are examples of tools on which chromium plate has proved advantageous. In one case, a flash plate on taps used to thread cold-worked 1010 steel improved tap life from 250 (for unplated taps) to 6000 parts per tap. The poor tool life of the unplated taps was caused by buildup of metal on the cutting edges. Hard chromium plating is not recommended for cold extrusion tools for severe applications where extreme heat and pressure are generated, because the plate is likely to crack and spall and may be incompatible with phosphate-soap lubricants.

Part Salvage. Hard chromium plating is sometimes used for restoring mismachined or worn surfaces. Since 1970, the use of this process for part salvage has been frequently replaced by thermal spraying and plasma coatings, which can be applied more quickly. The fact that a chromium deposit can significantly reduce fatigue strength must be considered in determining whether chromium plating can be safely used.

Hard chromium plating is used to restore to original dimensions the worn surfaces of large crankshafts for diesel and gas engines and for compressors. In these applications, in which coating thicknesses usually range from 125 to 1250 μm (5 to 50 mils), the excellent wearing qualities and low coefficient of friction of chromium are highly advantageous. The plate is prevented from depositing in fillet areas as a precaution against fatigue failure.

The extremely close dimensional tolerances specified for components of compressors for jet aircraft engines are not always correctly met in machining. Hard chromium plating is sometimes used to salvage mismachined parts. Most frequently mismachined are the diameters of rotor disks and spacers. The maximum thickness of plate on these components, which are made of 4130 and 4340 steels, generally does not exceed 380 μm (15 mils).

Other Applications. Hard chromium plate is applied to printing plates and stereotypes, especially to those intended for long runs, because compared to other materials or coatings used for this application, it wipes cleaner, provides sharper reproduction, and increases the length of press runs. It is used on press rams because of its excellent resistance to corrosion, seizing, galling, and other forms of wear.

Selection Factors

The decision to use hard chromium plating on a specific part should take into account the following characteristics:

- The inherent hardness and wear resistance of electrodeposited chromium
- The thickness of chromium required
- The shape, size, and construction of the part to be plated
- The type of metal from which the part is made
- Masking requirements (for parts that are to be selectively plated)
- Dimensional requirements (that is, whether or not mechanical finishing is required and can be accomplished in accordance with desired tolerances)

The hardness of chromium electrodeposits is a function of the type of chemistry selected and the plating conditions. In general, chromium plated in the bright range is optimally hard. Typically bright chromium deposits from conventional plating solutions have hardness values of 850 to 950 HV; those from mixed-catalyst solutions have values of 900 to 1000 hV; and those from fluoride-free chemistries have values of 950 to 1100 HV or higher.

Size. Frequently, a very large part can be plated in sections or can be rotated so that only a portion of the part is immersed in the plating solution at any given time. The latter method has been used to plate large cylinders up to 4 m (12 ft) in diameter and up to 18 m (60 ft) long. When this technique is used, all of the surface to be plated that is exposed to the atmosphere must remain wet with plating solution.

Journal surfaces of the largest diesel crankshafts and bores of large naval guns and M-16 rifles are hard chromium plated on a production basis. Internal surfaces of very large cylinders have been plated by closing off the ends of each cylinder and retaining the plating solution with it.

Base Metal. Most hard chromium deposits are applied to parts made of ferrous alloys; however, numerous aerospace applications require the chromium plating of aluminum and nickel-base alloys. From the standpoint of processing, hard chromium plate may be applied to steels, regardless of their surface hardness or chemical composition, provided that the base metal is hard enough to support the chromium layer in service. Similarly, cast irons can be plated provided that the surface is capable of conducting the required current and is reasonably free of voids, pits, gross silicate inclusions, massive segregation, slivers, and feather edges.

Plating Solutions

Chromic acid is the source of metal in hard chromium plating solutions. However, a chromic acid solution does not deposit chromium unless a definite amount of catalyst is present. If there is either too much or too little catalyst, no chromium metal is deposited. Catalysts that have proved successful are acid anions, the first of which to be used was sulfate. Substitution of fluoride ions present in complex acid radicals for a portion of the sulfate improves the chromium-plating operation. In the late 1980s, a fluoride-free proprietary solution was developed. The secondary catalyst in this chemistry is a stable organic species. Reflecting this difference in catalyst, the principal types of solutions are designated as conventional sulfate (also called Sargent or Fink); mixed-catalyst, which refers to the sulfate and fluoride chemistry; and fluoride-free (proprietary) catalyst.

The fatigue limit of high-strength steel (steels with ultimate tensile strengths of 1240 MPa, or 180 ksi, and above) may be reduced by about 50% when chromium plated because of the inherent crack structure of hard chromium. However, special techniques using shot peening and postplate heat treatments may be used to retain most of the original fatigue strength.

Conventional Sulfate Solutions. Composition of conventional chromic acid solutions catalyzed by sulfate can vary widely, provided the ratio by weight of chromic acid to sulfate radical is within the range between 75 and 120 to 1. Throwing power, or distribution of plate, is optimum at ratios between 90 and 110 to 1; however, in the range between 75 and 90 to 1, brighter deposits are obtained, less burning occurs, and a higher current density can be used.

Solutions containing chromic acid in a concentration as low as 50 g/L (7 oz/gal) have been reported but are not practical for production because:

- Their plating range is too limited
- The solutions are more sensitive to contamination
- They have a higher electrical resistance
- They require a higher voltage for operation

Compositions and operating conditions for two chromic acid/sulfate solutions (low and high concentrations) for hard chromium plating are given in Table 2. The low-concentration solution is widely used for hard chromium plating because it minimizes dragout losses and associated environmental problems. The high-concentration solution has the advantage of being less sensitive to concentration changes; it is also easier to control and has better throwing power. Because the high-concentration solution is more conductive, it can be operated at lower voltages and heats up less in operation.

Table 2 Sulfate baths for hard chromium plating

Type of oath	Chromic acid[a]		Sulfate[a]		Current density		Bath temperature	
	g/L	oz/gal	g/L	oz/gal	A/dm^2	A/in.^{2}	°C	°F
Low concentration	250	33	2.5	0.33	31-62	2-4	52-63	125-145
High concentration	400	53	4.0	0.53	16-54	1-3.5	43-63	110-145

(a) Concentration usually can deviate ±10% without creating problems. It is recommended that adjustments be such that the concentrations listed above lie in the middle of the range permitted. For example, chromic acid can fluctuate by ±23 g/L (±3 oz/gal); therefore, the concentration range should be 225-270 g/L (30 to 36 oz/gal), rather than 205-250 g/L (27 to 33 oz/gal).

If available voltage is limited, it may be preferable to operate a solution with higher conductivity in the range of 300 to 405 g/L (40 to 54 oz/gal) of chromic acid, even though current efficiency is lower than with the less concentrated solutions. The lower current efficiency is offset by increased current density obtainable because of better solution conductivity. Usually, the best range of operation is from 195 to 300 g/L (26 to 40 oz/gal) of chromic acid. Even within this range, the solution containing 195 g/L (26 oz/gal) has the highest current efficiency, while the solution containing 300 g/L (40 oz/gal) has the best conductivity.

The mixed-catalyst solutions are similar to conventional sulfate solutions in conductivity, but they produce harder deposits and have higher intrinsic current efficiency than conventional solutions under identical conditions. They also have a higher current efficiency at higher concentration. Mixed-catalyst solutions can increase production rates 40 to 60% and more over those obtainable with conventional solutions, due to the greater current efficiencies of the mixed-catalyst solutions and their ability to operate at higher current densities without creating harmful effects on the deposit. One limitation of mixed-catalyst solutions is that they cause etching of unplated iron surfaces at areas of low current density, with a resulting increase in contamination that reduces the life of the solution. This etching can be prevented on significant surfaces by masking areas not to be plated. Mixed-catalyst solutions are seldom used on aluminum or copper substrates because of the attack by the fluoride chemicals.

Fluoride-free solution, a proprietary chemistry, is based on chromic acid, sulfate, and a stable organic catalyst. It provides deposit speeds and current density ranges slightly in excess of those obtained with mixed-catalyst solutions. Because the solution contains no fluorides or other halogens, it does not cause etching on exposed unplated surfaces or attack aluminum or copper substrates. These features alleviate the need for excessive protective masking operations. As with the mixed-catalyst chemistry, the fluoride-free solution provides much greater plating throughput while consuming about one-third less electricity than the conventional solution.

Deposit hardness and corrosion resistance improve as one moves from the conventional sulfate solution to the mixed-catalyst solution and on to the fluoride-free solution.

Solution Control

Chromium-plating solutions of all three types must be subjected to periodic chemical analyses for control of solution composition. With the exception of catalyst analysis, the species and methods are identical for all chemistries. Solution control can be simplified if a record is kept of the way a particular chromium solution changes in composition during its use. Change in chemical composition depends on the number of ampere-hours of current passed through the solution, the dragout of solution, and spray losses. Also, evaporation losses, if not compensated for, usually cause the concentration to change by about 2 to 5% during a day's operation. A complete solution analysis should be made at periodic intervals (weekly or monthly, depending on production rate) and the solution should be brought into proper balance.

Chromic acid content can be semi-quantitatively determined simply by placing a hydrometer in the plating solution, provided that other contaminants, such as iron or copper, are not present in significant quantities. Hydrometers calibrated in ounces of chromic acid per gallon at the operating temperature of the solution are available. Baumé hydrometers can be used in samples cooled to the calibration temperature marked on the hydrometer; the reading can be converted to concentration by using Table 3. Impurities cause the Baumé reading to be higher than is warranted by the actual chromic acid content. Periodically, the chromic acid content should be quantitatively determined by chemical titration and a notation made of the differences between the contents as shown by chemical analysis and by hydrometer readings. Hydrometer readings should then be corrected by that amount. When a hydrometer reading shows 30 to 38 g/L (4 to 5 oz/gal) more chromic acid than is actually present, the solution should be discarded, because this is caused by a high metallic impurity level. Adjustments in chromic acid concentration are simplified by the use of Table 4.

Table 3 Determination of chromic acid in chromium baths with a Baumé hydrometer

Direct conversion of degrees Baumé to ounces of chromic acid per gallon, at 25 °C (77 °F)

°Bé	**Chromic acid**	
	g/L	**oz/gal**
10.5	113	15.0
11.0	119	15.8
11.5	124	16.5
12.0	130	17.3
12.5	137	18.2
13.0	144	19.1
13.5	149	19.8
14.0	153	20.4
14.5	159	21.2
15.0	165	22.0
15.5	172	22.9
16.0	178	23.7
16.5	184	24.5
17.0	191	25.4
17.5	198	26.3

18.0	204	27.2
18.5	211	28.1
19.0	218	29.0
19.5	224	29.8
20.0	230	30.9
20.5	237	31.5
21.0	244	32.4
21.5	250	33.3
22.0	257	34.2
22.5	264	35.1
23.0	271	36.0
23.5	279	37.1
24.0	287	38.2
24.5	294	39.1
25.0	301	40.0
25.5	308	4.09
26.0	315	41.9
26.5	323	42.9
27.0	331	44.0
27.5	338	45.0
28.0	346	46.0

28.5	354	47.1
29.0	362	48.2
29.5	370	49.2
30.0	378	50.2
30.5	387	51.5
31.0	399	53.0
31.5	406	54.0
32.0	415	55.2

Note: Impurities will cause the Baumé hydrometer reading to be higher than is warranted by the actual content of chromic acid.

Table 4 Conversion equivalents for chromic acid concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Chromic acid required, kg(lb) = g/L(oz/gal) CrO_3 to be added × bath volume, in liters (gallons)/16

Chromic acid to be added		**Chromic acid required, kg (lb), at volume of bath, L (gal), of:**									
g/L	**oz/gal**	**380 (100)**	**760 (200)**	**1140 (300)**	**1510 (400)**	**1890 (500)**	**2270 (600)**	**2650 (700)**	**3030 (800)**	**3410 (900)**	**3790 (1000)**
4.0	0.5	1.4 (3.1)	2.9 (6.3)	4.3 (9.4)	5.7 (12.5)	7.1 (15.6)	8.5 (18.8)	9.9 (21.9)	11.3 (25.0)	12.7 (28.1)	14.2 (31.2)
7.5	1.0	2.8 (6.2)	5.7 (12.5)	8.5 (18.8)	11.3 (25.0)	14.2 (31.2)	17.0 (37.5)	19.9 (43.8)	22.7 (50.0)	25.5 (56.3)	28.3 (62.5)
11.0	1.5	4.3 (9.4)	8.5 (18.8)	12.8 (28.2)	17.0 (37.5)	21.3 (46.9)	25.5 (56.3)	29.8 (65.6)	34.0 (75.0)	38.3 (84.4)	42.5 (93.8)
15.0	2.0	5.7 (12.5)	11.3 (25.0)	17.0 (37.5)	22.7 (50.0)	28.3 (62.5)	34.0 (75.0)	39.7 (87.5)	45.3 (100.0)	51.3 (113.0)	56.7 (125.0)
19.0	2.5	7.1 (15.6)	14.2 (31.2)	21.3 (46.9)	28.3 (62.5)	35.4 (78.1)	42.5 (93.8)	49.4 (109.0)	56.7 (125.0)	61.0 (141.0)	70.8 (156.0)
22.0	3.0	8.5 (18.8)	17.0 (37.5)	25.5 (56.3)	34.0 (75.0)	42.6 (93.8)	51.3 (113.0)	59.4 (131.0)	68.0 (150.0)	76.7 (169.0)	85.3 (188.0)

26.0	3.5	9.9 (21.9)	19.8 (43.7)	29.8 (65.6)	39.7 (87.5)	49.4 (109.0)	59.4 (131.0)	69.4 (153.0)	79.4 (175.0)	89.4 (197.0)	99.3 (219.0)
30.0	4.0	11.3 (25.0)	22.7 (50.0)	34.0 (75.0)	45.3 (100.0)	56.7 (125.0)	68.0 (150.0)	79.4 (175.0)	90.7 (200.0)	102.0 (225.0)	113.0 (250.0)
34.0	4.5	12.7 (28.1)	25.5 (56.2)	38.3 (84.4)	51.3 (113.0)	64.0 (141.0)	76.7 (169.0)	89.4 (197.0)	102.0 (225.0)	115.0 (253.0)	127.0 (281.0)
37.0	5.0	14.2 (31.2)	28.3 (62.5)	42.5 (93.8)	56.7 (125.0)	70.8 (156.0)	85.3 (188.0)	99.3 (219.0)	113.0 (250.0)	128.0 (281.0)	142.0 (312.0)
41.0	5.5	15.6 (34.4)	31.2 (68.7)	46.7 (103.0)	62.6 (138.0)	78.0 (172.0)	93.4 (206.0)	109.0 (241.0)	125.0 (275.0)	140.0 (309.0)	156.0 (344.0)
45.0	6.0	17.0 (37.5)	34.0 (75.0)	51.3 (113.0)	68.0 (150.0)	85.3 (188.0)	102.0 (225.0)	119.0 (262.0)	136.0 (300.0)	153.0 (338.0)	170.0 (375.0)
49.0	6.5	18.4 (40.6)	36.8 (81.2)	55.3 (122.0)	73.9 (163.0)	92.1 (203.0)	111.0 (244.0)	129.0 (284.0)	147.0 (325.0)	162.0 (365.0)	184.0 (406.0)
52.0	7.0	19.8 (43.7)	39.7 (87.5)	59.4 (131.0)	79.4 (175.0)	99.3 (219.0)	119.0 (262.0)	139.0 (306.0)	159.0 (350.0)	179.0 (394.0)	198.0 (437.0)
56.0	7.5	21.3 (46.9)	42.5 (93.8)	64.0 (141.0)	85.3 (188.0)	106.0 (234.0)	128.0 (281.0)	149.0 (328.0)	170.0 (375.0)	191.0 (422.0)	213.0 (469.0)
60.0	8.0	22.7 (50.0)	45.4 (100.0)	68.0 (150.0)	90.7 (200.0)	113.0 (250.0)	136.0 (300.0)	159.0 (350.0)	181.0 (400.0)	204.0 (450.0)	227.0 (500.0)
64.0	8.5	24.1 (53.1)	48.1 (106.0)	72.1 (159.0)	96.6 (213.0)	121.0 (266.0)	145.0 (319.0)	169.0 (372.0)	193.0 (425.0)	216.0 (477.0)	241.0 (531.0)
67.0	9.0	25.5 (56.2)	51.3 (113.0)	76.7 (169.0)	102.0 (225.0)	127.0 (281.0)	153.0 (338.0)	179.0 (394.0)	204.0 (450.0)	230.0 (506.0)	255.0 (562.0)
71.0	9.5	26.9 (59.4)	54.0 (119.0)	80.7 (178.0)	108.0 (238.0)	135.0 (297.0)	161.0 (356.0)	189.0 (416.0)	215.0 (475.0)	243.0 (535.0)	269.0 (594.0)
75.0	10.0	28.3 (62.5)	56.7 (125.0)	85.3 (188.0)	113.0 (250.0)	142.0 (312.0)	170.0 (375.0)	199.0 (438.0)	227.0 (500.0)	255.0 (563.0)	284.0 (625.0)

Chromic acid content can also be determined by various analytical procedures. Some of these procedures use standard solutions that can be used for other determinations; this may be the deciding factor as to which procedure to use. The following procedure is simple and quite rapid:

Reagents

- *Acid mixture:* Mix 1 part sulfuric acid, 1 part phosphoric acid, and 1 part water.
- *Ferrous ammonium sulfate (FAS) 0.1 N:* Dissolve 40 g/L (5.3 oz/gal) FAS · $6H_2O$ and add 25 mL/L concentrated sulfuric acid. When in use, keep about 6500 mm^2 (10 $in.^2$) of aluminum metal in the container to maintain constant normality.
- Orthophenanthroline ferrous sulfate complex indicator
- *Potassium dichromate, 0.1000 N:* dissolve 4.900 g (0.173 oz) of $K_2Cr_2O_7$ (CP grade) and dilute to a liter.

Standardization of FAS

- 1. Pipette 25 mL of potassium dichromate standard into a 250 mL Erlenmeyer flask and dilute to 85 mL.
- 2. Add 15 mL of acid mixture and 3 drops of indicator.
- 3. Titrate with FAS to clear orange endpoint. Normality of FAS = 2.5 / (mL of FAS).

Procedure

- 1(a). Pipette 10 mL of chromium solution into a 250 mL volumetric flask and dilute to volume. Pipette a 10 mL aliquot into a 250 mL Erlenmeyer flask.
- 1(b). Pipette 0.4 mL of chromium solution sample into a 250 mL Erlenmeyer flask, using a 1 mL pipette graduated in hundredths of a milliliter.
- 2. Add 50 mL of water, 15 mL of acid mixture, and 3 drops of indicator.
- 3. Titrate with FAS to clear orange end point. Chromic acid in g/L = (mL of FAS) × (*N* of FAS) × (83.3). Chromic acid in oz/gal = (mL of FAS) × (*N* of FAS) (11.12).

Use either step 1(a) or 1(b), followed by steps 2 and 3. Step 1(b) is slightly less accurate than 1(a) but is much faster.

Sulfate in a chromium solution can be determined to a high degree of accuracy by a gravimetric method, or with reasonable accuracy using the much faster centrifuge method. Unless there is some reason for great precision, the centrifuge method is entirely satisfactory. Most graduated centrifuge tubes can be calibrated for sulfate; however, the technique should be checked regularly by analysis of a standard solution, or by the gravimetric technique.

With the centrifuge method, the amount of insoluble material in the sample must be determined before sulfate is precipitated. This can be done by running a blank sample or centrifuging the sample before precipitating the sulfate. Because sulfate determinations are made in duplicate, it is advisable to determine how closely the two tubes match in calibration. This can be done by pouring a small amount of mercury into first one tube and then the other. These tubes should be marked to be used together, and a notation should be made, if necessary, as to the amount of correction needed in the reading. Adjustments of sulfate concentration in chromium solutions can be simplified by using Table 5.

Table 5 Conversion equivalents for adjusting sulfate concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Sulfuric acid (66 °Bé) fluid oz, = 0.522 × oz/gal H_2SO_4 to be added × bath volume, gal

Sulfuric acid to be added		Sulfuric acid (66 °Bé) required, mL (fluid oz), at volume of bath, L (gal), of:									
g/L	oz/gal	380 (100)	760 (200)	1140 (300)	1515 (400)	1890 (500)	2270 (600)	2650 (700)	3030 (800)	3410 (900)	3790 (1000)
0.08	0.01	15 (0.5)	30 (1.0)	47 (1.6)	62 (2.1)	77 (2.6)	92 (3.1)	109 (3.7)	124 (4.2)	139 (4.7)	154 (5.2)

0.15	0.02	30 (1.0)	62 (2.1)	92 (3.1)	124 (4.2)	154 (5.2)	186 (6.3)	216 (7.3)	249 (8.4)	278 (9.4)	308 (10.4)
0.22	0.03	47 (1.6)	92 (3.1)	139 (4.7)	186 (6.3)	231 (7.8)	284 (9.6)	323 (10.9)	370 (12.5)	417 (14.1)	465 (15.7)
0.30	0.04	62 (2.1)	124 (4.2)	186 (6.3)	249 (8.4)	308 (10.4)	370 (12.5)	432 (14.6)	494 (16.7)	556 (18.8)	619 (20.9)
0.37	0.05	77 (2.6)	154 (5.2)	231 (7.8)	308 (10.4)	385 (13.0)	462 (15.6)	539 (18.2)	619 (20.9)	696 (23.5)	773 (26.1)
0.45	0.06	92 (3.1)	186 (6.3)	284 (9.6)	370 (12.5)	462 (15.6)	556 (18.8)	648 (21.9)	740 (25.0)	835 (28.2)	926 (31.3)
0.53	0.07	110 (3.7)	216 (7.3)	323 (10.9)	432 (14.6)	539 (18.2)	648 (21.9)	758 (25.6)	864 (29.2)	974 (32.9)	1080 (36.5)
0.60	0.08	124 (4.2)	249 (8.4)	370 (12.5)	494 (16.7)	619 (20.9)	740 (25.0)	864 (29.2)	989 (33.4)	1113 (37.6)	1237 (41.8)
0.67	0.09	139 (4.7)	278 (9.4)	417 (14.1)	556 (18.8)	696 (23.5)	835 (28.2)	974 (32.9)	1143 (38.6)	1252 (42.3)	1391 (47.0)
0.75	0.10	154 (5.2)	308 (10.4)	465 (15.7)	619 (20.9)	773 (26.1)	926 (31.3)	1080 (36.5)	1237 (41.8)	1391 (47.0)	1545 (52.2)

Note: To neutralize excess sulfuric acid (thereby lowering the sulfate content) in a chromium bath, add approximately 1.5 g/L (0.2 oz/gal) of barium carbonate for each 0.8 g/L (0.1 oz/gal) of excess sulfuric acid. Additions of barium carbonate should be made slowly to the bath.

Contamination. In the operation of any chromium solution, the solution should be kept free of excessive amounts of contamination. Introduction of copper, iron, or trivalent chromium seriously decreases the conductivity of the solution and requires the use of a higher operating voltage to produce a given current density.

Trivalent chromium can be formed by the decomposition of organics, but more often it results from too low a ratio of anode-to-cathode area, a condition always encountered in plating interior surfaces cylinders. Trivalent chromium can be reoxidized to hexavalent chromium by electrolyzing the solution at 60 to 66 °C (140 to 150 °F), with an anode-to-cathode area ratio of about 30 to 1, and using a cathode current density of about 60 A/dm^2 (4 A/in.^{2}). About 50 A · h/L (200 A · h/gal) is required for reoxidizing 15 g/L (2 oz/gal) of trivalent chromium; ordinarily, this operation is performed during the weekend shutdown period.

Removal of copper, iron, and other contaminants is usually accomplished by disposing of part or all of the solution, or where permissible, by ion exchange or electrodialysis techniques. In addition to reducing the conductivity of the solution, impurities, particularly iron and trivalent chromium, also reduce current efficiency. (This is especially true for the mixed-catalyst type of chemistry because these contaminants reduce the activity of the fluoride catalyst.) Normally, the presence of 10 g/L (1.5 oz/gal) of iron in solution reduces cathode current efficiency by about 30%. Iron and trivalent chromium can produce rougher deposits with more treeing. Other contaminants affect the throwing power and coverage.

Mandrel Test. When difficulties are experienced with the hard chromium production solution, it may be useful to use the mandrel test, so named because it is usually performed by plating a low-carbon steel rod or mandrel (9.5 mm diameter by 75 mm long, or $\frac{3}{8}$ in. diameter by 3 in. long) with a conforming circular anode to give uniform current distribution. A convenient procedure is to use 540 mL of the solution in a 600 mL beaker made of heat-resistant glass. The steel mandrel is buffed to a bright finish, and the top 25 mm (1 in.) that projects out of the solution and into a holder is stopped-off to indicate the exact size of the plating area.

The mandrel is immersed in the test solution, which is heated to 55 °C (130 °F) in a water solution, treated anodically at 15 A/dm^2 (1 A/in.^{2}) for 15 s, and then plated at 30 A/dm^2 (2 A/in.^{2}) for 1 h. The temperature of the water solution should be reduced to about 52 °C (125 °F) during plating to compensate for the heat generated by the current. The mandrel is then removed, rinsed, dried, and inspected.

Better temperature control through the plating process is obtained by using 1 L of solution in a 1.5 L beaker. The solution is heated with a 125 W quartz heater controlled by a thermoregulator and relay. The process operates at 55 °C (130 °F).

A hard chromium solution in proper adjustment gives a bright plate under these conditions. If the deposit is dull, the solution is contaminated or out of balance. Burning on the bottom edge of the mandrel also indicates that the solution is out of adjustment. A high content of trivalent chromium causes dullness and growth of metal whiskers from the bottom edge of the mandrel.

Current efficiency and plating speed can be checked with the same setup, but this is more conveniently done with a flat steel panel and flat anodes. A polished steel panel, 25 by 75 mm (1 by 3 in.), can be used, with the bottom 50 mm (2 in.) marked off as the plating area. Plating conditions would be 30 A/dm^2 (2 A/in.^{2}) for 15 min at 55 °C (130 °F), but other conditions can be tested as desired. The steel panel is accurately weighed before and after plating (without current reversal). Current efficiency, thickness of chromium, and plating speed are calculated as follows:

- Current efficiency, % = (weight, in grams, of chromium × 100) / (ampere-hours × 0.323)
- Thickness of deposit, mils = (weight, in grams, of chromium) / (4 × 0.116)
- Plating speed, mils/h = (thickness of deposit, in mils × 60) / plating time, min

Process Control

In addition to solution composition, the principal variables that must be controlled for satisfactory hard chromium plating are the anodes, the current density, and the solution temperature.

Anodes. In contrast to other plating solutions, which use soluble anodes to supply the solution with a large part of the metal ion being plated, chromium plating solutions are operated with insoluble lead alloy anodes. Usually about 7% Sn or Sb or a combination of the two are used to alloy the lead. As a consequence of using inert anodes, additions of chromic acid must be made to keep the plating solution supplied with chromium metal ions.

A coating of lead peroxide forms on the lead alloy anodes during electrolysis. This coating is usually dark charcoal brown, which indicates that the anodes are functioning correctly. The presence of an orange-to-yellow lead chromate coating indicates that the anodes are not passing current properly. Periodic cleaning of the anodes and their hooks is mandatory for efficient operation.

Insoluble antimonial lead (93Pb, bal Sb + Sn) and lead-tin alloy (93Pb-7Sn) are the most widely used anode materials in chromium plating solutions. These alloys minimize corrosion of the anode; the antimony in the first composition stiffens the anode against shape changes. Each anode must have sufficient cross-sectional area to pass the requisite current without overheating. If high current densities are to be used with mixed-catalyst or fluoride-free solutions, it may be necessary to use larger anode cross sections than would be the case in the low-current-density conventional solutions. In any case the bottom of each anode should be at least 150 mm (6 in.) above the bottom of the plating tank to avoid possible electrical shorts.

Conductivity of the chromium solution is based on chromic acid concentration. Concentrations higher than 250 g/L (33 oz/gal) require lower operating voltage; however, current efficiency decreases with increasing chromic acid concentration. Concentrations below about 180 g/L are usually impractical unless high-voltage rectifiers are available.

Current Density and Efficiency. Cathode current efficiency varies with current density and temperature of the plating solution. Efficiency increases significantly with increasing current density and slightly with decreasing temperature. These two variables have a definite effect on the appearance and hardness of the deposit. A high solution temperature results in a milky, dull, and softer deposit at lower current efficiencies, unless the current density is increased substantially. Raising current density causes the deposit to change successively at specific temperatures (Table 6). Because tank time is an important economic factor, the highest rates of deposition that are produced by the highest available currents may determine which plating solution temperature is most useful.

Table 6 Effect of bath temperature and current density on appearance and hardness of chromium deposits plated from a conventional sulfate solution

Bath contained 406 g/L CrO_3; ratio of CrO_3 to SO_4 ranged from 90-to-1 to 100-to-1

Current density		Appearance of deposit	Hardness[(a)], DPH
A/dm^2	A/in.^{2}		
Plating bath at 43 °C (110 °F)			
Below 8.53	Below 0.55	Dull matte	[(b)]
8.53	0.55	Semibright	695
17.1	1.10	Bright	900
25.6	1.65	Bright, pebbly	Over 940
34.1	2.20	Dull, nodular[(c)]	Over 940
Plating bath at 49 °C (120 °F)			
Below 10.9	Below 0.70	Dull matte	510-595
10.9	0.70	Semibright	695
21.7	1.40[(d)]	Bright	900
32.6	2.10	Bright, pebbly	Over 940
43.4	2.80	Dull, nodular[(c)]	Over 940
Plating bath at 54 °C (130 °F)			
Below 14.0	Below 0.90	Dull matte	510-595
14.0	0.90	Semibright	695

27.9	1.80[d]	Bright	900
41.9	2.70	Bright, pebbly	Over 940
55.8	3.60	Dull, nodular[c]	Over 940

(a) Hardness of mounted and unmounted specimens was determined with a tester employing a Vickers diamond, a load of 200 g, and a magnifaction of 200×. Mounted specimens were mounted flat (not cross section).

(b) Current density too low to plate a sufficient amount of chromium for hardness test.

(c) Specimens polished lightly to smooth out nodules.

(d) Optimum current density

Deposition Rates. Times required to plate hard chromium deposits of various thicknesses are shown as a function of current density in Table 7 (for low-concentration solutions) and Table 8 (for high-concentration solutions).

Table 7 Rates of deposition of hard chromium from low-concentration baths

Thickness of plate		**Plating time, h:min, at current density, A/dm^2 (A/in.^{2}), of:**		
µm	**mils**	**31 (2.0)**	**47 (3.0)**	**62 (4.0)**
Conventional sulfate bath[a]				
25	1	1:05	0:40	0:25
50	2	2:05	1:20	0:55
125	5	5:20	3:20	2:20
Mixed catalyst bath[b]				
25	1	0:50	0:30	0:20
50	2	1:40	1:00	0:40
125	5	4:05	2:25	1:45

Fluoride-free bath(c)				
25	1	0:40	0:27	0:17
50	2	1:25	0:53	0:37
125	5	3:35	2:15	1:30

(a) Bath containing 250 g/L (33 oz/gal) of chromic acid with 100-to-1 ratio of chromic acid to sulfate, operated at 54 °C (130 °F).

(b) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F).

(c) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F)

Table 8 Rates of deposition of hard chromium from high-concentration baths

Thickness of plate		**Plating time, h:min, at current density of:**				
µm	**mils**	**23 A/dm^2 (1.5 A/in.^{2})**	**31 A/dm^2 (2.0 A/in.^{2})**	**39 A/dm^2 (2.5 A/in.^{2})**	**47 A/dm^2 (3.0 A/in.^{2})**	**54 A/dm^2 (3.5 A/in.^{2})**
Conventional sulfate bath(a)						
25	1	2:20	1:35	1:15	0:55	0:45
50	2	4:35	3:10	2:30	1:55	1:30
125	5	11:30	8:00	6:15	4:40	3:50
255	10	23:00	16:00	12:30	9:25	7:35
380	15	34:30	24:00	18:45	14:05	11:25
510	20	46:00	32:00	25:00	18:50	15:10
Mixed catalyst bath(b)						
25	1	2:00	1:10	0:55	0:40	0:30
50	2	4:00	2:20	1:50	1:20	1:00

125	5	10:00	5:50	4:30	3:20	2:30
255	10	20:00	12:00	9:00	6:40	5:00
380	15	30:00	18:00	13:00	10:00	7:30
510	20	40:00	24:00	18:00	16:40	12:30
Fluoride-free solution(c)						
25	1	1:50	1:05	0:50	0:37	0:27
50	2	3:40	2:10	1:40	1:15	0:55
125	5	9:10	5:30	4:10	3:10	2:15
255	10	18:20	11:00	8:20	6:20	4:30
380	15	27:30	16:30	12:30	9:30	6:45
510	20	36:40	22:00	16:40	12:40	9:00

(a) Chromic acid content, 400 g/L (53 oz/gal); ratio of chromic acid to sulfate, 100:1; operating temperature, 55 °C (130 °F).

(b) Chromic acid content, 400 g/L (53 oz/gal); sulfate content, 1.5 g/L (0.20 oz/gal); contains sufficient fluoride catalyst to give 100-to-1 ratio results.

(c) Chromic acid content, 400 g/L (53 oz/gal); contains appropriate amount of proprietary catalyst; operating temperature, 55 °C (130 °F)

Solution temperature affects both the conductivity and the current required. If limited power is available, satisfactory hard chromium plating deposits can be obtained at lower temperatures (43 to 49 °C, or 110 to 120 °F), but if power supply is adequate, it is advantageous to work at higher temperatures (up to 60 °C, or 140 °F) because of the faster deposition rate and the improved durability of the deposit. At 43 to 49 °C (110 to 120 °F), current densities of 8 to 30 A/dm^2 ($\frac{1}{2}$ to 2 A/in.^{2}) are satisfactory; at 60 to 66 °C (140 to 150 °F), 45 to 60 A/dm^2 (3 to 4 A/in.^{2}) may be required, and as high as 80 to 90 A/dm^2 (5 to 6 A/in.^{2}) can sometimes be needed. At all temperatures, increased agitation will allow higher current densities.

Control of solution temperature to within a narrow range is necessary because of the marked influence of temperature on deposition rate and deposit quality. An increase of 2 °C (5 °F) in mean solution temperature, for example, can cause a reduction of 5% or more in mean chromium thickness, thus necessitating a sizable adjustment in either plating time or current density. The solution temperature should be maintained within 1 °C (2 °F). Solution temperature is usually controlled automatically. Manual control is impractical for a production operation.

For automatic control, it is important that the thermostat be placed in the plating solution in a location where it can readily sense any significant change in solution temperature. Obviously, the thermostat must not be in close proximity to a heating or cooling pipe or to an electric heating element. Location of the thermostat is greatly simplified when an external heat exchanger is used and the solution is pumped from the heat exchanger to the solution. Rapid movement of the solution or air agitation helps to promote temperature uniformity.

Problems and Corrective Procedures

Faulty operation of a chromium-plating solution can result in slow plating speed or deposits with undesirable characteristics. The problems encountered in hard chromium plating are similar for all three chemistries. Possible causes and suggested corrective procedures include:

Poor coverage

- Low chromic acid content
- Low ratio of chromic acid content to total catalyst content. Correct by adding chromic acid or by precipitating sulfate, if too high, with barium carbonate.
- Temperature too high
- Current density too low
- Passive or scaled anodes. Correct by cleaning and reactivating anodes, using high current density until uniform gassing is obtained, and checking for good anode contact.
- Rack contacts too heavily built up with metal, causing rack to rob plate
- Thieves too large or too close
- Open holes preventing uniform plate in adjacent areas. Correct by using nonconducting plugs in holes.
- Gas entrapment preventing plating solution from reaching some areas. Correct by positioning parts in solution so that all gases can escape or by agitating parts while they are plating.

Burnt deposits

- Ratio of chromic acid to total catalysts too high. Correct by adding necessary catalyst or by lowering chromic acid content.
- Current density too high
- Temperature too low
- Large parts were colder than solution temperature when plating began.
- Some parts, in a load of different parts, receive too much current. Correct by adjusting anodes and contacts to ensure that each part receives correct current density.
- Excessive amount of anode within a given area for the part being plated. Correct by eliminating all excess anodes in the tank, designing the shape of conforming anodes to minimize current density at high-density areas, and, if necessary, using nonconducting shields at these areas.

Slow plating speed

- Chromic acid content too high
- Ratio of chromic acid to total catalyst too high
- Temperature too high
- Current density too low
- Scaled anodes
- Insufficient or inadequate sizes of conductors in anode or cathode circuits
- Thief obtains too much current. Correct by redesigning thief or by removing nodules from thief.
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- High contact resistance on busbars, racks, or jigs. Correct by cleaning contacts to lower contact resistance. Do not always rely on voltage for control, because it does not indicate the conditions present on the part; instead, control by amperage.

- Large variety of parts in same tank prohibiting proper current density for each part
- Tank overcrowded with parts
- High content of metallic impurities. Correct by discarding a portion of solution; readjust after dilution.

Nodular deposits

- Insufficient etching before plating in relation to thickness of deposit. Correct by increasing etching time.
- Rough surface before plating
- Chromic acid content too high. Correct by removing portion of solution; dilute the remainder and adjust.
- Low temperature
- Low sulfate content
- Current density too high

Pitted deposits

- Marking dye not completely removed
- Material suspended in solution. Correct by filtering out suspended material.
- Surface-activating agents caused deep pits when plating thick deposits. Correct by discarding as much of the solution as necessary to eliminate pits and replace with fresh solution. Prevent by discontinuing use of mist suppressors. Plastic parts that decompose, such as floats, can form decomposition products that also create pits.
- Gas bubbles adhering to part. Correct by improving surface finish before plating and by agitating part occasionally during plating.
- Part is magnetized. Correct by demagnetizing.
- Magnetic particles in the solution. Correct by removing particles with magnet.
- Insufficient cleaning prior to plating
- Particles falling on work from anodes or thieves. Correct by improving design of anodes and thieves and by cleaning both regularly to remove loose particles.
- Carbon smut on surface. Correct by scrubbing before plating.
- Excessively etched surface during reverse-etch or stripping operation

Poor adhesion

- Insufficient or no etching before plating
- Contaminants not completely removed from surfaces during cleaning
- Excessive grinding rate at edges or sharp projections, where base metal fractures and it may appear that plated material did not adhere
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- Current interruption during plating
- Cold solution

Macrocracks

- Highly stressed base metal; cracks are visible during grinding or when heat is applied. Correct by relieving stresses in base metal.
- Grinding at too fast a rate (heat checks)

Equipment

The discussion of equipment that follows is confined largely to considerations that are specific to chromic acid plating processes. Mixed-catalyst and fluoride-free solutions have essentially the same equipment requirements as conventional sulfate solutions, except that all parts of the electrical system may need to be heavier to accommodate the increased current used. Equipment requirements for plating three specific parts are given in Table 9.

Table 9 Process and equipment requirements for hard chromium plating using conventional solutions

Item	**Area of part**		**Area of load**		**No. of pieces/ 8 h**	**Thickness of plate**		**Current density**		**Plating time, min**	**Temperature of bath**		**No. of work rods**	**Tank dimensions**	
	mm^2	**in.^{2}**	**mm^2**	**in.^{2}**		**µm**	**mil**	**A/dm^2**	**A/in.^{2}**		**°C**	**°F**		**mm**	**in.**
Small cutting tools	4,800	7.5	967,000	1500	10,000	1.3	0.05	30	2	5	50	120	1	1500 × 760 × 910	60 × 30 × 36
Shafts	20,000	30	600,000	930	200	25	1	30	2	63	50	120	2	1800 × 910 × 910	72 × 36 × 36
Gun barrels(a)	15,000	23	543,000	828	180	25	1	45	3	40	54	130	2	2400 × 910 × 610	96 × 36 ×

(a) Plating of inside diameter 30-caliber gun barrels

Tanks and Linings. Figure 1 illustrates a hard chromium plating tank arrangement. Most tanks for chromium plating are made of steel and lined with an acid-resisting material. Because of their excellent resistance to corrosion by chromic acid, lead alloys containing antimony or tin may be used as tank linings.

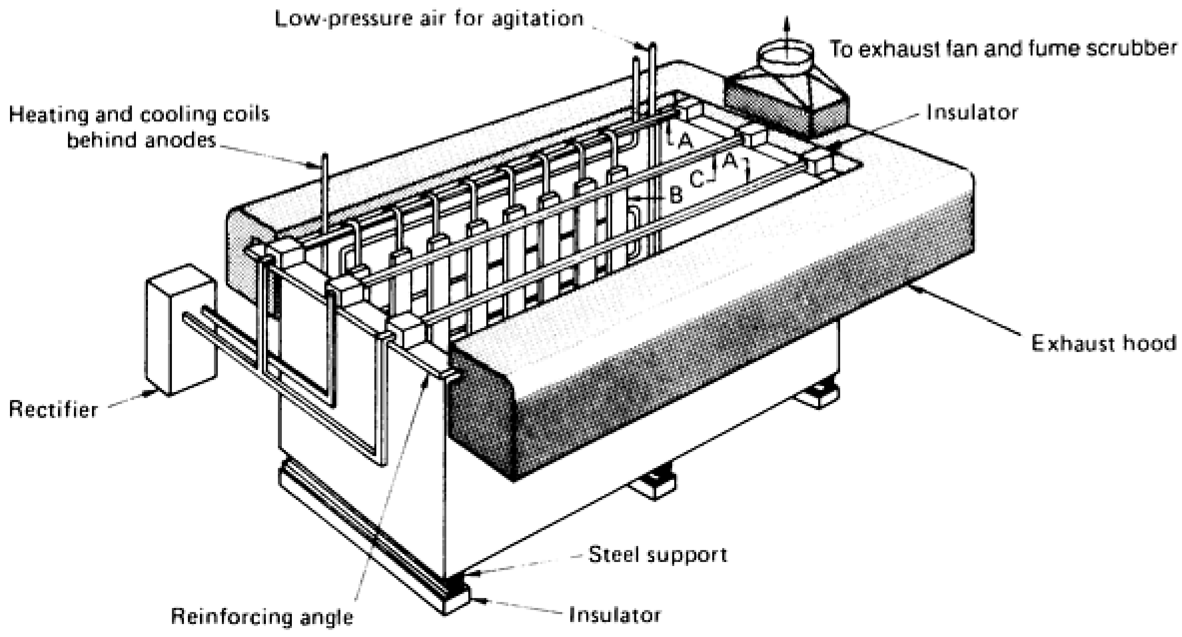


Fig. 1 Tank and accessory equipment used for hard chromium plating. A, anode rods; B, lead or lead-tin anodes; C, cathode rod

Acid-resistant brick has been used as a lining material. Because of its electrical insulating characteristics, acid-resistant brick lining has the advantage over metal linings of reducing possible current losses or stray currents. Some installations combine a lead lining or plastic sheet lining with an acid-resistant brick facing. With fluoride-containing solutions, a brick lining is suitable only for temporary use.

Almost invariably, plasticized polyvinyl chloride is used for all three types of chromium plating solutions, provided that the solution temperature does not exceed 66 °C (150 °F). Sheets of this plastic are cemented to tank walls and welded at joints and corners. Other plastic materials are equally resistant to chemical attack but are more likely to fail at the welds when exposed to an oxidizing acid. Fiberglass utilizing either polyester or epoxy is unsatisfactory for use in mixed-catalyst solutions, because exposed fiberglass will be attacked by the secondary fluoride catalyst.

Design specifications for low-carbon steel tanks for chromium plating are given in Table 10. Lining materials for low-carbon steel tanks are given in Table 11. Steel tanks should be supported at least 100 mm (4 in.) from the floor; steel I-beams are used to provide this support and are mandatory when side bracing is required. To provide insulation, reinforced strips of resin-bonded glass fiber can be placed between the floor and the I-beams. Glass brick can be used as insulation between electrodes and the plating tank.

Table 10 Design specifications for low-carbon steel tanks for hard chromium plating

Size of tank				Thickness of low-carbon steel		Width of rim		Tank reinforcing
Length		Depth						
m	ft	m	ft	mm	in.	mm	in.	
Up to 1	Up to 4	Under 0.9	Under 3	5	$\frac{3}{16}$	50	2	No
Up to 1	Up to 4	Over 0.9	Over 3	5	$\frac{3}{16}$	50	2	Yes
1-4	4-12	All	All	6	$\frac{1}{4}$	75	3	Yes

Table 11 Lining materials for low-carbon steel tanks for hard chromium plating

Tank length		Lining material					
		Lead alloy(a)		PVC(b)		Brick(c)	
m	ft	kg/m^2	lb/ft^2	mm	in.	mm	in.

Up to 2	Up to 6	40	8	5(d)	$\frac{3}{16}$(d)	100	4
2-4	6-12	50	10	5(d)	$\frac{3}{16}$(d)	100	4
Over 4	Over 12	60	12	5(d)	$\frac{3}{16}$(d)	100	4

(a) Antimonial lead, or lead-tin alloy.

(b) Plasticized polyvinyl chloride.

(c) Acid-resistant brick. For further protection, brick may be backed up with 39 kg/m^2 (8 lb/ft^2) of antimonial lead or lead-tin alloy, or with plasticized polyvinyl chloride sheet.

(d) Lining should be 10 mm ($\frac{3}{8}$ in.) thick at top to 0.3 m (1 ft) below top of tank.

Heating and Cooling. Steam heating coils and cooling coils can be made of antimonial lead or silver-bearing lead. Titanium coils are preferred for conventional and fluoride-free plating solutions because of their relatively low cost and long life. Tantalum or niobium-clad coils should be used for mixed-catalyst solutions due to the fluoride attack on titanium. These coils are mounted on tank walls behind the anodes. Steel pipes carrying steam and cooling water to the tank must have a nonconducting section in each leg, so that the coils cannot become an electrical ground back through the power plant system.

Electric immersion heaters sheathed in fused quartz are suitable for heating chromic acid solutions. The quartz is fragile and must be handled with care. Similar immersion heaters are sheathed in either tantalum, titanium, or lead alloy. It is sometimes feasible to heat and cool a chromic acid solution by piping the liquid to a tube bundle, concentric, or tube heat exchanger located outside the plating tank. Preferably, heat exchanger tubes should be made of tantalum or titanium. This method has the disadvantage of requiring pumping of the solution.

Temperature-control planning should begin with selection of the volume of solution required in the plating solution. An ideal volume consists of 1 L or more of solution for each 13 W of plating power (1 gal or more of solution for each 50 W of plating power). About 60% of this plating power (30 W) produces heat and maintains the solution at temperature in an uninsulated tank of standard design. Power applications in excess of 13 W/L (50 W/gal) require cooling of the plating solution and cause relatively rapid changes in solution composition.

Agitation. A chromium-plating solution should be agitated periodically, particularly when the solution is being started, to prevent temperature stratification. Air agitation is effective, but oil from an air pump must not be permitted to leak into the air system. Preferably, the air should come from an oil-free low-pressure blower. A perforated pipe of rigid polyvinyl chloride may be used to distribute air in the solution.

Busbars. Anode and cathode busbars are usually made of round or rectangular copper bar stock. These rods should be adequately supported to prevent them from sagging under the weight of anodes and work. Generally, selection of bar size is determined by allowing 1 cm^2 of cross-sectional area for each 150 A (1 in^2 of cross-sectional area for each 1000 A), although mechanical strength for load support is also a factor in determining rod size. Anode and cathode rods are supported above the tank rim by insulators, which may be made of brick, porcelain, or plastic. Even metallic supports can be used if a strip of electrical insulating material is placed between the plating tank and the busbar.

Power Sources. Although dynamos or motor-generator sets were once the usual sources of power for low-voltage direct current for plating, rectifiers are now regularly used. In general, use of motor-generator sets is now restricted to larger and more permanent installations. Originally, plating rectifiers were made of copper oxide or magnesium-copper sulfide, but these have been largely replaced by silicon rectifiers. Silicon is favored for plating rectifiers because of its high resistance to thermal overload and small space requirement. Hard chromium platers often start plating on a piece by sweeping up applied voltage and current from very low values to the high values used for plating. Because silicon-controlled rectifiers have high ripple at low output, the output should be filtered. Tap-switch controls, however, produce relatively low ripple over the entire output range.

A 6 V power source can be used for chromium plating, but it is generally desirable or necessary to operate with 9 to 12 V available. Chromium plating requires full-wave rectification with a three-phase input and full control, giving a ripple less than 5% and no current interruptions. If a rectifier becomes partially burned out, it may single phase to some degree, and this can cause dull or laminated, peeling deposits.

Fume Exhaust. A chromium-plating process produces a chromic acid mist, which is toxic. The maximum allowable concentration for 8 h continuous exposure is 0.1 mg of chromic acid mist per cubic meter of air. This concentration value is in accordance with recommendations by the American Conference of Governmental Industrial Hygienists. Because of the extreme toxicity of this mist, it is mandatory to provide adequate facilities for removing it. The minimum ventilation rate should be 60 m^3/min per square meter (200 ft^3/min per square foot) of solution surface area. (It should be noted that these regulations are presently under revision and are subject to changes.)

Generally, fumes are exhausted from a chromium plating tank by means of lateral exhaust vents along both long sides of the tank. For narrow tanks, up to 600 mm (24 in.) wide, a lateral exhaust on one side of the tank should be adequate unless strong cross-drafts exist. Velocity of the air at the lateral exhaust hood slots should be 600 m/min (2000 ft/min) or more.

In the design of ductwork, condensate duct traps should be included to capture chromic acid solution. Drains from these traps should be directed to a special container and not to the sewer. In this way, chromic acid solutions can be returned to the tank or recovery system or be safely destroyed. A fume scrubber or a demister should also be included in the system to remove most of the chromic acid fumes before exhausted air is emitted to the atmosphere. Many communities have air pollution regulations requiring fume scrubbers. Fume exhaust ductwork may be made of carbon steel and coated with acid-resistant paint. Modern construction uses chlorinated polyvinyl chloride.

Rinse Facilities. Rinsing the work after chromium plating prevents it from becoming stained or discolored. Insufficient rinsing can result in contamination of cleaning solutions during subsequent cycling of racks. Multiple rinsing facilities are recommended. After being plated, parts should be rinsed in a nonrunning reclaim tank, which can be used to recover part of the chromium solution dragout. After they are rinsed in the reclaim tank, plated parts should be rinsed in counterflowing cold water and hot water tanks. Water should cascade from the hot water tank to the cold water tank. A multiple counterflowing arrangement requires much less water than two separate rinsing tanks.

If rinse water is being returned to a chromic acid waste disposal unit, the flow of water into the hot water tank should be controlled automatically by a conductivity-sensing element in the cold water tank. At a predetermined concentration of chromic acid in the cold water, the water inlet to the hot water tank should flow, causing an overflow of cold water to the waste disposal unit. This arrangement decreases the amount of water consumed and minimizes the required capacity of the waste disposal unit.

Cold water rinse tanks may be coated, sprayed, or otherwise lined with plasticized polyvinyl chloride. Hot water rinse tanks may be constructed of types 347, 304, or 316 stainless steel, or they may be made of carbon steel and lined with lead. Reinforced polyester glass fiber also may be used for either hot water or cold water rinse tanks.

Spray rinsing also effectively removes residual chromic acid. Because spraying does not always reach recessed areas, sprays should be positioned above a dip rinse. As parts are removed from the dip rinse, they may be sprayed with clean water, which, in turn, is returned to the dip tank.

Maintenance. Following is a maintenance schedule for a still tank installation for hard chromium plating:

- *Daily:* Check temperature. Check concentration of solution by density measurements. Clean busbars and electrical connections. Remove any parts that fall from racks.

- *Weekly:* Analyze for chromic acid and sulfate contents.
- *Monthly:* Remove all sludge and parts from tank, using a hoe and dragging the bottom. If tank is used for plating inside diameters, analyze for trivalent chromium.
- *Semiannually:* Check tanks for leaks and condition of lining. Clean and inspect rectifiers or motor-generating units. Check ammeter calibration.
- *As necessary:* Analyze for trivalent chromium, iron, nickel, copper, and zinc. Check condition of anodes.

This schedule is intended only as a guide; local conditions determine exact requirements. The rate of variation of solution constituents depends on the volume of solution, the method of operation for the solution, and the type and amount of work.

Racks and Fixtures

The following recommendations are offered regarding the design and use of plating racks:

- Racks should be designed to hold workpieces in a favorable position for plating uniformly on significant surfaces and to facilitate racking and unracking.
- Workpieces with protruding sections should be racked so that parts shield each other. If this is not possible, a current thief should be used to reduce current density at the protruding points.
- Electrical contact with the part should be made on an insignificant surface.
- The contact or rack tip should be rigid enough to hold workpieces securely and maintain positive contact. When the work is heavy enough to ensure positive contact, a hook often suffices.
- To minimize solution losses due to dragout, the work should be hung as nearly vertical as possible, with the lower edge of the work tilted from the horizontal to permit runoff at a corner rather than a whole edge. When recessed areas cannot be racked to allow proper runoff, provision should be made for drain holes or perhaps tilting of the rack when it is being withdrawn from the solution.

Although the design of racks and the methods of racking vary greatly, two basic types of racks are generally used. The first type consists of a single high-conductivity bar on which suitable supports have been mounted for holding the work to be plated; this rack is the cathode side of the plating circuit. The second type consists of two elements, the cathode and the anode; the work is held by the cathode and the cathode is attached to, but insulated from, the anode. Both types of racks are illustrated in Fig. 2. To prevent deposition of chromium or attack by the plating solution on parts of the rack that are immersed in the solution, these parts are covered with nonconducting material such as water-resistant tape, special insulating lacquer, or plastisol coatings.

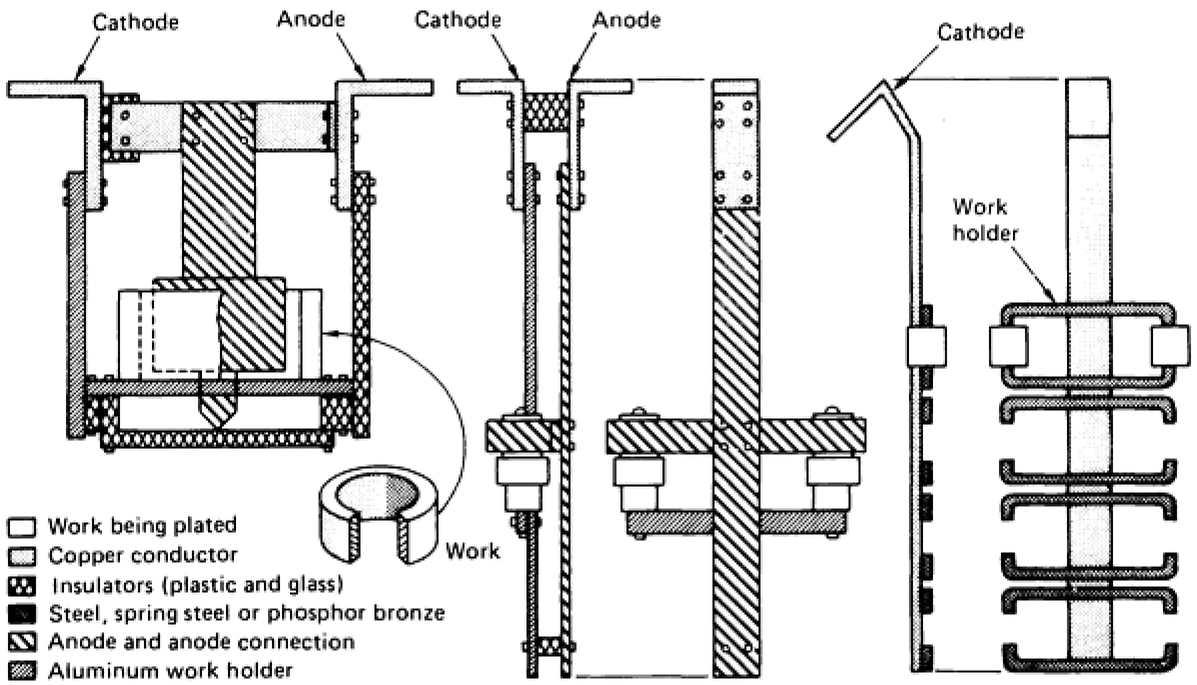


Fig. 2 Racks used in hard chromium plating

Surface Preparation

All soils and passive films must be removed from surfaces of ferrous and nonferrous metals before they are hard chromium plated. In addition to cleaning, certain surface-activating processes are often important in preparing the base metal for hard chromium plating. The processes include etching of steel, preplate machining, and nonferrous metals preparation.

Etching of steel before plating is needed to ensure adherence of the chromium deposit. Anodic etching is preferred for this purpose. Slight etching by acid immersion may be used for highly finished surfaces, but with possible sacrifice of maximum adherence.

Steel can be etched anodically in the chromium plating solution at its operating temperature for plating. A reversing switch is used so that the steel to be plated can serve as the anode for 10 s to 1 min (usually 30 s to 1 min) at a current density of about 15 to 45 A/dm^2 (1 to 3 A/in^2). Tank voltage should ordinarily be 4 to 6 V. Because mixed-catalyst solutions chemically attack the steel, causing etching of the surface, shorter electrochemical etching time frequently is required than is the case with conventional or fluoride-free chemistries. This process has the disadvantage of causing the solution to become contaminated with iron from the work and with copper from the conductors.

As an alternative, steel may be anodically etched in a separate chromic acid solution without sulfate additions and containing 120 to 450 g/L (16 to 60 oz/gal) of chromic acid. Solution temperature may range from room temperature to that of the chromic acid plating solution, or even higher, provided that current density and time of treatment are adjusted to suit the type of work being processed.

A sulfuric acid solution (specific gravity 1.53 to 1.71) may be used for anodic etching, provided that the solution temperature is held below 30 °C (86 °F), and preferably below 25 °C (77 °F). The time of treatment may vary from 30 to 60 s and the current density may vary from about 15 to 45 A/dm^2 (1 to 3 A/in^2) at tank voltages ordinarily between 4 and 6 V. A lead-lined tank with lead cathodes should be used. With the use of a sulfuric acid solution, however, two difficulties may be encountered. First, if the rinsing following etching is incomplete, the drag-in of sulfuric acid throws the chromium plating solution out of balance with respect to the ratio of chromic acid to sulfate. Second, in handling parts that are difficult to manipulate, there is danger that surfaces exposed to air more than a very short time will rust and that finely finished surfaces will be overetched.

For high-carbon steel, a sulfuric acid solution of 250 to 1000 g/L (33 to 133 oz/gal), used at a temperature of not more than 30 °C (86 °F) and preferably below 25 °C (77 °F), is effective for anodic etching. The addition of 125 g/L (16.6 oz/gal) of sodium sulfate, based on the anhydrous salt, is of benefit for many grades of steel. Anodic treatment in this solution usually does not exceed 1 min at a current density of about 15 A/dm^2 (1 A/in^2) (range of 15 to 45 A/dm^2, or 1 to 3 A/in^2). High acid content, high current density, and low temperature (within the ranges specified) minimize the attack on the base metal and produce a smoother surface. This sulfuric acid solution is stable and not appreciably affected by iron buildup.

Preplate Machining. Metal debris on the surface should be removed before etching (an activation procedure). The use of abrasive-coated papers is common, as is the use of successively finer grit stones in honing and grinding. To prepare a sound surface in superfinishing, 600-grit stones may be used. Electropolishing is sometimes used to remove highly stressed metal and metal debris from the surface of cold-worked steel. This process improves bond strength and corrosion resistance of electroplated coatings. It accomplishes this function without formation of smut, which may result from anodic etching. This treatment is not recommended for parts that are subjected to critical fatigue stresses and that are expensive to manufacture.

Preparation of Nonferrous Metals. Aluminum, in common with certain other metals, quickly develops a natural, passive oxide film after exposure to preplating cleaning cycles. This film must be removed before aluminum is plated. The most widely used method of preparing aluminum for plating involves a zincating treatment, which may be followed by a thin 5 μm (0.2 mil) copper electrodeposit. However, it is possible to plate chromium directly over the zincate.

Aluminum parts used in hydraulic systems require a nickel undercoat before being plated, to provide corrosion protection to all plated surfaces that are not completely and constantly immersed in hydraulic fluid or similarly protective fluids. A minimum thickness of 10 to 15 μm (0.4 to 0.6 mil) of nickel is usually specified. This undercoat may also be required for steel parts in similar applications.

Titanium and titanium alloys, as well as magnesium, also form a tight, stable oxide coating and are therefore difficult to plate. These metals can be pretreated with an electroless nickel plate or a coating deposited from a high-chloride nickel strike solution.

Variations in Plate Thickness

Variations in the thickness of hard chromium plate depend primarily on the potential field distribution. Potential field is controlled by the placement of anodes, shields, thieves, and other parts, as well as the relative position of the sides and surface of the tank. Variations in plate thickness also depend on surface preparation, control of solution conditions, and uniformity of the power source.

Methods of Measuring Plate Thickness. Several methods and types of instruments are available for determining the thickness of plate. These include electrolytic stripping, microscopic measurements of cross sections, torsion dynamometer measurements made with magnets of various strengths, measurement by eddy current instruments, and accurate measurement of the dimensions of the part before and after plating to determine thickness by difference.

Electrolytic stripping and microscopic measurements of cross sections are destructive methods that are most frequently used for purposes of verification, calibration, and sampling of production runs. When calibrating instruments with prototype plated parts, using microscopic measurements of cross sections as umpire checks, several calibration reference curves may be required, depending on the parts being plated.

Measurements by properly calibrated eddy current or torsion dynamometer instruments are affected by the surface finish of the deposit, width and thickness of the piece, surface contour, and composition of the base material. With a properly calibrated instrument, thickness measurements are usually within 10% of the actual thickness. Individual thickness measurements should not be used as the basis for acceptance or rejection; however, an average of several determinations from a well-calibrated instrument is an acceptable measure of the mean thickness from a controlled process.

The normal variation in plate thickness that can be expected when plating the outside diameter of cylinders, rods, or round parts racked as cylinders is ±0.2μm/μm (±0.2 mil/mil) of plate intended. This has been determined over a period of several years by average quality level thickness measurements on piston rings racked as cylinders.

This normal variation of 20% was confirmed in an actual production situation. In plating identical parts to a consistent thickness requirement, sample checks from 74 loads (110,000 parts) representing 27 days of operation were made to determine the plating tolerances that could be expected. The plating cycle was set to provide a plate thickness of 200 to 230 μm (8 to 9 mils) to meet a final requirement for a minimum plate thickness of 150 μm (6 mils) after light stock removal during the subsequent finishing operation. Results of this analysis are shown in Fig. 3.

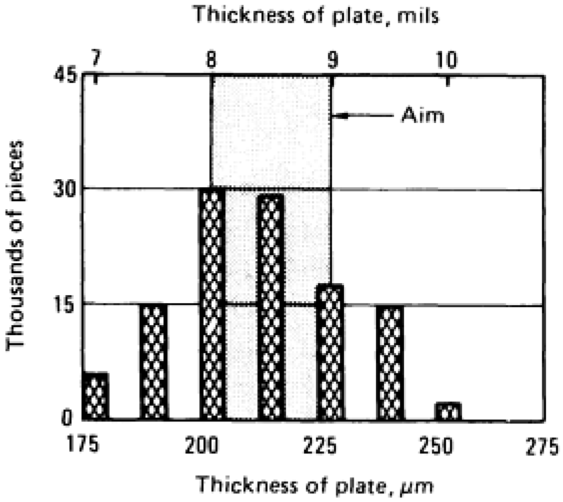


Fig. 3 Variations in hard chromium plate thickness for 74 loads, representing 110,000 parts of the same design plated over a period of 27 days of operation. Target thickness was 200 to 230 μm (8 to 9 mils) of hard chromium. Average thickness for the 74 loads was 215 μm (8.4 mils).

The throwing power of chromium-plating solutions is related to the ratio of chromic acid concentration to the catalyst concentration. Higher ratios give better throwing power at a given temperature and current density. This is evidenced by the fact that when a very low current density is present on certain areas of irregularly shaped parts, the cathode efficiency at that low current density is less for a solution high in sulfate than for a solution with lower sulfate content. Therefore, less metal is deposited on the areas of low current density from a solution of high catalyst content.

The current density at which no metal deposits is greater for high catalyst solutions than for lower catalyst solutions. Also, metal deposits from a solution of low catalyst concentration at a current density that would be too low for depositing from a solution with high catalyst concentration. Thus, the following factors must be considered to ensure successful plating of complex shapes: chemical balance, operating variables, type of anode, and design of fixtures or racks.

Chromium plating requires far more attention to the variables that affect current distribution than cadmium, zinc, copper, or nickel plating. It is theoretically impossible to obtain the same current density at an inside corner as on the flat adjacent to it. An outside corner without shielding or thieving always has the highest current density and hence the greatest plate thickness. Conforming anodes, shields, and thieves may be used to minimize thickness variation, but except on the simplest shapes, they do not eliminate it.

Some metal is deposited at low current densities in most other plating solutions, but in chromic acid solutions there is a minimum current density for a given solution at a given temperature below which no metal is deposited. If an area of an internal or irregular shape receives less than this minimum current density, no deposition of metal occurs in this area. This explains why it is so difficult to chromium plate recesses and internal shapes without special anodes. Special hardware, in the form of thieves or shields, is required for lowering the current density on areas such as edges to prevent excessive buildup of deposit.

In most electroplating solutions, the primary current distribution on an irregular object can be improved by increasing the tank anode-to-cathode distance. However, beyond a minimum distance, which depends on the shape of the part, no further improvement can be attained.

Because of the low throwing power of hard chromium plating solutions, an increase in the anode-to-cathode distance does not result in even plating of sharp reentrant surfaces such as those formed by internal angles. For plating parts containing shapes of this type, conforming anodes and/or current shields must be used.

Figure 4 illustrates the relation between thickness of deposit and distance of the anode from the part being plated. In this instance, an alternative to an increase in the anode distance is the use of an anode contoured to the curvature of the part.

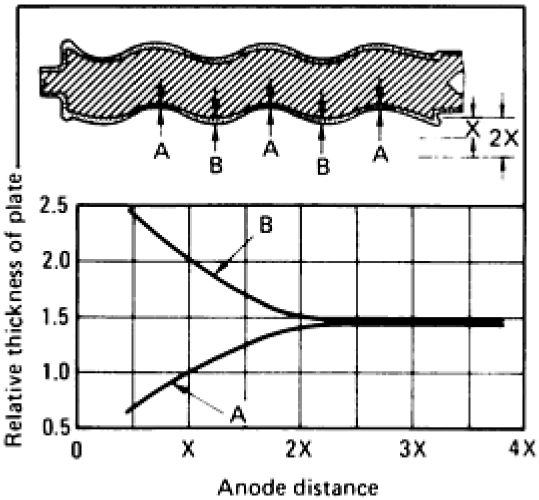


Fig. 4 Variation in thickness of chromium plate on feedworm as a function of the distance of the anode from the part. Values of *x* are about 25 mm (1 in.) or more.

Special Anodes. When the part contains sharp, narrow recesses, such as grooves, a reduction of the anode distance may help to increase the thickness of the deposit at the bottom of the grooves. However, some parts with sharp-cornered grooves, bosses, and undercuts cannot be uniformly covered even when contoured anodes are used. Examples of parts in this category and the areas of heavy deposits are illustrated in Fig. 5.

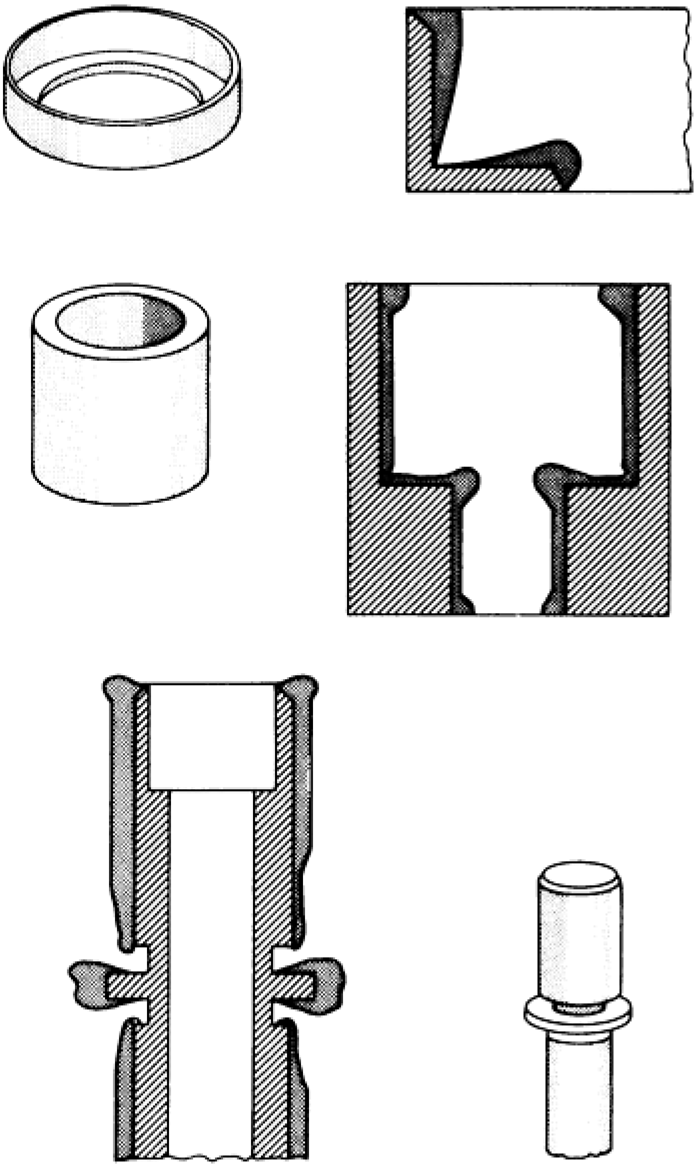


Fig. 5 Parts difficult to plate uniformly with hard chromium, even with the use of specially contoured anodes. Variations in plate thickness shown are approximately to scale.

Anodes used for plating recesses can be directly connected to the power supply, or they can be bipolar in nature. The bipolar anode has no direct electrical connection and takes advantage of the fact that current follows the path of least resistance. Bipolar anodes are an interesting curiosity that may have application in rare instances; however, direct connection of the anode to the positive direct current through a rheostat and ammeter, if required, is far more controllable.

The deposit on internal shapes can also be affected by the evolution of gas that occurs during plating. Gas can cause streaked deposits or produce a taper in a long bore. To minimize this effect, the parts should be positioned in a manner that permits the gas to move rapidly away from the part.

Because of fabrication problems encountered with lead alloys, complex-shaped anodes are made of steel, then coated with lead to produce the effect of solid lead anodes. These composite anodes are more economical and lighter in weight. However, the base metal can be destroyed if there are pores or throughholes in the lead alloy coatings. Brass or copper should never be used on the anode side, as they dissolve rapidly and seriously contaminate the solution. Low-carbon steel may be used alone for short runs, and lead-coated steel may be used for longer service.

Crack Patterns and Other Characteristics of Hard Chromium Plate

The quality of hard chromium plate is evaluated chiefly from the standpoint of thickness and thickness distribution, appearance, crack pattern, crack size, porosity, roughness, and adhesion of the plate to the base metal.

Surface Cracks. During the deposition of chromium deposits, microcracks form to relieve the internal stress. These cracks subsequently fill in with plated chromium. The chromium in these former cracks is more easily etched and has a different refractive index than the surrounding deposits. For this reason, with the use of a microscope one can determine where and how many microcracks were present at one time on the surface of the deposit. The pattern usually consists of crack-free areas and plateaus completely surrounded by crack boundaries. The plateaus from an average conventional sulfate solution are 2 to 3 times larger than those from a mixed-catalyst solution; that is, there are more cracks per inch in a deposit from the average mixed-catalyst solution. The fluoride-free chemistry gives yet an additional factor of 2 to 3 times more microcracks.

Interestingly, the more microcracks present, the shorter the penetration into the deposit of each one (i.e., with the conventional solution, a microcrack can extend all the way through a 1 mil thick deposit, while in the fluoride-free solution deposit they extend very short distances). Since these (former) cracks provide the pathway for corrosion, it is desirable to have as many discontinuities as possible as one progresses through the deposit to the substrate. It is for this reason that in corrosion applications, the solution that provides the greatest amount of microcracking possible is used.

Crack-Free Deposits. It is possible to plate chromium with virtually no microcracks. This is done by altering the current density and temperature, altering the catalyst concentrations, or using pulsed-current or periodic-reverse plating. Crack-free deposits are gray and have very poor wear properties. The corrosion resistance is also very poor due to residual stresses in the deposit, which eventually (in a few days or months) cause large cracks that extend through the entire deposit.

Some specialized applications for this type of deposit include broaches, cams, dies for metal forming, metalworking rolls, and stamping dies for embossing silverware. Complicated shapes create a large range of current densities and are difficult to plate with a crack-free surface. Corners, edges, or other high-current-density areas are most likely to crack during plating.

Porous Chromium. Although the cracks or porosity that characterize chromium deposits are not desirable for resistance to corrosion, a porous structure can be advantageous in wear applications in which lubrication is required, because it promotes wetting action and provides oil retention after initial lubrication. Engine cylinders are the outstanding application.

Most chromium-plated cylinder surfaces consist of some form of interrupted surface, generally porous chromium. An interrupted surface may be obtained by electrolytic or chemical etching of chromium after it is plated on a smoothly honed bore, as with porous chromium, or by preroughening the bore by shot blasting, knurling, or tooling and then reproducing this roughness in the final chromium plate or by machining in roughness after plating.

Two distinct types of porous chromium are produced. One has pinpoint porosity with many microscopic depressions in a honed chromium surface. This has been used in all types of engine cylinders except aircraft. The other type is also finish honed but is broken by randomly connected channels, leaving isolated bearing plateaus. For both types, the percentage of porosity is generally controlled between 20 and 50% of the total area. Average plateau diameter is further controlled between 0.25 to 0.75 mm (0.010 to 0.030 in.) with the channel type of porosity. Porosity as low as 5% approaches dense chromium and is susceptible to scoring because of sparse oil distribution. High porosity, such as 75%, may cause high initial ring wear and high oil consumption. In normal engine service, cylinders coated with chromium of optimum porosity give wear rates one-third to one-tenth better than those of uncoated cast iron or steel, hardened or unhardened.

Several methods--electrochemical, mechanical, and combinations of both--have been developed to provide controlled porosity in heavy chromium deposits. Mechanical methods entail either severe grit blasting of the surface to be plated or roughening of the surface with a fine knurling tool. The roughened surface is reproduced by the deposit. Using a patterned mask, the surface can also be roughened by chemical or electrochemical means before plating The most widely used techniques, however, involve chemical or electrochemical etching of the chromium deposit after plating. Note that the pattern or crack density and the size of the plateaus are largely determined by the composition (ratio) of the solution, and the plating temperature.

Etching is performed on plated thicknesses ranging from 120 to 180 μm (5 to 7 mils). Porosity is developed after plating by electrochemically etching anodically in chromic acid solution. The etched surface is finished by honing, polishing, or lapping. Metal removal that exceeds the depth of porosity must be avoided. To avoid accelerated wear in service, finished surfaces must be thoroughly cleaned of abrasive and chromium particles.

Quality Control Tests. Usually, visual examination is sufficient for determining appearances and roughness of the surface of hard chromium plate. Magnetic particle inspection can be used to examine chromium plate up to 100 μm (4 mils) thick for cracks after grinding. The as-plated deposit prior to postfinishing should be as smooth as the base metal before plating and should be free of pits and nodules. The deposit should not exhibit excessive thickness variation. Particularly, deposits with dendritic growths (trees) should be rejected. Adequate plating control requires that such dendritic deposits occur on thieves rather than in functional areas.

For process development and quality verification, destructive testing may be used to determine the crack pattern and bond between the plate and base metal. The crack pattern can be developed by etchants such as a hot 50 vol% hydrochloric acid aqueous solution, or by short etching in a chromium plating solution.

The quality of the bond can be determined by punch testing, bend testing, examining the bond line metallographically, or judging of ground or hammered samples. Well-bonded chromium, because of its low ductility, does not fail by pulling away from the bond line; however, it fails by cracking and spalling if it is subjected to excessive stress or distortion in 45° diagonal tension.

Excessive porosity of thin (less than 25 μm, or 1 mil, thick) chromium plate on steel can be determined by applying an acidified copper sulfate solution to the plated areas. The pores permit the solution to copper coat steel by displacement, and the degree of copper coating thus indicates the degree of porosity. Porosity can also be determined by the ferroxyl test described in *Metal Finishing Guidebook,* 1982.

The mandrel test can also be used in quality control. If a portion of the chromium plate is made anodic for 3 min at 15 A/dm^2 (1 A/in^2) in a solution containing 250 g/L (33 oz/gal) chromic acid at 60 °C (140 °F), the crack pattern is developed. Counting the crack density under the microscope is an excellent procedure for noting the constancy of the composition (mainly ratio) and the temperature of the solution.

Hardness of Plate

Valid hardness measurements of chromium deposits are difficult to make, and values are dependent on test conditions, so hardness values should not ordinarily be used as quality control specifications and routine criteria. Rather, the as-plated brightness can serve as an indication of hardness.

The hardness of chromium plate cannot be accurately determined by the common hardness testers, such as Brinell and Rockwell, because hard chrome is generally too thin for these tests. The indentation produced in these tests distorts the base metal and is influenced by it, which usually results in low hardness readings.

The most reliable and most widely accepted hardness values are those obtained with the Vickers 136 diamond pyramid indenter or the Knoop indenter. With these, the hardness test must be made on a carefully prepared and polished surface, preferably on a cross section of the plate, to eliminate any possible influence of the base metal on the hardness values obtained.

Cracks in the chromium plate influence the hardness values, depending on the type of indenter used and the load applied. In general, lighter loads are more sensitive to hardness variations and result in higher hardness values. Cracks influence values obtained with heavy loads more than values obtained with light loads. Also, because of the smaller area covered by the Vickers 136 diamond pyramid indenter, hardness values determined with this indenter are influenced less by underlying cracks than values obtained with the Knoop indenter.

When conducting microhardness tests, it is important to make sharp and accurate impressions, particularly when using light loads. Also, when hardness values are reported, the load, type of indenter, and optical system used should be indicated. The importance of stating the load and type of indenter is shown by the following data obtained on chromium plate from one plating cycle (each range or average represents 25 tests):

Load, g	Hardness value	
	136° diamond pyramid	Knoop indenter
100	950-1110 (1040 avg)	940-1090 (1025 avg)

In an investigation of the scratch hardness of chromium deposits of all types, it was observed that bright or semibright deposits had the best combination of hardness and wear resistance, regardless of plating conditions. In this investigation, the wear resistance was measured by means of a specially constructed abrasion hardness machine. The machine contained a small grinding wheel that revolved at 18 rpm. The number of revolutions required to grind through a 25 μm (1 mil) deposit on steel was an indication of the abrasion hardness. Results are summarized in Table 12, which shows the relation between the appearance of deposits and their hardness and resistance to abrasive wear.

Table 12 Relation between appearance and hardness of hard chromium plate deposited from conventional solutions

Average appearance	Average scratch hardness[(a)], HB	Average relative abrasive hardness
Matte (cold bath)	640	25
Milky	830	100
Slightly milky	990	290
Bright	1000	300
Slighty frosty	1005	300
Frosty (smooth)	1020	235
Frosty (rough)	1060	125
Burnt	1165	110

(a) Converted to Brinell scale from values obtained with a Bierbaum microcharacter using a 9 g (0.3 oz) load

The effect of temperature on the hardness of electrodeposited chromium is often a significant factor in applications involving wear resistance. The electrodeposited metal begins to decrease in hardness when it is exposed to temperatures above about 205 °C (400 °F). Hardness decreases progressively with an increase in temperature (Fig. 6). As the hardness of chromium plate decreases, its resistance to wear may be affected adversely. Chromium plate should not be used for wear resistance in applications where service temperature exceeds 420 °C (790 °F).

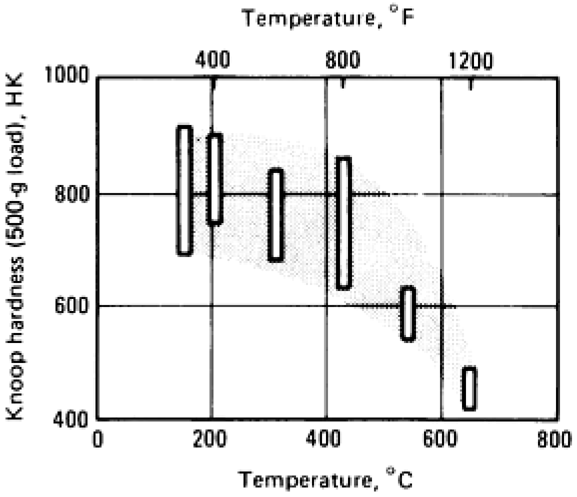


Fig. 6 Effect of annealing temperature on the hardness of chromium plate deposited during a single cycle in a mixed-catalyst solution. All data represent 25 measurements of each condition; every readable impression was accepted as valid. Heating cycles of 1 h were used.

Cost

The electroplating of hard chromium is very cost-effective, giving a high throughput with reliable, reproducible quality deposits that are unattainable by any alternative technology. The important cost factors are capital and labor expenses, followed by electricity, and, lastly, chemicals, which are relatively inexpensive. Almost always the fluoride-free solution is the least expensive chemistry to operate, followed by mixed-catalyst and then conventional sulfate solutions. Although the chemical costs increase going from conventional to mixed-catalyst to fluoride-free solutions, this increase is offset by savings in electrical costs, capacity improvements, and deposit quality improvements.

Factors that affect the relative cost of plating, regardless of the solution used, include the shape of the part, the design and arrangement of anodes, and special finishing techniques. Labor charges for hard chromium plating may be higher than for other plating processes, largely because many chromium plating operations are performed manually. Also, more labor is required to prepare some parts for plating or for finishing after plating.

The cost of plating increases with the complexity of the part design. Parts containing sharp notches, section changes, and unplated areas of cross-holes necessitate more handling during preparation and finishing than parts of simple shape. Also, anodes must more precisely conform to the shape of such parts for accurate control of plating thickness. Defects associated with chrome plate, such as dendritic growths and excessive buildups on external corners, can be minimized with tooling and special techniques. Depending on the nature of the part, these may increase costs. Special finishing techniques, primarily grinding and lapping, are required. Often a heat treatment of plated parts is necessary before they are ground or lapped.

For surfaces that are difficult to finish mechanically, even greater care must be taken in design and construction of anodes to approximate desired results closely. The cost of anode design and construction must be amortized over the number of parts plated. If sufficient production is required, refinement of masking and anodizing generally pays with decreased postplate finishing. Costs are affected also by the quality of the plate. Hard, high-quality plating finished to a bright luster is very expensive because of the rigid controls required in its production. As with other plating processes, costs vary because of local utility charges and ordinances pertaining to disposal of wastes. The availability of power and water, and the quality of the water available, can significantly affect cost. Safety requirements and waste disposal methods can be responsible for at least a 20% difference in plating costs among different plants.

Removal of Chromium Plate

Most manufacturers require salvage of misplated parts because of their high value. Further, in the aircraft industry, business machine industry, and plastic mold industry, significant numbers of parts are run for the life of the deposit and then overhauled by stripping worn deposits and replating.

Methods of Stripping. Chemical, electrochemical, or mechanical methods are used to remove hard chromium deposits. When the base material is steel, brass, copper, or nickel, hydrochloric acid at any concentration over 10 vol% and at room temperature or above removes chromium. In some operations, inhibitors are added to the acid solution to minimize attack on the steel substrate.

Chromium is removed electrochemically from steel or nickel by the use of any convenient heavy-duty alkaline cleaner at room temperature or above, at 5 to 6 V with anodic current. This method is unsatisfactory for nickel-base alloys, which should be stripped chemically in hydrochloric acid. Chromium may be stripped from aluminum by making the part the anode in a cold chromium (nonfluoride) plating solution or in conventional chromic acid or sulfuric acid anodizing solutions. Aluminum alloys with a high alloy content and alloys subjected to various heat treatments all react differently in stripping solutions, so precautions must be taken to prevent attack on the base metal. Anodic stripping operations result in formation of oxide films on the base metal. These films should be removed by one of the conventional deoxidizing processes prior to replating.

Stripping of chromium deposits from high-strength steel must be performed electrochemically in an alkaline solution. The parts are then stress relieved at 190 °C (375 °F) for a minimum of 3 h. The following solutions and operating conditions are recommended for removing chromium deposits from the materials indicated. Proprietary formulations having a longer operational life are also available.

Removal from steel or nickel-plated steel

- Sodium hydroxide, 45 to 320 g/L (6 to 30 oz/gal); anodic treatment at 3 to 8 A/dm^2) (0.2 to 0.5 A/in^2); solution temperature, 21 to 71 °C (70 to 160 °F)
- Anhydrous sodium carbonate, 45 to 60 g/L (6 to 8 oz/gal); anodic treatment at 2.5 to 5.5 A/dm^2 (0.15 to 0.35 A/in^2); solution temperature, 21 to 66 °C (70 to 150 °F). Use 2.3 A/dm^2 (0.15 A/in^2) with solution temperature of 66 °C (150 °F) to reduce possibility of pitting alloy steel.
- Sodium hydroxide, 52 g/L (7 oz/gal); sodium carbonate, 30 g/L (4 oz/gal); anodic treatment at 8 A/dm^2 (0.5 A/in.^{2})
- Concentrated hydrochloric acid at room temperature
- Hydrochloric acid, 50 vol%, at room temperature

Removal from aluminum and aluminum alloys

- Sulfuric acid, 67 vol%; glycerin, 5 vol%; anodic treatment at 1 to 3 A/dm^2 (0.1 to 0.2 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Removal from magnesium and magnesium alloys

- Anhydrous sodium carbonate, 50 g/L (6.5 oz/gal); anodic treatment at 2 to 5 A/dm^2 (0.15 to 0.30 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Grinding is used occasionally to remove heavy chromium deposits. Most defective chromium deposits are observed during subsequent grinding for finishing, so it is sometimes expedient to continue grinding to remove all of the plate and then replate. In the grinding of heavy deposits for the removal of several thousandths of an inch of chromium to attain required dimensions or surface finish, the most important requisites for successful results are:

- A soft grinding wheel
- A sufficient amount of coolant
- A light cut
- Correct peripheral speed
- Freedom from vibration
- Frequent wheel dressing

Because chromium is hard and brittle, a soft grinding wheel is essential. A hard wheel forms a glazed surface, which results in a temperature rise that causes the chromium to crack. A soft wheel breaks down rapidly enough to prevent formation of a glaze; however, too soft a wheel is not economical because of rapid wheel wear. Good performance can be obtained with an aluminum oxide resin-bonded wheel of about 60 grit and H-grade (hardness).

To prevent or minimize glazing, the contact area should be flooded with a coolant. Usually, the coolant is water with a small amount of soluble oil. Because of its hardness, excess chromium cannot be removed as rapidly as when grinding most other materials. The maximum thickness of metal removed should not exceed 5 μm (0.2 mil) per pass, and this amount should be reduced if there is any evidence of cracking. The optimum grinding speed is about 20.4 m/s (4000 sfm).

Effective grinding requires a rigid machine. Any appreciable vibration can cause cracking of chromium because of uneven contact pressure, and it also results in a wavy surface. Factors essential for a rigid machine include a well-fitting spindle bearing, a balanced wheel, a heavy bed, and a well-supported workpiece. Whenever there is the least indication of glazing or nonuniform wheel surface, the wheel should be dressed with a diamond point. Adherence to the preceding recommendations will result in a good surface with a finish of 0.35 to 0.5 μm (14 to 20 μin.). Subsequent lapping (240 grit) will produce a finish of 0.1 to 0.3 μm (5 to 10 μin.).

Special care should be taken when grinding chromium-plated parts made from high-strength steel (steel with an ultimate tensile strength of 1240 MPa, or 180 ksi, and above) that are to be used in stressed applications. Numerous failures have occurred due to formation of untempered martensite caused by the heat of the grinding operation. For information and guidelines on grinding chromium-plated high-strength steel parts, see military specification MIL-STD-866B.

Hydrogen Embrittlement

The susceptibility of chromium-plated parts to hydrogen embrittlement is affected by hardening of the steel, grinding, surface defects, pickling, cathodic cleaning, and the depth of plate relative to the thickness and hardness of the part being plated. (It should be noted that the chemistry of the chromium plating solution is not a factor.) Unless the hydrogen absorbed during pickling and cathodic cleaning is removed, subsequent plating further embrittles the part to such an extent that breakage can occur during plating. This effect becomes more prevalent with increasing hardness of steel and on parts of thin cross section.

The thickness of plate on thin steel sections is of importance from the standpoint of notch effect. This was illustrated in an actual production setting. Thin sections of steel, 2.5 by 0.5 mm (0.10 by 0.020 in.) and 25 to 38 mm (1 to 1 $\frac{1}{2}$ in.) long, were plated with chromium to a thickness of 8 to 13 μm (0.3 to 0.5 mil). The hardness of the steel was 57 to 59 HRC. These parts were aligned by being bent until permanently set. When the thickness of the chromium plate was increased to range from 15 to 23 μm (0.6 to 0.9 mil), the parts would break before taking a set. Baking them at 205 °C (400 °F) for 4 days did not relieve this condition. It was necessary to decrease the hardness of the steel to 53 to 55 HRC to prevent breakage of parts with heavier plate.

Stress Relieving before Plating. Surfaces to be chromium plated must be free from stresses induced during machining, grinding, or hardening. Stresses from the hardening operation may be further increased during grinding and result in microcracks. If the hardness of the steel is less than 40 HRC, it is unlikely that any damaging effect will occur as a result of residual stress. Steel with a hardness exceeding 40 HRC should be stress relieved before it is plated by heating at 150 to 230 °C (300 to 450 °F).

Baking after Plating. Steel parts with a hardness above 40 HRC should be baked at a temperature of at least 190 °C (375 °F) for 4 h after plating to ameliorate the effects of hydrogen embrittlement. This treatment should be started as soon as possible, preferably within 15 min after plating. The fatigue strength of parts subjected to alternating stresses is reduced by the baking treatment, so such parts should be shot peened before plating.

The use of shot peening and baking, as related to the hardness of steel to be chromium plated, is described in federal specification QQ-C-320B, amendment 1, as follows:

- Plated parts below 40 HRC and subject to static loads or designed for limited life under dynamic loads, or combination thereof, shall not require shot peening prior to plating or baking after plating.
- Plated parts below 40 HRC that are designed for unlimited life under dynamic loads shall be shot

peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated.

- Plated parts with a hardness of 40 HRC, or above, and subject to static loads or designed for limited life under dynamic loads, or combinations thereof, shall be baked after plating at 190 ± 14 °C (375 ± 25 °F) for not less than 3 h.
- Plated parts with a hardness of 40 HRC, or above, and designed for unlimited life under dynamic loads, shall be shot peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated. After plating, parts shall be baked at 190 °C (375 °F) for not less than 3 h.

Safety Precautions

All applicable OSHA, EPA, and local regulations pertaining to electroplating in general and specifically to chromium plating should be carefully reviewed and strictly followed. Material Safety Data Sheet forms should always be available, and precautions should be carefully noted, especially with respect to the incapability of mixing certain chemicals.

Personnel should wear rubber gloves, rubber aprons, and face shields when making additions to any plating or cleaning solution. Tank operators should wear proper protective clothing and eye protection at all times.

Health and safety concerns related to the use of chromium and possible alternative plating technologies are discussed in the article "Chromium Elimination" in this Volume.

Recovery and Disposal of Wastes

Chromic acid wastes may be either recovered or destroyed, and the choice of process should be based on a comparison of initial costs, labor costs for operation and maintenance, chemical costs, space requirements, and utility costs. The volume of wastes and the value of the chromic acid and rinse water saved can greatly influence the choice.

Local, state, and federal authorities are constantly increasing their attention to antipollution programs. Strict regulations are being enforced regarding the allowable limits for chromic acid wastes that leave the plating plant in any form. The prevailing limits for chromic acid contamination of waste water range from about 0.05 to 5 ppm. These limits vary for each locality, depending on the uses of the receiving body of water, supplementary water flows that affect dilution, and the ability of sewage plants to handle wastes. A new plater must check with federal, state, and local authorities to determine what limits are applicable at that time.

Preventive Measures. The problem of waste disposal can be greatly minimized if suitable measures are taken to minimize the amount of wastes produced. The following practices contribute to minimizing wastes:

- Extend drainage periods to permit more solution to return to the tank. In hand operations, this is made possible by providing a drainage bar over the tank to hold racks.
- Provide drip boards to return solution lost when going from tank to tank.
- If possible, rack parts in such a way as to eliminate cupping action.
- Use reclaim rinse tanks. The rinse solution can be used to maintain the level of liquid in the processing tank. Sometimes concentration methods may be profitable to facilitate use of rinse waters.
- Control drag-in of water to permit use of reclaim rinse tanks.
- Complete recovery should be used only in conjunction with technologies for the removal of metallic impurities.

Disposal of chromic acid wastes is most commonly based on reduction of hexavalent chromium to the trivalent form and, in either a batch or a continuous operation, precipitating the trivalent metal hydroxide by means of an alkali. The actual chemicals used vary from locality to locality, depending on cost and availability. Chromic acid is first neutralized to a suitable pH and is then reduced with one of the sulfite compounds (sodium sulfite, sodium metabisulfite), sulfur dioxide, ferrous sulfate, iron, copper, or brass. After completion of reduction, trivalent chromium is precipitated as hydroxide with alkali. The amount of chemicals required to complete reduction can be governed by laboratory analysis, or, because the reaction is solely one of oxidation-reduction, it may be controlled automatically by use of electrodes.

The most commonly used reducing agent for large plants is sulfur dioxide gas. It can be obtained in liquid form in cylinders of various sizes, is comparatively inexpensive, and can be fed directly into the treatment tank. The rate of addition is easily controlled and gas is delivered from the cylinder under its own pressure. A lower initial acidity is required because the gas forms sulfurous acid when dissolved in water. The operating pH is 2 to 3, and the ratio of sulfur dioxide to chromic acid used commercially is slightly under 3 to 1. The sulfur dioxide method lends itself readily to an automatic system because the gas feed can be controlled by a flowmeter, and the reaction can be controlled by oxidation-reduction potentials.

Ferrous sulfate also is a widely used reducing chemical, especially in localities where large quantities are available from pickling plants. The quantity required can be easily determined by titration. The ratio of ferrous sulfate to chromic acid varies between 5 and 16 to 1. Reduction of chromium is followed by neutralization with lime or caustic. Above a pH of 7, the metals precipitate as hydroxides, together with calcium sulfate. The main disadvantage of the ferrous sulfate method is the large volumes of sludge that have to be handled.

The sulfite-containing compounds generally are slightly more expensive than sulfur dioxide or ferrous sulfate. In addition, several difficulties are involved in sulfite treatment, such as solubility, loss of hydrogen sulfide through hydrolysis, slightly lower pH, and, occasionally, the need for additional treatment to complete the process.

Regardless of the chemical treatment selected, all chromic acid disposal systems require collection, treatment, and settling tanks. The operating procedure consists of chemical additions, mixing, separation of precipitated metal, clarification, and sludge disposal. Variations in equipment design affect economy, time and labor requirements, and equipment costs.

In recent years several new companies have been formed that recycle chromium plating wastes into new products, thereby avoiding the long-term potential liabilities of landfill operations. No matter what method of waste disposal is selected, the plater is well advised to know what happens to the wastes and what the liability could be.

Stopoff Media for Selective Plating

During plating, part surfaces that are not to be plated may need to be protected from the solution by stopoff media, such as lacquers, foils, tapes, waxes, and machined reusable fixtures. Stopoff media must adhere well to the metal surface, not become soft at the temperature of the solution or brittle at room temperatures, be resistant to solutions used for cleaning, etching, and plating, and be easy to remove after plating.

Lacquers used to prevent surfaces from being plated can be easily applied by brushing, spraying, or dipping. After plating, the lacquer can be stripped off or dissolved in an appropriate solvent.

Lead sheet, foil, and wire not only provide a positive stopoff but also act as thieves to aid in current distribution. Lead can be pounded into holes, keyways, or slots and trimmed with a sharp knife.

Tapes of several kinds are used as stopoff media. They vary from adhesive tapes backed with lead foil to tapes made of vinyl and other plastics. Lead foil tapes combine a specially compounded lead foil with a highly pressure-sensitive adhesive to provide a quick and convenient stopoff for short runs. The lead backing is useful as a thief in areas of high current density, or it can be lacquered when used in areas of low current density for equalizing current distribution. It is soft enough to conform to various configurations. Vinyl and other plastic tapes are soft and pliable and have extruded edges for providing a lead-free seal on almost any contour.

Sheet Materials. For large production runs, it is convenient to make stop-off forms that can be reused many times. Plastic sheet, generally 0.1 to 0.15 mm (0.004 to 0.006 in.) thick, is excellent for masking simple plates, cylinders, or other configurations. Steel sheet is sometimes substituted for plastic if it is desirable to equalize current distribution. To prevent plating or corrosion of the base metal, the plastic or steel stopoff must adhere firmly to the area being masked. Snug-fitting cylinders can be made to fit inside or outside diameters. To mask areas that are flat or of irregular shape, lacquer may be used to glue the stop-off material to the part; the lacquer may be removed with a thinner after plating.

Waxes. Several waxes designed for use as stopoffs are obtainable commercially. The use of a dip tank, thermostatically controlled to maintain the temperature at 15 to 20 °C (30 to 40 °F) above the melting point of the wax, makes the use of these materials comparatively fast and simple. The portion of the part to be plated can be covered with masking tape to prevent wax from adhering, or, if desired, the whole part can be coated and the wax stripped with a knife from areas to be plated. The wax mixture should have a melting point low enough to allow removal of the bulk with boiling water. Because they evolve poisonous fumes when heated, waxes containing chlorinated naphthalene must be used with exhaust equipment. High-melting-point mineral and vegetable waxes are not dangerous to use.

Decorative Chromium Plating

Revised by: James H. Lindsay, General Motors; Donald L. Snyder, Atotech USA Inc.

Introduction

DECORATIVE CHROMIUM PLATING is different from hard chromium plating in terms of thickness and the type of undercoating used. The average thickness of decorative plating is actually very thin, usually not more than 1.25 μm (50 μin.). A decorative chromium deposit is used primarily for its pleasing blue-white color. Its highly reflective appearance is maintained in service because chromium can resist tarnish, chemicals, scratches, and wear. If the deposit is defect-free, then a level of corrosion resistance also is provided, because the deposit acts as a physical barrier to the environment. Decorative chromium is applied over undercoatings, such as nickel or copper and nickel, which give the chromium bright, semibright, or satin cosmetic appearances. Corrosion protection depends on the choice of undercoating, as well as the type of chromium being applied. Parts made from steel, copper and its alloys, zinc, stainless steel, and aluminum are typically plated with nickel-chromium or copper-nickel-chromium.

Most decorative chromium coatings have been applied using hexavalent chromium processes that are based on chromic anhydride. However, since 1975, trivalent chromium processes have become available commercially. They are increasing in importance because of their increased throwing and covering powers and because they offer environmental advantages. Both systems are considered in detail in this article.

Chromium Electrodeposits

Decorative chromium plating baths generally produce deposits that range from 0.13 to 1.25 μm (5 to 50 μin.) in thickness. These deposits generally reproduce the finish of the substrate, or, in a multilayer system, the undercoating that is applied prior to the chromium layer. Optimum luster of the final chromium deposit is obtained by plating the substrate coating to a uniformly bright condition. If the substrate is nonuniform, grainy, hazy, or dull, then it should be polished and buffed to a uniformly high luster before being plated with chromium. When a final chromium coating over a uniformly bright substrate is hazy in certain areas, these areas can be buffed on a wheel or the coating can be stripped and the substrate replated. Buffing of chromium is not allowed when corrosive service conditions will be encountered.

In addition to being lustrous, the final chromium deposit should cover all significant areas. When there is not adequate coverage, because of an improperly operated chromium bath, the chromium should be stripped, the substrate reactivated, if necessary, and the part replated.

Decorative chromium that has been applied over nickel, the typical undercoating, is readily stripped by immersion in a 1:1 solution of hydrochloric acid. An alternate method involves treating the part anodically in an alkaline cleaning solution. However, this method requires reactivation of the nickel surface prior to replating, which is typically accomplished by immersion in dilute sulfuric or hydrochloric acid. Cathodic, but never anodic, alkaline cleaning can also be used for activation.

Excessively high current densities, improper temperatures, and passivated substrates can produce hazy, nonuniform chromium deposits. Operating conditions for chromium plating should be in the specified ranges. Properly operated nickel baths and other similar precautions also are necessary to ensure uniformly lustrous chromium deposits.

The adhesion of chromium to an active or properly prepared substrate is usually not a problem. However, if chromium is plated on an undercoating that has been improperly applied and has questionable adhesion, then blistering or exfoliation can occur, either immediately after chromium plating or during storage or service. Organizations that generate standards, such as ASTM, can provide procedures for checking adhesion if a related method has not been specified in the purchase agreement for the part being plated.

Microporosity and Microcracking. The key to the corrosion durability offered by decorative chromium deposits lies in controlling the type, size, and distribution of microdiscontinuities that form in the deposit. These can occur as either pores or cracks. In an outdoor corrosive environment, as well as in accelerated corrosion tests, corrosion has been observed to proceed by galvanic cell action between the nickel and the chromium, with the nickel acting anodically. Microcracks or micropores in the chromium expose the underlying nickel through a uniform, diffuse network of discontinuities. Because the rate of corrosion penetration through the nickel layer is a function of the anodic current density of the corrosion cell, the reduction of current density that is obtained by the increase in exposed nickel area prolongs the time required to penetrate a given thickness of nickel. The advantage of such a system lies in its ability to provide long-term corrosion protection without developing easily visible fine surface pits in the nickel, which eventually become corrosion sites. The use of microdiscontinuous chromium makes the surface pits much smaller, which means that the substrate will be protected from corrosion for a longer time. However, after excessive corrosion, these fine pits will become visible as a haze on the corroded surface.

Chromium deposits, up to a thickness of 0.13 μm (5 μin.), that are obtained from hexavalent processes are somewhat porous. Because porosity decreases with increasing thickness, at approximately 0.5 μm (20 μin.), the deposits become nearly pore-free when plated (Fig. 1). However, because of the hard, brittle nature of the highly stressed chromium deposits, they quickly become cracked during storage or service. These cracks do not improve the corrosion resistance, as do deposits with intentionally developed micropores or microcracks.

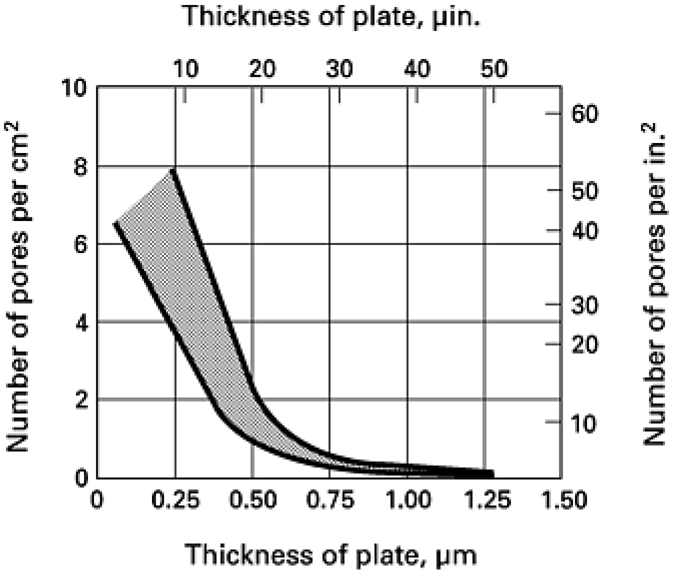


Fig. 1 Porosity in chromium plate as a function of plate thickness. Chromium deposited in low-temperature baths begins to crack at 75 μm (3000 μin.).

Except when special hexavalent chromium processes and conditions are used, hexavalent chromium deposits that are more than 0.5 μm (20 μin.) thick will have visible nondecorative microcracks. In contrast, chromium deposits from trivalent processes are microporous up to thicknesses of 0.5 to 0.6 μm (20 to 25 μin.), above which they become microcracked. Both features enhance the corrosion resistance of the part.

When hexavalent chromium is deposited from solutions operated below 50 °C (120 °F), the deposit will begin to craze when it exceeds 0.5 μm (20 μin.) in thickness, and a macrocrack pattern visible to the unaided eye will appear. This pattern generally has 5 to 10 cracks/cm (12.5 to 25 cracks/in.).

Either microcracked or microporous chromium deposits can be produced by altering the nature of the nickel undercoating. Microporous chromium can be obtained by plating over a thin layer of nickel deposited from a solution containing very fine, nonconductive particles. Chromium will not plate over these particles, which creates a microporous deposit with pore densities proportional to the amount of inert particles and additives in the nickel solution. An average pore density of

10,000 pores/cm^2 (60,000 pores/in^2) is the typical minimum specified for enhanced corrosion resistance. A disadvantage of this process is the addition of an extra nickel plating tank between the bright nickel and the chromium tanks. The pore count is also current-density dependent, and chromium deposits of 0.3 to 0.4 μm (12 to 16 μin.) in thickness have a tendency to bridge over the inert particles and reduce the pore count.

Trivalent chromium deposits provide pore counts of more than 16,000 pores/cm^2 (100,000 pores/in^2), without any special procedures. The pore count also is rather current-density independent.

Another very common method for obtaining microporous chromium deposits is to mildly blast the chromium deposit with an abrasive, such as sand or aluminum oxide. The brittle chromium fractures where it is hit by the particles, thus causing a microporous deposit to form. This method permits the pore count to be varied, based on the amount of particles used, and is independent of current density.

Microporous chromium is the most common microdiscontinuous chromium deposit used in North America to enhance the corrosion resistance of the decorative nickel-chromium type of electrodeposit. Microcracked chromium is somewhat more popular in the rest of the world.

Microcracking can be produced by using a thin layer, approximately 1.25 μm (50 μin.), of a highly stressed nickel deposit between the bright nickel and chromium deposits. Approximately 0.25 μm (10 μin.) of chromium is typically used with this procedure. A crack density of 275 to 790 cracks/cm (700 to 2000 cracks/in.) is typically produced. Thicker chromium deposits are required with other microcracking methods.

Microcracked chromium deposits can be obtained from systems using either a single or a dual specially formulated chromium solution. An example of the latter is duplex chromium. Although single-deposit systems are easier to operate, conditions that favor the formation of microcracks, such as high solution temperature, low chromic-acid concentration, and high fluoride content, usually have an adverse effect on the covering power of the chromium deposit. Duplex chromium systems have resolved this problem by using two successive chromium baths. The first obtains coverage and the second creates the microcrack pattern.

Satisfactory coatings are not too difficult to obtain on parts with relatively simple shapes, but complex parts can present a serious problem because it is difficult to obtain adequately thick chromium in areas of low current density. Auxiliary anodes can be used to increase the thickness in these areas.

Influence of Design on Quality and Cost

The cost of electroplating is often greatly influenced by the complexity of the workpiece. Simple shapes can be processed through all cleaning and plating sequences, with a minimum of approximately 33 μm (1300 μin.) of copper and nickel and 0.25 μm (10 μin.) of chromium, in approximately 50 min. Providing these minimum thicknesses on complex shapes requires longer plating periods, special fixturing, special anodes, and current shields. Plating costs are increased by each of these factors, although buffing and cleaning costs may be unchanged. Equipment and overhead costs per workpiece also increase in direct proportion to the plating time. In addition, the cost of materials is increased, because more metal is plated unnecessarily on projections and other areas of high current density. Figure 2 indicates the approximate increase of plating costs with plating time at a fixed current density.

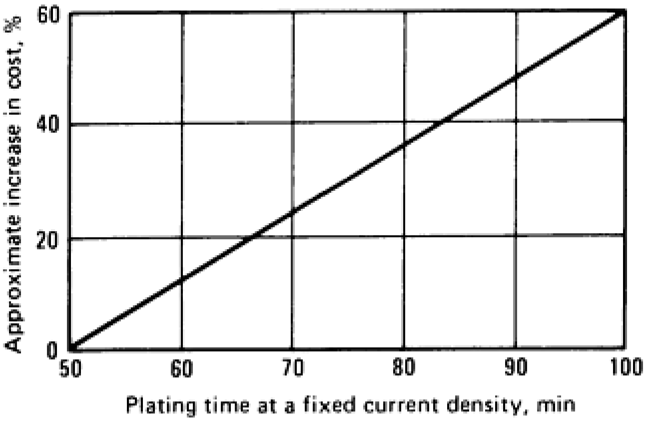
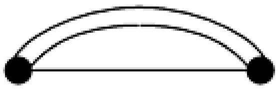
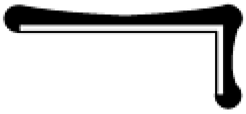
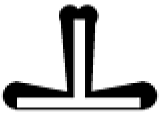
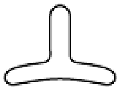
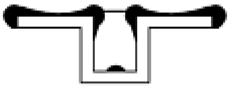
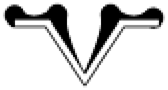
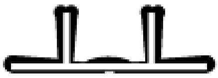
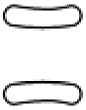
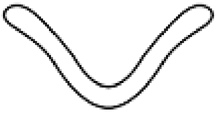
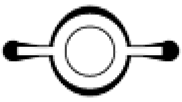


Fig. 2 Plating cost-time relationship

Extreme workpiece complexity can preclude the application of a truly corrosion-protective deposit by conventional plating procedures. The influence of some design features on platability and plating cost are described in Table 1.

Table 1 Influence of design on platability of zinc-base die castings

Design feature	Influence on platability	Better design
	**Convex surface.** Ideal shape. Easy to plate to uniform thickness, especially where edges are rounded.	
	**Flat surface.** Not as desirable as crowned surface. Use 0.015 mm/mm (0.015 in./in.) crown to hide undulations caused by uneven buffing.	
	**Sharply angled edge.** Undesirable. Reduced thickness of plate at center areas. Requires increased plating time for depositing minimum thickness of durable plate. All edges should be rounded. Edges that contact painted surfaces should have a 0.8 mm ($\frac{1}{32}$ in.) min radius.	
	**Flange.** Large flange with sharp inside angles should be avoided to minimize plating costs. Use generous radius on inside angles and taper abutment.	
	**Slots.** Narrow, closely spaced slots and holes cannot be plated properly with some metals (e.g., nickel and chromium) unless corners are rounded.	
	**Blind hole.** Must usually be exempted from minimum thickness requirements.	
	**Sharply angled indentation.** Increases plating time and cost for attaining a specified minimum thickness and reduces the durability of the plated part.	
	**Flat-bottom groove.** Inside and outside angles should be rounded generously to minimize plating costs.	
	**V-shaped groove.** Deep grooves cannot be plated satisfactorily; should be avoided. Shallow, rounded grooves are better.	
	**Fins.** Increase plating time and costs for attaining a specified minimum thickness and reduce the durability of the plated part.	

	**Ribs.** Narrow ribs with sharp angles usually reduce platability; wide ribs with rounded edges impose no problem. Taper each rib from its center to both sides and round off edges. Increase spacing, if possible.	
	**Deep scoop.** Increases time and cost for plating specified minimum thickness.	
	**Spearlike jut.** Buildup on jut robs corners of electroplate. Crown base and round all corners.	
	**Ring.** Platability depends on dimensions. Round corners; crown from center line, sloping toward both sides.	

Note: Distribution of electroplate on design shapes is intentionally exaggerated by solid black outline. Cross-hatched areas indicate part before plating.

Hexavalent Chromium Plating

The first hexavalent chromium plating bath used for decorative plating, sometimes referred to as the conventional bath, consisted of an aqueous solution of chromic anhydride (CrO_3) and a small amount of soluble sulfate ($SO_4^=$), referred to as the catalyst. The latter was added as sulfuric acid or as a soluble sulfate salt, such as sodium sulfate. When dissolved in water, the chromic anhydride forms chromic acid, which is believed to exist in the following equilibrium:

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$$

The ratio of chromic acid to sulfate, generally given as the weight ratio of chromic anhydride to sulfate, governs the current efficiency for chromium metal deposition. The cathode current efficiency also is affected by solution variables, such as concentration of chromic acid, temperature, and content of metallic impurities. The latter variable is an important consideration for commercial operations, because an excessively high content of impurities such as copper, iron, zinc, and nickel seriously affects bath conductivity, cathode current efficiency, and both throwing and covering power, even if the ratio of chromic anhydride to sulfate is within optimum limits for the application.

Most decorative chromium is deposited within these operating limits:

- Chromic anhydride, 200 to 400 g/L (27 to 54 oz/gal)
- Chromic anhydride-to-sulfate ratio, 80:1 to 125:1
- Cathode current density, 810 to 1880 A/m^2 (75 to 175 A/ft^2)

These wide limits encompass a broad variety of decorative applications. As of 1994, the trend is toward using chromic-anhydride concentrations of 250 to 300 g/L (33 to 40 oz/gal) and avoiding more highly concentrated baths and their attendant environmental and recovery concerns. The ratio of chromic acid to sulfate ion is usually maintained at levels near 100:1.

With the development of duplex, microcracked, and crack-free applications, specialized bath compositions and operating conditions have come into use. However, many of these are either proprietary or are not subjects of general agreement. The compositions and operating conditions for a general, additive-free, decorative chromium plating bath and a bright, crack-free bath are given in Table 2.

Table 2 Compositions and operating conditions for two chromium plating baths

Constituent or condition	General decorative bath	Bright, crack-free bath
Chromic acid	250 g/L (33.0 oz/gal)	260-300 g/L (35-40 oz/gal)
Ratio of chromic acid to sulfate	100:1 to 125:1	150:1
Operating temperature	38-49 °C (100-120 °F)	52-54 °C (125-130 °F)
Cathode current density	810 - 1885 A/m^2 (75 - 175 A/ft^2)	2690 - 3230 A/m^2 (250 - 300 A/ft^2)

To meet specific requirements for plating speed, nickel activation, and crack pattern, the chromium anhydride and sulfate concentrations should be properly correlated with temperature and cathode current-density limits. In preparing a bath and establishing operating conditions, these relationships should be considered:

- An increase in the temperature of the bath, except for mixed-catalyst baths, will decrease the cathode efficiency, decrease the number of cracks per unit length, decrease coverage at low current density, increase the limiting current density at which burning occurs, and increase passivating action on nickel.
- An increase in the weight ratio of chromic anhydride to sulfate will decrease the crack density and increase the nickel passivity. The chromium will whitewash (have a milky appearance) when plated over passive nickel.
- An increase in sulfate, at a constant chromic-acid concentration, temperature, and cathode current density, will increase the cathode current efficiency to an upper limit; beyond this point, any further increase in sulfate concentration can cause a decrease in cathode current efficiency.

In dilute chromic-acid solutions containing as low as 150 g/L (20 oz/gal) of sulfate, any small carryover of soluble sulfates from earlier solutions can quickly upset the balance of the solution. However, dilute solutions do have a higher cathode efficiency and a slightly wider bright range, although they require higher tank voltages to maintain desired current density. Even when other plating conditions (such as temperature and current density) are held constant, the plating operation can be seriously disrupted by any change in the ratio of chromic acid to sulfate.

Because there are advantages and disadvantages to using either high or low chromic-acid contents, some compromise is necessary. The size and shape of the article to be plated and the available equipment and power often determine exactly which solution should be used. In decorative chromium plating, all variables must be kept in the proper relationship. Frequent bath analysis and prompt adjustments are essential to maintain balanced conditions.

Mixed-Catalyst Baths. Since the mid-1950s, a number of mixed-catalyst proprietary chromium plating baths have been developed. The advantages of these baths are increased cathode current efficiencies, increased activating action on nickel and stainless steel, improved coverage at low current density, broader bright plating ranges, and improved decorative chromium applications, including dual, microcracked, and bright or dull crack-free.

Mixed-catalyst compositions contain chromic acid, sulfate, and fluorine compounds (frequently, fluosilicate ions) as active ingredients. Proprietary baths, formulated to regulate the concentration of catalyst ions, contain strontium, calcium, or potassium salts, to control the solubility of fluosilicate ions. Details on mixed-catalyst compositions are provided in several U.S. patents and at least one British patent (see "Selected References" at the end of this article). Most control requirements applicable to standard baths also apply to proprietary baths.

With the exception of ratio control, the problems associated with low, medium, or high chromic-acid concentrations in mixed-catalyst baths are the same as those for conventional chromium baths. After optimum conditions are found, the same close control must be maintained to prevent mischromes (absence of plate) in areas of low current density and blue, matte, or burnt deposits in areas of high current density. Because supplies for mixed-catalyst solutions are more expensive than chromic acid alone, using less-concentrated solutions can provide a cost advantage.

Baths for Microcracked Chromium. Typically, two chromium solutions are used successively to produce microcracked chromium plate. The first chromium solution can either be conventional or proprietary and is operated in a normal manner. A plating time of 8 min is preferred when recessed areas are involved, although plating times of 5 to 6 min are often used. Surging of the current can be used to increase coverage. Composition ranges and operating conditions for nonproprietary, first-plating solutions that are used to plate steel and zinc parts are given in Table 3.

Table 3 Bath compositions and conditions for plating microcracked chromium

Substrate material	Constituents				Chromic anhydride to sulfate ratio	Temperature		Current density	
	Chromic acid		Fluoride						
	g/L	oz/gal	g/L	oz/gal		°C	°F	A/m^2	A/ft^2
First plating bath									
Steel	338-375	45-50	. . .	. . .	100:1	46-52	115-125	1075-1615	100-150
Zinc	375-413	50-55	. . .	. . .	140:1	46-52	115-125	1290-1720	120-160
Second plating bath									
Steel	165-195	22-26	1.5-2.25	0.20-0.30	180:1	43-54	120-130	970-1345	90-125

The second chromium solution is similar to the first and can be either proprietary or nonproprietary. The chromic-acid concentration is lower and fluosilicate ions must be present in the bath to promote cracking. The plating time is approximately the same as in the first solution, 5 to 8 min, and current surging can be used, if desired. Composition ranges and operating conditions for the second chromium bath also are given in Table 3. The plating conditions are governed by the nature of the parts being plated. Solutions for parts having deep recesses should have a higher chromic acid and fluoride content and a lower sulfate content. However, thickness must be weighed against other influences on microcrack formation. For this reason, operating conditions can be established on a firm basis only by actual operation with the parts to be processed. On simple shapes, the second plating bath formulation can be used alone.

The use of a rinse or rinses between the two chromium solutions is not essential to the process, but it may help to avoid control problems, because of drag-out from the first chromium solution into the low-concentration second solution. When used, these rinses can be operated as reclaim tanks to minimize drag-out losses.

Solution Control. Regardless of which chromium bath is used, periodic analyses are required. Information on control procedures is provided in the article "Industrial (Hard) Chromium Plating" in this Volume.

Temperature. All chromium plating solutions require the control of temperature, current density, and solution composition. The exact temperature at which bright, milky, frosty, or burnt deposits occur depends on solution composition and current density. Chromium plating is usually performed within the range of 38 to 60 °C (100 to 140 °F), but the most common operating range is from 46 to 52 °C (115 to 125 °F). At room temperature, the bright plating range is impractically narrow. In a process set up to plate at 50 °C (120 °F) with all variables properly controlled, the temperature need vary only 1.5 or 2 °C (3 or 4 °F) to move the electrodeposit out of the clear, bright range. Consequently, an accurate temperature controller and facilities for rapid cooling and heating of the bath are essential. Temperature variation outside the bright operating range can either cause an unacceptably high rejection rate or necessitate costly stripping and replating operations. The preheating of heavy parts is necessary to avoid plating solution cooling and temperature fluctuation.

Current Density. The standard sulfate bath is usually operated at 1075 to 1720 A/m^2 (100 to 160 A/ft^2). A current density of about 1075 A/m^2 (100 A/ft^2) is used for solutions maintained at 38 °C (100 °F). A higher current density, sometimes as high as 3230 A/m^2 (300 A/ft^2), is required for solutions operated at 55 °C (130 °F). The choice for a specific use depends on such variables as the complexity of the articles being plated and the equipment available. After the current density has been established, close control must be maintained.

Changes in the ratio of chromic acid to sulfate require compensating adjustments in current density. If the sulfate content is increased (lower ratio), then current density must be increased to maintain full coverage in areas of low current density. If the sulfate content is decreased (higher ratio), then current density must be decreased to prevent burning in areas of high current density.

An increase in temperature may require an increase in current density to ensure full coverage in areas of low current density. A decrease in temperature may require a decrease in current density to prevent gray (burnt) deposits in areas of high current density.

As chromic-acid content increases, higher current densities can be used. The average cathode efficiency of most conventional chromium solutions is about 13% over a wide range of concentration, making it possible to plate for shorter times when using the most concentrated solution. Rectifiers with low ripple, not exceeding 5%, must be used to maintain trouble-free, uniform deposition.

Anodes. In chromium plating, insoluble lead or lead-alloy anodes are almost always used. Chromium metal is supplied by the chromic acid in the electrolyte.

Pure lead anodes are often attacked excessively by idle baths, which causes the formation of a heavy sludge of lead chromate on the bottom of the tank, making pure lead anodes impractical for all but continuous operations. During plating, a coating of lead peroxide forms on the anode. The coating favors oxidation of trivalent chromium at the anode. However, when the bath is idle, the coating dissolves to some extent in the solution, making attack on the anode possible.

To reduce the attack of the chromic-acid bath on the anode, several lead alloys are used. For conventional sulfate baths, 6 to 8% antimonial (Sb) lead is preferred, whereas for solutions containing fluoride, lead alloys with 4 to 7% Sn are used.

For an anode to provide optimum throwing power and coverage, it must be positioned properly in relation to the workpiece and have a continuous, uniform film of lead peroxide on the entire surface. Anodes with crusty surfaces have low conductivity and should be cleaned periodically by wire brushing or alkaline cleaning to ensure proper current distribution. The function of the anode is not only to conduct the plating current, but to oxidize trivalent chromium, which forms at the cathode, back to hexavalent chromium. To accomplish this, the anode area should be adjusted to provide the optimum anode current density for the oxidation necessary to keep the trivalent chromium at the desired level, usually 0.25 to 1.0 g/L (0.033 to 0.13 oz/gal). In decorative chromium plating, an anode-to-cathode area ratio of 2:1 is common for proper reoxidation and balance. If trivalent chromium continues to increase above the desired level, then the anode area should be increased to the point where the trivalent chromium concentration remains stable. Overheating of the bath can occur if the anode area is so small that resistive heating becomes a factor.

Anodes with round cross sections are most commonly used. When maximum anode area is desired, corrugated, ribbed, ridged, and multi-edged anodes are used. The round anode is preferred, because its surface is active on its entire circumference, enabling it to carry higher amperage at lower voltage. The absence of inactive areas on this anode minimizes the formation of lead chromate film, reducing maintenance requirements. If the weight of the anode presents a problem, then hollow, round anodes can be used. Although such anodes provide a 25 to 40% reduction in weight, their current-carrying capacity is less than that of solid anodes.

Anodes are manufactured by extrusion. Contact with the bus bar can be provided by a copper hook homogeneously burned to the extruded anode. Pure nickel, nickel-plated copper, and lead-coated copper are also used for hooks. Several hook styles are used, but the knife-edge hook is preferred. The hook and the top of the anode are covered with plastisol for protection against corrosion by fumes and drag-out drip. Bags typically used to cover the anodes in nickel- and copper-plating processes should not be used in chromium-plating processes. Roughness that is due to nonuniform anode corrosion is not a problem in chromium-plating operations. Therefore, the resulting particles do not have to be captured by the bags.

Control of Current Distribution. Chromium plating baths have poorer throwing and covering power than most other plating baths. To obtain thickness and coverage in areas of low current density, special auxiliary anodes are sometimes used.

Any workpiece of complex shape constitutes a problem of proper current distribution when nonconforming anodes are used. The current density and the thickness on a workpiece varies from highest on corners, edges, and areas closest to the anode to lowest on recesses and areas distant from the anode. Variations in current density result in differences of cathode efficiency, which accentuate the problems of uneven plate, burning, or complete absence of plate. These problems can be overcome, to some extent, by special racking and shielding techniques, such as:

- Wide spacing of concave parts on rack
- Increasing the distance between workpiece and anode
- Intentional shielding of a projection on one piece with a depression on an adjacent one
- Orienting areas of low current density toward the periphery of the fixture
- Moving the parts in the center of the rack closer to the anodes than those on the periphery of the rack

Improved coverage on areas of low current density can be achieved with striking, that is, plating at high current density for a short period of time. The striking time duration is kept to a minimum, usually 5 to 20 s, to avoid burning. Plating is continued at normal current density after the strike.

Current Shields. A nonconducting plate or panel (current shield) can be mounted on the plating rack to direct current away from areas of high current density or to direct additional current into areas of low current density. Figure 3 illustrates the use of a device to divert some of the current that would otherwise cause excessive current density and possible burning at the work areas closest to the anodes. The position and size of current shields are extremely important for their effective use and can be established best by trial and error. The use of shields, however, is always accompanied by some increase in drag-out.

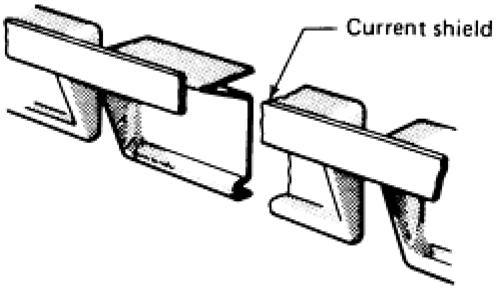


Fig. 3 Current shield

Thieves or robbers made of metal conductors can be positioned near edges and points to shunt away current from these areas. Rods with a diameter of 9.5 to 16 mm ($\frac{3}{8}$ to $\frac{5}{8}$ in.) are sometimes suspended vertically on both ends of a plating rack to prevent burning or rough plate on the edges of the cathodes. Maintenance of robbers is of utmost importance, because they can be the source of large drag-out losses if metal is allowed to build up excessively.

Auxiliary Anodes. Special racks and auxiliary anodes are used only when conventional techniques fail to produce satisfactory coatings. Parts with deep recesses, such as coffeepots and small appliance housings, require auxiliary anodes. Auxiliary anodes are also used for parts with concave surfaces that are difficult to plate uniformly (Fig. 4). Auxiliary anodes also offer potential cost reductions by directing the plate into areas of minimum plate thickness without the penalty of overplating areas of high current density. The use of such devices should be considered even for some parts that do not present serious problems in meeting specifications for plate thickness. The shapes of many die castings make the use of auxiliary anodes particularly applicable. The current supply for auxiliary anodes can be the same as the major plating circuit with a separate current control, such as a rheostat. Greater flexibility is obtained if a separate current source is used for the auxiliary anodes.

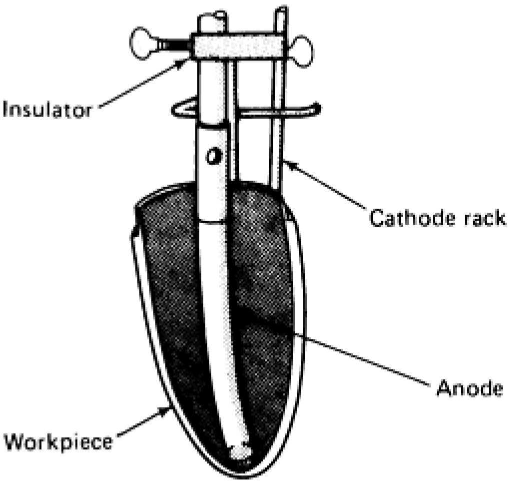


Fig. 4 Use of auxiliary anode for a part difficult to plate to uniform thickness because of concave surface

Auxiliary anodes are mounted on the plating rack, insulated from cathode current-carrying members, and provided with means of direct connection to the anodic side of the electrical circuit (Fig. 5). In still tanks, the connection can simply be a flexible cable equipped with battery clamps. In fully automatic machines, cables are permanently mounted on the carriers, and contact brushes riding on an anode rail are provided to pick up the current. Connections must be positive. An interruption or drastic reduction of current could cause the auxiliary anode to function as a robber or shield, resulting in local interruption of plate, with consequent darkening and loss of adhesion.

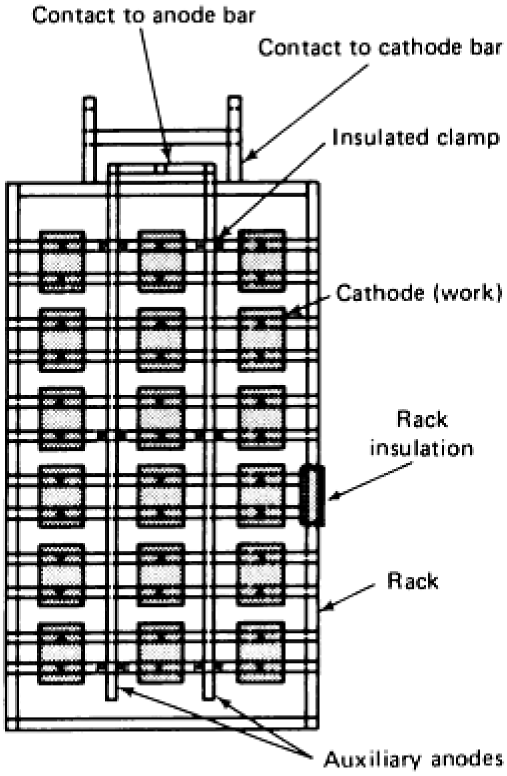


Fig. 5 Rack assembly for decorative chromium plating

The auxiliary anode need not follow the contour of the part closely. An anode-to-work spacing of 13 mm ($\frac{1}{2}$ in.) or slightly more is usually effective. The auxiliary anode mounting must be designed carefully to prevent the anode from interfering with efficient racking and unracking of parts. The anode can be designed for removal while parts are being loaded on the rack, but good contact must be preserved. The auxiliary anode should be held rigidly to prevent it from short circuiting against the cathode.

Some platers connect auxiliary anodes electrically only during chromium plating, a practice that is usually satisfactory for still tank operation, where an anode can be physically mounted immediately before chromium plating. In an automatic plating machine, however, the auxiliary anode should be connected in the acid-copper bath, the nickel bath (at least, in the last half of the tank), and the chromium bath to avoid low thicknesses and low current density effects that could detract from appearance and cause difficulty in chromium plating.

Unless they are made of insoluble material, auxiliary anodes are consumed in plating. Their design should therefore permit easy replacement. Plastisol-coated steel bushings with locking screw heads protected by stop-off lacquer are satisfactory. As anodes become thin, they must be carefully inspected for replacement to avoid shorting out. The diameter of rod used should be as large as is compatible with the size of the part and with construction requirements to minimize the need for frequent replacement. A diameter of 13 mm ($\frac{1}{2}$ in.) is suitable for a variety of parts, ranging from small brackets to instrument panels and moldings. On larger parts, diameters as large as 25 mm (1 in.) or specially cast sections can be useful.

Bags should not be used on auxiliary anodes, because of the resulting solution contamination from drag-in. Avoiding roughness from bare anodes requires serious consideration if the anodes are to be immersed in copper and nickel undercoating baths. Roughness is not a problem when the anode is to be immersed only in the chromium solution. Lead-alloy or steel anode material has been used satisfactorily for this purpose. Graphite rods also have been used to a limited extent. Auxiliary anodes are most frequently made of platinized titanium.

Bipolar anodes are a special variation of auxiliary anodes, in which current is not supplied by external connection. In use, collector plates are mounted at the cathodic end (the end closest to the tank anodes) of the bipolar anode to draw current from a larger section of the bath. Bipolar anodes can be used on conveyorized systems when a special bus bar is unavailable. Although adequate for some purposes, bipolar anodes are usually less effective than other auxiliary anodes and must be carefully maintained to avoid the problems of roughness from loosely adherent deposits of nickel and chromium on the collector plates. The metal deposited on the collector plates is often not reusable.

Stop-offs are not widely used in decorative chromium plating. However, when selective plating is required, a number of materials have the necessary qualifications, including ease of application and removal, resistance to hot cleaners and plating solutions, and excellent adherence and electrical insulation characteristics during use.

Special racks are sometimes used to prevent plating solution from entering tapped holes and areas where plate is not wanted. Figure 6 shows a plated lever with a 7.92 mm (0.312 in.) diameter hole that had to be free of plate. If conventional racking had been used, then the hole would have had to be reamed to remove the plate.

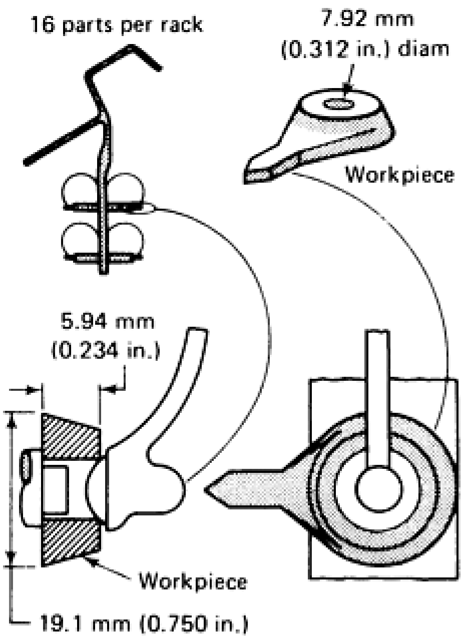


Fig. 6 Racking arrangement to prevent plating of chromium in the hole of a shift lever

Tanks. Chromium plating tanks can be constructed of steel and lined with flexible plastic-type materials, such as fiberglass or polyvinyl chloride (sheet form or sprayed) or lead alloy (6% Sb). Lead-alloy linings should be approximately 3.2 mm ($\frac{1}{8}$ in.) thick. Plastic liners should range in thickness from 2.4 to 4.8 mm ($\frac{3}{32}$ to $\frac{3}{16}$ in.). Plastic linings are preferred, particularly for proprietary baths with fluoride-containing anions, which may have a greater rate of attack on lead linings. Rubber mats or plastisol-coated metal ribs are often used to protect the sides or bottoms of lead-lined tanks from shorts that are due to either accidental contact or being punctured by dropped anodes or workpieces. Lead linings can cause serious bipolarity problems, because of their electrical conductivity.

Heating. Chromium plating tanks can be heated internally or externally. Internal heating, by steam coils or electric immersion heaters, is usually used for small tanks. External heating by heat exchangers is used for large tanks. Coils for internal heating can be made of lead, a lead alloy such as 4% Sn or 6% Sb, or tantalum. Titanium can be used for baths that do not contain fluoride ions. Immersion heaters should be quartz-covered. Heat exchangers can be made of tantalum, lead alloy (4% Sn or 6% Sb), high-silicon cast iron, or heat-resistant glass. Tantalum is preferred for heating coils or heat exchangers when proprietary solutions containing fluoride ions are used, because titanium is attacked by the fluoride. Consultation with vendors on specific material/process compatibility is suggested.

Plating Cycles. Typical system cycles for the application of six decorative chromium plating systems to identical workloads are given in Table 4. Each system is identified by the specific combination of metals successively deposited, the total thickness of plate, and the total plating time. The plating times and power requirements listed in Table 4 are theoretical values for perfect coverage. In practice, these values would be considerably higher to ensure adequate plate thickness in all areas. Table 5 provides the requirements for the design of several installed machines for the continuous plating of zinc die castings of average complexity. The higher-than-normal designed current density is related to potential future needs that exceed present requirements.

Table 4 Typical system cycles

System	Cycles	Total plate		Total time, min(a)
		µm	µin.	

Cu + Ni + Cr	A, B, D, F	50	1970	48
Cu + Cr	A, B, F	20	790	14
Ni + Cr	D, F	30	1180	36
Ni + Cr + Cr	D, G	32	1260	41.5
Ni + Ni + Cr	C, E, F	30	1180	36
Ni + Ni + Cr + Cr	C, E, G	32	1260	41.5

Operating parameters	
A: Copper strike	
Current density	325 A/m^2 (30 A/ft^2)
Plating time	2 min
Heat[(b)]	49-65 °C (120-150 °F)
Filtration	Yes
Agitation	Optional
B: Acid copper plate, high speed, bright (20 µm, or 790 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	10 min
Heat[(b)]	21-27 °C (70-80 °F)
Filtration and agitation	Yes
C: Nickel plate, semibright (23 µm, or 900 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time(100% efficiency)	26 min

Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
D: Nickel plate, bright (30 μm or 1180 μin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
E: Nickel plate, bright (8 μm, or 315 μin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
F: Chromium plate (0.3 μm, or μin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time	
Conventional (10% efficiency)	2 min
High speed (25% efficiency)	54 s
Heat(b)(c)	46-65 °C (115-150 °F)

Filtration and agitation	No
Ventilation(d)	Yes
G: Chromium plate, microcracked (0.64 µm, or 25 µin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time (25% efficiency)	2.5 min
Heat(b)(c)	45-65 °C (115-150 °F)
Filtration and agitation	No
Ventilation(d)	Yes

(a) Power requirements and plating times given are theoretical values for perfect coverage. In practice, these values would be approximately doubled to ensure adequate thickness of plate in all areas. Table 5 has data for practical conditions.

(b) For operating temperature indicated.

(c) Cooling as well as heating may be required.

(d) Chemical suppressant (mist or spray) may be used in addition to ventilation.

Table 5 Design basis of equipment for continuous chromium plating of zinc-base die castings

Metal deposited	**Designed current density**		**Minimum thickness of plate**		**Nominal thickness of plate**		**Plating time, min**
	A/m^2	**A/ft^2**	**µm**	**µin.(a)**	**µm**	**µin.**	
Copper cyanide strike	1075	100	. . .	. . .	0.25	10	3-4
Bright copper	320	30	15	590	20	790	25-30
Semibright nickel	810	75	15	590	20	790	30
Bright nickel	1075	100	5	197	7.5	295	17
First chromium	2150	200	0.3	12	0.5	20	6.5

Second chromium	1615	150	0.25	10	0.5	20	6.5

(a) On parts of moderate complexity

Maintenance. The importance of proper solution maintenance and electrical, mechanical, and other equipment used in plating processes cannot be overemphasized. Table 6 identifies the daily, weekly, monthly, and annual inspection and correction operations that should enable the setup of an adequate maintenance program for chromium plating.

Table 6 Chromium plating maintenance schedule

Frequency	Action
Daily	Fill plating tank with solution from save-rinse and boil-down tanks.
	Stir solution thoroughly, using low-pressure air agitation.
	Check solution for chromic acid, sulfate, and anti-spray additives; make corrective additions.
	Check temperature controls for satisfactory operation; adjust temperature to proper range.
	Inspect plating racks; repair as necessary.
	Check ground lights to see that plating circuits are clear; do not start plating until grounds are clear.
	Put dummy cathodes in tanks and electrolyze solutions at maximum voltage for 15 to 30 min at start of each day.
	Check hull cell.
Weekly	Boil down the save-rinse solution.
	Check auxiliary catalyst; make additions as necessary.
Monthly	Check solution for metallic impurity content (iron, zinc, copper, nickel).
	Clean and straighten anodes.
	Check solution for trivalent chromium content.
Annually	Check all ammeters and ampere-hour meters.
	Inspect and adjust all temperature controllers.

	Clean and repair outside of all tanks; clean and repair all ventilation hoods and ducts.
	Pump out solution, remove sludge. Clean and inspect tank and heating coil; repair as needed. Disconnect all bus bar connections; clean, draw-file and reconnect, including all anode and cathode joints. Inspect anodes; clean, straighten or replace as required.

Troubleshooting. Plating problems can still develop, even when proper maintenance is used. Some typical plating problems and solutions are given in Table 7. Examples of actual problems and solutions used with a variety of chromium-plated parts are given in Table 8.

Table 7 Chromium plating problems and corrections

Defect	Possible cause	Possible remedy
Poor covering power or low deposit thickness	Temperature too high	Adjust temperature to standard range.
	Current density too low	Increase current density.
	Low chromic acid	Adjust chromic acid to standard range.
	Fluoride catalyst too high	Reduce concentration (by dilution).
	Low chromic acid to sulfate ratio	Adjust ratio.
	Poor electrical contact	Correct electrical contact.
	Bath contamination	Remove impurities.
Burning in high current density areas	Temperature too low	Adjust temperature to standard range.
	Current density too high	Reduce current density.
	Chromic acid low	Raise chromic acid.
	High chromic acid/sulfate ratio	Adjust ratio.
	Fluoride catalyst too low	Adjust concentration of fluoride catalyst.
Deposit color nonuniform	Underlying surface not clean or active	Remove any interfering films and provide active surface.
	Bipolarity during entrance to chromium	Enter bath with precontact (live entry).

	Bath contamination by metallic impurities	Analyze bath, remove impurities.

Table 8 Case histories of plating problems

Condition	Cause and correction
Passivation	Nickel-plated business machine parts were stored submerged in cold water to await barrel chromium plating. Although these parts were acid activated before chromium plating, chromium coverage was poor to nil on parts that had been stored for only a few hours. To remedy the problem, parts were stored submerged in a 10% solution of potassium bitartrate (cream of tartar). After several days of storage, the parts could be electrolytically reactivated and barrel chromium plated satisfactorily.
Burning	Although bath composition and temperature were carefully controlled, burnt chromium deposits occurred on die castings plated at moderate amperage. This resulted from nonuniform distribution of current caused by the corrosion of mounting blocks attaching the bus bar to the anode bar. The situation was corrected by welding the bus bar to the anode rail, eliminating mounting blocks.
Poor electrical contact	L-shaped die-cast frames approximately 0.09 m^2 (1 ft^2) in area, although plated in identical racks in an automatic plating machine,exhibited nonuniformity of plate and, in some racks, burnt deposits. This was found to be caused by variations in current from rack to rack in the plating machine. To correct this, mechanical joints were eliminated from the electrical circuit. The mechanical joints were replaced by welding cables from the carrier contact brushes to the rack mounting bar.
Mischromes	Mischromes (absence of chromium on certain areas) occurred on die-cast window frames that occupied the lower portions of racks during plating in a full-return-type automatic plating machine. These defects were caused by the presence of short anodes at the exit end of the nickel plating tank. Replacement with anodes of the correct length solved the problem.
Inadequate rinsing	Inadequate rinsing after chromium plating, which failed to remove small amounts of bath impurities,resulted in nonuniform appearance of the plate on zinc die castings. The parts were given a hot rinse at 93 °C (200 °F) before customary room-temperature rinses to remove bath impurities.

Trivalent Chromium Plating

The use of the trivalent chromium ion, instead of the hexavalent ion, in solution to deposit chromium has been of interest for many years. The first commercially successful decorative trivalent chromium process began in England in 1975 and in the United States in 1976. Environmental, safety, and productivity advantages have been the driving forces for the commercialization of trivalent chromium processes.

Hexavalent chromium ions are also considered carcinogenic and can cause skin ulcerations. The trivalent chromium ion is estimated to be about 100 times less toxic than hexavalent chromium ions.

Trivalent chromium processes have reduced misting to the extent that scrubbers, such as those used with hexavalent chromium processes, are presently not required to meet federal and state air-quality discharge standards. Waste-treatment costs are reduced by a factor of 10, because less than one-tenth of the chromium contained in hexavalent processes is used in the trivalent process (8 to 23 g/L, or 1 to 3 oz/gal, versus 115 to 300 g/L, or 15 to 40 oz/gal). In addition, the solution drains faster, so that less solution is removed with the parts. Finally, the chromium in the rinse water is already in the trivalent state, which eliminates the expensive and sludge-volume-building reduction step required with hexavalent chromium ions.

Some of the trivalent chromium processes plate up to three times faster than hexavalent chromium processes. This increases productivity in some shops. Increased throwing and covering powers, lack of burning, and tolerance to current interruptions and ripple also reduce rejects and can increase the allowable number of parts on a rack.

One of the main difficulties with the development of trivalent chromium baths was the formation of hexavalent chromium at the insoluble anodes during plating. Hexavalent chromium ions are a contaminant in trivalent chromium processes. They initially cause a poor deposit appearance and eventually result in the cessation of plating.

Two well-known proprietary approaches were developed to address the problem of hexavalent chromium formation during plating. The oldest and most frequently used technique incorporates several lines of defense against hexavalent chromium ions. Under normal operating conditions, hexavalent chromium cannot form. If it does manage to get into the plating solution, then it is reduced to the trivalent state, which eliminates it as a contaminant. This technique is referred to as the single-cell process, in contrast to the second technique, which isolates the insoluble graphite anodes from the trivalent-chromium-containing plating solution to restrict the formation of hexavalent chromium.

This second technique, commonly referred to as the double-cell, or shielded anode, method, uses an ion-selective membrane to create a barrier around the anode. Conventional lead anodes are used in a 10% sulfuric-acid electrolyte. The membrane keeps the trivalent chromium from contacting the anode, thereby preventing the formation of hexavalent chromium.

Solution Compositions. Depending on the process used and its operating conditions, the trivalent chromium ion content typically ranges from 5 to 20 g/L (0.67 to 2.67 oz/gal). It is introduced as a water-soluble salt and forms a stable specie upon combining with the stabilizing agents/catalysts. These agents permit the trivalent chromium ion to be stable in solution until it is plated out at the cathode. However, the stability process is not strong enough to interfere with the normal precipitation sequence used with chromium during waste treatment.

In comparison to hexavalent chromium solutions, which have good conductivity, the conductivity of the relatively high-pH and low-metal-content trivalent plating solution is increased by the addition of conductivity salts/buffers. Lower amperes but higher volts are required for trivalent chromium processes, compared with hexavalent chromium process requirements. Surfactants are added to reduce the surface tension of the solution for mist suppression, as well as to act as additives in the plating operation.

Solution Operation. The typical operating conditions for trivalent chromium processes are summarized in Table 9. High current density spiking at the onset of plating increases the already excellent covering and throwing powers of trivalent chromium processes, when compared with those of hexavalent processes. In general, wherever nickel can be plated, trivalent chromium can be plated. Hexavalent chromium processes fall short, particularly around holes and slots and in low current density areas. Process control, while plating at high current densities, is not a serious concern for trivalent processes, because they have less tendency to produce burnt deposits, compared with hexavalent processes. However, some earlier trivalent processes did produce thick deposits, over 1.3 μm (50 μin.). This thickness is sufficient to produce macrocracking. The cathode efficiency decreases with increasing current density. Therefore, the plating speed does not increase proportionally with an increase in current density.

Table 9 Typical operating conditions for trivalent chromium processes

Parameter	**Value**
pH	2.3-4.0
Temperature	27-50 °C (80-122 °F)
Current density	
Cathode	430-1400 A/m^2 (40-130 A/ft^2)
Anode	540 A/m^2 (50 A/ft^2)

Agitation	Mild air
Rectifier voltage	6-15 V
Deposition rate	
Single-cell process	0.20-0.25 μm/min (8-10 μin./min)
Double-cell process	0.08-0.10μm/min (3-4 μin./min)

Once the operating range has been established for a particular plating installation, the pH and temperature must be controlled well, because they influence plating speed, covering power, and color. The buffering ability of the solution is strong enough that large pH fluctuations do not occur. As the pH increases, the plating rate decreases, but the covering power increases. In general, trivalent chromium deposits do not have the blue-white color of hexavalent chromium deposits. Generally, they have a deeper, slightly darker appearance. However, the newer trivalent processes can produce deposits very close in appearance to hexavalent chromium deposits. In most cases, the color difference is noticeable only when the part is placed next to a hexavalent chromium-plated part.

Temperature. Depending on the process selected, either cooling or heating might be required for temperature control to maintain a bath at desired operating parameters. When lower operating temperatures are desired, some degree of cooling might be required to offset the power used for deposition. Cooler operating temperatures increase the covering power of the process, but slightly darken the color.

Anodes and Agitation. Anode current density should be maintained below 540 A/m^2 (50 A/ft^2) to promote anode life and consistent bath operation. The insoluble graphite anode used in the single-cell process should last indefinitely, if it is not physically damaged. Lead anodes will form protective insoluble films as long as the anodic current density is properly maintained in the double-cell process, resulting in a limited production of lead salts. Mild and uniform air agitation is used around the parts to assist in obtaining metal distribution and appearance.

Contamination Control. The major contributor to a change in appearance of the trivalent chromium deposits is solution contamination. Trivalent chromium solutions are much more sensitive to bath contamination, but are much more easily purified than are hexavalent chromium solutions. Organic contaminants, a minor problem, are typically removed by filtration through carbon. Organic contamination appears in the chromium deposit as white smears that resemble a pattern typically associated with poor cleaning.

Inorganic contaminants, such as iron, nickel, copper, and zinc, cause the deposit to have dark streaks and/or to lose covering power. The newest and easiest method for removing inorganic impurities is to continuously purify the plating solution by passing it through a specially designed resin. Using this technique, the inorganic impurity levels can be maintained much below the level that will cause any operational or appearance problems.

Three other general methods can be used to remove these contaminants. The slowest approach is to plate them out whenever the bath is not being used for production. An alternative method is to set a small plating unit, connected by a recirculating pump, to the main plating tank. Dummy sheets are used in the small unit to continuously plate out impurities without interrupting production.

A third method that is available for some processes is to use chemical purifiers that can remove large quantities of inorganic contaminants during one or two hours of downtime. Although this method is very fast, it has two disadvantages. The chemical precipitates the impurities within the plating bath. The precipitation itself does not cause any plating problems, but the precipitates could adhere to the parts as they leave the tank, causing them to have an objectionable white film. If chemical purifiers are improperly used, then the solution chemistry can be affected, resulting in a darker deposit and poorcoverage.

Plating Problems and Corrections. Some of the plating problems experienced with trivalent chromium baths can be ascribed to common operational problems. Poor coverage is typically due to low pH, high temperature, low current density, or lead or zinc contamination. Dark clouds or smudges on the work can arise from metallic contamination or low complexant or surfactant concentrations. White patches on the work can be caused by high concentrations of surfactants or other organics, lead contamination, or high wetting agent concentration in the nickel bath used prior to chromium plating.

Trivalent and Hexavalent Deposit Comparisons. The choice of chromium plating solution, whether hexavalent or trivalent, depends on the individual application under consideration. The characteristics of these processes are compared in Table 10.

Table 10 Trivalent and hexavalent chromium comparison

Parameter	**Trivalent chromium**	**Hexavalent chromium**
Throwing power	Good	Poor
Covering power	Good	Poor
Current interruptions	Completely tolerant	Intolerant
Rectifier ripple	Completely tolerant	Intolerant
Deposit structure (microdiscontinuous):		
Single cell	Microporous and microcracked	Special processes required
Double cell	Microporous	. . .
Ease of burning	Very difficult	Easy
Ease of rinsing	Easy	Moderate
Color buffing requirement	Never	Occasional
Filtering requirement:		
Single cell	Only after purification	Never
Double cell	Daily with carbon	. . .
Conditioning/dummying:		
Single cell	Never	Start up to each day

Double cell	Start up and routinely	. . .
Passivity of nonplated surfaces	Needs post dip	"Chromate" surfaces
Color of deposit:		
Single cell:		
Ambient temperature	Pewter or stainless steel	Blue-white
Elevated temperature	Metallic white	. . .
Double cell:		
Elevated temperature	Metallic white	. . .
Waste treatment	Easy	Moderate
Relative safety	Similar to nickel	Similar to cyanide
Misting	Almost eliminated	Heavy
Odor	Almost eliminated	Strong and dangerous

Nickel Plating

Revised by George A. Di Bari, International Nickel Inc.

Introduction

THE NICKEL PLATING PROCESS is used extensively for decorative, engineering, and electroforming purposes because the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and the operating parameters of the plating solution. Decorative applications account for about 80% of the nickel consumed in plating; 20% is consumed for engineering and electroforming purposes. Autocatalytic (electroless) nickel plating processes are commercially important but are outside the scope of this section. The annual worldwide consumption of nickel for electroplating is approximately 180 million pounds (81,700 metric tons) and accounts for 11 to 12% of world nickel consumption. Some basic information about nickel and common nickel salts for plating is given in the following table:

Nickel	Atomic weight 58.69. Valency 2. Specific gravity 8.90. Plating rate, at 100% cathode efficiency, 1.095 g/A · h (0.039 oz/A · h)

Nickel salts	
Nickel chloride	Formula is $NiCl_2 \cdot 6H_2O$. Contains 24.7% Ni.
Nickel sulfate	Formula is $NiSO_4 \cdot 6H_2O$. Contains 22.3% Ni.
Nickel sulfamate	Formula is $Ni(NH_2SO_3)_2$. Contains 23.2% Ni.
Nickel carbonate	Formula is $NiCO_3$. Contains about 46% Ni.

Decorative Plating. Modern decorative nickel plating solutions contain organic additives that modify the electrocrystallization process so that mirror-bright, highly-leveled nickel coatings are deposited directly from solution. Prior to the introduction of "organic" baths, decorative nickel coatings were produced by polishing nickel-plated parts mechanically, a practice that continued from 1870 to about 1945. Thin layers of chromium were electrodeposited over polished nickel coatings for the first time in 1927 to prevent the "yellowing" or tarnishing of nickel in outdoor atmospheres, and that practice continues with the "as-deposited" bright nickel coatings now available. An effort to develop improved decorative, electroplated nickel coatings began in the late 1940s and led to the development of multilayer nickel coatings (early 1950s) and microdiscontinuous chromium coatings (mid- to late 1960s). Modern multilayer nickel coatings in combination with microdiscontinuous chromium are capable of protecting and enhancing the appearance of most metals and alloys, plateable plastics, and other materials for extended periods of time.

Engineering Plating. The engineering applications of nickel plating include those where a fully bright appearance is not required. Engineering nickel deposits are usually sulfur-free and matte in appearance. These deposits may be specified to improve corrosion and wear resistance, to salvage or build up worn or undersized parts, to modify magnetic properties, to prepare surfaces for enameling or for organic coating, to function as diffusion barriers in electronic applications and for other purposes. Engineering applications exist in the chemical, nuclear, telecommunications, consumer electronics, and computer industries.

Electroforming. Nickel electroforming is electrodeposition applied to the manufacture of nickel products of various kinds, and it differs from electroplating in one major respect. In electroplating, the coating is metallurgically bonded to the substrate and is an integral part of the surface. In electroforming, nickel is deposited onto a mandrel or mold nonadherently so that the nickel can be separated from the mandrel when it is removed from the plating solution. Electroforming applications include the fabrication of molds and dies, mesh, and other products that are indispensable to operations in the textile, aerospace, communication, electronics, automotive, photocopying, and entertainment industries. Additional information is available in the article "Electroforming" in this Volume.

Basic Process Considerations

Before describing decorative, engineering, and electroforming plating processes, some basic facts are reviewed that make it possible to control the nickel plating process, predict the amount of nickel deposited, and estimate nickel coating thickness.

The Basic Process. Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent positively charged ions (Ni^{++}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode, where metallic nickel is dissolved to form divalent positively charged ions, which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode.

Hydrogen Evolution and Cathode Efficiency. The discharge of nickel ions is not the only reaction that can occur at the cathode; a small percentage of the current is consumed in the discharge of hydrogen ions from water. This reduces the cathode efficiency for nickel deposition from 100% to 92 to 97%, depending on the nature of the electrolyte. The discharged hydrogen atoms form bubbles of hydrogen gas at the cathode surface.

Anode Efficiency. Under normal conditions the efficiency of dissolution at the anode is 100% and no hydroxyl ions are discharged from the water. If the pH of the solution is too high, however, hydroxyl ions may be discharged in preference to the dissolution of nickel, and oxygen will be evolved. Under those conditions, the nickel anode becomes passive and ceases to dissolve nickel. Activated nickel anode materials are available commercially that resist the onset of passivity and replenish the solution with nickel ions over a wide range of plating conditions.

Nickel Ion and pH Changes. Under normal operating conditions, the nickel ion concentration and the pH of the solution will slowly increase as plating proceeds. The rate of increase in nickel ion concentration depends on the difference between cathode and anode efficiencies. Because cathode efficiencies may vary from 92 to 97%, whereas anode efficiency is always 100%, the rate of increase in nickel ion concentration depends on the nature of the plating solution and not on the type of soluble nickel anode material that is used.

Faraday's Law for Nickel. The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time (Faraday's Law). The proportionality constant is equal to M divided by nF, where M is the molecular weight, n is the number of electrons involved in the electrochemical reaction, and F is Faraday's constant, equal to 96,500 coulombs (ampere-seconds). For nickel, the constant is 1.095 g/A · h. The constant for nickel deposition is calculated assuming that cathode efficiency is 100%; because a small part of the current goes to discharge hydrogen, the constant must be adjusted by multiplying by the cathode efficiency (for example, $1.095 \times 0.955 = 1.046$).

Faraday's Law for nickel may be expressed as $m = 1.095\ (a)\ (l)\ (t)$, where m is the amount of nickel deposited at the cathode (or dissolved at the anode), in grams; l is the current that flows through the plating tank, in amperes; t is the time that the current flows, in hours; and a is the current efficiency ratio for the reaction of interest. In almost all cases, the anode efficiency is 100% ($a = 1$). The cathode efficiency may vary from 92 to 97% and accordingly, a will vary from 0.92 to 0.97.

Average Nickel Thickness. The nickel electrodeposition data compiled in Table 1 have been calculated on the assumption that cathode efficiency is 95.5%, which approximates the case for most nickel plating solutions. From the table, one can estimate the time required to deposit a specified thickness of nickel at a specified current density. If the plating process is operated at 5 A/dm^2, for example, it takes about 20 min to deposit a nickel coating with an average thickness of 20 µm.

Table 1 Nickel electrodeposition data

Deposit thickness, µm	**Weight per unit area, g/dm^2**	**Amp hours per unit, A · h/dm^2**	**Time (min) required to obtain deposit at current density (A/dm^2) of:**									
			0.5	**1**	**1.5**	**2**	**3**	**4**	**5**	**6**	**8**	**10**
2	0.18	0.17	20	10	6.8	5.1	3.4	2.6	2.0	1.7	1.3	1
4	0.36	0.34	41	20	14	10	6.8	5.1	4.1	3.4	2.6	2
6	0.53	0.51	61	31	20	15	10	7.7	6.1	5.1	3.8	3.1
8	0.71	0.68	82	41	27	20	13	10	8.2	6.8	5.1	4.1
10	0.89	0.85	100	51	34	26	17	13	10	8.5	6.4	5.1

12	1.1	1.0	120	61	41	31	20	15	12	10	7.7	6.1
14	1.2	1.2	140	71	48	36	24	18	14	12	8.9	7.1
16	1.4	1.4	160	82	54	41	27	20	16	14	10	8.2
18	1.6	1.5	180	92	61	46	31	23	18	15	11	9.2
20	1.8	1.7	200	100	68	51	34	26	20	17	13	10
40	3.6	3.4	410	200	140	100	68	51	41	34	26	20

Note: Values are based on 95.5% cathode efficiency.

The data in Table 1 provide a means of estimating the average coating thickness. The actual thickness on an individual part depends on the uniformity of current density distribution. Under practical plating conditions, the thickness of the nickel on a batch of parts is measured in one or more trials, and adjustments are made, if necessary, as to how the parts are placed in the tank relative to the anode and how they are positioned on the plating racks. In some cases, shields and auxiliary anodes may be required to obtain acceptable thickness uniformity. Shields are made of nonconductive materials and may be placed on the anode, on the cathode, or between electrodes to block or control current flow. Auxiliary anodes may be either soluble or insoluble, and they are placed closer to the cathode than principal anodes so as to direct current to a recessed or relatively small area on the cathode. With care, current density distribution and coating thickness can be made reasonably uniform and predictable.

The Watts Solution and Deposit Properties

The nickel plating solution described by Watts in 1916 was a major milestone in the development of nickel plating technology. The solution eventually replaced all others in use up to that time. It remains the basis of most decorative nickel plating processes, and it is used for engineering applications and for electroforming. It is operated at elevated temperatures and is capable of being used with high current densities.

The composition of the modern Watts bath is included in Table 2. The constituents of the Watts bath have several functions.

- *Nickel sulfate* is available in commercially pure forms, is relatively inexpensive, and is the major source of the nickel ions in solution. A high nickel sulfate concentration is used when high current densities are required.
- *Nickel chloride* serves primarily to improve anode corrosion, but it also increases conductivity and uniformity of coating thickness distribution. Excessive amounts of chloride increase the corrosivity of the solution and the internal stress of the deposits. (*Internal stress* refers to forces created within the deposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur, and other elements. Internal stress is either tensile [contractile] or compressive [expansive] and may cause plating problems if excessively high.)
- *Boric acid* is used in nickel plating solutions for buffering purposes; its concentration may affect the appearance of the deposits. The deposit may first become frosty in high current density areas at 30 g/L (4 oz/gal) of boric acid, and then as the boric acid concentration approaches 15 to 23 g/L (2 to 3 oz/gal), the deposit may be burnt and cracked. No effect on appearance is observed at high boric acid concentrations up to saturation (45 g/L, or 6 oz/gal).
- *Wetting agents or surfactants,* formulated specifically for nickel plating solutions, are almost always added to control pitting. Their function is to lower the surface tension of the plating solution so that air

and hydrogen bubbles do not cling to the parts being plated.

Table 2 Nickel electroplating solutions

Electrolyte composition, [(a)] **g/L**	**Watts nickel**	**Nickel sulfamate**	**Typical semibright bath**[(b)]
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	225 to 400	. . .	300
Nickel sulfamate, Ni $(SO_3NH_2)_2$	. . .	300 to 450	. . .
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30 to 60	0 to 30	35
Boric acid, H_3BO_3	30 to 45	30 to 45	45
Operating conditions			
Temperature, °C	44 to 66	32 to 60	54
Agitation	Air or mechanical	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2	3 to 11	0.5 to 30	3 to 10
Anodes	Nickel	Nickel	Nickel
pH	2 to 4.5	3.5 to 5.0	3.5 to 4.5
Mechanical properties[(c)]			
Tensile strength, MPa	345 to 485	415 to 610	. . .
Elongation, %	10 to 30	5 to 30	8 to 20
Vickers hardness, 100 gram load	130 to 200	170 to 230	300 to 400
Internal stress, MPa	125 to 210 (tensile)	0 to 55 (tensile)	35 to 200 (tensile)

(a) Antipitting agents formulated for nickel plating are often added to control pitting.

(b) Organic additives available from plating supply houses are required for semibright nickel plating.

(c) Typical properties of *bright* nickel deposits are as follows: elongation, 2 to 5%; Vickers hardness, 100 gram load, 600 to 800; internal stress, 12 to 25 MPa (compressive).

Good-quality nickel deposits can be produced within the ranges of solution pH, temperature, and current density given in Table 2. Although the maximum current density given in the table is 11 A/dm^2, higher rates of plating are possible with increased solution agitation and flow rates.

The physical and mechanical properties of nickel deposited from Watts solutions are affected by the operating conditions and chloride content of the solution as shown in Fig. 1, 2, 3, and 4. Figures 1, 2, and 3 show how pH, current density, and temperature affect properties such as internal stress, hardness, percent elongation, and tensile strength. Figure 4 shows how the chloride content affects those properties; the maximum ductility and softest deposits are produced when 25% of the nickel in solution is present as nickel chloride. Reference 2 is a comprehensive source of mechanical property data for electrodeposited nickel, nickel alloys, and nickel composite coatings.

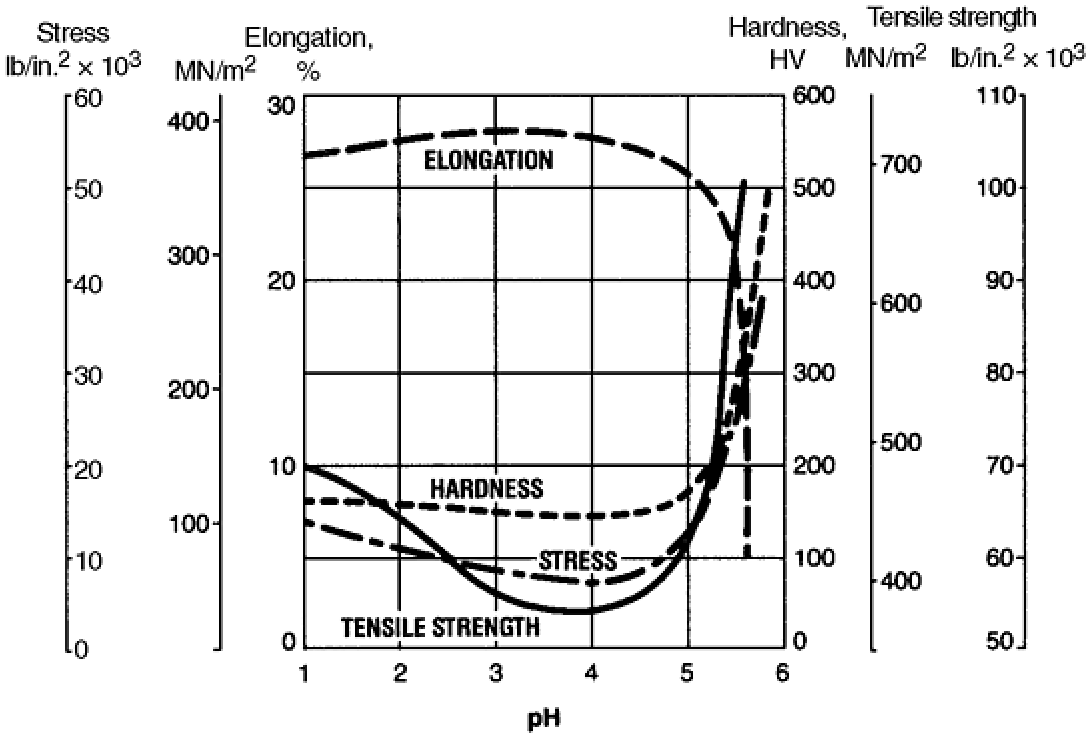


Fig. 1 Variation in internal stress, tensile strength, ductility, and hardness with pH. Watts bath operated at 54 °C and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

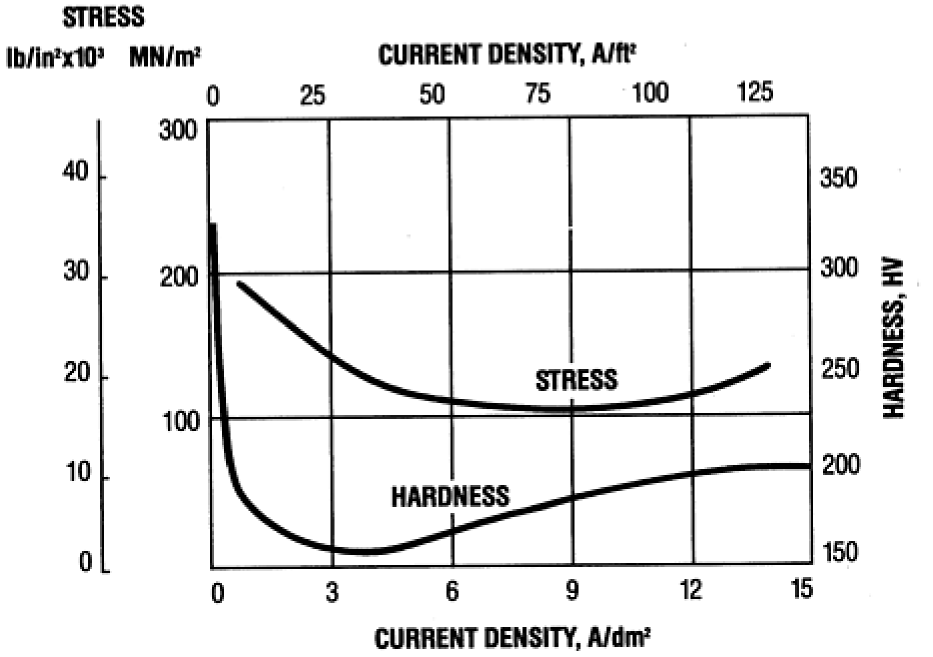


Fig. 2 Variation in internal stress and hardness with current density. Watts bath operated at 54 °C and pH 3.0. Internal stress is tensile (indicated by a positive number). Source: Ref 1

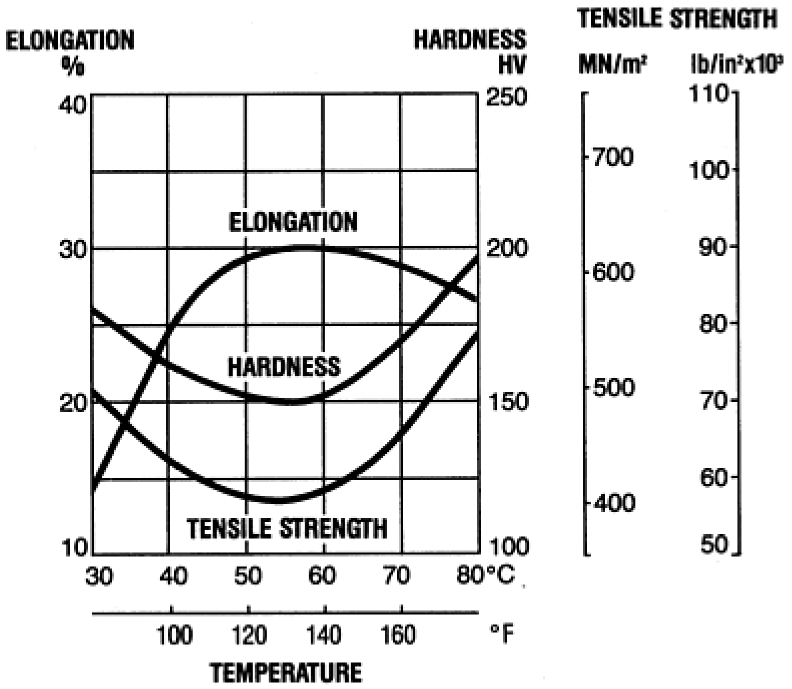


Fig. 3 Variation in elongation, tensile strength, and hardness with temperature. Watts bath operated at 54 °C and 5 A/dm^2. Source: Ref 1

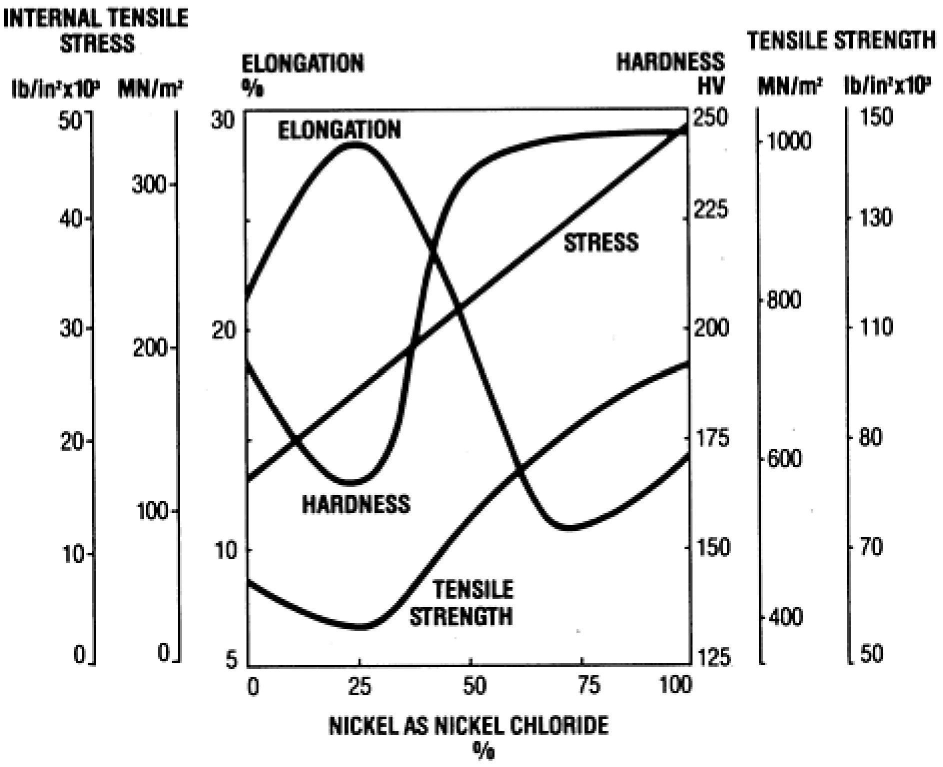


Fig. 4 Variation in internal stress, elongation, tensile strength, and hardness with chloride content in deposits from Watts solutions operated at 55 °C, pH 3.0, and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

The nickel plating processes used for decorative, engineering, and electroforming purposes are discussed in the following sections.

References cited in this section

1. *Plating,* Vol 39 (No. 365), 1952, p 1229
2. W.H. Safranek, *The Properties of Electrodeposited Alloys--A Handbook,* 2nd ed., American Electroplaters and Surface Finishers Society 1986

Decorative Nickel Plating Processes and Multilayer Coatings

The technology of decorative nickel plating has been improved continuously over the years. Prime examples include development of the organic bright nickel solutions, introduction of semibright nickel plating processes, development of multilayer nickel coatings, and the use of microdiscontinuous chromium in combination with multilayer nickel. The major result of these developments has been a remarkable improvement in the corrosion performance of decorative nickel plus chromium coatings without the need to increase deposit thickness.

Bright nickel plating solutions are modifications of the Watts formulation given in Table 2, but they contain organic and other additives that act to produce a fully bright finish suitable for immediate chromium plating without mechanical finishing. Portions of the addition agent molecules may be incorporated into the deposit, resulting in a hard, fine-grain coating that contains incorporated sulfur. The sulfur causes the deposit to be electrochemically more reactive than sulfur-free matte, polished, or semibright nickel deposits. Decomposition products of the additives accumulate in solution with time and are removed by purification with activated carbon. In modern solutions, continuous filtration through active carbon removes deleterious decomposition products without significant removal of the addition agents themselves.

Several substances--organic and inorganic--are used at appropriate concentrations to achieve brightness, leveling, and control of internal stress. (Leveling is the ability of the deposit to become smoother than the surface on which it is deposited as the thickness of the nickel is increased.) The substances used as additives in bright nickel plating solutions may be described by the following three terms: *carriers, auxiliary brighteners,* and *brighteners.* The terminology is not standardized, however, and alternative terms mentioned in the literature are shown in parentheses.

Carriers (brighteners of the first class, secondary brighteners, control agents, ductilizers) are usually aromatic organic compounds. They are the principal source of the sulfur codeposited with the nickel. Their main function is to refine grain structure and provide deposits with increased luster compared with matte or full deposits from baths without additives. Some of these additives can be used in Watts solution or high-chloride versions of the Watts solution (for example, solutions with 115 g/L nickel chloride). This class of brightener widens the bright range when used in combination with the auxiliary brighteners and brighteners discussed below. Some examples of carriers are saccharin (o-sulfobenzoic imide), paratoluene sulfonamide, benzene sulfonamide, benzene monosulfonate (sodium salt), ortho sulfobenzaldehyde (sodium salt), and naphthalene 1,3,6-trisulfonate (sodium salt). Carriers are used in concentrations of about 1 to 25 g/L (0.1 to 3 oz/gal), either singly or in combination. They are not consumed rapidly by electrolysis, and consumption is primarily by dragout and by losses during batch carbon treatment. (Batch treatment involves interrupting production and transferring the plating solution to a separate treatment tank where it is treated with activated carbon, filtered, and returned to the main tank.) The stress-reducing property of carriers is increased if they contain amido or imido nitrogen. For example, saccharin is a most effective stress reducer and often helps to decrease or eliminate hazes. It is generally used as sodium saccharin at a concentration of 0.5 to 4.0 g/L (0.07 to 0.5 oz/gal).

Auxiliary brighteners may be either organic or inorganic. Their functions are to augment the luster attainable with the carriers and brighteners and to increase the rate of brightening and leveling. Some examples are sodium allyl sulfonate; zinc, cobalt, cadmium (for rack and barrel plating); and 1,4-butyne 2-diol. The concentration of these additives may vary from about 0.1 to 4 g/L (0.01 to 0.5 oz/gal). The rate of consumption depends on the type of compound and may vary widely. These compounds may be of aromatic or aliphatic types and usually are heterocyclic or unsaturated. The inorganic metallic ions--zinc, cobalt, cadmium--are not often used anymore as auxiliary brighteners.

Brighteners (brighteners of the second class, primary brighteners, leveling agents), when used in combination with carriers and auxiliary brighteners, produce bright to brilliant deposits having good ductility and leveling characteristics over a wide range of current densities. Some of the compounds used as brighteners include reduced fuchsin, phenosafranin, thiourea, 1,4-butyne diol, n-allylquinolinium bromide) and 5-aminobenzimidazolethiol-2. Materials of this type generally are used in concentrations of 0.005 to 0.2 g/L (0.0006 to 0.02 oz/gal); an excess of brighteners may cause serious embrittlement. The rates of consumption of these materials may vary within wide limits.

Modern bright nickel plating solutions employ combinations of additives similar to those described and are formulated to produce bright deposits over a wide range of current densities. The deposits have excellent leveling or scratch-filling characteristics, produce deposits with fair ductility and low internal stress, produce bright deposits in areas of low current density, permit use of high average current densities and bath temperatures, are less sensitive to metallic contaminants than some of the solutions first commercialized, permit continuous purification of the plating solution by use of activated carbon on filters, produce breakdown products that can be removed by activated carbon, and are not overly sensitive to anode effects.

Multilayer Decorative Plating. The single-layer bright nickel coatings produced from solutions containing organic additives are less resistant to corrosion than polished nickel coatings. The lower corrosion resistance is due to the presence of small amounts of sulfur that originate from the organic additives present in solution. The amount of sulfur that is incorporated depends on exactly how the process is formulated and controlled. Single-layer bright nickel coatings are suitable for use in mildly corrosive service using a nickel thickness of 10 to 20 μm (0.39 to 0.79 mil). For severe and very severe conditions of exposure, especially where longtime resistance to corrosion is required, multilayer nickel coatings with microdiscontinuous chromium are used. The principal types are double- and triple- layer coatings.

Double-layer coatings involve the electrodeposition of two layers of nickel, one semibright and one bright, before the application of chromium. The first layer (semibright) is deposited from a Watts-type formulation containing one or more sulfur-free organic additives. Semibright nickel deposits contain less than 0.005 wt% S and are semilustrous, smooth, and fine-grain over a wide current density range. The deposits have a columnar structure and good ductility. The typical composition and operating conditions for a semibright nickel plating bath are given in Table 2. Deposit internal stress increases with increasing nickel chloride content; deposits also tend to be nonuniform in color and leveling at high chloride levels. The concentrations of the organic additives for semibright nickel solutions are usually fairly low, from 0.05 to 0.5 g/L (0.006 to 0.06 oz/gal). Examples of these additives are 1,4-butyne diol (or other aliphatic compounds with olefinic or acetylenic unsaturation), formaldehyde, coumarin, and ethylene cyanohydrin. There are two families of semibright nickel plating processes that are usually referred to as *coumarin* and *noncoumarin* types. The latter were introduced more recently and offer advantages. Semibright nickel plating solutions usually contain anionic surfactants and antipitting agents, singly or in combination.

The bright nickel layer deposited on top of the semibright one may range in thickness from 5 to 8 μm (0.2 to 0.3 mil), or about 20 to 35% of the total nickel thickness. Ideally, it should be plated from a bath that is compatible with the semibright additive, or additives, because in most double-layer systems the semibright additive functions as either a brightener or an auxiliary brightener in the bright nickel bath.

Triple-layer coatings are similar to double-layer coatings except that a thin, high-sulfur-containing layer is deposited between the semibright and bright layers. The thin layer must contain greater than 0.15 wt% S. Some of the requirements for double- and triple-layer nickel coatings are summarized in Table 3. Why multilayer coatings improve corrosion performance is discussed in the section "Corrosion Performance" in this article.

Table 3 Requirements for double- or triple-layer nickel coatings

Type of nickel coating[(a)]	**Specific elongation, %**	**Sulfur content, wt%**	**Thickness as a percentage of total nickel thickness**	
			Double-layer	**Triple-layer**
Bottom (s--semibright)	Greater than 8	Less than 0.005	Greater than 60 (but at least 75 for steel)	Greater than 50 (but not more than 70)
Middle (b--high-sulfur bright)	. . .	Greater than 0.15	. . .	10 max
Top (b--bright)	. . .	Between 0.04 and	Greater than 10, but less than 40	Equal to or greater than 30

(a) s,semibright nickel layer applied prior to bright nickel; b, fully bright nickel layer that contains the amount of sulfur specified

Microdiscontinuous Chromium. Decorative, electrodeposited nickel coatings, whether single- or multilayer, are most often used in combination with electrodeposited chromium. The thin layer of chromium, initially applied over nickel to prevent tarnishing, now provides added resistance to corrosion because of the developments discussed in this and the next section.

Conventional or regular chromium deposits are low-porosity coatings, whereas microdiscontinuous chromium deposits have a high, controlled degree of microporosity or microcracking. Controlled microporosity or microcracking in the chromium is achieved by depositing a special nickel strike on top of the bright nickel layer just prior to chromium plating. When it is plated over with chromium, the thin layer of nickel, usually about 1 to 2 μm (0.04 to 0.08 mil), helps create microcracks or micropores in the chromium. Microporosity may also be achieved without the use of a special nickel layer by means of the Pixie process, a patented process that involves postplating treatment of the chromium to increase porosity on a microscopic scale. Traditionally, the chromium is deposited from conventional hexavalent processes, but within the last ten years, trivalent chromium plating processes have grown in popularity.

Microcracked chromium is produced by depositing the thin layer of nickel from a special bath formulated to produce nickel with a high internal tensile stress. When the chromium deposit is chromium plated, the thin nickel and the chromium then crack. Varying the conditions under which the nickel layer is deposited can provide variations in the crack density over a range of from 30 cracks/mm (750 cracks/in.) to 80 cracks/mm (2000 cracks/in.). The nickel bath usually consists of a basic nickel chloride electrolyte with additives that provide additional stress, such as the ammonium ion. Boric acid is not used, but other buffers such as the acetate ion may be added. Proprietary organic additives are also used to enhance the brightness and the ability of the deposit to crack, especially in the low-current-density areas. Temperature and pH are controlled to vary the crack density; low temperature (23 °C, or 73 °F) and high pH (4.5) favor higher crack densities; high temperature (36 °C, or 97 °F) and low pH (3.5) favor lower crack densities. Cracking of the chromium deposit must occur subsequent to chromium plating. Aging or the use of a hot water dip may be necessary to promote the formation of all microcracks.

Microporous chromium is produced from Watts-type nickel baths using air agitation and containing very fine inert particles, usually inorganic, and the normal additives used for bright nickel plating. Chromium, plated over the resulting nickel-particle matrix, deposits around the particles, creating pores. The nickel baths are operated much like bright nickel solutions, with the exception that filtration cannot be performed. In some instances, auxiliary additives permit reduction of the particle concentration in the plating bath and still provide high pore densities. Pore densities can vary according to the concentration of particles, agitation rates, and additives. Generally, a minimum pore density of 100 pores/mm^2 (64,000 pores/in.^{2}) is specified. In either case, chromium thicknesses should not be allowed to exceed about 0.5 μm (0.02 mil) or the cracks and pores will start to heal.

Microcracked chromium deposits can also be produced directly from chromium baths by increasing thickness, or by depositing chromium over chromium. The latter, dual-layer chromium technique is no longer popular.

Corrosion Performance. The remarkable corrosion resistance of modern decorative nickel-plus-chromium coatings depends on the use of multilayer nickel in combination with microdiscontinuous chromium. The improved performance of multilayer nickel coatings is due to the fact that the combination of layers of nickel have different electrochemical reactivities. If one measures the corrosion potentials of various nickel deposits in the same electrolyte, one finds that the bright nickel deposits display more active dissolution potentials than do the semibright nickels. If bright and semibright nickel deposits (for example, in the form of foils separated from the substrate) are electrically connected in the electrolyte, electrons will flow from the bright nickel to the semibright nickel. The result is that the rate of corrosion of the bright nickel is increased, whereas the rate of corrosion of the semibright nickel is decreased. In a composite coating consisting of bright nickel over semibright nickel, this is manifested by enhanced lateral corrosion of the bright nickel layer and delayed penetration of the semibright nickel layer.

The extent to which bright nickel protects the underlying semibright nickel layer by sacrificial action is dependent on the difference between the corrosion potentials of the semibright and bright nickel. The difference should be at least 100 mV (as measured by the simultaneous thickness and electrochemical potential, or STEP test, described in the section "Quality Control of Nickel Plating" in this article), differences in potential are beneficial, especially in low-current-density areas of complicated parts. If the difference becomes too great, appearance suffers because of the accelerated corrosion of the bright nickel layer; that is, there is an optimum value that represents a compromise between preventing basis metal attack and controlling superficial corrosion. The result is that penetration of the coating and exposure of the underlying substrate occur slowly. Multilayer nickel coatings are thus more protective than single-layer bright nickel coatings of equal thickness.

The rate of pit penetration through the nickel layers varies inversely with the number of microdiscontinuities in the chromium layer. Pit penetration may occur rapidly with low-porosity, conventional chromium. When corrosion takes place at a pore in conventional chromium, the large cathodic area of chromium surrounding the pore accelerates the corrosion of the nickel, and pitting may occur rapidly. With microdiscontinuous chromium, a large number of microscopic pores or cracks are deliberately induced in the chromium deposit so that corrosion can start at many sites. The available corrosion current has to be spread over a myriad number of tiny corrosion cells, so that the rate of corrosion of the nickel is greatly reduced. For example, the approximate depth of pitting of nickel after 16 h of CASS testing (ASTM B 368, "Copper-Accelerated Acetic Acid Salt Spray [Fog] Testing") was 10 to 20 μm with conventional chromium and 1 to 6 μm with microdiscontinuous chromium.

Corrosion studies conducted by plating suppliers, nickel producers, and groups such as ASTM Committee B-8 have confirmed that multilayer nickel coatings are significantly more protective than single-layer bright nickel coatings, that microdiscontinuous chromium coatings provide more protection than conventional chromium coatings, and that the corrosion protection of decorative, electroplated nickel-plus-chromium coatings is directly proportional to nickel thickness and to the ratio of semibright and bright nickel in multilayer coatings. Table 4 is based on the results of a study conducted at the LaQue Center for Corrosion Technology, Wrightsville Beach, NC, and it summarizes the types of coatings that protected standard panels from corrosion for more than 15 years outdoors in a severe marine atmosphere.

Table 4 Coating systems on steel giving best performance after 15 years of outdoor marine exposure and 96 h of CASS testing

Type and thickness of coating, µm			ASTM performance ratings[(a)]	
Copper	**Nickel[(b)]**	**Chromium[(c)]**	**Outdoor marine, 15 years**	**CASS, 96 h**
. . .	38d	1.5 mc	10/8	10/8
12	26d	1.5 mc	10/9	10/8
. . .	38d	0.25 mp	10/7	10/7
12	26d	0.25 mp	10/9	10/7

Note: CASS testing ("Copper-Accelerated Acetic Salt Spray [Fog] Testing") is conducted according to ASTM B 368.

(a) A two-number system has been adopted by ASTM for rating panels after corrosion testing. The first, the protection number, is based on the percentage of the base metal that is defective due to corrosion. A rating of 10 on steel indicates that the panel did not rust. The second, the appearance number, is similarly based on percentage of defective area, but it rates the extent to which corrosion of the base metal as well as superficial corrosion, detract from the overall appearance. Appearance ratings of 7, 8, or 9 indicate that 0.25 to 0.5%, 0.1 to .25%, or 0 to 0.1% of the area, respectively, is defective due to superficial staining and corrosion.

(b) d, double layer. The double-layer nickel coatings in the program differed in reactivity. For details see G.A. DiBari and F.X. Carlin, Decorative Nickel/Chromium Electrodeposits on Steel--15 Years Corrosion Performance Data, *Plating and Surface Finishing,* May 1985, p 128.

(c) mc, microcracked; mp, microporous. The type of microcracked chromium used in this study is based on the addition of selenium compounds to a conventional chromium bath to obtain microcracking. Consistent crack patterns were obtained at the chromium thicknesses given in the table.

Standards and Recommended Thicknesses. ASTM B 456 provides information on specific requirements for decorative nickel-plus-chromium coatings to achieve acceptable performance under five different conditions of service. The standard defines several classes of coatings that differ in thickness and type, and it classifies the various coating systems according to their resistance to corrosion. The standard specifies the requirements for double- and triple-layer nickel coatings (Table 3), and it gives the classification numbers of coatings appropriate for each service condition number. For example, Table 5 specifies decorative nickel-plus-chromium coatings on steel.

Table 5 Decorative nickel-plus-chromium coatings on steel

Service condition number (typical applications)	Coating designation[(a)]	Minimum nickel thickness, µm
SC 5--Extended very severe (exterior automotive where long-time corrosion protection is a requirement)	Fe/Ni35d Cr mc	35
	Fe/Ni35d Cr mp	35
SC 4--Very severe (exterior automotive, boat fittings)	Fe/Ni40d Cr r	40

	Fe/Ni30d Cr mp	30
	Fe/Ni30d Cr mc	30
SC 3--Severe (patio and lawn furniture, bicycles, hospital furniture and cabinets)	Fe/Ni30d Cr r	30
	Fe/Ni25d Cr mp	25
	Fe/Ni25d Cr mc	25
	Fe/Ni40p; Cr r	40
	Fe/Ni30p Cr mp	30
	Fe/Ni30p Cr mc	30
SC 2--Moderate service (stove tops, oven liners, office furniture, golf club shafts, plumbing fixtures and bathroom accessories)	Fe/Ni20b Cr r	20
	Fe/Ni15b Cr mp	15
	Fe/Ni15b Cr mc	15
SC 1--Mild (toaster bodies, interior automotive accessories, trim for major appliances, fans, light fixtures)	Fe/Ni10b Cr r	10

(a) b, electrodeposited single-layer bright nickel; d, double-layer or multilayer nickel coating; r, regular or conventional chromium; mc, microcracked chromium; mp, microporous chromium. The numerals in the designations denote the thickness of the nickel coating in microns. The thickness of the chromium is assumed to be 0.3 μm unless otherwise specified. When permitted by the purchaser, copper may be used as an undercoat for nickel, but it cannot be substituted for any of the part of the nickel specified. Results of several test programs have raised doubt about whether coating systems involving regular chromium are satisfactory for SC 4 and SC 3.

The service condition number characterizes the severity of the corrosion environment, 5 being the most severe and 1 being the least severe. The classification number is a way to specify the details of the coating in an abbreviated fashion. For example, the classification number Fe/Ni30d Cr mp indicates that the coating is applied to steel (Fe) and consists of 30 μm of double-layer nickel (d) with a top layer of microporous (mp) chromium that is 0.3 μm thick. (The thickness value of the chromium is not included in the classification number unless its thickness is different from 0.3 μm.) The type of nickel is designated by the following symbols: "b" for electrodeposited single-layer bright nickel, "d" for double- or multilayer nickel coatings, "p" for dull, satin, or semibright nickel deposits, and "s" for polished dull or semibright electrodeposited nickel. The type of chromium is given by the following symbols: "r" for regular or conventional chromium, "mp" for microporous chromium, and "mc" for microcracked chromium.

Decorative nickel-iron alloy plating processes were introduced to conserve nickel and to lower anode material costs by substituting a portion of the nickel with iron. Decorative nickel-iron alloy deposits have full brightness, high leveling, excellent ductility, and good receptivity for chromium. Nickel-iron can be plated on steel, brass, aluminum, zinc die castings, or plastic substrates in either barrel or rack equipment. The operation and the proprietary additives used in commercially available processes are similar to those in conventional bright nickel plating. In addition, the bath requires special additives to stabilize the ferrous and ferric ions so that hydroxide compounds do not form and precipitate. The stabilizers are either complexers or reducing agents, depending on the nature of the proprietary process. The processes should be controlled within the limits recommended by plating supply houses. Deposits on steel or copper that is subsequently chromium plated have had good acceptance for interior applications as a substitute for bright nickel. Decorative nickel-iron alloy deposits are not often used for outdoor applications where corrosion conditions are severe, because the deposits tend to form a fine, superficial brown stain relatively quickly. The rate at which this occurs depends on the iron content of the deposits, and those with less than 15% Fe have been used in outdoor applications.

Engineering and Electroforming Processes

Electrodeposited nickel coatings are applied in engineering applications to modify or improve surface properties, such as corrosion resistance, hardness, wear, and magnetic properties. Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous, mirror-like deposits described in previous sections are not usually required. Nickel electroforming is the specialized use of the nickel plating process to produce or reproduce articles by electroplating onto a mandrel that is subsequently separated from the deposit.

Watts and Nickel Sulfamate Processes. The two most popular solutions for depositing engineering nickel coatings and for electroforming, Watts nickel and nickel sulfamate, have been included in Table 2. The table summarizes the chemical composition, operating conditions, and typical mechanical property data for deposits from these solutions. The Watts solution is relatively inexpensive and easy to control; it has already been discussed.

Nickel sulfamate solutions are widely used for electroforming because of the low internal stress of the deposits, high rates of deposition, and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness, as influenced by geometric factors (the shape and relative positioning of anode and cathode), and by the electrochemical characteristics of the solution (conductivity, cathode polarization, and cathode efficiency). Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those that would be produced in the absence of cathode polarization and cathode efficiency effects. Because of the very high solubility of nickel sulfamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting lower operating temperatures and higher plating rates.

A small amount of nickel chloride is usually added to nickel sulfamate solutions to minimize anode passivity, especially at high current densities. If nickel chloride is not added, sulfur-containing nickel anode materials with about 0.02% S are essential to avoid anodic oxidation of the sulfamate ion, which can result in the uncontrolled and unpredictable production of sulfur-containing compounds that act as stress reducers and that cannot easily be removed from solution. Bromide ions, instead of chloride, are sometimes added to nickel sulfamate solutions to promote anode dissolution.

Nickel sulfamate is so soluble that it cannot be readily recrystallized from solution. It is commercially available as a concentrated solution, usually prepared by reacting high-purity nickel powder with sulfamic acid under controlled conditions. Nickel sulfamate plating solutions are more expensive than those based on commercial grades of nickel sulfate and nickel chloride. The extra cost of using solutions that are as pure as possible is more than offset by savings in the preliminary purification procedures necessary otherwise.

Prolonged use of sulfamate solutions at temperatures above 60 °C (140 °F) or at a pH of less than 3.0 can hydrolyze the nickel sulfamate to the less soluble form of nickel ammonium sulfate. The ammonium and sulfate ions produced from the hydrolysis increase the internal tensile stress and hardness of the deposits.

Nickel electrodeposited from a well-purified sulfamate bath containing no stress-reducing agent and operated at 46 °C (115 °F), a pH of 4.0, and a current density of 2.0 A/dm^2 (20 A/ft^2) has a residual tensile stress varying from 15 to 40 MPa (2 to 6 ksi). The stress in a deposit produced from a similarly operated Watts bath would be about 170 MPa (25 ksi).

Sulfamate nickel plating baths are especially useful for applications requiring low residual stress in the electrodeposited nickel, such as in electroforming, and for coating objects that are susceptible to fatigue cracking. Steel crankshafts that are nickel plated for resistance to corrosion and wear should be coated with a low-stress nickel deposit, such as sulfamate nickel, to minimize loss of fatigue strength. The fatigue limit of nickel-plated steel is reduced almost proportionally to the amount of residual tensile stress in the nickel plate, and the use of compressively stressed deposits provides additional benefits.

Other nickel plating solutions for engineering applications are listed in Table 6, along with available mechanical properties of the deposits. Many of these solutions were developed to meet specific engineering requirements; all are used to a lesser extent than Watts and nickel sulfamate solutions.

Table 6 Other nickel plating solutions and some properties of the deposits

Type	Composition[(a)],g/L	pH	Temperature, °C	Cathode current density, A/dm^2	Vickers hardness, 100 g load	Tensile strength, MPa	Elongation, %	Internal stress, MPa
Fluoborate	Nickel fluoborate, 225-300 Nickel chloride, 0-15 Boric acid, 15-30	2.5-4	38-70	3-30	125-300	380-600	5-30	90-200
Hard nickel	Nickel sulfate, 180 Ammonium chloride, 25 Boric acid, 30	5.6-5.9	43-60	2-10	350-500	990-1100	5-8	300
All-chloride	Nickel chloride, 225-300 Boric acid, 30-35	1-4	50-70	2.5-10	230-260	620-930	4-20	275-340
All-sulfate	Nickel sulfate, 225-410 Boric acid, 30-45	1.5-4	38-70	1-10	180-275	410-480	20	120
Sulfate chloride	Nickel sulfate, 150-225 Nickel chloride, 150-225 Boric acid, 30-45	1.5-2.5	43-52	2.5-15	150-280	480-720	5-25	210-280
High sulfate	Nickel sulfate, 75-110 Sodium sulfate, 75-110 Ammonium chloride, 15-35 Boric acid, 15	5.3-5.8	20-32	0.5-2.5	. . .	. . .	. . .	. . .
Black nickel (sulfate bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24-32	0.15	. . .	. . .	. . .	. . .
Black nickel	Nickel chloride, 75 Zinc chloride, 30	5.0	24-32	0.15-0.6	. . .	. . .	. . .	. . .

(chloride bath)	Ammonium chloride, 30 Sodium thiocyanate, 15							
Nickel phosphorus	Nickel sulfate, 170 or 330 Nickel chloride, 35-55 Boric acid, 0 or 4 Phosphoric acid, 50 or 0 Phosphorous acid, 2-40	0.5-3.0	60-95	2-5	. . .	. . .	. . .	. . .

(a) The formulas of the compounds in the table are as follows: nickel fluoborate, $Ni(BF_4)_2$; nickel sulfate, $NiSO_4 \cdot 6H_2O$; nickel chloride, $NiCl_2 \cdot 6H_2O$; boric acid, H_3BO_3; ammonium chloride, NH_4Cl; ammonium sulfate, $(NH_4)_2SO_4$; sodium sulfate, Na_2SO_4; phosphoric acid, H_3PO_4; phosphorous acid, H_3PO_3; zinc sulfate, $ZnSO_4 \cdot 7H_2O$; zinc chloride, $ZnCl_2$; sodium thiocyanate, NaSCN.

Fluoborate. The fluoborate solution listed in Table 6 can be used over a wide range of nickel concentrations, temperatures, and current densities. The fluoborate anion is aggressive, and some materials that contact the solution are chemically attacked. Silica filter aids cannot be used on a continuous basis, although cellulose filters are satisfactory. Lead, titanium, and high-silicon cast iron are readily attacked. Stainless steels containing 20% Cr, 25 to 30% Ni, and 2 to 3% Mo are resistant. Anode materials can be encased in Vinyon, polypropylene, or Orlon anode bags to prevent insoluble particles and anode residues from entering the plating solution; nylon bags are unsuitable. Only sleeve-type glass electrodes for pH measurement should be used because of the formation of relatively insoluble potassium fluoborate with permanent junction types. The mechanical and physical properties of deposits produced by the fluoborate bath are similar to those from Watts solutions. The nickel fluoborate solution has been used primarily for high-speed deposition of thick nickel.

Hard Nickel. Developed especially for engineering applications, this solution is applied where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required (without the use of sulfur-containing organic addition agents). Close control of pH, temperature, and current density is necessary for this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature. The internal stress is slightly higher than in deposits from Watts solutions. The disadvantages of the hard nickel bath are its tendency to form nodules on edges and the low annealing temperature (230 °C, or 450 °F) of its deposits. Hard nickel deposits are used primarily for buildup or salvage purposes. For optimum results, the ammonium ion concentration should be maintained at 8 g/L (1.1 oz/gal). In those applications where the part being plated is not going to be exposed to elevated temperatures in service, it is simpler to add organic compounds such as saccharin, p-toluene sulfonamide, p-benzene sulfonamide, or other carriers to Watts or sulfamate solutions to achieve hardness without increased internal stress. Because the additives introduce 0.03% S (or more), this approach cannot be used for parts that will be exposed to high temperatures where sulfur severely embrittles the nickel deposit.

All-Chloride. The principal advantage of the all-chloride bath (Table 6) is its ability to operate effectively at high cathode current densities. Other advantages include its high conductivity, its slightly better throwing power, and a reduced tendency to form nodular growths on edges. Deposits from this electrolyte are smoother, finer-grain, harder, and stronger than those from Watts solutions, and more highly stressed. Because of the partial solubility of lead chloride, lead cannot be used in contact with the all-chloride solution. Mists from this solution are corrosive to the superstructure, vents, and other plant equipment, if not well protected. The solution has been used to some extent for salvaging undersize or worn shafts and gears.

All-sulfate has been applied for electrodepositing nickel where the principal or auxiliary anodes are insoluble. For example, insoluble auxiliary or conforming anodes may be required to plate the insides of steel pipes and fittings. To prevent pitting, hydrogen peroxide may be added to all-sulfate solutions, provided they contain no wetting agents or organic stress reducers. Oxygen is evolved at insoluble anodes in the all-sulfate solution, and as a result, the nickel concentration and pH decrease during plating. The pH is controlled and the nickel ion concentration is maintained by adding nickel carbonate. Another procedure that has been used in low-pH solutions replenishes the nickel electrolytically by employing a replenishment tank with nickel anodes; the current in the replenishment tank is periodically reversed to keep the nickel anodes actively dissolving in the absence of chlorides. The insoluble anodes in all-sulfate solutions may be lead, carbon, graphite, or platinum. If a small anode area is required, solid platinum (in the form of wire) may be used; for large anode areas, platinum-plated or platinum-clad titanium is recommended. In some forms, carbon and graphite are too fragile; lead has the disadvantage of forming loose oxide layers, especially if it is immersed in other solutions in the course of a plating cycle. In chloride-free solution, pure nickel is almost insoluble and may function as an internal anode if properly bagged.

Sulfate/Chloride. The sulfate/chloride solution given in Table 6 has roughly equivalent amounts of nickel sulfate and nickel chloride and was developed to overcome some of the disadvantages of the all-chloride solution. It has high conductivity and can be operated at high current densities. Although the internal stress of the deposits is higher than in deposits from Watts solutions, the stress is lower than in the all-chloride solution. The other properties are about midway between those for deposits from Watts and all-chloride solutions. Lead may not be used for equipment in contact with this solution because of the high chloride content.

High Sulfate. The high-sulfate bath was developed for plating nickel directly on zinc-base die castings. It may also be used to plate nickel on aluminum that has been given a zincate or comparable surface preparation treatment. The high sulfate and low nickel contents, together with the high pH, provide good throwing power with little attack of the zinc. The deposits are less ductile and more highly stressed than nickel deposited from a Watts bath. For this reason, high sulfate nickel is sometimes used as a thin undercoating for more ductile nickel. In general, the deposition of copper from a cyanide solution directly on zinc-base die castings prior to the deposition of nickel is simpler and more reliable.

Black Nickel. There are at least two formulations for producing black nickel deposits; these incorporate zinc and thiocyanate (CNS^-) ions. Table 6 gives the composition and operating conditions for a sulfate and a chloride black nickel plating bath. The process was developed for decorative reasons--color matching and blending. The black nickel deposit has little wear or corrosion resistance and is usually deposited over a layer of nickel deposited from a bright or dull nickel plating solution. It is in commercial use, but it is limited in its applications.

Nickel phosphorus solutions result in the electrodeposition of nickel phosphorus alloys that are analogous to electroless deposits using sodium hypophosphite as the reducing agent. The hardness of the electrolytic deposits can be increased by heat treatment in the same way that the hardness of electroless nickel deposits can be increased, with maximum hardness occurring at 400 °C (750 °F). The phosphorus content of the deposits is best controlled by frequent additions of phosphite or phosphorous acid. The electrodeposition of nickel phosphorus alloys is receiving increased attention because deposits with greater than 10% P are amorphous and therefore have enhanced resistance to corrosion.

Nickel Alloy Plating and Composites. Although discussion of alloy plating is beyond the scope of this article, it should be noted that nickel alloy plating processes of commercial importance include nickel-iron (without brighteners), nickel-cobalt, nickel-palladium, and tin-nickel. An alloy plating process that is growing in importance is zinc-nickel, containing 8 to 12% Ni. In addition, the incorporation of inert particles within a nickel matrix is possible, and coatings that incorporate silicon carbide, diamonds, mica, polytetrafluoroethylene, and other materials are being applied for engineering purposes. Detailed information is available in the articles "Nickel Alloy Plating" and "Zinc Alloy Plating" in this Volume.

Quality Control of Nickel Plating

Achieving high quality involves controlling the bath composition, the purity of the plating solution, and the thickness and uniformity of the deposits. Eliminating rejects, troubleshooting, and the testing of deposits are important aspects of process and product control.

Control of Solution Composition. Control of the composition of the plating bath is one of the most important factors contributing to the quality of nickel deposits. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter, the composition and pH of the solution must be controlled within specified limits, and contamination by metallic and organic substances must be prevented.

Purification Techniques and Starting Up a New Bath. Before any freshly prepared nickel plating bath is used, contaminants such as iron, copper, zinc, and organics present in trace quantities in commercial salts must be removed to obtain the best results. Several treatments are available for purifying a freshly prepared nickel plating solution.

High-pH treatment consists of adding nickel carbonate to the hot solution until a pH of 5.0 to 5.5 is obtained. This precipitates the hydroxides of metals such as iron, aluminum, and silicon, which in turn frequently absorb other impurities. Addition of hydrogen peroxide oxidizes iron to the ferric state, making it more easily precipitated at high pH, and frequently destroys organic impurities.

Treatment with activated carbon removes organic impurities.

Electrolytic purification removes most of the harmful metallic and organic impurities. A complete purification procedure for a Watts solution would comprise the following steps:

1. Use a separate treatment tank (not the plating tank) to dissolve the nickel sulfate and nickel chloride in hot water at 38 to 49 °C (100 to 120 °F) to about 80% of desired volume.
2. Add 1 to 2 m/L (0.8 to 1.6 pints/100 gal) of 30% hydrogen peroxide (agitate briefly and allow to settle for 1 h).
3. Add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) activated carbon and agitate thoroughly.
4. Heat to 66 °C (150 °F), then add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) of nickel carbonate to the solution, with agitation to adjust the pH to 5.2 to 5.5. More nickel carbonate may be required and the mixture should be stirred to assist the dissolution of the carbonate. Allow to settle 8 to 16 h.
5. Filtering into the plating tank.
6. Add and dissolve boric acid; add water to bring bath up to its desired volume.
7. Electrolytically purify by using a large area of nickel plated corrugated steel sheets as cathodes. The average cathode current density should be 0.5 A/dm^2 (5 A/ft^2), and treatment should continue until 0.5 to 1.3 A · h/L (2 to 5 A · h/gal) have passed through the solution. The solution should be agitated and the temperature held at 49 to 60 °C (120 to 140 °F). It is useful to prepare deposits at normal current densities at some point to check appearance, stress, and sulfur content. If not acceptable, continue dummying until the properties are acceptable.
8. Remove the dummy cathodes and adjust the pH of the solution to the desired value.

Controlling the Main Constituents. The following basic constituents of nickel plating baths must be regularly controlled: the nickel metal content; the chloride concentration; the boric acid; and any organic addition agents. Nickel metal concentration is maintained between 60 and 80 g/L (8.0 and 10.5 oz/gal) in most commercial applications. It is desirable to have a minimum of 23 g/L (3 oz/gal) of nickel chloride in the solution to promote anode corrosion. (The chloride content is not critical for anode corrosion when sulfur-activated anode materials are used.) Boric acid is the most commonly used buffering agent for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance. It is available in a purified form and is inexpensive. Organic addition agents must be controlled within the limits specified by the suppliers of proprietary processes, and they must be replenished due to losses from dragout, electrolytic consumption, and the effects of carbon filtration (or batch treatment).

Procedures exist for chemical analysis of nickel, chloride, boric acid, and organic addition agents in nickel plating solutions, and modern instrumental techniques are available to monitor the main ingredients on a regular basis with improved precision. High-performance liquid chromatography is one of the improved techniques for controlling organics that is growing in popularity.

Controlling pH, Temperature, Current Density, and Water Quality. The pH of the nickel plating solution will rise during normal operation of the bath, necessitating regular additions of acid to maintain the pH within the prescribed limits. A decrease in pH accompanied by a decrease in nickel ion concentration indicates that the process is not functioning properly.

The operating temperature may have a significant effect on the properties of the deposits, and it should be maintained within specified limits (±2 °C) of the recommended value. In general, most commercial nickel plating baths are operated between 38 to 60 °C (100 to 140 °F).

The nickel plating process should be operated at specified current densities by estimating the surface area of the parts and calculating the total current required. The practice of operating the process at a fixed voltage is not recommended.

Controlling cathode current density is essential for accurately predicting average nickel thickness, for achieving uniform coating thickness on complicated shapes, and for producing deposits with consistent and predictable properties.

Since current density determines the rate of deposition, it must be as uniform as possible to achieve uniformly thick nickel deposits. The nickel plating solution has an electrical resistance, and almost all components to be plated have prominent surfaces that are nearer the anode than recessed areas. The current density is greater at the prominences because the anode-to-cathode distance is shorter and therefore has less electrical resistance. The apportioning of the current in this way is called *current distribution.* This means that the recessed areas receive a thinner nickel deposit than the prominent ones. Current distribution is controlled by proper rack design and proper placement of components on those racks, by the use of nonconducting shields and baffles, and by the use of auxiliary anodes, when necessary. With care, relatively good thickness distribution can be achieved.

The quality of the water used in making up the bath and in replacing water lost by evaporation is important. Demineralized water should be used, especially if the local tap water has a high calcium content (greater than 200 ppm). Filtering the water before it is added to the plating tank is a useful precaution to eliminate particles that can cause rough deposits.

Controlling Impurities. Inorganic, organic, and gaseous impurities may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities from the plating shop can improve the quality of the deposits, as well as productivity and profitability. The presence of small quantities of inorganic or organic contamination may result in plating defects.

Inorganic contaminants arise from numerous sources, including nickel salts of technical grade, hard water, carryover from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, and dirt from structures above the tank and from parts that fall into the solution and are not removed. The following table lists maximum limits for metallic impurities in nickel plating baths:

Contaminant	**Maximum concentration, ppm**
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20
Calcium	[a]

Note: The limits may be different when several contaminants are present at the same time, and complexing agents are a part of the solution formulation.

(a) pH-dependent; will precipitate at the saturation point

The degree of contamination by many inorganic materials may be controlled by continuous filtration and dummying, that is, by electrolysis of the plating solution at 0.2 to 0.5 A/dm^2 (2 to 5 A/ft^2). This may be accomplished on a batch basis or continuously by installing a dummy compartment and overflow dam at one end of the plating tank. Solution from the filter is pumped into the bottom of the dummy compartment, up past the corrugated cathode sheets, over the dam, into the plating section of the tank, out through a bottom outlet at the far end of the tank, and back to the filter. Solid particles and soluble metallic impurities (for example, copper, zinc, lead) are removed simultaneously by this procedure.

Organic contaminants may arise from many sources, including buffing compounds, lubricating oil dropped from overhead equipment, sizing from anode bags, weaving lubricants on plastic anode bags, uncured rack coatings or stopoff lacquers, adhesives on certain types of masking tape, decomposition products from wetting agents, organic stabilizers in hydrogen peroxide, paint spray, and new or patched rubber tank linings. Many organic contaminants can be effectively removed from nickel plating solutions by adsorption on activated carbon on either a batch or a continuous basis. On a batch basis, the solution is transferred to a spare tank, heated to 60 to 71 °C (140 to 160 °F), stirred for several hours with a slurry of 6 g/L (5 lb/100 gal) minimum of activated carbon, permitted to settle, and then filtered back into the plating tank. It is usually necessary to do a complete chemical analysis and adjust the composition of the solution after this type of treatment.

For solutions in which organic contamination is a recurring problem, continuous circulation of the solution through a filter, coated at frequent intervals with small amounts of fresh activated carbon, is recommended. When continuous carbon filtration is used, the wetting agent in the solution must be replenished and controlled more carefully, to prevent pitting of the nickel deposits.

Gaseous contamination of nickel plating solutions usually consists of dissolved air or carbon dioxide. Dissolved air in small amounts may lead to a type of pitting characterized by a teardrop pattern. Dissolved air in the plating solution usually can be traced to entrainment of air in the pumping system when the solution is circulated. If this occurs, the circulating pump and valves should be checked and modified, if necessary. Nickel plating solutions can be purged of dissolved air by heating to a temperature at least 6 °C (10 °F) higher than the normal operating temperature for several hours. The solution is cooled to the operating temperature before plating is resumed. Dissolved carbon dioxide in a nickel plating solution is usually found after nickel carbonate has been added to raise the pH, and it is liberated from warm nickel plating solutions after several hours. If solutions containing carbon dioxide are scheduled for immediate use, they should be purged by a combination of heating and air agitation for approximately 1 h at 6 °C (10 °F) or more above the normal plating temperature.

Effects of Impurities on Bright Nickel Plating. The presence of impurities is especially troublesome in decorative nickel plating. Contamination by zinc, aluminum, and copper is most often caused by the dissolution of zinc-base die castings that have fallen from racks into the plating tank and have been permitted to remain there. Inadequate rinsing before nickel plating increases the drag-in of metallic elements. The presence of cadmium and lead may be attributed to a number of sources, including lead-lined equipment and tanks, impure salts, and drag-in of other plating solutions on poorly rinsed racks. Chromium is almost always carried into the nickel solution on rack tips that have not been chromium stripped, or on poorly maintained racks that have been used in a chromium plating tank and have trapped chromium plating solution in holes, pockets, and tears in the rack coating.

Metallic contaminants affect bright nickel deposition in several ways. Aluminum and silicon produce hazes, generally in areas of medium to high current density. Aluminum and silicon may also cause a fine roughness called "salt and pepper" or "stardust." Iron produces various degrees of roughness, particularly at high pH. Calcium contributes to needlelike roughness as a result of the precipitation of calcium sulfate when calcium in solution exceeds the saturation point of 0.5 g/L (0.06 oz/gal) at 60 °C (140 °F). Chromium as chromate causes dark streaks, high-current-density gassing, and possibly peeling. After reduction to the trivalent form by reaction with organic materials in the solution or at the cathode, chromium may produce hazing and roughness effects similar to those produced by iron, silicon, and aluminum. Copper, zinc, cadmium, and lead affect areas of low current density, producing hazes and dark-to-black deposits.

Organic contaminants may also produce hazes or cloudiness on a bright deposit, or they can result in a degradation of mechanical properties. Haze defects may appear at any current density, or they may be confined to narrow current density ranges.

Mechanical defects producing hairline cracks, called *macrocracking,* may be encountered if the coating is sufficiently stressed as a result of solution contamination. These cracks usually appear in areas of heavier plating thickness (higher current density) but are not necessarily confined to those areas.

Eliminating Rejects/Troubleshooting. The production of defective plated parts or rejects may be associated with the presence in solution of soluble and insoluble impurities. The nature of the coating defect is often an indication of the source of the problem. Common defects include roughness, pitting, blistering (often associated with poor preparation of the surface prior to plating), high stress and low ductility, discoloration, burning at high-current-density areas, and failure to meet thickness specifications.

Roughness is usually caused by the incorporation of insoluble particles in the deposit. In bright nickel baths, chlorine generated at an auxiliary anode that is close to the cathode can react with organic additives to form an insoluble material that is incorporated in the deposit. Insoluble particles may enter the solution from many sources: incomplete polishing of the base metal so that slivers of metal protrude from the surface, incomplete cleaning of the surface so that soil particles remain on the surface, detached flakes of deposit from improperly cleaned racks, dust carried into the tank from metal polishing operations and other activities, insoluble salts and metallic residues from the anode, and others.

Roughness from incomplete polishing, cleaning, and inadequate rack maintenance is avoided by good housekeeping, regular inspection, and control. Roughness caused by dust can be controlled by isolating surface preparation and metal polishing operations from the plating area, by providing a supply of clean air, and by removing dirt from areas near and above the tanks. Roughness caused by the precipitation of calcium sulfate can be avoided by using demineralized water. Continuous filtration of the plating solution so as to turn over the solution at least once an hour is important for minimizing roughness problems. Anode residues must be retained within anode bags, and care should be taken not to damage the bags or allow the solution level to rise above the tops of the bags.

Pitting is caused by many factors, including adhesion of air or hydrogen bubbles to the parts being plated. Air should be expelled as already mentioned. Pitting from adherent hydrogen bubbles can result from a solution that is chemically out of balance, has too low a pH, or is inadequately agitated. Other sources of pitting include incorrect racking of complicated components, too low a concentration of wetting or antipitting agents, the use of incompatible wetting agents, the presence of organic contaminants, the presence of copper ions and other inorganic impurities, incomplete cleaning of the base material, and incomplete dissolution of organic additives that may form oily globules. Pitting is therefore avoided by maintaining the composition of the plating solution within specified limits, controlling the pH and temperature, and preventing impurities of all kinds from entering the solution.

Blistering may be associated with poor adhesion resulting from poor or incorrect surface preparation prior to plating. Nickel can be deposited adherently on most metals and alloys, plastics, and other materials by following standard methods of preparation and activation, including the proper use of intermediate deposits such as cyanide copper, acid copper, and acid nickel chloride strikes. Standard procedures for the preparation of materials prior to electroplating can be found in handbooks and in the *Annual Book of ASTM Standards,* Volume 0.205. Blistering may also be related to incomplete removal of grease, dirt, or oxides, formation of metal soaps from polishing compounds, or formation of silica films from cleaning solutions. In the case of zinc-base die castings or aluminum castings, blistering during or immediately after plating may be due to surface porosity and imperfections that trap plating solution under the coating.

High stress and low ductility usually occur when organic addition agents are out of balance, and also because of the presence of organic and inorganic impurities. Solutions must be maintained in a high state of purity.

Discoloration in low-current-density areas is most likely the consequence of metallic contamination of the plating solution. The effects can be evaluated systematically by plating over a reproducible range of current densities on a Hull cell cathode. Hull cells are available from plating supply houses and are shaped so that nickel can be deposited onto a standard panel over a predictable range of current densities. The variation in current density over the face of the panel is achieved by placing the panel at a specified angle to the anode. Bent panels that are L-shape and plated with the recessed area facing the anode can also be used to assess discoloration at low-current-density areas, and they may provide information on roughness problems.

Burning at high current densities can be caused by applying the full load on the rectifier to the lowest parts on a rack as it is lowered into the tank. This can be controlled by applying a reduced load or ramping the current during immersion of the rack. Burning can also be caused by exceeding the recommended maximum cathode current density, the presence of phosphates in solution introduced via contaminated activated carbon, or incorrect levels of organic additives.

Failure to meet thickness specifications is most frequently due to the application of too low a current and/or too short a plating time. This can be avoided by measuring the area of the parts to be plated, then calculating the total current required for a specified current density and plating for the appropriate time (see Table 1). Another major cause of failure to meet thickness requirements is nonuniform distribution of current leading to insufficient deposition in low-current-density areas. Poor electrical contacts and stray currents can also cause thin deposits, and anode and cathode bars, hooks, and contacts should be kept clean.

Controlling and Testing Deposit Properties. The requirements for testing electrodeposited nickel coatings may vary significantly, depending on the application. In almost all decorative applications, the appearance and the thickness of the deposit should be controlled and monitored on a regular basis. The plated surface must be free of defects such as blisters, roughness, pits, cracks, discoloration, stains, and unplated areas. It must also have the required finish--bright, satin, or semibright. Quality can only be maintained by checking the thickness of a specified number of plated parts. In decorative, electrodeposited multilayer coatings, it is also important to control the sulfur contents of the deposits, the relative thicknesses of individual layers, the ductility of the semibright nickel layer, and the difference in the electrochemical potentials between individual layers. Requirements for corrosion performance and adhesion may also be specified and may require additional testing.

In engineering and electroforming applications, it may be necessary to monitor the mechanical properties, including hardness, tensile strength, ductility, and internal stress, as well as wear resistance and other properties. Some of the more important test methods are briefly outlined below. Additional details can be found in the standard test methods collected in the *Annual Book of ASTM Standards.*

Thickness may be measured using a variety of techniques. The coulometric method described in ISO 2177 and ASTM B 504 can be used to measure the chromium and nickel thicknesses, as well as the thickness of copper undercoats, if present. The coulometric method measures the quantity of electrical energy required to deplate a small, carefully defined area of the component under test. A cell is sealed to the test surface and filled with the appropriate electrolyte, and a cathode is inserted. The component is made the anode, and the circuit is connected to the power supply via an electronic coulometer. By integrating time in seconds with the current passing, the electronic coulometer provides a direct reading in coulombs; modern instruments provide a direct reading of thickness. The completion of the deplating is shown by a marked change in the applied voltage. For routine control of production, it is convenient to monitor nickel thickness nondestructively by means of a magnetic gage, calibrating the gage at intervals with standard samples. Instruments for measuring thickness by beta backscatter, X-ray spectrometry, and eddy current techniques are also available. The traditional method of measuring thickness by microscopic examination of a metallographically prepared cross section of the plated part is still employed, but it is time-consuming, expensive, and destructive.

The simultaneous thickness and electrochemical potential (STEP) test was developed to measure the difference in electrochemical potential between semibright and bright nickel layers in multilayer nickel deposits on parts that are plated in production. It is similar to the coulometric method just described. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved at the same time that the thickness of the individual layers is being measured. For example, with a double-layer nickel coating, a relatively large change in potential occurs when the bright nickel layer has dissolved and the semibright nickel layer begins to be attacked. The potential difference is related to the overall corrosion resistance of the double-layer coating and should be greater than 100 mV. Details can be found in ASTM B 764.

Corrosion testing may be specified and may require the plater to perform accelerated corrosion tests on a specified number of production parts as part of an overall quality assurance requirement. Three accelerated corrosion tests are recognized internationally: the Copper-Accelerated Acetic Acid Salt Spray (CASS), the Corrodkote, and the Acetic Acid Salt Spray tests. The CASS test is the one most widely used. The CASS and Corrodkote tests were developed when conventional chromium was the only type of chromium available; when the accelerated tests are used to evaluate microdiscontinuous chromium coatings, the surface appearance deteriorates more rapidly than in real-world environments. Details of these three tests can be found in ISO 1456 as well as in ASTM standards. The salt spray tests involve the application of the corrosive solution in the form of a spray or fog inside a fog cabinet or room made or lined with glass, rubber, or resistant plastics. The Corrodkote test involves applying a corrosive slurry to parts and exposing them to high, controlled humidity in a suitable chamber or cabinet; the slurry is formulated to simulate road mud containing corrosive salts. The CASS and Corrodkote tests were developed to control the quality of decorative, electrodeposited nickel-chromium-plated parts for exterior automotive use under severe conditions of corrosion and abrasion. CASS and other corrosion test requirements are specified in ASTM B 456 for nickel-plus-chromium coatings applied to steel, zinc alloys, or copper alloys. Similar information for nickel-plus-chromium coatings on plastics is given in ASTM B 604.

Ductility testing is used in decorative nickel plating to test that the percent elongation of semibright nickel deposits is greater than 8, and to verify that bright nickel solutions are in good working condition. The simple test described in ISO 1456 and in ASTM B 489 is based on bending a test strip of the deposit over a mandrel of specified diameter until the two ends of the strip are parallel. Other tests based on hydraulic or mechanical bulge testing are available. The percent elongation can also be determined by traditional mechanical testing by machining a test sample from relatively thick electroformed nickel and subjecting it to a tensile test. Because ductility is affected by the thickness of the coating, ductility should be measured at the actual thickness specified in a specific end use.

Other useful tests described in ASTM standards include adhesion (B 571), internal stress measurements with the spiral contractometer (B 636), and microhardness testing (B 578), among others.

Nickel Anode Materials

Most nickel plating processes are operated with soluble nickel anode materials. Nickel from the anode is converted into ions that enter the plating solution to replace those discharged at the cathode. In addition, the anode distributes current to the parts being plated and influences metal distribution.

The simplest way to satisfy anode requirements is to suspend nickel bars from hooks placed on an anode bar so that the nickel, not the hook, is immersed in the plating solution. Nickel anode materials are encased in cloth anode bags to prevent insoluble anode residues from entering the solution and causing roughness at the cathode. The use of bars or electrolytic nickel strip is still practiced but has been supplanted in most regions of the world by the use of titanium anode baskets. The baskets used in nickel plating are generally made of titanium mesh strengthened by solid strips of titanium at tops, bottoms, and edges. The baskets are encased in cloth anode bags, suspended on the anode bar by hooks that are an integral part of the baskets, and loaded with small pieces of nickel. The mesh facilitates the free flow of plating solution. Baskets that incorporate hoppers at the tops facilitate basket loading and help prevent pieces of nickel from falling into the tank.

Titanium anode baskets were quickly accepted because of their many advantages. The basket anode is large and unchanging, ensuring a uniform anode area giving constant current distribution and consistent thickness for repeat batches of the same work. Anode maintenance involves topping-up the load to keep the baskets filled. Conforming baskets can be made in virtually any size and shape. The anode-to-cathode distance can be made constant, thereby contributing to good current distribution. Lowest-cost, primary forms of nickel can be used to fill the baskets. Baskets can be semiautomatically or automatically filled with nickel, and that practice is growing in progressive plating shops. One limitation is that titanium cannot be used in concentrated fluoborate solutions or those containing fluoride ions; small amounts of fluoride in solution activate titanium, causing it to corrode.

The available forms of nickel for titanium baskets include high-purity electrolytic nickel squares about 25 × 25 mm, pure electrolytic nickel in button-like shapes about 22 mm in diameter, and sulfur-activated, electrolytic nickel button-shape pieces about 25 mm in diameter. Other popular forms of nickel for plating with baskets are made in spherical shapes by a gas-refining process; the spherical forms are also available in sulfur-free and sulfur-containing grades.

The sulfur-activated forms dissolve relatively uniformly at high current densities and at 100% anode efficiency even in the absence of chloride ions, whereas sulfur-free forms dissolve nonuniformly and require the presence of chloride ions in solution to dissolve efficiently. The need for chloride ions is due to the tendency for pure nickel to become passive in nickel sulfate solutions. Although the tendency for passivity persists even in the presence of chlorides, the chloride ion attacks the passive oxide film that forms when current flows through the anode, and nickel can be dissolved through pits on the surface. The sulfur-containing materials do not form oxide films, and they dissolve at low anode potentials. The small amount of sulfur in the nickel lowers the surface resistance to current flow, the practical effect being to reduce power costs. The unique advantage of the spherical forms of nickel is product flowability, which facilitates automatic basket loading and filling of conforming, semicylindrical, and other complicated basket shapes.

The anode affects the quality of nickel primarily through its effect on current distribution and thickness uniformity. Most anode materials available today are made to strict specifications of purity and are unlikely to introduce significant amounts of impurities into the solution.

Environmental, Health, and Safety Considerations

Strict environmental regulations are being imposed on the plating industry worldwide. The major problem facing nickel platers is to prevent nickel and other metallic ions from entering the environment via plant effluents. The most widely used method of removing metallic elements from effluents is to precipitate nickel and other metals in sludges as hydroxides or sulfides. The solid waste is then disposed of in landfills. Because the number of landfill sites is limited, and because disposal of solid waste is expensive, the recovery of metallic elements by applying reverse osmosis, ion exchange, electrotwinning, and other methods is economically appealing. Nickel producers accept nickel-containing sludges for recycling through smelters or special plants. The recovery of metallic elements is technically possible and will become important in the future.

Environmental regulations vary from state to state. Platers need to become familiar with all applicable local regulations and comply with them. Although there was great resistance to compliance in the early 1970s, most electroplaters in the United States are complying with existing regulations. In some cases, the recycling and recovery of salts and metals, coupled with the conservation of water and energy, have led to economies in plating operations that partially offset the cost of compliance.

The adoption and enforcement of strict environmental regulations arises from concern with the possible effects of metal contaminants on human health. Although the general perception is that these health effects are completely understood, the reality is that our knowledge is extremely limited. It is only when metals are present in high concentrations and in very specific forms that they are definitely known to be toxic.

In the nickel plating shop, three types of exposure are possible: Nickel and its compounds may be inadvertently ingested, nickel-containing solutions may be allowed to remain on the skin for long periods of time, and nickel and its compounds may be taken into the body by breathing. Although nickel and its compounds are not considered acutely toxic, it is advisable to avoid ingesting even small amounts of these substances by taking some simple precautions--wearing work gloves, washing one's hands before eating, and not eating in the workplace. Some workers may develop a skin rash or dermatitis after persistent contact with nickel and its salts. People who have become so sensitized should avoid contact with nickel and its compounds. To avoid becoming sensitized, one should limit skin contact with nickel and its compounds. In the plating shop, this may mean wearing work gloves and washing one's hands immediately after coming in contact with nickel plating solutions.

On the basis of available information, enhanced risk of cancer appears to be confined to the inhalation of high concentrations of dusts containing nickel subsulfides and oxides under conditions previously existing in certain nickel refineries. Although similar health problems have not been observed in plating shops and other workplaces where nickel is found, it is recommended that precautions be taken to avoid dispersing nickel-containing dusts or sprays into the air. Airborne concentrations of nickel should be kept below the permissible exposure limits established by law. This is not only the law, but good common sense. Simple housekeeping and personal hygiene can help prevent the release of toxic substances to the environment and minimize the possible effects of metallic contaminants on human health.

Iron Plating

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Introduction

IRON has been electrodeposited for many years. One of the earliest references to iron electroplating is in Langbein's *Electrodeposition of Metals,* published in 1894 as the English translation of a German treatise. In that translation there is a reference to "Mr. Alfred Smee (who made) many discoveries in the deposition of antimony, platinum, gold, silver, iron, copper and zinc. In publishing his experiments, in 1841, he originated the very appropriate term 'electro-metallurgy' for the process of working in metals by means of electrolysis" (Ref 1). A paper published in 1930 was titled "The Production of Electrolytic Iron Printing Plates" (Ref 2). It appears, though, that the largest body of published papers and patents were written in the 1950s and 1960s, although a small number of new papers on this topic are published every year.

Iron has been electroplated from a variety of electrolytes. These include chloride, sulfate, sulfamate, fluoroborate, sulfonate, and various combinations of these electrolytes. Perhaps the widest use of iron plating has been in electroforming, where thicknesses of 6 mm (0.25 in.) are common. The bath parameters of these electroplating solutions are as varied as the parts that are plated in them, and the resulting coatings have widely divergent characteristics according to the specific characteristics desired in the finished product.

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2. W. Safranek, *The Properties of Electrodeposited Metals and Alloys,* 2nd ed., American Electroplaters and Surface Finishers Society, 1986, p 215

Advantages and Limitations

Iron is the least expensive metal available. This is partly because it makes up 5% of the earth's crust, making it second in abundance to aluminum among the metals and fourth in abundance behind oxygen, silicon, and aluminum among the elements. Iron, which largely constitutes the core, is the most abundant element in the Earth as a whole (about 35%). This abundance, plus the fact that iron is easily extracted from concentrated ore sources, is what makes it so inexpensive. In addition, the human body contains approximately 4.5 g of iron. The average adult human requires 10 to 20 mg of dietary iron each day to maintain good health. This human requirement, coupled with the vast abundance of iron around us, makes iron an unlikely candidate for environmental controls, at least on the metal itself. Also, the physical properties of the deposited metal can be altered very easily by adjustments in electrolyte, temperature, pH, and addition agents. The ability to "design" a coating to meet a specific need, coupled with the environmental friendliness of iron, has caused a recent upsurge in interest in this electrodeposited metal.

The primary limitations of iron electrodeposition are the innate corrosion properties that affect all iron and steel, although electrodeposited iron appears to be more corrosion resistant than ordinary iron, probably because of its higher purity. Even with better resistance, a protective coating of some kind must be applied to the deposit to prevent corrosion.

An additional limitation seems to be obtaining consistent properties from one batch of parts to another. There is evidence that iron baths function best when they are run in a full production mode. Intermittent operation creates problems in restoring the electrolyte to proper operating condition. Many baths are highly corrosive to ordinary equipment. Pitting and roughness can be a problem if the bath is not controlled properly. Extreme brittleness can result from the presence of codeposited hydrated Fe(III) or Fe(II) oxide as well as codeposition of organic additive breakdown products.

Principal Applications

Today the principal applications for electrodeposited iron are in the production of solder gun tips, the electroplating of iron onto aluminum automobile engine parts, and the electroforming of iron foils for certain magnetic applications. In the past there was a large market for electroformed stampers, engraving plates, and textile rollers, but these iron applications have been almost totally replaced by nickel plating. However, as environmental concerns about nickel increase, a return to iron plating will become increasingly probable. Interest is increasing in the use of nickel-iron alloys containing up to 40% Fe as a substitute for the more expensive and potentially toxic nickel deposits.

Process Description

Table 1 shows some typical iron plating bath parameters. It should be noted that the addition of various organic additives can change the properties of the deposit to a high degree. These are addressed in the Section "Properties of the Deposited Materials and Modified Surfaces" in this article.

Table 1 Typical iron plating solutions

Bath type	Composition	pH	Temperature, °C	Current density

	Component	**g/L**	**Molarity**		**°C**	**A/m^2**	**A/ft^2**
Sulfate	Fe^{++}	48	0.86	2.8-3.5	32-65	215-430	20-40
	(a)	240	0.86				
Double sulfate	Fe^{++}	36-51	0.64-0.92	2.5-3.5	24-65	215-645	20-60
	(b)	250-400	0.64-1.2				
Chloride	Fe^{++}	84-125	1.5-2.25	0.5-1.0	85 min	215-1075	20-100
	(c)	300-450	1.5-2.25				
	(d)	300	2.7				
Sulfate-chloride	Fe^{++}	60	1.08	2.5-3.5	27-70	215-540	20-50
	(a)	250	0.9				
	(c)	36	0.18				
	(e)	20	0.37				
Fluoborate	Fe^{++}	55	1	3.0-3.5	57-63	430-970	40-90
	(f)	227	1				
	(g)	10	0.17				
Sulfamate	Fe^{++}	75	1.35	2.5-3.5	60 max	215-430	20-40
	(h)	30-38	0.25-0.32				
Sulfonate	Fe^{++}	150	2.7	1.2-1.8	60-82	430-860	40-80
	(g)	50	0.81				
	(i)	275	2.7				

(a) Ferrous sulfate (7-hydrate).

(b) Ferrous ammonium sulfate (6-hydrate).

(c) Ferrous chloride (4-hydrate).

(d) Calcium chloride.

(e) Ammonium chloride.

(f) Ferrous fluoborate.

(g) Sodium chloride.

(h) Ammonium sulfamate.

(i) Ferrous sulfonate

In addition, there are many baths that have been reported for both the electrolytic and electroless deposition of iron alloys. Alloys are attracting more interest as replacements for nickel, but this chapter will address only electrodeposited pure iron deposits.

Processing Equipment

Because many of the electrolytes used in iron plating are very corrosive, it is necessary to choose the most corrosion-resistant materials for the processing equipment. This means at least a lined steel or stainless steel tank. However, considering the potential problems with liners, it is advisable to have tanks made out of polypropylene. The high temperatures of some of the baths make polyethylene a poor choice for tank construction.

Filters should be chlorinated polyvinyl chloride or polypropylene. Magnetically coupled pumps do not work well because of the high molar concentration of most of the solutions. Centrifugal pumps require seals, which do not hold up well in hot acidic solutions. In-tank pump and filter assemblies are highly recommended because any solution that leaves the tank and dries leaves a red-brown stain that can be a major problem in maintaining good housekeeping. There should be provision for regular carbon treatment. Care must be exercised to prevent the pump from aspirating air that aggravates the problem of oxidation.

Agitation can be mechanical or provided by the pump and filter. Air agitation should not be used because it will increase the oxidation of the ferrous to ferric iron that causes brittle, dark deposits.

Heaters should be Teflon-covered titanium except for those to be used in fluoroborate baths, which should be Teflon-coated stainless steel. Steam-heated tanks usually do not get enough for baths with higher temperatures, but they are acceptable for lower-temperature baths.

Anodes should be pure electrolytic iron (often called ARMCO iron) and should be bagged with glass fiber (except in fluoborate solutions) or Dynel anode bags to retain the sludge that comes from the anodes. In certain cases low-carbon steel anodes can be used, but these can cause incorporation of carbon into the deposit, which could cause the deposit to be very hard. This could be a problem if one of the required deposit characteristics is low hardness.

Properties of the Deposited Materials and / or Modified Surfaces

Table 2 shows some of the characteristics of deposits produced in various baths. It also shows a few instances where postplate heat treatment was used to change the stress characteristics of a deposit and some of the changes that additives can make in a deposit.

Table 2 Properties of electrodeposited iron coatings

Basic bath	Additives	Ultimate tensile strength		Elongation, %	Hardness, HV
		MPa	ksi		
Sulfate	None	572-614	83-89	3.0-3.5	250
	NaCl	354	51.4	5.5	200
	Boric acid + urea	. . .	. . .	. . .	480-720
	Oxalic acid	. . .	. . .	. . .	600-615
	NaCl + citric acid(a)	. . .	. . .	. . .	1000-1100
Double sulfate	NaCl + antioxidant	. . .	. . .	. . .	600-700
Chloride	None	421-434	61-63	5.0-18.0	<100
	NaCl	448-593	65-86	4.0-18.0	150-530
	Glycerol	786-883	114-128	. . .	360-380
Sulfate-chloride	Amidopyrine(b)	. . .	. . .	. . .	500-750
Fluoborate	Boric acid	. . .	. . .	. . .	575
Sulfamate	Formic acid(c)	676-1068	98-155	. . .	1200-1500
Sulfonate	Antioxidant 15 g/L	. . .	. . .	. . .	650-750
	Antioxidant 1.5 g/L	. . .	. . .	. . .	350-400

(a) Properties are for parts stress relieved by heat treatment for 1 h at 250 °C (480 °F).

(b) Properties are for parts stress relieved by heat treatment for 2 h at 200-300 °C (392-572 °F).

(c) Properties are for parts stress relieved by heat treatment for 24 h at 190 °C (374 °F).

Other additives can be used in various combinations with various baths. Organic additives (acetic acid, arginine, dextrin, glycerin, glycine, saccharin, sugar, and thiourea) are grain refiners as a general rule. They induce stress by the inclusion of their breakdown products in the coating. Inorganic additives (manganese chloride and potassium chloride) increase conductivity. A wetting agent (sodium lauryl sulfate) can be used to reduce pitting. The additive characteristics overlap each other and can change with current density, temperature, pH, and concentration.

References cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

4. S.T. Packman, unpublished data

Environmental Considerations

Iron metal does not pose any special waste disposal considerations unless associated radicals are hazardous (Ref 3). In fact, most publicly owned treatment works (POTWs) like to see iron introduced into the sewer system because it acts as a "getter" for the sulfides in the system, thereby reducing the hydrogen sulfide that can form. The only waste treatment required for iron baths is the adjustment of the pH to a value within the operating range specified in a facility's waste disposal permit. The only exception to this rule is the fluoroborate bath, which could introduce fluorides to the waste disposal system. Most POTWs have fluoride limits that have to be considered when designing a waste disposal system. Boron also has limits in some geographical areas. Local permitting agencies can provide detailed information. Compared to other metal finishing operations, iron is very easy to keep in compliance.

Reference cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

Health and Safety Considerations

As in all metal finishing operations, good judgment should be exercised when operating an iron plating bath. Eye protection, clothing protection, and gloves should be used. Most of the baths are highly corrosive and can have detrimental effects on surrounding equipment. This is especially true of the chloride and fluoroborate baths. High corrosion potentials coupled with current efficiencies in the range of 82 to 87% probably indicate that air emission equipment is necessary. The sulfate, sulfamate, and sulfonate baths are less corrosive and, even though they run at low pH, should require only general ventilation equipment.

Cadmium Plating

Revised by Milton F. Stevenson, Sr., Anoplate Corporation

Introduction

Electrodeposits of cadmium are used to protect steel and cast iron against corrosion. Because cadmium is anodic to iron, the underlying ferrous metal is protected at the expense of the cadmium plate even if the cadmium becomes scratched or nicked, exposing the substrate.

Cadmium is usually applied as a thin coating (less than 25 μm or 1000 μin. thick) intended to withstand atmospheric corrosion. It is seldom used as an undercoating for other metals, and its resistance to corrosion by most chemicals is low.

Besides having excellent corrosion protective properties, cadmium has many useful engineering properties, including natural lubricity. When corrosion products are formed on cadmium-electroplated parts, they are not voluminous, and there is minimal change in dimension. These two properties are responsible for the wide use of cadmium on moving parts or threaded assemblies.

Cadmium has excellent electrical conductivity and low contact resistance. Noncorrosive fluxes can be used to produce top-quality soldered sections. Steel that is coated with cadmium can be formed and shaped because of the ductility of the cadmium. Malleable iron, cast iron, powdered metals, and other hard-to-plate surfaces can be coated with cadmium, and materials used for adhesives bond very well to cadmium-coated surfaces.

Cadmium is highly toxic, and health, safety, and environmental concerns are driving the reduction or elimination of its use for many applications. See the section "Toxicity of Cadmium" in this article and the article "Cadmium Elimination" in this Volume for more information.

Plating Baths

Most cadmium plating is done in cyanide baths, which generally are made by dissolving cadmium oxide in a sodium cyanide solution. Sodium cyanide provides conductivity and makes the corrosion of the cadmium anodes possible.

Cyanide Baths. Compositions and operating conditions of four cyanide baths are given in Tables 1(a) and 1(b). Note that for each of these baths a ratio of total sodium cyanide to cadmium metal is indicated; maintenance of the recommended ratio is important to the operating characteristics of the bath.

Table 1(a) Compositions of cadmium plating cyanide solutions

Solution No.	Ratio of total sodium cyanide to cadmium metal	Composition[(a)]									
		Cadmium oxide		Cadmium metal		Sodium cyanide		Sodium hydroxide[(b)]		Sodium carbonate[(c)]	
		g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	4:1	23	3	19.8	2.62	78.6	10.4	14.4	1.90	30-75	4-10
2	7:1	23	3	19.8	2.62	139	18.4	14.4	1.90	30-45	4-6
3	5:1	26	3.5	23.1	3.06	116	15.3	16.6	2.19	30-60	4-8

(a) Metal-organic agents are added to cyanide solutions to produce fine-grain deposits. The addition of excessive quantities of these agents should be avoided, because this will cause deposits to be of inferior quality and to have poor resistance to corrosion. The addition of these agents to solutions used for plating cast iron is not recommended.

(b) Sodium hydroxide produced by the cadmium oxide used. In barrel plating, 7.5 g/L (1 oz/gal) is added for conductivity.

(c) Sodium carbonate produced by decomposition of sodium cyanide and absorption of carbon dioxide, and by poor anode efficiency. Excess sodium carbonate causes anode polarization, rough coatings, and lower efficiency. Excess sodium carbonate may be reduced by freezing, or by treatment with calcium sulfate.

Table 1(b) Operating conditions of cadmium plating cyanide solutions

Solutions No.	Current density[(a)]				Operating temperature		Remarks
	Range		Average				
	A/m^2	A/ft^2	A/m^2	A/ft^2	°C	°F	
1	55-650	5-60	270	25	27-32	80-90	For use in still tanks. Good efficiency, fair throwing power. Also used in bright barrel plating
2	110-860	10-80	270	25	27-32	80-90	For use in still tanks and automatic plating. High throwing power, uniform deposits, fair efficiency. Not for use in barrel plating
3	55-970	5-90	380	35	24-29	75-85	Primarily for use in still tanks, but can be used in automatic plating and barrel plating. High efficiency and good throwing power
4	55-	5-	540	50	27-	80-	Used for plating cast iron. High speed and high efficiency[(b)]

(a) For uniform deposits from cyanide solutions, the use of a current density of at least 215 A/m^2 (20 A/ft^2) is recommended. Agitation and cooling of solution are required at high current densities.

(b) Agitation and cooling are required when current density is high (above 215 A/m^2, or 20 A/ft^2).

For still tank or automatic plating of steel, selection of a bath on the basis of cyanide-to-metal ratio depends on the type of work being plated and the results desired:

- For parts with no recesses and when protection of the basis metal is the sole requirement, Solution 1 in Table 1(a) (ratio, 4 to 1) is recommended.
- For plating parts with deep recesses and when a bright, uniform finish is required, Solution 2 in Table 1(a) (ratio, 7 to 1) is recommended.
- For all-purpose bright plating of various shapes, Solution 3 in Table 1(a) (ratio, 5 to 1) is recommended.
- For high-speed, high-efficiency plating, Solution 4 in Table 1(a) (ratio, 4.5 to 1) is recommended.

Although the use of brighteners produces maximum improvement in uniformity and throwing power (that is, the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped cathode) in Solution 3 in Tables 1(a) and 1(b), brighteners also improve these properties in Solutions 1 and 2.

Normally, the sodium hydroxide content of cyanide baths is not critical. Usual limits are 7.5 to 26 g/L (1.0 to 3.5 oz/gal); the preferred concentration for best results is 15 ± 4 g/L (2 ± 0.5 oz/gal). Sodium hydroxide contributes to conductivity and, in excess, affects the current-density range for obtaining bright plate. Analytical procedures useful in the maintenance of cyanide baths are outlined in the section "Chemical Analysis of Cyanide Cadmium Plating Baths" in this article.

In recent years, the need for pollution control of cyanide solutions has led to the development of noncyanide cadmium electroplating baths, shown in Table 2. Noncyanide baths generate little hydrogen embrittlement and are used to electroplate hardened, high-strength steels. Both the sulfate and the fluoborate baths have been used for some time as a substitute for cyanide baths, and working data are available. The fluoborate bath is characterized by high cathode efficiency, good stability, and relatively little production of hydrogen embrittlement (see the section "Selective Plating" in this article). The major disadvantage of the fluoborate bath is its poor throwing power. It is widely used in barrel plating operations. If this bath is used for still plating at high current density, air agitation is desirable. Wire and strip geometries can readily be plated in a fluoborate bath. Practically all of the other acid-type baths shown in Table 2 are supplied to electroplaters as proprietary baths. Because each proprietary bath has its own peculiarities, it is advisable to obtain all proper operating information from the supplier to obtain the desired results.

Table 2 Concentration of commercial noncyanide cadmium plating baths

Bath	**Proprietary(a)**		**Fluoborate(b)**		**Acid sulfate(c)**
	g/L	**oz/gal**	**g/L**	**oz/gal**	
Ammonium chloride	11-23	1.5-3.0	. . .	. . .	. . .
Ammonium fluoborate	. . .	. . .	60	8	. . .
Ammonium sulfate	75-115	10-15	. . .	. . .	. . .
Boric acid	. . .	. . .	27	3.6	. . .
Cadmium	4-11	0.5-1.5	95	12.6	. . .
Cadmium fluoborate	. . .	. . .	244	32.2	. . .
Cadmium oxide	. . .	. . .	. . .	. . .	7.6-11 g/L (1.0-1.5 oz/gal)

(a) Proprietary requires a current density of 22 to 160 A/m^2 (2 to 15 A/ft^2) and an operating temperature of 16 to 38 °C (61 to 100 °F).

(b) Fluoborate requires a current density of 325 to 650 A/m^2 (30 to 60 A/ft^2) and an operating temperature of 21 to 38 °C (70 to 100 °F).

(c) Acid sulfate requires a current density of 110 to 660 A/m^2 (10 to 61 A/ft^2) and an operating temperature of 16 to 32 °C (61 to 90 °F).

Brighteners. The most widely used, and probably the safest, brightening agents for cyanide baths are organics such as:

- Aldehydes
- Ketones
- Alcohols
- Furfural
- Dextrin
- Gelatin
- Milk sugar

- Molasses
- Piperonal
- Some sulfonic acids

These materials form complexes with the electrolyte in cyanide baths and influence the orientation and growth of electrodeposited crystals, resulting in the formation of fine longitudinal crystals, and hence a bright deposit. Care should be taken not to add the brighteners in too large an amount. Too much brightener can result in dullness, pitting, blistering, and general poor quality and appearance. It is difficult to remove the excess brightener. Many organic brighteners are available as proprietary materials. When these are used, manufacturers' recommendations regarding amounts and other conditions of use should be followed.

Another method of brightening consists of the use of trace quantities of metallic nickel, cobalt, molybdenum, and selenium. The concentration of these elements in the bath is much more critical than the concentration of the organic brighteners. Poor bright dipping qualities or poor ductility and corrosion resistance of the coating may result from an excess of these metals. Certain proprietary brighteners contain both metallic and organic compounds. Brighteners for the noncyanide baths are also proprietary products.

Rough or pitted deposits should not be encountered in a well-balanced, carefully operated bath. However, if the concentration of metal is too low or the ratio of metal to cyanide varies from recommended values, roughness may result. Other factors that may contribute are contamination by dust, dirt, oil, metallic particles, or soap. Excessive concentrations of sodium carbonate and too high a temperature or current density also promote surface roughness.

Pitted deposits usually are the result of metallic impurities or an excessive amount of decomposed organic addition agents. The interfering metals are antimony, lead, silver, arsenic, tin and thallium. Pitting may also result from the presence of nitrates.

Correction of roughness or pitting may require a complete solution clean-up, including removal of excess sodium carbonate, purification with zinc dust, treatment with activated carbon, and filtration.

Formation and Elimination of Carbonate. Sodium carbonate forms in the cyanide bath as a result of the decomposition of sodium cyanide and the reaction of sodium cyanide with carbon dioxide from the air. The preferred method of agitation, if used, is mechanical because air agitation accelerates the buildup of carbonates.The buildup also results from failure to keep ball anode racks full or from the use of a large area of insoluble steel anodes.

Maximum concentrations of sodium carbonate that can be present in the bath without adverse effect on operating efficiency and deposit characteristics depend on the metal content of the bath. For example, carbonate can be present in concentrations up to 60 g/L (8 oz/gal) if the metal content is 19 g/L (2.5 oz/gal), and up to 30 g/L (4 oz/gal) if metal content is 30 g/L (4oz/gal), without deleterious effects. Exceeding these concentrations results in anode polarization, depletion of the metal content of the bath, and poor, irregular, and dull deposits.

To remove carbonates, the preferred method is to freeze them out by reducing the temperature to 1 to 3 °C (35 to 40 °F) in an outside treatment tank. This lowers the solubility of the carbonates, and the resulting precipitate is allowed to settle. The next step is to pump or filter the clear solution back to the plating tank, readjust the solution based on analysis, and properly dispose of the settled precipitate and solution. It is also possible to remove carbonates by treating the solution with calcium sulfate or calcium cyanide. The equipment supplier should be consulted about which procedure should be applied. Continuous purification equipment that maintains a preset level of carbonate is now available in state-of-the-art equipment.

Purification and Filtration. Whenever it is convenient, continuous filtration is advisable. If a solution is contaminated by impurities such as copper, tin, lead, or other metals, the following treatment is recommended.

Transfer the solution to an auxiliary tank of the same size as the plating tank; stir in 0.7 to 1 kg (1.5 to 2 lb) of purified zinc dust per 400 L (100 gal). Continue to stir for about 1 h, then allow to settle for no more than 6 h. Filter through a well-packed filter. If the solution contains excess organic impurities, such as decomposed brighteners, it should be treated with activated carbon and filtered. Pumps and filter parts should be made of iron or steel for alkaline cyanide baths. The solution attacks brass or bronze, and heavy copper contamination results.

Anodes

The anode system for cadmium plating from a cyanide solution consists of ball-shape cadmium anodes in a spiral cage of bare steel (Fig. 1). The spherical shape provides a large surface area in relation to weight, without a large investment in cadmium. Ball anodes also make it possible to maintain an approximately constant anode area, and little or no anode scrap is produced. Cadmium balls are usually 50 mm (2 in.) in diameter and weigh 0.6 kg ($1\frac{1}{4}$ lb) per ball.

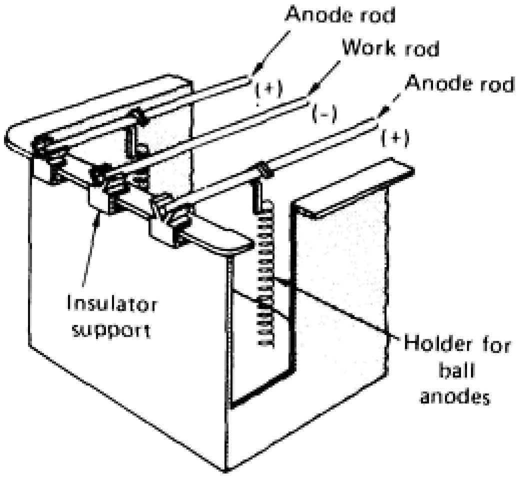


Fig. 1 Unagitated plating tank with spiral steel holders to secure cadmium ball anodes

If a cadmium cyanide solution is to be left idle for an extended period of time (a week or more), the steel anode cages should be removed from the solution, because the galvanic cell set up between the steel and the cadmium anodes will accelerate chemical dissolution of the anodes when the current is off.

When cadmium is plated from an acid solution, such as the fluoborate bath, ball anodes in uncoated steel cages cannot be used, because the steel would dissolve. Rather, bar anodes of elliptical or oval cross section, 460 to 2440 mm (18 to 96 in.) long, are used.

The use of bar anodes in a cyanide solution results in a high percentage of waste, because they must be removed and replaced when the cross-sectional area decreases, or they will dissolve preferentially at the solution level and drop to the bottom of the plating tank.

Purity of the anode is of great importance, especially if a bright deposit is to be produced. The typical composition range for cadmium anodes is as follows:

Element	**Composition, %**
Cadmium	99.95-99.97
Lead	0.008-0.03
Iron	0.005-0.008

Copper	0.002-0.01
Arsenic	0-0.001
Zinc	0-0.001

Anode composition complying with Federal Specification QQ-A-671 is:

Element(s)	**Composition**
Cadmium	99.9% min
Silver, lead, tin	0.05% max (total)
Arsenic, antimony, thallium	0.005% max

Insoluble anodes, which are made of low-carbon steel strip or wire, offer no particular advantage except where inside anodes are necessary or for special applications in which they are required because of a need to reduce metal concentration in the plating bath. When insoluble anodes are used, their total area should be 10 to 15% of the total anode area. Insoluble anodes accelerate the formation of carbonate.

Current Density

Cyanide cadmium baths may be operated over a wide range of cathode current densities, as indicated in Table 1(b). In a properly formulated bath operated within its intended current-density range, the cathode efficiency is 90% ± about 5%. Thus, to apply a 25 μ(1000 μin.) deposit of cadmium requires 120 A · h/m^2 (11 A · h/ft^2).

The ranges of current density given in Table 1(b) are suggested limiting values. Choice of current density is governed mainly by the type of work being plated; for example, low current densities are suitable for small lightweight parts, current densities up to 430 A/m^2 (40 A/ft^2) for medium-weight parts of fairly uniform shape, and high current densities for uniformly shaped heavy parts such as cylinders and shafts.

Baths containing 19 g/L (2.5 oz/gal) of cadmium are suitable for general use at current densities up to 270 A/m^2 (25 A/ft^2); higher concentrations of cadmium, up to 38 g/L (5 oz/gal), permit operation at higher current density.

A bath containing 19 g/L (2.5 oz/gal) of cadmium is suitable for barrel plating, where average current density may be about 55 A/m^2 (25 A/ft^2). Such a bath is also suitable for many still tank or automatic plating applications in which current densities do not exceed 270 A/m^2 (25 A/ft^2). At higher current densities, burning may result, with attendant dull, rough deposits that lack decorative and protective qualities. Where higher current densities are required, baths of higher metal content should be used.

Too low a current density (less than 55 A/m^2, or 5 A/ft^2) particularly in still tank or automatic plating, can result in excessively long plating times and inferior appearance of deposits.

The recommended range of current densities for plating with a fluoborate bath is 320 to 650 A/m^2 (30 to 60 A/ft^2). Even near 650 A/m^2 (60 A/ft^2), however, the bath has poor throwing power.

Deposition Rates

Among plating baths used commercially to deposit common metals (other than precious metals), cadmium cyanide baths are high in both throwing and covering power; only alkaline tin and cyanide copper have greater throwing power. Based on Haring-Blum cell measurements, the throwing power of cadmium cyanide baths is rated between 40 and 45%, with a distance ratio of 5. Therefore, the distance between the anode and the work is not critical, although as the distance is increased, current density and efficiency decrease, and current distribution is altered.

Table 3 lists the times required to plate cadmium deposits from 3 to 18 μm (120 to 720 μin.) thick. These times are predicated on 90% cathode efficiency.

Table 3 Time for plating cadmium to a given thickness at various current densities

Data based on 90% cathode efficiency, in a cyanide bath

Thickness of plate		Plating time in minutes at current density specified					
μm	μin.	54 A/m^2 (5 A/ft^2)	110 A/m^2 (10 A/ft^2)	160 A/m^2 (15 A/ft^2)	215 A/m^2 (20 A/ft^2)	270 A/m^2 (25 A/ft^2)	325 A/m^2 (30 A/ft^2)
3	120	13.0	6.5	4.3	3.2	2.6	2.2
5	200	26.0	13.0	8.6	6.4	5.2	4.4
8	320	39.0	19.5	13.9	9.6	7.8	6.6
10	400	52.0	26.0	18.2	12.8	10.4	8.8
13	520	65.0	32.5	22.5	16.0	13.0	11.0
15	600	78.0	39.0	25.8	19.2	15.6	13.2
18	720	91.0	45.5	30.4	22.4	18.2	15.4

Bath Temperature

Typical operating temperature ranges for cyanide baths are given in Table 1(b). Data for noncyanide baths are shown in Table 2. In general, satisfactory plating results are obtained by controlling bath temperature within ±3 °C (±5 °F) during plating. When greater precision is required, temperature should be controlled within ±1 °C (±2 °F).

Plating Equipment

Considerations specific to the operation of cadmium cyanide baths in conventional plating equipment are discussed here, with attention to the materials of construction used.

Still Tanks. Usually, unlined steel tanks are used for alkaline cadmium plating; however, steel tanks with plastic linings are useful in preventing stray tank currents. Another advantage is that lined tanks may satisfy the diking requirements of the Occupational Safety and Health Administration (OSHA). Double tanks and containment berms must be considered with the current regulations. Rubber and plastics used for tank linings should be tested for compatibility with the plating bath, to prevent contamination from constituents of the lining. Vinyl plastisols are compatible, commercially available, and require no further testing.

Filters and cooling coils may also be made of steel. Equipment for fume control should be used; such equipment in some cases is required by local ordinances. A typical tank arrangement is shown in Fig. 1. Equipment for baths other than the cyanide must be made acid-resistant.

Barrels may be made of hard rubber, polypropylene, acrylic resins, phenol-formaldehyde or melamine-formaldehyde laminates, or expanded or perforated sheet steel coated with vinyl plastisol. The plastisol coating is about 3.2 mm ($\frac{1}{8}$ in.) thick and is resistant to the standard barrel plating solutions and temperatures. Usually, doors and wall ends are of the same material.

Perforated cylinders for oblique barrels also have perforated bottoms and are made of the same materials used for perforated cylinders of horizontal barrels.

Anodes used for barrel plating may be bar- or ball-shape. For maximum current density, the anodes are curved to shorten the path of the current. Curved solid anodes are placed on insulated supports, whereas anode balls are placed in curved holders tied together at the lower ends.

Figure 2 illustrates schematically the use of barrel equipment for cadmium plating. Although not shown in the illustration, barrel installations are equipped with plate coils to remove the excess heat caused by the high current used in the plating bath.

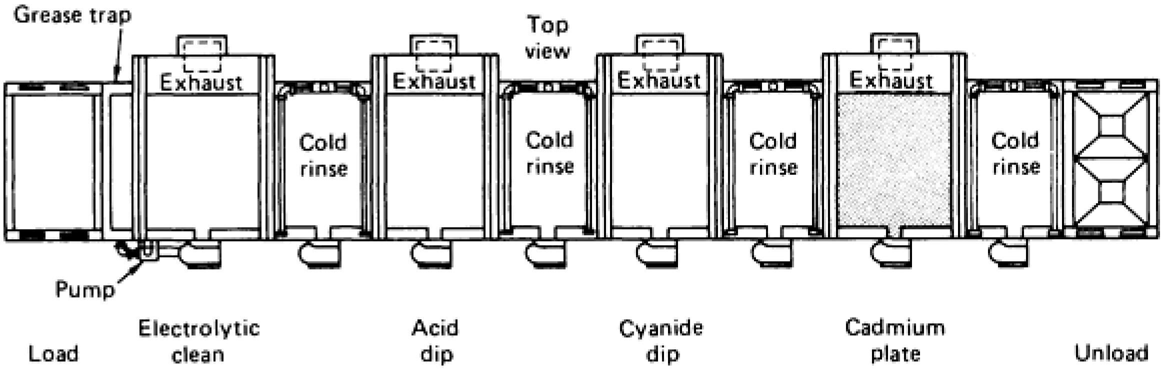


Fig. 2 Schematic showing cadmium plating installation that incorporates the barrel method

Automatic plating machines may be of either the straight-line or the return type. In straight-line plating machines, the work is loaded at one end, carried through the various phases of the cleaning and finishing cycles, and unloaded at the opposite end. Such a machine is considered a heavy-duty unit, because it can be designed for large racks and heavy loads.

Loading and unloading of the return machine is performed in the same area; the work follows an elliptical path, as indicated by the schematic layout of Fig. 3. This unit can be designed for either light or heavy loads.

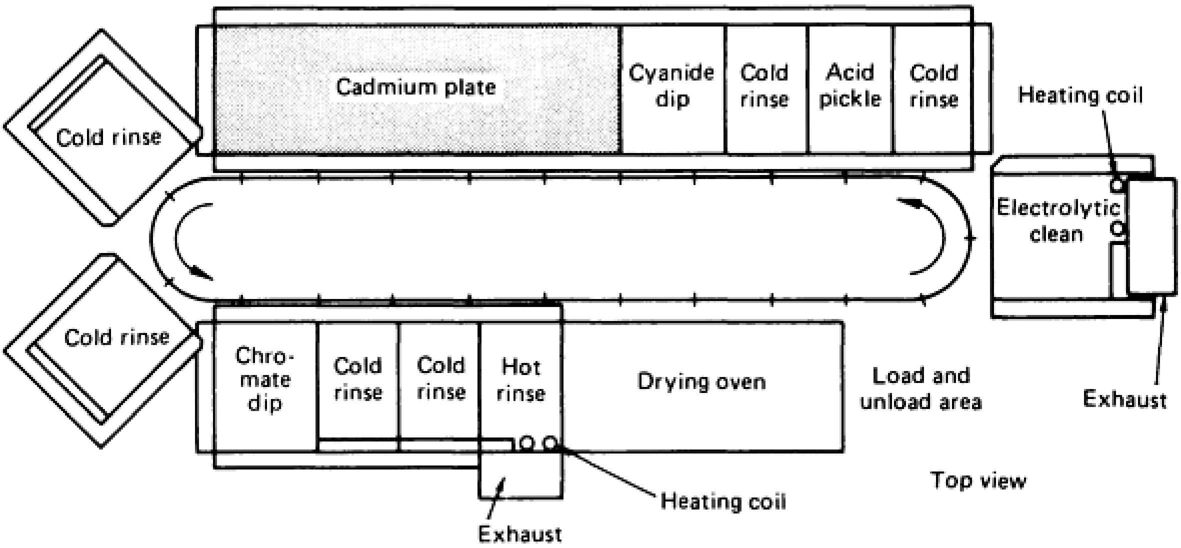


Fig. 3 Schematic showing process sequence for automatic cadmium plating installation

Both types of automatic machines may be continuous, with the work load in constant motion, or intermittent, in which case the motion of the carriers stops for a predetermined time after the work is immersed in each solution.

Power for cadmium plating is provided by rectifiers, which can be of silicon-controlled-rectifier (SCR) thyristor or tapswitch type. If the SCR type is used, attention should be paid to reducing ripple through a filter choke. This is necessary because bright cadmium is sensitive to a high-ripple current, which produces a dull finish on coatings plated in the medium- and high-current density range.

The rectifier elements are silicon. SCR rectifiers offer the advantage of remote control, finer control, computer interface, and constant current-voltage availability. Tap switch rectifiers offer the advantage of lower cost and eliminate the need for ripple filter chokes.

Rinse Tanks. Although longer tank life will be obtained if rinse tanks are lined or coated with polyvinyl chloride or rubber, all rinsing, with the exception of the rinse following hydrochloric acid pickling, may be done in unlined steel tanks. The use of unlined steel tanks for rinsing following pickling or acid plating is not recommended.

Racking of parts for cadmium plating is subject to the same considerations as in the electrodeposition of other metals. Information on design and use of plating racks is available in the article "Industrial (Hard) Chromium Plating" in this Volume.

Maintenance. Table 4 is a typical schedule of maintenance for plating and auxiliary equipment.

Table 4 Recommended maintenance schedule for plating and auxiliary equipment

Daily Check anodes; replenish when necessary. Check all contacts, anode and cathode. Check solution levels. Check bath temperatures and controls. Check bath composition, if possible, using chemical analysis and plating cell test., Probe tank bottom for lost parts. Check motors for signs of overheating, arcing, or failure. Check amperage and voltage to work.

Check lubrication on automatic equipment.

Weekly

Probe tank bottom for lost parts, if not checked daily.
Check rubber tank linings for damage.
Filter plating bath, unless constant filtration is used.
Check bath analysis, chemically and with plating cell, and make additions and corrections, if these functions are not performed more frequently.
Oil equipment.
Clean all contacts.
Check for preventive-maintenance items that cannot be repaired during the week.
Dump and replenish cleaning lines where necessary

Monthly

Pump plating solution to purification tank; treat for impurities, if necessary.
Inspect tank linings while plating tanks are empty; repair if necessary.
Inspect and clean heat exchangers or plate coils if accumulation or buildup exists.
Blow out and check rectifier stacks for condition and power delivery.
Check for arcing or scored armatures on generators. Blow out coils.
Perform general preventive maintenance examination of all equipment.

Semiannually

Clean out exhaust systems.
Repair exhaust fans.
Check all motors.
Repaint where necessary.
Inspect and clean out all floor drains.
Check for leaks and cross connections between cyanide and acid drains.

Selection of Plating Method

Selection of plating method involves both technical and economic factors. Still plating, with parts racked, is the oldest and most universally used plating method. Barrel plating, limited to smaller parts that can be tumbled in the plating bath, is popular because many parts can be plated at one time. Automatic hoist units offer a means of mechanizing the still-tank rack or the barrel.

Still tanks are suitable for all types of work. They are used for small production quantities, in general, and for all quantities of parts that cannot be plated in barrel or automatic systems, because of a need for auxiliary anodes or special handling or because plating dimensions are critical.

Example 1: Cadmium Plating of Valve Bodies and Baffle Plates in Still Tanks.

Valve bodies and baffle plates are typical of many parts that are plated in still tanks (see Table 5). To cadmium plate the production quantities of these parts given in Table 5, the equipment required is:

Equipment	Specification
Plating tank (1440 L, or 380 gal)	2.7 by 0.76 by 0.76 m (9 by 2 $\frac{1}{2}$ by 2 $\frac{1}{2}$ ft)
Other tanks (420 L, or 110 gal)	0.91 by 0.76 by 0.76 m (3 by 2 $\frac{1}{2}$ by 2 $\frac{1}{2}$ ft)
Power rectifier (600 A)	1.5 to 6 V
Dimensions of rectifier	0.76 by 0.91 by 2.1 m (2 $\frac{1}{2}$ by 3 by 7 ft)
Total floor space of equipment and access area	2.0 by 4.6 m (6 $\frac{1}{2}$ by 15 ft)
Number of racks	15

Other tanks include a cleaning tank, an acid pickle tank, a hot-water rinse tank, and three cold-water rinse tanks.

Table 5 Equipment requirements for cadmium plating of valve bodies and baffle plates in still tanks

Production requirements	Valve body	Baffle plate
Weight per piece	1.1 kg (2 $\frac{1}{2}$ lb)	0.2 kg (0.5 lb)
Pieces plated per hour	210	175
Area plated per hour	6.5 m^2 (70 ft^2)	11.1 m^2 (120 ft^2)
Minimum thickness	8 μm (320 μin.)	4 μm (160 μin.)

Barrel plating may be used for parts up to 100 mm (4 in.) long and 50 mm (2 in.) thick. Parts such as machine bolts, nuts, and washers are ideal for barrel plating. Conversely, intricate shapes, such as ornaments and complex castings of brittle metals with small sections that fracture easily, should not be barrel plated; the tumbling action may damage these parts, and variation in plating thickness and appearance may result. Intricate designs incorporating recessed or shielded areas may present problems in plating coverage, luster, and appearance. Barrel plating is not applicable for parts requiring heavy plate. Usually, 8 to 13 μm (320 to 520 μin.) is the maximum thickness of plate applied.

Example 2: Barrel Plating of Small Coil Springs and Brush Holders.

Small coil springs and brush holders are illustrative of parts suitable for barrel plating. Production requirements for plating these parts in horizontal barrels are given in Table 6. Equipment specifications are as follows:

Equipment	Specification
Plating tank (1330 L, or 350 gal)	1.8 by 1.2 by 0.76 m (6 by 4 by $2\frac{1}{2}$ ft)
Other tanks (605 L, or 160 gal)	0.91 by 1.2 by 0.76 m (3 by 4 by $2\frac{1}{2}$ ft)
Power rectifier (2000 A)	9 to 15 V
Dimensions of rectifier	0.91 by 1.2 by 2.4 m (3 by 4 by 8 ft)
Centrifugal dryer	0.61 by 0.61 by 0.76 m (2 by 2 by $2\frac{1}{2}$ ft)
Baking oven	1.2 by 0.91 by 2.4 m (4 by 3 by 8 ft)
Equipment floor space	12 m^2 (125 ft^2)
Access area behind line	6.3 m^2 (68 ft^2)
Access area in front	9.3 m^2 (100 ft^2)

Other tanks in the list above refer to cleaning tanks, acid pickle tanks, hot-water tanks, and three cold-water rinse tanks.

Table 6 Production requirements for cadmium plating of coil springs and brush holders in a horizontal barrel

Production requirements	Coil spring	Brush holder

Weight per piece	14 g ($\frac{1}{2}$ oz)	9 g ($\frac{5}{16}$ oz)
Pieces plated per hour	7200	3800
Area plated per hour	22 m^2 (240 ft^2)	17 m^2 (180 ft^2)
Minimum thickness	4 μm (160 μin.)	8 μm (320 μin.)

Automatic Plating. The primary selection factor for automatic plating is cost. The volume of work must be sufficient to warrant installation of the equipment.

Example 3: Cadmium Plating of Voltage-Regulator Bases on Automatic Equipment.

Voltage-regulator bases were cadmium plated, to a minimum thickness of 3.8 μm (152 μin.), in automatic equipment at the rate of 2640 pieces/h.

Production requirements:

Factor	**Specification**
Weight per piece	170 g (0.37 lb)
Pieces plated per hour	2640
Area to be plated per hour	53 m^2 (570 ft^2)
Minimum plate thickness	4 μm (160 μin.)

Equipment requirements:

Factor	**Specification**
Dimensions of full automatic plating unit	21 by 3.4 by 2.8 m(70 by 11 by 9 ft)
Width of access space on sides of unit	0.76 m (3 ft)

Width of access space on load end of unit	3.1 m (10 ft)
Motor-generator set	15 V, 7500 A
Dimensions of motor-generator set	3.1 by 3.1 by 2.4 m(10 by 10 by 8 ft)

Example 4: Cadmium Plating of Electrical-Outlet Receptacles with Automatic Equipment.

A quantity of 12,000 to 14,000 electrical-outlet receptacles per eight-hour day were required in order to justify the use of a small automatic plating system of 3800L (1000 gal) solution capacity with a single lane of rods and workpieces and plating 4 to 5 μm (160 to 200 μin.) of cadmium. When the size and shape of the parts are such that either automatic or still-tank plating processes may be used, the racking requirement is often the most important factor in determining the relative economy of still-tank and automatic plating. Two kinds of automated plating equipment are available, the regular return machine and the programmed hoist unit, which is an automated straight-line unit. The latter equipment is much less expensive to purchase.

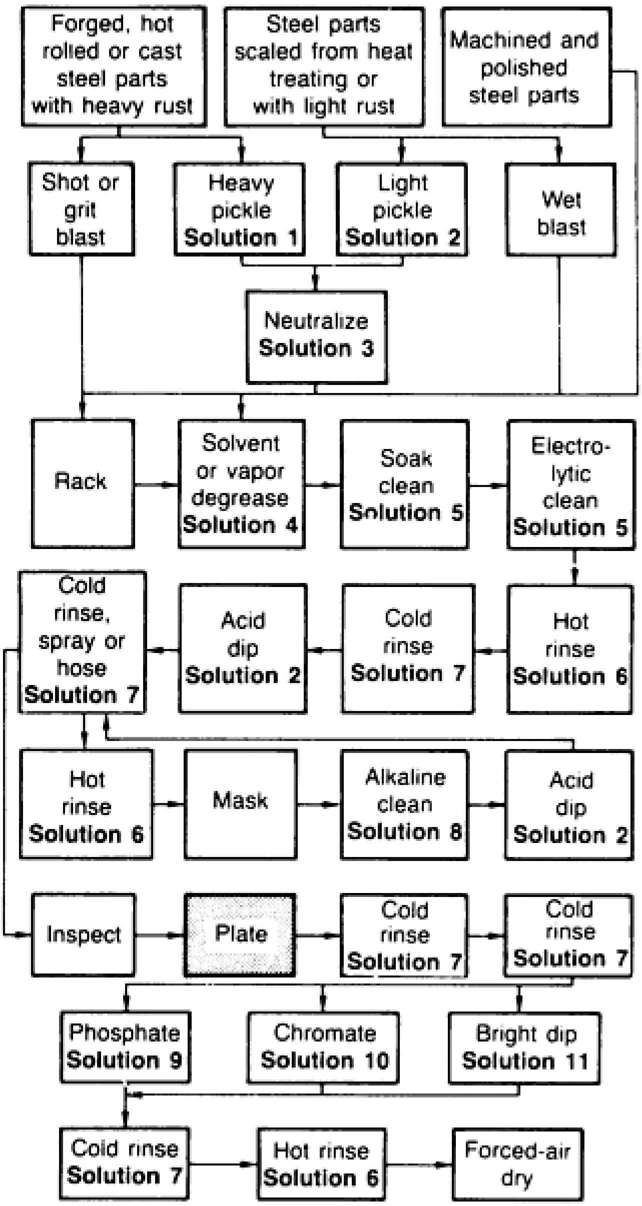
Cleaning and rinsing are essential operations in any plating sequence. Figures 2 and 3 show the number of tanks or stations required for such operations in typical barrel and automatic processes. In Fig. 4, where cleaning, rinsing, and postplating operations are indicated for various initial conditions of the work surface, the plating step itself is a rather inconspicuous item in the flow chart of the total finishing process. Table 7 shows variations in processing techniques for still-tank, barrel, or automatic plating to a thickness of less than 13 μm (520 μin.).

Table 7 Conditions for plating cadmium to a thickness of less than 13 μm (520 μin.)

Process variable	Still tank	Barrel	Automatic
Soak cleaning			
Alkali, g/L (oz/gal)	53 (6)	106 (12)	70 (8)
Temperature, °C (°F)	82 (180)	82 (180)	82 (180)
Time, min	2-3	5	3-5
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Electrolytic cleaning			
Alkali, g/L (oz/gal)	70 (8)	. . .	70 (8)

Temperature, °C (°F)	82 (180)	. . .	82 (180)
Time, min	$\frac{1}{2}$-1	. . .	1-3
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Acid dipping			
HCl, vol%	10-50	10-50	10-50
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{8}$-1	3	$\frac{1}{2}$ to >1
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Cyanide dipping			
NaCN, g/L (oz/gal)	30-45 (4-6)	30-45 (4-6)	30-45 (4-6)
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Plating			
Temperature, °C (°F)	29 (85)	29 (85)	29 (85)

Current density, A/m^2 (A/ft^2)	270 (25)	9-15 V	270 (25)
Time, min	10	30	10
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	2	$\frac{1}{2}$
Bright dipping			
HNO_3, vol%	$\frac{1}{4}-\frac{1}{2}$	$\frac{1}{4}-\frac{1}{2}$	$\frac{1}{4}-\frac{1}{2}$
Temperature, °C (°F)	82 (180)	Ambient	Ambient
Time, min	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{2}$
Rinsing			
Temperature, °C (°F)	. . .	71-82 (160-180)	82 (180)
Time, min	. . .	2	$\frac{1}{2}$
Drying			
Temperature, °C (°F)	82-105 (180-220)	82-105 (180-220)	82-105 (180-220)
Time, min	1-3	5	1-3



Solution No.	**Composition**	**Amount**	**Temperature**		**Immersion time**
			°C	**°F**	
1	H_2SO_4	8-12 vol%	71-93	160-200	10-120 s
2	HCl	20-50 vol%	RT	RT	10-120 s
3	Na_2CO_3	75-90 g/L (10-12 oz/gal)	RT	RT	15-60 s[(a)]

4	Petroleum solvent	. . .	RT	RT	$\frac{1}{2}$-3 min
5	Alkali(b)	60-75 g/L(b) (8-10 oz/gal)	82-93(b)	180-200(b)	$\frac{1}{2}$-3 min
6	Water	. . .	82-93(c)	180-200(c)	5-15 s
7	Water(d)	. . .	RT	RT	5-15 s
8	Alkali	60-75 g/L (8-10 oz/gal)	66 max	150 max	$\frac{1}{2}$-1 min
9	(e)	(e)	(e)	(e)	$\frac{1}{2}$-1 min
10	(e)	(e)	(e)	(e)	30 s
11	NaCN	45-60 g/L (6-8 oz/gal)	RT	RT	5-15 s

Note: For cast iron, the solutions, conditions, and procedure are the same as for steel, except that cast iron parts, after being thoroughly washed in cold water following the acid dip, are dipped for 5 s in a room-temperature (RT) cyanide solution (NaCN, 45 to 60 g/L, or 6 to 8 oz/gal) and then again rinsed in cold water, before proceeding to inspection, plating, and post-treatments.

(a) When solution is sprayed, time is 5 to 15 s.

(b) Heavy-duty cleaner. For electrolytic cleaning, concentration of alkali is 45 to 60 g/L (6 to 8 oz/gal), temperature is 82 °C (180 °F), and time is 1 to 3 min.

(c) When a spray rinse is used, water temperature is 71 to 82 °C (160 to 180 °F).

(d) Immersion or spray rinsing.

(e) Proprietary compounds

Fig. 4 Flow diagram showing cadmium plating operation relative to overall cleaning and post-treatment operations for steel and cast iron components

In the case of Fig. 2, 3, and 4 and Table 7, it is important to consider double or triple overflow rinses to control both water usage and pollution control costs. The use of dead rinses, following process tanks, is equally important.

Variations in Plate Thickness

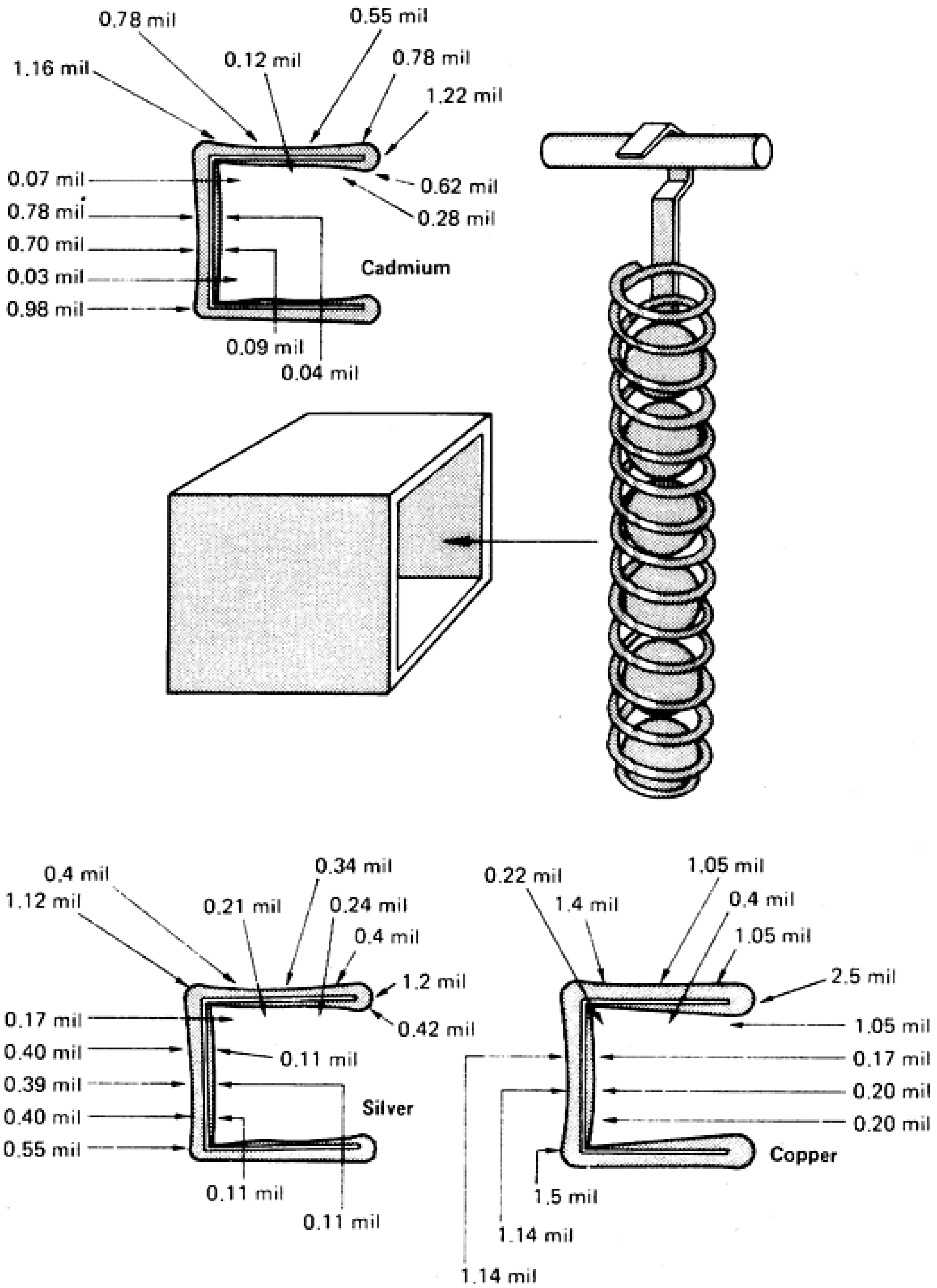
For adequate protection of steel, the thicknesses of cadmium in Table 8 are recommended. The shape of a part can markedly influence uniformity of the electrodeposit. Parts of simple design, such as socket wrenches and bathroom hardware, can be plated with a high degree of uniformity of plate thickness. On such parts, about 90% uniformity would be anticipated.

Table 8 Recommended thicknesses of cadmium

Environmental exposure	**Description**	**Thickness**		**Uses**
		µm	**µin.**	
Mild	Exposure to indoor atmospheres with rare condensation. Minimum wear and abrasion	5	200	Springs, lock washers, fasteners
Moderate	Exposure mostly to dry indoor atmospheres. Subject to occasional condensation, wear, or abrasion	8	320	Television and radio chassis, threaded parts, screws, bolts, radio parts instruments
Severe	Exposure to condensation, infrequent wetting by rain, cleaners	13	520	Washing machine parts, military hardware, electronic parts for tropical service
Very severe	Frequent exposure to moisture, saline solutions, and	25	1000	. . .

Threaded fasteners present a special problem, because of variations in contour and because of tolerance requirements. These items ordinarily are barrel plated, and thicknesses of 3 to 4 µm (120 to 160 µin.) are usually specified.

Throwing Power. The effect of shape on uniformity of deposit thickness is exemplified by the open-ended box (100 mm, or 4 in., cube) of Fig. 5. The open end of the box is pointed toward one of the anodes, to produce the most desirable condition for this shape without auxiliary thief rings, shields, bipolar anodes, insoluble anodes, or other devices. Results of plating such boxes with cadmium, silver, and copper, all deposited from cyanide baths, are shown in Fig. 5. These diagrams illustrate two facts: thickness of plate varies significantly from place to place on the simplest shape; and various plating baths have different throwing powers or abilities to plate uniformly over the surface, regardless of shape.



Plating bath	Thickness ratio[(a)]	
	Side	Bottom
Cadmium	1:4.25	1:12

Copper	1:3.0	1:6
Silver	1:2.5	1:5

(a) Ratio of average plate thickness of inside of average plate thickness on outside

Fig. 5 Plate thickness deposited on the cross section of a cube-shape workpiece to show throwing power of cadmium relative to that of silver or copper in a cyanide bath. Open ends of the 100 mm (4 in.) cubes were pointed toward ball anodes during plating.

The data on cyanide baths tabulated in Fig. 5 show that cadmium has appreciably less throwing power than silver or copper. However, cyanide cadmium has greater throwing power than nickel, chromium, iron, cyanide zinc, acid tin, acid cadmium, acid copper, or acid zinc. Normally, metals plated from cyanide or alkaline baths are more uniformly distributed than metals from acid baths. As design becomes more complex, uniform thickness of plate is more difficult to achieve without the use of special conforming anodes.

Example 5: Plate Thickness Variation in a Workpiece Plated without Use of Conforming Anodes.

A cylindrical, cup-shape production part that was plated without the use of conforming anodes is shown in Fig. 6. Thickness of plate varied from a minimum of 6 μm (240 μin.) to a maximum of 25 μm (1000 μin.).

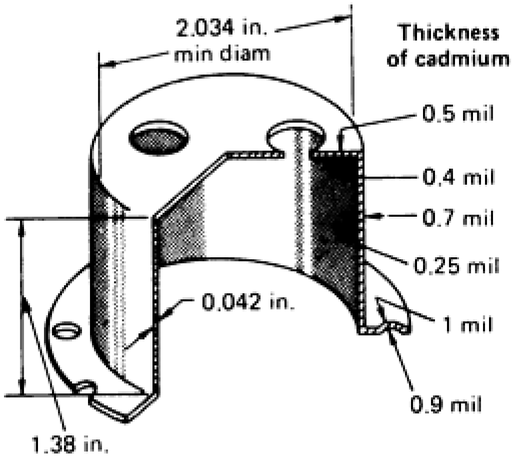


Fig. 6 Variations in plate thickness obtained on a workpiece plated without the use of conforming anodes

Conforming Anodes. Parts of complex shape with stringent dimensional requirements, such as those shown in Fig. 7 and 8, require the use of special techniques, conforming anodes, and shields, in order to obtain the required uniformity of plate thickness.

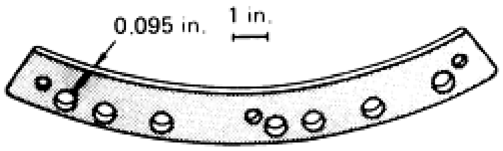


Fig. 7 Application of shields to obtain shim having a uniform cadmium plating. The 305 mm (12 in.) long and 38 mm (1 in.) wide shim was plated to the required thickness of 13 ± 5 μm (520 ± 200 μin.).

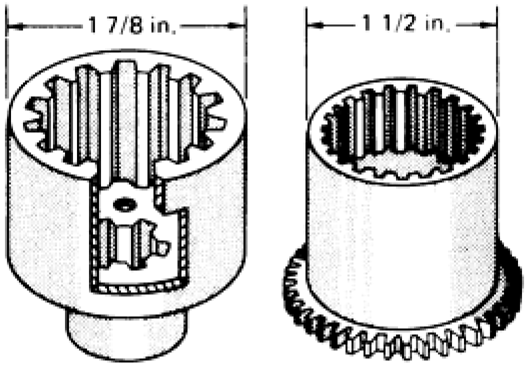


Fig. 8 Couplings that were uniformly cadmium plated with the aid of a 6.4 mm ($\frac{1}{4}$ in.) diameter anode centered in the bore during the plating operation. Plating thickness ranges from 8 to 13 μm (320 to 520 μin.).

Example 6: Application of Shields to Produce Uniform Cadmium-Plated Shim.

A shim, 305 mm (12 in.) long by 40 mm ($1\frac{1}{2}$ in.) wide by 2.4 mm (0.095 in.) thick, is shown in Fig. 7. Parallelism of all sides, as well as plate thickness, was extremely critical. When this part was plated in a simple rack, plate thickness varied from 13 μm (520 μin.) at the center to 50 to 75 μm (0.002 to 0.003 μin.) at the edges and ends.

By using shields that approximated the outline of the shim, it was possible to plate cadmium all over to a depth of 13 ± 5 μm (520 ± 200 μin.). The part was gently agitated in a still bath.

Example 7: Uniform Internal and External Cadmium Plating of Splined Couplings.

A coupling that required 8 to 13 μm (320 to 520 μin.) all over, except for the last 6.4 mm ($\frac{1}{4}$ in.) of the outside diameter of the small end, is shown in Fig. 8. The internal splines on both large and small bores were checked with plug gages and a single-tooth gage to ensure uniformity of plate thickness. To obtain the required uniformity, a 6.4 mm ($\frac{1}{4}$ in.) diameter anode was centered in the bore during plating. Although the outer surface of the large end of the coupling accumulated a heavier coating than other areas, general plate-thickness uniformity met requirements.

Example 8: Uniform Cadmium Plating of Coupling Leaving External Teeth Unplated.

A coupling that, except for the external teeth, was cadmium plated all over to a specified depth of 8 to 13 μm (320 to 520 μin.) is also shown in Fig. 8. Spline and internal bore dimensions were critical and had to be held to a tolerance of ±5 μm (±200 μin.) after plating. Again, uniformity of plate thickness was achieved by centering a 6.4 mm ($\frac{1}{4}$ in.) diameter anode in the bore during plating.

Simple cylindrical, cuboid, and channel shapes, such as those shown in Fig. 9, usually require conforming anodes in order to achieve complete coverage of plate and reasonable plating uniformity. Dimensional limits that definitely require the use of an internal anode are indicated for each geometric shape.

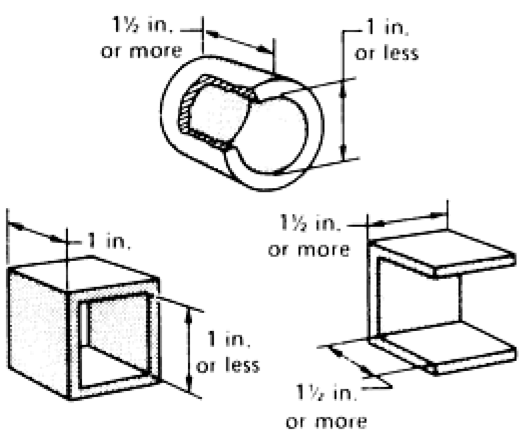


Fig. 9 Typical workpiece configurations with accompanying dimensions that require the use of conforming anodes to ensure uniform plate thickness

Normal Variations. Even under preferred production conditions, some variation in plate thickness must be anticipated. Usually, this normal scatter is acceptable and falls within the specified range of allowable variation.

In general, barrel plating produces greater variations in thickness than still plating. In barrel plating, factors such as the weight, size, and shape of the part usually exert a greater influence on uniformity of plate thickness than they do in still or automatic plating.

Screws, nuts, and other small parts of fairly regular shape will usually coat uniformly in barrel plating. Parts that are likely to nest because they have large flat areas or cup-shape recesses exhibit wide variations in coating thickness. Variations decrease somewhat as the thickness of plate increases.

Variations in plate thickness obtained on production parts are detailed in the example that follows:

Example 9: Histogram Showing Thickness Distribution of 90 Cadmium-Plated Components.

The small cylindrical part shown in Fig. 10 was plated in a horizontal barrel. The load contained about 5000 pieces. Thickness of plate was measured with a magnetic gage on 90 parts from each load. Plating thickness ranged from 5 to 14 μm (200 to 560 μin.).

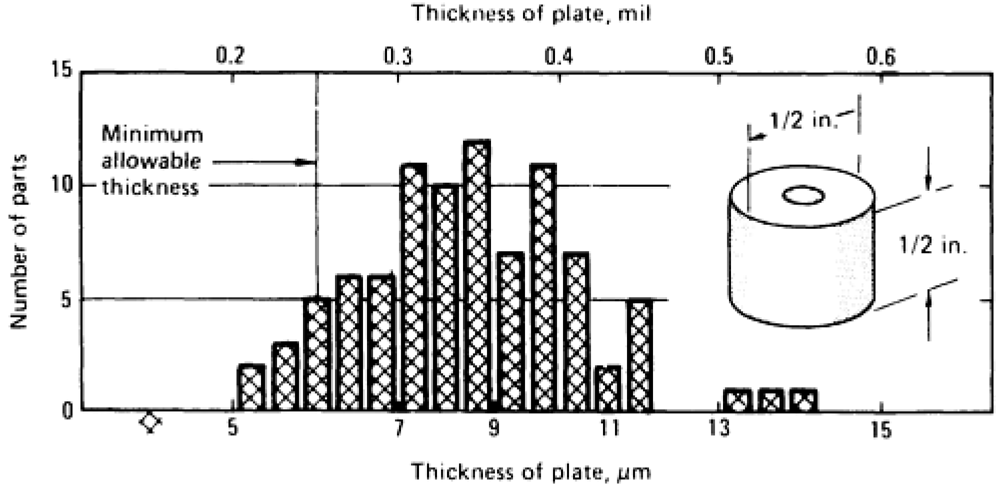


Fig. 10 Thickness distribution for cadmium plating of 90 samples that were evaluated from a 5000-piece

production lot

Other Application Factors

Aside from considerations of cost of very large plating systems, there are no size limitations on parts that can be cadmium plated, provided a tank of adequate size and other essential equipment are available. When a very large part is to be plated, jet plating methods may sometimes be used, rather than constructing a very large plating tank. In the jet technique, a steady stream of solution impinges against the part to be plated until the required thickness of plate is obtained. Because of the rapid movement of the solution, very high current densities can be used. The quality of the plate is comparable to that obtained by conventional methods.

Another technique that can be used on large parts is selective (or brush) plating. Detailed information is available in the article "Selective Plating" in this Volume.

Hardness. The hardness of the basis metal has little or no effect on the successful deposition of cadmium. However, the harder steels are likely to be more highly alloyed and may produce difficult-to-remove smuts from excessive pickling or chemical cleaning. Pickling is also a source of hydrogen embrittlement, which may be particularly harmful to hardened and stressed parts.

Springs often are electroplated with cadmium for protection against corrosion and abrasion. The following example deals with failure of a cadmium-plated compression spring that was not properly treated to release hydrogen.

Example 10: Baking of Cadmium-Plated 6150 Alloy Steel to Eliminate Hydrogen Embrittlement.

A spring used in a high-temperature relief valve under intermittent loading had dimensions and specifications as follows: wire size, 8.76 mm (0.345 in.); outside diameter of spring, 50 mm (2 in.); length, 75 mm (3 in.); six coils; 6150 alloy steel at 43 HRC; stress relieved immediately after coiling. The plating sequence was:

1. Alkaline clean.
2. Rinse in cold water.
3. Electroplate with cadmium 8 μm (320 μin.) thick.
4. Rinse in hot water.
5. Relieve hydrogen embrittlement in boiling water $\frac{1}{2}$ h.

The spring broke with a shatter fracture typical of that caused by hydrogen embrittlement. The corrective action was to bake the spring at 190 °C (375 °F) for 5 h.

For additional information on this subject, refer to the section "Hydrogen Embrittlement" in this article.

Service Temperature. Cadmium-plated, high-strength steel parts that are subjected to heavy loading should never be used at temperatures above 230 °C (450 °F). Cadmium melts at 320 °C (610 °F); at temperatures approaching 260 °C (500 °F), damage occurs that adversely affects mechanical properties.

Diffused Coatings. The aviation industry has developed an application for cadmium for low-alloy steel jet engine parts. The substrate is first plated with 10 μm (400 μin.) of nickel and then 5 μm (200 μin.) of cadmium. The alloy is diffused at 340 °C (645 °F) for about 1 h. Coverage with nickel must be complete, because cadmium can detrimentally affect the steel substrate when heated above the melting point of cadmium. In this way, an alloy with a very high melting point can be formed. Low-alloy steel parts that operate in jet engines at a temperature of 540 °C (1005 °F) were coated with this diffused alloy. After operating for 1 h at 540 °C (1005 °F), the parts withstood 100 h of salt spray without rusting. Cadmium can also be plated on copper and zinc, as well as on nickel.

Solderability. Although cadmium usually solders well with solders of the 60% tin, 40% lead type, using an inactive rosin flux, its performance may sometimes be unaccountably erratic. Solderability can be improved and made more consistent by predepositing a thin (3 to 4 μm, or 120 to 160 μin.) layer of copper. If the final cadmium deposit is at least 4 μm (160 μin.) thick, the copper coating will not adversely affect corrosion resistance in mild indoor atmospheres. It is important for health and safety reasons to see the section "Toxicity of Cadmium" in this article.

Cadmium on Stainless. Cadmium can be successfully plated over stainless steels and heat-resisting chromium-nickel alloys if the basis metal is first activated and given a light coating of nickel in a nickel chloride-hydrochloric acid bath (U.S. Patent 2,437,409). Composition and operating conditions for this bath are as follows:

Factor	**Specification**
Nickel chloride	240 g/L (32 oz/gal)
Hydrochloric acid (1.16 sp gr)	120 g/L (16 oz/gal)
Temperature	Room temperature
Current density	55 to 2150 A/m^2 (50 to 200 A/ft^2)
Time	2 to 4 min
Anodes	Nickel

Plating of Cast Iron

Cast iron is difficult to plate because of the graphite flakes or nodules in the microstructure. The larger the graphite inclusions, the more difficult the plating operation. Cast iron parts with unmachined surfaces should be cleaned by mechanical methods, such as shot blasting or tumbling, before plating. Heavy pickling should be avoided if possible, because it produces smut that is difficult to remove. However, light pickling is required after abrasive cleaning, to activate the surface for plating.

Pickling should be followed by a thorough water rinse and a cyanide dip (see note in the table accompanying Fig. 4). Any carryover of acid to the cyanide dip must be avoided, because the combination of these chemicals generates a highly poisonous hydrocyanic gas. The fluoborate solution described in Tables 1(a) and 1(b) is excellent for plating cast iron parts without deep recesses. The cyanide solutions in Tables 1(a) and 1(b) also may be used, provided no metal-organic grain-refining agents have been added. Current density on the high side of the indicated ranges is recommended, to establish a continuous film of cadmium on the iron as soon as possible.

Cadmium Versus Zinc

In rural areas, cadmium and zinc are generally considered to offer equal protection. However, zinc is superior to cadmium in industrial environments (Table 9). In uncontaminated marine atmospheres, zinc and cadmium give approximately equal protection. When the comparison is made at a distance of 24 m (80 ft) from the ocean, cadmium gives significantly greater protection than zinc. Although it is used to a limited extent in the paper and textile industries, cadmium plate has poor resistance to chemicals commonly used in these processes and also to the chemicals of the petroleum and pharmaceutical industries.

Table 9 Protection against rusting imparted to steel in selected atmospheres by 25μm (1000μin.) of cadmium plate or zinc plate

Test location	Atmosphere	Time required for 5 to 10% rusting, yr	
		Cadmium	**Zinc**
New York, NY	Industrial	2	4
Pittsburgh, PA	Industrial	3	4
Sandy Hook, NJ	Marine, Industrial	6	5
State College, PA	Rural	>11	>11
Key West, FL	Marine	>7	>9

Source:ASTM

One reason for preferring cadmium to zinc is that cadmium plate forms a smaller amount of corrosion products than zinc, particularly in marine atmospheres. Cadmium also retains its initial appearance for a longer time. This is an important consideration in applications where a buildup of corrosion products would have a detrimental effect, such as preventing the flow of current in electrical components or the movement of closely fitting parts such as hinges. For such applications, cadmium should be chosen in preference to zinc. Cadmium is preferable to zinc for plating cast iron.

Cadmium Substitutes

There is increased pressure, both domestically and internationally, for reduced usage, or even elimination of cadmium plating for health, safety, and environmental reasons. There have been several zinc alloy baths developed that work for specific applications, but none duplicates all the properties of cadmium. There are many instances, however, where the use of cadmium plating is not essential and zinc or zinc alloy deposits could be substituted, because both give adequate anodic protection, and there was no functional purpose when cadmium was chosen in the first place.

Chemical Analysis of Cyanide Cadmium Plating Baths

Table 10 lists analytical tests that may be applied to cyanide cadmium plating baths to determine their contents of cadmium metal, sodium cyanide, sodium hydroxide, and sodium carbonate.

Table 10 Analytical tests for determining concentration of selected chemical constituents of cyanide cadmium plating baths

Test constituent	Component			
	Cadmium metal	**Sodium cyanide (total)**	**Sodium Hydroxide**	**Sodium Carbonate**
Reagents	Hydrochloric or sulfuric acid (concentrated) Ammonium hydroxide (concentrated) Eriochrome black "T" indicator (0.5% solution in alcohol) Formaldehyde (8% solution in water)	Ammonium hydroxide (concentrated) Potassium iodide (10% solution in water) Silver nitrate (13 g/L, or	LaMotte sulfo-orange indicator Sulfuric acid, standard (0.94	Barium chloride (10% solution in water) Methyl orange-xylene cyanole

	Disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA), 0.575*M* solution (21.4 g/L, or 2.85 oz/gal)	1.7 oz/gal solution in water)	*N*)	indicator solution Hydrochloric acid, standard (0.7 *N*)
Procedure	1. Pipette exactly 2 mL (0.07 oz) of plating bath into a 250 mL (8.5 oz) Erlenmeyer flask, and dilute to about 100 mL (3.4 oz) with distilled water. 2. Neutralize this dilution to a faint white precipitate with hydrochloric or sulfuric acid. This can be conveniently done from the burette of standard sulfuric acid (0.94 *N* used for the caustic titration, or by the addition of a 50% solution of hydrochloric acid from an eyedropper. If no precipitate appears, as may happen with a new bath, thymolphthalein can be used as an indicator and will change from blue to colorless on neutralization. 3. Add 10 mL (0.34 oz) of concentrated ammonium hydroxide and about $\frac{3}{4}$ mL of Eriochrome indicator. 4. Zero the burette. 5. Add 8 mL (0.27 oz) of 8% formaldehyde solution. 6. Titrate immediately with EDTA solution. The color change is from red to blue, and it is sharpest when the solution is titrated as soon as possible after the formaldehyde has been added. A rapid titration will also give a sharper end point. Occasionally, the presence of impurities in the bath will prevent the attainment of a clear blue end point, but the color will prevent the attainment of a clear blue end point, but the color change is still sharp, from a red to a purplish blue.	1. Pipette a 2 mL (0.07 oz)sample of plating bath into a 250 mL (8.5 oz) flask. 2. Add to the sample about 50 mL (1.7 oz) distilled water, 5 to 7 mL (0.17 to 0.24 oz) of ammonium hydroxide, and 2 to 3 mL (0.07 to 0.10 oz) of potassium iodide solution. 3. Titrate with silver nitrate solution to the first stable faint yellowish turbidity.	1. Pipette 10 mL (0.34 oz) of the plating bath into a 250 ml (8.5 oz) flask. 2. Add to the sample about $\frac{1}{2}$ mL (0.017 oz) of indicator solution. 3. Titrate with the sulfuric acid to the color change from orange to yellow.	1. Pipette 10 mL (0.34 oz) of plating bath into a 250 mL (8.5 oz) beaker, add to it about 100 mL (3.4 oz) of water, and heat to boiling. 2. Stir into boiling bath dilution about 20 mL of barium chloride solution; cover mixture; allow to stand warm for about $\frac{1}{4}$ to $\frac{1}{2}$ h. 3. Filter, using No. 41 Whatman filter paper, and wash precipitate and flask at least 2 or 3 times with hot distilled water. 4. Place paper and precipitate in the original beaker, add about 10 mL (0.34 oz) of hot distilled water and 3 or 4 drops of indicator. 5. Titrate with the hydrochloric acid (while stirring) to the first permanent color change from green to purple.
Calculation	Milliliters of EDTA solution used × 0.432 = ounces per gallon, cadmium metal	Milliliters of silver nitrate used × 0.5 = ounces per gallon, total sodium cyanide	Milliliters of sulfuric acid used × 0.5 = ounces per gallon, sodium hydroxide	Milliliters of hydrochloric acid used × 0.5 = ounces per gallon, sodium carbonate

Methods for Measuring Thickness of Cadmium Plate

There are many nondestructive and destructive methods for measuring the thickness of cadmium deposits (Table 11). The most widely used are magnetic, coulometric, and eddy-current methods, as well as x-ray spectrometry and microscopic cross-sectioning. Other reliable methods, including the chemical drop test, may be used. Detailed information on most methods can be obtained from ASTM specification B 659-85 ("Standard Guide for Measuring Thickness of Metallic and Inorganic Coatings") (Ref 1) and ISO Standards.

Table 11 Methods applicable to measuring cadmium coating thickness on selected ferrous and nonferrous substrates per ASTM B 659

Substrates	**Measurement technique**

	Beta backscatter[(a)]	**Coulometric[(b)]**	**Magnetic[(c)]**
Magnetic steel (including corrosion-resisting steel)	X	X	X
Nonmagnetic stainless steels	X	X	. . .
Copper and alloys	X	X	. . .
Zinc and alloys	X	. . .	. . .
Aluminum and alloys	X	X	. . .
Magnesium and alloys	X	. . .	. . .
Nickel	X	X	. . .
Glass sealing nickel-cobalt-iron alloys (UNS No. K94610)	X	. . .	X
Nonmetals	X	X	. . .
Titanium	X	. . .	. . .

Source: Ref 1

(a) ASTM B 567; ISO 3543.

(b) ASTM B 504; ISO 2177.

(c) ASTM B 499; ISO 2178.

Reference cited in this section

1. 1989 Annual Book of ASTM Standards, Vol 2.05 *(Metallic and Inorganic Coatings; Metal Powders, Sintered P/M Structural Parts)*, ASTM, 1989, p 441-443

Solutions for Stripping Cadmium Plate

Electrodeposited cadmium can be stripped chemically from the basis metal by immersion in one of the following solutions: ammonium nitrate, inhibited hydrochloric acid, chromic acid with a sulfuric acid addition, and ammonium persulfate with an ammonium hydroxide addition. Electrolytic stripping is performed in a solution of sodium cyanide with an addition of sodium hydroxide. Compositions of these stripping solutions, and the immersion times to be used with them, are given in Table 12.

Table 12 Solutions for stripping electrodeposited cadmium

Solution[a]	Composition	Amount		Immersion time, min[b]
		g/L	oz/gal	
1	Ammonium nitrate	105-136	14-18	10-20
2[c]	Hydrochloric acid (1.18 sp gr), undiluted	. . .	. . .	10-20
	Antimony trioxide	15	2	. . .
3	Chromic acid	203	26.8	5-10
	Sulfuric acid (95%)	48[d]	6.4[e]	. . .
4	Ammonium persulfate	51	6.7	5-10
	Ammonium hydroxide	96.8[d]	12.8[e]	. . .
5[f]	Sodium cyanide	60-91	8-12	10-20

(a) Solutions are listed in order of preference; all solutions are used at room temperature.

(b) Immersion times are for deposits 8 to 13 μm (320 to 520 μin.) thick.

(c) Solution should not be used on stressed or hardened parts.

(d) mL/L.

(e) fl oz/gal.

(f) Solution for stripping electrolytically; 540 to 1080 A/m^2 (50 to 100 A/ft^2) and 6 to 8 V; part to be stripped is made the anode.

Toxicity of Cadmium

Two hazardous consequences attend the use of cadmium in contact with food products: acute poisoning resulting from the ingestion of cadmium dissolved from containers or from food-handling equipment; and poisoning from the inhalation of fumes of cadmium oxide, if cadmium-plated vessels or food-handling equipment is heated.

Acute poisoning has resulted from the ingestion of cadmium salts derived from cadmium-plated vessels in which any acid foods have been stored for even short periods of time; therefore, cadmium should not be used on food containers of any kind. Fatal poisoning is more apt to result from the inhalation of dust or fumes of cadmium salts and cadmium oxide. These are the kinds of exposure encountered in industrial operations when cadmium-plated parts are heated or soldered. Exposure to dust or fumes of cadmium should be avoided and safety / OSHA regulations should be followed. The complete regulatory text of the cadmium rule and appendixes is published in the Federal Register 57 (178): 42102-42463, 14 September 1992. Among its provisions, the rule requires employers to adhere to a new personal exposure limit (5 g/ μm^3), provide medical surveillance, monitor exposure level, and maintain proper records.

Deposits of cadmium on the sides or bottom of a tank previously used for cadmium plating should not be burned off, because the fumes from this operation are highly toxic. These deposits should be removed mechanically or deplated. For high-efficiency deplating, the solution used contains 45 to 60 g/L (6 to 8 oz/gal) of sodium cyanide and 23 to 30 g/L (3 to 4 oz/gal) of sodium hydroxide in water; the tank is the anode, and steel sheets or scrap steel parts are the cathodes. Just like the production solutions presented in Table 1(a), the resulting solution must be treated with the utmost care. The proper handling of cyanide solutions should be discussed with the proper vendors, and internal safety departments must train operators in the safe use of these solutions. Disposal issues must be part of waste treatment management practices. Additional information is available in the article "Cadmium Elimination" in this Volume.

Selective Plating

When plating must be applied to only certain areas of parts, the areas not to be plated must be stopped off or masked, which means they must be covered with materials that will not conduct current, such as waxes, lacquers, or rubber tape.

Waxes. Ordinarily, a petroleum-derived wax is used for stopping off. The wax must not contain any oil or other organic materials that will dissolve in the plating solution and contaminate it. It must also be capable of adhering tightly to the part, to prevent the plating solution from coming in contact with the stopped-off area.

Before being applied, the wax is heated in a pot to about 27 °C (80 °F) above its melting point, so that it does not solidify too rapidly and will adhere more readily. Still-better adhesion is obtained if parts are warmed on a hot plate before the wax is applied.

Parts must be positioned so that only the area to be coated is placed in the molten wax. This means that, normally, only end areas or protrusions can be stopped off with wax. The wax can be applied with camel's hair brushes, but this is time-consuming if many parts are to be treated. For a large number of similar parts, a fixture can be used that will dip each part to the proper depth.

A sharp, uniform demarcation between plated and nonplated areas can be obtained by the use of pressure-sensitive tape and wax, following either of two procedures:

- Apply the tape to the part so that the trailing edge of the tape follows the demarcation line; dip that portion of the part to be left unplated in molten wax so as to overlap the trailing edge of the tape slightly; and then remove the wax when it has solidified.
- Apply the tape to the part so that the leading edge follows the demarcation; dip that portion of the part to be left unplated in molten wax so as to overlap partly the trailing edge of the tape; and then, when the wax has solidified, plate the part without removing the tape.

Waxing must be done carefully, so that areas that are to be plated have no wax on them. If wax does get on areas to be plated, it must be thoroughly removed. After plating and postplating treatments, the wax is removed from parts by placing them in hot water.

Lacquers may be used instead of wax as stop-off coatings, but their use is generally limited to instances in which the plating bath is operated at a temperature at which the wax would melt. Lacquer is applied by dipping or painting the areas to be stopped off. Normally, two to four coats of lacquer must be applied. One disadvantage of lacquer is that it is difficult and time-consuming to get all of it off. Heavier coatings prevent leakage and make stripping easier.

Plastic Tape. For stopping off irregular areas of heavy parts that cannot be dipped or that are too large to be painted (e.g., splines, large shafts, or bearing shoulders), a plastic tape is used. The tape is wound tightly and stretched over the irregular areas. To prevent leakage, each turn should overlap the preceding one at least half-way. At the edge of the stopoff 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								

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.

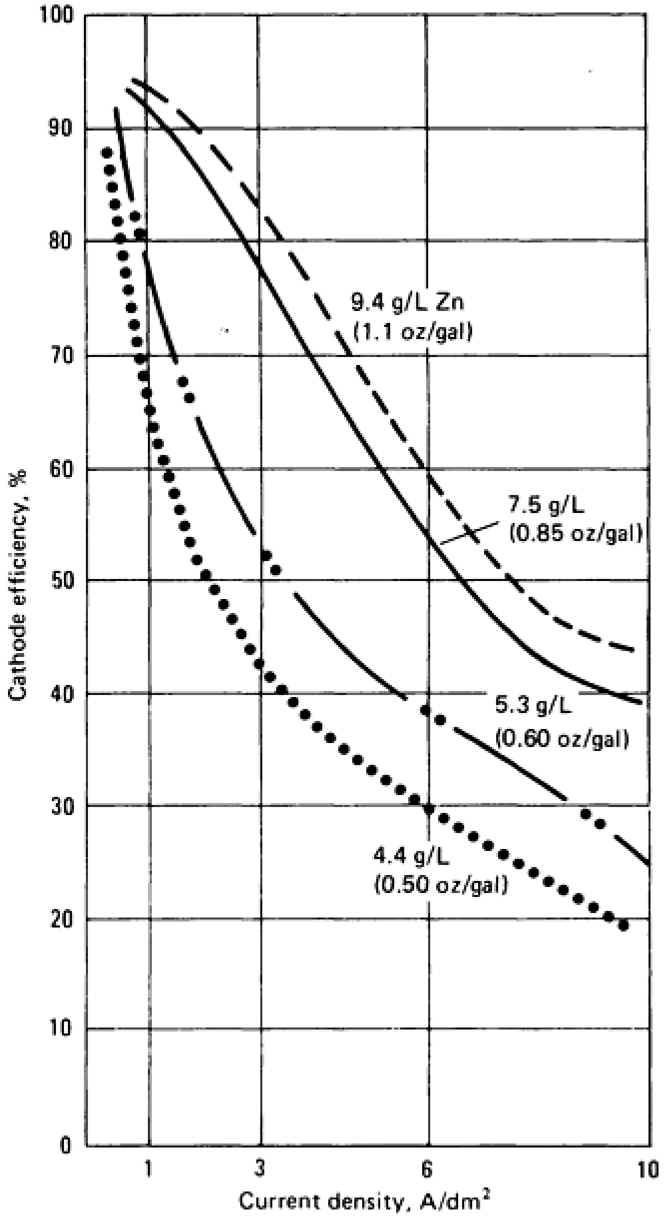


Fig. 1 Cathode current efficiency of alkaline noncyanide zinc baths as related to zinc metal contents. NaOH, 80 g/L (11 oz/gal); Na_2CO_3, 15 g/L (2 oz/gal)

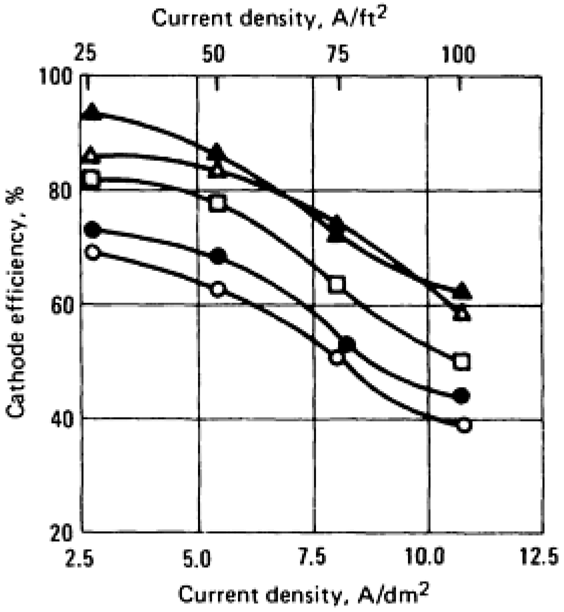


Fig. 2 Effect of zinc and sodium hydroxide concentration on the cathode efficiency of noncyanide zinc solutions. Temperature: 26 °C (77 °F). d : 7.5 g/L (1 oz/gal) Zn, 75 g/L (10 oz/gal) NaOH; •: 7.5 g/L (1.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; V : 11 g/L (1.5 oz/gal) Zn, 110 g/L (15 oz/gal) NaOH;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

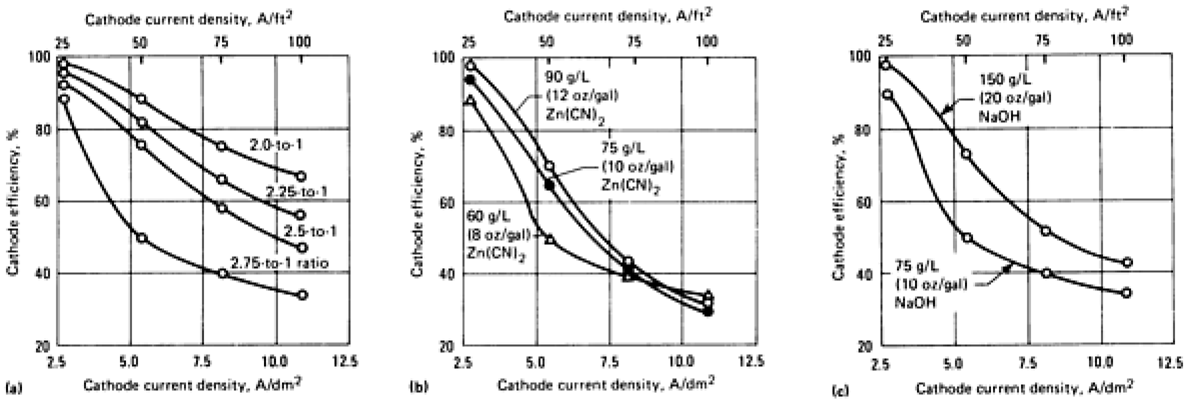


Fig. 3 Effects of bath composition variables and cathode current density on cathode efficiency in cyanide zinc plating. (a) Effect of NaCN/Zn ratio. 60 g/L (8 oz/gal) Zn (CN); 17.5 to 43.7 g/L (2.33 to 5.82 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.0-to-1 to 2.75-to-1 ratios of NaCN to zinc. Temperature: 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

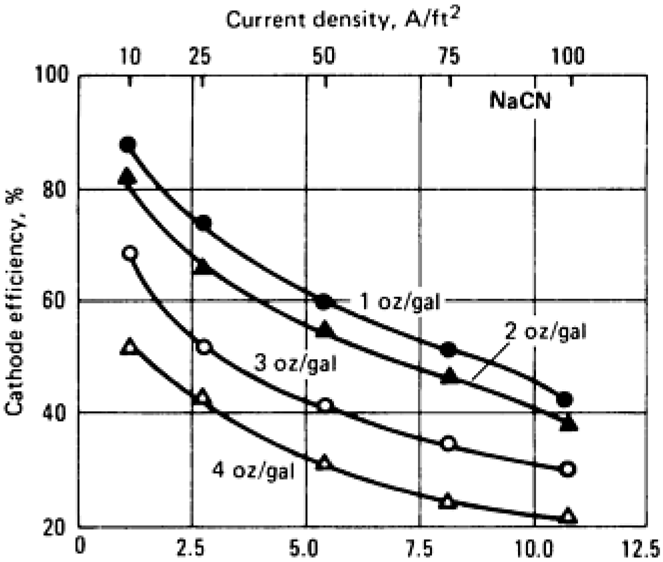


Fig. 4 Effect of sodium cyanide concentration on the cathode efficiency of low-cyanide zinc solutions. d :20 g/L

(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.

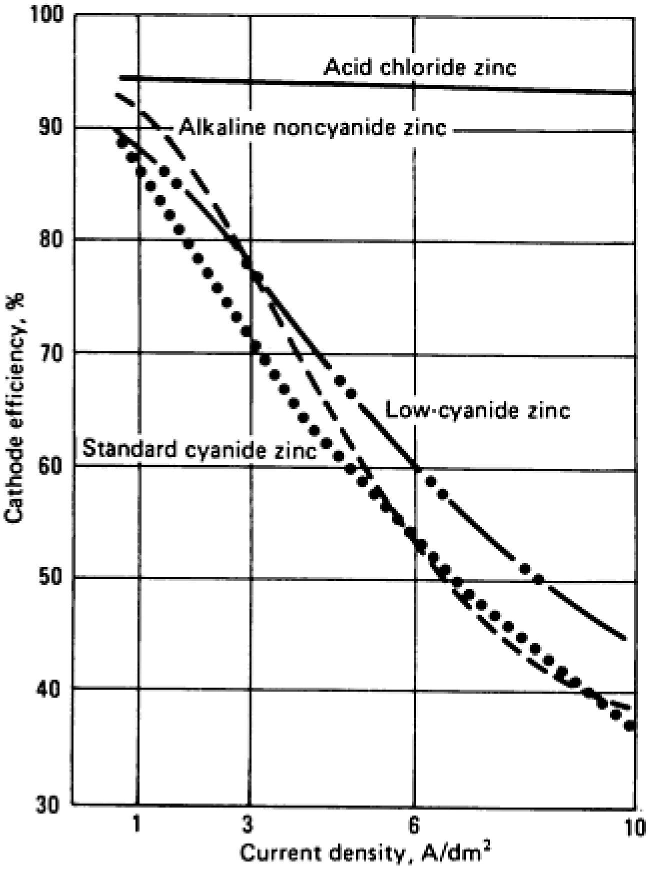


Fig. 5 Comparison of cathode current efficiencies of bright zinc plating electrolytes

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.

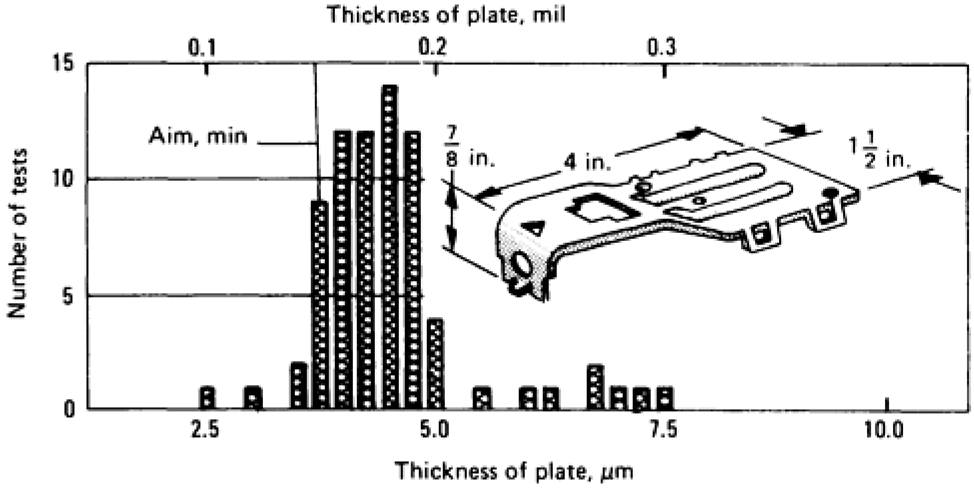


Fig. 6 Variation in thickness of zinc plate obtained in automatic plating in cyanide zinc bath, 75 tests

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).

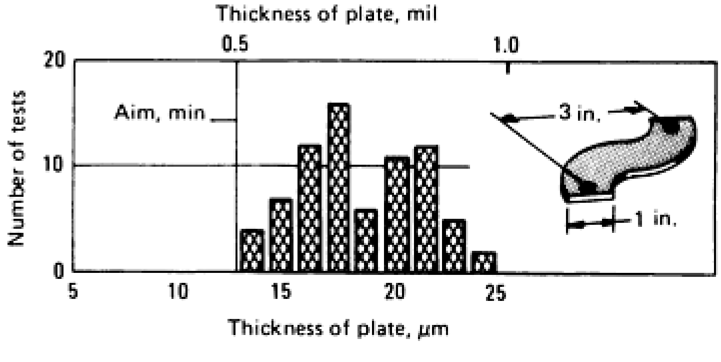


Fig. 7 Variation in thickness of zinc plate obtained in barrel plating a 3.2 mm ($\frac{1}{8}$ in.) thick part in a cyanide zinc

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.

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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.

Acknowledgement

Special thanks are due to Milton F. Stevenson, Jr., Anoplate Corporation, for providing information for this article.

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).

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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).

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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

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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

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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

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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.

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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.

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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

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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.

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18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205
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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.

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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.

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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.

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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

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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

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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:

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

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.

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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

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Zinc Alloy Plating

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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

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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.

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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).

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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.

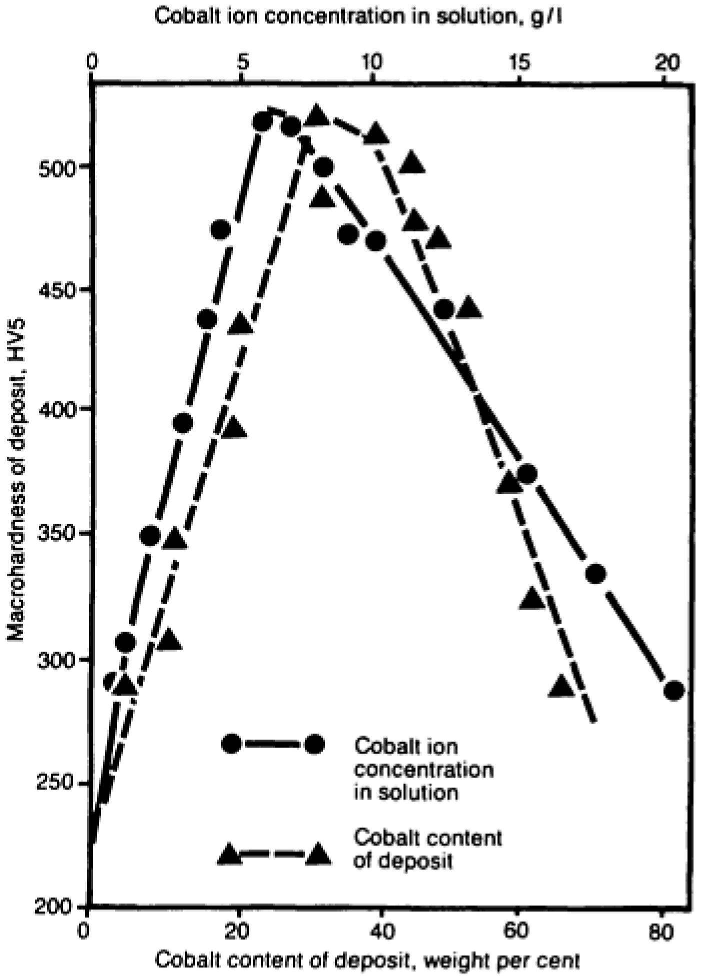

Fig. 1 Relationship between deposit hardness and cobalt concentration in the sulfamate solution and in the deposit

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.

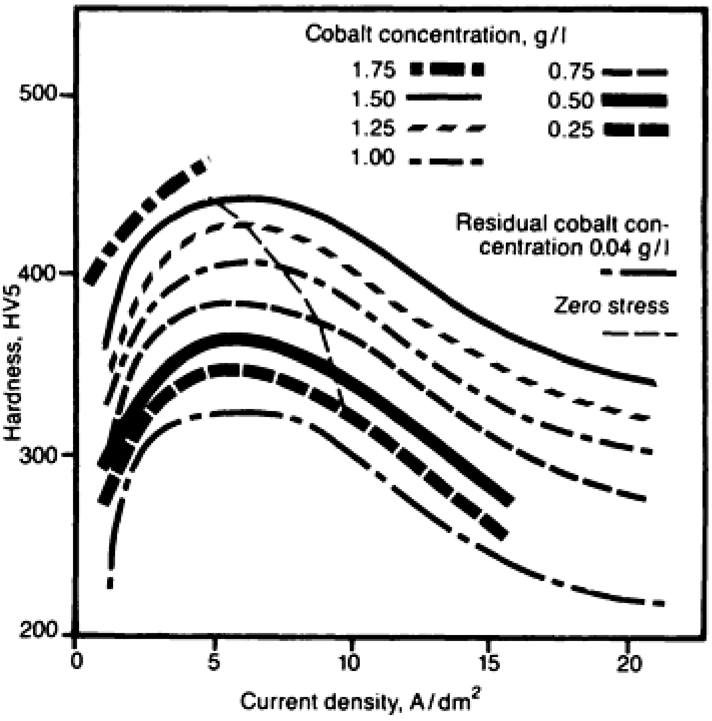

Fig. 2 Relationship between current density and alloy deposit hardness for various cobalt concentrations in solution with superimposed zero stress contour

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).

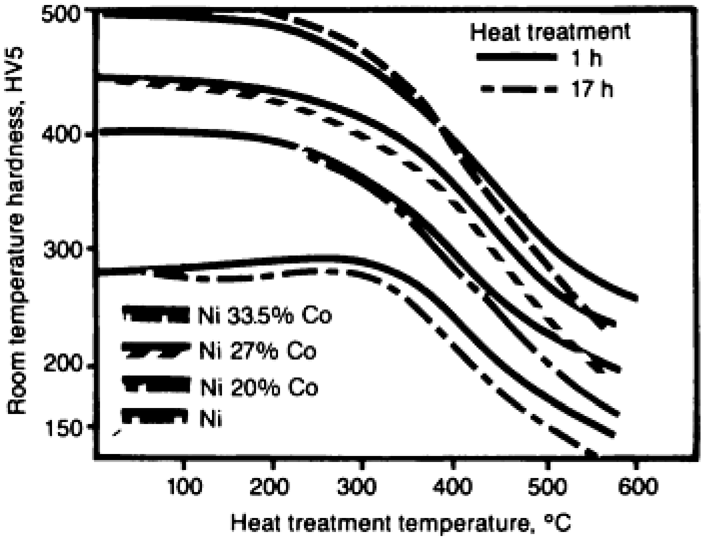

Fig. 3 Room-temperature hardness of electroformed nickel and nickel-cobalt alloys after heating

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).

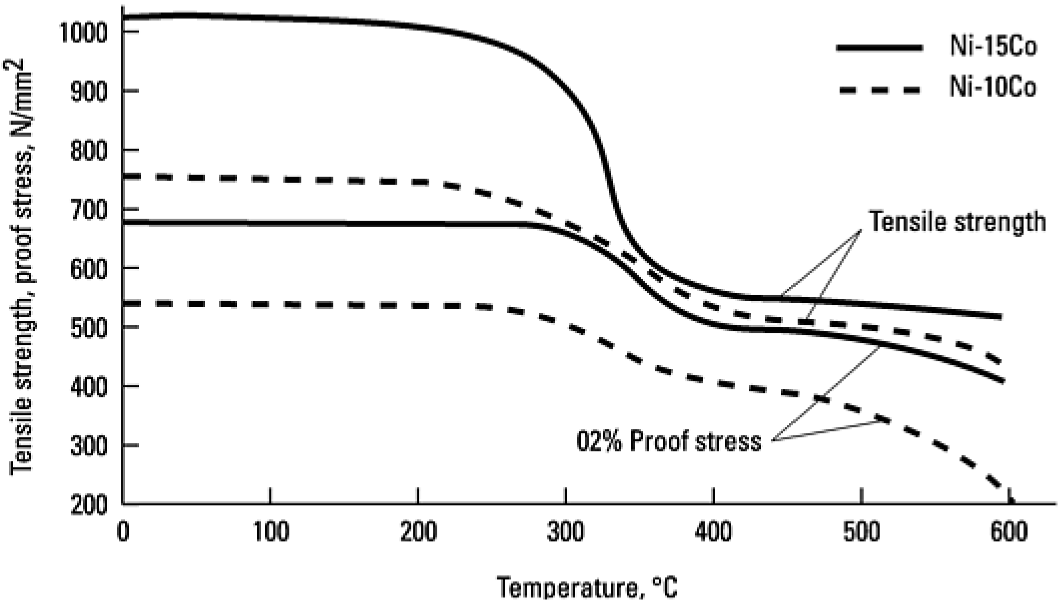

Fig. 4 Effect of heat treatment on the mechanical properties of Ni-10Co and Ni-15Co alloys

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).

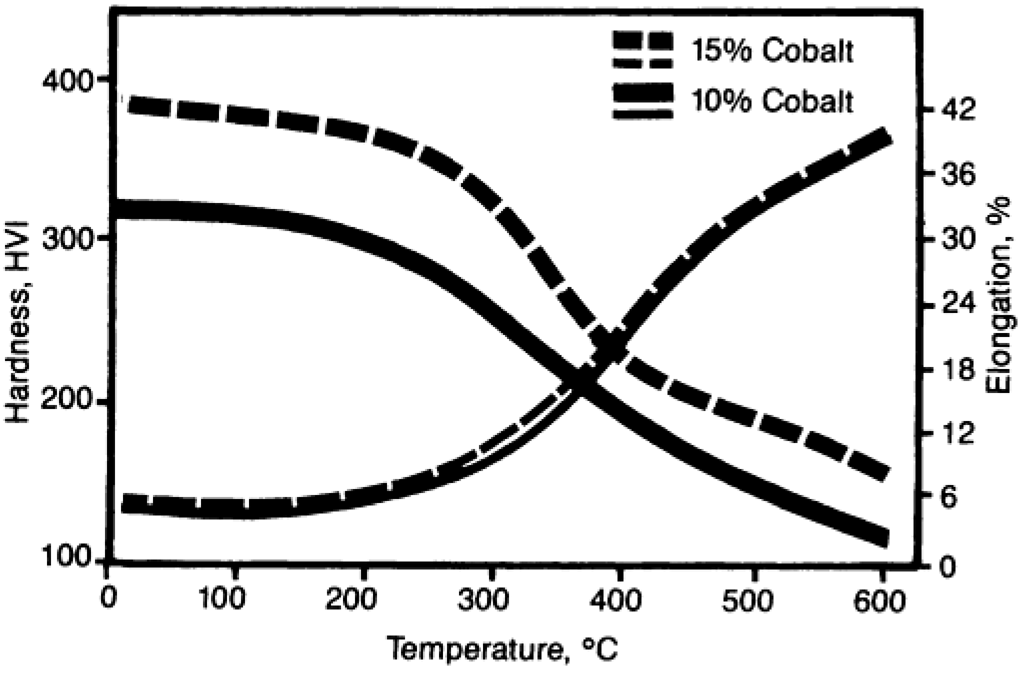

Fig. 5 Hardness and elongation of Ni-10Co and Ni-15Co alloys after heating to various temperatures

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.

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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).

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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.

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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).

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Chromium Alloy Plating

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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

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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

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Multiple-Layer Alloy Plating

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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.

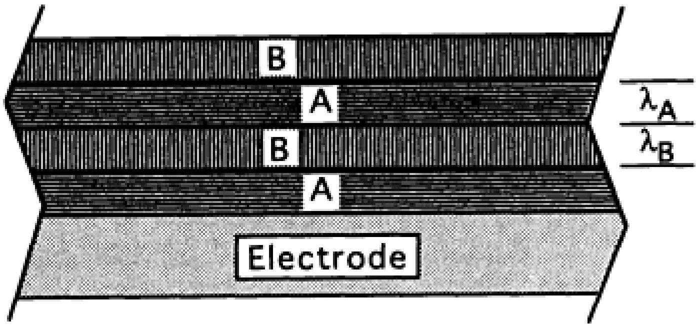

Fig. 1 Schematic representation of a multiple-layer alloy consisting of alternating lamellae of species A and species B. The thicknesses of the A and B layers are given by λ_A and λ_B, respectively. The modulation wavelength that characterizes the multiple-layer superlattice structure is $\lambda = \lambda_A + \lambda_B$. 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.

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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%).

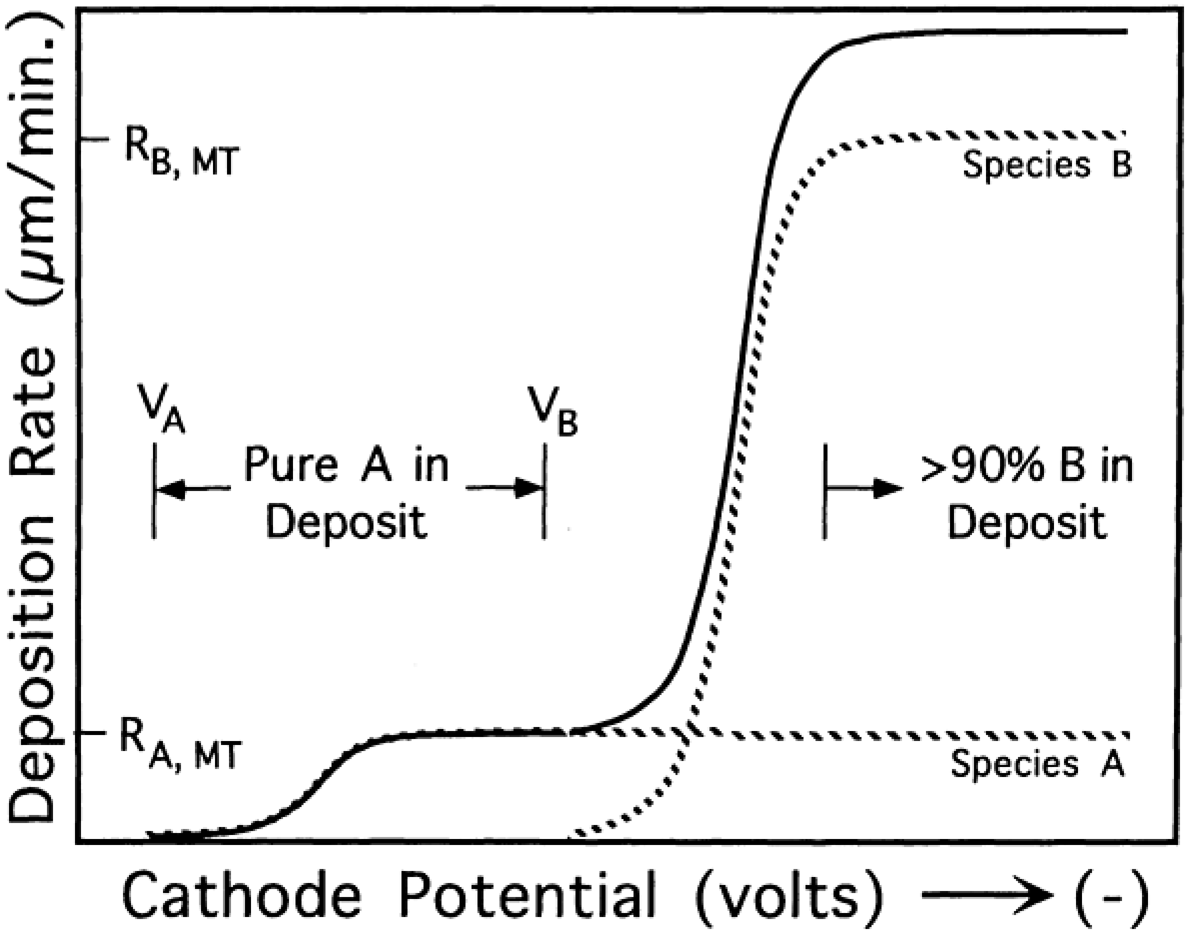

Fig. 2 Schematic of ideal deposition rate vs. applied cathodic potential characteristics for electroplating an A/B multiple-layer alloy. The dashed lines denote deposition rates for plating each individual species, and the solid line represents the total deposition rate. Note that pure A is deposited 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)	$\lambda Ni/\lambda Cu$	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.

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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.

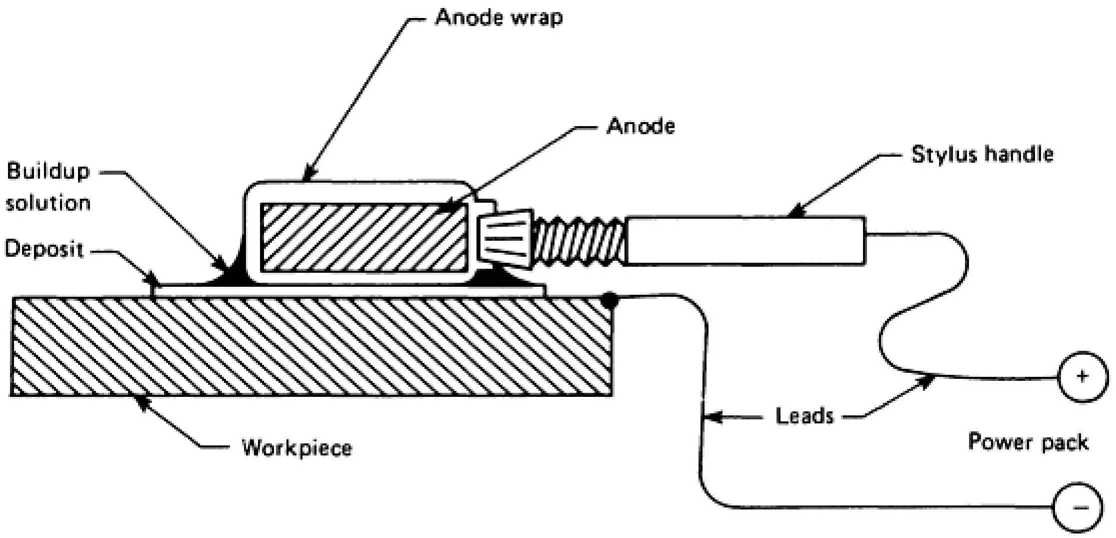

Fig. 1 Manual operation of selective plating process. Source: Ref 1

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

The following individuals contributed to the revision of this article: Robert R. Brookshire and Lester Simmons, Brushtronics Engineering; Francine Hammer, Joseph C. Norris, and Derek Vanek, SIFCO Selective Plating; and Beldon Hutchinson, Liquid Development Co.

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

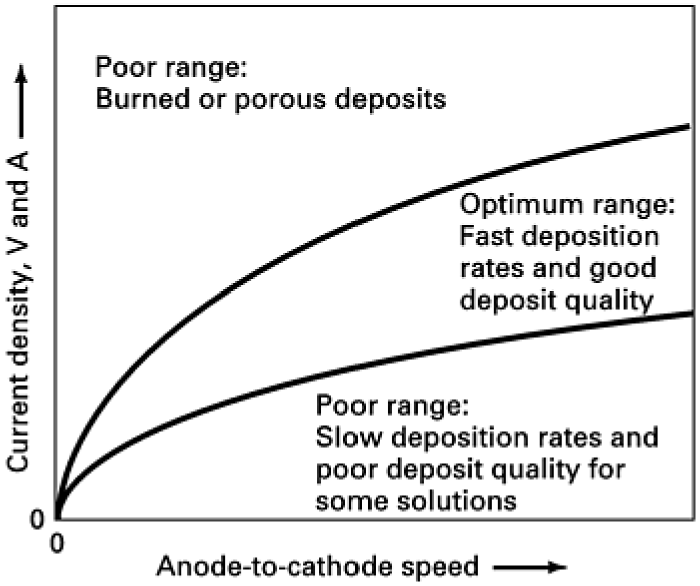

Fig. 2 Relationship between current density and anode-to-cathode speed. Source: Ref 3

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.

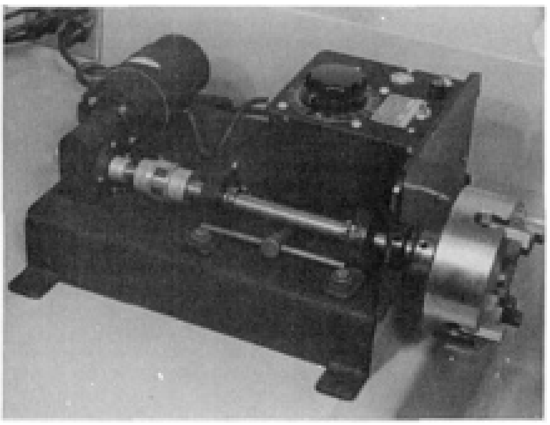

Fig. 3 Turning head. Courtesy of SIFCO Selective Plating

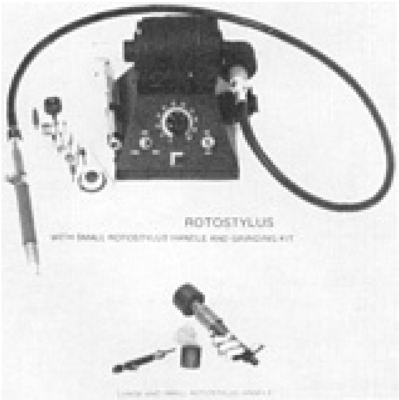

Fig. 4 Rotostylus. Courtesy of SIFCO Selective Plating

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.

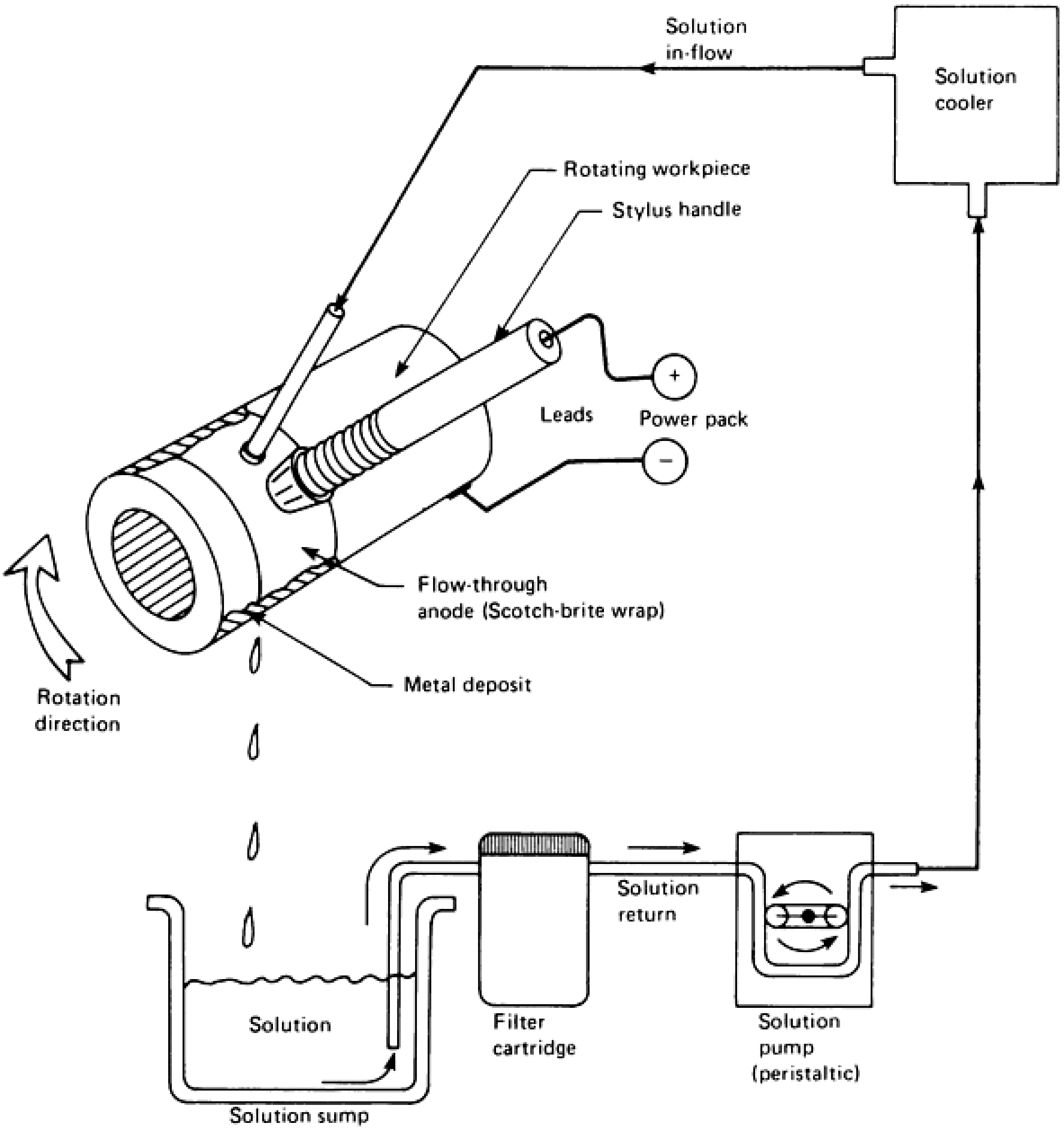

Fig. 5 Flow-through deposition. Courtesy of Vanguard Pacific, Inc.

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).

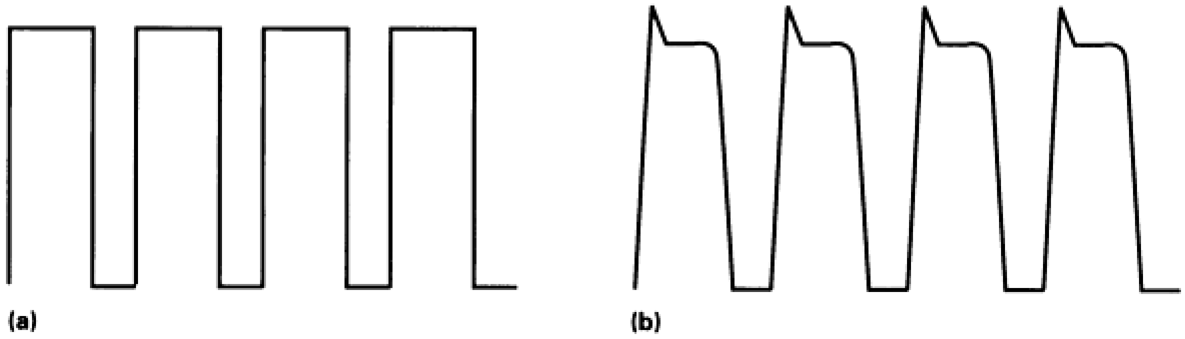

Fig. 1 Current patterns in conventional pulsed-current plating. (a) Ideal pattern. (b) Typical pattern as seen using an oscilloscope

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.

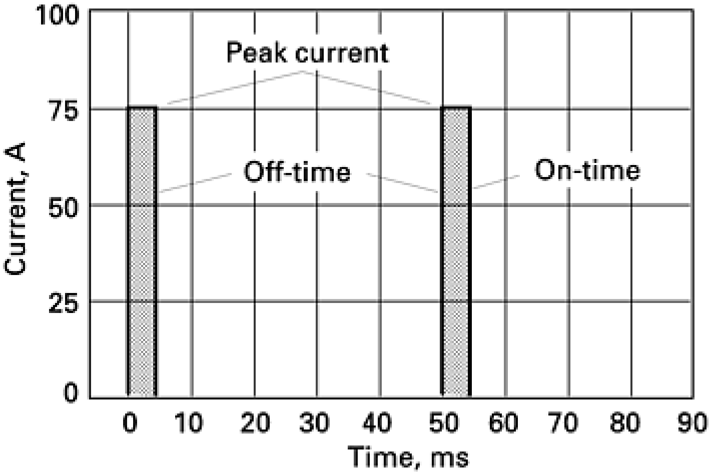

Fig. 2 Constant-current pulse plating with an on-time of 5 ms, an off-time of 45 ms, and a peak current of 75 A. Because the current is on one-tenth of the time, the average current is 7.5 A.

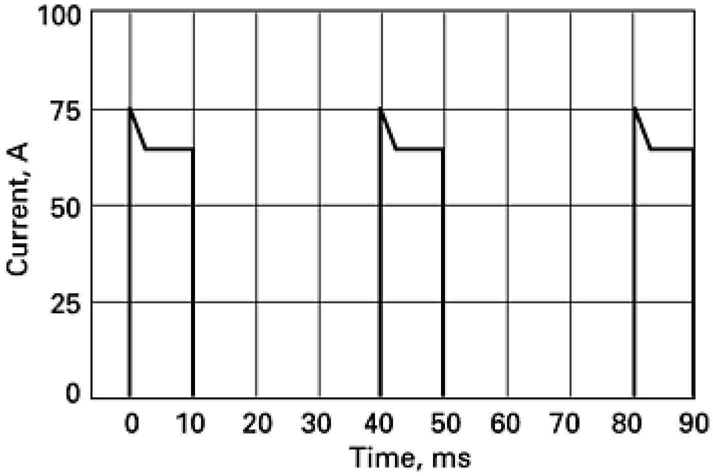

Fig. 3 Typical current pattern for constant-voltage pulse plating. The current falls during the on-time because of the increasing resistance of the cathode. On-time, 10 ms; off-time, 30 ms

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.

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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.

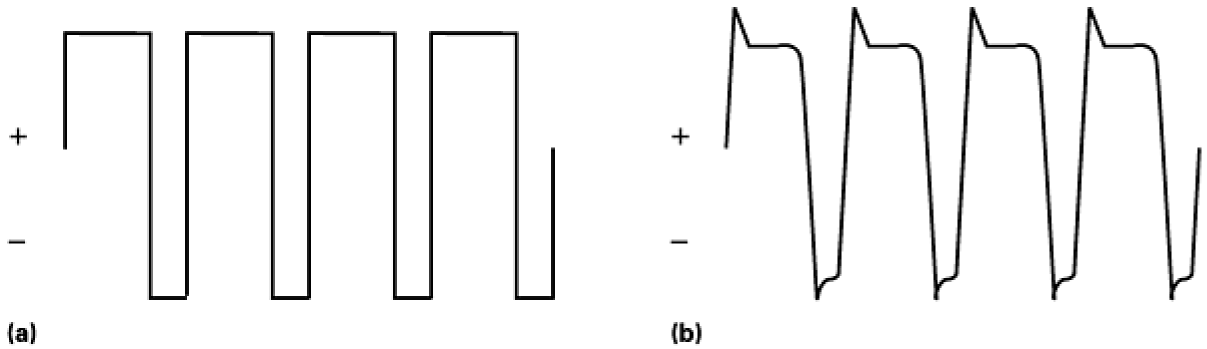

Fig. 4 Current patterns in periodic-reverse pulsed-current plating. (a) Ideal pattern. (b) Pattern of a slow-response control unit as seen using an oscilloscope

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.

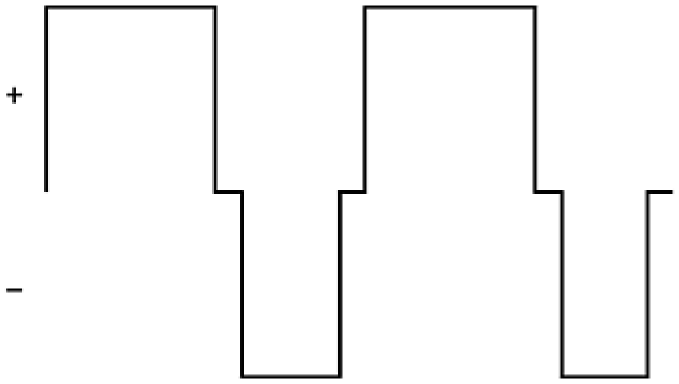

Fig. 5 Square-wave current pattern of the forward and reverse envelopes in periodic-reverse pulse plating

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.

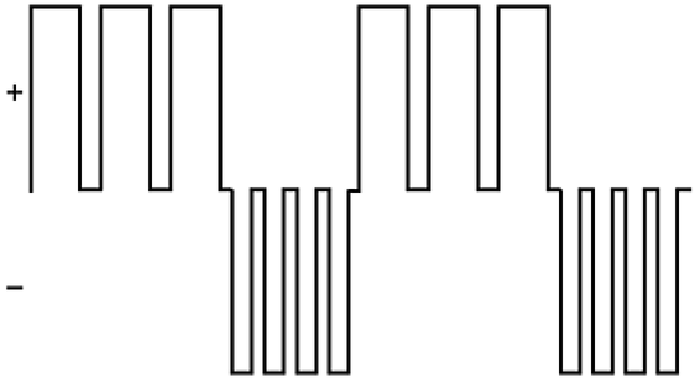

Fig. 6 Current pattern for periodic-reverse pulse plating in which pulse frequencies have been superimposed on the forward and reverse envelopes

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.)

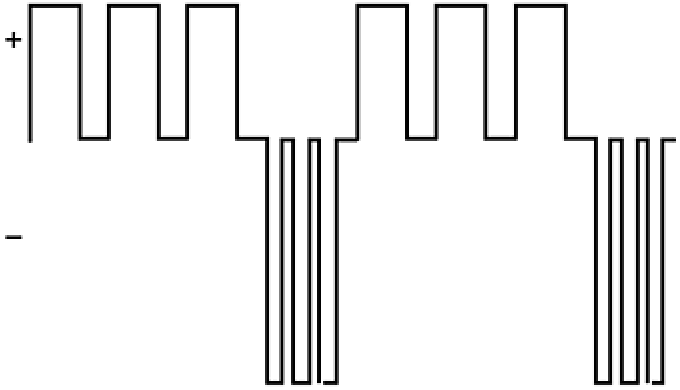

Fig. 7 Current pattern for periodic-reverse pulse plating in which pulse frequencies of different current densities have been superimposed on the forward and reverse envelopes

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.

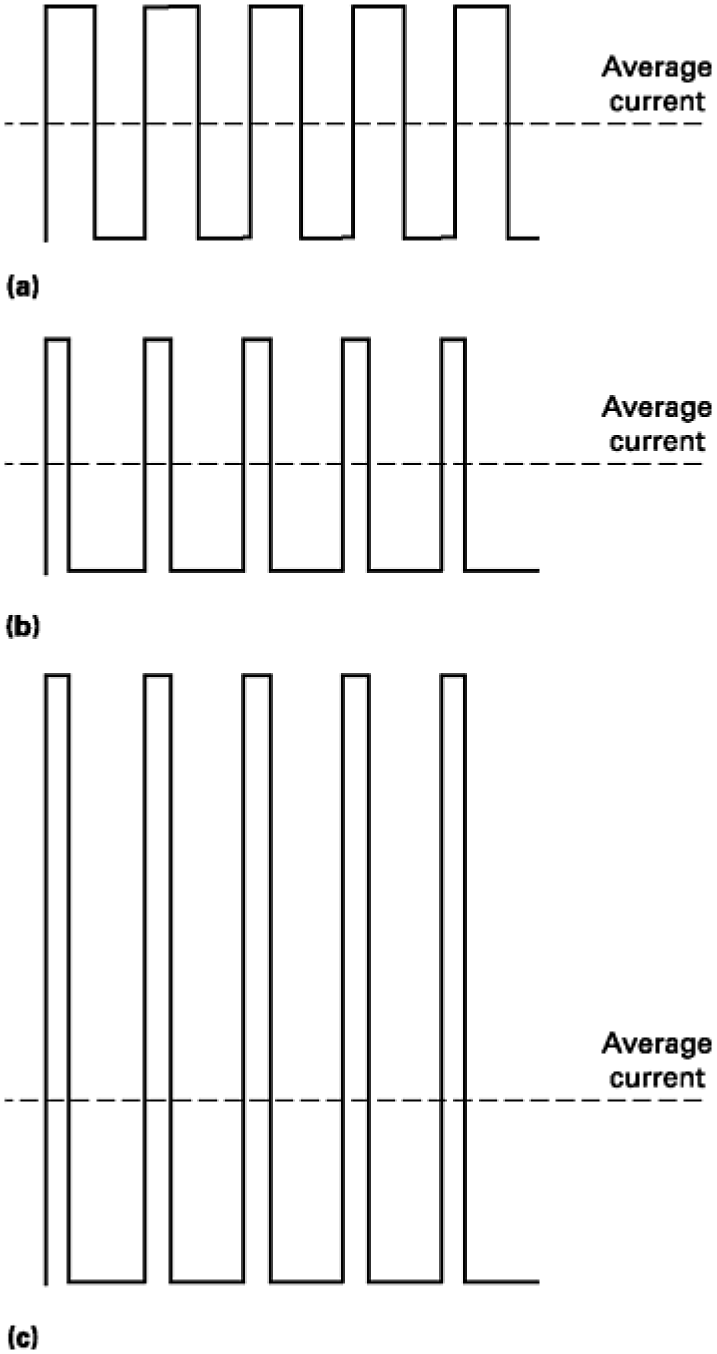

Fig. 8 Effect of changes in the duty cycle on constant-average-current and constant-voltage pulsed-current plating. (a) 50% duty cycle, with average current 50% of the peak value. (b) Duty cycle reduced to 25% in constant-voltage mode; average current drops with duty cycle. (c) Duty cycle reduced to 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.

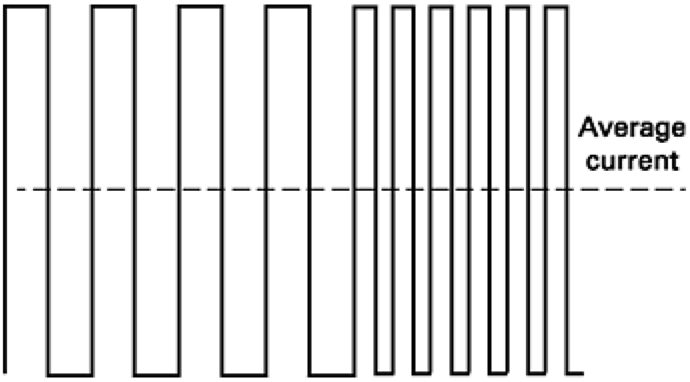

Fig. 9 Effect of change of frequency on current pattern in pulsed-current plating. Only pulse width is altered; peak current, average current, and duty cycle remain constant.

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.

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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.

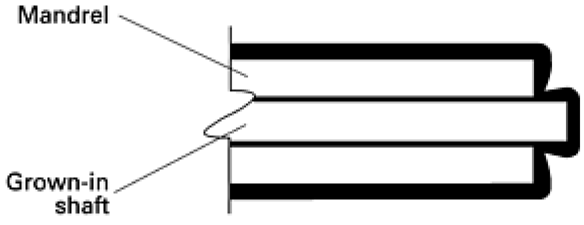
Use fillets at least equal to metal deposit thickness for strong inside corners.

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

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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:

$$(H_2PO_2)^- + H_2O \frac{Catalyst}{Heat} \rightarrow H^+ + (HPO_3)^{-2} + 2H_{abs} \qquad \textbf{(Eq 1)}$$

$$Ni_2 + 2H_{abs} \rightarrow Ni + 2H^+ \qquad \textbf{(Eq 2)}$$

$$(H_2PO_2)^- + H_{abs} \rightarrow H_2O + OH^- + P \qquad \textbf{(Eq 3)}$$

$$(H_2PO_2)^- + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2 \qquad \textbf{(Eq 4)}$$

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).

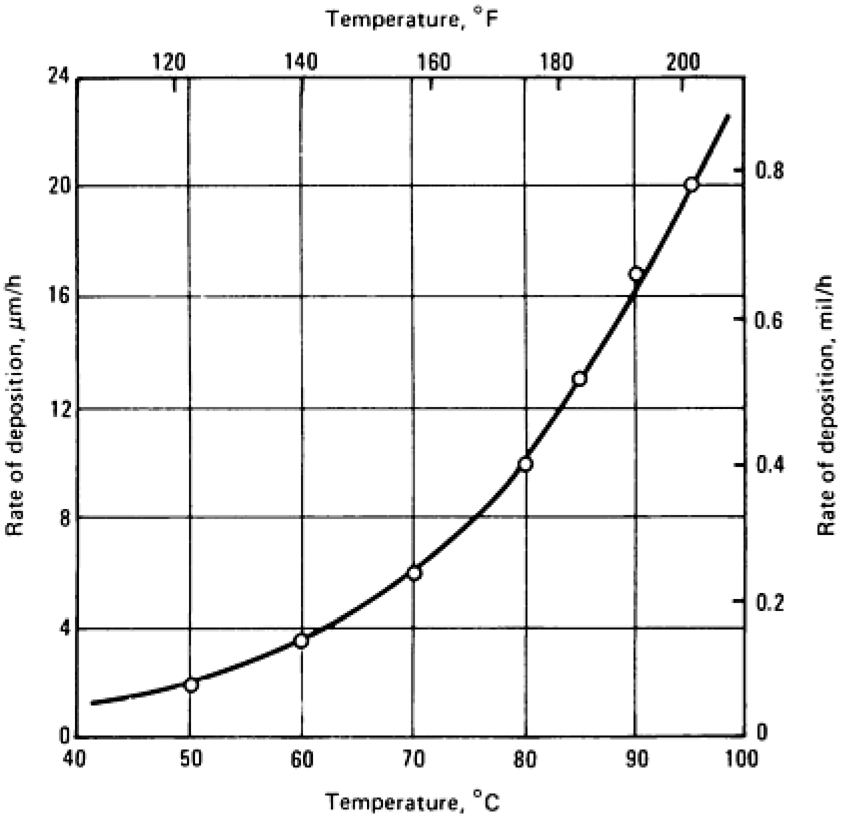

Fig. 1 Effect of solution temperature on the rate of deposition. Tests conducted on bath 3 at 5 pH

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).

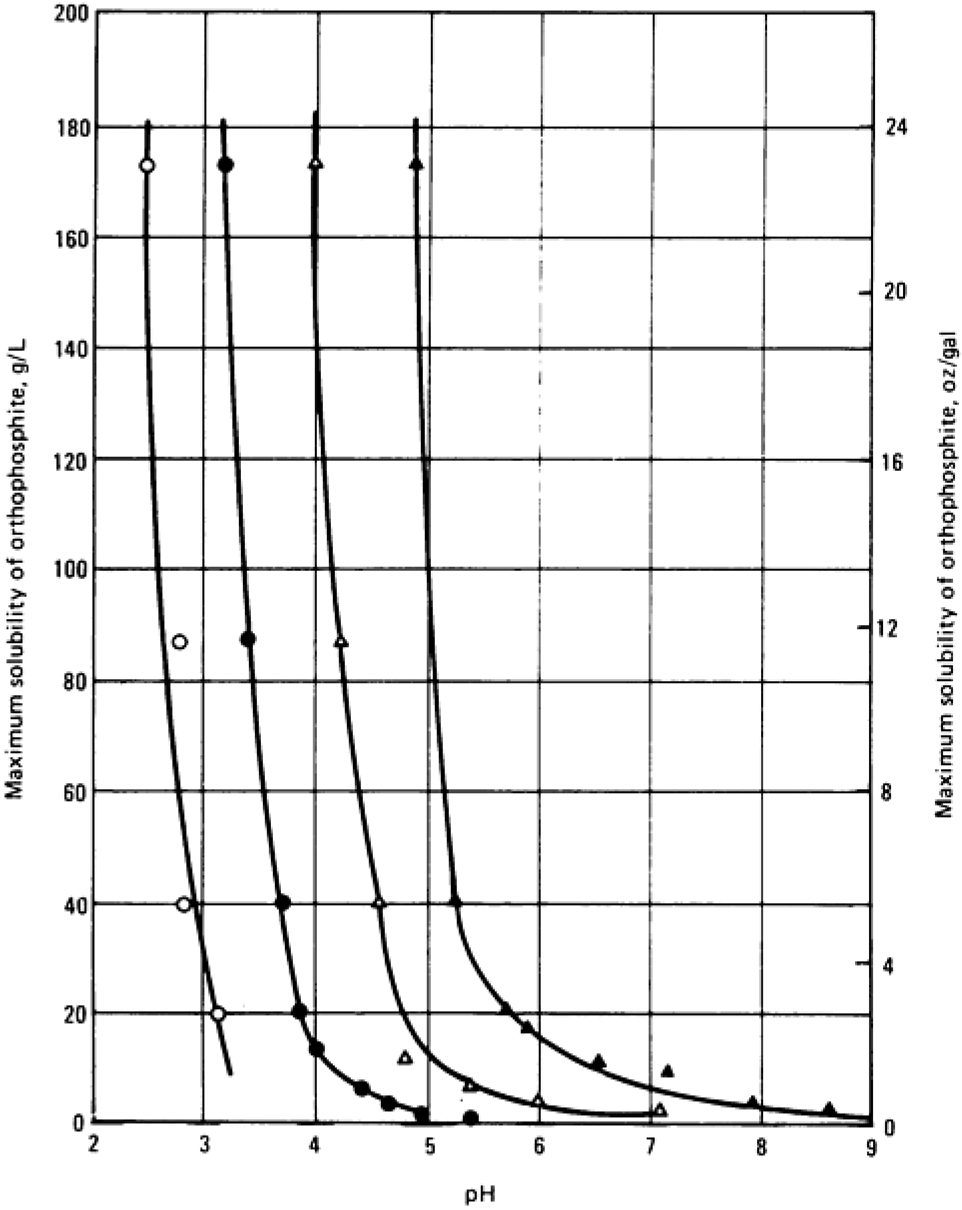

Fig. 2 Limits of solubility for orthophosphite in electroless nickel solutions. Solutions contain 30 g/L (4 oz/gal) nickel chloride ($NiCl_2$) and 10 g/L (1.3 oz/gal) sodium hypophosphite (NaH_2PO_2). d , without a complexing agent; •, with 15 g/L (2 oz/gal) citric acid; V , with 39 g/L (5.2 oz/gal) 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).

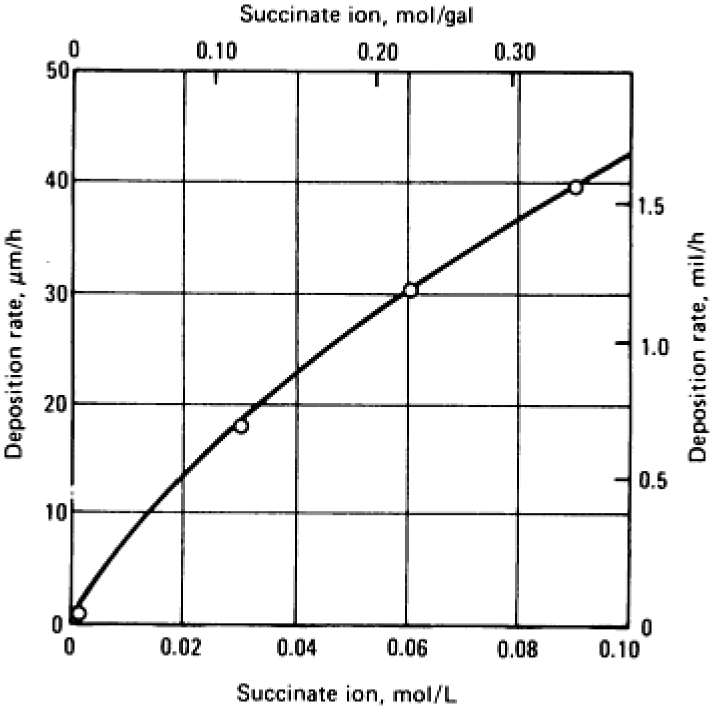

Fig. 3 Effect of succinate additions on the plating rate of an electroless nickel solution. Solutions contain 16 g/L (2.1 oz/gal) nickel chloride ($NiCl_2$) and 24 g/L (3.2 oz/gal) sodium hypophosphite (NaH_2PO_2). 5 g/L (0.7 oz/gal) ammonium hydroxide (NH_4OH) and 1 mg/L (4 mg/gal) lead at 5 pH and 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.

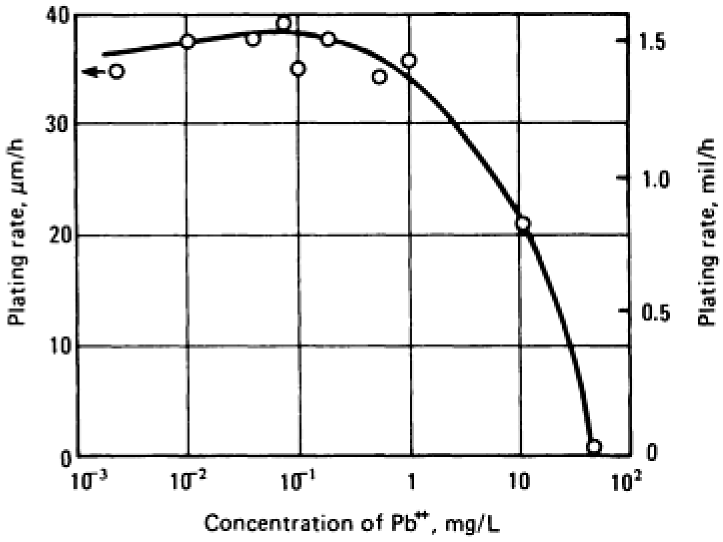

Fig. 4 Effect of lead additions on plating rate in a hypophosphite-reduced succinate-based bath. Bath at 4.6 pH and 95 °C (205 °F). Solutions containing less than 0.1 mg (0.4 mg/gal) Pb^{2+} were unstable.

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).

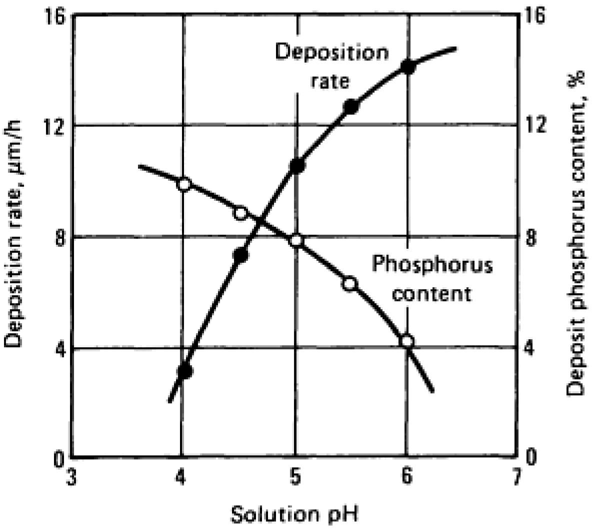

Fig. 5 Effect of solution pH on deposition rate and deposit phosphorus content

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.

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Temperature, °C (°F)	22-30 (72-86)	43-60 (110-140)
Current density, A/dm^2 (A/ft^2)	1.0-3.0 (10-30)	1.0-7.0 (10-70)
Cathode efficiency	. . .	95-100%
Voltage at tank, V	2-5	2-6
pH, electrometric(a)	8.0-8.5	8.0-8.7
Anodes(b)	Copper	Copper
Anode:cathode ratio	2:1	2:1

(a) May be maintained with pyrophosphoric acid and potassium hydroxide.

(b) OFHC anodes

Copper pyrophosphate bath characteristics are intermediate between those of cyanide and acid baths and are very similar to those of the high-efficiency cyanide bath. Electrode efficiencies are 100%; throwing power and plating rates are good. The bath also operates at an almost neutral pH. Deposits from pyrophosphate baths are fine-grain and semibright. For pyrophosphate plating on steel, zinc die castings, magnesium, or aluminum, a preliminary strike should be used. For striking, a dilute cyanide or pyrophosphate copper, nickel, or other solution may be used.

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Acid Plating Baths

Electrodeposition of copper from acid baths is used extensively for electroforming, electrorefining, and decorative electroplating. Acid copper plating baths contain copper in the bivalent form and are more tolerant of ionic impurities than alkaline baths. They also have less macro throwing power and poorer metal distribution. Acid baths have excellent micro throwing power, resulting in the ability to fill or level scratches, grooves, or other substrate conditions, and additionally they are effective in sealing porous substrates. In most instances the smooth deposits produced by these solutions reduce or eliminate the need for mechanical smoothing for various substrates. A cyanide, noncyanide copper, or nickel strike must be applied to steel or zinc-alloy die castings before they are plated in acid copper solutions. Acid copper solutions cannot be used directly over substrates that are attacked by the high acidity or those where the copper forms an immersion deposit. Immersion deposits usually have poor adhesion to the substrate. Concentration limits and operating conditions of acid copper plating baths are given in Table 4.

Table 4 Compositions and operating conditions of acid copper plating baths

Constituent or condition	**Copper sulfate bath**		**Copper fluoborate bath**	
	General	**Printed circuit through-hole**	**Low copper**	**High copper**
Bath composition, g/L (oz/gal)				
Copper sulfate, $CuSO_4 \cdot 5H_2O$	200-240 (27-32)	60-110 (8-15)	. . .	. . .
Sulfuric acid, H_2SO_4	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Copper fluoborate, $Cu(BF_4)_2$	. . .	. . .	225 (30)	450 (60)
Fluoboric acid, HBF_4	. . .	. . .	To pH	40 (5)
Bath analysis, g/L (oz/gal)				
Copper	50-60 (7-8)	15-28 (2-4)	8 (1)	16 (2)
Sulfuric acid	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Specific gravity at 25 °C (77 °F)	. . .	. . .	1.17-1.18	1.35-1.37
Operating conditions				
Temperature, °C (°F)	20-50 (68-120)	20-40 (68-105)	20-70 (68-160)	20-70 (68-160)
Current density, A/dm^2 (A/ft^2)	2.0-10.0 (20-100)	0.1-6.0 (1-6)	7.0-13.0 (70-130)	12-35 (120-350)
Cathode efficiency, %	95-100	95-100	95-100	95-100
Voltage, V	6	6	6	6-12
pH	. . .	. . .	0.8-1.7	<0.6
Anodes	Copper(a)	Copper(a)	Copper(b)	Copper(b)

(a) Phosphorized copper (0.02-0.08% P) is recommended.

(b) High-purity, oxygen-free, nonphosphorized copper is recommended.

The copper sulfate bath is the most frequently used of the acid copper electrolytes and has its primary use in electroforming. In this application, the advantages of acid copper lie in its strength and ductility. Acid copper sulfate is used to plate thick deposits over 150 μm (6 mils) on large nickel-plated rolls; it is then engraved to electroform textile printing screens. It is also used extensively for the application of copper as an undercoating for bright nickel-chromium plating, especially for automotive components. Plates and rolls have been plated with acid copper sulfate for graphic arts and rotogravure printing where thicknesses of 500 μm (20 mils) or more are not uncommon. Bright acid copper sulfate baths are used extensively as an underlayer in decorative plating of the plastic trim found on automobiles, appliances, and various housewares. By altering the composition of the copper sulfate bath, it can be used in through-hole plating of printed circuit boards where a deposit ratio of 1 to 1 in the hole-to-board surface is desired. In some applications, acid copper sulfate solutions are used to plate over electroless deposited copper or nickel. With additives, the bath produces a bright deposit with good leveling characteristics or a semibright deposit that is easily buffed. Where copper is used as an undercoating, deposit thicknesses will generally range up to about 50 μm (2 mils).

The copper fluoborate bath produces high-speed plating and dense deposits up to any required thickness, usually 500 μm (20 mils). This bath is simple to prepare, stable, and easy to control. Operating efficiency approaches 100%. Deposits are smooth and attractive. Deposits from the low-copper bath operated at 49 °C (120 °F) are soft and are easily buffed to a high luster. The addition of molasses to either the high copper or the low copper bath operated at 49 °C (120 °F) results in deposits that are harder and stronger. Good smoothness of coatings up to 500 μm (20 mils) thick can be obtained without addition agents. For greater thicknesses, addition agents must be used to avoid excessive porosity.

Surface Preparation Considerations

Careful cleaning and preparation of the substrate material being plated is required for the effective electrodeposition of copper. Surface oils and greases, buffing compounds, rust, scale, and oxides, especially around weld or solder areas must be thoroughly removed before copper plating to ensure adhesion and to minimize contamination of the plating bath. However, before considering any preparation, it is important to know the type of substrate being used as well as any substrate surface conditions that may be present. This information is important because the preparation cycles used prior to copper plating can vary considerably, depending on the alloy or type of substrate. Also, substrate heat treatment variations can contribute to complications in surface preparation. Because there are also variations in organic and inorganic soil conditions on the work to be plated, preparation cycles should include adequate cleaning, rinsing, and activation steps to ensure quality deposits. Some of the cleaning methods used to prepare substrate surfaces prior to copper plating include soak or electrolytic alkaline cleaning, alkaline derusting, vapor degreasing, and solvent cleaning.

Good rinsing between preparation steps is a very important and often-overlooked step in the preparation cycle. Time, temperature, and concentration considerations should be applied to rinsing techniques as well as to the cleaning processing solutions. Often, rinse times are too short, immersion temperatures are too cold, and the water flow rate is too low to adequately rinse cleaner films from the surfaces.

The activation step is usually carried out with the use of an acid to remove inorganic soils, oxides, or cleaner films from the surfaces. The acid used depends on the type of substrate to be plated. The most commonly used acids in preplate processes are hydrochloric acid and sulfuric acid. More information about the techniques used in these preparation processes is found in the Section "Surface Cleaning" in this Volume. Specifications and practices for copper electroplating are given in Table 5.

Table 5 Specifications and standards for copper electroplating

Specification	**Uses**
Copper plating	
AMS 2418	Copper plating
MIL-C-14550 (Ord)	Copper plating

ASTM B 503	Recommended practice for use of copper and nickel electroplating solution for electroforming
Copper plating in multiplate systems	
ASTM B 456	Specification for electrodeposited coatings of copper plus nickel plus chromium and nickel plus chromium
ASTM B 200	Specification for electrodeposited coatings of lead and lead-tin alloys on steel and ferrous alloys
AMS 2412	Plating silver, copper strike, low bake
AMS 2413	Silver and rhodium plating
AMS 2420	Plating, aluminum for solderability, zincate process
AMS 2421	Plating, magnesium for solderability, zincate process
QQ-N-290	Nickel plating (electrodeposited)
Surface preparation	
ASTM A 380	Practice for cleaning and descaling stainless steel parts, equipment, and systems
ASTM B 183	Practice for preparation of low-carbon steel for electroplating
ASTM B 242	Practice for preparation of high-carbon steel for electroplating
ASTM B 252	Recommended practice for preparation of zinc alloy die castings for electroplating
ASTM B 253	Practice for preparation of aluminum alloys for electroplating
ASTM B 254	Practice for preparation of and electroplating on stainless steel
ASTM B 281	Practice for preparation of copper and copper-base alloys for electroplating and conversion coatings
ASTM B 319	Guide for preparation of lead and lead alloys for electroplating
ASTM B 322	Practice for cleaning metals prior to electroplating
ASTM B 480	Practice for preparation of magnesium and magnesium alloys for electroplating
ASTM B 481	Practice for preparation of titanium and titanium alloys for electroplating

MIL-HDBK-132 (Ord)	Military handbook, protective finishes

Cyanide Baths. Although the dilute cyanide and Rochelle cyanide baths exert a significant cleaning action on the surface of the parts during the plating operation, thorough cleaning of parts to be plated in these baths is still necessary.

The high-efficiency sodium cyanide and potassium cyanide electrolytes have virtually no surface-cleaning ability during plating because of the absence of hydrogen evolution. Parts to be plated in these electrolytes must be thoroughly cleaned. Parts also must receive first a dilute cyanide copper strike about 1.3 μm (0.05 mil) thick.

Noncyanide Alkaline Baths. Unlike cyanide baths, noncyanide alkaline baths do not offer any cleaning, and parts plated in these electrolytes must first be thoroughly cleaned, rinsed, and activated. If being used as a strike prior to acid copper or other similar deposit, a minimum thickness of 5.2 μm (0.2 mil) is desired. These systems can be plated directly on properly prepared steel, brass, stainless steel, zincated aluminum, lead-tin, and most high-quality, properly prepared zinc-base die castings (Ref 4, 5). One advantage of the noncyanide electrolyte is the fact that accidental drag-in of acids poses no hazard of the evolution of poisonous cyanide gas, which could occur with cyanide copper electrolytes.

Pyrophosphate Baths. If pyrophosphate electrolytes are to be used, conventional cleaning cycles are generally satisfactory. A preliminary strike should be applied to steel, zinc-base die castings, magnesium, and aluminum. The strike solution may be a dilute cyanide copper, dilute pyrophosphate copper, or nickel. If a cyanide copper strike is used, adequate rinsing or, preferably, a mild acid dip following the strike is recommended before final pyrophosphate copper plating.

Acid Baths. When sulfate or fluoborate copper is to be deposited, steel or zinc must first receive a cyanide or noncyanide alkaline copper or nickel strike. With complete coverage, the strike may be as thin as 2 μm (0.08 mil). After the strike, the parts should be dipped in a dilute solution of sulfuric acid to neutralize solution retained from the alkaline strike bath. The parts should be rinsed thoroughly before acid copper plating. Nickel or nickel alloy parts, when surface activated by reverse-current etching in sulfuric acid, can be plated directly, provided contact is made to the work with the current or power on before immersion into the acid copper solution.

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Bath Composition and Operating Variables

The compositions and analyses given in Tables 1, 2, 3, and 4 for cyanide, noncyanide alkaline, pyrophosphate, and acid copper plating baths may be varied within the control limits to satisfy requirements for specific applications.

Current density can be altered to effect more efficient control and to increase the deposition rate of copper. The data in Table 6 can be used as a guide to the selection of current density.

Table 6 Estimated time required for plating copper (valence 1) to a given thickness at 100% cathode efficiency

Cyanide baths contain copper with a valence of 1. For baths containing copper with a valence of 2, such as noncyanide alkaline, sulfate, pyrophosphate, and fluoborate baths, double the time values given in this table. Values must be corrected for losses in cathode efficiency by adding the difference between the actual cathode efficiency and 100%; for example, for 70% cathode efficiency, add 30% to values in table to determine estimated time.

Thickness of plate	**Plating time, min**[(a)] **at current density, A/dm^2 (A/ft^2)**

µm	mils	1.0 (10)	1.5 (15)	2.0 (20)	2.5 (25)	3.0 (30)	3.5 (35)	4.0 (40)	4.5 (45)
2	0.08	4	3	2	2	2	1	1	1
5	0.2	11	8	6	5	4	3	3	2
10	0.4	23	15	11	9	8	6	6	5
20	0.8	45	30	23	18	15	13	11	9
30	1.2	68	45	34	27	23	19	17	14
40	1.6	90	60	45	36	30	26	23	18
50	2.0	113	75	57	45	38	32	28	23
60	2.4	136	90	68	54	45	39	34	27
70	2.8	158	106	79	63	53	45	40	32
80	3.1	181	120	90	72	60	52	45	36

(a) To nearest whole value

Impurities. The degree of control required to protect copper plating baths from impurities varies with the type of bath and the method of processing used. Known causes of roughness in copper deposits are:

- Dragover from cleaners, which results in the formation of insoluble silicates in the electrolyte
- Poor anode corrosion
- Insoluble metallic sulfides because of sulfide impurities
- Organic matter in the water used for composition, especially in rinse tanks
- Insoluble carbonates because of calcium and magnesium in hard water
- Oil from overhead conveyors
- Airborne dust or particles

If the level of impurities reaches a critical point, causing poor results, a batch carbon treatment or circulation through a carbon-packed filter may be required. For the noncyanide processes, a sulfur-free carbon pack must be maintained on the bath and changed weekly. Lead and cyanide are contaminants to these systems and tend to cause a black smutted deposit. When converting a plating line from a cyanide system to a noncyanide electrolyte, all associated equipment must be cleaned and thoroughly washed to ensure no cyanide contamination.

Caution: Cyanide remains in the system. Acids can be used only after all traces of cyanide have been eliminated.

Purity of Water Used in Composition. The purity of the water used in the composition of the baths is important for all plating operations. Iron in the water causes roughness in the deposit if the pH of the electrolyte is above 3.5 where iron can be precipitated. Chlorides in concentrations greater than about 0.44 g/L (0.05 oz/gal) promote the formation of nodular deposits. Calcium, magnesium, and iron precipitate in the bath. Organic matter may cause pitting of deposits.

When plating in sodium or potassium, high-efficiency electrolytes and distilled, deionized, softened, or good quality tap water may be used for solution composition and for replenishment. Tap water with high contents of calcium and/or iron should not be used, because it may cause roughness of the deposit. Softened water should be used with care, especially in plating baths where chloride contents are critical, such as bright copper sulfate baths.

Agitation during plating permits the use of higher current densities, which create rapid deposition of copper. The amount of increase permissible in current density varies for the different baths. Preferred methods of agitation for the types of baths are:

Cyanide baths	Cathode movement, air agitation, or both
Pyrophosphate baths	Air agitation
Acid baths	Cathode movement, air agitation, or both
Noncyanide baths	Vigorous air agitation

When air agitation is used, all airline pipes should be made of inert material or coated with an inert material to prevent attack by the electrolytes. The air used for agitation must be clean to avoid bath contamination. Filtered air from a low-pressure blower is required.

Ultrasonic vibration also has been used for the agitation of copper plating baths. This method does not largely improve the properties or appearance of electroplates, but it can improve plating speed by permitting an increase in the current density without the hazard of burning the parts. Increased plating speed does not necessarily justify the increased cost and complexity of ultrasonic operation, because the high-speed baths can usually be operated with a fairly high current density at nearly 100% efficiency.

Plating in Dilute Cyanide Baths

In the dilute cyanide bath, corrosion of the anodes increases with increasing concentration of free cyanide. Low free-cyanide content may cause rough deposits due to anode polarization; however, excessive free cyanide lowers cathode efficiency, resulting in thinner deposits per unit of time. Modifications of the pH, or alkalinity, of the strike compositions are used for striking various substrates. For use on steel, additional NaOH or KOH improves the conductivity of the solution and aids in protecting steel anode baskets, tanks, and other steel fixtures from corrosion. For use on zinc-base die castings, the hydroxide concentration is kept in the range of 1.3 to 3.8 g/L (0.2 to 0.5 oz/gal). For use on zincated aluminum alloys, the pH should be reduced to approximately 9.7 to 10.0 with sodium bicarbonate. The operator should keep adding tartaric acid or sodium bicarbonate to the solution to maintain the desired pH range (e.g., 10.0 to 10.5 for plating on aluminum alloys.

The dilute copper cyanide bath can be operated at room temperature, but the general practice is to operate the bath between 32 and 49 °C (90 and 120 °F) to increase the rate of deposition and to improve anode dissolution. This electrolyte is usually operated with a cathode current density of 1 to 1.5 A/dm^2 (10 to 15 A/ft^2). The tank voltage is normally between 4 and 6 V.

Agitation of the bath produces more uniform composition throughout the electrolyte, more uniform anode corrosion, and an increase in current densities where the brightest deposits are obtained. Current densities in excess of 5 A/dm^2 (50 A/ft^2) have been applied successfully by using air agitation of the solution and agitating the work.

Continuous filtration is preferred for dilute cyanide baths. Organic contamination or suspended matter in the strike is frequently responsible for roughness of copper plate subsequently deposited in the cyanide copper plating bath. Hexavalent chromium in the strike causes blistering of the deposit. Proprietary additives can be used to improve the bath operation, as well as aid in the control of organic and inorganic contaminants. These proprietary additives consist of organic complexing agents, such as tartrate salts. Organic reducing agents are used to control impurities such as hexavalent chromium. Wetting agents (surfactants) are used to control organic contaminants and to lower the surface tension of the plating solution, to allow better throwing power of copper over substrate irregularities, and to aid drainage and rinsing.

Plating in Rochelle Cyanide Baths

Rochelle electrolytes with lower metal concentrations can be used both for striking applications and, with higher metal concentrations, for plating applications. Rochelle salts produce some grain refinement, reduce the effects of some metallic contaminants, and aid in anode corrosion by increasing the anode current density range before anode polarization occurs. The Rochelle electrolyte can also be used for periodic-reverse plating with good results. Barrel plating with a Rochelle bath requires a variation in the chemistry. When plating parts that tend to nest or stick together during the barrel rotation, it is necessary to increase the free cyanide to 25 to 30 g/L (3 to 4 oz/gal) or slightly higher to obtain adequate coverage on the nested parts.

Rochelle baths usually are operated at a current density between 2 and 5 A/dm^2 (20 and 50 A/ft^2). Substituting potassium salts for sodium salts in the baths with higher metal concentration, up to 38 g/L (5 oz/gal) copper, can increase the allowable current density to 6 A/dm^2 (60 A/ft ^{2}), with the penalty of lowering the cathode efficiency. The Rochelle baths are usually operated at between 54 and 71 °C (130 and 160 °F) for best efficiency. The rate of deposition is higher at the higher temperatures. A high-efficiency electrolyte having a higher metal concentration can be operated at up to 77 °C (170 °F). For copper plating zinc-base die castings, the electrolyte is best operated at 60 to 71 °C (140 to 160 °F), provided the pH of the bath is maintained between 11.6 and 12.3. An increase in the operating temperature of Rochelle cyanide baths increases the efficiency of the anode and cathode; however, free cyanide decomposes more rapidly, which increases carbonate formation. An increase in agitation causes an increase in anode efficiency, but this also increases carbonate formation. Carbonates are always present in cyanide copper solutions from oxidation of the cyanide and, also, from adsorption of carbon dioxide from the air that reacts with the alkali in solution. Carbonates from a sodium copper cyanide plating solution can be removed by cooling the solution, which precipitates the less soluble sodium carbonate. High carbonate concentrations lower the anode efficiency, which accelerates additional carbonate formation in addition to producing rough or porous plated deposits (Ref 6).

Rochelle copper baths should be maintained at a pH between 12.2 and 13.0. Anode efficiency may be prohibitively low if the pH is too high. Raising the pH also decreases the voltage drop across the anode film. Figure 1 shows a buffer curve for adjusting the pH of Rochelle electrolytes.

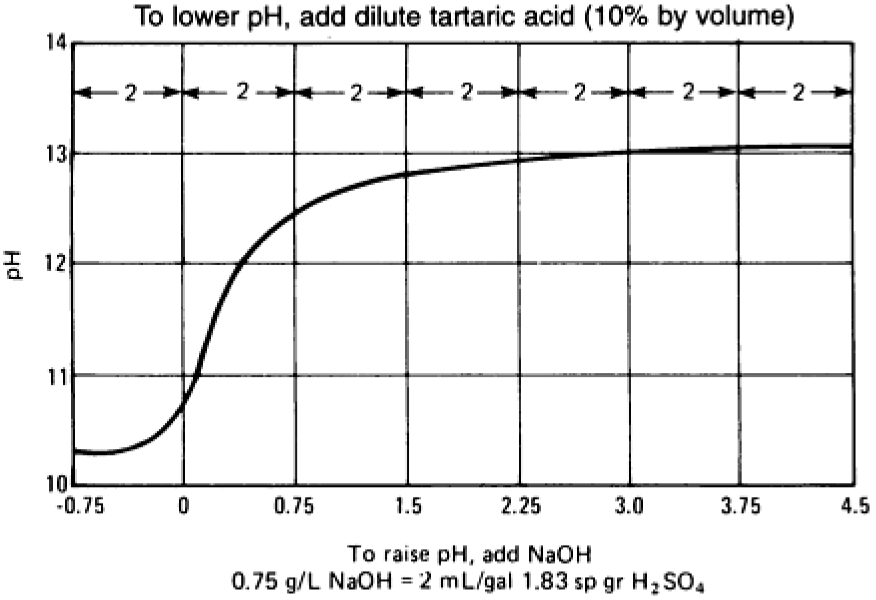

Fig. 1 Buffer curve for adjusting the pH of Rochelle electrolytes. Source: Ref 7

Conductivity of the bath is improved by raising the free alkali cyanide and the concentration of the copper complexes. When depositing copper directly on steel, brass, or copper, conductivity can be improved by the addition of 2 to 15 g/L ($\frac{1}{4}$ to 2 oz/gal) of sodium hydroxide. Sodium hydroxide concentrations should be reduced if the electrolyte is used to deposit copper onto zinc-base die castings, aluminum, or magnesium.

Rochelle baths can become contaminated during plating of zinc-base die castings. Zinc contamination can be removed by electrolysis of the bath at room temperature, at the current density that produces the most brassy or off-color deposit, usually 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2). Iron, which forms complexes with cyanide, cannot be removed readily from the bath and causes a reduction in current efficiency. Drag-in of chloride ion from acid dips must be kept very low to prevent iron buildup due to dissolution of steel equipment. Bipolarity of steel tanks or heat exchangers should be avoided.

The Rochelle bath is susceptible to organic contamination, which can be controlled by the use of wetting agents. Organic contaminants should be removed by periodic batch treatment of the electrolyte with activated carbon, followed by filtration. Organic contamination is especially high in barrel plating. A low-foaming, free-rinsing surfactant or a dispersion agent must be used in barrel plating baths to prevent organic contamination from adversely affecting the quality of the plated deposit. Organic contamination can be controlled with carbon treatment methods. Continuous filtration of cyanide electrolytes is recommended to eliminate particulate matter or salts, which can result in rough deposits.

Increase in the current density or the presence of lead in the Rochelle cyanide bath causes an increase in the stresses of copper plate. These stresses can be reduced by increasing the concentration of copper in Rochelle baths. The addition of 15 g/L (2 oz/gal) of potassium thiocyanate produces an expansion stress instead of the usual contraction stress. Figure 2 shows stress in thin copper electrodeposits plated from a cyanide solution onto stainless steel.

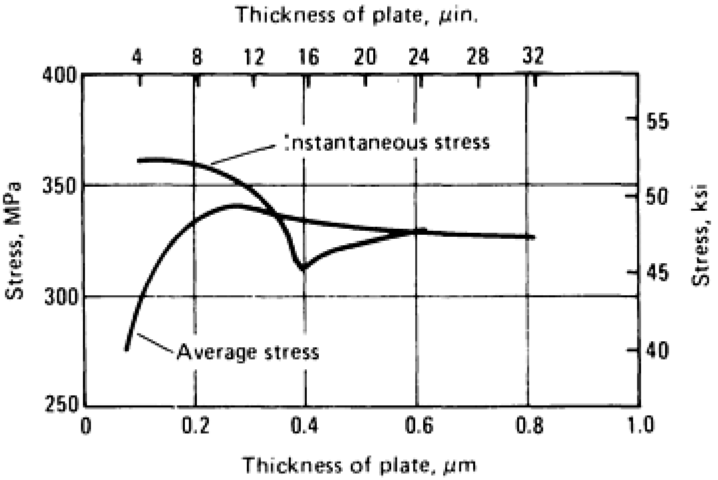

Fig. 2 Stress in thin copper plate deposited on stainless steel spirals. Stainless steel spirals are 0.127 mm (0.005 in.) thick. Source: Ref 8

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Plating in High-Efficiency Sodium and Potassium Cyanide Baths

High-efficiency sodium and potassium cyanide baths allow the use of higher current densities. Cyanide plating baths typically decrease in cathode efficiency, or speed of deposition, with increasing current, which accounts for the good plate distribution (throwing power). The cathode efficiency approaches 100% only at low current densities, often $10A/dm^2$ or less. With more practical current densities of 2.0 to 3.0 A/dm^2, the cathode efficiency may drop 20%, especially with lower agitation rates. The sodium or potassium constituent improves the conductivity of the bath.

Operation of the sodium cyanide and potassium cyanide electrolytes at 66 to 74 °C (150 to 165 °F) produces quality deposits. Temperatures in excess of 74 °C (165 °F) allow the use of higher current densities, but breakdown of the cyanide becomes excessive at elevated temperatures. The anode current densities are limited by polarization, resulting in poor anode efficiency and higher voltage requirements. The cathode current densities are limited by burning of the deposit, resulting in reduced efficiency, loss of brightness, and roughness. These limits are higher in the potassium cyanide electrolyte.

Agitation of sodium cyanide and potassium cyanide high-efficiency baths is important for achieving maximum plating speed. Agitation can be accomplished by solution movement, cathode-rod movement, or use of air. Each type of agitation improves the maximum allowable current densities, with air agitation providing the greatest improvement. However, it should be noted that carbonate levels in air-agitated baths tend to increase at a greater rate than baths using mechanical agitation. All three types of agitation may be used within a single bath. Solution movement can be accomplished by mixing or by the flow of solution through filtration equipment. Cathode-rod movement of about 1 to 2 m/min (3 to 7 ft/min) allows increased plating rates. Gentle air agitation should be supplied by the use of a low-pressure blower that has a clean, filtered air source. Care must be taken to use clean, oil-free air for agitation to avoid contamination of the plating solution.

Filtration is also essential when operating high-efficiency cyanide copper electrolytes, especially for plating deposits thicker than 13 μm (0.5 mil). Filtration equipment should have the capability of one to two complete turnovers of the solution each hour while removing particulate matter from the electrolyte. Roughness of the copper deposits from particulate matter is often caused by faulty cleaning or by the formation of metallic copper or cuprous oxide particles at the anodes. Suspended dirt or solid matter in the cyanide copper electrolyte also causes surface roughness. Anode bags of proper size, material, weight, and weave are beneficial in retaining particulate matter formed at the anode. Other foreign particles introduced into the cyanide copper electrolyte are removed by the filtration equipment.

Carbonate buildup in high-efficiency copper cyanide baths can adversely affect the bath operation. High concentrations of carbonate reduce plating efficiency and speed. Excessive carbonates also affect the smoothness of the deposits. Carbonate contents of 120 to 150 g/L (16 to 20 oz/gal) or more may result in lower plating efficiency and plating speed. Excessive carbonates can also lower and reduce the acceptable plating range. These effects are more pronounced in a sodium cyanide bath than in a potassium cyanide bath.

The primary source of carbonate formation is the breakdown of cyanide as a result of poor anode efficiency. Operating cyanide electrolytes at temperatures above the recommended levels can also result in carbonate formation. Operating temperatures above about 74 °C (165 °F) cause decomposition of the cyanide ion. Air containing high levels of carbon dioxide should not be used in air-agitated systems, because the carbon dioxide is dissolved by the alkaline plating solution, also forming carbonate. The air source for air-agitated systems should be placed where it provides a clean, fresh supply.

Excessive carbonates can be removed by freezing or precipitation with lime or proprietary additives. Sodium cyanide baths can be treated either by precipitation or freezing. Potassium cyanide baths can only be treated by precipitation. Freezing is not effective for potassium cyanide baths because of the high solubility of the carbonate salts.

Current interruption cycles frequently improve the operating range of high-efficiency sodium or potassium copper cyanide plating solutions. Current interruption cycles generally allow the use of higher current densities while maintaining bath efficiency. Current interruption cycles also improve the brightness of the copper deposits, and in some cases they give excellent deposit brightness from bright plating baths that are so contaminated that acceptable deposits cannot be produced when using continuous direct current.

Current interruption cycles in the range of 8 to 15 s plating time followed by 1 to 3 s current interruption are generally used. Plating times of less than 8 s and current interruptions of more than 3 s lower the net plating rate. Plating times of more than 15 s and current interruption of less than 1 s reduce the benefits obtained by using a current interruption cycle.

The use of periodic current reversal can also be used to great advantage in high-efficiency copper cyanide plating solutions. This technique involves plating parts in the conventional manner for a selected time and then deplating for a shorter period by reversing the current. Shorter periodic reversal cycles, such as 2 to 40 s of plating followed by 1 to 10 s of deplating (reversal), result in improved deposit brightness similar to that obtained with current interruption. A major advantage in using periodic reversal is the degree of leveling that can be achieved, particularly when relatively long reversal cycles are used. These longer cycles, in excess of 45 s direct with reverse cycles in excess of 10 s, can provide leveling characteristics in excess of 50%. The use of periodic reversal permits the use of higher plating and deplating current densities.

The leveling characteristics of the deposit are improved by increasing the reversal current, whereas cycle efficiency is increased by lowering the reversal current. Figure 3 shows cycle efficiency for periodic-reverse plating. Figure 4 indicates thickness of deposit as a function of cycle efficiency.

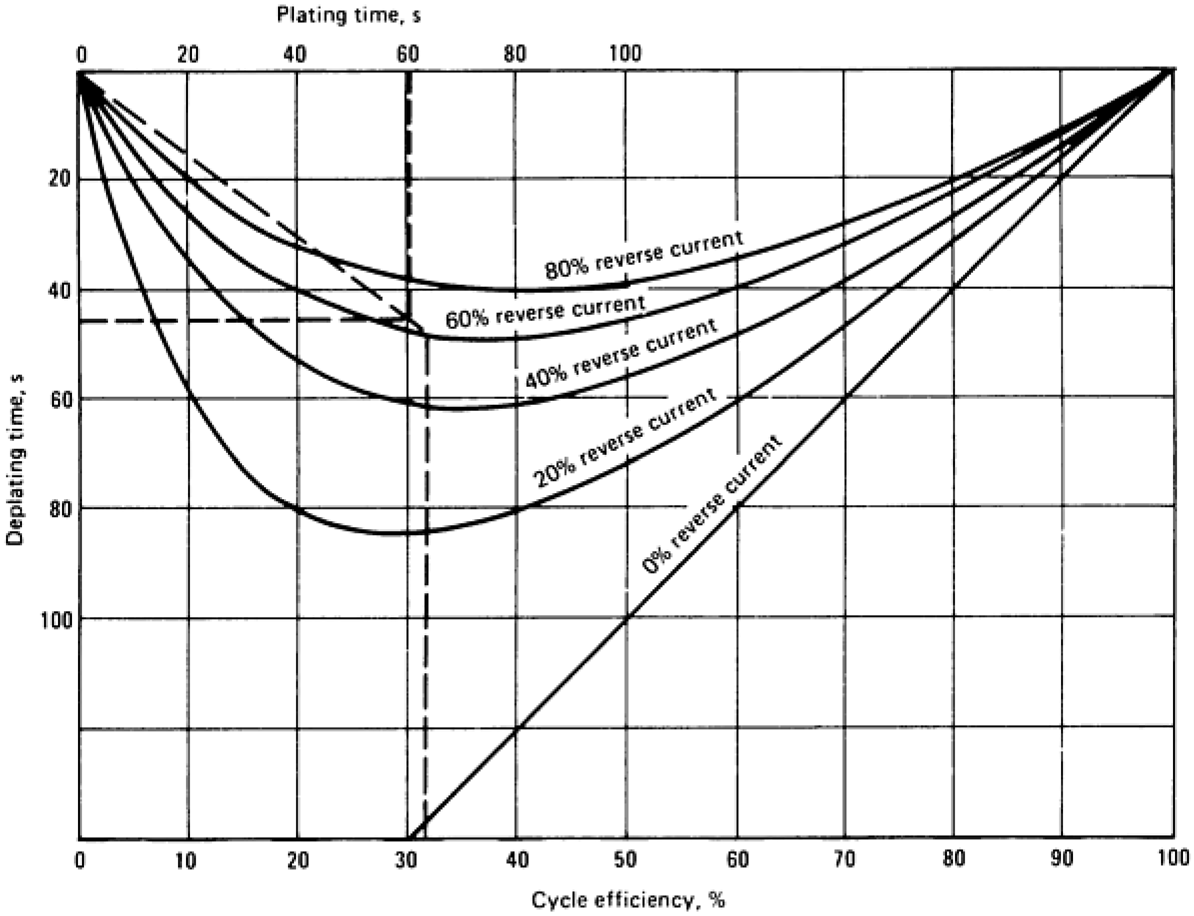

Fig. 3 Cycle efficiency during copper plating with periodic current reversal. Source: Ref 9

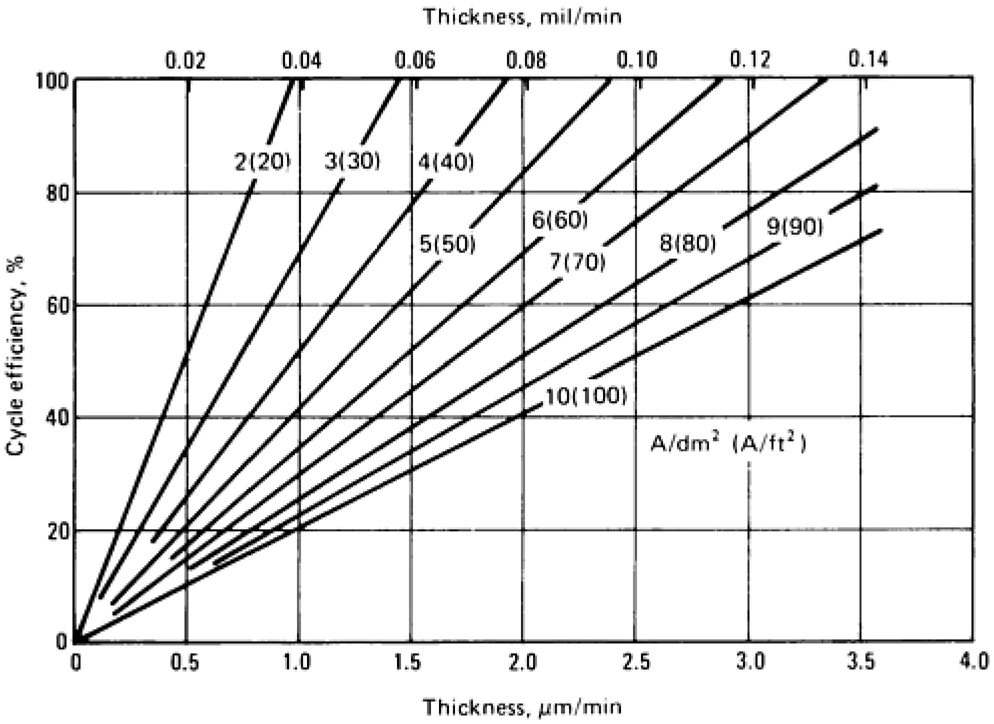

Fig. 4 Thickness of copper deposits as a function of cycle efficiency and current density during plating with periodic current reversal. Source: Ref 9

Another current-interrupting scheme being used for this and other copper plating systems is pulse plating. This normally involves a pulse power source (rectifier) that produces square-wave current pulses. *Square wave* conventionally suggests a pulse with a rise-and-fall time of approximately 10 to 85 μs and a standard frequency of 150 and 10,000 cycles. The periodic interruption of the current with proper time sequences allows much faster plating without surface burning, produces finer grain deposits, and increases throwing power and distribution.

Proprietary additives are used in high-efficiency copper cyanide baths to improve anode corrosion, increase both anode and cathode efficiencies, and control contamination. Organic and metallic additives are also used to improve deposit characteristics and brightness. These additives produce deposits ranging from matte to full-bright.

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Plating in Noncyanide Copper Baths

The development and refinement of proprietary noncyanide copper baths continues today. The copper deposit from these systems is a fine-grain, dense deposit (Ref 3). The noncyanide copper systems exhibit excellent throwing and covering power, even in deeply recessed areas. In addition to eliminating the cyanide, these processes operate at much lower copper metal concentrations of 7.5 to 13.5 g/L (1 to 2 oz/gal). As a result, they offer additional savings in lowering waste treatment costs. Copper sulfate is the source of copper ions for these systems. The plating electrolytes producing these deposits are very stable compared to those of cyanide copper processes, because there is no decomposition of cyanide resulting in carbonate buildup.

Over the typical current density range of 0.5 to 3.5 A/dm^2 (5 to 35 A/ft^2), the cathode efficiency of noncyanide systems approaches 100%. The good efficiency tends to offset the lower deposition rate of divalent copper electrolysis compared to that of monovalent copper systems. Agitation has a dramatic effect on deposit appearance and cathode efficiency. To obtain a uniform, fine-grain deposit over a wide current density range, air agitation is required for these systems. Lack of agitation produces dull, burned deposits at average current densities of 1.5 to 2.0 A/dm^2 (15 to 20 A/ft^2).

Of the commercially available systems, one process is affected by the buildup of cuprous ions in the cupric phosphonate system, which results in rough, nonadherent copper deposits (Ref 10). To overcome this effect, the process uses continuous electrolysis carried out in an auxiliary tank with special ceramic or platinized anodes to oxidize the cuprous to cupric.

Because the operating pH of these systems is in the range of 9 to 10, these baths can be used as both strikes and plates. There are no special adjustments required for processing zinc diecast and zincated aluminum, as there are in cyanide copper plating. At pH values below 9, the deposits are brighter but adhesion is adversely affected. Values greater than 10 cause high-current-density dullness and can reduce the limiting current density.

These systems, unlike the cyanide systems, are more susceptible to metallic and organic contaminants. Iron, lead, and silver are critical impurities that should be removed by low-current-density electrolytic treatments. Organic impurities are treated using hydrogen peroxide and carbon treatments on a regular basis. Continuous filtration through a 10 μm retention-size cartridge is beneficial for the noncyanide systems. Occasional carbon filtration using a sulfur-free carbon can be used to control organic contamination. Noncyanide systems have very little tolerance to cyanide contamination. When converting cyanide plating lines to noncyanide processes, it is essential to clean and leach out all the cyanide from the tank linings, racks, filters, heaters, plating barrels, and any associated equipment.

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Plating in Pyrophosphate Baths

Copper pyrophosphate plating baths offer a number of desirable features. Copper pyrophosphate forms a highly soluble and conductive complex when dissolved in potassium pyrophosphate solution. Potassium salts are preferred because of their higher solubilities. Copper pyrophosphate plating baths operate at nearly 100% cathode efficiency and provide good throwing power. They are noncorrosive because the operating pH is near neutral. Concentration limits and operating conditions for copper pyrophosphate baths are given in Table 3.

Pyrophosphate forms a highly soluble complex with copper. Excess pyrophosphate is necessary to increase the conductivity of the bath and to effect proper corrosion of the anodes. Ammonia assists anode corrosion, helps enhance the luster of the deposit, and aids pH control. Nitrate allows the use of higher operating current densities by inhibiting the reduction of hydrogen at the upper end of the current density range. The pH of the pyrophosphate bath is maintained between 8.0 and 8.8. A high pH reduces anode efficiency, and a low pH reduces the throwing power of the solution and the stability of the complex compound in solution with the formation of orthophosphate. The pH of the bath can be lowered with pyrophosphoric acid and raised with potassium hydroxide. Good agitation is also essential for consistent operation. Air agitation provides for good performance of the anodes and cathodes and is preferred to cathode agitation.

Pyrophosphate electrolytes can be operated at current densities up to 7.0 A/dm^2 (70 A/ft^2) or higher. The operating current density can be increased by agitating the solution or by increasing the temperature of the bath. The anode current density should be maintained between 2 and 4 A/dm^2 (20 and 40 A/ft^2).

High bath temperatures should be avoided, because excessive formation of orthophosphate occurs. Orthophosphate formed by the hydrolysis of pyrophosphate is beneficial up to about 90 g/L (12 oz/gal), because it promotes anode corrosion and acts as a buffer. Above this concentration, conductivity and bright plating range are decreased and banded deposits are obtained. Orthophosphate cannot be removed chemically from the solution. The concentration can be reduced only by discarding the bath or diluting and rebuilding the pyrophosphate plating solution.

Copper pyrophosphate plating baths are susceptible to organic contamination, including oil and excess or decomposed addition agents. These are removed by treatment with activated carbon and filtration. Cyanide and lead also contaminate the bath. Cyanide is removed by treatment with hydrogen peroxide and lead by electrolysis. Precautionary methods, such as proper cleaning, adequate rinsing, and good solution control and maintenance, prevent these contaminants from entering or building up in the bath, avoiding the need for frequent purification. Copper pyrophosphate solutions are tolerant of other metallic contamination.

Proprietary brighteners are available that refine the grain structure, impart leveling characteristics, and act as brighteners. However, decomposition products from an excessive additive concentration cause stress and brittle deposits. Thus, for quality deposits, additives should be added to the bath on an as-consumed basis.

Plating in Acid Sulfate Baths

The chemical composition of acid sulfate baths is simple. Copper sulfate pentahydrate and sulfuric acid are the primary constituents of the copper sulfate electrolyte. The metal ions are furnished by the copper sulfate. Sulfuric acid increases solution conductivity and helps prevent the formation of basic cuprous or cupric crystals on the anodes and the tank, which causes poor anode corrosion and roughness. Low sulfuric acid contents produce more high-current-density burn, poorer leveling, more low-current-density dullness, and more nodular deposits. High sulfuric acid has less effect on the deposit but increases the anode dissolution. With cathode efficiencies of 95 to 100%, the copper sulfate bath is easy to operate and control.

Many copper sulfate plating solutions require the use of additives to produce smooth, fine-grain, bright, leveled, and ductile deposits. Most of the addition agents used in copper sulfate plating solutions are proprietary formulations. These proprietary additives are capable of producing the desired characteristics in the copper deposit, and deposit hardness can be increased where necessary.

In copper sulfate systems that produce bright deposits, a catalyst must be added in addition to the primary constituents to avoid streaky deposits. This catalyst is chloride, which is maintained between 0.02 to 0.1 g/L (0.003 to 0.01 oz/gal), or 20 to 100 ppm. The chloride, usually added as hydrochloric acid, inhibits rough nodular plate from forming. Low chloride can cause dark deposits on the edges and high-current-density areas of the work, loss of leveling, loss of brightness, pitting, and poor anode corrosion. High chloride causes streaks, increased brightener usage, and loss of leveling and brightness in the bright bath formulations. High chloride can be reduced with zinc dust treatments or precipitation with silver.

If solution agitation or work movement is minimal, current densities should not exceed about 4.5 A/dm^2 (45 A/ft^2), because excessive anode polarization may occur and the deposits can be spongy. Where higher current densities are desired, such as for electrotypes or wire plating, air agitation is used. Air agitation is necessary to accelerate ionic diffusion and produce high-quality, fine-grain deposits where current densities are in excess of 10 A/dm^2 (100 A/ft^2).

The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper sulfate bath is less significant than the effect of changes in cathode current densities. An increase in temperature results in higher conductivity and reduced anode and cathode polarization. Increased temperature also reduces the tensile strength of deposits and increases grain size. Excessive temperatures should be avoided in copper sulfate baths where proprietary brightener formulations are used, because reduced plating ranges, excessive additive use, and solution contamination from additive breakdown result.

Care must be taken to avoid accelerated buildup of copper metal, as in cases where dragout rates are low or improper anode-to-cathode ratios are maintained. An increase in the concentration of the copper sulfate increases the solution resistivity and slightly reduces the anode and cathode polarization. Copper sulfate concentrations in excess of 248 g/L (33 oz/gal) may result in salt crystallization in the plating solution. Normal bath composition is restored by discarding a portion of the bath and adding water and sulfuric acid.

To improve the throwing power of some bright copper sulfate baths used for plating printed circuit boards, a low copper sulfate and high sulfuric acid electrolyte is used. The use of this electrolyte allows a nearly equal deposit distribution when plating the through-holes of the printed circuit board.

In sulfate electrolytes, impurities such as silver, gold, arsenic, and antimony can codeposit with copper. Arsenic and antimony cause copper deposits to be brittle and rough, and silver may cause roughness. Nickel and iron impurities reduce the conductivity of the plating bath. Lead impurities do not codeposit with copper; however, they precipitate in the electrolyte. Soluble silicates may precipitate onto the work. Organic contamination from decomposition products of addition agents, tank linings, and anode bags can cause brittle or discolored deposits. These organics can be removed from the electrolyte by treating it with activated carbon.

Plating in Fluoborate Baths

Copper fluoborate and fluoboric acid are the primary constituents of the copper fluoborate electrolyte. The metal ions are furnished by the copper fluoborate, which is more soluble than copper sulfate used in the sulfate bath, and the anode current density is not critical. Therefore, the metal-ion concentration in the fluoborate bath can be more than twice that in the copper sulfate solution, and this permits higher cathode current densities. The cupric salts in the fluoborate bath are highly ionized, except for small amounts of less ionized complex salts formed with certain addition agents.

In the copper fluoborate bath, the anode current density can be as high as 40 A/dm^2 (400 A/ft^2) without excessive anode polarization. The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper fluoborate bath is less significant than the effect of changes in cathode current density.

Agitation is preferred for the fluoborate bath, although acceptable deposits 25 μm (1 mil) thick have been produced in a high-concentration bath without agitation and with current density maintained at 35 A/dm^2 (350 A/ft^2). When agitation is used, a low-concentration bath operated at a current density of 4 to 5 A/dm^2 (40 to 50 A/ft^2) is preferred.

Although fluoborate baths containing no additives can produce dense and smooth deposits up to 500 μm (20 mils) thick, additives may be used to aid in the deposition of brighter or more uniform coatings or to assist in control of plating conditions. Although deposits from fluoborate baths are easily buffed to a high luster, brighteners of acetyl thiourea can be added to the electrolyte to produce bright coatings. The addition of free acid to the bath increases solution conductivity, reduces anode and cathode polarization, and prevents the precipitation of basic salts. Hard deposits and minimum edge effects result when molasses (1 mL/L, or 0.1 fluid oz/gal) is added to the electrolyte. If the pH of these baths exceeds 1.7, deposits become dull, dark, and brittle.

The resistivity of fluoborate electrolytes is reduced if the concentration of fluoboric acid exceeds 15 g/L (2 oz/gal) or if the concentration of copper fluoborate exceeds 220 g/L (29 oz/gal). In the fluoborate bath, the metal-ion concentration can be more than double that in a copper sulfate solution containing 50 to 75 g/L (6.7 to 10 oz/gal) of sulfuric acid.

In the fluoborate electrolytes, silver, gold, arsenic, and antimony may co-deposit with copper, but the effects of such impurities in this electrolyte have not been reported. Lead is the only metallic impurity known to interfere with the deposition of ductile copper deposits. Additions of sulfuric acid precipitate the lead. As with the sulfate electrolytes, organic impurities sometimes cause deposits to be brittle or discolored. They can be removed by treating the bath with activated carbon

Wastewater Control and Treatment

Increasing regulations governing discharge water have led to improved techniques for reducing the quantities of wastes that must be treated. These techniques have not only reduced the quantity of wastewater to be treated, but have also reduced the quantity of chemicals used and have lowered water consumption. These methods can be applied to any plating operation. Many references are available, including Ref 11, that cover waste treatment technologies.

The use of counterflow rinses has reduced water consumption and wastewaters while maintaining adequate rinsing between plating operations. Reduced dragout of plating electrolytes can be accomplished by allowing processed parts leaving the plating solution to drain into the plating solution. Drip pans also reduce the amount of electrolyte dragout.

Closed-loop systems have dramatically reduced wastewater, lowered water consumption, and diminished chemical usage. Closed-loop systems allow recovery of rinse waters and chemicals by evaporative, reverse osmosis, or ion exchange recovery methods. Care must be exercised when using closed-loop systems, especially with copper plating, to keep impurities and contaminants from preplate operations out of the copper plating bath where they will be trapped by the closed-loop operation.

In any plating operation, wastewaters must be treated to reduce the hazardous materials to meet regulations. The general procedures for treating copper plating electrolytes and rinse waters resulting from copper plating systems are:

- Cyanide-bearing solutions require oxidation of the cyanide with an oxidizing agent such as chlorine or hypochlorite, followed by precipitation of the heavy metals.
- Noncyanide alkaline solutions are pH-adjusted and have calcium chloride added to precipitate the

copper.

- Pyrophosphate wastes require low pH hydrolysis to orthophosphate, followed by precipitation of the heavy metals.
- Acid sulfate and fluoborate wastes are pH-adjusted to precipitate the copper.

Reference cited in this section

11. J.W. Patterson, *Industrial Waste Water Treatment Technology,* 2nd ed., Butterworth Publishers, 1985

Copper Plating Equipment

Construction materials for equipment are indicated in Table 7. Construction materials for racks and anodes are given in Table 8.

Table 7 Materials of construction for equipment basic to copper plating

Tank linings are of rubber or plastic(a), or Koroseal.

Plating bath	**Heating coils**	**Filters**	**Filter aids**
Dilute cyanide	Low-carbon steel Teflon(b)	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Rochelle cyanide	Low-carbon steel Teflon(b)	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
High-efficiency cyanide	Low-carbon steel Teflon(b)	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Pyrophosphate	Stainless steel Teflon(b)	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Noncyanide alkaline(c)	Stainless steel Titanium	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Acid copper sulfate	Titanium(d) Teflon(b)	Rubber- or vinyl-lined steel	Diatomite Cellulose
Fluoborate	Carbon(d) Teflon(b)	Rubber- or vinyl-lined steel	Diatomite Cellulose

(a) Of approved compositions; in the absence of data on bath contamination and effects on deposits, compatibility tests are required.

(b) Dupont trademark.

(c) Polypropylene filter cartridges may be used.

(d) Also for cooling coils, if bath is used below 32 °C (90 °F)

Table 8 Materials for anodes and racks for use in copper plating

Racks are made of copper(a).

Plating bath	**Anodes**
Dilute cyanide	Copper; steel
Rochelle cyanide	Copper(b)(c)(d)
High-efficiency cyanide	Copper(b)(c)(d)
Noncyanide alkaline	Copper(d)
Pyrophosphate	Copper(b)(c)(d)
Acid copper sulfate	Copper(e)
Fluoborate	Copper(d)

(a) Racks are generally coated with an inert plastic coating to prevent plating.

(b) Cast copper, high purity.

(c) Rolled copper, high purity.

(d) Oxygen-free high-purity copper.

(e) Phosphorized copper

Tanks. For cyanide copper solutions, low-carbon steel tanks are suitable. Polypropylene tanks with adequate reinforcing may also be used, provided that the operating temperature is not excessive. Low-carbon steel tanks should be lined with rubber, polyvinylchloride, or another synthetic material that is not susceptible to attack by the cyanide plating solution. This will prevent bipolar effects, which may rob current from significant areas of the work. Tanks for alkaline noncyanide copper, copper pyrophosphate, acid copper sulfate, and copper fluoborate solutions should be of similar construction. Low-carbon steel tanks used for these solutions must be lined with the above materials to prevent the solutions from attacking the low-carbon steel, resulting in short tank life and immersion deposits. New tanks, as well as all other equipment coming in contact with the plating solution, should be leached before use to remove any materials that may leach into the plating solution and cause poor quality deposits. Leaching solutions should be similar to the plating solution to be used, such as a 15 to 30 g/L (2 to 4 oz/gal) caustic solution for copper cyanide or noncyanide copper equipment, or a 5 to 10% sulfuric acid solution for acid copper sulfate. When converting a tank or line that contained cyanide to a noncyanide electrolyte, it is essential to leach out all residual cyanide from the tank lining and any associated equipment.

Barrels. High-speed copper plating solutions for barrel plating are being used in product operations. Polypropylene barrels have been used successfully for prolonged periods.

Anodes. The types of copper anodes used in each of the copper plating solutions are indicated in Table 8. High-purity copper anodes are recommended. Anodes with a lesser purity may form heavy sludges during electrolysis and contribute appreciably to roughness of the deposit. Anodes used for acid copper plating solutions should be phosphorized. These contain a small percentage of phosphorus, which helps to control chemical dissolution and limits the buildup rate of copper in the acid solution. These types should not be used in alkaline cyanide or noncyanide electrolytes, because anode polarization will develop and cause deposit roughness and more difficult copper metal control.

Copper anodes are available in many forms, such as bars, balls, or chips. Bars are suspended from the anode bar. Balls or chips are placed in titanium baskets.

The anode area in a copper plating solution should be controlled and maintained. If the anode area is not maintained, it decreases as the copper is dissolved and the anode current density rises, resulting in increased polarization and formation of undesirable films. These films can restrict current flow or sluff from the anode and cause roughness in the plating solution.

Anode Bags. Bags made of cotton, Dynel, or polypropylene are used in copper plating solutions. Cotton bags are preferred for cyanide copper solutions, and Dynel or polypropylene are used in the acid copper solutions. Bags are used to keep the fine particles formed at the anode from migrating to the cathode, resulting in roughness. The weave and weight of the anode bag are most important. The bag material must be capable of retaining the particles formed at the anode and at the same time allow the plating solution to flow freely around the anode. Anode bags are not generally used in pyrophosphate baths, because they interfere with dissolution of the anode by decreasing the circulation of the solution around the anode.

Characteristics of Copper Plate

Variations in processing during surface preparation or during plating have significant effects on the quality of the copper electrodeposit. Certain variations can adversely affect the adhesion of copper to the substrate metal. Variations also can affect brightness, porosity, blistering, roughness, hardness, solderability, and leveling.

Brightness. Bright copper coatings are generally obtained by the addition of brighteners to the electrolyte, although buffing of the electrodeposited coating provides a high luster. Plating from high-concentration cyanide baths with current interruption or periodic reversal of current also improves the luster of the copper coating.

Buffing or electropolishing the work before plating it in an electrolyte not containing a brightener results in the deposition of a smooth and sometimes semibright coating. If an electrolyte containing a brightener is used, the luster of the coating is enhanced. The high cost of labor is a primary concern when buffing is considered as the method of brightening the coatings. Plating from high-efficiency cyanide baths with current interruption or periodic reversal of current also improves the luster of the deposits. Improved casting techniques and mechanical finishing before plating can improve the quality of the copper deposit.

Adhesion. Careful selection of substrate surface and proper preparation of the surface before plating are important for good adhesion. In general, cast and other porous surfaces are less receptive to good-quality electrodeposited coatings than wrought surfaces.

The kind of material to be electroplated with copper is another important consideration. For magnesium-base or aluminum-base die castings, the zincate layer between the substrate and the copper deposit is a critical control factor. For a properly activated stainless steel surface, a controlling factor for ensured adhesion of copper is the speed with which the workpiece is immersed in the bath. Some brighteners, especially organic brighteners, may adversely affect adhesion of subsequent electrodeposited coatings. Adhesion of copper electrodeposits from acid baths can be ensured only if a strike from a cyanide copper bath precedes copper plating.

Porosity. The degree of porosity in a copper coating can be controlled by the kind of copper plating bath selected, the composition and control of the electrolyte, the basis material to be plated, and the condition of the surface to be plated. The degree of porosity on the surface of the metal to be plated also dictates the techniques needed to minimize porosity in the coating. A porous surface has high surface area and requires high current density for efficient plating.

Blistering of copper plate, particularly when the plated work is subjected to heat, occurs mostly on zinc-base die castings. Blistering can also occur on parts made of magnesium or aluminum in any form, as a result of poor quality of castings, poor surface preparation, or both. Blistering of copper plate on zinc-base die castings plated in a cyanide strike electrolyte and then subjected to heat can be reduced by lowering the pH of the cyanide strike bath from the range of 12.0 to 12.6 to about 10. Caution must be used because operation at a pH value this low may result in the release of poisonous hydrogen cyanide gas. It is imperative that the plating bath be thoroughly vented.

Blistering of copper-plated magnesium and aluminum, especially during subsequent soldering or heating in service, is caused by poor adhesion at the zincate-copper interface. Unfortunately, blistering often does not become evident until subsequent electrodeposits have been applied and the coating has been subjected to heat. Exposing all copper-plated magnesium and aluminum parts to controlled heat representative of that to be subsequently encountered is good practice. This causes blistering before deposition of subsequent metal coatings if there is poor adhesion at the interface.

Roughness in copper deposits is often caused by foreign particles present in the bath as the result of faulty cleaning, or by the migration to the cathode of metallic copper or cuprous oxide particles that form at the anode. Such roughness is especially likely to occur with the sodium cyanide high-concentration electrolytes and can be prevented by using anode bags.

Solderability of the coating is good when the copper surface is free of oxide, the coating is thick enough, and the adhesion of the copper plate is superior. Direct soldering of electrodeposited copper is not unusual for parts that are subsequently contained in hermetically sealed units.

Soldering is a routine operation for aluminum and magnesium electronic parts used in aerospace applications. A copper strike and copper plate frequently comprise the initial metal coating over the zincated surfaces of these parts, after which electrodeposits of other metals are applied before soldering. A top coat of tin, or of cadmium plate that has been chromate conversion coated, is a particularly effective means of producing a good combination of solderability and corrosion resistance for parts exposed to the atmosphere.

Hardness. Without the use of addition agents, cyanide electrolytes produce harder coatings than acid baths. With the use of addition agents, the hardness of copper deposits from any electrolyte can be increased. Hardness of the electrodeposit is generally associated with fine grain, but hardness can be increased by introducing preferred crystal orientation in the absence of grain refinement. Changes in the copper sulfate or sulfuric acid concentration of acid baths have little effect on the hardness of copper plate.

Leveling has a significant effect on the appearance of the copper coating, as well as on the appearance of the final product when other metals are subsequently plated over the copper. Often, the substrate metal does not have the degree of smoothness that is desired of the plated surface. Metal substrate surfaces can be mechanically or chemically worked to reduce surface roughness before electroplating; however, some copper electrolytes can produce substantial leveling in the deposited coating, thus reducing cost related to elaborate prepolishing or other means of smoothing the surface. The high-concentration potassium cyanide electrolytes produce excellent leveling when certain addition agents are added and interrupted current or periodic reversal is used during plating. Although somewhat less effective, high-concentration sodium cyanide baths, mixed sodium and potassium electrolytes, and Rochelle cyanide electrolytes also have good leveling characteristics with interrupted or periodically reversed current. Acid copper sulfate electrolytes also provide very good leveling characteristics.

Copper in Multiplate Systems

Electrodeposited copper is widely used as a basis for subsequent plated coatings in multiplate systems. The use of copper plate in copper-nickel-chromium systems is discussed in the article "Decorative Chromium Plating" in this Volume.

Cost

The cost of copper plating is influenced largely by the type of installation. In a modern, automated, multiple-phase shop, brighteners and wetting agents probably are the greatest cost factor. In a still-tank operation, the cost of labor is of major importance. An increase in current density reduces cost because of the reduction in time required to deposit a given thickness of coating.

For a routine plating operation, the cost of the copper deposited can be estimated with the aid of Fig. 5. For example, Fig. 5 shows that 120 g (4 oz) of copper is required for plating an area of 0.7 m^2 (7 ft^2) with a coating 20 μm (0.8 mil) thick. The cost of the copper coating is obtained by multiplying the weight of copper required by the cost of copper anodes. For areas larger than 2.4 m^2 (10 ft^2), multiply by the proper factor.

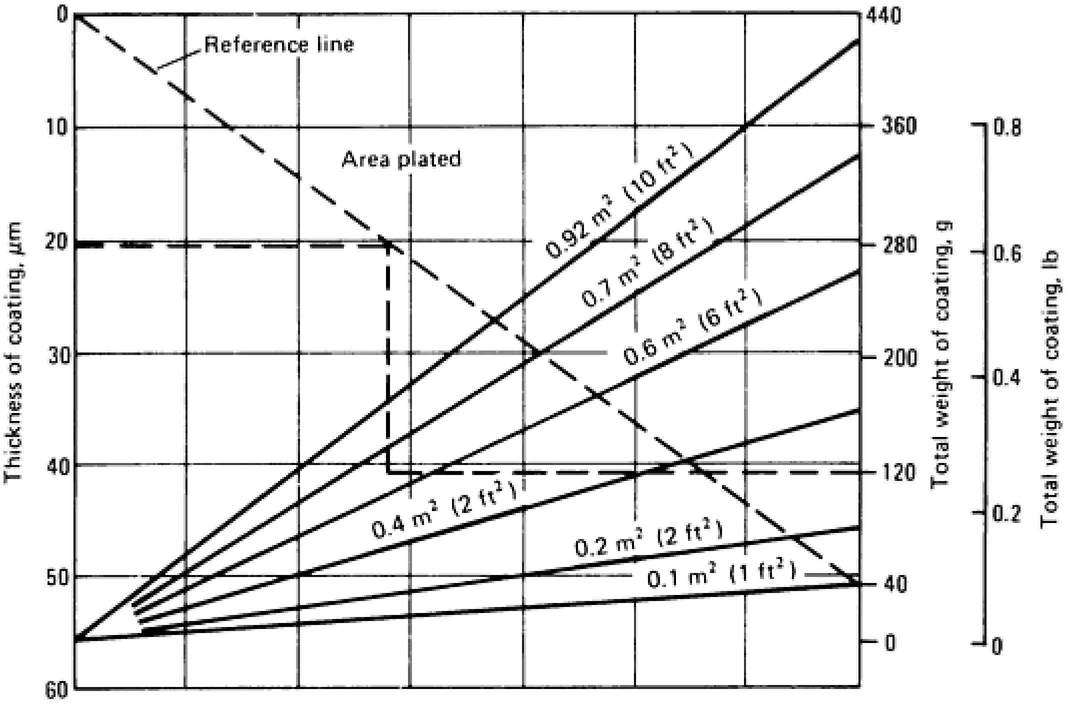


Fig. 5 Copper required for covering an area with a specific thickness

Industrial (Hard) Chromium Plating

Revised by Kenneth R. Newby, Atotech USA

Introduction

HARD CHROMIUM PLATING is produced by electrodeposition from a solution containing chromic acid (CrO_3) and a catalytic anion in proper proportion. The metal so produced is extremely hard and corrosion resistant. The process is used for applications where excellent wear and/or corrosion resistance is required. This includes products such as piston rings, shock absorbers, struts, brake pistons, engine valve stems, cylinder liners, and hydraulic rods. Other applications are for aircraft landing gears, textile and gravure rolls, plastic rolls, and dies and molds. The rebuilding of mismachined or worn parts comprises large segments of the industry. One specialized application is a thin chromium layer used as a lacquer adhesive layer in the manufacture of "tin" cans.

Hard chromium plating is also known as industrial, functional, or engineering chromium plating. It differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase the service life of functional parts by providing a surface with a low coefficient of friction that resists galling, abrasive and lubricated wear, and corrosion. Another major purpose is to restore dimensions of undersized parts.
- Hard chromium normally is deposited to thicknesses ranging from 2.5 to 500 μm (0.1 to 20 mils) and for certain applications to considerably greater thicknesses, whereas decorative coatings seldom exceed 1.3 μm (0.05 mil).
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is

applied over undercoats of nickel or of copper and nickel.

Principal Uses

The major uses of hard chromium plating are for wear-resistance applications, improvement of tool performance and tool life, and part salvage. Table 1 lists parts to which hard chromium plate is applied and representative data regarding plate thickness and plating times. Plating times can be reduced by using high-efficiency or mixed-catalyst solutions.

Table 1 Typical thicknesses and plating times for selected applications of hard chromium plating

Part	**Base metal**	**Thickness of plate**		**Plating time**[(a)]
		µm	**mils**	
Computer printer type	Carbon steel	25	1	60 min
Face seals	Steel or copper	75-180	3-7	10 h
Aircraft engine parts	Nickel-based alloys, high strength steel	75-180	3-7	10 h
Plastic molds	Tool steel	5-13	0.2-0.5	30 min
Textile guides	Steel	5-100	0.2-4	20-240 min
Piston rings	Steel or cast iron	150-255	6-10	8 h
Balls for ball valves	Brass or steel	7.5-13	0.3-0.5	20 min
Micrometers	Steel	7.5-13	0.3-0.5	20 min
Golf ball molds	Brass or steel	7.5-25	0.3-1	20-60 min
Lock cases	Brass	5-7.5	0.2-0.3	20 min
Cylinder	Cast iron	255	10	300 min
Bushing	1018 carburized, 56 HRC	25	1	45 min
Crankshafts	Steel	255-3800	10-150	. . .
Cutting tools	Tool steel	1.3	0.05	5 min
Forming and drawing dies	Steel	25	1	60 min

Part	Base metal	Thickness of plate		Plating time[(a)]
		µm	mils	
Gage	Steel	125	5	150 min
Gun barrels, 30 caliber[(b)]	Steel	25	1	40 min
Hydraulic cylinder	1045 steel	13	0.5	40 min
Pin	Steel	13	0.5	30 min
Pin	1045 steel, 60 HRC	125	5	40 min
Plug gage	1040 steel, 55 HRC	125	5	150 min
Relief-valve plunger	1113 steel, soft	100	4	60 min
Ring gage	Steel	205	8	240 min
Rolls	Steel	13-255	0.5-10	20-300 min

(a) Times shown are for conventional plating solutions; plating times for the proprietary fluoride-free solution are half of those shown.

(b) M-16 rifle, barrel and chamber

Wear Resistance. Extensive performance data indicate the effectiveness of chromium plate in reducing the wear of piston rings caused by scuffing and abrasion. The average life of a chromium-plated ring is approximately five times that of an unplated ring made of the same base metal. Piston rings for most engines have a chromium plate thickness of 100 to 200 μm (4 to 8 mils) on the bearing face, although thicknesses up to 250 µm (10 mils) are specified for some heavy-duty engines.

In the automotive industry, hard chromium is also applied to shock absorber rods and struts to increase their resistance to wear and corrosion. Valve stems are plated with a flash coating (about 2.5 µm, or 0.1 mil) to reduce wear. Hydraulic shafts for all kinds of equipment are plated with 20 to 30 µm (0.8 to 1.2 mil) of hard chromium to increase service life.

Tooling Applications. Various types of tools are plated with chromium to minimize wear, prevent seizing and galling, reduce friction, and/or prevent or minimize corrosion. Steel or beryllium copper dies for molding of plastics are usually plated with chromium, especially when vinyl or other corrosive plastic materials are to be molded. Plating thicknesses of 2.5 to 125 µm (0.1 to 5 mils) usually are recommended for preventing wear in parts sticking in molds and for reducing frequency of polishing when plastics that attack steel or beryllium copper are being molded. Chromium-plated dies should not be used when plastics containing fire-retardant chlorides are molded.

The service life of plug gages and other types of gages may be prolonged by hard chromium plating. Most gage manufacturers provide chromium-plated gages. Records in one plant indicate that plug gages made from hardened O1 tool steel wore 0.0025 mm (0.0001 in.) after gaging 5000 cast iron parts. Hard chromium plating of these gages allowed the gaging of 40,000 parts per 0.0025 mm (0.0001 in.) of wear.

Worn gages can be salvaged by being built up with hard chromium plate. Also, chromium plate provides steel gages with good protection against rusting in normal exposure and handling. Chromium plating is not recommended, however, for gages that are subjected to impact at exposed edges during operation.

Deep drawing tools often are plated with chromium, in thicknesses up to 100 μm (4 mils), for improvement of tool performance and/or building up of worn areas. The life of draw rings and punches may be prolonged by plating. In addition, plating reduces frictional force on punches and facilitates removal of workpieces from punches in instances where sticking is encountered with plain steel surfaces. If deep drawing tools are chromium plated, the base metal should be harder than 50 HRC. Steel dies used for drawing bars and tubes are often plated with relatively heavy thicknesses (up to 250 μm, or 10 mils) of chromium to minimize die wear, reduce friction, and prevent seizing and galling.

The service life of cutting tools is often extended by chromium plate, in thicknesses ranging from less than 2.5 to 13 μm (0.1 to 0.5 mil). Taps and reamers are examples of tools on which chromium plate has proved advantageous. In one case, a flash plate on taps used to thread cold-worked 1010 steel improved tap life from 250 (for unplated taps) to 6000 parts per tap. The poor tool life of the unplated taps was caused by buildup of metal on the cutting edges. Hard chromium plating is not recommended for cold extrusion tools for severe applications where extreme heat and pressure are generated, because the plate is likely to crack and spall and may be incompatible with phosphate-soap lubricants.

Part Salvage. Hard chromium plating is sometimes used for restoring mismachined or worn surfaces. Since 1970, the use of this process for part salvage has been frequently replaced by thermal spraying and plasma coatings, which can be applied more quickly. The fact that a chromium deposit can significantly reduce fatigue strength must be considered in determining whether chromium plating can be safely used.

Hard chromium plating is used to restore to original dimensions the worn surfaces of large crankshafts for diesel and gas engines and for compressors. In these applications, in which coating thicknesses usually range from 125 to 1250 μm (5 to 50 mils), the excellent wearing qualities and low coefficient of friction of chromium are highly advantageous. The plate is prevented from depositing in fillet areas as a precaution against fatigue failure.

The extremely close dimensional tolerances specified for components of compressors for jet aircraft engines are not always correctly met in machining. Hard chromium plating is sometimes used to salvage mismachined parts. Most frequently mismachined are the diameters of rotor disks and spacers. The maximum thickness of plate on these components, which are made of 4130 and 4340 steels, generally does not exceed 380 μm (15 mils).

Other Applications. Hard chromium plate is applied to printing plates and stereotypes, especially to those intended for long runs, because compared to other materials or coatings used for this application, it wipes cleaner, provides sharper reproduction, and increases the length of press runs. It is used on press rams because of its excellent resistance to corrosion, seizing, galling, and other forms of wear.

Selection Factors

The decision to use hard chromium plating on a specific part should take into account the following characteristics:

- The inherent hardness and wear resistance of electrodeposited chromium
- The thickness of chromium required
- The shape, size, and construction of the part to be plated
- The type of metal from which the part is made
- Masking requirements (for parts that are to be selectively plated)
- Dimensional requirements (that is, whether or not mechanical finishing is required and can be accomplished in accordance with desired tolerances)

The hardness of chromium electrodeposits is a function of the type of chemistry selected and the plating conditions. In general, chromium plated in the bright range is optimally hard. Typically bright chromium deposits from conventional plating solutions have hardness values of 850 to 950 HV; those from mixed-catalyst solutions have values of 900 to 1000 hV; and those from fluoride-free chemistries have values of 950 to 1100 HV or higher.

Size. Frequently, a very large part can be plated in sections or can be rotated so that only a portion of the part is immersed in the plating solution at any given time. The latter method has been used to plate large cylinders up to 4 m (12 ft) in diameter and up to 18 m (60 ft) long. When this technique is used, all of the surface to be plated that is exposed to the atmosphere must remain wet with plating solution.

Journal surfaces of the largest diesel crankshafts and bores of large naval guns and M-16 rifles are hard chromium plated on a production basis. Internal surfaces of very large cylinders have been plated by closing off the ends of each cylinder and retaining the plating solution with it.

Base Metal. Most hard chromium deposits are applied to parts made of ferrous alloys; however, numerous aerospace applications require the chromium plating of aluminum and nickel-base alloys. From the standpoint of processing, hard chromium plate may be applied to steels, regardless of their surface hardness or chemical composition, provided that the base metal is hard enough to support the chromium layer in service. Similarly, cast irons can be plated provided that the surface is capable of conducting the required current and is reasonably free of voids, pits, gross silicate inclusions, massive segregation, slivers, and feather edges.

Plating Solutions

Chromic acid is the source of metal in hard chromium plating solutions. However, a chromic acid solution does not deposit chromium unless a definite amount of catalyst is present. If there is either too much or too little catalyst, no chromium metal is deposited. Catalysts that have proved successful are acid anions, the first of which to be used was sulfate. Substitution of fluoride ions present in complex acid radicals for a portion of the sulfate improves the chromium-plating operation. In the late 1980s, a fluoride-free proprietary solution was developed. The secondary catalyst in this chemistry is a stable organic species. Reflecting this difference in catalyst, the principal types of solutions are designated as conventional sulfate (also called Sargent or Fink); mixed-catalyst, which refers to the sulfate and fluoride chemistry; and fluoride-free (proprietary) catalyst.

The fatigue limit of high-strength steel (steels with ultimate tensile strengths of 1240 MPa, or 180 ksi, and above) may be reduced by about 50% when chromium plated because of the inherent crack structure of hard chromium. However, special techniques using shot peening and postplate heat treatments may be used to retain most of the original fatigue strength.

Conventional Sulfate Solutions. Composition of conventional chromic acid solutions catalyzed by sulfate can vary widely, provided the ratio by weight of chromic acid to sulfate radical is within the range between 75 and 120 to 1. Throwing power, or distribution of plate, is optimum at ratios between 90 and 110 to 1; however, in the range between 75 and 90 to 1, brighter deposits are obtained, less burning occurs, and a higher current density can be used.

Solutions containing chromic acid in a concentration as low as 50 g/L (7 oz/gal) have been reported but are not practical for production because:

- Their plating range is too limited
- The solutions are more sensitive to contamination
- They have a higher electrical resistance
- They require a higher voltage for operation

Compositions and operating conditions for two chromic acid/sulfate solutions (low and high concentrations) for hard chromium plating are given in Table 2. The low-concentration solution is widely used for hard chromium plating because it minimizes dragout losses and associated environmental problems. The high-concentration solution has the advantage of being less sensitive to concentration changes; it is also easier to control and has better throwing power. Because the high-concentration solution is more conductive, it can be operated at lower voltages and heats up less in operation.

Table 2 Sulfate baths for hard chromium plating

Type of oath	Chromic acid(a)		Sulfate(a)		Current density		Bath temperature	
	g/L	oz/gal	g/L	oz/gal	A/dm^2	A/in.^{2}	°C	°F
Low concentration	250	33	2.5	0.33	31-62	2-4	52-63	125-145
High concentration	400	53	4.0	0.53	16-54	1-3.5	43-63	110-145

(a) Concentration usually can deviate ±10% without creating problems. It is recommended that adjustments be such that the concentrations listed above lie in the middle of the range permitted. For example, chromic acid can fluctuate by ±23 g/L (±3 oz/gal); therefore, the concentration range should be 225-270 g/L (30 to 36 oz/gal), rather than 205-250 g/L (27 to 33 oz/gal).

If available voltage is limited, it may be preferable to operate a solution with higher conductivity in the range of 300 to 405 g/L (40 to 54 oz/gal) of chromic acid, even though current efficiency is lower than with the less concentrated solutions. The lower current efficiency is offset by increased current density obtainable because of better solution conductivity. Usually, the best range of operation is from 195 to 300 g/L (26 to 40 oz/gal) of chromic acid. Even within this range, the solution containing 195 g/L (26 oz/gal) has the highest current efficiency, while the solution containing 300 g/L (40 oz/gal) has the best conductivity.

The mixed-catalyst solutions are similar to conventional sulfate solutions in conductivity, but they produce harder deposits and have higher intrinsic current efficiency than conventional solutions under identical conditions. They also have a higher current efficiency at higher concentration. Mixed-catalyst solutions can increase production rates 40 to 60% and more over those obtainable with conventional solutions, due to the greater current efficiencies of the mixed-catalyst solutions and their ability to operate at higher current densities without creating harmful effects on the deposit. One limitation of mixed-catalyst solutions is that they cause etching of unplated iron surfaces at areas of low current density, with a resulting increase in contamination that reduces the life of the solution. This etching can be prevented on significant surfaces by masking areas not to be plated. Mixed-catalyst solutions are seldom used on aluminum or copper substrates because of the attack by the fluoride chemicals.

Fluoride-free solution, a proprietary chemistry, is based on chromic acid, sulfate, and a stable organic catalyst. It provides deposit speeds and current density ranges slightly in excess of those obtained with mixed-catalyst solutions. Because the solution contains no fluorides or other halogens, it does not cause etching on exposed unplated surfaces or attack aluminum or copper substrates. These features alleviate the need for excessive protective masking operations. As with the mixed-catalyst chemistry, the fluoride-free solution provides much greater plating throughput while consuming about one-third less electricity than the conventional solution.

Deposit hardness and corrosion resistance improve as one moves from the conventional sulfate solution to the mixed-catalyst solution and on to the fluoride-free solution.

Solution Control

Chromium-plating solutions of all three types must be subjected to periodic chemical analyses for control of solution composition. With the exception of catalyst analysis, the species and methods are identical for all chemistries. Solution control can be simplified if a record is kept of the way a particular chromium solution changes in composition during its use. Change in chemical composition depends on the number of ampere-hours of current passed through the solution, the dragout of solution, and spray losses. Also, evaporation losses, if not compensated for, usually cause the concentration to change by about 2 to 5% during a day's operation. A complete solution analysis should be made at periodic intervals (weekly or monthly, depending on production rate) and the solution should be brought into proper balance.

Chromic acid content can be semi-quantitatively determined simply by placing a hydrometer in the plating solution, provided that other contaminants, such as iron or copper, are not present in significant quantities. Hydrometers calibrated in ounces of chromic acid per gallon at the operating temperature of the solution are available. Baumé hydrometers can be used in samples cooled to the calibration temperature marked on the hydrometer; the reading can be converted to concentration by using Table 3. Impurities cause the Baumé reading to be higher than is warranted by the actual chromic acid content. Periodically, the chromic acid content should be quantitatively determined by chemical titration and a notation made of the differences between the contents as shown by chemical analysis and by hydrometer readings. Hydrometer readings should then be corrected by that amount. When a hydrometer reading shows 30 to 38 g/L (4 to 5 oz/gal) more chromic acid than is actually present, the solution should be discarded, because this is caused by a high metallic impurity level. Adjustments in chromic acid concentration are simplified by the use of Table 4.

Table 3 Determination of chromic acid in chromium baths with a Baumé hydrometer

Direct conversion of degrees Baumé to ounces of chromic acid per gallon, at 25 °C (77 °F)

°Bé	Chromic acid	
	g/L	oz/gal
10.5	113	15.0
11.0	119	15.8
11.5	124	16.5
12.0	130	17.3
12.5	137	18.2
13.0	144	19.1
13.5	149	19.8
14.0	153	20.4
14.5	159	21.2
15.0	165	22.0
15.5	172	22.9
16.0	178	23.7
16.5	184	24.5
17.0	191	25.4
17.5	198	26.3

18.0	204	27.2
18.5	211	28.1
19.0	218	29.0
19.5	224	29.8
20.0	230	30.9
20.5	237	31.5
21.0	244	32.4
21.5	250	33.3
22.0	257	34.2
22.5	264	35.1
23.0	271	36.0
23.5	279	37.1
24.0	287	38.2
24.5	294	39.1
25.0	301	40.0
25.5	308	4.09
26.0	315	41.9
26.5	323	42.9
27.0	331	44.0
27.5	338	45.0
28.0	346	46.0

28.5	354	47.1
29.0	362	48.2
29.5	370	49.2
30.0	378	50.2
30.5	387	51.5
31.0	399	53.0
31.5	406	54.0
32.0	415	55.2

Note: Impurities will cause the Baumé hydrometer reading to be higher than is warranted by the actual content of chromic acid.

Table 4 Conversion equivalents for chromic acid concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Chromic acid required, kg(lb) = g/L(oz/gal) CrO_3 to be added × bath volume, in liters (gallons)/16

Chromic acid to be added		**Chromic acid required, kg (lb), at volume of bath, L (gal), of:**									
g/L	**oz/gal**	**380 (100)**	**760 (200)**	**1140 (300)**	**1510 (400)**	**1890 (500)**	**2270 (600)**	**2650 (700)**	**3030 (800)**	**3410 (900)**	**3790 (1000)**
4.0	0.5	1.4 (3.1)	2.9 (6.3)	4.3 (9.4)	5.7 (12.5)	7.1 (15.6)	8.5 (18.8)	9.9 (21.9)	11.3 (25.0)	12.7 (28.1)	14.2 (31.2)
7.5	1.0	2.8 (6.2)	5.7 (12.5)	8.5 (18.8)	11.3 (25.0)	14.2 (31.2)	17.0 (37.5)	19.9 (43.8)	22.7 (50.0)	25.5 (56.3)	28.3 (62.5)
11.0	1.5	4.3 (9.4)	8.5 (18.8)	12.8 (28.2)	17.0 (37.5)	21.3 (46.9)	25.5 (56.3)	29.8 (65.6)	34.0 (75.0)	38.3 (84.4)	42.5 (93.8)
15.0	2.0	5.7 (12.5)	11.3 (25.0)	17.0 (37.5)	22.7 (50.0)	28.3 (62.5)	34.0 (75.0)	39.7 (87.5)	45.3 (100.0)	51.3 (113.0)	56.7 (125.0)
19.0	2.5	7.1 (15.6)	14.2 (31.2)	21.3 (46.9)	28.3 (62.5)	35.4 (78.1)	42.5 (93.8)	49.4 (109.0)	56.7 (125.0)	61.0 (141.0)	70.8 (156.0)
22.0	3.0	8.5 (18.8)	17.0 (37.5)	25.5 (56.3)	34.0 (75.0)	42.6 (93.8)	51.3 (113.0)	59.4 (131.0)	68.0 (150.0)	76.7 (169.0)	85.3 (188.0)

26.0	3.5	9.9 (21.9)	19.8 (43.7)	29.8 (65.6)	39.7 (87.5)	49.4 (109.0)	59.4 (131.0)	69.4 (153.0)	79.4 (175.0)	89.4 (197.0)	99.3 (219.0)
30.0	4.0	11.3 (25.0)	22.7 (50.0)	34.0 (75.0)	45.3 (100.0)	56.7 (125.0)	68.0 (150.0)	79.4 (175.0)	90.7 (200.0)	102.0 (225.0)	113.0 (250.0)
34.0	4.5	12.7 (28.1)	25.5 (56.2)	38.3 (84.4)	51.3 (113.0)	64.0 (141.0)	76.7 (169.0)	89.4 (197.0)	102.0 (225.0)	115.0 (253.0)	127.0 (281.0)
37.0	5.0	14.2 (31.2)	28.3 (62.5)	42.5 (93.8)	56.7 (125.0)	70.8 (156.0)	85.3 (188.0)	99.3 (219.0)	113.0 (250.0)	128.0 (281.0)	142.0 (312.0)
41.0	5.5	15.6 (34.4)	31.2 (68.7)	46.7 (103.0)	62.6 (138.0)	78.0 (172.0)	93.4 (206.0)	109.0 (241.0)	125.0 (275.0)	140.0 (309.0)	156.0 (344.0)
45.0	6.0	17.0 (37.5)	34.0 (75.0)	51.3 (113.0)	68.0 (150.0)	85.3 (188.0)	102.0 (225.0)	119.0 (262.0)	136.0 (300.0)	153.0 (338.0)	170.0 (375.0)
49.0	6.5	18.4 (40.6)	36.8 (81.2)	55.3 (122.0)	73.9 (163.0)	92.1 (203.0)	111.0 (244.0)	129.0 (284.0)	147.0 (325.0)	162.0 (365.0)	184.0 (406.0)
52.0	7.0	19.8 (43.7)	39.7 (87.5)	59.4 (131.0)	79.4 (175.0)	99.3 (219.0)	119.0 (262.0)	139.0 (306.0)	159.0 (350.0)	179.0 (394.0)	198.0 (437.0)
56.0	7.5	21.3 (46.9)	42.5 (93.8)	64.0 (141.0)	85.3 (188.0)	106.0 (234.0)	128.0 (281.0)	149.0 (328.0)	170.0 (375.0)	191.0 (422.0)	213.0 (469.0)
60.0	8.0	22.7 (50.0)	45.4 (100.0)	68.0 (150.0)	90.7 (200.0)	113.0 (250.0)	136.0 (300.0)	159.0 (350.0)	181.0 (400.0)	204.0 (450.0)	227.0 (500.0)
64.0	8.5	24.1 (53.1)	48.1 (106.0)	72.1 (159.0)	96.6 (213.0)	121.0 (266.0)	145.0 (319.0)	169.0 (372.0)	193.0 (425.0)	216.0 (477.0)	241.0 (531.0)
67.0	9.0	25.5 (56.2)	51.3 (113.0)	76.7 (169.0)	102.0 (225.0)	127.0 (281.0)	153.0 (338.0)	179.0 (394.0)	204.0 (450.0)	230.0 (506.0)	255.0 (562.0)
71.0	9.5	26.9 (59.4)	54.0 (119.0)	80.7 (178.0)	108.0 (238.0)	135.0 (297.0)	161.0 (356.0)	189.0 (416.0)	215.0 (475.0)	243.0 (535.0)	269.0 (594.0)
75.0	10.0	28.3 (62.5)	56.7 (125.0)	85.3 (188.0)	113.0 (250.0)	142.0 (312.0)	170.0 (375.0)	199.0 (438.0)	227.0 (500.0)	255.0 (563.0)	284.0 (625.0)

Chromic acid content can also be determined by various analytical procedures. Some of these procedures use standard solutions that can be used for other determinations; this may be the deciding factor as to which procedure to use. The following procedure is simple and quite rapid:

Reagents

- *Acid mixture:* Mix 1 part sulfuric acid, 1 part phosphoric acid, and 1 part water.
- *Ferrous ammonium sulfate (FAS) 0.1 N:* Dissolve 40 g/L (5.3 oz/gal) FAS · $6H_2O$ and add 25 mL/L concentrated sulfuric acid. When in use, keep about 6500 mm^2 (10 $in.^2$) of aluminum metal in the container to maintain constant normality.
- Orthophenanthroline ferrous sulfate complex indicator
- *Potassium dichromate, 0.1000 N:* dissolve 4.900 g (0.173 oz) of $K_2Cr_2O_7$ (CP grade) and dilute to a liter.

Standardization of FAS

- 1. Pipette 25 mL of potassium dichromate standard into a 250 mL Erlenmeyer flask and dilute to 85 mL.
- 2. Add 15 mL of acid mixture and 3 drops of indicator.
- 3. Titrate with FAS to clear orange endpoint. Normality of FAS = 2.5 / (mL of FAS).

Procedure

- 1(a). Pipette 10 mL of chromium solution into a 250 mL volumetric flask and dilute to volume. Pipette a 10 mL aliquot into a 250 mL Erlenmeyer flask.
- 1(b). Pipette 0.4 mL of chromium solution sample into a 250 mL Erlenmeyer flask, using a 1 mL pipette graduated in hundredths of a milliliter.
- 2. Add 50 mL of water, 15 mL of acid mixture, and 3 drops of indicator.
- 3. Titrate with FAS to clear orange end point. Chromic acid in g/L = (mL of FAS) × (N of FAS) × (83.3). Chromic acid in oz/gal = (mL of FAS) × (N of FAS) (11.12).

Use either step 1(a) or 1(b), followed by steps 2 and 3. Step 1(b) is slightly less accurate than 1(a) but is much faster.

Sulfate in a chromium solution can be determined to a high degree of accuracy by a gravimetric method, or with reasonable accuracy using the much faster centrifuge method. Unless there is some reason for great precision, the centrifuge method is entirely satisfactory. Most graduated centrifuge tubes can be calibrated for sulfate; however, the technique should be checked regularly by analysis of a standard solution, or by the gravimetric technique.

With the centrifuge method, the amount of insoluble material in the sample must be determined before sulfate is precipitated. This can be done by running a blank sample or centrifuging the sample before precipitating the sulfate. Because sulfate determinations are made in duplicate, it is advisable to determine how closely the two tubes match in calibration. This can be done by pouring a small amount of mercury into first one tube and then the other. These tubes should be marked to be used together, and a notation should be made, if necessary, as to the amount of correction needed in the reading. Adjustments of sulfate concentration in chromium solutions can be simplified by using Table 5.

Table 5 Conversion equivalents for adjusting sulfate concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Sulfuric acid (66 °Bé) fluid oz, = 0.522 × oz/gal H_2SO_4 to be added × bath volume, gal

Sulfuric acid to be added		**Sulfuric acid (66 °Bé) required, mL (fluid oz), at volume of bath, L (gal), of:**									
g/L	**oz/gal**	**380 (100)**	**760 (200)**	**1140 (300)**	**1515 (400)**	**1890 (500)**	**2270 (600)**	**2650 (700)**	**3030 (800)**	**3410 (900)**	**3790 (1000)**
0.08	0.01	15 (0.5)	30 (1.0)	47 (1.6)	62 (2.1)	77 (2.6)	92 (3.1)	109 (3.7)	124 (4.2)	139 (4.7)	154 (5.2)

0.15	0.02	30 (1.0)	62 (2.1)	92 (3.1)	124 (4.2)	154 (5.2)	186 (6.3)	216 (7.3)	249 (8.4)	278 (9.4)	308 (10.4)
0.22	0.03	47 (1.6)	92 (3.1)	139 (4.7)	186 (6.3)	231 (7.8)	284 (9.6)	323 (10.9)	370 (12.5)	417 (14.1)	465 (15.7)
0.30	0.04	62 (2.1)	124 (4.2)	186 (6.3)	249 (8.4)	308 (10.4)	370 (12.5)	432 (14.6)	494 (16.7)	556 (18.8)	619 (20.9)
0.37	0.05	77 (2.6)	154 (5.2)	231 (7.8)	308 (10.4)	385 (13.0)	462 (15.6)	539 (18.2)	619 (20.9)	696 (23.5)	773 (26.1)
0.45	0.06	92 (3.1)	186 (6.3)	284 (9.6)	370 (12.5)	462 (15.6)	556 (18.8)	648 (21.9)	740 (25.0)	835 (28.2)	926 (31.3)
0.53	0.07	110 (3.7)	216 (7.3)	323 (10.9)	432 (14.6)	539 (18.2)	648 (21.9)	758 (25.6)	864 (29.2)	974 (32.9)	1080 (36.5)
0.60	0.08	124 (4.2)	249 (8.4)	370 (12.5)	494 (16.7)	619 (20.9)	740 (25.0)	864 (29.2)	989 (33.4)	1113 (37.6)	1237 (41.8)
0.67	0.09	139 (4.7)	278 (9.4)	417 (14.1)	556 (18.8)	696 (23.5)	835 (28.2)	974 (32.9)	1143 (38.6)	1252 (42.3)	1391 (47.0)
0.75	0.10	154 (5.2)	308 (10.4)	465 (15.7)	619 (20.9)	773 (26.1)	926 (31.3)	1080 (36.5)	1237 (41.8)	1391 (47.0)	1545 (52.2)

Note: To neutralize excess sulfuric acid (thereby lowering the sulfate content) in a chromium bath, add approximately 1.5 g/L (0.2 oz/gal) of barium carbonate for each 0.8 g/L (0.1 oz/gal) of excess sulfuric acid. Additions of barium carbonate should be made slowly to the bath.

Contamination. In the operation of any chromium solution, the solution should be kept free of excessive amounts of contamination. Introduction of copper, iron, or trivalent chromium seriously decreases the conductivity of the solution and requires the use of a higher operating voltage to produce a given current density.

Trivalent chromium can be formed by the decomposition of organics, but more often it results from too low a ratio of anode-to-cathode area, a condition always encountered in plating interior surfaces cylinders. Trivalent chromium can be reoxidized to hexavalent chromium by electrolyzing the solution at 60 to 66 °C (140 to 150 °F), with an anode-to-cathode area ratio of about 30 to 1, and using a cathode current density of about 60 A/dm^2 (4 $A/in.^2$). About 50 A · h/L (200 A · h/gal) is required for reoxidizing 15 g/L (2 oz/gal) of trivalent chromium; ordinarily, this operation is performed during the weekend shutdown period.

Removal of copper, iron, and other contaminants is usually accomplished by disposing of part or all of the solution, or where permissible, by ion exchange or electrodialysis techniques. In addition to reducing the conductivity of the solution, impurities, particularly iron and trivalent chromium, also reduce current efficiency. (This is especially true for the mixed-catalyst type of chemistry because these contaminants reduce the activity of the fluoride catalyst.) Normally, the presence of 10 g/L (1.5 oz/gal) of iron in solution reduces cathode current efficiency by about 30%. Iron and trivalent chromium can produce rougher deposits with more treeing. Other contaminants affect the throwing power and coverage.

Mandrel Test. When difficulties are experienced with the hard chromium production solution, it may be useful to use the mandrel test, so named because it is usually performed by plating a low-carbon steel rod or mandrel (9.5 mm diameter by 75 mm long, or $\frac{3}{8}$ in. diameter by 3 in. long) with a conforming circular anode to give uniform current distribution. A convenient procedure is to use 540 mL of the solution in a 600 mL beaker made of heat-resistant glass. The steel mandrel is buffed to a bright finish, and the top 25 mm (1 in.) that projects out of the solution and into a holder is stopped-off to indicate the exact size of the plating area.

The mandrel is immersed in the test solution, which is heated to 55 °C (130 °F) in a water solution, treated anodically at 15 A/dm^2 (1 A/in.^{2}) for 15 s, and then plated at 30 A/dm^2 (2 A/in.^{2}) for 1 h. The temperature of the water solution should be reduced to about 52 °C (125 °F) during plating to compensate for the heat generated by the current. The mandrel is then removed, rinsed, dried, and inspected.

Better temperature control through the plating process is obtained by using 1 L of solution in a 1.5 L beaker. The solution is heated with a 125 W quartz heater controlled by a thermoregulator and relay. The process operates at 55 °C (130 °F).

A hard chromium solution in proper adjustment gives a bright plate under these conditions. If the deposit is dull, the solution is contaminated or out of balance. Burning on the bottom edge of the mandrel also indicates that the solution is out of adjustment. A high content of trivalent chromium causes dullness and growth of metal whiskers from the bottom edge of the mandrel.

Current efficiency and plating speed can be checked with the same setup, but this is more conveniently done with a flat steel panel and flat anodes. A polished steel panel, 25 by 75 mm (1 by 3 in.), can be used, with the bottom 50 mm (2 in.) marked off as the plating area. Plating conditions would be 30 A/dm^2 (2 A/in.^{2}) for 15 min at 55 °C (130 °F), but other conditions can be tested as desired. The steel panel is accurately weighed before and after plating (without current reversal). Current efficiency, thickness of chromium, and plating speed are calculated as follows:

- Current efficiency, % = (weight, in grams, of chromium × 100) / (ampere-hours × 0.323)
- Thickness of deposit, mils = (weight, in grams, of chromium) / (4 × 0.116)
- Plating speed, mils/h = (thickness of deposit, in mils × 60) / plating time, min

Process Control

In addition to solution composition, the principal variables that must be controlled for satisfactory hard chromium plating are the anodes, the current density, and the solution temperature.

Anodes. In contrast to other plating solutions, which use soluble anodes to supply the solution with a large part of the metal ion being plated, chromium plating solutions are operated with insoluble lead alloy anodes. Usually about 7% Sn or Sb or a combination of the two are used to alloy the lead. As a consequence of using inert anodes, additions of chromic acid must be made to keep the plating solution supplied with chromium metal ions.

A coating of lead peroxide forms on the lead alloy anodes during electrolysis. This coating is usually dark charcoal brown, which indicates that the anodes are functioning correctly. The presence of an orange-to-yellow lead chromate coating indicates that the anodes are not passing current properly. Periodic cleaning of the anodes and their hooks is mandatory for efficient operation.

Insoluble antimonial lead (93Pb, bal Sb + Sn) and lead-tin alloy (93Pb-7Sn) are the most widely used anode materials in chromium plating solutions. These alloys minimize corrosion of the anode; the antimony in the first composition stiffens the anode against shape changes. Each anode must have sufficient cross-sectional area to pass the requisite current without overheating. If high current densities are to be used with mixed-catalyst or fluoride-free solutions, it may be necessary to use larger anode cross sections than would be the case in the low-current-density conventional solutions. In any case the bottom of each anode should be at least 150 mm (6 in.) above the bottom of the plating tank to avoid possible electrical shorts.

Conductivity of the chromium solution is based on chromic acid concentration. Concentrations higher than 250 g/L (33 oz/gal) require lower operating voltage; however, current efficiency decreases with increasing chromic acid concentration. Concentrations below about 180 g/L are usually impractical unless high-voltage rectifiers are available.

Current Density and Efficiency. Cathode current efficiency varies with current density and temperature of the plating solution. Efficiency increases significantly with increasing current density and slightly with decreasing temperature. These two variables have a definite effect on the appearance and hardness of the deposit. A high solution temperature results in a milky, dull, and softer deposit at lower current efficiencies, unless the current density is increased substantially. Raising current density causes the deposit to change successively at specific temperatures (Table 6). Because tank time is an important economic factor, the highest rates of deposition that are produced by the highest available currents may determine which plating solution temperature is most useful.

Table 6 Effect of bath temperature and current density on appearance and hardness of chromium deposits plated from a conventional sulfate solution

Bath contained 406 g/L CrO_3; ratio of CrO_3 to SO_4 ranged from 90-to-1 to 100-to-1

Current density		**Appearance of deposit**	**Hardness[(a)], DPH**
A/dm²	**A/in.²**		
Plating bath at 43 °C (110 °F)			
Below 8.53	Below 0.55	Dull matte	[(b)]
8.53	0.55	Semibright	695
17.1	1.10	Bright	900
25.6	1.65	Bright, pebbly	Over 940
34.1	2.20	Dull, nodular[(c)]	Over 940
Plating bath at 49 °C (120 °F)			
Below 10.9	Below 0.70	Dull matte	510-595
10.9	0.70	Semibright	695
21.7	1.40[(d)]	Bright	900
32.6	2.10	Bright, pebbly	Over 940
43.4	2.80	Dull, nodular[(c)]	Over 940
Plating bath at 54 °C (130 °F)			
Below 14.0	Below 0.90	Dull matte	510-595
14.0	0.90	Semibright	695

27.9	1.80[d]	Bright	900
41.9	2.70	Bright, pebbly	Over 940
55.8	3.60	Dull, nodular[c]	Over 940

(a) Hardness of mounted and unmounted specimens was determined with a tester employing a Vickers diamond, a load of 200 g, and a magnifaction of 200×. Mounted specimens were mounted flat (not cross section).

(b) Current density too low to plate a sufficient amount of chromium for hardness test.

(c) Specimens polished lightly to smooth out nodules.

(d) Optimum current density

Deposition Rates. Times required to plate hard chromium deposits of various thicknesses are shown as a function of current density in Table 7 (for low-concentration solutions) and Table 8 (for high-concentration solutions).

Table 7 Rates of deposition of hard chromium from low-concentration baths

Thickness of plate		Plating time, h:min, at current density, A/dm^2 (A/in.^{2}), of:		
µm	**mils**	**31 (2.0)**	**47 (3.0)**	**62 (4.0)**
Conventional sulfate bath[a]				
25	1	1:05	0:40	0:25
50	2	2:05	1:20	0:55
125	5	5:20	3:20	2:20
Mixed catalyst bath[b]				
25	1	0:50	0:30	0:20
50	2	1:40	1:00	0:40
125	5	4:05	2:25	1:45

Fluoride-free bath(c)				
25	1	0:40	0:27	0:17
50	2	1:25	0:53	0:37
125	5	3:35	2:15	1:30

(a) Bath containing 250 g/L (33 oz/gal) of chromic acid with 100-to-1 ratio of chromic acid to sulfate, operated at 54 °C (130 °F).

(b) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F).

(c) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F)

Table 8 Rates of deposition of hard chromium from high-concentration baths

Thickness of plate		**Plating time, h:min, at current density of:**				
µm	**mils**	**23 A/dm^2 (1.5 A/in.^{2})**	**31 A/dm^2 (2.0 A/in.^{2})**	**39 A/dm^2 (2.5 A/in.^{2})**	**47 A/dm^2 (3.0 A/in.^{2})**	**54 A/dm^2 (3.5 A/in.^{2})**
Conventional sulfate bath(a)						
25	1	2:20	1:35	1:15	0:55	0:45
50	2	4:35	3:10	2:30	1:55	1:30
125	5	11:30	8:00	6:15	4:40	3:50
255	10	23:00	16:00	12:30	9:25	7:35
380	15	34:30	24:00	18:45	14:05	11:25
510	20	46:00	32:00	25:00	18:50	15:10
Mixed catalyst bath(b)						
25	1	2:00	1:10	0:55	0:40	0:30
50	2	4:00	2:20	1:50	1:20	1:00

125	5	10:00	5:50	4:30	3:20	2:30
255	10	20:00	12:00	9:00	6:40	5:00
380	15	30:00	18:00	13:00	10:00	7:30
510	20	40:00	24:00	18:00	16:40	12:30
Fluoride-free solution(c)						
25	1	1:50	1:05	0:50	0:37	0:27
50	2	3:40	2:10	1:40	1:15	0:55
125	5	9:10	5:30	4:10	3:10	2:15
255	10	18:20	11:00	8:20	6:20	4:30
380	15	27:30	16:30	12:30	9:30	6:45
510	20	36:40	22:00	16:40	12:40	9:00

(a) Chromic acid content, 400 g/L (53 oz/gal); ratio of chromic acid to sulfate, 100:1; operating temperature, 55 °C (130 °F).

(b) Chromic acid content, 400 g/L (53 oz/gal); sulfate content, 1.5 g/L (0.20 oz/gal); contains sufficient fluoride catalyst to give 100-to-1 ratio results.

(c) Chromic acid content, 400 g/L (53 oz/gal); contains appropriate amount of proprietary catalyst; operating temperature, 55 °C (130 °F)

Solution temperature affects both the conductivity and the current required. If limited power is available, satisfactory hard chromium plating deposits can be obtained at lower temperatures (43 to 49 °C, or 110 to 120 °F), but if power supply is adequate, it is advantageous to work at higher temperatures (up to 60 °C, or 140 °F) because of the faster deposition rate and the improved durability of the deposit. At 43 to 49 °C (110 to 120 °F), current densities of 8 to 30 A/dm^2 ($\frac{1}{2}$ to 2 A/in.^{2}) are satisfactory; at 60 to 66 °C (140 to 150 °F), 45 to 60 A/dm^2 (3 to 4 A/in.^{2}) may be required, and as high as 80 to 90 A/dm^2 (5 to 6 A/in.^{2}) can sometimes be needed. At all temperatures, increased agitation will allow higher current densities.

Control of solution temperature to within a narrow range is necessary because of the marked influence of temperature on deposition rate and deposit quality. An increase of 2 °C (5 °F) in mean solution temperature, for example, can cause a reduction of 5% or more in mean chromium thickness, thus necessitating a sizable adjustment in either plating time or current density. The solution temperature should be maintained within 1 °C (2 °F). Solution temperature is usually controlled automatically. Manual control is impractical for a production operation.

For automatic control, it is important that the thermostat be placed in the plating solution in a location where it can readily sense any significant change in solution temperature. Obviously, the thermostat must not be in close proximity to a heating or cooling pipe or to an electric heating element. Location of the thermostat is greatly simplified when an external heat exchanger is used and the solution is pumped from the heat exchanger to the solution. Rapid movement of the solution or air agitation helps to promote temperature uniformity.

Problems and Corrective Procedures

Faulty operation of a chromium-plating solution can result in slow plating speed or deposits with undesirable characteristics. The problems encountered in hard chromium plating are similar for all three chemistries. Possible causes and suggested corrective procedures include:

Poor coverage

- Low chromic acid content
- Low ratio of chromic acid content to total catalyst content. Correct by adding chromic acid or by precipitating sulfate, if too high, with barium carbonate.
- Temperature too high
- Current density too low
- Passive or scaled anodes. Correct by cleaning and reactivating anodes, using high current density until uniform gassing is obtained, and checking for good anode contact.
- Rack contacts too heavily built up with metal, causing rack to rob plate
- Thieves too large or too close
- Open holes preventing uniform plate in adjacent areas. Correct by using nonconducting plugs in holes.
- Gas entrapment preventing plating solution from reaching some areas. Correct by positioning parts in solution so that all gases can escape or by agitating parts while they are plating.

Burnt deposits

- Ratio of chromic acid to total catalysts too high. Correct by adding necessary catalyst or by lowering chromic acid content.
- Current density too high
- Temperature too low
- Large parts were colder than solution temperature when plating began.
- Some parts, in a load of different parts, receive too much current. Correct by adjusting anodes and contacts to ensure that each part receives correct current density.
- Excessive amount of anode within a given area for the part being plated. Correct by eliminating all excess anodes in the tank, designing the shape of conforming anodes to minimize current density at high-density areas, and, if necessary, using nonconducting shields at these areas.

Slow plating speed

- Chromic acid content too high
- Ratio of chromic acid to total catalyst too high
- Temperature too high
- Current density too low
- Scaled anodes
- Insufficient or inadequate sizes of conductors in anode or cathode circuits
- Thief obtains too much current. Correct by redesigning thief or by removing nodules from thief.
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- High contact resistance on busbars, racks, or jigs. Correct by cleaning contacts to lower contact resistance. Do not always rely on voltage for control, because it does not indicate the conditions present on the part; instead, control by amperage.

- Large variety of parts in same tank prohibiting proper current density for each part
- Tank overcrowded with parts
- High content of metallic impurities. Correct by discarding a portion of solution; readjust after dilution.

Nodular deposits

- Insufficient etching before plating in relation to thickness of deposit. Correct by increasing etching time.
- Rough surface before plating
- Chromic acid content too high. Correct by removing portion of solution; dilute the remainder and adjust.
- Low temperature
- Low sulfate content
- Current density too high

Pitted deposits

- Marking dye not completely removed
- Material suspended in solution. Correct by filtering out suspended material.
- Surface-activating agents caused deep pits when plating thick deposits. Correct by discarding as much of the solution as necessary to eliminate pits and replace with fresh solution. Prevent by discontinuing use of mist suppressors. Plastic parts that decompose, such as floats, can form decomposition products that also create pits.
- Gas bubbles adhering to part. Correct by improving surface finish before plating and by agitating part occasionally during plating.
- Part is magnetized. Correct by demagnetizing.
- Magnetic particles in the solution. Correct by removing particles with magnet.
- Insufficient cleaning prior to plating
- Particles falling on work from anodes or thieves. Correct by improving design of anodes and thieves and by cleaning both regularly to remove loose particles.
- Carbon smut on surface. Correct by scrubbing before plating.
- Excessively etched surface during reverse-etch or stripping operation

Poor adhesion

- Insufficient or no etching before plating
- Contaminants not completely removed from surfaces during cleaning
- Excessive grinding rate at edges or sharp projections, where base metal fractures and it may appear that plated material did not adhere
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- Current interruption during plating
- Cold solution

Macrocracks

- Highly stressed base metal; cracks are visible during grinding or when heat is applied. Correct by relieving stresses in base metal.
- Grinding at too fast a rate (heat checks)

Equipment

The discussion of equipment that follows is confined largely to considerations that are specific to chromic acid plating processes. Mixed-catalyst and fluoride-free solutions have essentially the same equipment requirements as conventional sulfate solutions, except that all parts of the electrical system may need to be heavier to accommodate the increased current used. Equipment requirements for plating three specific parts are given in Table 9.

Table 9 Process and equipment requirements for hard chromium plating using conventional solutions

Item	Area of part		Area of load		No. of pieces/ 8 h	Thickness of plate		Current density		Plating time, min	Temperature of bath		No. of work rods	Tank dimensions	
	mm^2	$in.^2$	mm^2	$in.^2$		μm	mil	A/dm^2	$A/in.^2$		°C	°F		mm	in.
Small cutting tools	4,800	7.5	967,000	1500	10,000	1.3	0.05	30	2	5	50	120	1	1500 × 760 × 910	60 × 30 × 36
Shafts	20,000	30	600,000	930	200	25	1	30	2	63	50	120	2	1800 × 910 × 910	72 × 36 × 36
Gun barrels(a)	15,000	23	543,000	828	180	25	1	45	3	40	54	130	2	2400 × 910 × 610	96 × 36 × 24

(a) Plating of inside diameter 30-caliber gun barrels

Tanks and Linings. Figure 1 illustrates a hard chromium plating tank arrangement. Most tanks for chromium plating are made of steel and lined with an acid-resisting material. Because of their excellent resistance to corrosion by chromic acid, lead alloys containing antimony or tin may be used as tank linings.

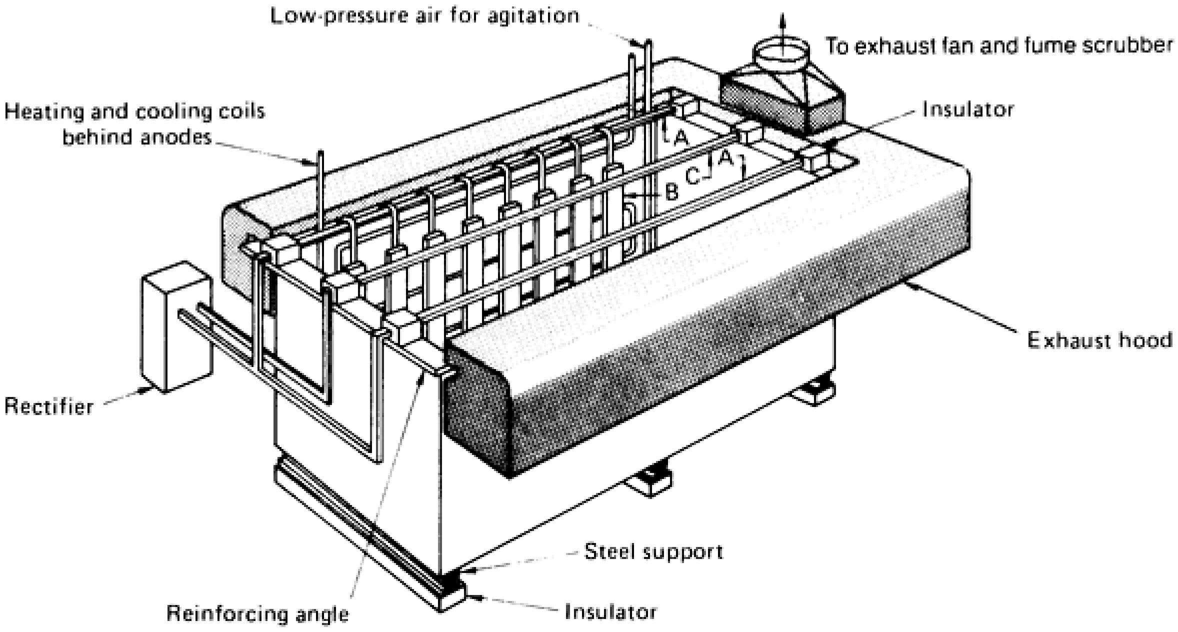


Fig. 1 Tank and accessory equipment used for hard chromium plating. A, anode rods; B, lead or lead-tin anodes; C, cathode rod

Acid-resistant brick has been used as a lining material. Because of its electrical insulating characteristics, acid-resistant brick lining has the advantage over metal linings of reducing possible current losses or stray currents. Some installations combine a lead lining or plastic sheet lining with an acid-resistant brick facing. With fluoride-containing solutions, a brick lining is suitable only for temporary use.

Almost invariably, plasticized polyvinyl chloride is used for all three types of chromium plating solutions, provided that the solution temperature does not exceed 66 °C (150 °F). Sheets of this plastic are cemented to tank walls and welded at joints and corners. Other plastic materials are equally resistant to chemical attack but are more likely to fail at the welds when exposed to an oxidizing acid. Fiberglass utilizing either polyester or epoxy is unsatisfactory for use in mixed-catalyst solutions, because exposed fiberglass will be attacked by the secondary fluoride catalyst.

Design specifications for low-carbon steel tanks for chromium plating are given in Table 10. Lining materials for low-carbon steel tanks are given in Table 11. Steel tanks should be supported at least 100 mm (4 in.) from the floor; steel I-beams are used to provide this support and are mandatory when side bracing is required. To provide insulation, reinforced strips of resin-bonded glass fiber can be placed between the floor and the I-beams. Glass brick can be used as insulation between electrodes and the plating tank.

Table 10 Design specifications for low-carbon steel tanks for hard chromium plating

Size of tank				**Thickness of low-carbon steel**		**Width of rim**		**Tank reinforcing**
Length		**Depth**						
m	**ft**	**m**	**ft**	**mm**	**in.**	**mm**	**in.**	
Up to 1	Up to 4	Under 0.9	Under 3	5	$\frac{3}{16}$	50	2	No
Up to 1	Up to 4	Over 0.9	Over 3	5	$\frac{3}{16}$	50	2	Yes
1-4	4-12	All	All	6	$\frac{1}{4}$	75	3	Yes
Over 4	Over 12	All	All	10	$\frac{3}{8}$	75	3	Yes

Table 11 Lining materials for low-carbon steel tanks for hard chromium plating

Tank length		**Lining material**					
		Lead alloy(a)		**PVC(b)**		**Brick(c)**	
m	**ft**	**kg/m^2**	**lb/ft^2**	**mm**	**in.**	**mm**	**in.**

Up to 2	Up to 6	40	8	5(d)	$\frac{3}{16}$(d)	100	4
2-4	6-12	50	10	5(d)	$\frac{3}{16}$(d)	100	4
Over 4	Over 12	60	12	5(d)	$\frac{3}{16}$(d)	100	4

(a) Antimonial lead, or lead-tin alloy.

(b) Plasticized polyvinyl chloride.

(c) Acid-resistant brick. For further protection, brick may be backed up with 39 kg/m^2 (8 lb/ft^2) of antimonial lead or lead-tin alloy, or with plasticized polyvinyl chloride sheet.

(d) Lining should be 10 mm ($\frac{3}{8}$ in.) thick at top to 0.3 m (1 ft) below top of tank.

Heating and Cooling. Steam heating coils and cooling coils can be made of antimonial lead or silver-bearing lead. Titanium coils are preferred for conventional and fluoride-free plating solutions because of their relatively low cost and long life. Tantalum or niobium-clad coils should be used for mixed-catalyst solutions due to the fluoride attack on titanium. These coils are mounted on tank walls behind the anodes. Steel pipes carrying steam and cooling water to the tank must have a nonconducting section in each leg, so that the coils cannot become an electrical ground back through the power plant system.

Electric immersion heaters sheathed in fused quartz are suitable for heating chromic acid solutions. The quartz is fragile and must be handled with care. Similar immersion heaters are sheathed in either tantalum, titanium, or lead alloy. It is sometimes feasible to heat and cool a chromic acid solution by piping the liquid to a tube bundle, concentric, or tube heat exchanger located outside the plating tank. Preferably, heat exchanger tubes should be made of tantalum or titanium. This method has the disadvantage of requiring pumping of the solution.

Temperature-control planning should begin with selection of the volume of solution required in the plating solution. An ideal volume consists of 1 L or more of solution for each 13 W of plating power (1 gal or more of solution for each 50 W of plating power). About 60% of this plating power (30 W) produces heat and maintains the solution at temperature in an uninsulated tank of standard design. Power applications in excess of 13 W/L (50 W/gal) require cooling of the plating solution and cause relatively rapid changes in solution composition.

Agitation. A chromium-plating solution should be agitated periodically, particularly when the solution is being started, to prevent temperature stratification. Air agitation is effective, but oil from an air pump must not be permitted to leak into the air system. Preferably, the air should come from an oil-free low-pressure blower. A perforated pipe of rigid polyvinyl chloride may be used to distribute air in the solution.

Busbars. Anode and cathode busbars are usually made of round or rectangular copper bar stock. These rods should be adequately supported to prevent them from sagging under the weight of anodes and work. Generally, selection of bar size is determined by allowing 1 cm^2 of cross-sectional area for each 150 A (1 in^2 of cross-sectional area for each 1000 A), although mechanical strength for load support is also a factor in determining rod size. Anode and cathode rods are supported above the tank rim by insulators, which may be made of brick, porcelain, or plastic. Even metallic supports can be used if a strip of electrical insulating material is placed between the plating tank and the busbar.

Power Sources. Although dynamos or motor-generator sets were once the usual sources of power for low-voltage direct current for plating, rectifiers are now regularly used. In general, use of motor-generator sets is now restricted to larger and more permanent installations. Originally, plating rectifiers were made of copper oxide or magnesium-copper sulfide, but these have been largely replaced by silicon rectifiers. Silicon is favored for plating rectifiers because of its high resistance to thermal overload and small space requirement. Hard chromium platers often start plating on a piece by sweeping up applied voltage and current from very low values to the high values used for plating. Because silicon-controlled rectifiers have high ripple at low output, the output should be filtered. Tap-switch controls, however, produce relatively low ripple over the entire output range.

A 6 V power source can be used for chromium plating, but it is generally desirable or necessary to operate with 9 to 12 V available. Chromium plating requires full-wave rectification with a three-phase input and full control, giving a ripple less than 5% and no current interruptions. If a rectifier becomes partially burned out, it may single phase to some degree, and this can cause dull or laminated, peeling deposits.

Fume Exhaust. A chromium-plating process produces a chromic acid mist, which is toxic. The maximum allowable concentration for 8 h continuous exposure is 0.1 mg of chromic acid mist per cubic meter of air. This concentration value is in accordance with recommendations by the American Conference of Governmental Industrial Hygienists. Because of the extreme toxicity of this mist, it is mandatory to provide adequate facilities for removing it. The minimum ventilation rate should be 60 m^3/min per square meter (200 ft^3/min per square foot) of solution surface area. (It should be noted that these regulations are presently under revision and are subject to changes.)

Generally, fumes are exhausted from a chromium plating tank by means of lateral exhaust vents along both long sides of the tank. For narrow tanks, up to 600 mm (24 in.) wide, a lateral exhaust on one side of the tank should be adequate unless strong cross-drafts exist. Velocity of the air at the lateral exhaust hood slots should be 600 m/min (2000 ft/min) or more.

In the design of ductwork, condensate duct traps should be included to capture chromic acid solution. Drains from these traps should be directed to a special container and not to the sewer. In this way, chromic acid solutions can be returned to the tank or recovery system or be safely destroyed. A fume scrubber or a demister should also be included in the system to remove most of the chromic acid fumes before exhausted air is emitted to the atmosphere. Many communities have air pollution regulations requiring fume scrubbers. Fume exhaust ductwork may be made of carbon steel and coated with acid-resistant paint. Modern construction uses chlorinated polyvinyl chloride.

Rinse Facilities. Rinsing the work after chromium plating prevents it from becoming stained or discolored. Insufficient rinsing can result in contamination of cleaning solutions during subsequent cycling of racks. Multiple rinsing facilities are recommended. After being plated, parts should be rinsed in a nonrunning reclaim tank, which can be used to recover part of the chromium solution dragout. After they are rinsed in the reclaim tank, plated parts should be rinsed in counterflowing cold water and hot water tanks. Water should cascade from the hot water tank to the cold water tank. A multiple counterflowing arrangement requires much less water than two separate rinsing tanks.

If rinse water is being returned to a chromic acid waste disposal unit, the flow of water into the hot water tank should be controlled automatically by a conductivity-sensing element in the cold water tank. At a predetermined concentration of chromic acid in the cold water, the water inlet to the hot water tank should flow, causing an overflow of cold water to the waste disposal unit. This arrangement decreases the amount of water consumed and minimizes the required capacity of the waste disposal unit.

Cold water rinse tanks may be coated, sprayed, or otherwise lined with plasticized polyvinyl chloride. Hot water rinse tanks may be constructed of types 347, 304, or 316 stainless steel, or they may be made of carbon steel and lined with lead. Reinforced polyester glass fiber also may be used for either hot water or cold water rinse tanks.

Spray rinsing also effectively removes residual chromic acid. Because spraying does not always reach recessed areas, sprays should be positioned above a dip rinse. As parts are removed from the dip rinse, they may be sprayed with clean water, which, in turn, is returned to the dip tank.

Maintenance. Following is a maintenance schedule for a still tank installation for hard chromium plating:

- *Daily:* Check temperature. Check concentration of solution by density measurements. Clean busbars and electrical connections. Remove any parts that fall from racks.

- *Weekly:* Analyze for chromic acid and sulfate contents.
- *Monthly:* Remove all sludge and parts from tank, using a hoe and dragging the bottom. If tank is used for plating inside diameters, analyze for trivalent chromium.
- *Semiannually:* Check tanks for leaks and condition of lining. Clean and inspect rectifiers or motor-generating units. Check ammeter calibration.
- *As necessary:* Analyze for trivalent chromium, iron, nickel, copper, and zinc. Check condition of anodes.

This schedule is intended only as a guide; local conditions determine exact requirements. The rate of variation of solution constituents depends on the volume of solution, the method of operation for the solution, and the type and amount of work.

Racks and Fixtures

The following recommendations are offered regarding the design and use of plating racks:

- Racks should be designed to hold workpieces in a favorable position for plating uniformly on significant surfaces and to facilitate racking and unracking.
- Workpieces with protruding sections should be racked so that parts shield each other. If this is not possible, a current thief should be used to reduce current density at the protruding points.
- Electrical contact with the part should be made on an insignificant surface.
- The contact or rack tip should be rigid enough to hold workpieces securely and maintain positive contact. When the work is heavy enough to ensure positive contact, a hook often suffices.
- To minimize solution losses due to dragout, the work should be hung as nearly vertical as possible, with the lower edge of the work tilted from the horizontal to permit runoff at a corner rather than a whole edge. When recessed areas cannot be racked to allow proper runoff, provision should be made for drain holes or perhaps tilting of the rack when it is being withdrawn from the solution.

Although the design of racks and the methods of racking vary greatly, two basic types of racks are generally used. The first type consists of a single high-conductivity bar on which suitable supports have been mounted for holding the work to be plated; this rack is the cathode side of the plating circuit. The second type consists of two elements, the cathode and the anode; the work is held by the cathode and the cathode is attached to, but insulated from, the anode. Both types of racks are illustrated in Fig. 2. To prevent deposition of chromium or attack by the plating solution on parts of the rack that are immersed in the solution, these parts are covered with nonconducting material such as water-resistant tape, special insulating lacquer, or plastisol coatings.

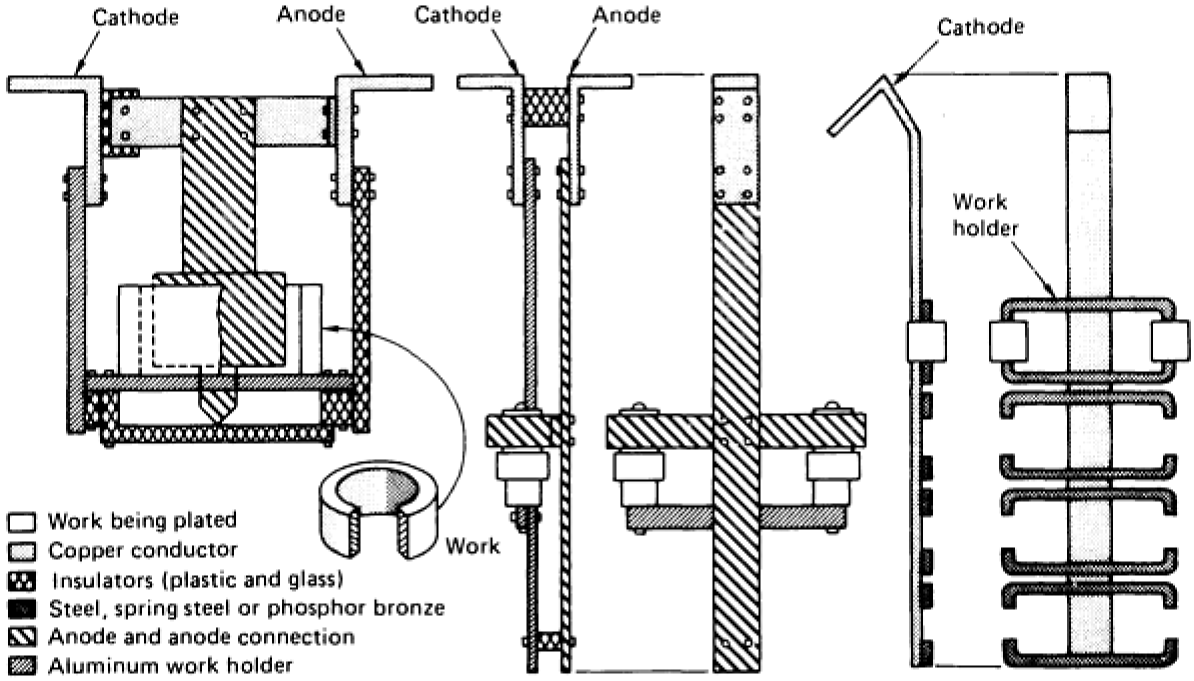


Fig. 2 Racks used in hard chromium plating

Surface Preparation

All soils and passive films must be removed from surfaces of ferrous and nonferrous metals before they are hard chromium plated. In addition to cleaning, certain surface-activating processes are often important in preparing the base metal for hard chromium plating. The processes include etching of steel, preplate machining, and nonferrous metals preparation.

Etching of steel before plating is needed to ensure adherence of the chromium deposit. Anodic etching is preferred for this purpose. Slight etching by acid immersion may be used for highly finished surfaces, but with possible sacrifice of maximum adherence.

Steel can be etched anodically in the chromium plating solution at its operating temperature for plating. A reversing switch is used so that the steel to be plated can serve as the anode for 10 s to 1 min (usually 30 s to 1 min) at a current density of about 15 to 45 A/dm^2 (1 to 3 A/in^2). Tank voltage should ordinarily be 4 to 6 V. Because mixed-catalyst solutions chemically attack the steel, causing etching of the surface, shorter electrochemical etching time frequently is required than is the case with conventional or fluoride-free chemistries. This process has the disadvantage of causing the solution to become contaminated with iron from the work and with copper from the conductors.

As an alternative, steel may be anodically etched in a separate chromic acid solution without sulfate additions and containing 120 to 450 g/L (16 to 60 oz/gal) of chromic acid. Solution temperature may range from room temperature to that of the chromic acid plating solution, or even higher, provided that current density and time of treatment are adjusted to suit the type of work being processed.

A sulfuric acid solution (specific gravity 1.53 to 1.71) may be used for anodic etching, provided that the solution temperature is held below 30 °C (86 °F), and preferably below 25 °C (77 °F). The time of treatment may vary from 30 to 60 s and the current density may vary from about 15 to 45 A/dm^2 (1 to 3 A/in^2) at tank voltages ordinarily between 4 and 6 V. A lead-lined tank with lead cathodes should be used. With the use of a sulfuric acid solution, however, two difficulties may be encountered. First, if the rinsing following etching is incomplete, the drag-in of sulfuric acid throws the chromium plating solution out of balance with respect to the ratio of chromic acid to sulfate. Second, in handling parts that are difficult to manipulate, there is danger that surfaces exposed to air more than a very short time will rust and that finely finished surfaces will be overetched.

For high-carbon steel, a sulfuric acid solution of 250 to 1000 g/L (33 to 133 oz/gal), used at a temperature of not more than 30 °C (86 °F) and preferably below 25 °C (77 °F), is effective for anodic etching. The addition of 125 g/L (16.6 oz/gal) of sodium sulfate, based on the anhydrous salt, is of benefit for many grades of steel. Anodic treatment in this solution usually does not exceed 1 min at a current density of about 15 A/dm^2 (1 A/in^2) (range of 15 to 45 A/dm^2, or 1 to 3 A/in^2). High acid content, high current density, and low temperature (within the ranges specified) minimize the attack on the base metal and produce a smoother surface. This sulfuric acid solution is stable and not appreciably affected by iron buildup.

Preplate Machining. Metal debris on the surface should be removed before etching (an activation procedure). The use of abrasive-coated papers is common, as is the use of successively finer grit stones in honing and grinding. To prepare a sound surface in superfinishing, 600-grit stones may be used. Electropolishing is sometimes used to remove highly stressed metal and metal debris from the surface of cold-worked steel. This process improves bond strength and corrosion resistance of electroplated coatings. It accomplishes this function without formation of smut, which may result from anodic etching. This treatment is not recommended for parts that are subjected to critical fatigue stresses and that are expensive to manufacture.

Preparation of Nonferrous Metals. Aluminum, in common with certain other metals, quickly develops a natural, passive oxide film after exposure to preplating cleaning cycles. This film must be removed before aluminum is plated. The most widely used method of preparing aluminum for plating involves a zincating treatment, which may be followed by a thin 5 μm (0.2 mil) copper electrodeposit. However, it is possible to plate chromium directly over the zincate.

Aluminum parts used in hydraulic systems require a nickel undercoat before being plated, to provide corrosion protection to all plated surfaces that are not completely and constantly immersed in hydraulic fluid or similarly protective fluids. A minimum thickness of 10 to 15 μm (0.4 to 0.6 mil) of nickel is usually specified. This undercoat may also be required for steel parts in similar applications.

Titanium and titanium alloys, as well as magnesium, also form a tight, stable oxide coating and are therefore difficult to plate. These metals can be pretreated with an electroless nickel plate or a coating deposited from a high-chloride nickel strike solution.

Variations in Plate Thickness

Variations in the thickness of hard chromium plate depend primarily on the potential field distribution. Potential field is controlled by the placement of anodes, shields, thieves, and other parts, as well as the relative position of the sides and surface of the tank. Variations in plate thickness also depend on surface preparation, control of solution conditions, and uniformity of the power source.

Methods of Measuring Plate Thickness. Several methods and types of instruments are available for determining the thickness of plate. These include electrolytic stripping, microscopic measurements of cross sections, torsion dynamometer measurements made with magnets of various strengths, measurement by eddy current instruments, and accurate measurement of the dimensions of the part before and after plating to determine thickness by difference.

Electrolytic stripping and microscopic measurements of cross sections are destructive methods that are most frequently used for purposes of verification, calibration, and sampling of production runs. When calibrating instruments with prototype plated parts, using microscopic measurements of cross sections as umpire checks, several calibration reference curves may be required, depending on the parts being plated.

Measurements by properly calibrated eddy current or torsion dynamometer instruments are affected by the surface finish of the deposit, width and thickness of the piece, surface contour, and composition of the base material. With a properly calibrated instrument, thickness measurements are usually within 10% of the actual thickness. Individual thickness measurements should not be used as the basis for acceptance or rejection; however, an average of several determinations from a well-calibrated instrument is an acceptable measure of the mean thickness from a controlled process.

The normal variation in plate thickness that can be expected when plating the outside diameter of cylinders, rods, or round parts racked as cylinders is ±0.2μm/μm (±0.2 mil/mil) of plate intended. This has been determined over a period of several years by average quality level thickness measurements on piston rings racked as cylinders.

This normal variation of 20% was confirmed in an actual production situation. In plating identical parts to a consistent thickness requirement, sample checks from 74 loads (110,000 parts) representing 27 days of operation were made to determine the plating tolerances that could be expected. The plating cycle was set to provide a plate thickness of 200 to 230 μm (8 to 9 mils) to meet a final requirement for a minimum plate thickness of 150 μm (6 mils) after light stock removal during the subsequent finishing operation. Results of this analysis are shown in Fig. 3.

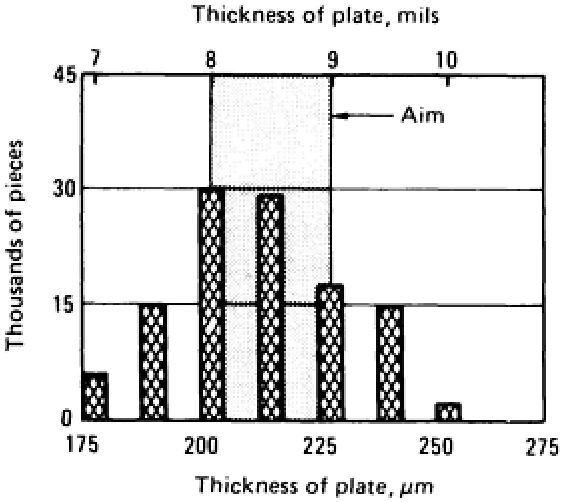


Fig. 3 Variations in hard chromium plate thickness for 74 loads, representing 110,000 parts of the same design plated over a period of 27 days of operation. Target thickness was 200 to 230 μm (8 to 9 mils) of hard chromium. Average thickness for the 74 loads was 215 μm (8.4 mils).

The throwing power of chromium-plating solutions is related to the ratio of chromic acid concentration to the catalyst concentration. Higher ratios give better throwing power at a given temperature and current density. This is evidenced by the fact that when a very low current density is present on certain areas of irregularly shaped parts, the cathode efficiency at that low current density is less for a solution high in sulfate than for a solution with lower sulfate content. Therefore, less metal is deposited on the areas of low current density from a solution of high catalyst content.

The current density at which no metal deposits is greater for high catalyst solutions than for lower catalyst solutions. Also, metal deposits from a solution of low catalyst concentration at a current density that would be too low for depositing from a solution with high catalyst concentration. Thus, the following factors must be considered to ensure successful plating of complex shapes: chemical balance, operating variables, type of anode, and design of fixtures or racks.

Chromium plating requires far more attention to the variables that affect current distribution than cadmium, zinc, copper, or nickel plating. It is theoretically impossible to obtain the same current density at an inside corner as on the flat adjacent to it. An outside corner without shielding or thieving always has the highest current density and hence the greatest plate thickness. Conforming anodes, shields, and thieves may be used to minimize thickness variation, but except on the simplest shapes, they do not eliminate it.

Some metal is deposited at low current densities in most other plating solutions, but in chromic acid solutions there is a minimum current density for a given solution at a given temperature below which no metal is deposited. If an area of an internal or irregular shape receives less than this minimum current density, no deposition of metal occurs in this area. This explains why it is so difficult to chromium plate recesses and internal shapes without special anodes. Special hardware, in the form of thieves or shields, is required for lowering the current density on areas such as edges to prevent excessive buildup of deposit.

In most electroplating solutions, the primary current distribution on an irregular object can be improved by increasing the tank anode-to-cathode distance. However, beyond a minimum distance, which depends on the shape of the part, no further improvement can be attained.

Because of the low throwing power of hard chromium plating solutions, an increase in the anode-to-cathode distance does not result in even plating of sharp reentrant surfaces such as those formed by internal angles. For plating parts containing shapes of this type, conforming anodes and/or current shields must be used.

Figure 4 illustrates the relation between thickness of deposit and distance of the anode from the part being plated. In this instance, an alternative to an increase in the anode distance is the use of an anode contoured to the curvature of the part.

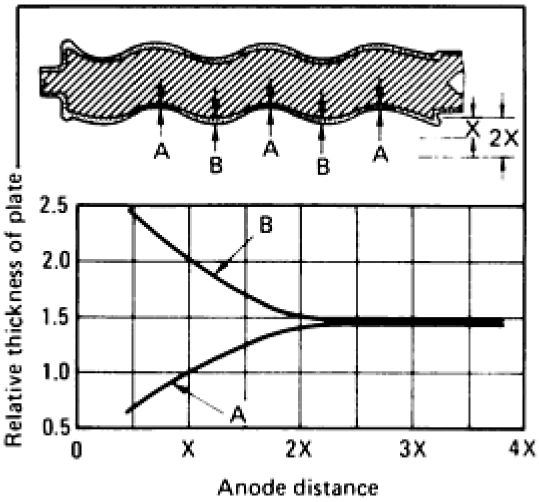


Fig. 4 Variation in thickness of chromium plate on feedworm as a function of the distance of the anode from the part. Values of *x* are about 25 mm (1 in.) or more.

Special Anodes. When the part contains sharp, narrow recesses, such as grooves, a reduction of the anode distance may help to increase the thickness of the deposit at the bottom of the grooves. However, some parts with sharp-cornered grooves, bosses, and undercuts cannot be uniformly covered even when contoured anodes are used. Examples of parts in this category and the areas of heavy deposits are illustrated in Fig. 5.

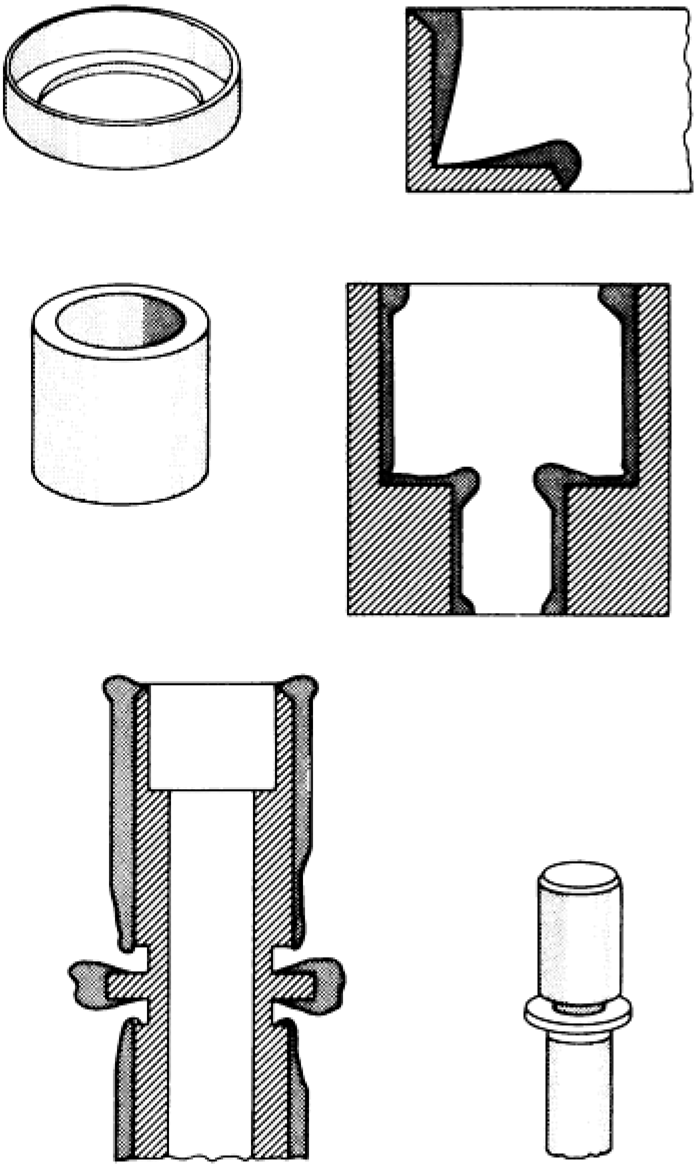


Fig. 5 Parts difficult to plate uniformly with hard chromium, even with the use of specially contoured anodes. Variations in plate thickness shown are approximately to scale.

Anodes used for plating recesses can be directly connected to the power supply, or they can be bipolar in nature. The bipolar anode has no direct electrical connection and takes advantage of the fact that current follows the path of least resistance. Bipolar anodes are an interesting curiosity that may have application in rare instances; however, direct connection of the anode to the positive direct current through a rheostat and ammeter, if required, is far more controllable.

The deposit on internal shapes can also be affected by the evolution of gas that occurs during plating. Gas can cause streaked deposits or produce a taper in a long bore. To minimize this effect, the parts should be positioned in a manner that permits the gas to move rapidly away from the part.

Because of fabrication problems encountered with lead alloys, complex-shaped anodes are made of steel, then coated with lead to produce the effect of solid lead anodes. These composite anodes are more economical and lighter in weight. However, the base metal can be destroyed if there are pores or throughholes in the lead alloy coatings. Brass or copper should never be used on the anode side, as they dissolve rapidly and seriously contaminate the solution. Low-carbon steel may be used alone for short runs, and lead-coated steel may be used for longer service.

Crack Patterns and Other Characteristics of Hard Chromium Plate

The quality of hard chromium plate is evaluated chiefly from the standpoint of thickness and thickness distribution, appearance, crack pattern, crack size, porosity, roughness, and adhesion of the plate to the base metal.

Surface Cracks. During the deposition of chromium deposits, microcracks form to relieve the internal stress. These cracks subsequently fill in with plated chromium. The chromium in these former cracks is more easily etched and has a different refractive index than the surrounding deposits. For this reason, with the use of a microscope one can determine where and how many microcracks were present at one time on the surface of the deposit. The pattern usually consists of crack-free areas and plateaus completely surrounded by crack boundaries. The plateaus from an average conventional sulfate solution are 2 to 3 times larger than those from a mixed-catalyst solution; that is, there are more cracks per inch in a deposit from the average mixed-catalyst solution. The fluoride-free chemistry gives yet an additional factor of 2 to 3 times more microcracks.

Interestingly, the more microcracks present, the shorter the penetration into the deposit of each one (i.e., with the conventional solution, a microcrack can extend all the way through a 1 mil thick deposit, while in the fluoride-free solution deposit they extend very short distances). Since these (former) cracks provide the pathway for corrosion, it is desirable to have as many discontinuities as possible as one progresses through the deposit to the substrate. It is for this reason that in corrosion applications, the solution that provides the greatest amount of microcracking possible is used.

Crack-Free Deposits. It is possible to plate chromium with virtually no microcracks. This is done by altering the current density and temperature, altering the catalyst concentrations, or using pulsed-current or periodic-reverse plating. Crack-free deposits are gray and have very poor wear properties. The corrosion resistance is also very poor due to residual stresses in the deposit, which eventually (in a few days or months) cause large cracks that extend through the entire deposit.

Some specialized applications for this type of deposit include broaches, cams, dies for metal forming, metalworking rolls, and stamping dies for embossing silverware. Complicated shapes create a large range of current densities and are difficult to plate with a crack-free surface. Corners, edges, or other high-current-density areas are most likely to crack during plating.

Porous Chromium. Although the cracks or porosity that characterize chromium deposits are not desirable for resistance to corrosion, a porous structure can be advantageous in wear applications in which lubrication is required, because it promotes wetting action and provides oil retention after initial lubrication. Engine cylinders are the outstanding application.

Most chromium-plated cylinder surfaces consist of some form of interrupted surface, generally porous chromium. An interrupted surface may be obtained by electrolytic or chemical etching of chromium after it is plated on a smoothly honed bore, as with porous chromium, or by preroughening the bore by shot blasting, knurling, or tooling and then reproducing this roughness in the final chromium plate or by machining in roughness after plating.

Two distinct types of porous chromium are produced. One has pinpoint porosity with many microscopic depressions in a honed chromium surface. This has been used in all types of engine cylinders except aircraft. The other type is also finish honed but is broken by randomly connected channels, leaving isolated bearing plateaus. For both types, the percentage of porosity is generally controlled between 20 and 50% of the total area. Average plateau diameter is further controlled between 0.25 to 0.75 mm (0.010 to 0.030 in.) with the channel type of porosity. Porosity as low as 5% approaches dense chromium and is susceptible to scoring because of sparse oil distribution. High porosity, such as 75%, may cause high initial ring wear and high oil consumption. In normal engine service, cylinders coated with chromium of optimum porosity give wear rates one-third to one-tenth better than those of uncoated cast iron or steel, hardened or unhardened.

Several methods--electrochemical, mechanical, and combinations of both--have been developed to provide controlled porosity in heavy chromium deposits. Mechanical methods entail either severe grit blasting of the surface to be plated or roughening of the surface with a fine knurling tool. The roughened surface is reproduced by the deposit. Using a patterned mask, the surface can also be roughened by chemical or electrochemical means before plating The most widely used techniques, however, involve chemical or electrochemical etching of the chromium deposit after plating. Note that the pattern or crack density and the size of the plateaus are largely determined by the composition (ratio) of the solution, and the plating temperature.

Etching is performed on plated thicknesses ranging from 120 to 180 μm (5 to 7 mils). Porosity is developed after plating by electrochemically etching anodically in chromic acid solution. The etched surface is finished by honing, polishing, or lapping. Metal removal that exceeds the depth of porosity must be avoided. To avoid accelerated wear in service, finished surfaces must be thoroughly cleaned of abrasive and chromium particles.

Quality Control Tests. Usually, visual examination is sufficient for determining appearances and roughness of the surface of hard chromium plate. Magnetic particle inspection can be used to examine chromium plate up to 100 μm (4 mils) thick for cracks after grinding. The as-plated deposit prior to postfinishing should be as smooth as the base metal before plating and should be free of pits and nodules. The deposit should not exhibit excessive thickness variation. Particularly, deposits with dendritic growths (trees) should be rejected. Adequate plating control requires that such dendritic deposits occur on thieves rather than in functional areas.

For process development and quality verification, destructive testing may be used to determine the crack pattern and bond between the plate and base metal. The crack pattern can be developed by etchants such as a hot 50 vol% hydrochloric acid aqueous solution, or by short etching in a chromium plating solution.

The quality of the bond can be determined by punch testing, bend testing, examining the bond line metallographically, or judging of ground or hammered samples. Well-bonded chromium, because of its low ductility, does not fail by pulling away from the bond line; however, it fails by cracking and spalling if it is subjected to excessive stress or distortion in 45° diagonal tension.

Excessive porosity of thin (less than 25 μm, or 1 mil, thick) chromium plate on steel can be determined by applying an acidified copper sulfate solution to the plated areas. The pores permit the solution to copper coat steel by displacement, and the degree of copper coating thus indicates the degree of porosity. Porosity can also be determined by the ferroxyl test described in *Metal Finishing Guidebook,* 1982.

The mandrel test can also be used in quality control. If a portion of the chromium plate is made anodic for 3 min at 15 A/dm^2 (1 A/in^2) in a solution containing 250 g/L (33 oz/gal) chromic acid at 60 °C (140 °F), the crack pattern is developed. Counting the crack density under the microscope is an excellent procedure for noting the constancy of the composition (mainly ratio) and the temperature of the solution.

Hardness of Plate

Valid hardness measurements of chromium deposits are difficult to make, and values are dependent on test conditions, so hardness values should not ordinarily be used as quality control specifications and routine criteria. Rather, the as-plated brightness can serve as an indication of hardness.

The hardness of chromium plate cannot be accurately determined by the common hardness testers, such as Brinell and Rockwell, because hard chrome is generally too thin for these tests. The indentation produced in these tests distorts the base metal and is influenced by it, which usually results in low hardness readings.

The most reliable and most widely accepted hardness values are those obtained with the Vickers 136 diamond pyramid indenter or the Knoop indenter. With these, the hardness test must be made on a carefully prepared and polished surface, preferably on a cross section of the plate, to eliminate any possible influence of the base metal on the hardness values obtained.

Cracks in the chromium plate influence the hardness values, depending on the type of indenter used and the load applied. In general, lighter loads are more sensitive to hardness variations and result in higher hardness values. Cracks influence values obtained with heavy loads more than values obtained with light loads. Also, because of the smaller area covered by the Vickers 136 diamond pyramid indenter, hardness values determined with this indenter are influenced less by underlying cracks than values obtained with the Knoop indenter.

When conducting microhardness tests, it is important to make sharp and accurate impressions, particularly when using light loads. Also, when hardness values are reported, the load, type of indenter, and optical system used should be indicated. The importance of stating the load and type of indenter is shown by the following data obtained on chromium plate from one plating cycle (each range or average represents 25 tests):

Load, g	Hardness value	
	136° diamond pyramid	Knoop indenter
100	950-1110 (1040 avg)	940-1090 (1025 avg)

In an investigation of the scratch hardness of chromium deposits of all types, it was observed that bright or semibright deposits had the best combination of hardness and wear resistance, regardless of plating conditions. In this investigation, the wear resistance was measured by means of a specially constructed abrasion hardness machine. The machine contained a small grinding wheel that revolved at 18 rpm. The number of revolutions required to grind through a 25 μm (1 mil) deposit on steel was an indication of the abrasion hardness. Results are summarized in Table 12, which shows the relation between the appearance of deposits and their hardness and resistance to abrasive wear.

Table 12 Relation between appearance and hardness of hard chromium plate deposited from conventional solutions

Average appearance	Average scratch hardness(a), HB	Average relative abrasive hardness
Matte (cold bath)	640	25
Milky	830	100
Slightly milky	990	290
Bright	1000	300
Slighty frosty	1005	300
Frosty (smooth)	1020	235
Frosty (rough)	1060	125
Burnt	1165	110

(a) Converted to Brinell scale from values obtained with a Bierbaum microcharacter using a 9 g (0.3 oz) load

The effect of temperature on the hardness of electrodeposited chromium is often a significant factor in applications involving wear resistance. The electrodeposited metal begins to decrease in hardness when it is exposed to temperatures above about 205 °C (400 °F). Hardness decreases progressively with an increase in temperature (Fig. 6). As the hardness of chromium plate decreases, its resistance to wear may be affected adversely. Chromium plate should not be used for wear resistance in applications where service temperature exceeds 420 °C (790 °F).

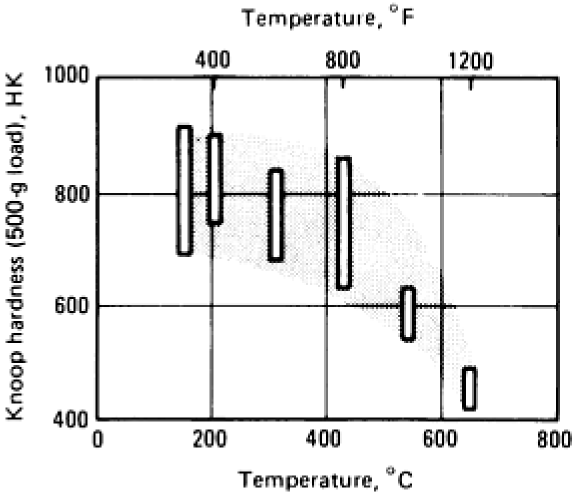


Fig. 6 Effect of annealing temperature on the hardness of chromium plate deposited during a single cycle in a mixed-catalyst solution. All data represent 25 measurements of each condition; every readable impression was accepted as valid. Heating cycles of 1 h were used.

Cost

The electroplating of hard chromium is very cost-effective, giving a high throughput with reliable, reproducible quality deposits that are unattainable by any alternative technology. The important cost factors are capital and labor expenses, followed by electricity, and, lastly, chemicals, which are relatively inexpensive. Almost always the fluoride-free solution is the least expensive chemistry to operate, followed by mixed-catalyst and then conventional sulfate solutions. Although the chemical costs increase going from conventional to mixed-catalyst to fluoride-free solutions, this increase is offset by savings in electrical costs, capacity improvements, and deposit quality improvements.

Factors that affect the relative cost of plating, regardless of the solution used, include the shape of the part, the design and arrangement of anodes, and special finishing techniques. Labor charges for hard chromium plating may be higher than for other plating processes, largely because many chromium plating operations are performed manually. Also, more labor is required to prepare some parts for plating or for finishing after plating.

The cost of plating increases with the complexity of the part design. Parts containing sharp notches, section changes, and unplated areas of cross-holes necessitate more handling during preparation and finishing than parts of simple shape. Also, anodes must more precisely conform to the shape of such parts for accurate control of plating thickness. Defects associated with chrome plate, such as dendritic growths and excessive buildups on external corners, can be minimized with tooling and special techniques. Depending on the nature of the part, these may increase costs. Special finishing techniques, primarily grinding and lapping, are required. Often a heat treatment of plated parts is necessary before they are ground or lapped.

For surfaces that are difficult to finish mechanically, even greater care must be taken in design and construction of anodes to approximate desired results closely. The cost of anode design and construction must be amortized over the number of parts plated. If sufficient production is required, refinement of masking and anodizing generally pays with decreased postplate finishing. Costs are affected also by the quality of the plate. Hard, high-quality plating finished to a bright luster is very expensive because of the rigid controls required in its production. As with other plating processes, costs vary because of local utility charges and ordinances pertaining to disposal of wastes. The availability of power and water, and the quality of the water available, can significantly affect cost. Safety requirements and waste disposal methods can be responsible for at least a 20% difference in plating costs among different plants.

Removal of Chromium Plate

Most manufacturers require salvage of misplated parts because of their high value. Further, in the aircraft industry, business machine industry, and plastic mold industry, significant numbers of parts are run for the life of the deposit and then overhauled by stripping worn deposits and replating.

Methods of Stripping. Chemical, electrochemical, or mechanical methods are used to remove hard chromium deposits. When the base material is steel, brass, copper, or nickel, hydrochloric acid at any concentration over 10 vol% and at room temperature or above removes chromium. In some operations, inhibitors are added to the acid solution to minimize attack on the steel substrate.

Chromium is removed electrochemically from steel or nickel by the use of any convenient heavy-duty alkaline cleaner at room temperature or above, at 5 to 6 V with anodic current. This method is unsatisfactory for nickel-base alloys, which should be stripped chemically in hydrochloric acid. Chromium may be stripped from aluminum by making the part the anode in a cold chromium (nonfluoride) plating solution or in conventional chromic acid or sulfuric acid anodizing solutions. Aluminum alloys with a high alloy content and alloys subjected to various heat treatments all react differently in stripping solutions, so precautions must be taken to prevent attack on the base metal. Anodic stripping operations result in formation of oxide films on the base metal. These films should be removed by one of the conventional deoxidizing processes prior to replating.

Stripping of chromium deposits from high-strength steel must be performed electrochemically in an alkaline solution. The parts are then stress relieved at 190 °C (375 °F) for a minimum of 3 h. The following solutions and operating conditions are recommended for removing chromium deposits from the materials indicated. Proprietary formulations having a longer operational life are also available.

Removal from steel or nickel-plated steel

- Sodium hydroxide, 45 to 320 g/L (6 to 30 oz/gal); anodic treatment at 3 to 8 A/dm^2) (0.2 to 0.5 A/in^2); solution temperature, 21 to 71 °C (70 to 160 °F)
- Anhydrous sodium carbonate, 45 to 60 g/L (6 to 8 oz/gal); anodic treatment at 2.5 to 5.5 A/dm^2 (0.15 to 0.35 A/in^2); solution temperature, 21 to 66 °C (70 to 150 °F). Use 2.3 A/dm^2 (0.15 A/in^2) with solution temperature of 66 °C (150 °F) to reduce possibility of pitting alloy steel.
- Sodium hydroxide, 52 g/L (7 oz/gal); sodium carbonate, 30 g/L (4 oz/gal); anodic treatment at 8 A/dm^2 (0.5 A/in.^{2})
- Concentrated hydrochloric acid at room temperature
- Hydrochloric acid, 50 vol%, at room temperature

Removal from aluminum and aluminum alloys

- Sulfuric acid, 67 vol%; glycerin, 5 vol%; anodic treatment at 1 to 3 A/dm^2 (0.1 to 0.2 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Removal from magnesium and magnesium alloys

- Anhydrous sodium carbonate, 50 g/L (6.5 oz/gal); anodic treatment at 2 to 5 A/dm^2 (0.15 to 0.30 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Grinding is used occasionally to remove heavy chromium deposits. Most defective chromium deposits are observed during subsequent grinding for finishing, so it is sometimes expedient to continue grinding to remove all of the plate and then replate. In the grinding of heavy deposits for the removal of several thousandths of an inch of chromium to attain required dimensions or surface finish, the most important requisites for successful results are:

- A soft grinding wheel
- A sufficient amount of coolant
- A light cut
- Correct peripheral speed
- Freedom from vibration
- Frequent wheel dressing

Because chromium is hard and brittle, a soft grinding wheel is essential. A hard wheel forms a glazed surface, which results in a temperature rise that causes the chromium to crack. A soft wheel breaks down rapidly enough to prevent formation of a glaze; however, too soft a wheel is not economical because of rapid wheel wear. Good performance can be obtained with an aluminum oxide resin-bonded wheel of about 60 grit and H-grade (hardness).

To prevent or minimize glazing, the contact area should be flooded with a coolant. Usually, the coolant is water with a small amount of soluble oil. Because of its hardness, excess chromium cannot be removed as rapidly as when grinding most other materials. The maximum thickness of metal removed should not exceed 5 μm (0.2 mil) per pass, and this amount should be reduced if there is any evidence of cracking. The optimum grinding speed is about 20.4 m/s (4000 sfm).

Effective grinding requires a rigid machine. Any appreciable vibration can cause cracking of chromium because of uneven contact pressure, and it also results in a wavy surface. Factors essential for a rigid machine include a well-fitting spindle bearing, a balanced wheel, a heavy bed, and a well-supported workpiece. Whenever there is the least indication of glazing or nonuniform wheel surface, the wheel should be dressed with a diamond point. Adherence to the preceding recommendations will result in a good surface with a finish of 0.35 to 0.5 μm (14 to 20 μin.). Subsequent lapping (240 grit) will produce a finish of 0.1 to 0.3 μm (5 to 10 μin.).

Special care should be taken when grinding chromium-plated parts made from high-strength steel (steel with an ultimate tensile strength of 1240 MPa, or 180 ksi, and above) that are to be used in stressed applications. Numerous failures have occurred due to formation of untempered martensite caused by the heat of the grinding operation. For information and guidelines on grinding chromium-plated high-strength steel parts, see military specification MIL-STD-866B.

Hydrogen Embrittlement

The susceptibility of chromium-plated parts to hydrogen embrittlement is affected by hardening of the steel, grinding, surface defects, pickling, cathodic cleaning, and the depth of plate relative to the thickness and hardness of the part being plated. (It should be noted that the chemistry of the chromium plating solution is not a factor.) Unless the hydrogen absorbed during pickling and cathodic cleaning is removed, subsequent plating further embrittles the part to such an extent that breakage can occur during plating. This effect becomes more prevalent with increasing hardness of steel and on parts of thin cross section.

The thickness of plate on thin steel sections is of importance from the standpoint of notch effect. This was illustrated in an actual production setting. Thin sections of steel, 2.5 by 0.5 mm (0.10 by 0.020 in.) and 25 to 38 mm (1 to 1 $\frac{1}{2}$ in.) long, were plated with chromium to a thickness of 8 to 13 μm (0.3 to 0.5 mil). The hardness of the steel was 57 to 59 HRC. These parts were aligned by being bent until permanently set. When the thickness of the chromium plate was increased to range from 15 to 23 μm (0.6 to 0.9 mil), the parts would break before taking a set. Baking them at 205 °C (400 °F) for 4 days did not relieve this condition. It was necessary to decrease the hardness of the steel to 53 to 55 HRC to prevent breakage of parts with heavier plate.

Stress Relieving before Plating. Surfaces to be chromium plated must be free from stresses induced during machining, grinding, or hardening. Stresses from the hardening operation may be further increased during grinding and result in microcracks. If the hardness of the steel is less than 40 HRC, it is unlikely that any damaging effect will occur as a result of residual stress. Steel with a hardness exceeding 40 HRC should be stress relieved before it is plated by heating at 150 to 230 °C (300 to 450 °F).

Baking after Plating. Steel parts with a hardness above 40 HRC should be baked at a temperature of at least 190 °C (375 °F) for 4 h after plating to ameliorate the effects of hydrogen embrittlement. This treatment should be started as soon as possible, preferably within 15 min after plating. The fatigue strength of parts subjected to alternating stresses is reduced by the baking treatment, so such parts should be shot peened before plating.

The use of shot peening and baking, as related to the hardness of steel to be chromium plated, is described in federal specification QQ-C-320B, amendment 1, as follows:

- Plated parts below 40 HRC and subject to static loads or designed for limited life under dynamic loads, or combination thereof, shall not require shot peening prior to plating or baking after plating.
- Plated parts below 40 HRC that are designed for unlimited life under dynamic loads shall be shot

peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated.
- Plated parts with a hardness of 40 HRC, or above, and subject to static loads or designed for limited life under dynamic loads, or combinations thereof, shall be baked after plating at 190 ± 14 °C (375 ± 25 °F) for not less than 3 h.
- Plated parts with a hardness of 40 HRC, or above, and designed for unlimited life under dynamic loads, shall be shot peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated. After plating, parts shall be baked at 190 °C (375 °F) for not less than 3 h.

Safety Precautions

All applicable OSHA, EPA, and local regulations pertaining to electroplating in general and specifically to chromium plating should be carefully reviewed and strictly followed. Material Safety Data Sheet forms should always be available, and precautions should be carefully noted, especially with respect to the incapability of mixing certain chemicals.

Personnel should wear rubber gloves, rubber aprons, and face shields when making additions to any plating or cleaning solution. Tank operators should wear proper protective clothing and eye protection at all times.

Health and safety concerns related to the use of chromium and possible alternative plating technologies are discussed in the article "Chromium Elimination" in this Volume.

Recovery and Disposal of Wastes

Chromic acid wastes may be either recovered or destroyed, and the choice of process should be based on a comparison of initial costs, labor costs for operation and maintenance, chemical costs, space requirements, and utility costs. The volume of wastes and the value of the chromic acid and rinse water saved can greatly influence the choice.

Local, state, and federal authorities are constantly increasing their attention to antipollution programs. Strict regulations are being enforced regarding the allowable limits for chromic acid wastes that leave the plating plant in any form. The prevailing limits for chromic acid contamination of waste water range from about 0.05 to 5 ppm. These limits vary for each locality, depending on the uses of the receiving body of water, supplementary water flows that affect dilution, and the ability of sewage plants to handle wastes. A new plater must check with federal, state, and local authorities to determine what limits are applicable at that time.

Preventive Measures. The problem of waste disposal can be greatly minimized if suitable measures are taken to minimize the amount of wastes produced. The following practices contribute to minimizing wastes:

- Extend drainage periods to permit more solution to return to the tank. In hand operations, this is made possible by providing a drainage bar over the tank to hold racks.
- Provide drip boards to return solution lost when going from tank to tank.
- If possible, rack parts in such a way as to eliminate cupping action.
- Use reclaim rinse tanks. The rinse solution can be used to maintain the level of liquid in the processing tank. Sometimes concentration methods may be profitable to facilitate use of rinse waters.
- Control drag-in of water to permit use of reclaim rinse tanks.
- Complete recovery should be used only in conjunction with technologies for the removal of metallic impurities.

Disposal of chromic acid wastes is most commonly based on reduction of hexavalent chromium to the trivalent form and, in either a batch or a continuous operation, precipitating the trivalent metal hydroxide by means of an alkali. The actual chemicals used vary from locality to locality, depending on cost and availability. Chromic acid is first neutralized to a suitable pH and is then reduced with one of the sulfite compounds (sodium sulfite, sodium metabisulfite), sulfur dioxide, ferrous sulfate, iron, copper, or brass. After completion of reduction, trivalent chromium is precipitated as hydroxide with alkali. The amount of chemicals required to complete reduction can be governed by laboratory analysis, or, because the reaction is solely one of oxidation-reduction, it may be controlled automatically by use of electrodes.

The most commonly used reducing agent for large plants is sulfur dioxide gas. It can be obtained in liquid form in cylinders of various sizes, is comparatively inexpensive, and can be fed directly into the treatment tank. The rate of addition is easily controlled and gas is delivered from the cylinder under its own pressure. A lower initial acidity is required because the gas forms sulfurous acid when dissolved in water. The operating pH is 2 to 3, and the ratio of sulfur dioxide to chromic acid used commercially is slightly under 3 to 1. The sulfur dioxide method lends itself readily to an automatic system because the gas feed can be controlled by a flowmeter, and the reaction can be controlled by oxidation-reduction potentials.

Ferrous sulfate also is a widely used reducing chemical, especially in localities where large quantities are available from pickling plants. The quantity required can be easily determined by titration. The ratio of ferrous sulfate to chromic acid varies between 5 and 16 to 1. Reduction of chromium is followed by neutralization with lime or caustic. Above a pH of 7, the metals precipitate as hydroxides, together with calcium sulfate. The main disadvantage of the ferrous sulfate method is the large volumes of sludge that have to be handled.

The sulfite-containing compounds generally are slightly more expensive than sulfur dioxide or ferrous sulfate. In addition, several difficulties are involved in sulfite treatment, such as solubility, loss of hydrogen sulfide through hydrolysis, slightly lower pH, and, occasionally, the need for additional treatment to complete the process.

Regardless of the chemical treatment selected, all chromic acid disposal systems require collection, treatment, and settling tanks. The operating procedure consists of chemical additions, mixing, separation of precipitated metal, clarification, and sludge disposal. Variations in equipment design affect economy, time and labor requirements, and equipment costs.

In recent years several new companies have been formed that recycle chromium plating wastes into new products, thereby avoiding the long-term potential liabilities of landfill operations. No matter what method of waste disposal is selected, the plater is well advised to know what happens to the wastes and what the liability could be.

Stopoff Media for Selective Plating

During plating, part surfaces that are not to be plated may need to be protected from the solution by stopoff media, such as lacquers, foils, tapes, waxes, and machined reusable fixtures. Stopoff media must adhere well to the metal surface, not become soft at the temperature of the solution or brittle at room temperatures, be resistant to solutions used for cleaning, etching, and plating, and be easy to remove after plating.

Lacquers used to prevent surfaces from being plated can be easily applied by brushing, spraying, or dipping. After plating, the lacquer can be stripped off or dissolved in an appropriate solvent.

Lead sheet, foil, and wire not only provide a positive stopoff but also act as thieves to aid in current distribution. Lead can be pounded into holes, keyways, or slots and trimmed with a sharp knife.

Tapes of several kinds are used as stopoff media. They vary from adhesive tapes backed with lead foil to tapes made of vinyl and other plastics. Lead foil tapes combine a specially compounded lead foil with a highly pressure-sensitive adhesive to provide a quick and convenient stopoff for short runs. The lead backing is useful as a thief in areas of high current density, or it can be lacquered when used in areas of low current density for equalizing current distribution. It is soft enough to conform to various configurations. Vinyl and other plastic tapes are soft and pliable and have extruded edges for providing a lead-free seal on almost any contour.

Sheet Materials. For large production runs, it is convenient to make stop-off forms that can be reused many times. Plastic sheet, generally 0.1 to 0.15 mm (0.004 to 0.006 in.) thick, is excellent for masking simple plates, cylinders, or other configurations. Steel sheet is sometimes substituted for plastic if it is desirable to equalize current distribution. To prevent plating or corrosion of the base metal, the plastic or steel stopoff must adhere firmly to the area being masked. Snug-fitting cylinders can be made to fit inside or outside diameters. To mask areas that are flat or of irregular shape, lacquer may be used to glue the stop-off material to the part; the lacquer may be removed with a thinner after plating.

Waxes. Several waxes designed for use as stopoffs are obtainable commercially. The use of a dip tank, thermostatically controlled to maintain the temperature at 15 to 20 °C (30 to 40 °F) above the melting point of the wax, makes the use of these materials comparatively fast and simple. The portion of the part to be plated can be covered with masking tape to prevent wax from adhering, or, if desired, the whole part can be coated and the wax stripped with a knife from areas to be plated. The wax mixture should have a melting point low enough to allow removal of the bulk with boiling water. Because they evolve poisonous fumes when heated, waxes containing chlorinated naphthalene must be used with exhaust equipment. High-melting-point mineral and vegetable waxes are not dangerous to use.

Decorative Chromium Plating

Revised by: James H. Lindsay, General Motors; Donald L. Snyder, Atotech USA Inc.

Introduction

DECORATIVE CHROMIUM PLATING is different from hard chromium plating in terms of thickness and the type of undercoating used. The average thickness of decorative plating is actually very thin, usually not more than 1.25 μm (50 μin.). A decorative chromium deposit is used primarily for its pleasing blue-white color. Its highly reflective appearance is maintained in service because chromium can resist tarnish, chemicals, scratches, and wear. If the deposit is defect-free, then a level of corrosion resistance also is provided, because the deposit acts as a physical barrier to the environment. Decorative chromium is applied over undercoatings, such as nickel or copper and nickel, which give the chromium bright, semibright, or satin cosmetic appearances. Corrosion protection depends on the choice of undercoating, as well as the type of chromium being applied. Parts made from steel, copper and its alloys, zinc, stainless steel, and aluminum are typically plated with nickel-chromium or copper-nickel-chromium.

Most decorative chromium coatings have been applied using hexavalent chromium processes that are based on chromic anhydride. However, since 1975, trivalent chromium processes have become available commercially. They are increasing in importance because of their increased throwing and covering powers and because they offer environmental advantages. Both systems are considered in detail in this article.

Chromium Electrodeposits

Decorative chromium plating baths generally produce deposits that range from 0.13 to 1.25 μm (5 to 50 μin.) in thickness. These deposits generally reproduce the finish of the substrate, or, in a multilayer system, the undercoating that is applied prior to the chromium layer. Optimum luster of the final chromium deposit is obtained by plating the substrate coating to a uniformly bright condition. If the substrate is nonuniform, grainy, hazy, or dull, then it should be polished and buffed to a uniformly high luster before being plated with chromium. When a final chromium coating over a uniformly bright substrate is hazy in certain areas, these areas can be buffed on a wheel or the coating can be stripped and the substrate replated. Buffing of chromium is not allowed when corrosive service conditions will be encountered.

In addition to being lustrous, the final chromium deposit should cover all significant areas. When there is not adequate coverage, because of an improperly operated chromium bath, the chromium should be stripped, the substrate reactivated, if necessary, and the part replated.

Decorative chromium that has been applied over nickel, the typical undercoating, is readily stripped by immersion in a 1:1 solution of hydrochloric acid. An alternate method involves treating the part anodically in an alkaline cleaning solution. However, this method requires reactivation of the nickel surface prior to replating, which is typically accomplished by immersion in dilute sulfuric or hydrochloric acid. Cathodic, but never anodic, alkaline cleaning can also be used for activation.

Excessively high current densities, improper temperatures, and passivated substrates can produce hazy, nonuniform chromium deposits. Operating conditions for chromium plating should be in the specified ranges. Properly operated nickel baths and other similar precautions also are necessary to ensure uniformly lustrous chromium deposits.

The adhesion of chromium to an active or properly prepared substrate is usually not a problem. However, if chromium is plated on an undercoating that has been improperly applied and has questionable adhesion, then blistering or exfoliation can occur, either immediately after chromium plating or during storage or service. Organizations that generate standards, such as ASTM, can provide procedures for checking adhesion if a related method has not been specified in the purchase agreement for the part being plated.

Microporosity and Microcracking. The key to the corrosion durability offered by decorative chromium deposits lies in controlling the type, size, and distribution of microdiscontinuities that form in the deposit. These can occur as either pores or cracks. In an outdoor corrosive environment, as well as in accelerated corrosion tests, corrosion has been observed to proceed by galvanic cell action between the nickel and the chromium, with the nickel acting anodically. Microcracks or micropores in the chromium expose the underlying nickel through a uniform, diffuse network of discontinuities. Because the rate of corrosion penetration through the nickel layer is a function of the anodic current density of the corrosion cell, the reduction of current density that is obtained by the increase in exposed nickel area prolongs the time required to penetrate a given thickness of nickel. The advantage of such a system lies in its ability to provide long-term corrosion protection without developing easily visible fine surface pits in the nickel, which eventually become corrosion sites. The use of microdiscontinuous chromium makes the surface pits much smaller, which means that the substrate will be protected from corrosion for a longer time. However, after excessive corrosion, these fine pits will become visible as a haze on the corroded surface.

Chromium deposits, up to a thickness of 0.13 μm (5 μin.), that are obtained from hexavalent processes are somewhat porous. Because porosity decreases with increasing thickness, at approximately 0.5 μm (20 μin.), the deposits become nearly pore-free when plated (Fig. 1). However, because of the hard, brittle nature of the highly stressed chromium deposits, they quickly become cracked during storage or service. These cracks do not improve the corrosion resistance, as do deposits with intentionally developed micropores or microcracks.

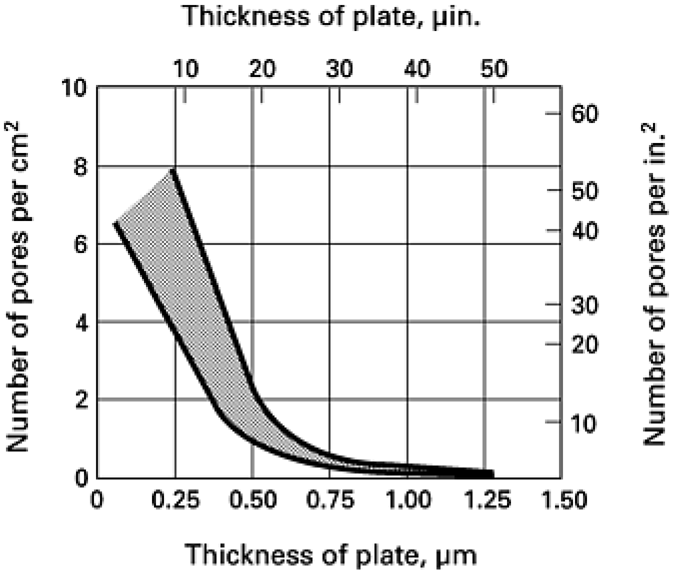


Fig. 1 Porosity in chromium plate as a function of plate thickness. Chromium deposited in low-temperature baths begins to crack at 75 μm (3000 μin.).

Except when special hexavalent chromium processes and conditions are used, hexavalent chromium deposits that are more than 0.5 μm (20 μin.) thick will have visible nondecorative microcracks. In contrast, chromium deposits from trivalent processes are microporous up to thicknesses of 0.5 to 0.6 μm (20 to 25 μin.), above which they become microcracked. Both features enhance the corrosion resistance of the part.

When hexavalent chromium is deposited from solutions operated below 50 °C (120 °F), the deposit will begin to craze when it exceeds 0.5 μm (20 μin.) in thickness, and a macrocrack pattern visible to the unaided eye will appear. This pattern generally has 5 to 10 cracks/cm (12.5 to 25 cracks/in.).

Either microcracked or microporous chromium deposits can be produced by altering the nature of the nickel undercoating. Microporous chromium can be obtained by plating over a thin layer of nickel deposited from a solution containing very fine, nonconductive particles. Chromium will not plate over these particles, which creates a microporous deposit with pore densities proportional to the amount of inert particles and additives in the nickel solution. An average pore density of

10,000 pores/cm^2 (60,000 pores/in^2) is the typical minimum specified for enhanced corrosion resistance. A disadvantage of this process is the addition of an extra nickel plating tank between the bright nickel and the chromium tanks. The pore count is also current-density dependent, and chromium deposits of 0.3 to 0.4 μm (12 to 16 μin.) in thickness have a tendency to bridge over the inert particles and reduce the pore count.

Trivalent chromium deposits provide pore counts of more than 16,000 pores/cm^2 (100,000 pores/in^2), without any special procedures. The pore count also is rather current-density independent.

Another very common method for obtaining microporous chromium deposits is to mildly blast the chromium deposit with an abrasive, such as sand or aluminum oxide. The brittle chromium fractures where it is hit by the particles, thus causing a microporous deposit to form. This method permits the pore count to be varied, based on the amount of particles used, and is independent of current density.

Microporous chromium is the most common microdiscontinuous chromium deposit used in North America to enhance the corrosion resistance of the decorative nickel-chromium type of electrodeposit. Microcracked chromium is somewhat more popular in the rest of the world.

Microcracking can be produced by using a thin layer, approximately 1.25 μm (50 μin.), of a highly stressed nickel deposit between the bright nickel and chromium deposits. Approximately 0.25 μm (10 μin.) of chromium is typically used with this procedure. A crack density of 275 to 790 cracks/cm (700 to 2000 cracks/in.) is typically produced. Thicker chromium deposits are required with other microcracking methods.

Microcracked chromium deposits can be obtained from systems using either a single or a dual specially formulated chromium solution. An example of the latter is duplex chromium. Although single-deposit systems are easier to operate, conditions that favor the formation of microcracks, such as high solution temperature, low chromic-acid concentration, and high fluoride content, usually have an adverse effect on the covering power of the chromium deposit. Duplex chromium systems have resolved this problem by using two successive chromium baths. The first obtains coverage and the second creates the microcrack pattern.

Satisfactory coatings are not too difficult to obtain on parts with relatively simple shapes, but complex parts can present a serious problem because it is difficult to obtain adequately thick chromium in areas of low current density. Auxiliary anodes can be used to increase the thickness in these areas.

Influence of Design on Quality and Cost

The cost of electroplating is often greatly influenced by the complexity of the workpiece. Simple shapes can be processed through all cleaning and plating sequences, with a minimum of approximately 33 μm (1300 μin.) of copper and nickel and 0.25 μm (10 μin.) of chromium, in approximately 50 min. Providing these minimum thicknesses on complex shapes requires longer plating periods, special fixturing, special anodes, and current shields. Plating costs are increased by each of these factors, although buffing and cleaning costs may be unchanged. Equipment and overhead costs per workpiece also increase in direct proportion to the plating time. In addition, the cost of materials is increased, because more metal is plated unnecessarily on projections and other areas of high current density. Figure 2 indicates the approximate increase of plating costs with plating time at a fixed current density.

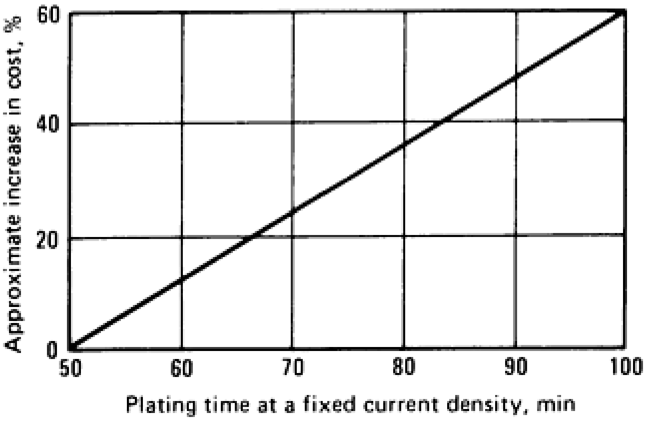
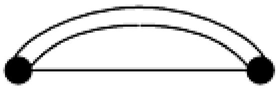
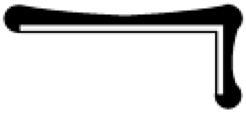
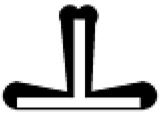
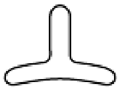
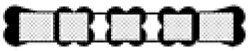
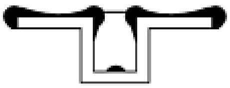
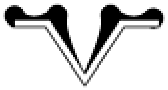
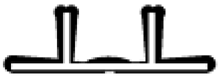
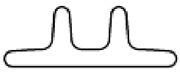
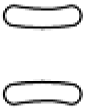
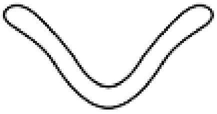
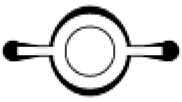


Fig. 2 Plating cost-time relationship

Extreme workpiece complexity can preclude the application of a truly corrosion-protective deposit by conventional plating procedures. The influence of some design features on platability and plating cost are described in Table 1.

Table 1 Influence of design on platability of zinc-base die castings

Design feature	Influence on platability	Better design
	**Convex surface.** Ideal shape. Easy to plate to uniform thickness, especially where edges are rounded.	
	**Flat surface.** Not as desirable as crowned surface. Use 0.015 mm/mm (0.015 in./in.) crown to hide undulations caused by uneven buffing.	
	**Sharply angled edge.** Undesirable. Reduced thickness of plate at center areas. Requires increased plating time for depositing minimum thickness of durable plate. All edges should be rounded. Edges that contact painted surfaces should have a 0.8 mm ($\frac{1}{32}$ in.) min radius.	
	**Flange.** Large flange with sharp inside angles should be avoided to minimize plating costs. Use generous radius on inside angles and taper abutment.	
	**Slots.** Narrow, closely spaced slots and holes cannot be plated properly with some metals (e.g., nickel and chromium) unless corners are rounded.	
	**Blind hole.** Must usually be exempted from minimum thickness requirements.	
	**Sharply angled indentation.** Increases plating time and cost for attaining a specified minimum thickness and reduces the durability of the plated part.	
	**Flat-bottom groove.** Inside and outside angles should be rounded generously to minimize plating costs.	
	**V-shaped groove.** Deep grooves cannot be plated satisfactorily; should be avoided. Shallow, rounded grooves are better.	
	**Fins.** Increase plating time and costs for attaining a specified minimum thickness and reduce the durability of the plated part.	

	**Ribs.** Narrow ribs with sharp angles usually reduce platability; wide ribs with rounded edges impose no problem. Taper each rib from its center to both sides and round off edges. Increase spacing, if possible.	
	**Deep scoop.** Increases time and cost for plating specified minimum thickness.	
	**Spearlike jut.** Buildup on jut robs corners of electroplate. Crown base and round all corners.	
	**Ring.** Platability depends on dimensions. Round corners; crown from center line, sloping toward both sides.	

Note: Distribution of electroplate on design shapes is intentionally exaggerated by solid black outline. Cross-hatched areas indicate part before plating.

Hexavalent Chromium Plating

The first hexavalent chromium plating bath used for decorative plating, sometimes referred to as the conventional bath, consisted of an aqueous solution of chromic anhydride (CrO_3) and a small amount of soluble sulfate ($SO_4^{=}$), referred to as the catalyst. The latter was added as sulfuric acid or as a soluble sulfate salt, such as sodium sulfate. When dissolved in water, the chromic anhydride forms chromic acid, which is believed to exist in the following equilibrium:

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$$

The ratio of chromic acid to sulfate, generally given as the weight ratio of chromic anhydride to sulfate, governs the current efficiency for chromium metal deposition. The cathode current efficiency also is affected by solution variables, such as concentration of chromic acid, temperature, and content of metallic impurities. The latter variable is an important consideration for commercial operations, because an excessively high content of impurities such as copper, iron, zinc, and nickel seriously affects bath conductivity, cathode current efficiency, and both throwing and covering power, even if the ratio of chromic anhydride to sulfate is within optimum limits for the application.

Most decorative chromium is deposited within these operating limits:

- Chromic anhydride, 200 to 400 g/L (27 to 54 oz/gal)
- Chromic anhydride-to-sulfate ratio, 80:1 to 125:1
- Cathode current density, 810 to 1880 A/m^2 (75 to 175 A/ft^2)

These wide limits encompass a broad variety of decorative applications. As of 1994, the trend is toward using chromic-anhydride concentrations of 250 to 300 g/L (33 to 40 oz/gal) and avoiding more highly concentrated baths and their attendant environmental and recovery concerns. The ratio of chromic acid to sulfate ion is usually maintained at levels near 100:1.

With the development of duplex, microcracked, and crack-free applications, specialized bath compositions and operating conditions have come into use. However, many of these are either proprietary or are not subjects of general agreement. The compositions and operating conditions for a general, additive-free, decorative chromium plating bath and a bright, crack-free bath are given in Table 2.

Table 2 Compositions and operating conditions for two chromium plating baths

Constituent or condition	General decorative bath	Bright, crack-free bath
Chromic acid	250 g/L (33.0 oz/gal)	260-300 g/L (35-40 oz/gal)
Ratio of chromic acid to sulfate	100:1 to 125:1	150:1
Operating temperature	38-49 °C (100-120 °F)	52-54 °C (125-130 °F)
Cathode current density	810 - 1885 A/m^2 (75 - 175 A/ft^2)	2690 - 3230 A/m^2 (250 - 300 A/ft^2)

To meet specific requirements for plating speed, nickel activation, and crack pattern, the chromium anhydride and sulfate concentrations should be properly correlated with temperature and cathode current-density limits. In preparing a bath and establishing operating conditions, these relationships should be considered:

- An increase in the temperature of the bath, except for mixed-catalyst baths, will decrease the cathode efficiency, decrease the number of cracks per unit length, decrease coverage at low current density, increase the limiting current density at which burning occurs, and increase passivating action on nickel.
- An increase in the weight ratio of chromic anhydride to sulfate will decrease the crack density and increase the nickel passivity. The chromium will whitewash (have a milky appearance) when plated over passive nickel.
- An increase in sulfate, at a constant chromic-acid concentration, temperature, and cathode current density, will increase the cathode current efficiency to an upper limit; beyond this point, any further increase in sulfate concentration can cause a decrease in cathode current efficiency.

In dilute chromic-acid solutions containing as low as 150 g/L (20 oz/gal) of sulfate, any small carryover of soluble sulfates from earlier solutions can quickly upset the balance of the solution. However, dilute solutions do have a higher cathode efficiency and a slightly wider bright range, although they require higher tank voltages to maintain desired current density. Even when other plating conditions (such as temperature and current density) are held constant, the plating operation can be seriously disrupted by any change in the ratio of chromic acid to sulfate.

Because there are advantages and disadvantages to using either high or low chromic-acid contents, some compromise is necessary. The size and shape of the article to be plated and the available equipment and power often determine exactly which solution should be used. In decorative chromium plating, all variables must be kept in the proper relationship. Frequent bath analysis and prompt adjustments are essential to maintain balanced conditions.

Mixed-Catalyst Baths. Since the mid-1950s, a number of mixed-catalyst proprietary chromium plating baths have been developed. The advantages of these baths are increased cathode current efficiencies, increased activating action on nickel and stainless steel, improved coverage at low current density, broader bright plating ranges, and improved decorative chromium applications, including dual, microcracked, and bright or dull crack-free.

Mixed-catalyst compositions contain chromic acid, sulfate, and fluorine compounds (frequently, fluosilicate ions) as active ingredients. Proprietary baths, formulated to regulate the concentration of catalyst ions, contain strontium, calcium, or potassium salts, to control the solubility of fluosilicate ions. Details on mixed-catalyst compositions are provided in several U.S. patents and at least one British patent (see "Selected References" at the end of this article). Most control requirements applicable to standard baths also apply to proprietary baths.

With the exception of ratio control, the problems associated with low, medium, or high chromic-acid concentrations in mixed-catalyst baths are the same as those for conventional chromium baths. After optimum conditions are found, the same close control must be maintained to prevent mischromes (absence of plate) in areas of low current density and blue, matte, or burnt deposits in areas of high current density. Because supplies for mixed-catalyst solutions are more expensive than chromic acid alone, using less-concentrated solutions can provide a cost advantage.

Baths for Microcracked Chromium. Typically, two chromium solutions are used successively to produce microcracked chromium plate. The first chromium solution can either be conventional or proprietary and is operated in a normal manner. A plating time of 8 min is preferred when recessed areas are involved, although plating times of 5 to 6 min are often used. Surging of the current can be used to increase coverage. Composition ranges and operating conditions for nonproprietary, first-plating solutions that are used to plate steel and zinc parts are given in Table 3.

Table 3 Bath compositions and conditions for plating microcracked chromium

Substrate material	Constituents				Chromic anhydride to sulfate ratio	Temperature		Current density	
	Chromic acid		Fluoride						
	g/L	oz/gal	g/L	oz/gal		°C	°F	A/m^2	A/ft^2
First plating bath									
Steel	338-375	45-50	. . .	. . .	100:1	46-52	115-125	1075-1615	100-150
Zinc	375-413	50-55	. . .	. . .	140:1	46-52	115-125	1290-1720	120-160
Second plating bath									
Steel	165-195	22-26	1.5-2.25	0.20-0.30	180:1	43-54	120-130	970-1345	90-125

The second chromium solution is similar to the first and can be either proprietary or nonproprietary. The chromic-acid concentration is lower and fluosilicate ions must be present in the bath to promote cracking. The plating time is approximately the same as in the first solution, 5 to 8 min, and current surging can be used, if desired. Composition ranges and operating conditions for the second chromium bath also are given in Table 3. The plating conditions are governed by the nature of the parts being plated. Solutions for parts having deep recesses should have a higher chromic acid and fluoride content and a lower sulfate content. However, thickness must be weighed against other influences on microcrack formation. For this reason, operating conditions can be established on a firm basis only by actual operation with the parts to be processed. On simple shapes, the second plating bath formulation can be used alone.

The use of a rinse or rinses between the two chromium solutions is not essential to the process, but it may help to avoid control problems, because of drag-out from the first chromium solution into the low-concentration second solution. When used, these rinses can be operated as reclaim tanks to minimize drag-out losses.

Solution Control. Regardless of which chromium bath is used, periodic analyses are required. Information on control procedures is provided in the article "Industrial (Hard) Chromium Plating" in this Volume.

Temperature. All chromium plating solutions require the control of temperature, current density, and solution composition. The exact temperature at which bright, milky, frosty, or burnt deposits occur depends on solution composition and current density. Chromium plating is usually performed within the range of 38 to 60 °C (100 to 140 °F), but the most common operating range is from 46 to 52 °C (115 to 125 °F). At room temperature, the bright plating range is impractically narrow. In a process set up to plate at 50 °C (120 °F) with all variables properly controlled, the temperature need vary only 1.5 or 2 °C (3 or 4 °F) to move the electrodeposit out of the clear, bright range. Consequently, an accurate temperature controller and facilities for rapid cooling and heating of the bath are essential. Temperature variation outside the bright operating range can either cause an unacceptably high rejection rate or necessitate costly stripping and replating operations. The preheating of heavy parts is necessary to avoid plating solution cooling and temperature fluctuation.

Current Density. The standard sulfate bath is usually operated at 1075 to 1720 A/m^2 (100 to 160 A/ft^2). A current density of about 1075 A/m^2 (100 A/ft^2) is used for solutions maintained at 38 °C (100 °F). A higher current density, sometimes as high as 3230 A/m^2 (300 A/ft^2), is required for solutions operated at 55 °C (130 °F). The choice for a specific use depends on such variables as the complexity of the articles being plated and the equipment available. After the current density has been established, close control must be maintained.

Changes in the ratio of chromic acid to sulfate require compensating adjustments in current density. If the sulfate content is increased (lower ratio), then current density must be increased to maintain full coverage in areas of low current density. If the sulfate content is decreased (higher ratio), then current density must be decreased to prevent burning in areas of high current density.

An increase in temperature may require an increase in current density to ensure full coverage in areas of low current density. A decrease in temperature may require a decrease in current density to prevent gray (burnt) deposits in areas of high current density.

As chromic-acid content increases, higher current densities can be used. The average cathode efficiency of most conventional chromium solutions is about 13% over a wide range of concentration, making it possible to plate for shorter times when using the most concentrated solution. Rectifiers with low ripple, not exceeding 5%, must be used to maintain trouble-free, uniform deposition.

Anodes. In chromium plating, insoluble lead or lead-alloy anodes are almost always used. Chromium metal is supplied by the chromic acid in the electrolyte.

Pure lead anodes are often attacked excessively by idle baths, which causes the formation of a heavy sludge of lead chromate on the bottom of the tank, making pure lead anodes impractical for all but continuous operations. During plating, a coating of lead peroxide forms on the anode. The coating favors oxidation of trivalent chromium at the anode. However, when the bath is idle, the coating dissolves to some extent in the solution, making attack on the anode possible.

To reduce the attack of the chromic-acid bath on the anode, several lead alloys are used. For conventional sulfate baths, 6 to 8% antimonial (Sb) lead is preferred, whereas for solutions containing fluoride, lead alloys with 4 to 7% Sn are used.

For an anode to provide optimum throwing power and coverage, it must be positioned properly in relation to the workpiece and have a continuous, uniform film of lead peroxide on the entire surface. Anodes with crusty surfaces have low conductivity and should be cleaned periodically by wire brushing or alkaline cleaning to ensure proper current distribution. The function of the anode is not only to conduct the plating current, but to oxidize trivalent chromium, which forms at the cathode, back to hexavalent chromium. To accomplish this, the anode area should be adjusted to provide the optimum anode current density for the oxidation necessary to keep the trivalent chromium at the desired level, usually 0.25 to 1.0 g/L (0.033 to 0.13 oz/gal). In decorative chromium plating, an anode-to-cathode area ratio of 2:1 is common for proper reoxidation and balance. If trivalent chromium continues to increase above the desired level, then the anode area should be increased to the point where the trivalent chromium concentration remains stable. Overheating of the bath can occur if the anode area is so small that resistive heating becomes a factor.

Anodes with round cross sections are most commonly used. When maximum anode area is desired, corrugated, ribbed, ridged, and multi-edged anodes are used. The round anode is preferred, because its surface is active on its entire circumference, enabling it to carry higher amperage at lower voltage. The absence of inactive areas on this anode minimizes the formation of lead chromate film, reducing maintenance requirements. If the weight of the anode presents a problem, then hollow, round anodes can be used. Although such anodes provide a 25 to 40% reduction in weight, their current-carrying capacity is less than that of solid anodes.

Anodes are manufactured by extrusion. Contact with the bus bar can be provided by a copper hook homogeneously burned to the extruded anode. Pure nickel, nickel-plated copper, and lead-coated copper are also used for hooks. Several hook styles are used, but the knife-edge hook is preferred. The hook and the top of the anode are covered with plastisol for protection against corrosion by fumes and drag-out drip. Bags typically used to cover the anodes in nickel- and copper-plating processes should not be used in chromium-plating processes. Roughness that is due to nonuniform anode corrosion is not a problem in chromium-plating operations. Therefore, the resulting particles do not have to be captured by the bags.

Control of Current Distribution. Chromium plating baths have poorer throwing and covering power than most other plating baths. To obtain thickness and coverage in areas of low current density, special auxiliary anodes are sometimes used.

Any workpiece of complex shape constitutes a problem of proper current distribution when nonconforming anodes are used. The current density and the thickness on a workpiece varies from highest on corners, edges, and areas closest to the anode to lowest on recesses and areas distant from the anode. Variations in current density result in differences of cathode efficiency, which accentuate the problems of uneven plate, burning, or complete absence of plate. These problems can be overcome, to some extent, by special racking and shielding techniques, such as:

- Wide spacing of concave parts on rack
- Increasing the distance between workpiece and anode
- Intentional shielding of a projection on one piece with a depression on an adjacent one
- Orienting areas of low current density toward the periphery of the fixture
- Moving the parts in the center of the rack closer to the anodes than those on the periphery of the rack

Improved coverage on areas of low current density can be achieved with striking, that is, plating at high current density for a short period of time. The striking time duration is kept to a minimum, usually 5 to 20 s, to avoid burning. Plating is continued at normal current density after the strike.

Current Shields. A nonconducting plate or panel (current shield) can be mounted on the plating rack to direct current away from areas of high current density or to direct additional current into areas of low current density. Figure 3 illustrates the use of a device to divert some of the current that would otherwise cause excessive current density and possible burning at the work areas closest to the anodes. The position and size of current shields are extremely important for their effective use and can be established best by trial and error. The use of shields, however, is always accompanied by some increase in drag-out.

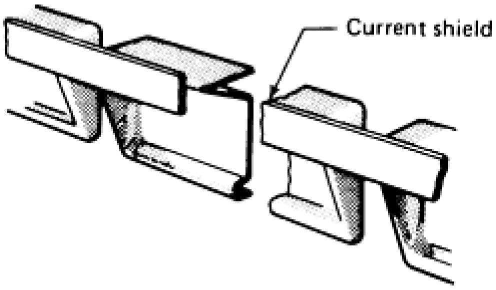


Fig. 3 Current shield

Thieves or robbers made of metal conductors can be positioned near edges and points to shunt away current from these areas. Rods with a diameter of 9.5 to 16 mm ($\frac{3}{8}$ to $\frac{5}{8}$ in.) are sometimes suspended vertically on both ends of a plating rack to prevent burning or rough plate on the edges of the cathodes. Maintenance of robbers is of utmost importance, because they can be the source of large drag-out losses if metal is allowed to build up excessively.

Auxiliary Anodes. Special racks and auxiliary anodes are used only when conventional techniques fail to produce satisfactory coatings. Parts with deep recesses, such as coffeepots and small appliance housings, require auxiliary anodes. Auxiliary anodes are also used for parts with concave surfaces that are difficult to plate uniformly (Fig. 4). Auxiliary anodes also offer potential cost reductions by directing the plate into areas of minimum plate thickness without the penalty of overplating areas of high current density. The use of such devices should be considered even for some parts that do not present serious problems in meeting specifications for plate thickness. The shapes of many die castings make the use of auxiliary anodes particularly applicable. The current supply for auxiliary anodes can be the same as the major plating circuit with a separate current control, such as a rheostat. Greater flexibility is obtained if a separate current source is used for the auxiliary anodes.

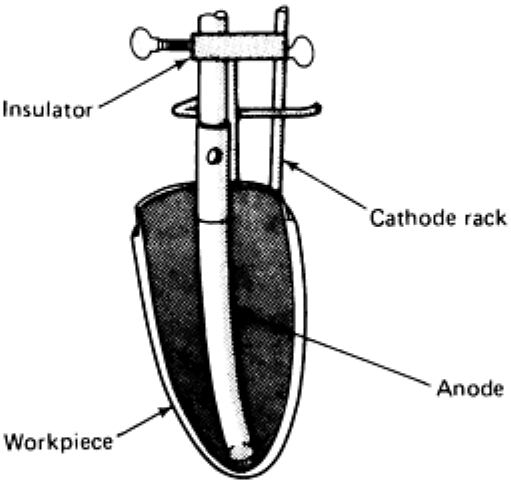


Fig. 4 Use of auxiliary anode for a part difficult to plate to uniform thickness because of concave surface

Auxiliary anodes are mounted on the plating rack, insulated from cathode current-carrying members, and provided with means of direct connection to the anodic side of the electrical circuit (Fig. 5). In still tanks, the connection can simply be a flexible cable equipped with battery clamps. In fully automatic machines, cables are permanently mounted on the carriers, and contact brushes riding on an anode rail are provided to pick up the current. Connections must be positive. An interruption or drastic reduction of current could cause the auxiliary anode to function as a robber or shield, resulting in local interruption of plate, with consequent darkening and loss of adhesion.

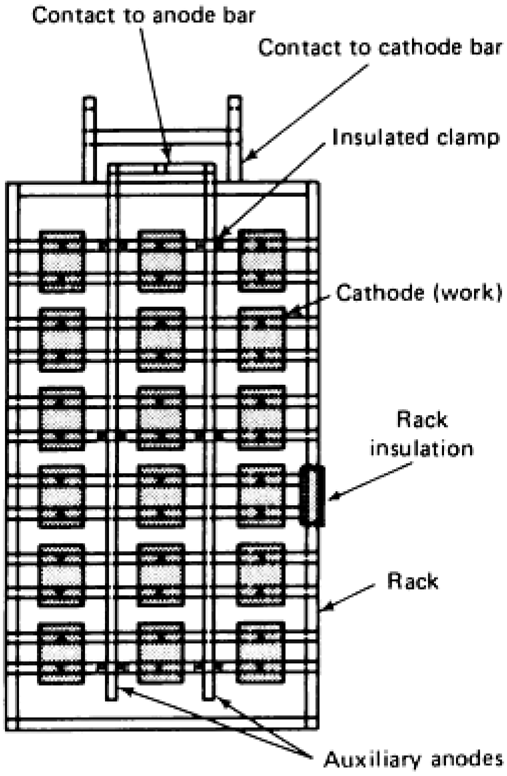


Fig. 5 Rack assembly for decorative chromium plating

The auxiliary anode need not follow the contour of the part closely. An anode-to-work spacing of 13 mm ($\frac{1}{2}$ in.) or slightly more is usually effective. The auxiliary anode mounting must be designed carefully to prevent the anode from interfering with efficient racking and unracking of parts. The anode can be designed for removal while parts are being loaded on the rack, but good contact must be preserved. The auxiliary anode should be held rigidly to prevent it from short circuiting against the cathode.

Some platers connect auxiliary anodes electrically only during chromium plating, a practice that is usually satisfactory for still tank operation, where an anode can be physically mounted immediately before chromium plating. In an automatic plating machine, however, the auxiliary anode should be connected in the acid-copper bath, the nickel bath (at least, in the last half of the tank), and the chromium bath to avoid low thicknesses and low current density effects that could detract from appearance and cause difficulty in chromium plating.

Unless they are made of insoluble material, auxiliary anodes are consumed in plating. Their design should therefore permit easy replacement. Plastisol-coated steel bushings with locking screw heads protected by stop-off lacquer are satisfactory. As anodes become thin, they must be carefully inspected for replacement to avoid shorting out. The diameter of rod used should be as large as is compatible with the size of the part and with construction requirements to minimize the need for frequent replacement. A diameter of 13 mm ($\frac{1}{2}$ in.) is suitable for a variety of parts, ranging from small brackets to instrument panels and moldings. On larger parts, diameters as large as 25 mm (1 in.) or specially cast sections can be useful.

Bags should not be used on auxiliary anodes, because of the resulting solution contamination from drag-in. Avoiding roughness from bare anodes requires serious consideration if the anodes are to be immersed in copper and nickel undercoating baths. Roughness is not a problem when the anode is to be immersed only in the chromium solution. Lead-alloy or steel anode material has been used satisfactorily for this purpose. Graphite rods also have been used to a limited extent. Auxiliary anodes are most frequently made of platinized titanium.

Bipolar anodes are a special variation of auxiliary anodes, in which current is not supplied by external connection. In use, collector plates are mounted at the cathodic end (the end closest to the tank anodes) of the bipolar anode to draw current from a larger section of the bath. Bipolar anodes can be used on conveyorized systems when a special bus bar is unavailable. Although adequate for some purposes, bipolar anodes are usually less effective than other auxiliary anodes and must be carefully maintained to avoid the problems of roughness from loosely adherent deposits of nickel and chromium on the collector plates. The metal deposited on the collector plates is often not reusable.

Stop-offs are not widely used in decorative chromium plating. However, when selective plating is required, a number of materials have the necessary qualifications, including ease of application and removal, resistance to hot cleaners and plating solutions, and excellent adherence and electrical insulation characteristics during use.

Special racks are sometimes used to prevent plating solution from entering tapped holes and areas where plate is not wanted. Figure 6 shows a plated lever with a 7.92 mm (0.312 in.) diameter hole that had to be free of plate. If conventional racking had been used, then the hole would have had to be reamed to remove the plate.

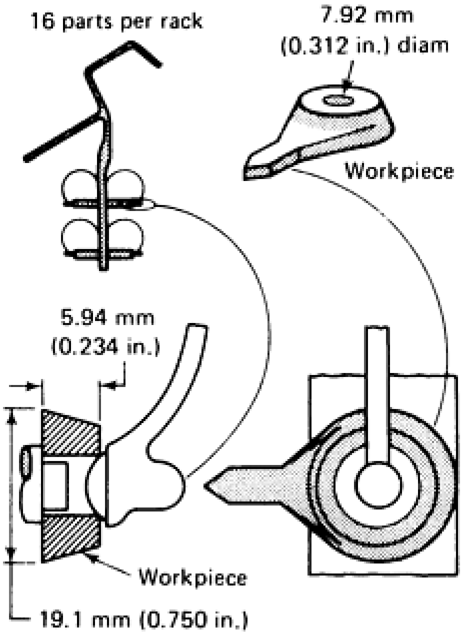


Fig. 6 Racking arrangement to prevent plating of chromium in the hole of a shift lever

Tanks. Chromium plating tanks can be constructed of steel and lined with flexible plastic-type materials, such as fiberglass or polyvinyl chloride (sheet form or sprayed) or lead alloy (6% Sb). Lead-alloy linings should be approximately 3.2 mm ($\frac{1}{8}$ in.) thick. Plastic liners should range in thickness from 2.4 to 4.8 mm ($\frac{3}{32}$ to $\frac{3}{16}$ in.). Plastic linings are preferred, particularly for proprietary baths with fluoride-containing anions, which may have a greater rate of attack on lead linings. Rubber mats or plastisol-coated metal ribs are often used to protect the sides or bottoms of lead-lined tanks from shorts that are due to either accidental contact or being punctured by dropped anodes or workpieces. Lead linings can cause serious bipolarity problems, because of their electrical conductivity.

Heating. Chromium plating tanks can be heated internally or externally. Internal heating, by steam coils or electric immersion heaters, is usually used for small tanks. External heating by heat exchangers is used for large tanks. Coils for internal heating can be made of lead, a lead alloy such as 4% Sn or 6% Sb, or tantalum. Titanium can be used for baths that do not contain fluoride ions. Immersion heaters should be quartz-covered. Heat exchangers can be made of tantalum, lead alloy (4% Sn or 6% Sb), high-silicon cast iron, or heat-resistant glass. Tantalum is preferred for heating coils or heat exchangers when proprietary solutions containing fluoride ions are used, because titanium is attacked by the fluoride. Consultation with vendors on specific material/process compatibility is suggested.

Plating Cycles. Typical system cycles for the application of six decorative chromium plating systems to identical workloads are given in Table 4. Each system is identified by the specific combination of metals successively deposited, the total thickness of plate, and the total plating time. The plating times and power requirements listed in Table 4 are theoretical values for perfect coverage. In practice, these values would be considerably higher to ensure adequate plate thickness in all areas. Table 5 provides the requirements for the design of several installed machines for the continuous plating of zinc die castings of average complexity. The higher-than-normal designed current density is related to potential future needs that exceed present requirements.

Table 4 Typical system cycles

System	Cycles	Total plate		Total time, min[(a)]
		µm	µin.	

Cu + Ni + Cr	A, B, D, F	50	1970	48
Cu + Cr	A, B, F	20	790	14
Ni + Cr	D, F	30	1180	36
Ni + Cr + Cr	D, G	32	1260	41.5
Ni + Ni + Cr	C, E, F	30	1180	36
Ni + Ni + Cr + Cr	C, E, G	32	1260	41.5

Operating parameters	
A: Copper strike	
Current density	325 A/m^2 (30 A/ft^2)
Plating time	2 min
Heat[(b)]	49-65 °C (120-150 °F)
Filtration	Yes
Agitation	Optional
B: Acid copper plate, high speed, bright (20 µm, or 790 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	10 min
Heat[(b)]	21-27 °C (70-80 °F)
Filtration and agitation	Yes
C: Nickel plate, semibright (23 µm, or 900 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time(100% efficiency)	26 min

Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
D: Nickel plate, bright (30 µm or 1180 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
E: Nickel plate, bright (8 µm, or 315 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
F: Chromium plate (0.3 µm, or µin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time	
Conventional (10% efficiency)	2 min
High speed (25% efficiency)	54 s
Heat(b)(c)	46-65 °C (115-150 °F)

Filtration and agitation	No
Ventilation[(d)]	Yes
G: Chromium plate, microcracked (0.64 µm, or 25 µin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time (25% efficiency)	2.5 min
Heat[(b)(c)]	45-65 °C (115-150 °F)
Filtration and agitation	No
Ventilation[(d)]	Yes

(a) Power requirements and plating times given are theoretical values for perfect coverage. In practice, these values would be approximately doubled to ensure adequate thickness of plate in all areas. Table 5 has data for practical conditions.

(b) For operating temperature indicated.

(c) Cooling as well as heating may be required.

(d) Chemical suppressant (mist or spray) may be used in addition to ventilation.

Table 5 Design basis of equipment for continuous chromium plating of zinc-base die castings

Metal deposited	**Designed current density**		**Minimum thickness of plate**		**Nominal thickness of plate**		**Plating time, min**
	A/m^2	**A/ft^2**	**µm**	**µin.[(a)]**	**µm**	**µin.**	
Copper cyanide strike	1075	100	. . .	. . .	0.25	10	3-4
Bright copper	320	30	15	590	20	790	25-30
Semibright nickel	810	75	15	590	20	790	30
Bright nickel	1075	100	5	197	7.5	295	17
First chromium	2150	200	0.3	12	0.5	20	6.5

Second chromium	1615	150	0.25	10	0.5	20	6.5

(a) On parts of moderate complexity

Maintenance. The importance of proper solution maintenance and electrical, mechanical, and other equipment used in plating processes cannot be overemphasized. Table 6 identifies the daily, weekly, monthly, and annual inspection and correction operations that should enable the setup of an adequate maintenance program for chromium plating.

Table 6 Chromium plating maintenance schedule

Frequency	Action
Daily	Fill plating tank with solution from save-rinse and boil-down tanks.
	Stir solution thoroughly, using low-pressure air agitation.
	Check solution for chromic acid, sulfate, and anti-spray additives; make corrective additions.
	Check temperature controls for satisfactory operation; adjust temperature to proper range.
	Inspect plating racks; repair as necessary.
	Check ground lights to see that plating circuits are clear; do not start plating until grounds are clear.
	Put dummy cathodes in tanks and electrolyze solutions at maximum voltage for 15 to 30 min at start of each day.
	Check hull cell.
Weekly	Boil down the save-rinse solution.
	Check auxiliary catalyst; make additions as necessary.
Monthly	Check solution for metallic impurity content (iron, zinc, copper, nickel).
	Clean and straighten anodes.
	Check solution for trivalent chromium content.
Annually	Check all ammeters and ampere-hour meters.
	Inspect and adjust all temperature controllers.

	Clean and repair outside of all tanks; clean and repair all ventilation hoods and ducts.
	Pump out solution, remove sludge. Clean and inspect tank and heating coil; repair as needed. Disconnect all bus bar connections; clean, draw-file and reconnect, including all anode and cathode joints. Inspect anodes; clean, straighten or replace as required.

Troubleshooting. Plating problems can still develop, even when proper maintenance is used. Some typical plating problems and solutions are given in Table 7. Examples of actual problems and solutions used with a variety of chromium-plated parts are given in Table 8.

Table 7 Chromium plating problems and corrections

Defect	Possible cause	Possible remedy
Poor covering power or low deposit thickness	Temperature too high	Adjust temperature to standard range.
	Current density too low	Increase current density.
	Low chromic acid	Adjust chromic acid to standard range.
	Fluoride catalyst too high	Reduce concentration (by dilution).
	Low chromic acid to sulfate ratio	Adjust ratio.
	Poor electrical contact	Correct electrical contact.
	Bath contamination	Remove impurities.
Burning in high current density areas	Temperature too low	Adjust temperature to standard range.
	Current density too high	Reduce current density.
	Chromic acid low	Raise chromic acid.
	High chromic acid/sulfate ratio	Adjust ratio.
	Fluoride catalyst too low	Adjust concentration of fluoride catalyst.
Deposit color nonuniform	Underlying surface not clean or active	Remove any interfering films and provide active surface.
	Bipolarity during entrance to chromium	Enter bath with precontact (live entry).

	Bath contamination by metallic impurities	Analyze bath, remove impurities.

Table 8 Case histories of plating problems

Condition	Cause and correction
Passivation	Nickel-plated business machine parts were stored submerged in cold water to await barrel chromium plating. Although these parts were acid activated before chromium plating, chromium coverage was poor to nil on parts that had been stored for only a few hours. To remedy the problem, parts were stored submerged in a 10% solution of potassium bitartrate (cream of tartar). After several days of storage, the parts could be electrolytically reactivated and barrel chromium plated satisfactorily.
Burning	Although bath composition and temperature were carefully controlled, burnt chromium deposits occurred on die castings plated at moderate amperage. This resulted from nonuniform distribution of current caused by the corrosion of mounting blocks attaching the bus bar to the anode bar. The situation was corrected by welding the bus bar to the anode rail, eliminating mounting blocks.
Poor electrical contact	L-shaped die-cast frames approximately 0.09 m^2 (1 ft^2) in area, although plated in identical racks in an automatic plating machine,exhibited nonuniformity of plate and, in some racks, burnt deposits. This was found to be caused by variations in current from rack to rack in the plating machine. To correct this, mechanical joints were eliminated from the electrical circuit. The mechanical joints were replaced by welding cables from the carrier contact brushes to the rack mounting bar.
Mischromes	Mischromes (absence of chromium on certain areas) occurred on die-cast window frames that occupied the lower portions of racks during plating in a full-return-type automatic plating machine. These defects were caused by the presence of short anodes at the exit end of the nickel plating tank. Replacement with anodes of the correct length solved the problem.
Inadequate rinsing	Inadequate rinsing after chromium plating, which failed to remove small amounts of bath impurities,resulted in nonuniform appearance of the plate on zinc die castings. The parts were given a hot rinse at 93 °C (200 °F) before customary room-temperature rinses to remove bath impurities.

Trivalent Chromium Plating

The use of the trivalent chromium ion, instead of the hexavalent ion, in solution to deposit chromium has been of interest for many years. The first commercially successful decorative trivalent chromium process began in England in 1975 and in the United States in 1976. Environmental, safety, and productivity advantages have been the driving forces for the commercialization of trivalent chromium processes.

Hexavalent chromium ions are also considered carcinogenic and can cause skin ulcerations. The trivalent chromium ion is estimated to be about 100 times less toxic than hexavalent chromium ions.

Trivalent chromium processes have reduced misting to the extent that scrubbers, such as those used with hexavalent chromium processes, are presently not required to meet federal and state air-quality discharge standards. Waste-treatment costs are reduced by a factor of 10, because less than one-tenth of the chromium contained in hexavalent processes is used in the trivalent process (8 to 23 g/L, or 1 to 3 oz/gal, versus 115 to 300 g/L, or 15 to 40 oz/gal). In addition, the solution drains faster, so that less solution is removed with the parts. Finally, the chromium in the rinse water is already in the trivalent state, which eliminates the expensive and sludge-volume-building reduction step required with hexavalent chromium ions.

Some of the trivalent chromium processes plate up to three times faster than hexavalent chromium processes. This increases productivity in some shops. Increased throwing and covering powers, lack of burning, and tolerance to current interruptions and ripple also reduce rejects and can increase the allowable number of parts on a rack.

One of the main difficulties with the development of trivalent chromium baths was the formation of hexavalent chromium at the insoluble anodes during plating. Hexavalent chromium ions are a contaminant in trivalent chromium processes. They initially cause a poor deposit appearance and eventually result in the cessation of plating.

Two well-known proprietary approaches were developed to address the problem of hexavalent chromium formation during plating. The oldest and most frequently used technique incorporates several lines of defense against hexavalent chromium ions. Under normal operating conditions, hexavalent chromium cannot form. If it does manage to get into the plating solution, then it is reduced to the trivalent state, which eliminates it as a contaminant. This technique is referred to as the single-cell process, in contrast to the second technique, which isolates the insoluble graphite anodes from the trivalent-chromium-containing plating solution to restrict the formation of hexavalent chromium.

This second technique, commonly referred to as the double-cell, or shielded anode, method, uses an ion-selective membrane to create a barrier around the anode. Conventional lead anodes are used in a 10% sulfuric-acid electrolyte. The membrane keeps the trivalent chromium from contacting the anode, thereby preventing the formation of hexavalent chromium.

Solution Compositions. Depending on the process used and its operating conditions, the trivalent chromium ion content typically ranges from 5 to 20 g/L (0.67 to 2.67 oz/gal). It is introduced as a water-soluble salt and forms a stable specie upon combining with the stabilizing agents/catalysts. These agents permit the trivalent chromium ion to be stable in solution until it is plated out at the cathode. However, the stability process is not strong enough to interfere with the normal precipitation sequence used with chromium during waste treatment.

In comparison to hexavalent chromium solutions, which have good conductivity, the conductivity of the relatively high-pH and low-metal-content trivalent plating solution is increased by the addition of conductivity salts/buffers. Lower amperes but higher volts are required for trivalent chromium processes, compared with hexavalent chromium process requirements. Surfactants are added to reduce the surface tension of the solution for mist suppression, as well as to act as additives in the plating operation.

Solution Operation. The typical operating conditions for trivalent chromium processes are summarized in Table 9. High current density spiking at the onset of plating increases the already excellent covering and throwing powers of trivalent chromium processes, when compared with those of hexavalent processes. In general, wherever nickel can be plated, trivalent chromium can be plated. Hexavalent chromium processes fall short, particularly around holes and slots and in low current density areas. Process control, while plating at high current densities, is not a serious concern for trivalent processes, because they have less tendency to produce burnt deposits, compared with hexavalent processes. However, some earlier trivalent processes did produce thick deposits, over 1.3 μm (50 μin.). This thickness is sufficient to produce macrocracking. The cathode efficiency decreases with increasing current density. Therefore, the plating speed does not increase proportionally with an increase in current density.

Table 9 Typical operating conditions for trivalent chromium processes

Parameter	**Value**
pH	2.3-4.0
Temperature	27-50 °C (80-122 °F)
Current density	
Cathode	430-1400 A/m^2 (40-130 A/ft^2)
Anode	540 A/m^2 (50 A/ft^2)

Agitation	Mild air
Rectifier voltage	6-15 V
Deposition rate	
Single-cell process	0.20-0.25 μm/min (8-10 μin./min)
Double-cell process	0.08-0.10μm/min (3-4 μin./min)

Once the operating range has been established for a particular plating installation, the pH and temperature must be controlled well, because they influence plating speed, covering power, and color. The buffering ability of the solution is strong enough that large pH fluctuations do not occur. As the pH increases, the plating rate decreases, but the covering power increases. In general, trivalent chromium deposits do not have the blue-white color of hexavalent chromium deposits. Generally, they have a deeper, slightly darker appearance. However, the newer trivalent processes can produce deposits very close in appearance to hexavalent chromium deposits. In most cases, the color difference is noticeable only when the part is placed next to a hexavalent chromium-plated part.

Temperature. Depending on the process selected, either cooling or heating might be required for temperature control to maintain a bath at desired operating parameters. When lower operating temperatures are desired, some degree of cooling might be required to offset the power used for deposition. Cooler operating temperatures increase the covering power of the process, but slightly darken the color.

Anodes and Agitation. Anode current density should be maintained below 540 A/m^2 (50 A/ft^2) to promote anode life and consistent bath operation. The insoluble graphite anode used in the single-cell process should last indefinitely, if it is not physically damaged. Lead anodes will form protective insoluble films as long as the anodic current density is properly maintained in the double-cell process, resulting in a limited production of lead salts. Mild and uniform air agitation is used around the parts to assist in obtaining metal distribution and appearance.

Contamination Control. The major contributor to a change in appearance of the trivalent chromium deposits is solution contamination. Trivalent chromium solutions are much more sensitive to bath contamination, but are much more easily purified than are hexavalent chromium solutions. Organic contaminants, a minor problem, are typically removed by filtration through carbon. Organic contamination appears in the chromium deposit as white smears that resemble a pattern typically associated with poor cleaning.

Inorganic contaminants, such as iron, nickel, copper, and zinc, cause the deposit to have dark streaks and/or to lose covering power. The newest and easiest method for removing inorganic impurities is to continuously purify the plating solution by passing it through a specially designed resin. Using this technique, the inorganic impurity levels can be maintained much below the level that will cause any operational or appearance problems.

Three other general methods can be used to remove these contaminants. The slowest approach is to plate them out whenever the bath is not being used for production. An alternative method is to set a small plating unit, connected by a recirculating pump, to the main plating tank. Dummy sheets are used in the small unit to continuously plate out impurities without interrupting production.

A third method that is available for some processes is to use chemical purifiers that can remove large quantities of inorganic contaminants during one or two hours of downtime. Although this method is very fast, it has two disadvantages. The chemical precipitates the impurities within the plating bath. The precipitation itself does not cause any plating problems, but the precipitates could adhere to the parts as they leave the tank, causing them to have an objectionable white film. If chemical purifiers are improperly used, then the solution chemistry can be affected, resulting in a darker deposit and poorcoverage.

Plating Problems and Corrections. Some of the plating problems experienced with trivalent chromium baths can be ascribed to common operational problems. Poor coverage is typically due to low pH, high temperature, low current density, or lead or zinc contamination. Dark clouds or smudges on the work can arise from metallic contamination or low complexant or surfactant concentrations. White patches on the work can be caused by high concentrations of surfactants or other organics, lead contamination, or high wetting agent concentration in the nickel bath used prior to chromium plating.

Trivalent and Hexavalent Deposit Comparisons. The choice of chromium plating solution, whether hexavalent or trivalent, depends on the individual application under consideration. The characteristics of these processes are compared in Table 10.

Table 10 Trivalent and hexavalent chromium comparison

Parameter	Trivalent chromium	Hexavalent chromium
Throwing power	Good	Poor
Covering power	Good	Poor
Current interruptions	Completely tolerant	Intolerant
Rectifier ripple	Completely tolerant	Intolerant
Deposit structure (microdiscontinuous):		
Single cell	Microporous and microcracked	Special processes required
Double cell	Microporous	. . .
Ease of burning	Very difficult	Easy
Ease of rinsing	Easy	Moderate
Color buffing requirement	Never	Occasional
Filtering requirement:		
Single cell	Only after purification	Never
Double cell	Daily with carbon	. . .
Conditioning/dummying:		
Single cell	Never	Start up to each day

Double cell	Start up and routinely	. . .
Passivity of nonplated surfaces	Needs post dip	"Chromate" surfaces
Color of deposit:		
Single cell:		
Ambient temperature	Pewter or stainless steel	Blue-white
Elevated temperature	Metallic white	. . .
Double cell:		
Elevated temperature	Metallic white	. . .
Waste treatment	Easy	Moderate
Relative safety	Similar to nickel	Similar to cyanide
Misting	Almost eliminated	Heavy
Odor	Almost eliminated	Strong and dangerous

Nickel Plating

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Introduction

THE NICKEL PLATING PROCESS is used extensively for decorative, engineering, and electroforming purposes because the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and the operating parameters of the plating solution. Decorative applications account for about 80% of the nickel consumed in plating; 20% is consumed for engineering and electroforming purposes. Autocatalytic (electroless) nickel plating processes are commercially important but are outside the scope of this section. The annual worldwide consumption of nickel for electroplating is approximately 180 million pounds (81,700 metric tons) and accounts for 11 to 12% of world nickel consumption. Some basic information about nickel and common nickel salts for plating is given in the following table:

Nickel	Atomic weight 58.69. Valency 2. Specific gravity 8.90. Plating rate, at 100% cathode efficiency, 1.095 g/A · h (0.039 oz/A · h)

Nickel salts	
Nickel chloride	Formula is $NiCl_2 \cdot 6H_2O$. Contains 24.7% Ni.
Nickel sulfate	Formula is $NiSO_4 \cdot 6H_2O$. Contains 22.3% Ni.
Nickel sulfamate	Formula is $Ni(NH_2SO_3)_2$. Contains 23.2% Ni.
Nickel carbonate	Formula is $NiCO_3$. Contains about 46% Ni.

Decorative Plating. Modern decorative nickel plating solutions contain organic additives that modify the electrocrystallization process so that mirror-bright, highly-leveled nickel coatings are deposited directly from solution. Prior to the introduction of "organic" baths, decorative nickel coatings were produced by polishing nickel-plated parts mechanically, a practice that continued from 1870 to about 1945. Thin layers of chromium were electrodeposited over polished nickel coatings for the first time in 1927 to prevent the "yellowing" or tarnishing of nickel in outdoor atmospheres, and that practice continues with the "as-deposited" bright nickel coatings now available. An effort to develop improved decorative, electroplated nickel coatings began in the late 1940s and led to the development of multilayer nickel coatings (early 1950s) and microdiscontinuous chromium coatings (mid- to late 1960s). Modern multilayer nickel coatings in combination with microdiscontinuous chromium are capable of protecting and enhancing the appearance of most metals and alloys, plateable plastics, and other materials for extended periods of time.

Engineering Plating. The engineering applications of nickel plating include those where a fully bright appearance is not required. Engineering nickel deposits are usually sulfur-free and matte in appearance. These deposits may be specified to improve corrosion and wear resistance, to salvage or build up worn or undersized parts, to modify magnetic properties, to prepare surfaces for enameling or for organic coating, to function as diffusion barriers in electronic applications and for other purposes. Engineering applications exist in the chemical, nuclear, telecommunications, consumer electronics, and computer industries.

Electroforming. Nickel electroforming is electrodeposition applied to the manufacture of nickel products of various kinds, and it differs from electroplating in one major respect. In electroplating, the coating is metallurgically bonded to the substrate and is an integral part of the surface. In electroforming, nickel is deposited onto a mandrel or mold nonadherently so that the nickel can be separated from the mandrel when it is removed from the plating solution. Electroforming applications include the fabrication of molds and dies, mesh, and other products that are indispensable to operations in the textile, aerospace, communication, electronics, automotive, photocopying, and entertainment industries. Additional information is available in the article "Electroforming" in this Volume.

Basic Process Considerations

Before describing decorative, engineering, and electroforming plating processes, some basic facts are reviewed that make it possible to control the nickel plating process, predict the amount of nickel deposited, and estimate nickel coating thickness.

The Basic Process. Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent positively charged ions (Ni^{++}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode, where metallic nickel is dissolved to form divalent positively charged ions, which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode.

Hydrogen Evolution and Cathode Efficiency. The discharge of nickel ions is not the only reaction that can occur at the cathode; a small percentage of the current is consumed in the discharge of hydrogen ions from water. This reduces the cathode efficiency for nickel deposition from 100% to 92 to 97%, depending on the nature of the electrolyte. The discharged hydrogen atoms form bubbles of hydrogen gas at the cathode surface.

Anode Efficiency. Under normal conditions the efficiency of dissolution at the anode is 100% and no hydroxyl ions are discharged from the water. If the pH of the solution is too high, however, hydroxyl ions may be discharged in preference to the dissolution of nickel, and oxygen will be evolved. Under those conditions, the nickel anode becomes passive and ceases to dissolve nickel. Activated nickel anode materials are available commercially that resist the onset of passivity and replenish the solution with nickel ions over a wide range of plating conditions.

Nickel Ion and pH Changes. Under normal operating conditions, the nickel ion concentration and the pH of the solution will slowly increase as plating proceeds. The rate of increase in nickel ion concentration depends on the difference between cathode and anode efficiencies. Because cathode efficiencies may vary from 92 to 97%, whereas anode efficiency is always 100%, the rate of increase in nickel ion concentration depends on the nature of the plating solution and not on the type of soluble nickel anode material that is used.

Faraday's Law for Nickel. The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time (Faraday's Law). The proportionality constant is equal to M divided by nF, where M is the molecular weight, n is the number of electrons involved in the electrochemical reaction, and F is Faraday's constant, equal to 96,500 coulombs (ampere-seconds). For nickel, the constant is 1.095 g/A · h. The constant for nickel deposition is calculated assuming that cathode efficiency is 100%; because a small part of the current goes to discharge hydrogen, the constant must be adjusted by multiplying by the cathode efficiency (for example, $1.095 \times 0.955 = 1.046$).

Faraday's Law for nickel may be expressed as $m = 1.095\ (a)\ (l)\ (t)$, where m is the amount of nickel deposited at the cathode (or dissolved at the anode), in grams; l is the current that flows through the plating tank, in amperes; t is the time that the current flows, in hours; and a is the current efficiency ratio for the reaction of interest. In almost all cases, the anode efficiency is 100% ($a = 1$). The cathode efficiency may vary from 92 to 97% and accordingly, a will vary from 0.92 to 0.97.

Average Nickel Thickness. The nickel electrodeposition data compiled in Table 1 have been calculated on the assumption that cathode efficiency is 95.5%, which approximates the case for most nickel plating solutions. From the table, one can estimate the time required to deposit a specified thickness of nickel at a specified current density. If the plating process is operated at 5 A/dm^2, for example, it takes about 20 min to deposit a nickel coating with an average thickness of 20 µm.

Table 1 Nickel electrodeposition data

Deposit thickness, µm	**Weight per unit area, g/dm^2**	**Amp hours per unit, A · h/dm^2**	**Time (min) required to obtain deposit at current density (A/dm^2) of:**									
			0.5	**1**	**1.5**	**2**	**3**	**4**	**5**	**6**	**8**	**10**
2	0.18	0.17	20	10	6.8	5.1	3.4	2.6	2.0	1.7	1.3	1
4	0.36	0.34	41	20	14	10	6.8	5.1	4.1	3.4	2.6	2
6	0.53	0.51	61	31	20	15	10	7.7	6.1	5.1	3.8	3.1
8	0.71	0.68	82	41	27	20	13	10	8.2	6.8	5.1	4.1
10	0.89	0.85	100	51	34	26	17	13	10	8.5	6.4	5.1

12	1.1	1.0	120	61	41	31	20	15	12	10	7.7	6.1
14	1.2	1.2	140	71	48	36	24	18	14	12	8.9	7.1
16	1.4	1.4	160	82	54	41	27	20	16	14	10	8.2
18	1.6	1.5	180	92	61	46	31	23	18	15	11	9.2
20	1.8	1.7	200	100	68	51	34	26	20	17	13	10
40	3.6	3.4	410	200	140	100	68	51	41	34	26	20

Note: Values are based on 95.5% cathode efficiency.

The data in Table 1 provide a means of estimating the average coating thickness. The actual thickness on an individual part depends on the uniformity of current density distribution. Under practical plating conditions, the thickness of the nickel on a batch of parts is measured in one or more trials, and adjustments are made, if necessary, as to how the parts are placed in the tank relative to the anode and how they are positioned on the plating racks. In some cases, shields and auxiliary anodes may be required to obtain acceptable thickness uniformity. Shields are made of nonconductive materials and may be placed on the anode, on the cathode, or between electrodes to block or control current flow. Auxiliary anodes may be either soluble or insoluble, and they are placed closer to the cathode than principal anodes so as to direct current to a recessed or relatively small area on the cathode. With care, current density distribution and coating thickness can be made reasonably uniform and predictable.

The Watts Solution and Deposit Properties

The nickel plating solution described by Watts in 1916 was a major milestone in the development of nickel plating technology. The solution eventually replaced all others in use up to that time. It remains the basis of most decorative nickel plating processes, and it is used for engineering applications and for electroforming. It is operated at elevated temperatures and is capable of being used with high current densities.

The composition of the modern Watts bath is included in Table 2. The constituents of the Watts bath have several functions.

- *Nickel sulfate* is available in commercially pure forms, is relatively inexpensive, and is the major source of the nickel ions in solution. A high nickel sulfate concentration is used when high current densities are required.
- *Nickel chloride* serves primarily to improve anode corrosion, but it also increases conductivity and uniformity of coating thickness distribution. Excessive amounts of chloride increase the corrosivity of the solution and the internal stress of the deposits. (*Internal stress* refers to forces created within the deposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur, and other elements. Internal stress is either tensile [contractile] or compressive [expansive] and may cause plating problems if excessively high.)
- *Boric acid* is used in nickel plating solutions for buffering purposes; its concentration may affect the appearance of the deposits. The deposit may first become frosty in high current density areas at 30 g/L (4 oz/gal) of boric acid, and then as the boric acid concentration approaches 15 to 23 g/L (2 to 3 oz/gal), the deposit may be burnt and cracked. No effect on appearance is observed at high boric acid concentrations up to saturation (45 g/L, or 6 oz/gal).
- *Wetting agents or surfactants,* formulated specifically for nickel plating solutions, are almost always added to control pitting. Their function is to lower the surface tension of the plating solution so that air

and hydrogen bubbles do not cling to the parts being plated.

Table 2 Nickel electroplating solutions

Electrolyte composition, (a) **g/L**	**Watts nickel**	**Nickel sulfamate**	**Typical semibright bath**(b)
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	225 to 400	. . .	300
Nickel sulfamate, Ni $(SO_3NH_2)_2$	. . .	300 to 450	. . .
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30 to 60	0 to 30	35
Boric acid, H_3BO_3	30 to 45	30 to 45	45
Operating conditions			
Temperature, °C	44 to 66	32 to 60	54
Agitation	Air or mechanical	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2	3 to 11	0.5 to 30	3 to 10
Anodes	Nickel	Nickel	Nickel
pH	2 to 4.5	3.5 to 5.0	3.5 to 4.5
Mechanical properties(c)			
Tensile strength, MPa	345 to 485	415 to 610	. . .
Elongation, %	10 to 30	5 to 30	8 to 20
Vickers hardness, 100 gram load	130 to 200	170 to 230	300 to 400
Internal stress, MPa	125 to 210 (tensile)	0 to 55 (tensile)	35 to 200 (tensile)

(a) Antipitting agents formulated for nickel plating are often added to control pitting.

(b) Organic additives available from plating supply houses are required for semibright nickel plating.

(c) Typical properties of *bright* nickel deposits are as follows: elongation, 2 to 5%; Vickers hardness, 100 gram load, 600 to 800; internal stress, 12 to 25 MPa (compressive).

Good-quality nickel deposits can be produced within the ranges of solution pH, temperature, and current density given in Table 2. Although the maximum current density given in the table is 11 A/dm^2, higher rates of plating are possible with increased solution agitation and flow rates.

The physical and mechanical properties of nickel deposited from Watts solutions are affected by the operating conditions and chloride content of the solution as shown in Fig. 1, 2, 3, and 4. Figures 1, 2, and 3 show how pH, current density, and temperature affect properties such as internal stress, hardness, percent elongation, and tensile strength. Figure 4 shows how the chloride content affects those properties; the maximum ductility and softest deposits are produced when 25% of the nickel in solution is present as nickel chloride. Reference 2 is a comprehensive source of mechanical property data for electrodeposited nickel, nickel alloys, and nickel composite coatings.

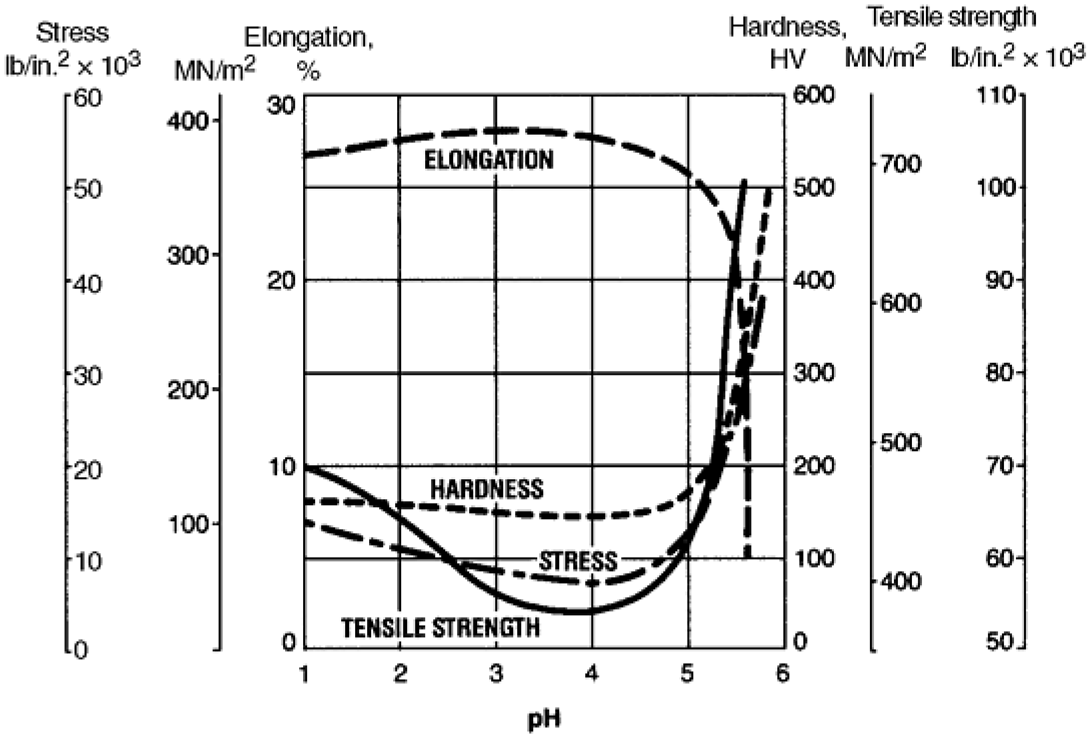

Fig. 1 Variation in internal stress, tensile strength, ductility, and hardness with pH. Watts bath operated at 54 °C and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

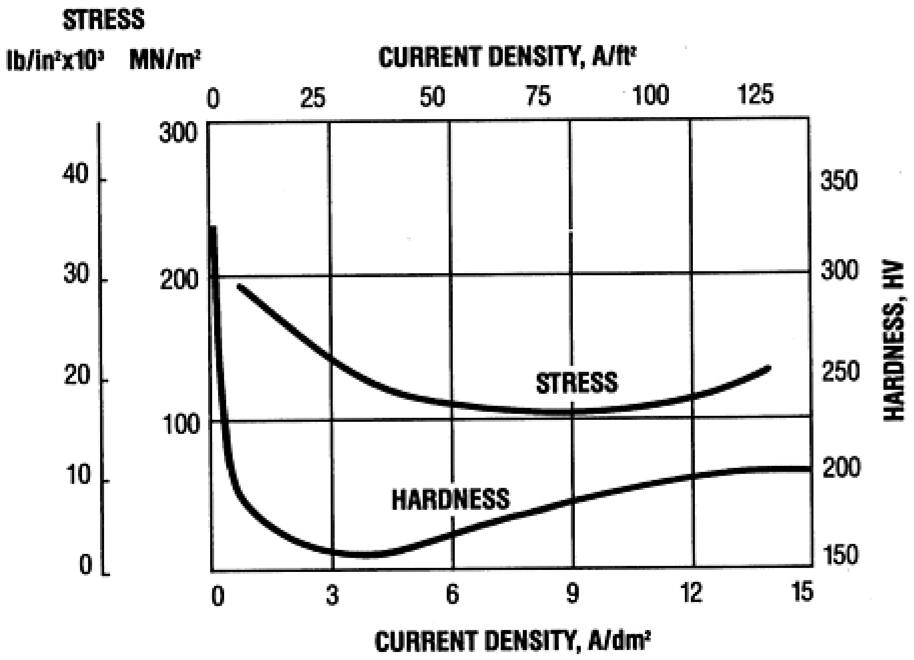

Fig. 2 Variation in internal stress and hardness with current density. Watts bath operated at 54 °C and pH 3.0. Internal stress is tensile (indicated by a positive number). Source: Ref 1

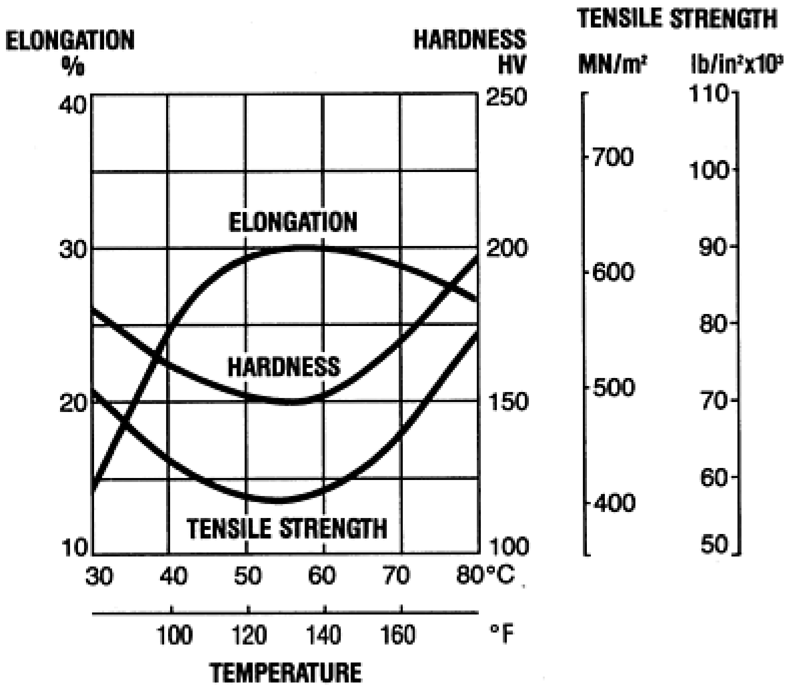

Fig. 3 Variation in elongation, tensile strength, and hardness with temperature. Watts bath operated at 54 °C and 5 A/dm^2. Source: Ref 1

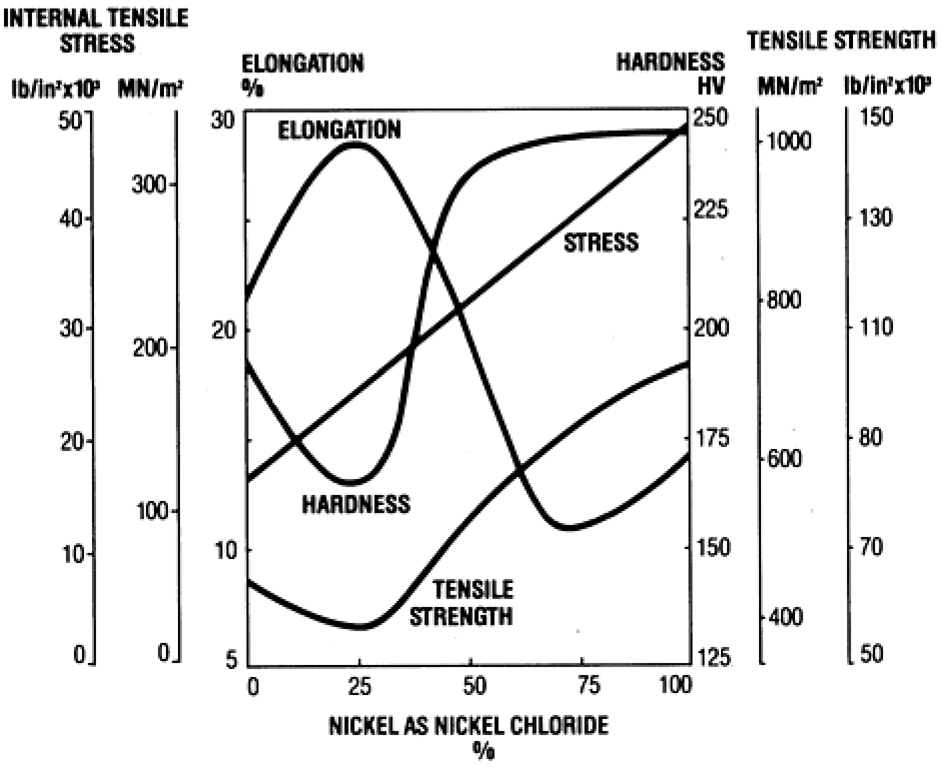

Fig. 4 Variation in internal stress, elongation, tensile strength, and hardness with chloride content in deposits from Watts solutions operated at 55 °C, pH 3.0, and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

The nickel plating processes used for decorative, engineering, and electroforming purposes are discussed in the following sections.

References cited in this section

1. *Plating,* Vol 39 (No. 365), 1952, p 1229
2. W.H. Safranek, *The Properties of Electrodeposited Alloys--A Handbook,* 2nd ed., American Electroplaters and Surface Finishers Society 1986

Decorative Nickel Plating Processes and Multilayer Coatings

The technology of decorative nickel plating has been improved continuously over the years. Prime examples include development of the organic bright nickel solutions, introduction of semibright nickel plating processes, development of multilayer nickel coatings, and the use of microdiscontinuous chromium in combination with multilayer nickel. The major result of these developments has been a remarkable improvement in the corrosion performance of decorative nickel plus chromium coatings without the need to increase deposit thickness.

Bright nickel plating solutions are modifications of the Watts formulation given in Table 2, but they contain organic and other additives that act to produce a fully bright finish suitable for immediate chromium plating without mechanical finishing. Portions of the addition agent molecules may be incorporated into the deposit, resulting in a hard, fine-grain coating that contains incorporated sulfur. The sulfur causes the deposit to be electrochemically more reactive than sulfur-free matte, polished, or semibright nickel deposits. Decomposition products of the additives accumulate in solution with time and are removed by purification with activated carbon. In modern solutions, continuous filtration through active carbon removes deleterious decomposition products without significant removal of the addition agents themselves.

Several substances--organic and inorganic--are used at appropriate concentrations to achieve brightness, leveling, and control of internal stress. (Leveling is the ability of the deposit to become smoother than the surface on which it is deposited as the thickness of the nickel is increased.) The substances used as additives in bright nickel plating solutions may be described by the following three terms: *carriers, auxiliary brighteners,* and *brighteners.* The terminology is not standardized, however, and alternative terms mentioned in the literature are shown in parentheses.

Carriers (brighteners of the first class, secondary brighteners, control agents, ductilizers) are usually aromatic organic compounds. They are the principal source of the sulfur codeposited with the nickel. Their main function is to refine grain structure and provide deposits with increased luster compared with matte or full deposits from baths without additives. Some of these additives can be used in Watts solution or high-chloride versions of the Watts solution (for example, solutions with 115 g/L nickel chloride). This class of brightener widens the bright range when used in combination with the auxiliary brighteners and brighteners discussed below. Some examples of carriers are saccharin (o-sulfobenzoic imide), paratoluene sulfonamide, benzene sulfonamide, benzene monosulfonate (sodium salt), ortho sulfobenzaldehyde (sodium salt), and naphthalene 1,3,6-trisulfonate (sodium salt). Carriers are used in concentrations of about 1 to 25 g/L (0.1 to 3 oz/gal), either singly or in combination. They are not consumed rapidly by electrolysis, and consumption is primarily by dragout and by losses during batch carbon treatment. (Batch treatment involves interrupting production and transferring the plating solution to a separate treatment tank where it is treated with activated carbon, filtered, and returned to the main tank.) The stress-reducing property of carriers is increased if they contain amido or imido nitrogen. For example, saccharin is a most effective stress reducer and often helps to decrease or eliminate hazes. It is generally used as sodium saccharin at a concentration of 0.5 to 4.0 g/L (0.07 to 0.5 oz/gal).

Auxiliary brighteners may be either organic or inorganic. Their functions are to augment the luster attainable with the carriers and brighteners and to increase the rate of brightening and leveling. Some examples are sodium allyl sulfonate; zinc, cobalt, cadmium (for rack and barrel plating); and 1,4-butyne 2-diol. The concentration of these additives may vary from about 0.1 to 4 g/L (0.01 to 0.5 oz/gal). The rate of consumption depends on the type of compound and may vary widely. These compounds may be of aromatic or aliphatic types and usually are heterocyclic or unsaturated. The inorganic metallic ions--zinc, cobalt, cadmium--are not often used anymore as auxiliary brighteners.

Brighteners (brighteners of the second class, primary brighteners, leveling agents), when used in combination with carriers and auxiliary brighteners, produce bright to brilliant deposits having good ductility and leveling characteristics over a wide range of current densities. Some of the compounds used as brighteners include reduced fuchsin, phenosafranin, thiourea, 1,4-butyne diol, n-allylquinolinium bromide) and 5-aminobenzimidazolethiol-2. Materials of this type generally are used in concentrations of 0.005 to 0.2 g/L (0.0006 to 0.02 oz/gal); an excess of brighteners may cause serious embrittlement. The rates of consumption of these materials may vary within wide limits.

Modern bright nickel plating solutions employ combinations of additives similar to those described and are formulated to produce bright deposits over a wide range of current densities. The deposits have excellent leveling or scratch-filling characteristics, produce deposits with fair ductility and low internal stress, produce bright deposits in areas of low current density, permit use of high average current densities and bath temperatures, are less sensitive to metallic contaminants than some of the solutions first commercialized, permit continuous purification of the plating solution by use of activated carbon on filters, produce breakdown products that can be removed by activated carbon, and are not overly sensitive to anode effects.

Multilayer Decorative Plating. The single-layer bright nickel coatings produced from solutions containing organic additives are less resistant to corrosion than polished nickel coatings. The lower corrosion resistance is due to the presence of small amounts of sulfur that originate from the organic additives present in solution. The amount of sulfur that is incorporated depends on exactly how the process is formulated and controlled. Single-layer bright nickel coatings are suitable for use in mildly corrosive service using a nickel thickness of 10 to 20 μm (0.39 to 0.79 mil). For severe and very severe conditions of exposure, especially where longtime resistance to corrosion is required, multilayer nickel coatings with microdiscontinuous chromium are used. The principal types are double- and triple- layer coatings.

Double-layer coatings involve the electrodeposition of two layers of nickel, one semibright and one bright, before the application of chromium. The first layer (semibright) is deposited from a Watts-type formulation containing one or more sulfur-free organic additives. Semibright nickel deposits contain less than 0.005 wt% S and are semilustrous, smooth, and fine-grain over a wide current density range. The deposits have a columnar structure and good ductility. The typical composition and operating conditions for a semibright nickel plating bath are given in Table 2. Deposit internal stress increases with increasing nickel chloride content; deposits also tend to be nonuniform in color and leveling at high chloride levels. The concentrations of the organic additives for semibright nickel solutions are usually fairly low, from 0.05 to 0.5 g/L (0.006 to 0.06 oz/gal). Examples of these additives are 1,4-butyne diol (or other aliphatic compounds with olefinic or acetylenic unsaturation), formaldehyde, coumarin, and ethylene cyanohydrin. There are two families of semibright nickel plating processes that are usually referred to as *coumarin* and *noncoumarin* types. The latter were introduced more recently and offer advantages. Semibright nickel plating solutions usually contain anionic surfactants and antipitting agents, singly or in combination.

The bright nickel layer deposited on top of the semibright one may range in thickness from 5 to 8 μm (0.2 to 0.3 mil), or about 20 to 35% of the total nickel thickness. Ideally, it should be plated from a bath that is compatible with the semibright additive, or additives, because in most double-layer systems the semibright additive functions as either a brightener or an auxiliary brightener in the bright nickel bath.

Triple-layer coatings are similar to double-layer coatings except that a thin, high-sulfur-containing layer is deposited between the semibright and bright layers. The thin layer must contain greater than 0.15 wt% S. Some of the requirements for double- and triple-layer nickel coatings are summarized in Table 3. Why multilayer coatings improve corrosion performance is discussed in the section "Corrosion Performance" in this article.

Table 3 Requirements for double- or triple-layer nickel coatings

Type of nickel coating[(a)]	**Specific elongation, %**	**Sulfur content, wt%**	**Thickness as a percentage of total nickel thickness**	
			Double-layer	**Triple-layer**
Bottom (s--semibright)	Greater than 8	Less than 0.005	Greater than 60 (but at least 75 for steel)	Greater than 50 (but not more than 70)
Middle (b--high-sulfur bright)	. . .	Greater than 0.15	. . .	10 max
Top (b--bright)	. . .	Between 0.04 and	Greater than 10, but less than 40	Equal to or greater than 30

(a) s,semibright nickel layer applied prior to bright nickel; b, fully bright nickel layer that contains the amount of sulfur specified

Microdiscontinuous Chromium. Decorative, electrodeposited nickel coatings, whether single- or multilayer, are most often used in combination with electrodeposited chromium. The thin layer of chromium, initially applied over nickel to prevent tarnishing, now provides added resistance to corrosion because of the developments discussed in this and the next section.

Conventional or regular chromium deposits are low-porosity coatings, whereas microdiscontinuous chromium deposits have a high, controlled degree of microporosity or microcracking. Controlled microporosity or microcracking in the chromium is achieved by depositing a special nickel strike on top of the bright nickel layer just prior to chromium plating. When it is plated over with chromium, the thin layer of nickel, usually about 1 to 2 μm (0.04 to 0.08 mil), helps create microcracks or micropores in the chromium. Microporosity may also be achieved without the use of a special nickel layer by means of the Pixie process, a patented process that involves postplating treatment of the chromium to increase porosity on a microscopic scale. Traditionally, the chromium is deposited from conventional hexavalent processes, but within the last ten years, trivalent chromium plating processes have grown in popularity.

Microcracked chromium is produced by depositing the thin layer of nickel from a special bath formulated to produce nickel with a high internal tensile stress. When the chromium deposit is chromium plated, the thin nickel and the chromium then crack. Varying the conditions under which the nickel layer is deposited can provide variations in the crack density over a range of from 30 cracks/mm (750 cracks/in.) to 80 cracks/mm (2000 cracks/in.). The nickel bath usually consists of a basic nickel chloride electrolyte with additives that provide additional stress, such as the ammonium ion. Boric acid is not used, but other buffers such as the acetate ion may be added. Proprietary organic additives are also used to enhance the brightness and the ability of the deposit to crack, especially in the low-current-density areas. Temperature and pH are controlled to vary the crack density; low temperature (23 °C, or 73 °F) and high pH (4.5) favor higher crack densities; high temperature (36 °C, or 97 °F) and low pH (3.5) favor lower crack densities. Cracking of the chromium deposit must occur subsequent to chromium plating. Aging or the use of a hot water dip may be necessary to promote the formation of all microcracks.

Microporous chromium is produced from Watts-type nickel baths using air agitation and containing very fine inert particles, usually inorganic, and the normal additives used for bright nickel plating. Chromium, plated over the resulting nickel-particle matrix, deposits around the particles, creating pores. The nickel baths are operated much like bright nickel solutions, with the exception that filtration cannot be performed. In some instances, auxiliary additives permit reduction of the particle concentration in the plating bath and still provide high pore densities. Pore densities can vary according to the concentration of particles, agitation rates, and additives. Generally, a minimum pore density of 100 pores/mm^2 (64,000 pores/in.^{2}) is specified. In either case, chromium thicknesses should not be allowed to exceed about 0.5 μm (0.02 mil) or the cracks and pores will start to heal.

Microcracked chromium deposits can also be produced directly from chromium baths by increasing thickness, or by depositing chromium over chromium. The latter, dual-layer chromium technique is no longer popular.

Corrosion Performance. The remarkable corrosion resistance of modern decorative nickel-plus-chromium coatings depends on the use of multilayer nickel in combination with microdiscontinuous chromium. The improved performance of multilayer nickel coatings is due to the fact that the combination of layers of nickel have different electrochemical reactivities. If one measures the corrosion potentials of various nickel deposits in the same electrolyte, one finds that the bright nickel deposits display more active dissolution potentials than do the semibright nickels. If bright and semibright nickel deposits (for example, in the form of foils separated from the substrate) are electrically connected in the electrolyte, electrons will flow from the bright nickel to the semibright nickel. The result is that the rate of corrosion of the bright nickel is increased, whereas the rate of corrosion of the semibright nickel is decreased. In a composite coating consisting of bright nickel over semibright nickel, this is manifested by enhanced lateral corrosion of the bright nickel layer and delayed penetration of the semibright nickel layer.

The extent to which bright nickel protects the underlying semibright nickel layer by sacrificial action is dependent on the difference between the corrosion potentials of the semibright and bright nickel. The difference should be at least 100 mV (as measured by the simultaneous thickness and electrochemical potential, or STEP test, described in the section "Quality Control of Nickel Plating" in this article), differences in potential are beneficial, especially in low-current-density areas of complicated parts. If the difference becomes too great, appearance suffers because of the accelerated corrosion of the bright nickel layer; that is, there is an optimum value that represents a compromise between preventing basis metal attack and controlling superficial corrosion. The result is that penetration of the coating and exposure of the underlying substrate occur slowly. Multilayer nickel coatings are thus more protective than single-layer bright nickel coatings of equal thickness.

The rate of pit penetration through the nickel layers varies inversely with the number of microdiscontinuities in the chromium layer. Pit penetration may occur rapidly with low-porosity, conventional chromium. When corrosion takes place at a pore in conventional chromium, the large cathodic area of chromium surrounding the pore accelerates the corrosion of the nickel, and pitting may occur rapidly. With microdiscontinuous chromium, a large number of microscopic pores or cracks are deliberately induced in the chromium deposit so that corrosion can start at many sites. The available corrosion current has to be spread over a myriad number of tiny corrosion cells, so that the rate of corrosion of the nickel is greatly reduced. For example, the approximate depth of pitting of nickel after 16 h of CASS testing (ASTM B 368, "Copper-Accelerated Acetic Acid Salt Spray [Fog] Testing") was 10 to 20 μm with conventional chromium and 1 to 6 μm with microdiscontinuous chromium.

Corrosion studies conducted by plating suppliers, nickel producers, and groups such as ASTM Committee B-8 have confirmed that multilayer nickel coatings are significantly more protective than single-layer bright nickel coatings, that microdiscontinuous chromium coatings provide more protection than conventional chromium coatings, and that the corrosion protection of decorative, electroplated nickel-plus-chromium coatings is directly proportional to nickel thickness and to the ratio of semibright and bright nickel in multilayer coatings. Table 4 is based on the results of a study conducted at the LaQue Center for Corrosion Technology, Wrightsville Beach, NC, and it summarizes the types of coatings that protected standard panels from corrosion for more than 15 years outdoors in a severe marine atmosphere.

Table 4 Coating systems on steel giving best performance after 15 years of outdoor marine exposure and 96 h of CASS testing

Type and thickness of coating, µm			**ASTM performance ratings**[(a)]	
Copper	**Nickel**[(b)]	**Chromium**[(c)]	**Outdoor marine, 15 years**	**CASS, 96 h**
. . .	38d	1.5 mc	10/8	10/8
12	26d	1.5 mc	10/9	10/8
. . .	38d	0.25 mp	10/7	10/7
12	26d	0.25 mp	10/9	10/7

Note: CASS testing ("Copper-Accelerated Acetic Salt Spray [Fog] Testing") is conducted according to ASTM B 368.

(a) A two-number system has been adopted by ASTM for rating panels after corrosion testing. The first, the protection number, is based on the percentage of the base metal that is defective due to corrosion. A rating of 10 on steel indicates that the panel did not rust. The second, the appearance number, is similarly based on percentage of defective area, but it rates the extent to which corrosion of the base metal as well as superficial corrosion, detract from the overall appearance. Appearance ratings of 7, 8, or 9 indicate that 0.25 to 0.5%, 0.1 to .25%, or 0 to 0.1% of the area, respectively, is defective due to superficial staining and corrosion.

(b) d, double layer. The double-layer nickel coatings in the program differed in reactivity. For details see G.A. DiBari and F.X. Carlin, Decorative Nickel/Chromium Electrodeposits on Steel--15 Years Corrosion Performance Data, *Plating and Surface Finishing,* May 1985, p 128.

(c) mc, microcracked; mp, microporous. The type of microcracked chromium used in this study is based on the addition of selenium compounds to a conventional chromium bath to obtain microcracking. Consistent crack patterns were obtained at the chromium thicknesses given in the table.

Standards and Recommended Thicknesses. ASTM B 456 provides information on specific requirements for decorative nickel-plus-chromium coatings to achieve acceptable performance under five different conditions of service. The standard defines several classes of coatings that differ in thickness and type, and it classifies the various coating systems according to their resistance to corrosion. The standard specifies the requirements for double- and triple-layer nickel coatings (Table 3), and it gives the classification numbers of coatings appropriate for each service condition number. For example, Table 5 specifies decorative nickel-plus-chromium coatings on steel.

Table 5 Decorative nickel-plus-chromium coatings on steel

Service condition number (typical applications)	**Coating designation**[(a)]	**Minimum nickel thickness, µm**
SC 5--Extended very severe (exterior automotive where long-time corrosion protection is a requirement)	Fe/Ni35d Cr mc	35
	Fe/Ni35d Cr mp	35
SC 4--Very severe (exterior automotive, boat fittings)	Fe/Ni40d Cr r	40

	Fe/Ni30d Cr mp	30
	Fe/Ni30d Cr mc	30
SC 3--Severe (patio and lawn furniture, bicycles, hospital furniture and cabinets)	Fe/Ni30d Cr r	30
	Fe/Ni25d Cr mp	25
	Fe/Ni25d Cr mc	25
	Fe/Ni40p; Cr r	40
	Fe/Ni30p Cr mp	30
	Fe/Ni30p Cr mc	30
SC 2--Moderate service (stove tops, oven liners, office furniture, golf club shafts, plumbing fixtures and bathroom accessories)	Fe/Ni20b Cr r	20
	Fe/Ni15b Cr mp	15
	Fe/Ni15b Cr mc	15
SC 1--Mild (toaster bodies, interior automotive accessories, trim for major appliances, fans, light fixtures)	Fe/Ni10b Cr r	10

(a) b, electrodeposited single-layer bright nickel; d, double-layer or multilayer nickel coating; r, regular or conventional chromium; mc, microcracked chromium; mp, microporous chromium. The numerals in the designations denote the thickness of the nickel coating in microns. The thickness of the chromium is assumed to be 0.3 μm unless otherwise specified. When permitted by the purchaser, copper may be used as an undercoat for nickel, but it cannot be substituted for any of the part of the nickel specified. Results of several test programs have raised doubt about whether coating systems involving regular chromium are satisfactory for SC 4 and SC 3.

The service condition number characterizes the severity of the corrosion environment, 5 being the most severe and 1 being the least severe. The classification number is a way to specify the details of the coating in an abbreviated fashion. For example, the classification number Fe/Ni30d Cr mp indicates that the coating is applied to steel (Fe) and consists of 30 μm of double-layer nickel (d) with a top layer of microporous (mp) chromium that is 0.3 μm thick. (The thickness value of the chromium is not included in the classification number unless its thickness is different from 0.3 μm.) The type of nickel is designated by the following symbols: "b" for electrodeposited single-layer bright nickel, "d" for double- or multilayer nickel coatings, "p" for dull, satin, or semibright nickel deposits, and "s" for polished dull or semibright electrodeposited nickel. The type of chromium is given by the following symbols: "r" for regular or conventional chromium, "mp" for microporous chromium, and "mc" for microcracked chromium.

Decorative nickel-iron alloy plating processes were introduced to conserve nickel and to lower anode material costs by substituting a portion of the nickel with iron. Decorative nickel-iron alloy deposits have full brightness, high leveling, excellent ductility, and good receptivity for chromium. Nickel-iron can be plated on steel, brass, aluminum, zinc die castings, or plastic substrates in either barrel or rack equipment. The operation and the proprietary additives used in commercially available processes are similar to those in conventional bright nickel plating. In addition, the bath requires special additives to stabilize the ferrous and ferric ions so that hydroxide compounds do not form and precipitate. The stabilizers are either complexers or reducing agents, depending on the nature of the proprietary process. The processes should be controlled within the limits recommended by plating supply houses. Deposits on steel or copper that is subsequently chromium plated have had good acceptance for interior applications as a substitute for bright nickel. Decorative nickel-iron alloy deposits are not often used for outdoor applications where corrosion conditions are severe, because the deposits tend to form a fine, superficial brown stain relatively quickly. The rate at which this occurs depends on the iron content of the deposits, and those with less than 15% Fe have been used in outdoor applications.

Engineering and Electroforming Processes

Electrodeposited nickel coatings are applied in engineering applications to modify or improve surface properties, such as corrosion resistance, hardness, wear, and magnetic properties. Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous, mirror-like deposits described in previous sections are not usually required. Nickel electroforming is the specialized use of the nickel plating process to produce or reproduce articles by electroplating onto a mandrel that is subsequently separated from the deposit.

Watts and Nickel Sulfamate Processes. The two most popular solutions for depositing engineering nickel coatings and for electroforming, Watts nickel and nickel sulfamate, have been included in Table 2. The table summarizes the chemical composition, operating conditions, and typical mechanical property data for deposits from these solutions. The Watts solution is relatively inexpensive and easy to control; it has already been discussed.

Nickel sulfamate solutions are widely used for electroforming because of the low internal stress of the deposits, high rates of deposition, and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness, as influenced by geometric factors (the shape and relative positioning of anode and cathode), and by the electrochemical characteristics of the solution (conductivity, cathode polarization, and cathode efficiency). Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those that would be produced in the absence of cathode polarization and cathode efficiency effects. Because of the very high solubility of nickel sulfamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting lower operating temperatures and higher plating rates.

A small amount of nickel chloride is usually added to nickel sulfamate solutions to minimize anode passivity, especially at high current densities. If nickel chloride is not added, sulfur-containing nickel anode materials with about 0.02% S are essential to avoid anodic oxidation of the sulfamate ion, which can result in the uncontrolled and unpredictable production of sulfur-containing compounds that act as stress reducers and that cannot easily be removed from solution. Bromide ions, instead of chloride, are sometimes added to nickel sulfamate solutions to promote anode dissolution.

Nickel sulfamate is so soluble that it cannot be readily recrystallized from solution. It is commercially available as a concentrated solution, usually prepared by reacting high-purity nickel powder with sulfamic acid under controlled conditions. Nickel sulfamate plating solutions are more expensive than those based on commercial grades of nickel sulfate and nickel chloride. The extra cost of using solutions that are as pure as possible is more than offset by savings in the preliminary purification procedures necessary otherwise.

Prolonged use of sulfamate solutions at temperatures above 60 °C (140 °F) or at a pH of less than 3.0 can hydrolyze the nickel sulfamate to the less soluble form of nickel ammonium sulfate. The ammonium and sulfate ions produced from the hydrolysis increase the internal tensile stress and hardness of the deposits.

Nickel electrodeposited from a well-purified sulfamate bath containing no stress-reducing agent and operated at 46 °C (115 °F), a pH of 4.0, and a current density of 2.0 A/dm^2 (20 A/ft^2) has a residual tensile stress varying from 15 to 40 MPa (2 to 6 ksi). The stress in a deposit produced from a similarly operated Watts bath would be about 170 MPa (25 ksi).

Sulfamate nickel plating baths are especially useful for applications requiring low residual stress in the electrodeposited nickel, such as in electroforming, and for coating objects that are susceptible to fatigue cracking. Steel crankshafts that are nickel plated for resistance to corrosion and wear should be coated with a low-stress nickel deposit, such as sulfamate nickel, to minimize loss of fatigue strength. The fatigue limit of nickel-plated steel is reduced almost proportionally to the amount of residual tensile stress in the nickel plate, and the use of compressively stressed deposits provides additional benefits.

Other nickel plating solutions for engineering applications are listed in Table 6, along with available mechanical properties of the deposits. Many of these solutions were developed to meet specific engineering requirements; all are used to a lesser extent than Watts and nickel sulfamate solutions.

Table 6 Other nickel plating solutions and some properties of the deposits

Type	Composition[(a)],g/L	pH	Temperature, °C	Cathode current density, A/dm^2	Vickers hardness, 100 g load	Tensile strength, MPa	Elongation, %	Internal stress, MPa
Fluoborate	Nickel fluoborate, 225-300 Nickel chloride, 0-15 Boric acid, 15-30	2.5-4	38-70	3-30	125-300	380-600	5-30	90-200
Hard nickel	Nickel sulfate, 180 Ammonium chloride, 25 Boric acid, 30	5.6-5.9	43-60	2-10	350-500	990-1100	5-8	300
All-chloride	Nickel chloride, 225-300 Boric acid, 30-35	1-4	50-70	2.5-10	230-260	620-930	4-20	275-340
All-sulfate	Nickel sulfate, 225-410 Boric acid, 30-45	1.5-4	38-70	1-10	180-275	410-480	20	120
Sulfate chloride	Nickel sulfate, 150-225 Nickel chloride, 150-225 Boric acid, 30-45	1.5-2.5	43-52	2.5-15	150-280	480-720	5-25	210-280
High sulfate	Nickel sulfate, 75-110 Sodium sulfate, 75-110 Ammonium chloride, 15-35 Boric acid, 15	5.3-5.8	20-32	0.5-2.5	. . .	. . .	. . .	. . .
Black nickel (sulfate bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24-32	0.15	. . .	. . .	. . .	. . .
Black nickel	Nickel chloride, 75 Zinc chloride, 30	5.0	24-32	0.15-0.6	. . .	. . .	. . .	. . .

(chloride bath)	Ammonium chloride, 30 Sodium thiocyanate, 15							
Nickel phosphorus	Nickel sulfate, 170 or 330 Nickel chloride, 35-55 Boric acid, 0 or 4 Phosphoric acid, 50 or 0 Phosphorous acid, 2-40	0.5-3.0	60-95	2-5	. . .	. . .	. . .	. . .

(a) The formulas of the compounds in the table are as follows: nickel fluoborate, $Ni(BF_4)_2$; nickel sulfate, $NiSO_4 \cdot 6H_2O$; nickel chloride, $NiCl_2 \cdot 6H_2O$; boric acid, H_3BO_3; ammonium chloride, NH_4Cl; ammonium sulfate, $(NH_4)_2SO_4$; sodium sulfate, Na_2SO_4; phosphoric acid, H_3PO_4; phosphorous acid, H_3PO_3; zinc sulfate, $ZnSO_4 \cdot 7H_2O$; zinc chloride, $ZnCl_2$; sodium thiocyanate, NaSCN.

Fluoborate. The fluoborate solution listed in Table 6 can be used over a wide range of nickel concentrations, temperatures, and current densities. The fluoborate anion is aggressive, and some materials that contact the solution are chemically attacked. Silica filter aids cannot be used on a continuous basis, although cellulose filters are satisfactory. Lead, titanium, and high-silicon cast iron are readily attacked. Stainless steels containing 20% Cr, 25 to 30% Ni, and 2 to 3% Mo are resistant. Anode materials can be encased in Vinyon, polypropylene, or Orlon anode bags to prevent insoluble particles and anode residues from entering the plating solution; nylon bags are unsuitable. Only sleeve-type glass electrodes for pH measurement should be used because of the formation of relatively insoluble potassium fluoborate with permanent junction types. The mechanical and physical properties of deposits produced by the fluoborate bath are similar to those from Watts solutions. The nickel fluoborate solution has been used primarily for high-speed deposition of thick nickel.

Hard Nickel. Developed especially for engineering applications, this solution is applied where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required (without the use of sulfur-containing organic addition agents). Close control of pH, temperature, and current density is necessary for this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature. The internal stress is slightly higher than in deposits from Watts solutions. The disadvantages of the hard nickel bath are its tendency to form nodules on edges and the low annealing temperature (230 °C, or 450 °F) of its deposits. Hard nickel deposits are used primarily for buildup or salvage purposes. For optimum results, the ammonium ion concentration should be maintained at 8 g/L (1.1 oz/gal). In those applications where the part being plated is not going to be exposed to elevated temperatures in service, it is simpler to add organic compounds such as saccharin, p-toluene sulfonamide, p-benzene sulfonamide, or other carriers to Watts or sulfamate solutions to achieve hardness without increased internal stress. Because the additives introduce 0.03% S (or more), this approach cannot be used for parts that will be exposed to high temperatures where sulfur severely embrittles the nickel deposit.

All-Chloride. The principal advantage of the all-chloride bath (Table 6) is its ability to operate effectively at high cathode current densities. Other advantages include its high conductivity, its slightly better throwing power, and a reduced tendency to form nodular growths on edges. Deposits from this electrolyte are smoother, finer-grain, harder, and stronger than those from Watts solutions, and more highly stressed. Because of the partial solubility of lead chloride, lead cannot be used in contact with the all-chloride solution. Mists from this solution are corrosive to the superstructure, vents, and other plant equipment, if not well protected. The solution has been used to some extent for salvaging undersize or worn shafts and gears.

All-sulfate has been applied for electrodepositing nickel where the principal or auxiliary anodes are insoluble. For example, insoluble auxiliary or conforming anodes may be required to plate the insides of steel pipes and fittings. To prevent pitting, hydrogen peroxide may be added to all-sulfate solutions, provided they contain no wetting agents or organic stress reducers. Oxygen is evolved at insoluble anodes in the all-sulfate solution, and as a result, the nickel concentration and pH decrease during plating. The pH is controlled and the nickel ion concentration is maintained by adding nickel carbonate. Another procedure that has been used in low-pH solutions replenishes the nickel electrolytically by employing a replenishment tank with nickel anodes; the current in the replenishment tank is periodically reversed to keep the nickel anodes actively dissolving in the absence of chlorides. The insoluble anodes in all-sulfate solutions may be lead, carbon, graphite, or platinum. If a small anode area is required, solid platinum (in the form of wire) may be used; for large anode areas, platinum-plated or platinum-clad titanium is recommended. In some forms, carbon and graphite are too fragile; lead has the disadvantage of forming loose oxide layers, especially if it is immersed in other solutions in the course of a plating cycle. In chloride-free solution, pure nickel is almost insoluble and may function as an internal anode if properly bagged.

Sulfate/Chloride. The sulfate/chloride solution given in Table 6 has roughly equivalent amounts of nickel sulfate and nickel chloride and was developed to overcome some of the disadvantages of the all-chloride solution. It has high conductivity and can be operated at high current densities. Although the internal stress of the deposits is higher than in deposits from Watts solutions, the stress is lower than in the all-chloride solution. The other properties are about midway between those for deposits from Watts and all-chloride solutions. Lead may not be used for equipment in contact with this solution because of the high chloride content.

High Sulfate. The high-sulfate bath was developed for plating nickel directly on zinc-base die castings. It may also be used to plate nickel on aluminum that has been given a zincate or comparable surface preparation treatment. The high sulfate and low nickel contents, together with the high pH, provide good throwing power with little attack of the zinc. The deposits are less ductile and more highly stressed than nickel deposited from a Watts bath. For this reason, high sulfate nickel is sometimes used as a thin undercoating for more ductile nickel. In general, the deposition of copper from a cyanide solution directly on zinc-base die castings prior to the deposition of nickel is simpler and more reliable.

Black Nickel. There are at least two formulations for producing black nickel deposits; these incorporate zinc and thiocyanate (CNS^-) ions. Table 6 gives the composition and operating conditions for a sulfate and a chloride black nickel plating bath. The process was developed for decorative reasons--color matching and blending. The black nickel deposit has little wear or corrosion resistance and is usually deposited over a layer of nickel deposited from a bright or dull nickel plating solution. It is in commercial use, but it is limited in its applications.

Nickel phosphorus solutions result in the electrodeposition of nickel phosphorus alloys that are analogous to electroless deposits using sodium hypophosphite as the reducing agent. The hardness of the electrolytic deposits can be increased by heat treatment in the same way that the hardness of electroless nickel deposits can be increased, with maximum hardness occurring at 400 °C (750 °F). The phosphorus content of the deposits is best controlled by frequent additions of phosphite or phosphorous acid. The electrodeposition of nickel phosphorus alloys is receiving increased attention because deposits with greater than 10% P are amorphous and therefore have enhanced resistance to corrosion.

Nickel Alloy Plating and Composites. Although discussion of alloy plating is beyond the scope of this article, it should be noted that nickel alloy plating processes of commercial importance include nickel-iron (without brighteners), nickel-cobalt, nickel-palladium, and tin-nickel. An alloy plating process that is growing in importance is zinc-nickel, containing 8 to 12% Ni. In addition, the incorporation of inert particles within a nickel matrix is possible, and coatings that incorporate silicon carbide, diamonds, mica, polytetrafluoroethylene, and other materials are being applied for engineering purposes. Detailed information is available in the articles "Nickel Alloy Plating" and "Zinc Alloy Plating" in this Volume.

Quality Control of Nickel Plating

Achieving high quality involves controlling the bath composition, the purity of the plating solution, and the thickness and uniformity of the deposits. Eliminating rejects, troubleshooting, and the testing of deposits are important aspects of process and product control.

Control of Solution Composition. Control of the composition of the plating bath is one of the most important factors contributing to the quality of nickel deposits. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter, the composition and pH of the solution must be controlled within specified limits, and contamination by metallic and organic substances must be prevented.

Purification Techniques and Starting Up a New Bath. Before any freshly prepared nickel plating bath is used, contaminants such as iron, copper, zinc, and organics present in trace quantities in commercial salts must be removed to obtain the best results. Several treatments are available for purifying a freshly prepared nickel plating solution.

High-pH treatment consists of adding nickel carbonate to the hot solution until a pH of 5.0 to 5.5 is obtained. This precipitates the hydroxides of metals such as iron, aluminum, and silicon, which in turn frequently absorb other impurities. Addition of hydrogen peroxide oxidizes iron to the ferric state, making it more easily precipitated at high pH, and frequently destroys organic impurities.

Treatment with activated carbon removes organic impurities.

Electrolytic purification removes most of the harmful metallic and organic impurities. A complete purification procedure for a Watts solution would comprise the following steps:

1. Use a separate treatment tank (not the plating tank) to dissolve the nickel sulfate and nickel chloride in hot water at 38 to 49 °C (100 to 120 °F) to about 80% of desired volume.
2. Add 1 to 2 m/L (0.8 to 1.6 pints/100 gal) of 30% hydrogen peroxide (agitate briefly and allow to settle for 1 h).
3. Add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) activated carbon and agitate thoroughly.
4. Heat to 66 °C (150 °F), then add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) of nickel carbonate to the solution, with agitation to adjust the pH to 5.2 to 5.5. More nickel carbonate may be required and the mixture should be stirred to assist the dissolution of the carbonate. Allow to settle 8 to 16 h.
5. Filtering into the plating tank.
6. Add and dissolve boric acid; add water to bring bath up to its desired volume.
7. Electrolytically purify by using a large area of nickel plated corrugated steel sheets as cathodes. The average cathode current density should be 0.5 A/dm^2 (5 A/ft^2), and treatment should continue until 0.5 to 1.3 A · h/L (2 to 5 A · h/gal) have passed through the solution. The solution should be agitated and the temperature held at 49 to 60 °C (120 to 140 °F). It is useful to prepare deposits at normal current densities at some point to check appearance, stress, and sulfur content. If not acceptable, continue dummying until the properties are acceptable.
8. Remove the dummy cathodes and adjust the pH of the solution to the desired value.

Controlling the Main Constituents. The following basic constituents of nickel plating baths must be regularly controlled: the nickel metal content; the chloride concentration; the boric acid; and any organic addition agents. Nickel metal concentration is maintained between 60 and 80 g/L (8.0 and 10.5 oz/gal) in most commercial applications. It is desirable to have a minimum of 23 g/L (3 oz/gal) of nickel chloride in the solution to promote anode corrosion. (The chloride content is not critical for anode corrosion when sulfur-activated anode materials are used.) Boric acid is the most commonly used buffering agent for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance. It is available in a purified form and is inexpensive. Organic addition agents must be controlled within the limits specified by the suppliers of proprietary processes, and they must be replenished due to losses from dragout, electrolytic consumption, and the effects of carbon filtration (or batch treatment).

Procedures exist for chemical analysis of nickel, chloride, boric acid, and organic addition agents in nickel plating solutions, and modern instrumental techniques are available to monitor the main ingredients on a regular basis with improved precision. High-performance liquid chromatography is one of the improved techniques for controlling organics that is growing in popularity.

Controlling pH, Temperature, Current Density, and Water Quality. The pH of the nickel plating solution will rise during normal operation of the bath, necessitating regular additions of acid to maintain the pH within the prescribed limits. A decrease in pH accompanied by a decrease in nickel ion concentration indicates that the process is not functioning properly.

The operating temperature may have a significant effect on the properties of the deposits, and it should be maintained within specified limits (±2 °C) of the recommended value. In general, most commercial nickel plating baths are operated between 38 to 60 °C (100 to 140 °F).

The nickel plating process should be operated at specified current densities by estimating the surface area of the parts and calculating the total current required. The practice of operating the process at a fixed voltage is not recommended.

Controlling cathode current density is essential for accurately predicting average nickel thickness, for achieving uniform coating thickness on complicated shapes, and for producing deposits with consistent and predictable properties.

Since current density determines the rate of deposition, it must be as uniform as possible to achieve uniformly thick nickel deposits. The nickel plating solution has an electrical resistance, and almost all components to be plated have prominent surfaces that are nearer the anode than recessed areas. The current density is greater at the prominences because the anode-to-cathode distance is shorter and therefore has less electrical resistance. The apportioning of the current in this way is called *current distribution.* This means that the recessed areas receive a thinner nickel deposit than the prominent ones. Current distribution is controlled by proper rack design and proper placement of components on those racks, by the use of nonconducting shields and baffles, and by the use of auxiliary anodes, when necessary. With care, relatively good thickness distribution can be achieved.

The quality of the water used in making up the bath and in replacing water lost by evaporation is important. Demineralized water should be used, especially if the local tap water has a high calcium content (greater than 200 ppm). Filtering the water before it is added to the plating tank is a useful precaution to eliminate particles that can cause rough deposits.

Controlling Impurities. Inorganic, organic, and gaseous impurities may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities from the plating shop can improve the quality of the deposits, as well as productivity and profitability. The presence of small quantities of inorganic or organic contamination may result in plating defects.

Inorganic contaminants arise from numerous sources, including nickel salts of technical grade, hard water, carryover from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, and dirt from structures above the tank and from parts that fall into the solution and are not removed. The following table lists maximum limits for metallic impurities in nickel plating baths:

Contaminant	**Maximum concentration, ppm**
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20
Calcium	(a)

Note: The limits may be different when several contaminants are present at the same time, and complexing agents are a part of the solution formulation.

(a) pH-dependent; will precipitate at the saturation point

The degree of contamination by many inorganic materials may be controlled by continuous filtration and dummying, that is, by electrolysis of the plating solution at 0.2 to 0.5 A/dm^2 (2 to 5 A/ft^2). This may be accomplished on a batch basis or continuously by installing a dummy compartment and overflow dam at one end of the plating tank. Solution from the filter is pumped into the bottom of the dummy compartment, up past the corrugated cathode sheets, over the dam, into the plating section of the tank, out through a bottom outlet at the far end of the tank, and back to the filter. Solid particles and soluble metallic impurities (for example, copper, zinc, lead) are removed simultaneously by this procedure.

Organic contaminants may arise from many sources, including buffing compounds, lubricating oil dropped from overhead equipment, sizing from anode bags, weaving lubricants on plastic anode bags, uncured rack coatings or stopoff lacquers, adhesives on certain types of masking tape, decomposition products from wetting agents, organic stabilizers in hydrogen peroxide, paint spray, and new or patched rubber tank linings. Many organic contaminants can be effectively removed from nickel plating solutions by adsorption on activated carbon on either a batch or a continuous basis. On a batch basis, the solution is transferred to a spare tank, heated to 60 to 71 °C (140 to 160 °F), stirred for several hours with a slurry of 6 g/L (5 lb/100 gal) minimum of activated carbon, permitted to settle, and then filtered back into the plating tank. It is usually necessary to do a complete chemical analysis and adjust the composition of the solution after this type of treatment.

For solutions in which organic contamination is a recurring problem, continuous circulation of the solution through a filter, coated at frequent intervals with small amounts of fresh activated carbon, is recommended. When continuous carbon filtration is used, the wetting agent in the solution must be replenished and controlled more carefully, to prevent pitting of the nickel deposits.

Gaseous contamination of nickel plating solutions usually consists of dissolved air or carbon dioxide. Dissolved air in small amounts may lead to a type of pitting characterized by a teardrop pattern. Dissolved air in the plating solution usually can be traced to entrainment of air in the pumping system when the solution is circulated. If this occurs, the circulating pump and valves should be checked and modified, if necessary. Nickel plating solutions can be purged of dissolved air by heating to a temperature at least 6 °C (10 °F) higher than the normal operating temperature for several hours. The solution is cooled to the operating temperature before plating is resumed. Dissolved carbon dioxide in a nickel plating solution is usually found after nickel carbonate has been added to raise the pH, and it is liberated from warm nickel plating solutions after several hours. If solutions containing carbon dioxide are scheduled for immediate use, they should be purged by a combination of heating and air agitation for approximately 1 h at 6 °C (10 °F) or more above the normal plating temperature.

Effects of Impurities on Bright Nickel Plating. The presence of impurities is especially troublesome in decorative nickel plating. Contamination by zinc, aluminum, and copper is most often caused by the dissolution of zinc-base die castings that have fallen from racks into the plating tank and have been permitted to remain there. Inadequate rinsing before nickel plating increases the drag-in of metallic elements. The presence of cadmium and lead may be attributed to a number of sources, including lead-lined equipment and tanks, impure salts, and drag-in of other plating solutions on poorly rinsed racks. Chromium is almost always carried into the nickel solution on rack tips that have not been chromium stripped, or on poorly maintained racks that have been used in a chromium plating tank and have trapped chromium plating solution in holes, pockets, and tears in the rack coating.

Metallic contaminants affect bright nickel deposition in several ways. Aluminum and silicon produce hazes, generally in areas of medium to high current density. Aluminum and silicon may also cause a fine roughness called "salt and pepper" or "stardust." Iron produces various degrees of roughness, particularly at high pH. Calcium contributes to needlelike roughness as a result of the precipitation of calcium sulfate when calcium in solution exceeds the saturation point of 0.5 g/L (0.06 oz/gal) at 60 °C (140 °F). Chromium as chromate causes dark streaks, high-current-density gassing, and possibly peeling. After reduction to the trivalent form by reaction with organic materials in the solution or at the cathode, chromium may produce hazing and roughness effects similar to those produced by iron, silicon, and aluminum. Copper, zinc, cadmium, and lead affect areas of low current density, producing hazes and dark-to-black deposits.

Organic contaminants may also produce hazes or cloudiness on a bright deposit, or they can result in a degradation of mechanical properties. Haze defects may appear at any current density, or they may be confined to narrow current density ranges.

Mechanical defects producing hairline cracks, called *macrocracking,* may be encountered if the coating is sufficiently stressed as a result of solution contamination. These cracks usually appear in areas of heavier plating thickness (higher current density) but are not necessarily confined to those areas.

Eliminating Rejects/Troubleshooting. The production of defective plated parts or rejects may be associated with the presence in solution of soluble and insoluble impurities. The nature of the coating defect is often an indication of the source of the problem. Common defects include roughness, pitting, blistering (often associated with poor preparation of the surface prior to plating), high stress and low ductility, discoloration, burning at high-current-density areas, and failure to meet thickness specifications.

Roughness is usually caused by the incorporation of insoluble particles in the deposit. In bright nickel baths, chlorine generated at an auxiliary anode that is close to the cathode can react with organic additives to form an insoluble material that is incorporated in the deposit. Insoluble particles may enter the solution from many sources: incomplete polishing of the base metal so that slivers of metal protrude from the surface, incomplete cleaning of the surface so that soil particles remain on the surface, detached flakes of deposit from improperly cleaned racks, dust carried into the tank from metal polishing operations and other activities, insoluble salts and metallic residues from the anode, and others.

Roughness from incomplete polishing, cleaning, and inadequate rack maintenance is avoided by good housekeeping, regular inspection, and control. Roughness caused by dust can be controlled by isolating surface preparation and metal polishing operations from the plating area, by providing a supply of clean air, and by removing dirt from areas near and above the tanks. Roughness caused by the precipitation of calcium sulfate can be avoided by using demineralized water. Continuous filtration of the plating solution so as to turn over the solution at least once an hour is important for minimizing roughness problems. Anode residues must be retained within anode bags, and care should be taken not to damage the bags or allow the solution level to rise above the tops of the bags.

Pitting is caused by many factors, including adhesion of air or hydrogen bubbles to the parts being plated. Air should be expelled as already mentioned. Pitting from adherent hydrogen bubbles can result from a solution that is chemically out of balance, has too low a pH, or is inadequately agitated. Other sources of pitting include incorrect racking of complicated components, too low a concentration of wetting or antipitting agents, the use of incompatible wetting agents, the presence of organic contaminants, the presence of copper ions and other inorganic impurities, incomplete cleaning of the base material, and incomplete dissolution of organic additives that may form oily globules. Pitting is therefore avoided by maintaining the composition of the plating solution within specified limits, controlling the pH and temperature, and preventing impurities of all kinds from entering the solution.

Blistering may be associated with poor adhesion resulting from poor or incorrect surface preparation prior to plating. Nickel can be deposited adherently on most metals and alloys, plastics, and other materials by following standard methods of preparation and activation, including the proper use of intermediate deposits such as cyanide copper, acid copper, and acid nickel chloride strikes. Standard procedures for the preparation of materials prior to electroplating can be found in handbooks and in the *Annual Book of ASTM Standards,* Volume 0.205. Blistering may also be related to incomplete removal of grease, dirt, or oxides, formation of metal soaps from polishing compounds, or formation of silica films from cleaning solutions. In the case of zinc-base die castings or aluminum castings, blistering during or immediately after plating may be due to surface porosity and imperfections that trap plating solution under the coating.

High stress and low ductility usually occur when organic addition agents are out of balance, and also because of the presence of organic and inorganic impurities. Solutions must be maintained in a high state of purity.

Discoloration in low-current-density areas is most likely the consequence of metallic contamination of the plating solution. The effects can be evaluated systematically by plating over a reproducible range of current densities on a Hull cell cathode. Hull cells are available from plating supply houses and are shaped so that nickel can be deposited onto a standard panel over a predictable range of current densities. The variation in current density over the face of the panel is achieved by placing the panel at a specified angle to the anode. Bent panels that are L-shape and plated with the recessed area facing the anode can also be used to assess discoloration at low-current-density areas, and they may provide information on roughness problems.

Burning at high current densities can be caused by applying the full load on the rectifier to the lowest parts on a rack as it is lowered into the tank. This can be controlled by applying a reduced load or ramping the current during immersion of the rack. Burning can also be caused by exceeding the recommended maximum cathode current density, the presence of phosphates in solution introduced via contaminated activated carbon, or incorrect levels of organic additives.

Failure to meet thickness specifications is most frequently due to the application of too low a current and/or too short a plating time. This can be avoided by measuring the area of the parts to be plated, then calculating the total current required for a specified current density and plating for the appropriate time (see Table 1). Another major cause of failure to meet thickness requirements is nonuniform distribution of current leading to insufficient deposition in low-current-density areas. Poor electrical contacts and stray currents can also cause thin deposits, and anode and cathode bars, hooks, and contacts should be kept clean.

Controlling and Testing Deposit Properties. The requirements for testing electrodeposited nickel coatings may vary significantly, depending on the application. In almost all decorative applications, the appearance and the thickness of the deposit should be controlled and monitored on a regular basis. The plated surface must be free of defects such as blisters, roughness, pits, cracks, discoloration, stains, and unplated areas. It must also have the required finish--bright, satin, or semibright. Quality can only be maintained by checking the thickness of a specified number of plated parts. In decorative, electrodeposited multilayer coatings, it is also important to control the sulfur contents of the deposits, the relative thicknesses of individual layers, the ductility of the semibright nickel layer, and the difference in the electrochemical potentials between individual layers. Requirements for corrosion performance and adhesion may also be specified and may require additional testing.

In engineering and electroforming applications, it may be necessary to monitor the mechanical properties, including hardness, tensile strength, ductility, and internal stress, as well as wear resistance and other properties. Some of the more important test methods are briefly outlined below. Additional details can be found in the standard test methods collected in the *Annual Book of ASTM Standards.*

Thickness may be measured using a variety of techniques. The coulometric method described in ISO 2177 and ASTM B 504 can be used to measure the chromium and nickel thicknesses, as well as the thickness of copper undercoats, if present. The coulometric method measures the quantity of electrical energy required to deplate a small, carefully defined area of the component under test. A cell is sealed to the test surface and filled with the appropriate electrolyte, and a cathode is inserted. The component is made the anode, and the circuit is connected to the power supply via an electronic coulometer. By integrating time in seconds with the current passing, the electronic coulometer provides a direct reading in coulombs; modern instruments provide a direct reading of thickness. The completion of the deplating is shown by a marked change in the applied voltage. For routine control of production, it is convenient to monitor nickel thickness nondestructively by means of a magnetic gage, calibrating the gage at intervals with standard samples. Instruments for measuring thickness by beta backscatter, X-ray spectrometry, and eddy current techniques are also available. The traditional method of measuring thickness by microscopic examination of a metallographically prepared cross section of the plated part is still employed, but it is time-consuming, expensive, and destructive.

The simultaneous thickness and electrochemical potential (STEP) test was developed to measure the difference in electrochemical potential between semibright and bright nickel layers in multilayer nickel deposits on parts that are plated in production. It is similar to the coulometric method just described. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved at the same time that the thickness of the individual layers is being measured. For example, with a double-layer nickel coating, a relatively large change in potential occurs when the bright nickel layer has dissolved and the semibright nickel layer begins to be attacked. The potential difference is related to the overall corrosion resistance of the double-layer coating and should be greater than 100 mV. Details can be found in ASTM B 764.

Corrosion testing may be specified and may require the plater to perform accelerated corrosion tests on a specified number of production parts as part of an overall quality assurance requirement. Three accelerated corrosion tests are recognized internationally: the Copper-Accelerated Acetic Acid Salt Spray (CASS), the Corrodkote, and the Acetic Acid Salt Spray tests. The CASS test is the one most widely used. The CASS and Corrodkote tests were developed when conventional chromium was the only type of chromium available; when the accelerated tests are used to evaluate microdiscontinuous chromium coatings, the surface appearance deteriorates more rapidly than in real-world environments. Details of these three tests can be found in ISO 1456 as well as in ASTM standards. The salt spray tests involve the application of the corrosive solution in the form of a spray or fog inside a fog cabinet or room made or lined with glass, rubber, or resistant plastics. The Corrodkote test involves applying a corrosive slurry to parts and exposing them to high, controlled humidity in a suitable chamber or cabinet; the slurry is formulated to simulate road mud containing corrosive salts. The CASS and Corrodkote tests were developed to control the quality of decorative, electrodeposited nickel-chromium-plated parts for exterior automotive use under severe conditions of corrosion and abrasion. CASS and other corrosion test requirements are specified in ASTM B 456 for nickel-plus-chromium coatings applied to steel, zinc alloys, or copper alloys. Similar information for nickel-plus-chromium coatings on plastics is given in ASTM B 604.

Ductility testing is used in decorative nickel plating to test that the percent elongation of semibright nickel deposits is greater than 8, and to verify that bright nickel solutions are in good working condition. The simple test described in ISO 1456 and in ASTM B 489 is based on bending a test strip of the deposit over a mandrel of specified diameter until the two ends of the strip are parallel. Other tests based on hydraulic or mechanical bulge testing are available. The percent elongation can also be determined by traditional mechanical testing by machining a test sample from relatively thick electroformed nickel and subjecting it to a tensile test. Because ductility is affected by the thickness of the coating, ductility should be measured at the actual thickness specified in a specific end use.

Other useful tests described in ASTM standards include adhesion (B 571), internal stress measurements with the spiral contractometer (B 636), and microhardness testing (B 578), among others.

Nickel Anode Materials

Most nickel plating processes are operated with soluble nickel anode materials. Nickel from the anode is converted into ions that enter the plating solution to replace those discharged at the cathode. In addition, the anode distributes current to the parts being plated and influences metal distribution.

The simplest way to satisfy anode requirements is to suspend nickel bars from hooks placed on an anode bar so that the nickel, not the hook, is immersed in the plating solution. Nickel anode materials are encased in cloth anode bags to prevent insoluble anode residues from entering the solution and causing roughness at the cathode. The use of bars or electrolytic nickel strip is still practiced but has been supplanted in most regions of the world by the use of titanium anode baskets. The baskets used in nickel plating are generally made of titanium mesh strengthened by solid strips of titanium at tops, bottoms, and edges. The baskets are encased in cloth anode bags, suspended on the anode bar by hooks that are an integral part of the baskets, and loaded with small pieces of nickel. The mesh facilitates the free flow of plating solution. Baskets that incorporate hoppers at the tops facilitate basket loading and help prevent pieces of nickel from falling into the tank.

Titanium anode baskets were quickly accepted because of their many advantages. The basket anode is large and unchanging, ensuring a uniform anode area giving constant current distribution and consistent thickness for repeat batches of the same work. Anode maintenance involves topping-up the load to keep the baskets filled. Conforming baskets can be made in virtually any size and shape. The anode-to-cathode distance can be made constant, thereby contributing to good current distribution. Lowest-cost, primary forms of nickel can be used to fill the baskets. Baskets can be semiautomatically or automatically filled with nickel, and that practice is growing in progressive plating shops. One limitation is that titanium cannot be used in concentrated fluoborate solutions or those containing fluoride ions; small amounts of fluoride in solution activate titanium, causing it to corrode.

The available forms of nickel for titanium baskets include high-purity electrolytic nickel squares about 25 × 25 mm, pure electrolytic nickel in button-like shapes about 22 mm in diameter, and sulfur-activated, electrolytic nickel button-shape pieces about 25 mm in diameter. Other popular forms of nickel for plating with baskets are made in spherical shapes by a gas-refining process; the spherical forms are also available in sulfur-free and sulfur-containing grades.

The sulfur-activated forms dissolve relatively uniformly at high current densities and at 100% anode efficiency even in the absence of chloride ions, whereas sulfur-free forms dissolve nonuniformly and require the presence of chloride ions in solution to dissolve efficiently. The need for chloride ions is due to the tendency for pure nickel to become passive in nickel sulfate solutions. Although the tendency for passivity persists even in the presence of chlorides, the chloride ion attacks the passive oxide film that forms when current flows through the anode, and nickel can be dissolved through pits on the surface. The sulfur-containing materials do not form oxide films, and they dissolve at low anode potentials. The small amount of sulfur in the nickel lowers the surface resistance to current flow, the practical effect being to reduce power costs. The unique advantage of the spherical forms of nickel is product flowability, which facilitates automatic basket loading and filling of conforming, semicylindrical, and other complicated basket shapes.

The anode affects the quality of nickel primarily through its effect on current distribution and thickness uniformity. Most anode materials available today are made to strict specifications of purity and are unlikely to introduce significant amounts of impurities into the solution.

Environmental, Health, and Safety Considerations

Strict environmental regulations are being imposed on the plating industry worldwide. The major problem facing nickel platers is to prevent nickel and other metallic ions from entering the environment via plant effluents. The most widely used method of removing metallic elements from effluents is to precipitate nickel and other metals in sludges as hydroxides or sulfides. The solid waste is then disposed of in landfills. Because the number of landfill sites is limited, and because disposal of solid waste is expensive, the recovery of metallic elements by applying reverse osmosis, ion exchange, electrotwinning, and other methods is economically appealing. Nickel producers accept nickel-containing sludges for recycling through smelters or special plants. The recovery of metallic elements is technically possible and will become important in the future.

Environmental regulations vary from state to state. Platers need to become familiar with all applicable local regulations and comply with them. Although there was great resistance to compliance in the early 1970s, most electroplaters in the United States are complying with existing regulations. In some cases, the recycling and recovery of salts and metals, coupled with the conservation of water and energy, have led to economies in plating operations that partially offset the cost of compliance.

The adoption and enforcement of strict environmental regulations arises from concern with the possible effects of metal contaminants on human health. Although the general perception is that these health effects are completely understood, the reality is that our knowledge is extremely limited. It is only when metals are present in high concentrations and in very specific forms that they are definitely known to be toxic.

In the nickel plating shop, three types of exposure are possible: Nickel and its compounds may be inadvertently ingested, nickel-containing solutions may be allowed to remain on the skin for long periods of time, and nickel and its compounds may be taken into the body by breathing. Although nickel and its compounds are not considered acutely toxic, it is advisable to avoid ingesting even small amounts of these substances by taking some simple precautions--wearing work gloves, washing one's hands before eating, and not eating in the workplace. Some workers may develop a skin rash or dermatitis after persistent contact with nickel and its salts. People who have become so sensitized should avoid contact with nickel and its compounds. To avoid becoming sensitized, one should limit skin contact with nickel and its compounds. In the plating shop, this may mean wearing work gloves and washing one's hands immediately after coming in contact with nickel plating solutions.

On the basis of available information, enhanced risk of cancer appears to be confined to the inhalation of high concentrations of dusts containing nickel subsulfides and oxides under conditions previously existing in certain nickel refineries. Although similar health problems have not been observed in plating shops and other workplaces where nickel is found, it is recommended that precautions be taken to avoid dispersing nickel-containing dusts or sprays into the air. Airborne concentrations of nickel should be kept below the permissible exposure limits established by law. This is not only the law, but good common sense. Simple housekeeping and personal hygiene can help prevent the release of toxic substances to the environment and minimize the possible effects of metallic contaminants on human health.

Iron Plating

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Introduction

IRON has been electrodeposited for many years. One of the earliest references to iron electroplating is in Langbein's *Electrodeposition of Metals,* published in 1894 as the English translation of a German treatise. In that translation there is a reference to "Mr. Alfred Smee (who made) many discoveries in the deposition of antimony, platinum, gold, silver, iron, copper and zinc. In publishing his experiments, in 1841, he originated the very appropriate term 'electro-metallurgy' for the process of working in metals by means of electrolysis" (Ref 1). A paper published in 1930 was titled "The Production of Electrolytic Iron Printing Plates" (Ref 2). It appears, though, that the largest body of published papers and patents were written in the 1950s and 1960s, although a small number of new papers on this topic are published every year.

Iron has been electroplated from a variety of electrolytes. These include chloride, sulfate, sulfamate, fluoroborate, sulfonate, and various combinations of these electrolytes. Perhaps the widest use of iron plating has been in electroforming, where thicknesses of 6 mm (0.25 in.) are common. The bath parameters of these electroplating solutions are as varied as the parts that are plated in them, and the resulting coatings have widely divergent characteristics according to the specific characteristics desired in the finished product.

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Advantages and Limitations

Iron is the least expensive metal available. This is partly because it makes up 5% of the earth's crust, making it second in abundance to aluminum among the metals and fourth in abundance behind oxygen, silicon, and aluminum among the elements. Iron, which largely constitutes the core, is the most abundant element in the Earth as a whole (about 35%). This abundance, plus the fact that iron is easily extracted from concentrated ore sources, is what makes it so inexpensive. In addition, the human body contains approximately 4.5 g of iron. The average adult human requires 10 to 20 mg of dietary iron each day to maintain good health. This human requirement, coupled with the vast abundance of iron around us, makes iron an unlikely candidate for environmental controls, at least on the metal itself. Also, the physical properties of the deposited metal can be altered very easily by adjustments in electrolyte, temperature, pH, and addition agents. The ability to "design" a coating to meet a specific need, coupled with the environmental friendliness of iron, has caused a recent upsurge in interest in this electrodeposited metal.

The primary limitations of iron electrodeposition are the innate corrosion properties that affect all iron and steel, although electrodeposited iron appears to be more corrosion resistant than ordinary iron, probably because of its higher purity. Even with better resistance, a protective coating of some kind must be applied to the deposit to prevent corrosion.

An additional limitation seems to be obtaining consistent properties from one batch of parts to another. There is evidence that iron baths function best when they are run in a full production mode. Intermittent operation creates problems in restoring the electrolyte to proper operating condition. Many baths are highly corrosive to ordinary equipment. Pitting and roughness can be a problem if the bath is not controlled properly. Extreme brittleness can result from the presence of codeposited hydrated Fe(III) or Fe(II) oxide as well as codeposition of organic additive breakdown products.

Principal Applications

Today the principal applications for electrodeposited iron are in the production of solder gun tips, the electroplating of iron onto aluminum automobile engine parts, and the electroforming of iron foils for certain magnetic applications. In the past there was a large market for electroformed stampers, engraving plates, and textile rollers, but these iron applications have been almost totally replaced by nickel plating. However, as environmental concerns about nickel increase, a return to iron plating will become increasingly probable. Interest is increasing in the use of nickel-iron alloys containing up to 40% Fe as a substitute for the more expensive and potentially toxic nickel deposits.

Process Description

Table 1 shows some typical iron plating bath parameters. It should be noted that the addition of various organic additives can change the properties of the deposit to a high degree. These are addressed in the Section "Properties of the Deposited Materials and Modified Surfaces" in this article.

Table 1 Typical iron plating solutions

Bath type	Composition	pH	Temperature, °C	Current density

	Component	g/L	Molarity		°C	A/m^2	A/ft^2
Sulfate	Fe^{++}	48	0.86	2.8-3.5	32-65	215-430	20-40
	(a)	240	0.86				
Double sulfate	Fe^{++}	36-51	0.64-0.92	2.5-3.5	24-65	215-645	20-60
	(b)	250-400	0.64-1.2				
Chloride	Fe^{++}	84-125	1.5-2.25	0.5-1.0	85 min	215-1075	20-100
	(c)	300-450	1.5-2.25				
	(d)	300	2.7				
Sulfate-chloride	Fe^{++}	60	1.08	2.5-3.5	27-70	215-540	20-50
	(a)	250	0.9				
	(c)	36	0.18				
	(e)	20	0.37				
Fluoborate	Fe^{++}	55	1	3.0-3.5	57-63	430-970	40-90
	(f)	227	1				
	(g)	10	0.17				
Sulfamate	Fe^{++}	75	1.35	2.5-3.5	60 max	215-430	20-40
	(h)	30-38	0.25-0.32				
Sulfonate	Fe^{++}	150	2.7	1.2-1.8	60-82	430-860	40-80
	(g)	50	0.81				
	(i)	275	2.7				

(a) Ferrous sulfate (7-hydrate).

(b) Ferrous ammonium sulfate (6-hydrate).

(c) Ferrous chloride (4-hydrate).

(d) Calcium chloride.

(e) Ammonium chloride.

(f) Ferrous fluoborate.

(g) Sodium chloride.

(h) Ammonium sulfamate.

(i) Ferrous sulfonate

In addition, there are many baths that have been reported for both the electrolytic and electroless deposition of iron alloys. Alloys are attracting more interest as replacements for nickel, but this chapter will address only electrodeposited pure iron deposits.

Processing Equipment

Because many of the electrolytes used in iron plating are very corrosive, it is necessary to choose the most corrosion-resistant materials for the processing equipment. This means at least a lined steel or stainless steel tank. However, considering the potential problems with liners, it is advisable to have tanks made out of polypropylene. The high temperatures of some of the baths make polyethylene a poor choice for tank construction.

Filters should be chlorinated polyvinyl chloride or polypropylene. Magnetically coupled pumps do not work well because of the high molar concentration of most of the solutions. Centrifugal pumps require seals, which do not hold up well in hot acidic solutions. In-tank pump and filter assemblies are highly recommended because any solution that leaves the tank and dries leaves a red-brown stain that can be a major problem in maintaining good housekeeping. There should be provision for regular carbon treatment. Care must be exercised to prevent the pump from aspirating air that aggravates the problem of oxidation.

Agitation can be mechanical or provided by the pump and filter. Air agitation should not be used because it will increase the oxidation of the ferrous to ferric iron that causes brittle, dark deposits.

Heaters should be Teflon-covered titanium except for those to be used in fluoroborate baths, which should be Teflon-coated stainless steel. Steam-heated tanks usually do not get enough for baths with higher temperatures, but they are acceptable for lower-temperature baths.

Anodes should be pure electrolytic iron (often called ARMCO iron) and should be bagged with glass fiber (except in fluoborate solutions) or Dynel anode bags to retain the sludge that comes from the anodes. In certain cases low-carbon steel anodes can be used, but these can cause incorporation of carbon into the deposit, which could cause the deposit to be very hard. This could be a problem if one of the required deposit characteristics is low hardness.

Properties of the Deposited Materials and / or Modified Surfaces

Table 2 shows some of the characteristics of deposits produced in various baths. It also shows a few instances where postplate heat treatment was used to change the stress characteristics of a deposit and some of the changes that additives can make in a deposit.

Table 2 Properties of electrodeposited iron coatings

Basic bath	Additives	Ultimate tensile strength		Elongation, %	Hardness, HV
		MPa	ksi		
Sulfate	None	572-614	83-89	3.0-3.5	250
	NaCl	354	51.4	5.5	200
	Boric acid + urea	. . .	. . .	. . .	480-720
	Oxalic acid	. . .	. . .	. . .	600-615
	NaCl + citric acid(a)	. . .	. . .	. . .	1000-1100
Double sulfate	NaCl + antioxidant	. . .	. . .	. . .	600-700
Chloride	None	421-434	61-63	5.0-18.0	<100
	NaCl	448-593	65-86	4.0-18.0	150-530
	Glycerol	786-883	114-128	. . .	360-380
Sulfate-chloride	Amidopyrine(b)	. . .	. . .	. . .	500-750
Fluoborate	Boric acid	. . .	. . .	. . .	575
Sulfamate	Formic acid(c)	676-1068	98-155	. . .	1200-1500
Sulfonate	Antioxidant 15 g/L	. . .	. . .	. . .	650-750
	Antioxidant 1.5 g/L	. . .	. . .	. . .	350-400

(a) Properties are for parts stress relieved by heat treatment for 1 h at 250 °C (480 °F).

(b) Properties are for parts stress relieved by heat treatment for 2 h at 200-300 °C (392-572 °F).

(c) Properties are for parts stress relieved by heat treatment for 24 h at 190 °C (374 °F).

Other additives can be used in various combinations with various baths. Organic additives (acetic acid, arginine, dextrin, glycerin, glycine, saccharin, sugar, and thiourea) are grain refiners as a general rule. They induce stress by the inclusion of their breakdown products in the coating. Inorganic additives (manganese chloride and potassium chloride) increase conductivity. A wetting agent (sodium lauryl sulfate) can be used to reduce pitting. The additive characteristics overlap each other and can change with current density, temperature, pH, and concentration.

References cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

4. S.T. Packman, unpublished data

Environmental Considerations

Iron metal does not pose any special waste disposal considerations unless associated radicals are hazardous (Ref 3). In fact, most publicly owned treatment works (POTWs) like to see iron introduced into the sewer system because it acts as a "getter" for the sulfides in the system, thereby reducing the hydrogen sulfide that can form. The only waste treatment required for iron baths is the adjustment of the pH to a value within the operating range specified in a facility's waste disposal permit. The only exception to this rule is the fluoroborate bath, which could introduce fluorides to the waste disposal system. Most POTWs have fluoride limits that have to be considered when designing a waste disposal system. Boron also has limits in some geographical areas. Local permitting agencies can provide detailed information. Compared to other metal finishing operations, iron is very easy to keep in compliance.

Reference cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

Health and Safety Considerations

As in all metal finishing operations, good judgment should be exercised when operating an iron plating bath. Eye protection, clothing protection, and gloves should be used. Most of the baths are highly corrosive and can have detrimental effects on surrounding equipment. This is especially true of the chloride and fluoroborate baths. High corrosion potentials coupled with current efficiencies in the range of 82 to 87% probably indicate that air emission equipment is necessary. The sulfate, sulfamate, and sulfonate baths are less corrosive and, even though they run at low pH, should require only general ventilation equipment.

Cadmium Plating

Revised by Milton F. Stevenson, Sr., Anoplate Corporation

Introduction

Electrodeposits of cadmium are used to protect steel and cast iron against corrosion. Because cadmium is anodic to iron, the underlying ferrous metal is protected at the expense of the cadmium plate even if the cadmium becomes scratched or nicked, exposing the substrate.

Cadmium is usually applied as a thin coating (less than 25 μm or 1000 μin. thick) intended to withstand atmospheric corrosion. It is seldom used as an undercoating for other metals, and its resistance to corrosion by most chemicals is low.

Besides having excellent corrosion protective properties, cadmium has many useful engineering properties, including natural lubricity. When corrosion products are formed on cadmium-electroplated parts, they are not voluminous, and there is minimal change in dimension. These two properties are responsible for the wide use of cadmium on moving parts or threaded assemblies.

Cadmium has excellent electrical conductivity and low contact resistance. Noncorrosive fluxes can be used to produce top-quality soldered sections. Steel that is coated with cadmium can be formed and shaped because of the ductility of the cadmium. Malleable iron, cast iron, powdered metals, and other hard-to-plate surfaces can be coated with cadmium, and materials used for adhesives bond very well to cadmium-coated surfaces.

Cadmium is highly toxic, and health, safety, and environmental concerns are driving the reduction or elimination of its use for many applications. See the section "Toxicity of Cadmium" in this article and the article "Cadmium Elimination" in this Volume for more information.

Plating Baths

Most cadmium plating is done in cyanide baths, which generally are made by dissolving cadmium oxide in a sodium cyanide solution. Sodium cyanide provides conductivity and makes the corrosion of the cadmium anodes possible.

Cyanide Baths. Compositions and operating conditions of four cyanide baths are given in Tables 1(a) and 1(b). Note that for each of these baths a ratio of total sodium cyanide to cadmium metal is indicated; maintenance of the recommended ratio is important to the operating characteristics of the bath.

Table 1(a) Compositions of cadmium plating cyanide solutions

Solution No.	Ratio of total sodium cyanide to cadmium metal	Composition[(a)]									
		Cadmium oxide		Cadmium metal		Sodium cyanide		Sodium hydroxide[(b)]		Sodium carbonate[(c)]	
		g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	4:1	23	3	19.8	2.62	78.6	10.4	14.4	1.90	30-75	4-10
2	7:1	23	3	19.8	2.62	139	18.4	14.4	1.90	30-45	4-6
3	5:1	26	3.5	23.1	3.06	116	15.3	16.6	2.19	30-60	4-8

(a) Metal-organic agents are added to cyanide solutions to produce fine-grain deposits. The addition of excessive quantities of these agents should be avoided, because this will cause deposits to be of inferior quality and to have poor resistance to corrosion. The addition of these agents to solutions used for plating cast iron is not recommended.

(b) Sodium hydroxide produced by the cadmium oxide used. In barrel plating, 7.5 g/L (1 oz/gal) is added for conductivity.

(c) Sodium carbonate produced by decomposition of sodium cyanide and absorption of carbon dioxide, and by poor anode efficiency. Excess sodium carbonate causes anode polarization, rough coatings, and lower efficiency. Excess sodium carbonate may be reduced by freezing, or by treatment with calcium sulfate.

Table 1(b) Operating conditions of cadmium plating cyanide solutions

Solutions No.	Current density[(a)]				Operating temperature		Remarks
	Range		Average				
	A/m^2	A/ft^2	A/m^2	A/ft^2	°C	°F	
1	55-650	5-60	270	25	27-32	80-90	For use in still tanks. Good efficiency, fair throwing power. Also used in bright barrel plating
2	110-860	10-80	270	25	27-32	80-90	For use in still tanks and automatic plating. High throwing power, uniform deposits, fair efficiency. Not for use in barrel plating
3	55-970	5-90	380	35	24-29	75-85	Primarily for use in still tanks, but can be used in automatic plating and barrel plating. High efficiency and good throwing power
4	55-	5-	540	50	27-	80-	Used for plating cast iron. High speed and high efficiency[(b)]

(a) For uniform deposits from cyanide solutions, the use of a current density of at least 215 A/m^2 (20 A/ft^2) is recommended. Agitation and cooling of solution are required at high current densities.

(b) Agitation and cooling are required when current density is high (above 215 A/m^2, or 20 A/ft^2).

For still tank or automatic plating of steel, selection of a bath on the basis of cyanide-to-metal ratio depends on the type of work being plated and the results desired:

- For parts with no recesses and when protection of the basis metal is the sole requirement, Solution 1 in Table 1(a) (ratio, 4 to 1) is recommended.
- For plating parts with deep recesses and when a bright, uniform finish is required, Solution 2 in Table 1(a) (ratio, 7 to 1) is recommended.
- For all-purpose bright plating of various shapes, Solution 3 in Table 1(a) (ratio, 5 to 1) is recommended.
- For high-speed, high-efficiency plating, Solution 4 in Table 1(a) (ratio, 4.5 to 1) is recommended.

Although the use of brighteners produces maximum improvement in uniformity and throwing power (that is, the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped cathode) in Solution 3 in Tables 1(a) and 1(b), brighteners also improve these properties in Solutions 1 and 2.

Normally, the sodium hydroxide content of cyanide baths is not critical. Usual limits are 7.5 to 26 g/L (1.0 to 3.5 oz/gal); the preferred concentration for best results is 15 ± 4 g/L (2 ± 0.5 oz/gal). Sodium hydroxide contributes to conductivity and, in excess, affects the current-density range for obtaining bright plate. Analytical procedures useful in the maintenance of cyanide baths are outlined in the section "Chemical Analysis of Cyanide Cadmium Plating Baths" in this article.

In recent years, the need for pollution control of cyanide solutions has led to the development of noncyanide cadmium electroplating baths, shown in Table 2. Noncyanide baths generate little hydrogen embrittlement and are used to electroplate hardened, high-strength steels. Both the sulfate and the fluoborate baths have been used for some time as a substitute for cyanide baths, and working data are available. The fluoborate bath is characterized by high cathode efficiency, good stability, and relatively little production of hydrogen embrittlement (see the section "Selective Plating" in this article). The major disadvantage of the fluoborate bath is its poor throwing power. It is widely used in barrel plating operations. If this bath is used for still plating at high current density, air agitation is desirable. Wire and strip geometries can readily be plated in a fluoborate bath. Practically all of the other acid-type baths shown in Table 2 are supplied to electroplaters as proprietary baths. Because each proprietary bath has its own peculiarities, it is advisable to obtain all proper operating information from the supplier to obtain the desired results.

Table 2 Concentration of commercial noncyanide cadmium plating baths

Bath	Proprietary(a)		Fluoborate(b)		Acid sulfate(c)
	g/L	oz/gal	g/L	oz/gal	
Ammonium chloride	11-23	1.5-3.0	. . .	. . .	. . .
Ammonium fluoborate	. . .	. . .	60	8	. . .
Ammonium sulfate	75-115	10-15	. . .	. . .	. . .
Boric acid	. . .	. . .	27	3.6	. . .
Cadmium	4-11	0.5-1.5	95	12.6	. . .
Cadmium fluoborate	. . .	. . .	244	32.2	. . .
Cadmium oxide	. . .	. . .	. . .	. . .	7.6-11 g/L (1.0-1.5 oz/gal)

(a) Proprietary requires a current density of 22 to 160 A/m^2 (2 to 15 A/ft^2) and an operating temperature of 16 to 38 °C (61 to 100 °F).

(b) Fluoborate requires a current density of 325 to 650 A/m^2 (30 to 60 A/ft^2) and an operating temperature of 21 to 38 °C (70 to 100 °F).

(c) Acid sulfate requires a current density of 110 to 660 A/m^2 (10 to 61 A/ft^2) and an operating temperature of 16 to 32 °C (61 to 90 °F).

Brighteners. The most widely used, and probably the safest, brightening agents for cyanide baths are organics such as:

- Aldehydes
- Ketones
- Alcohols
- Furfural
- Dextrin
- Gelatin
- Milk sugar

- Molasses
- Piperonal
- Some sulfonic acids

These materials form complexes with the electrolyte in cyanide baths and influence the orientation and growth of electrodeposited crystals, resulting in the formation of fine longitudinal crystals, and hence a bright deposit. Care should be taken not to add the brighteners in too large an amount. Too much brightener can result in dullness, pitting, blistering, and general poor quality and appearance. It is difficult to remove the excess brightener. Many organic brighteners are available as proprietary materials. When these are used, manufacturers' recommendations regarding amounts and other conditions of use should be followed.

Another method of brightening consists of the use of trace quantities of metallic nickel, cobalt, molybdenum, and selenium. The concentration of these elements in the bath is much more critical than the concentration of the organic brighteners. Poor bright dipping qualities or poor ductility and corrosion resistance of the coating may result from an excess of these metals. Certain proprietary brighteners contain both metallic and organic compounds. Brighteners for the noncyanide baths are also proprietary products.

Rough or pitted deposits should not be encountered in a well-balanced, carefully operated bath. However, if the concentration of metal is too low or the ratio of metal to cyanide varies from recommended values, roughness may result. Other factors that may contribute are contamination by dust, dirt, oil, metallic particles, or soap. Excessive concentrations of sodium carbonate and too high a temperature or current density also promote surface roughness.

Pitted deposits usually are the result of metallic impurities or an excessive amount of decomposed organic addition agents. The interfering metals are antimony, lead, silver, arsenic, tin and thallium. Pitting may also result from the presence of nitrates.

Correction of roughness or pitting may require a complete solution clean-up, including removal of excess sodium carbonate, purification with zinc dust, treatment with activated carbon, and filtration.

Formation and Elimination of Carbonate. Sodium carbonate forms in the cyanide bath as a result of the decomposition of sodium cyanide and the reaction of sodium cyanide with carbon dioxide from the air. The preferred method of agitation, if used, is mechanical because air agitation accelerates the buildup of carbonates.The buildup also results from failure to keep ball anode racks full or from the use of a large area of insoluble steel anodes.

Maximum concentrations of sodium carbonate that can be present in the bath without adverse effect on operating efficiency and deposit characteristics depend on the metal content of the bath. For example, carbonate can be present in concentrations up to 60 g/L (8 oz/gal) if the metal content is 19 g/L (2.5 oz/gal), and up to 30 g/L (4 oz/gal) if metal content is 30 g/L (4oz/gal), without deleterious effects. Exceeding these concentrations results in anode polarization, depletion of the metal content of the bath, and poor, irregular, and dull deposits.

To remove carbonates, the preferred method is to freeze them out by reducing the temperature to 1 to 3 °C (35 to 40 °F) in an outside treatment tank. This lowers the solubility of the carbonates, and the resulting precipitate is allowed to settle. The next step is to pump or filter the clear solution back to the plating tank, readjust the solution based on analysis, and properly dispose of the settled precipitate and solution. It is also possible to remove carbonates by treating the solution with calcium sulfate or calcium cyanide. The equipment supplier should be consulted about which procedure should be applied. Continuous purification equipment that maintains a preset level of carbonate is now available in state-of-the-art equipment.

Purification and Filtration. Whenever it is convenient, continuous filtration is advisable. If a solution is contaminated by impurities such as copper, tin, lead, or other metals, the following treatment is recommended.

Transfer the solution to an auxiliary tank of the same size as the plating tank; stir in 0.7 to 1 kg (1.5 to 2 lb) of purified zinc dust per 400 L (100 gal). Continue to stir for about 1 h, then allow to settle for no more than 6 h. Filter through a well-packed filter. If the solution contains excess organic impurities, such as decomposed brighteners, it should be treated with activated carbon and filtered. Pumps and filter parts should be made of iron or steel for alkaline cyanide baths. The solution attacks brass or bronze, and heavy copper contamination results.

Anodes

The anode system for cadmium plating from a cyanide solution consists of ball-shape cadmium anodes in a spiral cage of bare steel (Fig. 1). The spherical shape provides a large surface area in relation to weight, without a large investment in cadmium. Ball anodes also make it possible to maintain an approximately constant anode area, and little or no anode scrap is produced. Cadmium balls are usually 50 mm (2 in.) in diameter and weigh 0.6 kg ($1\frac{1}{4}$ lb) per ball.

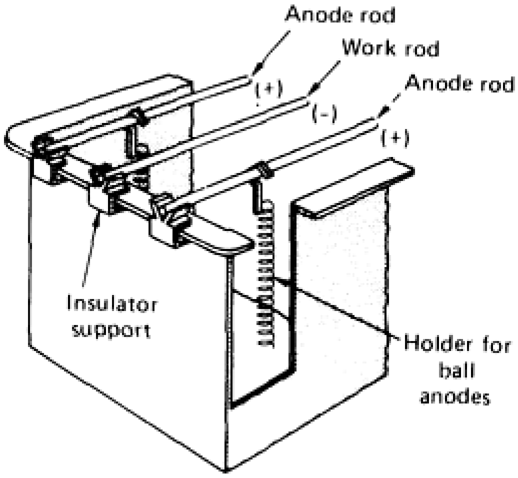


Fig. 1 Unagitated plating tank with spiral steel holders to secure cadmium ball anodes

If a cadmium cyanide solution is to be left idle for an extended period of time (a week or more), the steel anode cages should be removed from the solution, because the galvanic cell set up between the steel and the cadmium anodes will accelerate chemical dissolution of the anodes when the current is off.

When cadmium is plated from an acid solution, such as the fluoborate bath, ball anodes in uncoated steel cages cannot be used, because the steel would dissolve. Rather, bar anodes of elliptical or oval cross section, 460 to 2440 mm (18 to 96 in.) long, are used.

The use of bar anodes in a cyanide solution results in a high percentage of waste, because they must be removed and replaced when the cross-sectional area decreases, or they will dissolve preferentially at the solution level and drop to the bottom of the plating tank.

Purity of the anode is of great importance, especially if a bright deposit is to be produced. The typical composition range for cadmium anodes is as follows:

Element	**Composition, %**
Cadmium	99.95-99.97
Lead	0.008-0.03
Iron	0.005-0.008

Copper	0.002-0.01
Arsenic	0-0.001
Zinc	0-0.001

Anode composition complying with Federal Specification QQ-A-671 is:

Element(s)	**Composition**
Cadmium	99.9% min
Silver, lead, tin	0.05% max (total)
Arsenic, antimony, thallium	0.005% max

Insoluble anodes, which are made of low-carbon steel strip or wire, offer no particular advantage except where inside anodes are necessary or for special applications in which they are required because of a need to reduce metal concentration in the plating bath. When insoluble anodes are used, their total area should be 10 to 15% of the total anode area. Insoluble anodes accelerate the formation of carbonate.

Current Density

Cyanide cadmium baths may be operated over a wide range of cathode current densities, as indicated in Table 1(b). In a properly formulated bath operated within its intended current-density range, the cathode efficiency is 90% ± about 5%. Thus, to apply a 25 μ(1000 μin.) deposit of cadmium requires 120 A · h/m^2 (11 A · h/ft^2).

The ranges of current density given in Table 1(b) are suggested limiting values. Choice of current density is governed mainly by the type of work being plated; for example, low current densities are suitable for small lightweight parts, current densities up to 430 A/m^2 (40 A/ft^2) for medium-weight parts of fairly uniform shape, and high current densities for uniformly shaped heavy parts such as cylinders and shafts.

Baths containing 19 g/L (2.5 oz/gal) of cadmium are suitable for general use at current densities up to 270 A/m^2 (25 A/ft^2); higher concentrations of cadmium, up to 38 g/L (5 oz/gal), permit operation at higher current density.

A bath containing 19 g/L (2.5 oz/gal) of cadmium is suitable for barrel plating, where average current density may be about 55 A/m^2 (25 A/ft^2). Such a bath is also suitable for many still tank or automatic plating applications in which current densities do not exceed 270 A/m^2 (25 A/ft^2). At higher current densities, burning may result, with attendant dull, rough deposits that lack decorative and protective qualities. Where higher current densities are required, baths of higher metal content should be used.

Too low a current density (less than 55 A/m^2, or 5 A/ft^2) particularly in still tank or automatic plating, can result in excessively long plating times and inferior appearance of deposits.

The recommended range of current densities for plating with a fluoborate bath is 320 to 650 A/m^2 (30 to 60 A/ft^2). Even near 650 A/m^2 (60 A/ft^2), however, the bath has poor throwing power.

Deposition Rates

Among plating baths used commercially to deposit common metals (other than precious metals), cadmium cyanide baths are high in both throwing and covering power; only alkaline tin and cyanide copper have greater throwing power. Based on Haring-Blum cell measurements, the throwing power of cadmium cyanide baths is rated between 40 and 45%, with a distance ratio of 5. Therefore, the distance between the anode and the work is not critical, although as the distance is increased, current density and efficiency decrease, and current distribution is altered.

Table 3 lists the times required to plate cadmium deposits from 3 to 18 μm (120 to 720 μin.) thick. These times are predicated on 90% cathode efficiency.

Table 3 Time for plating cadmium to a given thickness at various current densities

Data based on 90% cathode efficiency, in a cyanide bath

Thickness of plate		**Plating time in minutes at current density specified**					
μm	**μin.**	**54 A/m^2 (5 A/ft^2)**	**110 A/m^2 (10 A/ft^2)**	**160 A/m^2 (15 A/ft^2)**	**215 A/m^2 (20 A/ft^2)**	**270 A/m^2 (25 A/ft^2)**	**325 A/m^2 (30 A/ft^2)**
3	120	13.0	6.5	4.3	3.2	2.6	2.2
5	200	26.0	13.0	8.6	6.4	5.2	4.4
8	320	39.0	19.5	13.9	9.6	7.8	6.6
10	400	52.0	26.0	18.2	12.8	10.4	8.8
13	520	65.0	32.5	22.5	16.0	13.0	11.0
15	600	78.0	39.0	25.8	19.2	15.6	13.2
18	720	91.0	45.5	30.4	22.4	18.2	15.4

Bath Temperature

Typical operating temperature ranges for cyanide baths are given in Table 1(b). Data for noncyanide baths are shown in Table 2. In general, satisfactory plating results are obtained by controlling bath temperature within ±3 °C (±5 °F) during plating. When greater precision is required, temperature should be controlled within ±1 °C (±2 °F).

Plating Equipment

Considerations specific to the operation of cadmium cyanide baths in conventional plating equipment are discussed here, with attention to the materials of construction used.

Still Tanks. Usually, unlined steel tanks are used for alkaline cadmium plating; however, steel tanks with plastic linings are useful in preventing stray tank currents. Another advantage is that lined tanks may satisfy the diking requirements of the Occupational Safety and Health Administration (OSHA). Double tanks and containment berms must be considered with the current regulations. Rubber and plastics used for tank linings should be tested for compatibility with the plating bath, to prevent contamination from constituents of the lining. Vinyl plastisols are compatible, commercially available, and require no further testing.

Filters and cooling coils may also be made of steel. Equipment for fume control should be used; such equipment in some cases is required by local ordinances. A typical tank arrangement is shown in Fig. 1. Equipment for baths other than the cyanide must be made acid-resistant.

Barrels may be made of hard rubber, polypropylene, acrylic resins, phenol-formaldehyde or melamine-formaldehyde laminates, or expanded or perforated sheet steel coated with vinyl plastisol. The plastisol coating is about 3.2 mm ($\frac{1}{8}$ in.) thick and is resistant to the standard barrel plating solutions and temperatures. Usually, doors and wall ends are of the same material.

Perforated cylinders for oblique barrels also have perforated bottoms and are made of the same materials used for perforated cylinders of horizontal barrels.

Anodes used for barrel plating may be bar- or ball-shape. For maximum current density, the anodes are curved to shorten the path of the current. Curved solid anodes are placed on insulated supports, whereas anode balls are placed in curved holders tied together at the lower ends.

Figure 2 illustrates schematically the use of barrel equipment for cadmium plating. Although not shown in the illustration, barrel installations are equipped with plate coils to remove the excess heat caused by the high current used in the plating bath.

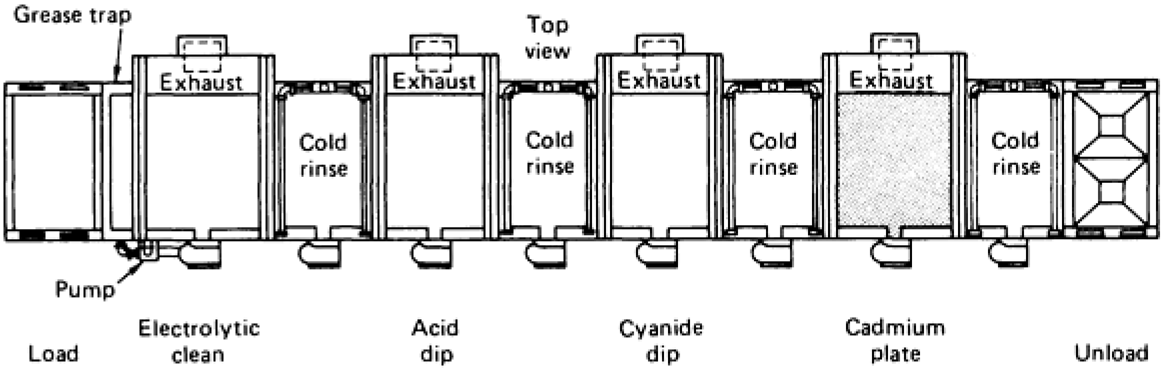


Fig. 2 Schematic showing cadmium plating installation that incorporates the barrel method

Automatic plating machines may be of either the straight-line or the return type. In straight-line plating machines, the work is loaded at one end, carried through the various phases of the cleaning and finishing cycles, and unloaded at the opposite end. Such a machine is considered a heavy-duty unit, because it can be designed for large racks and heavy loads.

Loading and unloading of the return machine is performed in the same area; the work follows an elliptical path, as indicated by the schematic layout of Fig. 3. This unit can be designed for either light or heavy loads.

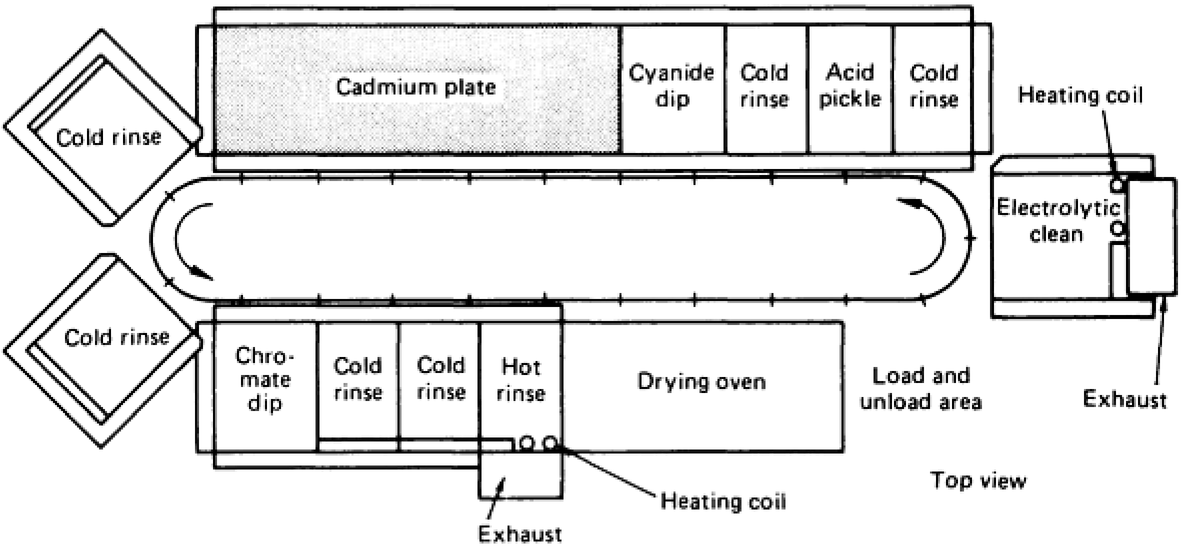


Fig. 3 Schematic showing process sequence for automatic cadmium plating installation

Both types of automatic machines may be continuous, with the work load in constant motion, or intermittent, in which case the motion of the carriers stops for a predetermined time after the work is immersed in each solution.

Power for cadmium plating is provided by rectifiers, which can be of silicon-controlled-rectifier (SCR) thyristor or tapswitch type. If the SCR type is used, attention should be paid to reducing ripple through a filter choke. This is necessary because bright cadmium is sensitive to a high-ripple current, which produces a dull finish on coatings plated in the medium- and high-current density range.

The rectifier elements are silicon. SCR rectifiers offer the advantage of remote control, finer control, computer interface, and constant current-voltage availability. Tap switch rectifiers offer the advantage of lower cost and eliminate the need for ripple filter chokes.

Rinse Tanks. Although longer tank life will be obtained if rinse tanks are lined or coated with polyvinyl chloride or rubber, all rinsing, with the exception of the rinse following hydrochloric acid pickling, may be done in unlined steel tanks. The use of unlined steel tanks for rinsing following pickling or acid plating is not recommended.

Racking of parts for cadmium plating is subject to the same considerations as in the electrodeposition of other metals. Information on design and use of plating racks is available in the article "Industrial (Hard) Chromium Plating" in this Volume.

Maintenance. Table 4 is a typical schedule of maintenance for plating and auxiliary equipment.

Table 4 Recommended maintenance schedule for plating and auxiliary equipment

Daily Check anodes; replenish when necessary. Check all contacts, anode and cathode. Check solution levels. Check bath temperatures and controls. Check bath composition, if possible, using chemical analysis and plating cell test., Probe tank bottom for lost parts. Check motors for signs of overheating, arcing, or failure. Check amperage and voltage to work.

Check lubrication on automatic equipment.

Weekly

Probe tank bottom for lost parts, if not checked daily.
Check rubber tank linings for damage.
Filter plating bath, unless constant filtration is used.
Check bath analysis, chemically and with plating cell, and make additions and corrections, if these functions are not performed more frequently.
Oil equipment.
Clean all contacts.
Check for preventive-maintenance items that cannot be repaired during the week.
Dump and replenish cleaning lines where necessary

Monthly

Pump plating solution to purification tank; treat for impurities, if necessary.
Inspect tank linings while plating tanks are empty; repair if necessary.
Inspect and clean heat exchangers or plate coils if accumulation or buildup exists.
Blow out and check rectifier stacks for condition and power delivery.
Check for arcing or scored armatures on generators. Blow out coils.
Perform general preventive maintenance examination of all equipment.

Semiannually

Clean out exhaust systems.
Repair exhaust fans.
Check all motors.
Repaint where necessary.
Inspect and clean out all floor drains.
Check for leaks and cross connections between cyanide and acid drains.
Check all items usually covered on annual or semiannual overhaul, such as solenoid valves, limit switches, relays, and automatic electrical equipment.

Selection of Plating Method

Selection of plating method involves both technical and economic factors. Still plating, with parts racked, is the oldest and most universally used plating method. Barrel plating, limited to smaller parts that can be tumbled in the plating bath, is popular because many parts can be plated at one time. Automatic hoist units offer a means of mechanizing the still-tank rack or the barrel.

Still tanks are suitable for all types of work. They are used for small production quantities, in general, and for all quantities of parts that cannot be plated in barrel or automatic systems, because of a need for auxiliary anodes or special handling or because plating dimensions are critical.

Example 1: Cadmium Plating of Valve Bodies and Baffle Plates in Still Tanks.

Valve bodies and baffle plates are typical of many parts that are plated in still tanks (see Table 5). To cadmium plate the production quantities of these parts given in Table 5, the equipment required is:

Equipment	Specification
Plating tank (1440 L, or 380 gal)	2.7 by 0.76 by 0.76 m (9 by $2\frac{1}{2}$ by $2\frac{1}{2}$ ft)
Other tanks (420 L, or 110 gal)	0.91 by 0.76 by 0.76 m (3 by $2\frac{1}{2}$ by $2\frac{1}{2}$ ft)
Power rectifier (600 A)	1.5 to 6 V
Dimensions of rectifier	0.76 by 0.91 by 2.1 m ($2\frac{1}{2}$ by 3 by 7 ft)
Total floor space of equipment and access area	2.0 by 4.6 m ($6\frac{1}{2}$ by 15 ft)
Number of racks	15

Other tanks include a cleaning tank, an acid pickle tank, a hot-water rinse tank, and three cold-water rinse tanks.

Table 5 Equipment requirements for cadmium plating of valve bodies and baffle plates in still tanks

Production requirements	Valve body	Baffle plate
Weight per piece	1.1 kg ($2\frac{1}{2}$ lb)	0.2 kg (0.5 lb)
Pieces plated per hour	210	175
Area plated per hour	6.5 m^2 (70 ft^2)	11.1 m^2 (120 ft^2)
Minimum thickness	8 µm (320 µin.)	4 µm (160 µin.)

Barrel plating may be used for parts up to 100 mm (4 in.) long and 50 mm (2 in.) thick. Parts such as machine bolts, nuts, and washers are ideal for barrel plating. Conversely, intricate shapes, such as ornaments and complex castings of brittle metals with small sections that fracture easily, should not be barrel plated; the tumbling action may damage these parts, and variation in plating thickness and appearance may result. Intricate designs incorporating recessed or shielded areas may present problems in plating coverage, luster, and appearance. Barrel plating is not applicable for parts requiring heavy plate. Usually, 8 to 13 μm (320 to 520 μin.) is the maximum thickness of plate applied.

Example 2: Barrel Plating of Small Coil Springs and Brush Holders.

Small coil springs and brush holders are illustrative of parts suitable for barrel plating. Production requirements for plating these parts in horizontal barrels are given in Table 6. Equipment specifications are as follows:

Equipment	**Specification**
Plating tank (1330 L, or 350 gal)	1.8 by 1.2 by 0.76 m (6 by 4 by $2\frac{1}{2}$ ft)
Other tanks (605 L, or 160 gal)	0.91 by 1.2 by 0.76 m (3 by 4 by $2\frac{1}{2}$ ft)
Power rectifier (2000 A)	9 to 15 V
Dimensions of rectifier	0.91 by 1.2 by 2.4 m (3 by 4 by 8 ft)
Centrifugal dryer	0.61 by 0.61 by 0.76 m (2 by 2 by $2\frac{1}{2}$ ft)
Baking oven	1.2 by 0.91 by 2.4 m (4 by 3 by 8 ft)
Equipment floor space	12 m^2 (125 ft^2)
Access area behind line	6.3 m^2 (68 ft^2)
Access area in front	9.3 m^2 (100 ft^2)

Other tanks in the list above refer to cleaning tanks, acid pickle tanks, hot-water tanks, and three cold-water rinse tanks.

Table 6 Production requirements for cadmium plating of coil springs and brush holders in a horizontal barrel

Production requirements	**Coil spring**	**Brush holder**

Weight per piece	14 g ($\frac{1}{2}$ oz)	9 g ($\frac{5}{16}$ oz)
Pieces plated per hour	7200	3800
Area plated per hour	22 m^2 (240 ft^2)	17 m^2 (180 ft^2)
Minimum thickness	4 μm (160 μin.)	8 μm (320 μin.)

Automatic Plating. The primary selection factor for automatic plating is cost. The volume of work must be sufficient to warrant installation of the equipment.

Example 3: Cadmium Plating of Voltage-Regulator Bases on Automatic Equipment.

Voltage-regulator bases were cadmium plated, to a minimum thickness of 3.8 μm (152 μin.), in automatic equipment at the rate of 2640 pieces/h.

Production requirements:

Factor	**Specification**
Weight per piece	170 g (0.37 lb)
Pieces plated per hour	2640
Area to be plated per hour	53 m^2 (570 ft^2)
Minimum plate thickness	4 μm (160 μin.)

Equipment requirements:

Factor	**Specification**
Dimensions of full automatic plating unit	21 by 3.4 by 2.8 m(70 by 11 by 9 ft)
Width of access space on sides of unit	0.76 m (3 ft)

Width of access space on load end of unit	3.1 m (10 ft)
Motor-generator set	15 V, 7500 A
Dimensions of motor-generator set	3.1 by 3.1 by 2.4 m(10 by 10 by 8 ft)

Example 4: Cadmium Plating of Electrical-Outlet Receptacles with Automatic Equipment.

A quantity of 12,000 to 14,000 electrical-outlet receptacles per eight-hour day were required in order to justify the use of a small automatic plating system of 3800L (1000 gal) solution capacity with a single lane of rods and workpieces and plating 4 to 5 μm (160 to 200 μin.) of cadmium. When the size and shape of the parts are such that either automatic or still-tank plating processes may be used, the racking requirement is often the most important factor in determining the relative economy of still-tank and automatic plating. Two kinds of automated plating equipment are available, the regular return machine and the programmed hoist unit, which is an automated straight-line unit. The latter equipment is much less expensive to purchase.

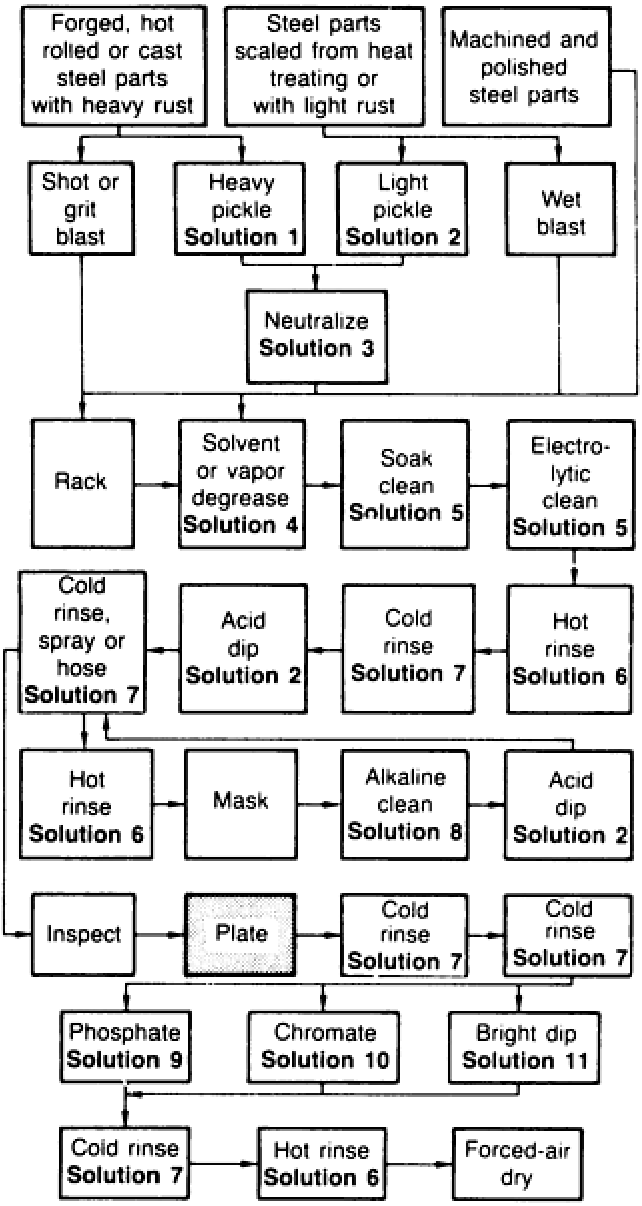
Cleaning and rinsing are essential operations in any plating sequence. Figures 2 and 3 show the number of tanks or stations required for such operations in typical barrel and automatic processes. In Fig. 4, where cleaning, rinsing, and postplating operations are indicated for various initial conditions of the work surface, the plating step itself is a rather inconspicuous item in the flow chart of the total finishing process. Table 7 shows variations in processing techniques for still-tank, barrel, or automatic plating to a thickness of less than 13 μm (520 μin.).

Table 7 Conditions for plating cadmium to a thickness of less than 13 μm (520 μin.)

Process variable	**Still tank**	**Barrel**	**Automatic**
Soak cleaning			
Alkali, g/L (oz/gal)	53 (6)	106 (12)	70 (8)
Temperature, °C (°F)	82 (180)	82 (180)	82 (180)
Time, min	2-3	5	3-5
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Electrolytic cleaning			
Alkali, g/L (oz/gal)	70 (8)	. . .	70 (8)

Temperature, °C (°F)	82 (180)	. . .	82 (180)
Time, min	$\frac{1}{2}$-1	. . .	1-3
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Acid dipping			
HCl, vol%	10-50	10-50	10-50
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{8}$-1	3	$\frac{1}{2}$ to >1
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Cyanide dipping			
NaCN, g/L (oz/gal)	30-45 (4-6)	30-45 (4-6)	30-45 (4-6)
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Plating			
Temperature, °C (°F)	29 (85)	29 (85)	29 (85)

Current density, A/m^2 (A/ft^2)	270 (25)	9-15 V	270 (25)
Time, min	10	30	10
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	2	$\frac{1}{2}$
Bright dipping			
HNO_3, vol%	$\frac{1}{4}-\frac{1}{2}$	$\frac{1}{4}-\frac{1}{2}$	$\frac{1}{4}-\frac{1}{2}$
Temperature, °C (°F)	82 (180)	Ambient	Ambient
Time, min	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{2}$
Rinsing			
Temperature, °C (°F)	. . .	71-82 (160-180)	82 (180)
Time, min	. . .	2	$\frac{1}{2}$
Drying			
Temperature, °C (°F)	82-105 (180-220)	82-105 (180-220)	82-105 (180-220)
Time, min	1-3	5	1-3



Solution No.	Composition	Amount	Temperature		Immersion time
			°C	°F	
1	H_2SO_4	8-12 vol%	71-93	160-200	10-120 s
2	HCl	20-50 vol%	RT	RT	10-120 s
3	Na_2CO_3	75-90 g/L (10-12 oz/gal)	RT	RT	15-60 s[(a)]

4	Petroleum solvent	. . .	RT	RT	$\frac{1}{2}$-3 min
5	Alkali(b)	60-75 g/L(b) (8-10 oz/gal)	82-93(b)	180-200(b)	$\frac{1}{2}$-3 min
6	Water	. . .	82-93(c)	180-200(c)	5-15 s
7	Water(d)	. . .	RT	RT	5-15 s
8	Alkali	60-75 g/L (8-10 oz/gal)	66 max	150 max	$\frac{1}{2}$-1 min
9	(e)	(e)	(e)	(e)	$\frac{1}{2}$-1 min
10	(e)	(e)	(e)	(e)	30 s
11	NaCN	45-60 g/L (6-8 oz/gal)	RT	RT	5-15 s

Note: For cast iron, the solutions, conditions, and procedure are the same as for steel, except that cast iron parts, after being thoroughly washed in cold water following the acid dip, are dipped for 5 s in a room-temperature (RT) cyanide solution (NaCN, 45 to 60 g/L, or 6 to 8 oz/gal) and then again rinsed in cold water, before proceeding to inspection, plating, and post-treatments.

(a) When solution is sprayed, time is 5 to 15 s.

(b) Heavy-duty cleaner. For electrolytic cleaning, concentration of alkali is 45 to 60 g/L (6 to 8 oz/gal), temperature is 82 °C (180 °F), and time is 1 to 3 min.

(c) When a spray rinse is used, water temperature is 71 to 82 °C (160 to 180 °F).

(d) Immersion or spray rinsing.

(e) Proprietary compounds

Fig. 4 Flow diagram showing cadmium plating operation relative to overall cleaning and post-treatment operations for steel and cast iron components

In the case of Fig. 2, 3, and 4 and Table 7, it is important to consider double or triple overflow rinses to control both water usage and pollution control costs. The use of dead rinses, following process tanks, is equally important.

Variations in Plate Thickness

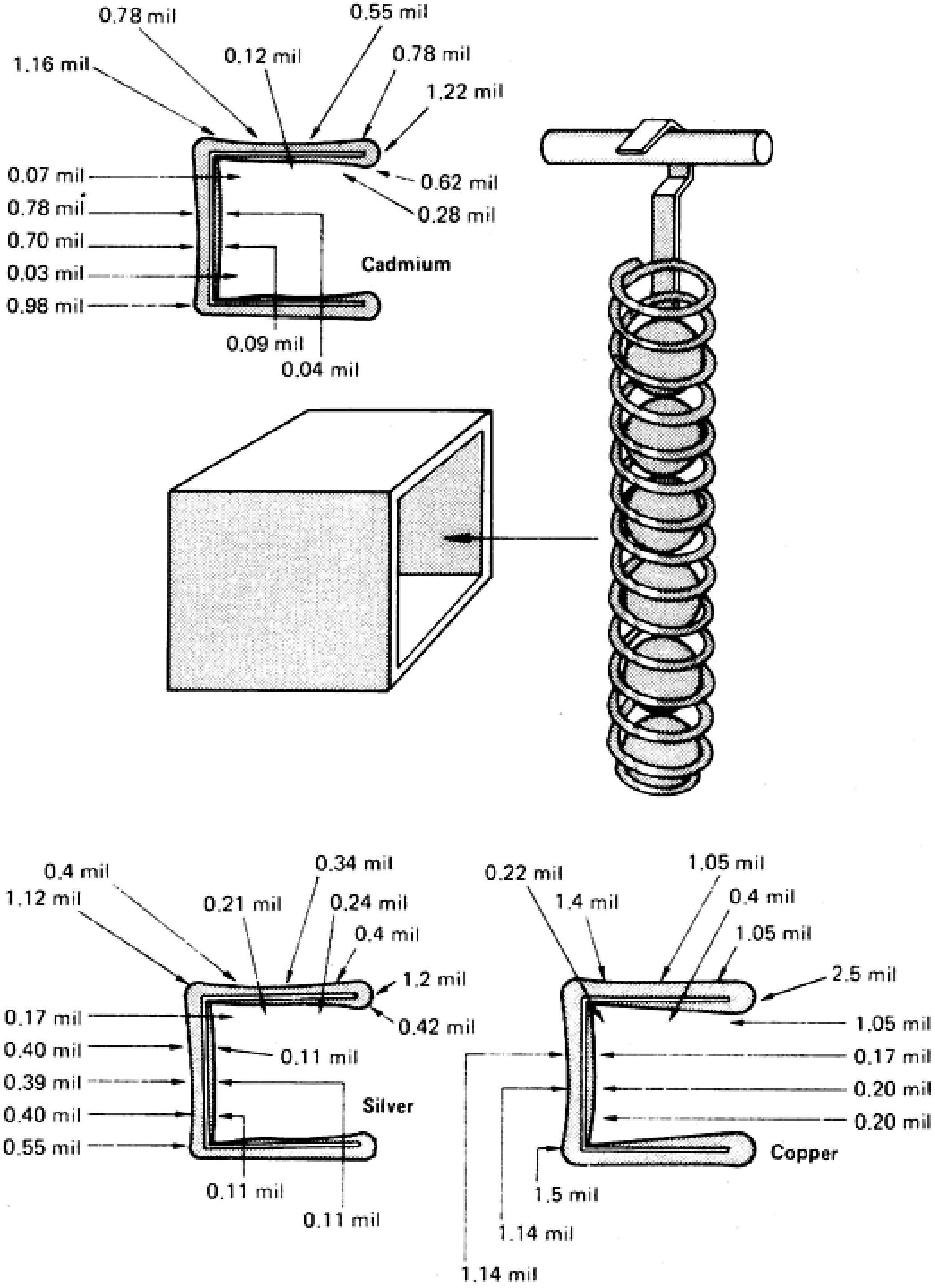
For adequate protection of steel, the thicknesses of cadmium in Table 8 are recommended. The shape of a part can markedly influence uniformity of the electrodeposit. Parts of simple design, such as socket wrenches and bathroom hardware, can be plated with a high degree of uniformity of plate thickness. On such parts, about 90% uniformity would be anticipated.

Table 8 Recommended thicknesses of cadmium

Environmental exposure	Description	Thickness		Uses
		µm	µin.	
Mild	Exposure to indoor atmospheres with rare condensation. Minimum wear and abrasion	5	200	Springs, lock washers, fasteners
Moderate	Exposure mostly to dry indoor atmospheres. Subject to occasional condensation, wear, or abrasion	8	320	Television and radio chassis, threaded parts, screws, bolts, radio parts instruments
Severe	Exposure to condensation, infrequent wetting by rain, cleaners	13	520	Washing machine parts, military hardware, electronic parts for tropical service
Very severe	Frequent exposure to moisture, saline solutions, and	25	1000	. . .

Threaded fasteners present a special problem, because of variations in contour and because of tolerance requirements. These items ordinarily are barrel plated, and thicknesses of 3 to 4 µm (120 to 160 µin.) are usually specified.

Throwing Power. The effect of shape on uniformity of deposit thickness is exemplified by the open-ended box (100 mm, or 4 in., cube) of Fig. 5. The open end of the box is pointed toward one of the anodes, to produce the most desirable condition for this shape without auxiliary thief rings, shields, bipolar anodes, insoluble anodes, or other devices. Results of plating such boxes with cadmium, silver, and copper, all deposited from cyanide baths, are shown in Fig. 5. These diagrams illustrate two facts: thickness of plate varies significantly from place to place on the simplest shape; and various plating baths have different throwing powers or abilities to plate uniformly over the surface, regardless of shape.



Plating bath	Thickness ratio(a)	
	Side	Bottom
Cadmium	1:4.25	1:12

Copper	1:3.0	1:6
Silver	1:2.5	1:5

(a) Ratio of average plate thickness of inside of average plate thickness on outside

Fig. 5 Plate thickness deposited on the cross section of a cube-shape workpiece to show throwing power of cadmium relative to that of silver or copper in a cyanide bath. Open ends of the 100 mm (4 in.) cubes were pointed toward ball anodes during plating.

The data on cyanide baths tabulated in Fig. 5 show that cadmium has appreciably less throwing power than silver or copper. However, cyanide cadmium has greater throwing power than nickel, chromium, iron, cyanide zinc, acid tin, acid cadmium, acid copper, or acid zinc. Normally, metals plated from cyanide or alkaline baths are more uniformly distributed than metals from acid baths. As design becomes more complex, uniform thickness of plate is more difficult to achieve without the use of special conforming anodes.

Example 5: Plate Thickness Variation in a Workpiece Plated without Use of Conforming Anodes.

A cylindrical, cup-shape production part that was plated without the use of conforming anodes is shown in Fig. 6. Thickness of plate varied from a minimum of 6 μm (240 μin.) to a maximum of 25 μm (1000 μin.).

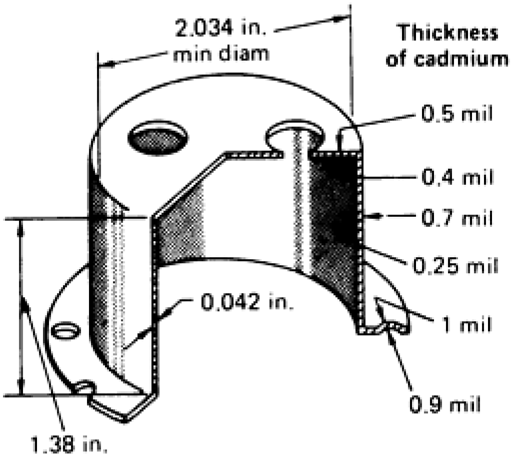


Fig. 6 Variations in plate thickness obtained on a workpiece plated without the use of conforming anodes

Conforming Anodes. Parts of complex shape with stringent dimensional requirements, such as those shown in Fig. 7 and 8, require the use of special techniques, conforming anodes, and shields, in order to obtain the required uniformity of plate thickness.

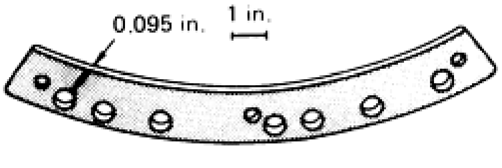


Fig. 7 Application of shields to obtain shim having a uniform cadmium plating. The 305 mm (12 in.) long and 38 mm (1 in.) wide shim was plated to the required thickness of 13 ± 5 μm (520 ± 200 μin.).

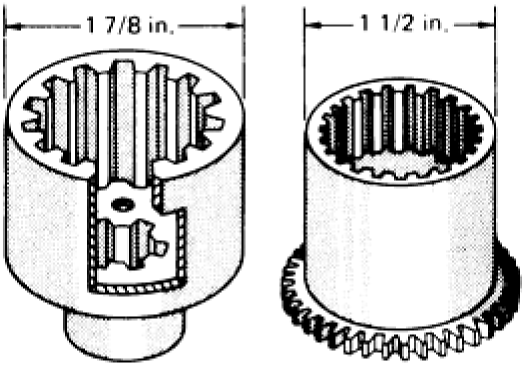


Fig. 8 Couplings that were uniformly cadmium plated with the aid of a 6.4 mm ($\frac{1}{4}$ in.) diameter anode centered in the bore during the plating operation. Plating thickness ranges from 8 to 13 μm (320 to 520 μin.).

Example 6: Application of Shields to Produce Uniform Cadmium-Plated Shim.

A shim, 305 mm (12 in.) long by 40 mm ($1\frac{1}{2}$ in.) wide by 2.4 mm (0.095 in.) thick, is shown in Fig. 7. Parallelism of all sides, as well as plate thickness, was extremely critical. When this part was plated in a simple rack, plate thickness varied from 13 μm (520 μin.) at the center to 50 to 75 μm (0.002 to 0.003 μin.) at the edges and ends.

By using shields that approximated the outline of the shim, it was possible to plate cadmium all over to a depth of 13 ± 5 μm (520 ± 200 μin.). The part was gently agitated in a still bath.

Example 7: Uniform Internal and External Cadmium Plating of Splined Couplings.

A coupling that required 8 to 13 μm (320 to 520 μin.) all over, except for the last 6.4 mm ($\frac{1}{4}$ in.) of the outside diameter of the small end, is shown in Fig. 8. The internal splines on both large and small bores were checked with plug gages and a single-tooth gage to ensure uniformity of plate thickness. To obtain the required uniformity, a 6.4 mm ($\frac{1}{4}$ in.) diameter anode was centered in the bore during plating. Although the outer surface of the large end of the coupling accumulated a heavier coating than other areas, general plate-thickness uniformity met requirements.

Example 8: Uniform Cadmium Plating of Coupling Leaving External Teeth Unplated.

A coupling that, except for the external teeth, was cadmium plated all over to a specified depth of 8 to 13 μm (320 to 520 μin.) is also shown in Fig. 8. Spline and internal bore dimensions were critical and had to be held to a tolerance of ±5 μm (±200 μin.) after plating. Again, uniformity of plate thickness was achieved by centering a 6.4 mm ($\frac{1}{4}$ in.) diameter anode in the bore during plating.

Simple cylindrical, cuboid, and channel shapes, such as those shown in Fig. 9, usually require conforming anodes in order to achieve complete coverage of plate and reasonable plating uniformity. Dimensional limits that definitely require the use of an internal anode are indicated for each geometric shape.

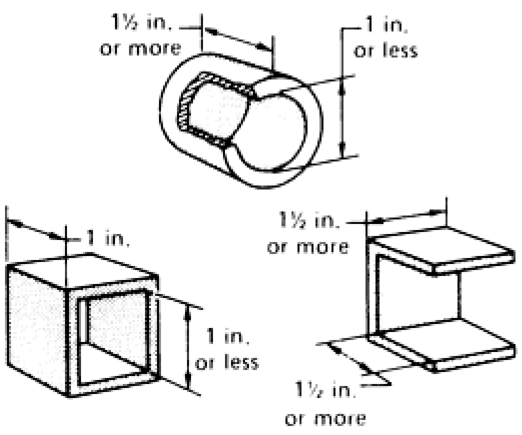


Fig. 9 Typical workpiece configurations with accompanying dimensions that require the use of conforming anodes to ensure uniform plate thickness

Normal Variations. Even under preferred production conditions, some variation in plate thickness must be anticipated. Usually, this normal scatter is acceptable and falls within the specified range of allowable variation.

In general, barrel plating produces greater variations in thickness than still plating. In barrel plating, factors such as the weight, size, and shape of the part usually exert a greater influence on uniformity of plate thickness than they do in still or automatic plating.

Screws, nuts, and other small parts of fairly regular shape will usually coat uniformly in barrel plating. Parts that are likely to nest because they have large flat areas or cup-shape recesses exhibit wide variations in coating thickness. Variations decrease somewhat as the thickness of plate increases.

Variations in plate thickness obtained on production parts are detailed in the example that follows:

Example 9: Histogram Showing Thickness Distribution of 90 Cadmium-Plated Components.

The small cylindrical part shown in Fig. 10 was plated in a horizontal barrel. The load contained about 5000 pieces. Thickness of plate was measured with a magnetic gage on 90 parts from each load. Plating thickness ranged from 5 to 14 μm (200 to 560 μin.).

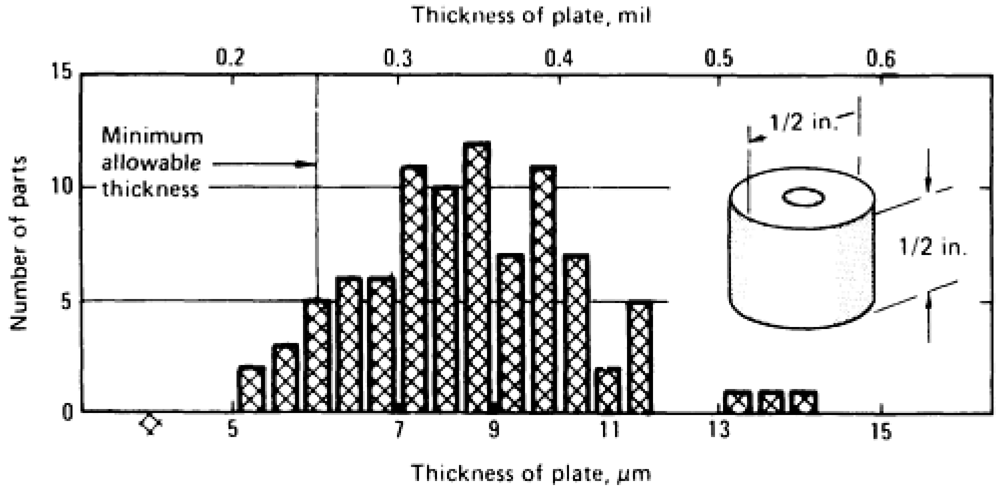


Fig. 10 Thickness distribution for cadmium plating of 90 samples that were evaluated from a 5000-piece

production lot

Other Application Factors

Aside from considerations of cost of very large plating systems, there are no size limitations on parts that can be cadmium plated, provided a tank of adequate size and other essential equipment are available. When a very large part is to be plated, jet plating methods may sometimes be used, rather than constructing a very large plating tank. In the jet technique, a steady stream of solution impinges against the part to be plated until the required thickness of plate is obtained. Because of the rapid movement of the solution, very high current densities can be used. The quality of the plate is comparable to that obtained by conventional methods.

Another technique that can be used on large parts is selective (or brush) plating. Detailed information is available in the article "Selective Plating" in this Volume.

Hardness. The hardness of the basis metal has little or no effect on the successful deposition of cadmium. However, the harder steels are likely to be more highly alloyed and may produce difficult-to-remove smuts from excessive pickling or chemical cleaning. Pickling is also a source of hydrogen embrittlement, which may be particularly harmful to hardened and stressed parts.

Springs often are electroplated with cadmium for protection against corrosion and abrasion. The following example deals with failure of a cadmium-plated compression spring that was not properly treated to release hydrogen.

Example 10: Baking of Cadmium-Plated 6150 Alloy Steel to Eliminate Hydrogen Embrittlement.

A spring used in a high-temperature relief valve under intermittent loading had dimensions and specifications as follows: wire size, 8.76 mm (0.345 in.); outside diameter of spring, 50 mm (2 in.); length, 75 mm (3 in.); six coils; 6150 alloy steel at 43 HRC; stress relieved immediately after coiling. The plating sequence was:

1. Alkaline clean.
2. Rinse in cold water.
3. Electroplate with cadmium 8 μm (320 μin.) thick.
4. Rinse in hot water.
5. Relieve hydrogen embrittlement in boiling water $\frac{1}{2}$ h.

The spring broke with a shatter fracture typical of that caused by hydrogen embrittlement. The corrective action was to bake the spring at 190 °C (375 °F) for 5 h.

For additional information on this subject, refer to the section "Hydrogen Embrittlement" in this article.

Service Temperature. Cadmium-plated, high-strength steel parts that are subjected to heavy loading should never be used at temperatures above 230 °C (450 °F). Cadmium melts at 320 °C (610 °F); at temperatures approaching 260 °C (500 °F), damage occurs that adversely affects mechanical properties.

Diffused Coatings. The aviation industry has developed an application for cadmium for low-alloy steel jet engine parts. The substrate is first plated with 10 μm (400 μin.) of nickel and then 5 μm (200 μin.) of cadmium. The alloy is diffused at 340 °C (645 °F) for about 1 h. Coverage with nickel must be complete, because cadmium can detrimentally affect the steel substrate when heated above the melting point of cadmium. In this way, an alloy with a very high melting point can be formed. Low-alloy steel parts that operate in jet engines at a temperature of 540 °C (1005 °F) were coated with this diffused alloy. After operating for 1 h at 540 °C (1005 °F), the parts withstood 100 h of salt spray without rusting. Cadmium can also be plated on copper and zinc, as well as on nickel.

Solderability. Although cadmium usually solders well with solders of the 60% tin, 40% lead type, using an inactive rosin flux, its performance may sometimes be unaccountably erratic. Solderability can be improved and made more consistent by predepositing a thin (3 to 4 μm, or 120 to 160 μin.) layer of copper. If the final cadmium deposit is at least 4 μm (160 μin.) thick, the copper coating will not adversely affect corrosion resistance in mild indoor atmospheres. It is important for health and safety reasons to see the section "Toxicity of Cadmium" in this article.

Cadmium on Stainless. Cadmium can be successfully plated over stainless steels and heat-resisting chromium-nickel alloys if the basis metal is first activated and given a light coating of nickel in a nickel chloride-hydrochloric acid bath (U.S. Patent 2,437,409). Composition and operating conditions for this bath are as follows:

Factor	**Specification**
Nickel chloride	240 g/L (32 oz/gal)
Hydrochloric acid (1.16 sp gr)	120 g/L (16 oz/gal)
Temperature	Room temperature
Current density	55 to 2150 A/m^2 (50 to 200 A/ft^2)
Time	2 to 4 min
Anodes	Nickel

Plating of Cast Iron

Cast iron is difficult to plate because of the graphite flakes or nodules in the microstructure. The larger the graphite inclusions, the more difficult the plating operation. Cast iron parts with unmachined surfaces should be cleaned by mechanical methods, such as shot blasting or tumbling, before plating. Heavy pickling should be avoided if possible, because it produces smut that is difficult to remove. However, light pickling is required after abrasive cleaning, to activate the surface for plating.

Pickling should be followed by a thorough water rinse and a cyanide dip (see note in the table accompanying Fig. 4). Any carryover of acid to the cyanide dip must be avoided, because the combination of these chemicals generates a highly poisonous hydrocyanic gas. The fluoborate solution described in Tables 1(a) and 1(b) is excellent for plating cast iron parts without deep recesses. The cyanide solutions in Tables 1(a) and 1(b) also may be used, provided no metal-organic grain-refining agents have been added. Current density on the high side of the indicated ranges is recommended, to establish a continuous film of cadmium on the iron as soon as possible.

Cadmium Versus Zinc

In rural areas, cadmium and zinc are generally considered to offer equal protection. However, zinc is superior to cadmium in industrial environments (Table 9). In uncontaminated marine atmospheres, zinc and cadmium give approximately equal protection. When the comparison is made at a distance of 24 m (80 ft) from the ocean, cadmium gives significantly greater protection than zinc. Although it is used to a limited extent in the paper and textile industries, cadmium plate has poor resistance to chemicals commonly used in these processes and also to the chemicals of the petroleum and pharmaceutical industries.

Table 9 Protection against rusting imparted to steel in selected atmospheres by 25μm (1000μin.) of cadmium plate or zinc plate

Test location	Atmosphere	Time required for 5 to 10% rusting, yr	
		Cadmium	Zinc
New York, NY	Industrial	2	4
Pittsburgh, PA	Industrial	3	4
Sandy Hook, NJ	Marine, Industrial	6	5
State College, PA	Rural	>11	>11
Key West, FL	Marine	>7	>9

Source:ASTM

One reason for preferring cadmium to zinc is that cadmium plate forms a smaller amount of corrosion products than zinc, particularly in marine atmospheres. Cadmium also retains its initial appearance for a longer time. This is an important consideration in applications where a buildup of corrosion products would have a detrimental effect, such as preventing the flow of current in electrical components or the movement of closely fitting parts such as hinges. For such applications, cadmium should be chosen in preference to zinc. Cadmium is preferable to zinc for plating cast iron.

Cadmium Substitutes

There is increased pressure, both domestically and internationally, for reduced usage, or even elimination of cadmium plating for health, safety, and environmental reasons. There have been several zinc alloy baths developed that work for specific applications, but none duplicates all the properties of cadmium. There are many instances, however, where the use of cadmium plating is not essential and zinc or zinc alloy deposits could be substituted, because both give adequate anodic protection, and there was no functional purpose when cadmium was chosen in the first place.

Chemical Analysis of Cyanide Cadmium Plating Baths

Table 10 lists analytical tests that may be applied to cyanide cadmium plating baths to determine their contents of cadmium metal, sodium cyanide, sodium hydroxide, and sodium carbonate.

Table 10 Analytical tests for determining concentration of selected chemical constituents of cyanide cadmium plating baths

Test constituent	Component			
	Cadmium metal	Sodium cyanide (total)	Sodium Hydroxide	Sodium Carbonate
Reagents	Hydrochloric or sulfuric acid (concentrated) Ammonium hydroxide (concentrated) Eriochrome black "T" indicator (0.5% solution in alcohol) Formaldehyde (8% solution in water)	Ammonium hydroxide (concentrated) Potassium iodide (10% solution in water) Silver nitrate (13 g/L, or	LaMotte sulfo-orange indicator Sulfuric acid, standard (0.94	Barium chloride (10% solution in water) Methyl orange-xylene cyanole

	Disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA), 0.575*M* solution (21.4 g/L, or 2.85 oz/gal)	1.7 oz/gal solution in water)	*N*)	indicator solution Hydrochloric acid, standard (0.7 *N*)
Procedure	1. Pipette exactly 2 mL (0.07 oz) of plating bath into a 250 mL (8.5 oz) Erlenmeyer flask, and dilute to about 100 mL (3.4 oz) with distilled water. 2. Neutralize this dilution to a faint white precipitate with hydrochloric or sulfuric acid. This can be conveniently done from the burette of standard sulfuric acid (0.94 *N* used for the caustic titration, or by the addition of a 50% solution of hydrochloric acid from an eyedropper. If no precipitate appears, as may happen with a new bath, thymolphthalein can be used as an indicator and will change from blue to colorless on neutralization. 3. Add 10 mL (0.34 oz) of concentrated ammonium hydroxide and about $\frac{3}{4}$ mL of Eriochrome indicator. 4. Zero the burette. 5. Add 8 mL (0.27 oz) of 8% formaldehyde solution. 6. Titrate immediately with EDTA solution. The color change is from red to blue, and it is sharpest when the solution is titrated as soon as possible after the formaldehyde has been added. A rapid titration will also give a sharper end point. Occasionally, the presence of impurities in the bath will prevent the attainment of a clear blue end point, but the color will prevent the attainment of a clear blue end point, but the color change is still sharp, from a red to a purplish blue.	1. Pipette a 2 mL (0.07 oz)sample of plating bath into a 250 mL (8.5 oz) flask. 2. Add to the sample about 50 mL (1.7 oz) distilled water, 5 to 7 mL (0.17 to 0.24 oz) of ammonium hydroxide, and 2 to 3 mL (0.07 to 0.10 oz) of potassium iodide solution. 3. Titrate with silver nitrate solution to the first stable faint yellowish turbidity.	1. Pipette 10 mL (0.34 oz) of the plating bath into a 250 ml (8.5 oz) flask. 2. Add to the sample about $\frac{1}{2}$ mL (0.017 oz) of indicator solution. 3. Titrate with the sulfuric acid to the color change from orange to yellow.	1. Pipette 10 mL (0.34 oz) of plating bath into a 250 mL (8.5 oz) beaker, add to it about 100 mL (3.4 oz) of water, and heat to boiling. 2. Stir into boiling bath dilution about 20 mL of barium chloride solution; cover mixture; allow to stand warm for about $\frac{1}{4}$ to $\frac{1}{2}$ h. 3. Filter, using No. 41 Whatman filter paper, and wash precipitate and flask at least 2 or 3 times with hot distilled water. 4. Place paper and precipitate in the original beaker, add about 10 mL (0.34 oz) of hot distilled water and 3 or 4 drops of indicator. 5. Titrate with the hydrochloric acid (while stirring) to the first permanent color change from green to purple.
Calculation	Milliliters of EDTA solution used × 0.432 = ounces per gallon, cadmium metal	Milliliters of silver nitrate used × 0.5 = ounces per gallon, total sodium cyanide	Milliliters of sulfuric acid used × 0.5 = ounces per gallon, sodium hydroxide	Milliliters of hydrochloric acid used × 0.5 = ounces per gallon, sodium carbonate

Methods for Measuring Thickness of Cadmium Plate

There are many nondestructive and destructive methods for measuring the thickness of cadmium deposits (Table 11). The most widely used are magnetic, coulometric, and eddy-current methods, as well as x-ray spectrometry and microscopic cross-sectioning. Other reliable methods, including the chemical drop test, may be used. Detailed information on most methods can be obtained from ASTM specification B 659-85 ("Standard Guide for Measuring Thickness of Metallic and Inorganic Coatings") (Ref 1) and ISO Standards.

Table 11 Methods applicable to measuring cadmium coating thickness on selected ferrous and nonferrous substrates per ASTM B 659

Substrates	**Measurement technique**

	Beta backscatter[a]	**Coulometric**[b]	**Magnetic**[c]
Magnetic steel (including corrosion-resisting steel)	X	X	X
Nonmagnetic stainless steels	X	X	. . .
Copper and alloys	X	X	. . .
Zinc and alloys	X	. . .	. . .
Aluminum and alloys	X	X	. . .
Magnesium and alloys	X	. . .	. . .
Nickel	X	X	. . .
Glass sealing nickel-cobalt-iron alloys (UNS No. K94610)	X	. . .	X
Nonmetals	X	X	. . .
Titanium	X	. . .	. . .

Source: Ref 1

(a) ASTM B 567; ISO 3543.

(b) ASTM B 504; ISO 2177.

(c) ASTM B 499; ISO 2178.

Reference cited in this section

1. 1989 Annual Book of ASTM Standards, Vol 2.05 *(Metallic and Inorganic Coatings; Metal Powders, Sintered P/M Structural Parts)*, ASTM, 1989, p 441-443

Solutions for Stripping Cadmium Plate

Electrodeposited cadmium can be stripped chemically from the basis metal by immersion in one of the following solutions: ammonium nitrate, inhibited hydrochloric acid, chromic acid with a sulfuric acid addition, and ammonium persulfate with an ammonium hydroxide addition. Electrolytic stripping is performed in a solution of sodium cyanide with an addition of sodium hydroxide. Compositions of these stripping solutions, and the immersion times to be used with them, are given in Table 12.

Table 12 Solutions for stripping electrodeposited cadmium

Solution[a]	Composition	Amount		Immersion time, min[b]
		g/L	oz/gal	
1	Ammonium nitrate	105-136	14-18	10-20
2[c]	Hydrochloric acid (1.18 sp gr), undiluted	. . .	. . .	10-20
	Antimony trioxide	15	2	. . .
3	Chromic acid	203	26.8	5-10
	Sulfuric acid (95%)	48[d]	6.4[e]	. . .
4	Ammonium persulfate	51	6.7	5-10
	Ammonium hydroxide	96.8[d]	12.8[e]	. . .
5[f]	Sodium cyanide	60-91	8-12	10-20
	Sodium hydroxide	15-30	2-4	. . .

(a) Solutions are listed in order of preference; all solutions are used at room temperature.

(b) Immersion times are for deposits 8 to 13 μm (320 to 520 μin.) thick.

(c) Solution should not be used on stressed or hardened parts.

(d) mL/L.

(e) fl oz/gal.

(f) Solution for stripping electrolytically; 540 to 1080 A/m^2 (50 to 100 A/ft^2) and 6 to 8 V; part to be stripped is made the anode.

Toxicity of Cadmium

Two hazardous consequences attend the use of cadmium in contact with food products: acute poisoning resulting from the ingestion of cadmium dissolved from containers or from food-handling equipment; and poisoning from the inhalation of fumes of cadmium oxide, if cadmium-plated vessels or food-handling equipment is heated.

Acute poisoning has resulted from the ingestion of cadmium salts derived from cadmium-plated vessels in which any acid foods have been stored for even short periods of time; therefore, cadmium should not be used on food containers of any kind. Fatal poisoning is more apt to result from the inhalation of dust or fumes of cadmium salts and cadmium oxide. These are the kinds of exposure encountered in industrial operations when cadmium-plated parts are heated or soldered. Exposure to dust or fumes of cadmium should be avoided and safety / OSHA regulations should be followed. The complete regulatory text of the cadmium rule and appendixes is published in the Federal Register 57 (178): 42102-42463, 14 September 1992. Among its provisions, the rule requires employers to adhere to a new personal exposure limit (5 g/μm^3), provide medical surveillance, monitor exposure level, and maintain proper records.

Deposits of cadmium on the sides or bottom of a tank previously used for cadmium plating should not be burned off, because the fumes from this operation are highly toxic. These deposits should be removed mechanically or deplated. For high-efficiency deplating, the solution used contains 45 to 60 g/L (6 to 8 oz/gal) of sodium cyanide and 23 to 30 g/L (3 to 4 oz/gal) of sodium hydroxide in water; the tank is the anode, and steel sheets or scrap steel parts are the cathodes. Just like the production solutions presented in Table 1(a), the resulting solution must be treated with the utmost care. The proper handling of cyanide solutions should be discussed with the proper vendors, and internal safety departments must train operators in the safe use of these solutions. Disposal issues must be part of waste treatment management practices. Additional information is available in the article "Cadmium Elimination" in this Volume.

Selective Plating

When plating must be applied to only certain areas of parts, the areas not to be plated must be stopped off or masked, which means they must be covered with materials that will not conduct current, such as waxes, lacquers, or rubber tape.

Waxes. Ordinarily, a petroleum-derived wax is used for stopping off. The wax must not contain any oil or other organic materials that will dissolve in the plating solution and contaminate it. It must also be capable of adhering tightly to the part, to prevent the plating solution from coming in contact with the stopped-off area.

Before being applied, the wax is heated in a pot to about 27 °C (80 °F) above its melting point, so that it does not solidify too rapidly and will adhere more readily. Still-better adhesion is obtained if parts are warmed on a hot plate before the wax is applied.

Parts must be positioned so that only the area to be coated is placed in the molten wax. This means that, normally, only end areas or protrusions can be stopped off with wax. The wax can be applied with camel's hair brushes, but this is time-consuming if many parts are to be treated. For a large number of similar parts, a fixture can be used that will dip each part to the proper depth.

A sharp, uniform demarcation between plated and nonplated areas can be obtained by the use of pressure-sensitive tape and wax, following either of two procedures:

- Apply the tape to the part so that the trailing edge of the tape follows the demarcation line; dip that portion of the part to be left unplated in molten wax so as to overlap the trailing edge of the tape slightly; and then remove the wax when it has solidified.
- Apply the tape to the part so that the leading edge follows the demarcation; dip that portion of the part to be left unplated in molten wax so as to overlap partly the trailing edge of the tape; and then, when the wax has solidified, plate the part without removing the tape.

Waxing must be done carefully, so that areas that are to be plated have no wax on them. If wax does get on areas to be plated, it must be thoroughly removed. After plating and postplating treatments, the wax is removed from parts by placing them in hot water.

Lacquers may be used instead of wax as stop-off coatings, but their use is generally limited to instances in which the plating bath is operated at a temperature at which the wax would melt. Lacquer is applied by dipping or painting the areas to be stopped off. Normally, two to four coats of lacquer must be applied. One disadvantage of lacquer is that it is difficult and time-consuming to get all of it off. Heavier coatings prevent leakage and make stripping easier.

Plastic Tape. For stopping off irregular areas of heavy parts that cannot be dipped or that are too large to be painted (e.g., splines, large shafts, or bearing shoulders), a plastic tape is used. The tape is wound tightly and stretched over the irregular areas. To prevent leakage, each turn should overlap the preceding one at least half-way. At the edge of the stop-