

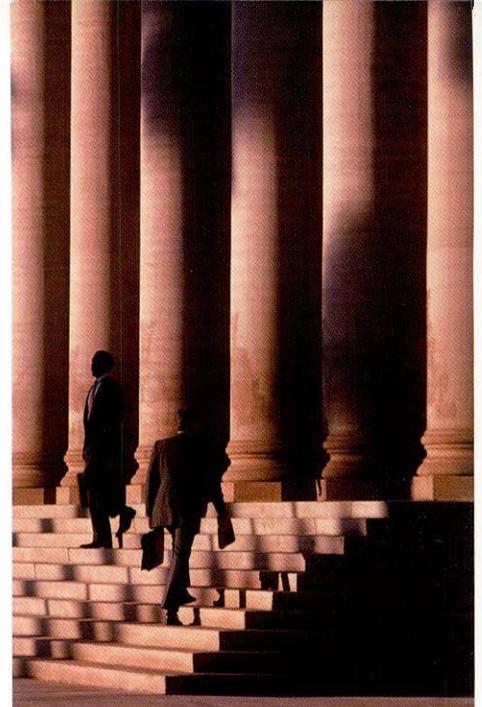
Quality Metal Finishing Guides



Metal Finishing Suppliers' Association

Hard Chrome





Introduction

The Metal Finishing Suppliers' Association (MFSA) is a trade association of companies and individuals involved in supplying chemicals, equipment, technology, and solutions to the surface finishing industry. One of the association's primary objectives is to promote the interests and further the welfare of its members and their customers while safeguarding the interests of the ultimate customer.

In 1960, MFSA initiated action to upgrade the durability of metal finishes. Known as the "Quality Metal Finishing Project" or QMF, this program was aimed at:

- 1) the promotion of technically sound specifications and standards in cooperation with interested trade and technical societies;
- 2) the provision of information to both producers and buyers of metal finished products;
- 3) the development of printed guides containing information on established standards and specifications, readily accessible for day-to-day use by the design engineer, the purchasing agent, and all those involved in the use of metal finished products.

Attribution

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Notice

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Quality

As an association promoting the interest and welfare of the producers and customers of the metal finishing industry, MFSA realizes that everyone suffers loss when products are sold that are inadequately finished for the intended application. MFSA wishes to encourage the industry to develop and maintain high-quality standards needed to guarantee the expected or promised service of the unit.

The industry needs to know how a high-quality metal finish can be achieved, how to select proper specifications for a given application, and how to control the release of products to assure that they meet the needs of the customer. At the same time, management must be confident that this know-how is based on sound engineering principles and incorporates a reasonable margin of safety.

There have been significant developments of standards for quality systems in the last few years that are applicable to metal finishing. These include:

- International Standards Organization; (ISO 9000; ISO 1456)
- American National Standards Institute/American Society for Quality Control; (ANSI/ASQC Q90)
- American Society for Testing and Materials; (ASTM B456)

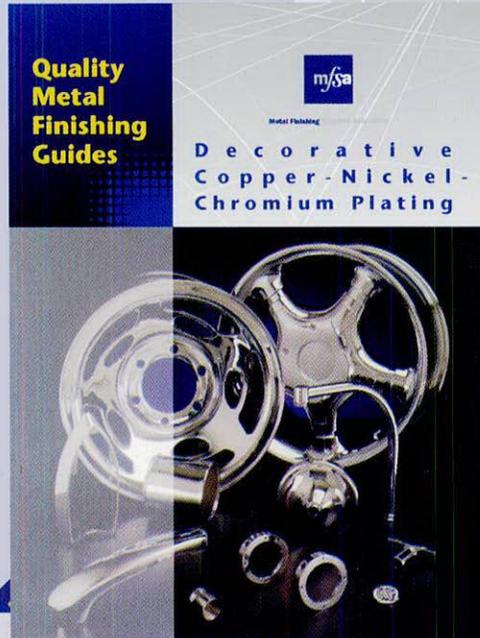
This manual will provide useful details on how to apply proven metal finishing engineering in your systems to help you maintain and improve your metal finishing quality.

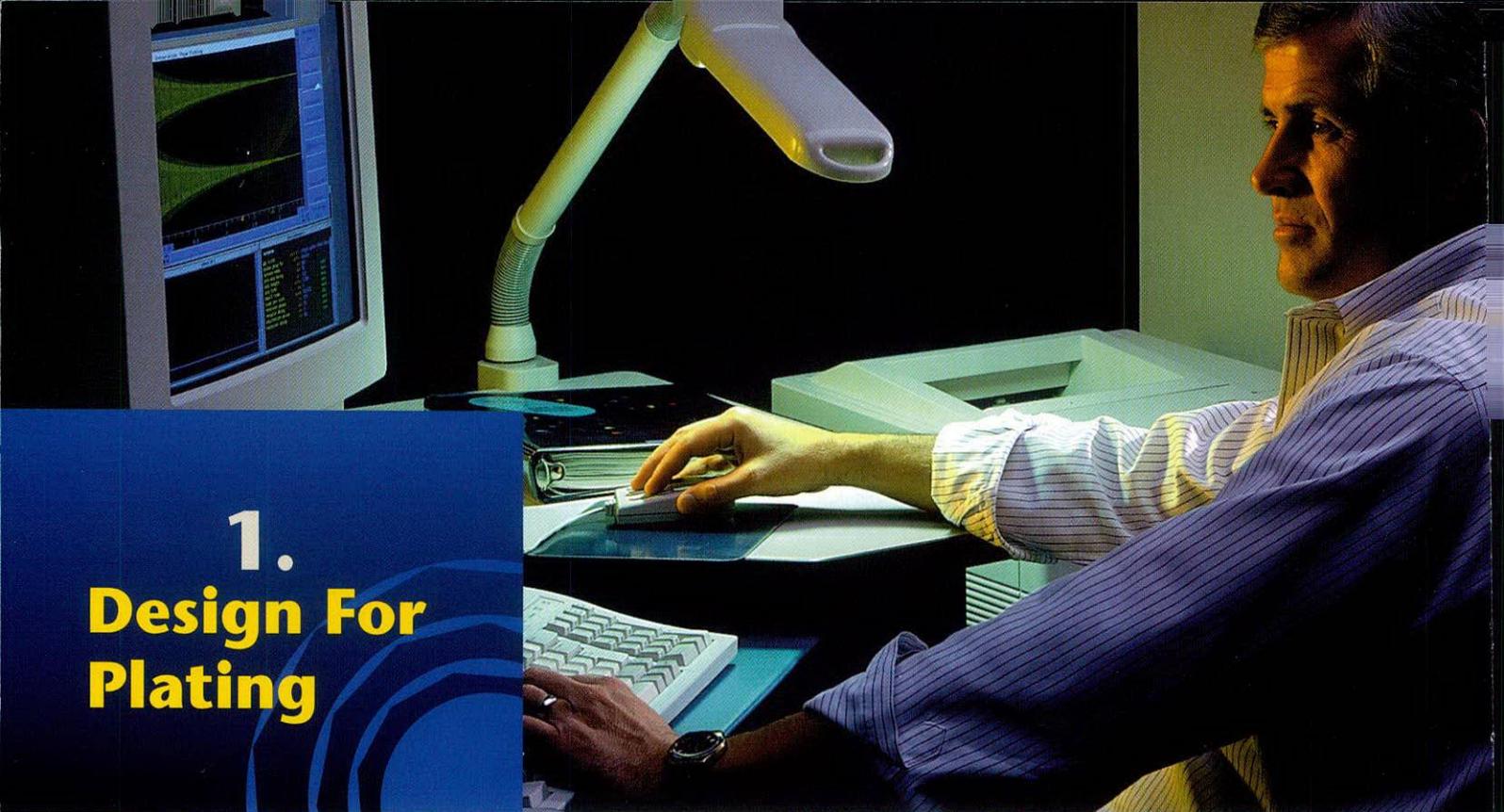
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Other QMF Guides:

- **Chemical Surface Preparation for Electroplated and Metallic Coatings**
- **Decorative Copper-Nickel Chromium Plating**
- **Decorative Precious Metal Plating**
- **Electroless Nickel Plating**
- **Pretreatment for Paint and Powder Coatings.**
- **Tin and Tin Alloy Coatings**
- **Zinc, Zinc Alloy and Cadmium Coatings**





1. Design For Plating

A program to improve and control the quality of a metal product should start at the desk of the designer. The metal finisher is restricted in what he or she can do by certain basic principles of mechanical finishing and of electroplating. The engineer should understand the limitations imposed by shape and size of components to facilitate quality finishing at an acceptable cost. The designer can exert as much influence on the quality attainable in finishing a part as can the electroplater. ASTM Standard B507 can provide the designer with helpful information.

Significant Surfaces

A most important term used in specifying metal finishes is “significant surfaces.” In most products the same standard of quality is not required over the entire surface. Instead, the quality specifications apply since compliance is expected only for the so-called “significant surfaces” defined by mutual agreement between the producer and purchaser as follows:

Significant surfaces are defined as those normally visible (directly or by reflection) which are essential to the appearance or serviceability of the article when assembled in normal position, or which can be the source of corrosion products that deface visible surfaces on the assembled article. When necessary, the significant surfaces shall be the subject of agreement between purchaser and manufacturer and shall be indicated on the drawings of the parts, or by the provision of suitably marked samples.

Design for Mechanical Finishing

Products which are to be coated are generally subjected to abrasive polishing with wheels or mass finishing techniques in preparation for the plating operations. This is done to aid in securing an attractive, uniform, mirror-like or satin appearance on the finished part. Mechanical finishing is an expensive operation. To reduce costs and assist the metal finisher in improving the appearance and quality of the product, the designer should consider certain rules applicable for parts requiring mechanical finishing:

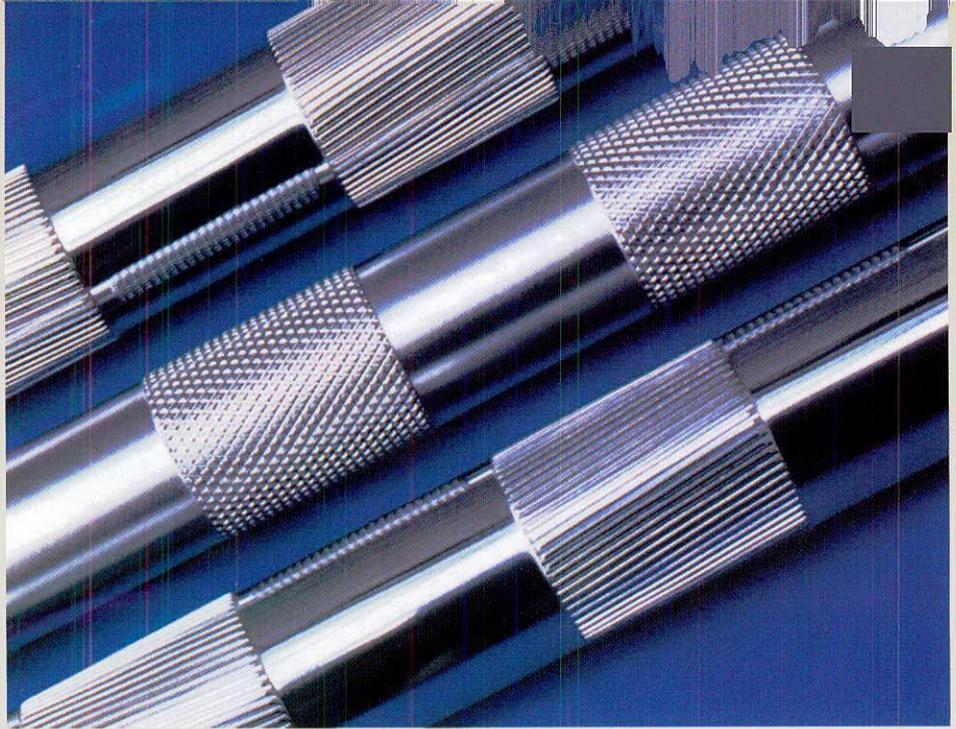
- Avoid blind holes, recesses and joint crevices which can retain polishing compounds and metal debris.
- Avoid intricate surface patterns which can be blurred by polishing operations.
- Significant surfaces should be exterior and reachable by ordinary polishing wheels or mass finishing media.
- Avoid sharp edges and protrusions which can cause excessive consumption of wheels or belts.

In small parts which are to be barrel processed, the above rules apply. This includes the requirement that the parts must be sturdy enough to withstand the multiple impacts of barrel rotation and will not entangle, causing damage or incomplete finishing. Whenever possible, small flat parts that tend to nest together should have ridges or dimples incorporated into their design to prevent such nesting.

Design for Racking, Draining and Air Entrapment

Most metal parts weighing more than a few grams, or that require a high degree of surface brilliance, are not plated in bulk in barrels, but are mounted on racks or fixtures for processing in cleaning and plating tanks. Design considerations relating to racked parts are described below.

- Consult the plating department to make certain that parts can be held securely on a plating rack with good electrical contact without masking a significant surface. Many difficult racking problems can be solved by minor design modification.
- Provide for good drainage of processing solutions from racked parts. Certain shapes tend to trap solution which then causes contamination by carry-over, possible corrosion of the part, and waste of materials. Carry-over aggravates the problem of waste disposal and adds excessive cost due to chemical losses. In design, avoid rolled edges, blind holes and spot-welded joints. Drain holes are especially helpful when they are included in the design of irregular shapes and tubular parts.
- Avoid shapes that can trap air on entry into processing tanks, if this air could block access of solution to areas requiring treatment. Wherever air can be trapped, hydrogen or oxygen gas may also accumulate during the cleaning or plating steps.



Design for Good Distribution of Electrodeposit Thickness

Simple shapes are always finished more uniformly and more economically than complex shapes. This is rule Number One for the designer.

One of the most important factors that determines the quality of a coating is its thickness on significant surfaces. Fundamental laws of electrochemistry (current distribution), operate to prevent uniform deposition of an electrodeposited coating on a cathode of any practical shape and size. Portions of the work which are nearer the anodes tend to receive a heavier deposit than those more distant from the anodes. Sharp edges or protrusions at all current densities tend to receive a disproportional

share of the current. The goal of the designer and the plater is to make thickness variations as small as possible. At the same time, it is appropriate to minimize the unnecessary waste of metal by excessive build-up on both significant and non-significant areas. The same variation in plating thickness found on plated articles also typically exists when comparing parts plated on different areas of plating racks. For example, parts racked on the perimeter of fixtures tend to exhibit more thickness than parts from the center of fixtures.

It is possible to estimate metal distribution ratios from models or mock-ups, but there are also empirical rules. These can guide the designer to improved uniformity of thickness, hence improved quality with greater economy. These general principles and various sketches illustrate what has been learned from practical experience:

- Avoid concave or perfectly flat significant surfaces. Convex or crowned areas receive more uniform coatings. Use a 0.4 mm per 25.4mm (0.015 inch per inch) crown–minimum.



- Edges should be rounded to a radius of at least 0.4 mm (1/64 inch) and, preferably to 0.8 mm (1/32 inch).
- Re-entrant angles or corners should be filleted with a generous radius. Make sure radii are as large as possible.
- Avoid concave recesses, grooves, or slots with width less than one-half the depth.
- Minimize the number of blind holes because these must usually be exempted from minimum thickness requirements. Where necessary, limit their depth to 50% of their width. Avoid diameters less than 6 mm (7/32 inch.)
- Countersink threaded holes to minimize electroplate thickness build-up at their peripheries and to facilitate insertion of fasteners after plating.
- If fins or ribs are required, reduce their height and specify a generous radius, 1.6 mm (1/16 inch) at each base. Round off tips with radii of a least 1.6 mm (1/16 inch). Multiple parallel fins should have spacing between centers equal to four times the width of the fin. Broad hollow ribs are preferred over slender solid ones.
- Adopt recessed letters and insignias in preference to raised letters and insignias, but round-off edges and provide gentle contours.
- Integrated studs for fasteners should be shortened as much as possible and inside angles at each base should be rounded generously. Tips should be similarly rounded.
- Studs or bosses with hollow centers should be shortened as much as possible and angled 90 degrees from the major plane of the part. All bosses should face the same direction.
- Assist the plater by clearly marking significant surfaces on part drawings.
- Avoid use of a variety of different base metals on any one part to be plated. The contact of dissimilar metals may

interfere with covering power or adhesion of the deposit due to galvanic action. It might also increase corrosion in service.

Design Features That Influence Electro-platability

The effect of the basic design of a product or component upon the effectiveness or durability of the plating used has been the subject of much study and research. Many failures for which the plater has been blamed can be attributed to the original design.

A major contribution to the plating industry was made by the Zinc Institute, Inc., when it sponsored a design study by Battelle Memorial Institute, which has resulted in the establishment of basic design principles to be applied to zinc die castings. The principles can be applied to other substrates.

The various shapes shown here provide the “dos and don’ts” of design configurations and their relationship to electroplating quality.

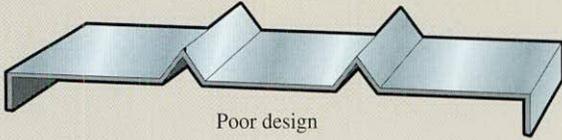
Feature	Influence On Electroplatability	Better Design
Flat-bottom grooves	Inside and outside angles should be rounded generously to minimize costs.	
V-shaped grooves	Deep, V-shaped grooves cannot be satisfactorily plated with corrosion protective nickel and chromium and should be avoided. Shallow, rounded grooves are better.	
Fins	Increase plating time and costs for a specified minimum thickness and reduce the durability of the plated part.	
Ribs	Narrow ribs with sharp angles usually reduce electroplatability; 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.	
Concave recesses	Electroplatability is dependent upon dimensions.	
Deep scoops	Increase plating time and costs for a specified minimum thickness.	
Spearlike Juts	Buildup on jut will rob corners from their share of electroplate. Crown the base and round off all corners.	
Rings	Electroplatability is dependent upon dimensions. Round off corners and crown from center line, sloping towards both sides.	

The distribution of electroplate is indicated in an exaggerated fashion.

ROUND OFF HIGH SPOTS

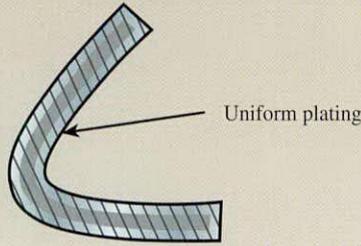


Good design

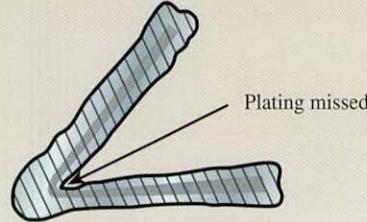


Poor design

AVOID SHARP INTERIOR ANGLES

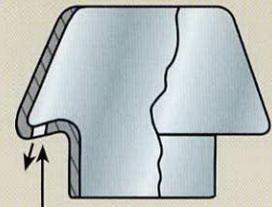


Uniform plating

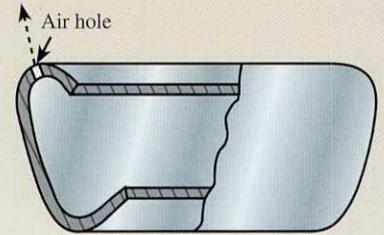


Plating missed

PLACE HOLES FOR DRAINING AND AIR ESCAPE



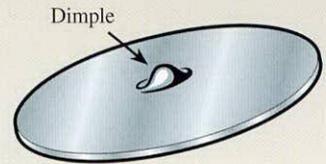
Drain hole



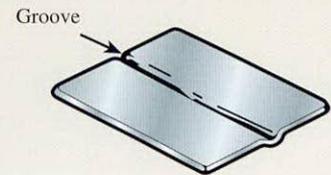
Air hole

Feature	Influence On Electroplatability	Better Design
Convex surfaces	Ideal shape. Easy to plate uniformly, especially where edges are rounded.	
Flat surfaces	Not as desirable as crowned surfaces. Use a 0.4mm/25.4mm (1/64 inch) crown to hide undulations caused by uneven buffing.	
Sharply angled edges	Undesirable. Reduced thickness at center areas and requires increased plating time for depositing a minimum thickness of durable electroplate. All edges should be rounded. (Edges that will contact painted surfaces should have a minimum radius of 0.8 mm [1/32 inch])	
Flanges	Large flanges with sharp inside angles should be avoided to minimize plating costs. Use a generous radius on inside angles and taper the abutment.	
Slots	Narrow, closely spaced slots and holes reduce electroplatability and cannot be properly plated with corrosion-protective nickel and chromium unless corners are rounded.	
Blind holes	Must usually be exempted from minimum-thickness requirements. Where necessary limit depth to 50% of width. Avoid diameters less than 6mm (7/32 inch).	
Sharply angled indentations	Increase plating time and costs for a specifically minimum thickness and reduce the durability of the plated part.	

AVOID STICKING WHEN BARREL PLATING



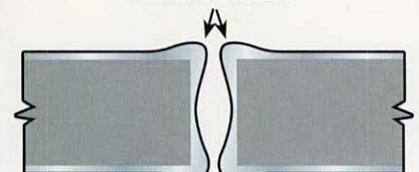
Dimple



Groove

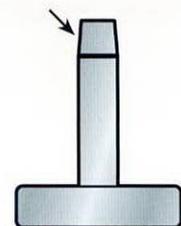
ALLOW FOR BUILDUP

Buildup reduces effective diameter



Hole

Tapered end to allow for buildup



Plug

The distribution of electroplate is indicated in an exaggerated fashion.

2. Specifying the finish



Functional or Hard Chrome- is the most commonly specified chromium deposit. These terms usually refer to a bright, smooth chromium deposit free from visible cracks, pits or nodules. The final deposit thickness at various locations on the part is generally specified.

Porous Chromium- is frequently specified for the cylinder liners of locomotive engines or aircraft piston engines. This type of deposit has the chromium surface etched or blasted following plating in order to provide for oil retention on the cylinder wall.

Thin Dense Chromium- is a deposit that is typically plated to no more than 0.2 mils in thickness. It is normally not subject to grinding following plating. Specifications for this type of deposit frequently require a micro-hardness such that only the Mixed Catalyst or High Speed Non-Fluoride chemistries are suitable.

Crack Free Chromium- is a deposit that does not have microcracks in it. It is most commonly used for either its unique surface texture, or as the under layer of a duplex chromium deposit which is thought by some to provide improved corrosion resistance. This claim is not universally accepted within the industry. Although it is possible to plate this type of deposit from either Conventional or High Speed Non-Fluoride chemistries, most commonly, variations of the Mixed Catalyst chemistry are used. The plated deposit is grey in color, relatively soft (600-750 Knoop) and not considered to be a good wear or corrosion resistant deposit by itself.

3. Physical properties of deposits

Deposit Properties

Hard chrome can be deposited from any of three general chemistries: Conventional, Mixed Catalyst, or High Speed Non-Fluoride. There are several variations or trade names for each of these systems. Each chemistry has applications for which it is best suited. Some of these differences relate to the physical properties of the finished product while some of them relate to the ease of plating and the productivity of the plating shop. Following is a brief description of each general type of chemistry:

Conventional

The conventional bath is the simplest and oldest chemistry for the plating of chromium. It has been in commercial use since the 1920s. The bath consists of chromic acid, which is the source of chromium metal, and a small amount of sulfate that serves as a catalyst for plating. While this chemistry does not give deposits with wear and corrosion properties as good as those provided by newer baths, it is still a widely used system which is suitable for almost any application. It is the best chemistry for plating "porous chromium" when etching is used to make pores in the deposit.

Mixed Catalyst

This chemistry, which was developed in the 1950s, consists of chromic acid and sulfate as in the conventional bath. In addition, a complex fluoride anion is added which increases the plating efficiency, as well as the deposit's hardness, wear, and corrosion properties relative to the conventional bath. The complex fluoride ion also helps to activate nickel and nickel alloy substrates, making good adhesion on these substrates easier to obtain. One drawback to this chemistry is that the combination of the complex fluoride

ion and the chromic acid will etch exposed steel, aluminum, and copper substrates. Hence, substrate surface areas made of these materials that are not to be plated, or that are in very low current density areas, must be protected from the solution by tape, wax, or some other inert material. The fluoride chemistry also requires different and more costly materials of construction for ancillary process equipment such as heat exchangers, cooling coils, etc.

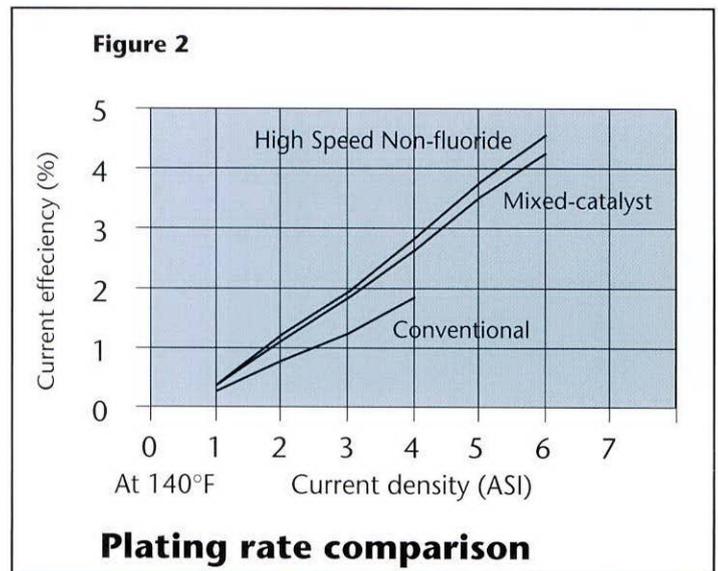
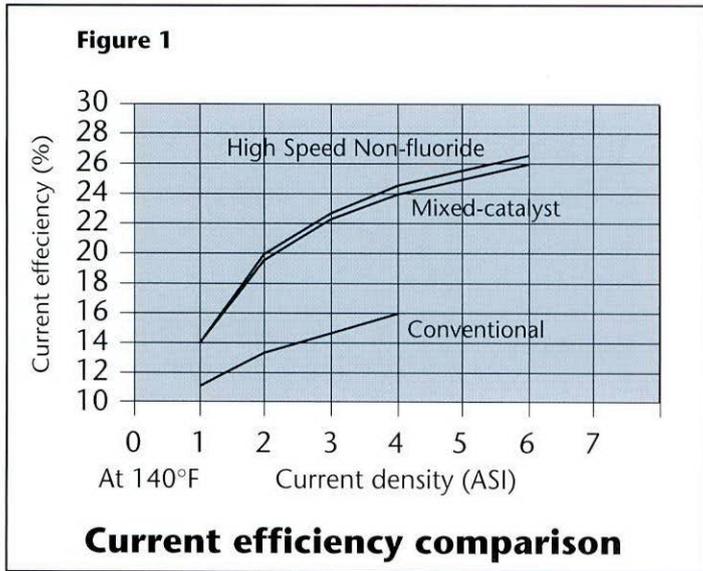
High speed non-fluoride

This chemistry was commercialized in the mid-1980s. It consists of chromic acid, sulfate, and an additional non-fluoride catalyst that alleviates the etching problems associated with the mixed catalyst chemistries. High Speed Non-Fluoride baths provide the same or greater plating efficiency improvements as the mixed catalyst system shows relative to the conventional bath. Deposits from this bath have the best wear and corrosion properties of the three chemistries. Shown below in chart form and graphs are some of the basic characteristics of the three different systems. The deposit properties are discussed in great detail in the next section.

Table I
Characteristics Of Chemistries And Deposits

	Conventional	Mixed Catalyst	High Speed Non-Fluoride
Plating Efficiency (%)	8-12	18-25	20-27
Typical Plating Rate (mil/hour)	0.5-1.0	1.0-2.5	1.0-3.5
Substrate Etching	No	Yes	No
Micro-Hardness (Knoop)	850-950	950-1050	1000-1100
Microcracks/Inch	300	800	>1000
Corrosion Resistance	Good	Better	Best
Wear Resistance	Good	Better	Best
Appearance	Semi-Bright	Bright	Brightest

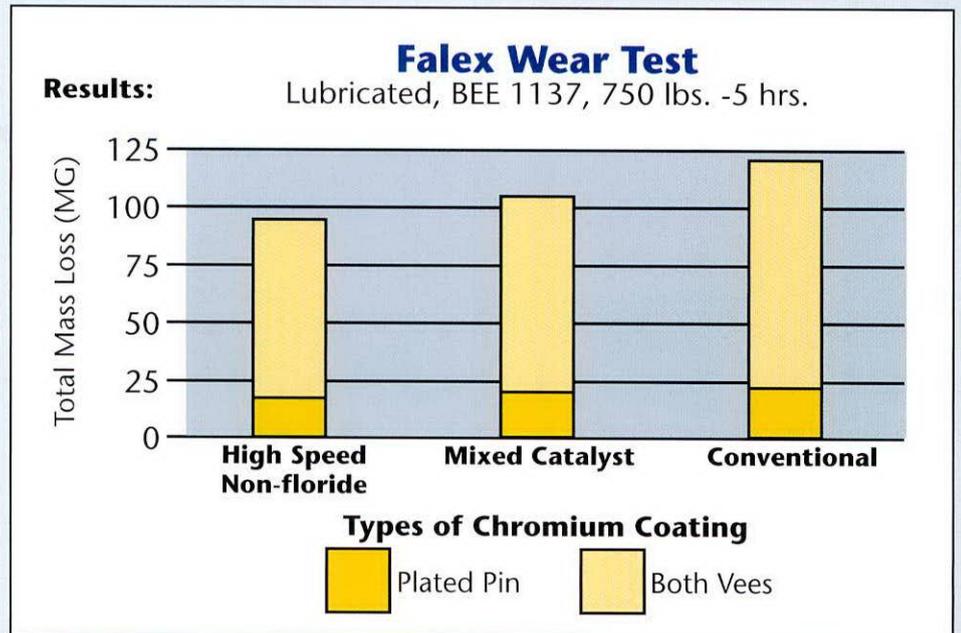
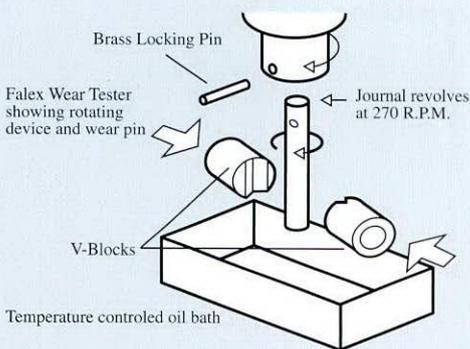
Hard chrome is most commonly specified because of its low coefficient of friction and its exceptional wear and corrosion resistance properties. The bath chemistry also influences the deposit smoothness or amount and size of nodules formed during the plating operation. Table I gives the chemical and physical properties of this deposit. Figures 1 and 2 contrast the performance of the three general types of hard chrome plating chemistries. Figures 3 and 4 compare deposit properties from three general types of hard chrome chemistries using two types of wear-testing.



The high hardness of plated chromium leads to the exceptional wear properties of this deposit. While all chromium deposits that plate a bright deposit have excellent wear resistance, studies have documented that the High-Speed, Non-Fluoride chemistry deposits have the best wear characteristics, and that the Conventional bath have the poorest.

Figure 3

METHOD: The Falex *Lubricated* Wear Tester used Conventional, Mixed Catalyst and High Speed Non-Fluoride hard chrome plated pins, revolving at 270 revolutions per minute between two unplated steel blocks while immersed in a temperature controlled oil bath. With a measured force, the blocks are pressed against the pin, creating wear which is calibrated by measuring the weight loss of both the pin and the blocks.



The Taber Abraser, illustrated in Figure 4, is the most commonly used test method for evaluating dry abrasive wear. The relative differences between the three types of chromium plating chemistries are shown alongside. Again, the relative wear characteristics for deposits are shown alongside.

METHOD: The Taber Abraser, an industry standard, was used to measure *dry* abrasive wear on samples, chrome-plated by each of the three plating processes: the Conventional, Mixed Catalyst and the High Speed Non-Fluoride Chromium Plating methods. The sample was placed on the instrument's revolving sample holder and a load was applied, rubbing against the sample's surface. A vacuum picked up residual particles to prevent their affecting the abrasiveness. The weight loss of the sample after a given number of revolutions provides an indication of its relative resistance to abrasive wear.

The Taber Abraser used to test the resistance of surfaces to dry abrasion

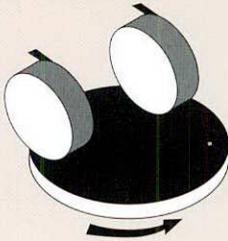


Figure 4

Chromium deposits also impart excellent corrosion protection to the substrate. Most commonly, this resistance to corrosion is measured by the Neutral Salt Spray Test (NSST), as specified by ASTM B117. How many hours of protection the deposit provides is the result of a combination of five major factors:

1. Quality of the substrate material
2. Preparation of the surface to be plated
3. Type of chromium plating bath
4. Thickness of the deposit
5. Post-plating treatment

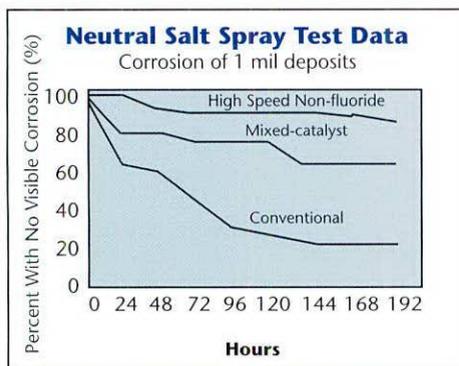
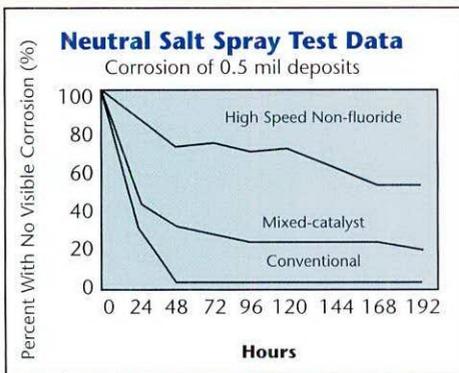
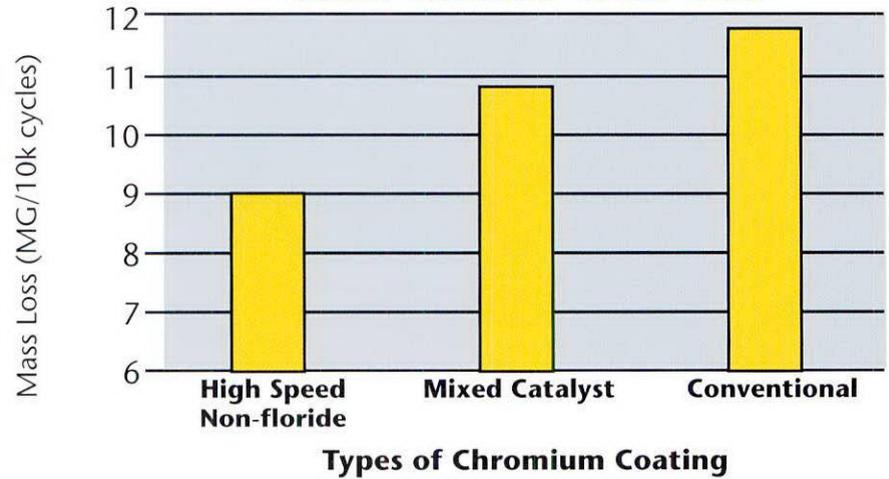


Figure 6 and 7

Results:

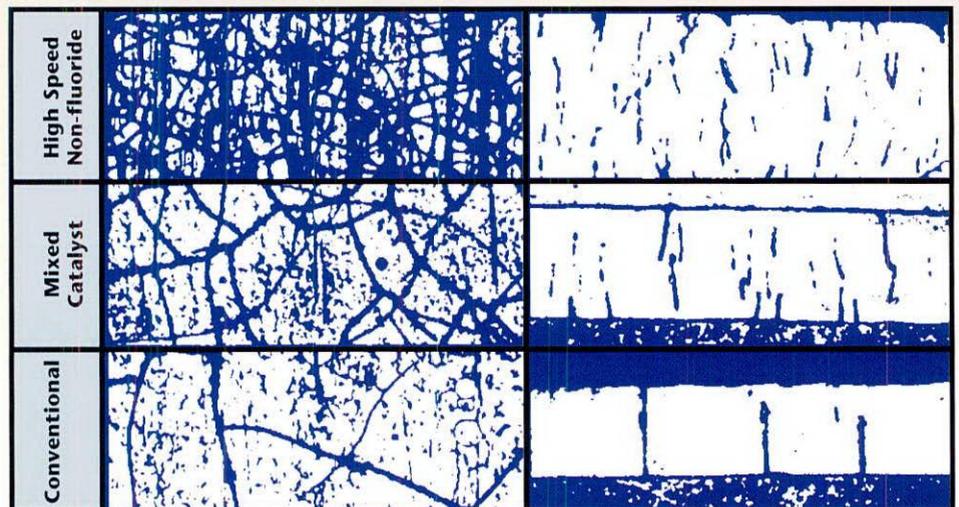
Taber Abraser Wear Test



Each of these factors needs to be controlled in order to obtain the best possible results on a continuous basis.

1. The substrate material needs to be uniform in composition and hardness, as well as free from surface defects and inclusions.
2. The pretreatment needs to provide as smooth a surface as is possible, taking into account design and economic considerations.

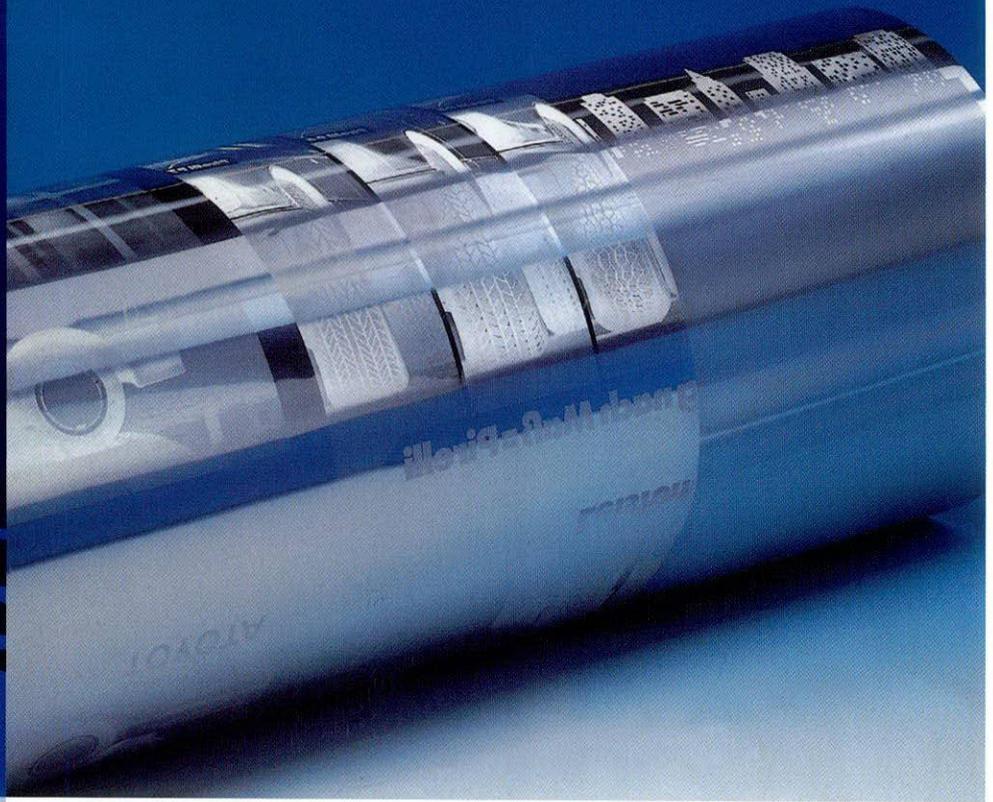
Figure 5 600x Surface View 200x Cross Section



3. The type of bath used determines the number of microcracks in the deposit and the depth of penetration through the deposit of each crack. See Figure 5. Deposits with low microcrack densities have microcracks that are longer and tend to extend to the substrate. In chromium deposits with a higher microcrack count, the microcracks are shorter and shallower, providing better protection to the substrate.
4. Chromium deposit thicknesses specified for corrosion resistance applications vary greatly and are strongly influenced by the specification for substrate roughness. The smoother the substrate, the thinner the deposit that is required for equivalent protection. Frequently shock absorbers and struts have thickness specifications of between 0.3 and 1.2 mils. Hydraulic shafts used for fluid power commonly specify 1-2 mils thickness.
5. The post plating treatment is normally a grinding and/or buffing operation. These processes tend to seal over top surfaces of the microcracks and fill in any porosity that may have been present.

4.

Functional or hard chrome plating



Bath Constituents

All hard chrome plating baths contain chromic acid (CrO_3) and sulfate ions (SO_4). These two constituents are the main ingredients and must be maintained at their proper limits to achieve the desired plating properties. In modern mixed catalyst and high-speed non-fluoride baths, further additives (so called "catalysts") are used to improve plating speed and control the physical properties of the electrodeposit.

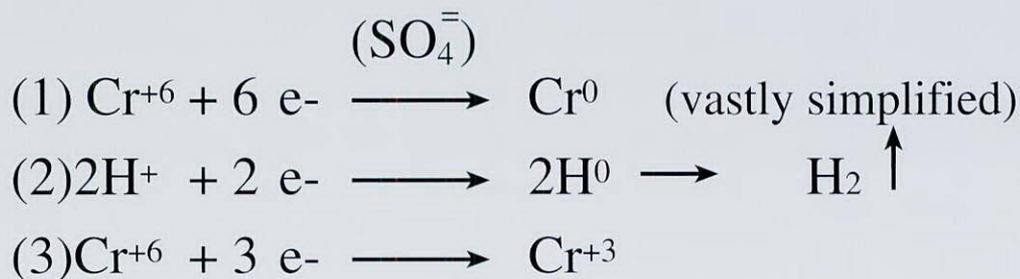
Chromic Acid (CrO_3) -- The chromic acid concentration is important for control of throwing power and deposit morphology. While the concentration range is about 20-60 oz/gal, the lower end of this range can only be used for simple shaped parts, as throwing power is very poor, while the high end of the range is used mostly for crack-free chromium plating. By far, the most common concentration for the chromic acid is 28-33 oz/gal. At this concentration, most hard chromium baths will perform as desired, as long as the other constituents and impurities are controlled properly.

Sulfate Ion (SO_4) -- The sulfate ion is normally added as sulfuric acid, although it is not generally critical if a sulfate salt is used. The specific concentration for the sulfate ion is not as critical as the ratio of the chromic acid to sulfate ion (CrO_3/SO_4). The CrO_3/SO_4 ratio must be controlled within specified limits for proper functioning of the bath and these limits will vary for each type of bath: Conventional, Mixed Catalyst, or High Speed Non-Fluoride bath. A conventional bath will require a CrO_3/SO_4 ratio of 80:1 - 130:1, with the most common ratio being 100:1. Since, in a mixed catalyst bath, the catalyst replaces part of the function of the sulfate, the CrO_3/SO_4 ratio is generally higher with a range of 150:1 - 250:1. The CrO_3/SO_4 ratio for a high speed non-fluoride bath is frequently controlled at closer to 90:1, but can be varied to enhance throwing power or to obtain smoother deposits.

Catalysts -- The introduction of catalysts to hard chrome plating greatly improves the plating rate. The mixed catalyst baths use fluoride (usually introduced as a silicofluoride, SiF_6) at about 0.3 - 0.4 oz/gal. While this improves the plating speed, the fluoride etches exposed areas of the part. More recent high-speed, non-fluoride baths use proprietary additives to eliminate this problem, while still retaining the improved plating rate.

Mechanism of Deposition

Cathode Reactions -- In its simplest form, the cathode reaction is ultimately the reaction of the hexavalent chromium ion Cr^{+6} with electrons to form chromium metal, Cr^0 . However, it is well known that a pure solution of chromic acid will not plate chromium metal, but instead will "plate" hydrogen gas. The actual mechanism is not completely understood, but it is clear that the sulfate ion is required for the electrodeposition of chromium to occur. When catalysts are added, they are also involved in the plating mechanism. Several details mechanistic studies have been performed and make interesting reading but many of the conclusions are still not fully accepted for plating parts under industrial conditions. Suffice it to say that the main competing reactions at the cathode are:



The predominate competing reaction of hydrogen ions to form hydrogen gas accounts for the low efficiency of chromium plating baths.

Anode Reactions

The anodes used in hard chrome plating are generally a lead alloy. The desired reaction at the lead anode is for the formation of lead dioxide (PbO_2). This is indicated by the formation of a brown to black surface on the anode, which shows that the anode is functioning normally. The competing reaction is for the formation of lead chromate (PbCrO_4), which has a yellow, powdery appearance.

The formation of the lead dioxide is important because this compound will conduct current and thus avoid polarization of the anode. The lead dioxide will also oxidize trivalent chromium (Cr^{+3}) back to hexavalent chromium (Cr^{+6}). This oxidation is required in order to avoid the buildup of excess trivalent chromium in the bath. The unbalanced, simplistic anode reactions are therefore:

New Anode in Tank



Anode in Use or When Current is Off



Anode in Use (Current On)



Major Anode Reactions





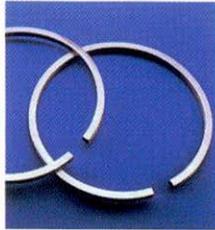
Surface Pretreatment

Chromium plating solutions have no inherent cleaning ability as do, for example, solutions containing cyanide. Thus it is critical that parts be free of oils, greases, buffing, and polishing compounds, finger-prints, paints, etc., before they are immersed in the plating bath. The base metal that is being plated will determine the proper cleaning cycle to remove whatever soils might be present.

Although a hard chrome bath is acidic, it is not intended to be used to remove rust or scale from parts before they are plated. If parts are badly rusted, or heavily scaled, they should be treated off-line to remove these coatings. If this can't easily be accomplished chemically, sand blasting, glass bead blasting, or vapor blasting is recommended. Durney's Electroplating Engineering Handbook contains a great deal of information on effective pretreatment methods.

Recommended Operating Parameters

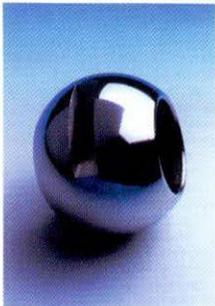
As with all plating baths, there are several variables that affect the performance of a hard chrome plating bath. While many of these variables depend on the type of application, the substrate in question, and the differences between plating shops, some general conditions can be addressed as being "normal" for hard chrome plating.



Temperature – The temperature of hard chrome plating baths will usually be within the range of 49-65° C (120-150° F). Temperatures below 49° C (120° F) will result in baths with a tendency to burn in the high current density regions. Temperatures above 65° C (150° F) can also lead to slow plating rates and milky deposits, although the higher temperature end of the range is used for crack-free chromium or when a smoother appearance is needed.



Current Density – While each type of part to be plated will have an optimum current density range, the current density range most often used for hard chrome plating is between 14-80 A/dm² (1 - 6 A/in² or 150 - 850 A/ft²). In order to achieve these high current densities, it is important to have the proper temperature or high current density burning will occur. Care also needs to be taken to ensure that rectifier ripple is within acceptable limits at the current actually being used. The ripple will increase dramatically in many rectifiers – especially SCR type units –when they are run below their maximum rated capacity.



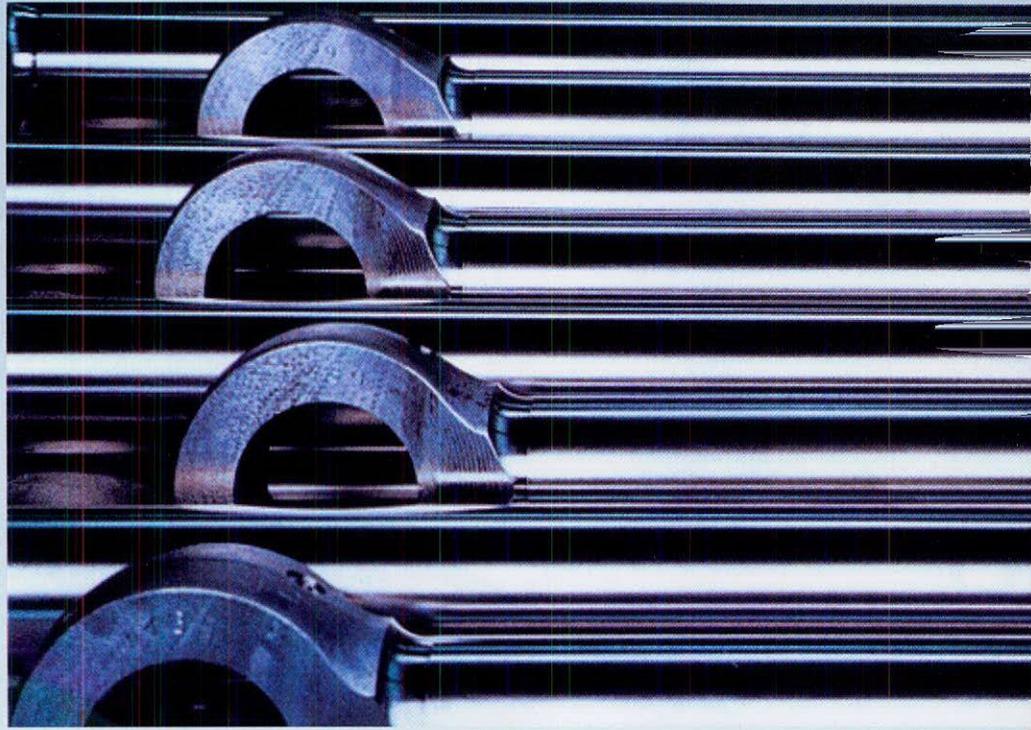
Agitation – Agitation is important in a hard chrome plating bath in order to maintain fresh plating solution and a uniform solution temperature on the surface to be plated. This can be achieved in several ways. Air agitation can be used, provided care is taken to remove any oil from the air supply. Another common source of agitation is to physically pump the solution so that the discharge from the pump is close to the parts to be plated, thus providing agitation near the cathode. A filtration system to provide both solution agitation and removal of sludge and other particulate contaminants may be used. It is also appropriate to point out that the vast amount of gas generated by the relatively inefficient plating in a chrome bath creates a natural pumping action, so auxiliary pumping may not be needed in all cases.

Anodes – Anodes are normally a lead alloy and are used at an anode to cathode area ratio of about 2:1. This anode to cathode ratio may be changed due to the level of trivalent chromium in the bath as discussed under the anode section.

Effects of Impurities and Methods of Removal

The common impurities found in hard chrome plating baths have the same effects irrespective of the specific type of chemistry being used. The most common impurity is the trivalent chromium ion, which is formed by one of the side reactions during plating. The build-up of trivalent chrome ion is magnified when there is significantly more cathode area in the plating bath than anode area, such as would occur if the majority of production work to be plated consisted of internal diameters.

The trivalent ion is re-oxidized to the hexavalent state at the anode. Thus – in a properly balanced plating operation – an equilibrium concentration, usually less than one oz/gal, is reached between the formation of trivalent chromium at the cathode and its re-oxidation at the anode. The effect on the bath of excess trivalent chromium ions is the same as other metallic ions such as iron and copper. (Iron is usually introduced into the bath from the etching step used prior to plating to obtain good adhesion, or in the case of the mixed catalyst chemistry from the etching of exposed steel substrates. Copper usually comes from etching by the chromic acid of the bus bars.) All of these metallic ions affect the bath by raising the solution's electrical resistance so that more voltage is required to conduct the same amount of current. This increases the electrical costs and the amount of heat generated in the bath. In severe cases, the rectifier will not have adequate voltage capability and the plating rate will be reduced because the same amount of current cannot flow due to the higher internal resistance of the electrolyte. Also, as the solution's electrical resistance is raised, the primary current distribution will be altered such that more current will flow to the high current density areas of the part being plated. This causes uneven plating thicknesses over the part and, in extreme cases, can result in nodular (burned) deposits. Metallic ions – other than



trivalent chrome – can be removed by bath dilution, ion exchange, or electro dialysis. Simple high current dummieing of the bath, using a small cathode area, and a large anode area, can reduce the concentration of trivalent chrome.

The most common troublesome anion is chloride, which typically enters the bath from poor quality water or drag-in from an activation or chloride based stripping tank somewhere ahead of the plating tank on the processing line. The chloride ion causes very rough deposits with poor physical properties. Additionally, since it is approximately ten times more powerful as a catalyst as the sulfate ion, it significantly increases the probability of production problems. It must be kept at levels below 10-15 ppm. Chloride can sometimes be removed by high current density dummy plating, using high anode area and low cathode area, in conjunction with good solution agitation. Theoretically, chloride ion can be precipitated from the plating bath as silver chloride by adding small amounts of silver oxide, but this is an expensive and unreliable method. The

best thing is to prevent the chloride ion from getting into the bath in the first place.

Nitrate and phosphate anions are serious poisons for chromium plating baths and significantly reduce the plating rate. The most common method by which these ions are introduced is through leaking steam coils that allow condensate that contains boiler treatment materials to enter the bath. Another possibility, especially in the case where aluminum parts are plated, is through drag-in of nitric acid from the zincating operation. There is no effective method for removing phosphate or nitrate ions.

Most organic impurities such as oils and greases do not cause a lasting problem to hard chrome plating solutions. They are usually oxidized to volatile products by the hot chromic acid. Trivalent ions are a product of this reaction and need to be re-oxidized at the anodes, as discussed above.

Anodes and Conforming Anodes

Insoluble anodes are used in hard chrome plating baths. In almost all instances the anodes are made of lead alloys such as lead:tin or lead:antimony. Less frequently, pure lead is used for the anodes. Occasionally platers will use steel anodes, although this is not recommended on a long-term basis since it will quickly introduce a significant quantity of iron to the plating bath. Iron will reduce the bath's conductivity and increase the deposit's roughness. Platinized titanium anodes are seldom used in mixed catalyst systems because fluorides or other halogens rapidly attack the titanium. Additionally, the high current densities typically used in hard chrome plating operations will rapidly remove the platinum coating from the titanium.

Pure lead, sometimes referred to as printers' lead, is soft and easy to bend to match the configuration of the parts being plated. This makes it very suitable for auxiliary anodes. However, pure lead has a short life, especially in baths containing fluorides.

Lead:tin alloys are generally recommended in baths that utilize fluoride as part of the catalyst system because this alloy is more resistant to attack by the fluoride than pure lead, or other lead alloys. The typical amount of tin added as an alloying ingredient is 3 to 7% by weight.

Antimony is added to lead to increase its strength and rigidity, an important consideration when large surfaces that are resistant to sagging are needed. The normal amount of antimony added is between 3 and 7% by weight.

Due to environmental regulations, a decreasing number of hard chrome plating operations make their own lead or lead alloy anodes. Those that do buy shapes or ingots of metal then cut or cast them into various patterns and sizes to suit their needs. This allows the anodes to be hand-shaped to conform to the work being plated. Cross-sectional areas of these anodes, which sometimes appear to be very large, must be sufficient to conduct all the current without significant voltage drops. A voltage drop would lead to non-uniform deposit thicknesses and offset the advantages of a conforming shape.

Two different anode/cathode arrangements are utilized in hard chrome plating: a three bus bar system, where two anode rails are positioned on opposite sides of the cathode rail; and a two bus bar system, where a single anode rail is used along with a single cathode rail. The triple bus bar configuration is the most common system.

The double bus bar arrangement requires a conforming anode that replicates the configuration of the part to be plated. A properly designed conforming anode will provide a relatively uniform deposit thickness, even on complex shaped parts. Conforming anodes are almost always used in conjunction with double bus bar fixtures that have a reversible configuration which allows parts to be either plated or reverse current activated simply by rotating the fixture 180 degrees in the plating bath. This rotation changes the polarity of the current flow.

A majority of plating shops rely on vendors for their lead or lead alloy anodes. They generally utilize the more popular triple bus bar plating station design that allows for increased productivity. While the lack of conforming anodes may require some additional grinding or machining of parts after plating, this is frequently less costly than the set-up cost for conforming anodes.

Masking Techniques

Hard chrome plating baths typically display poor covering power. Nevertheless, masking is an important consideration, and a challenge to the creativity of the hard chrome plater. Proper choice of the masking materials and proper placement of the mask or shield can have a tremendous effect on the uniformity of deposit thickness by forcing current to flow into certain areas while preventing it from flowing into other areas.

Masking materials can be either conductive or non-conductive:

Conductive masking materials produce a robbing effect that reduces deposit build-up in the area where the masking material is applied. Instead of the plating on the part, the chromium plates on the conductive mask. Examples of conductive masking materials are lead and aluminum tape, as well as simple "thiefs" made of almost any metal, such as steel, iron, copper, etc. A conductive mask is used to de-emphasize deposit build-up in a particular area by drawing the depositing metal onto itself.

Non-conductive masking materials work with an opposite approach. They cause a decrease in deposit thickness in the region behind the masked area by hermetically sealing the surface (no plating solution present) or by reducing the current flow behind themselves. Some shields will also slow the replenishment of metal ions after they have been plated out by decreasing solution movement. Examples of non-conducting masking materials that are commonly used in hard chrome plating operations include: various plastic and Mylar tapes, special high temperature resistant paints, Plexiglas or PVS sheets and tubing, waxes, rubber stoppers and plugs, wooden dowels, etc. Non-conductive masks may also be used to maximize deposit build-up just beyond their edges, but generally they are used to decrease deposit build-up in the area they completely cover.

A properly designed mask can save a substantial amount of time and money by eliminating unnecessary post plating machining and grinding.

Anodic Etching

(See Activation/Reactivation of Various Substrate Materials)

Post-Plate Baking (Hydrogen Embrittlement Relief)

Hydrogen embrittlement occurs in hard chrome plating almost entirely because of the low efficiency of chromium plating baths. Hydrogen atoms are formed on the surface of the substrate to be plated (usually steel) because of the electrolysis of water. In hard chrome baths, the electrolysis of water competes successfully with the electrodeposition of chromium, so there is a large amount of hydrogen on the substrate surface. These hydrogen atoms migrate into the steel substrate where they will eventually collect in small defects in the crystal structure and form molecular hydrogen gas. The pressure that results from the formation of this hydrogen gas in the substrate may cause the substrate to become brittle.

The majority of the hydrogen that enters the substrate can be removed by baking the plated parts at about 350-400F for 2-24 hours. Chromium electrodeposits are not a barrier that prevents the escape of the hydrogen gas when plated parts are baked. The actual time and temperature required for hydrogen embrittlement relief will vary with the type of substrate and the application. Normally, these requirements are specified by the final plating customer. As a general rule of thumb, the harder the steel substrate to be plated, the more rigorous the hydrogen

embrittlement relief procedure becomes to ensure that the hard chrome plated parts are not brittle. Hydrogen embrittlement relief should be done as soon as possible after the parts have been plated.

Grinding and Honing

Many of the parts that are hard chrome plated are coated with an extra thickness of chromium, over and above the amount needed to achieve the proper size, wear resistance, or corrosion resistance characteristics. This type of plating is generally referred to as "heavy plating". It differs from plating parts "to-size", the term used when objects are coated with a precise amount of chromium that produces the correct size or other specified characteristics directly out of the plating bath.

When parts are heavy plated, the excess coating is removed after plating by various mechanical means that produce the proper dimensions in critical areas. The most common method of post-plate finishing is by grinding on a lathe against a special grinding wheel.

Due to the extreme hardness of chromium deposits, only a very thin layer (typically about 0.1 mil) is removed with each pass of the grinding wheel over the surface being ground. If a large excess of chromium is deposited, then grinding is an expensive and time-consuming operation. In many instances the post-plate grinding operation can cost as much as the plating operation.

Internal surfaces are sometimes finished using a specialized grinding operation called honing. Honed parts allow for oil retention. Honing requires less excess thickness of chromium to produce the final finished dimension. Unfortunately, honing is not as precise as grinding. Thus, it is not used for the most demanding applications. Parts that are honed are generally not rotated on a lathe. Instead, they remain stationary while special fixtures that hold long, thin, rectangles of carbide are spun at high speeds against the plated surfaces to remove the excess chromium.

Stripping of Hard Chromium

Functional chromium electrodeposits are strippable. To minimize stripping time, many users grind off the chromium deposit as much as practical. For substrates of nickel, copper, brass, or bronze; the usual stripping method is by immersion in hydrochloric acid (HCl) solution at a concentration of 10-30% v/v of 20 Baumé HCl at a temperature between ambient and 49°C (120 F). Attack on the substrate will be very slow compared to the chromium stripping rate. For iron, steel, or stainless steel substrates, the usual stripping method is to make the part anodic in a caustic based proprietary stripper. The usual range of NaOH is 45-60 g/l (6-8 oz/gal) in the stripper solution. Temperature can vary from ambient to 71°C (160F). The stripping rate increases rapidly with temperature. During anodic stripping a current of 3-6 volts at 4.5-14 A/dm² (50-150 A/ft²) is used. The cathode material must be steel. There are also proprietary stripping additives that can be used, which will clean the work, inhibit anodic attack, and increase the stripping rate.

If HCl is used to strip ferrous alloys by immersion, care must be used to prevent excessive attack on the substrate. Similarly, copper and copper alloys stripped anodically must be run at the low end of the temperature and current density ranges to minimize substrate attack by the stripper.

Safe Handling of the Materials Used

The major source of concern when dealing with a hard chrome plating bath is the hexavalent chromium, which is carcinogenic. Once deposited on the part, the metallic chromium does not pose a health hazard. Thus the focus of a safety program for dealing with hard chrome plating should be when either adding chromic acid to the bath or operating the plating bath.

Since chromium is a very strong oxidizer, it will attack skin, clothes, and especially mucus membranes. When handling solid chromic acid flakes or crystals, a mask should be worn to prevent inhalation of chromic acid dust. Likewise, a face shield should be worn when dealing with chromic acid solutions to prevent splashing on the face or eyes. Hand protection in the form of gloves should be used around chromic acid and aprons and other protective clothing should be worn to minimize skin exposure.

The large amount of hydrogen and oxygen gas that are produced by chromium plating baths will result in a mist above an operating hard chrome plating tank. This mist contains chromic acid solution and therefore must be controlled. This can be accomplished by a good ventilation system that is coupled to a scrubber. Most systems now contain a unit that collects the chromium mist and returns it to the plating tank. This avoids getting chromium into the environment and is more efficient and economical for chromium platers.

EPA regulations limit the concentration of total chromium in the exhaust gas stream discharged to the atmosphere to not exceed 0.015 milligrams per dry standard cubic meter (mg/dscm) for new and existing large facilities and below 0.03 mg/dscm for existing small facilities. Along with the ventilation

and scrubber system, this may require that mist suppressants be added to the plating bath. These operate either by forming a foam blanket on the tank that prevents the mist and/or by reducing the surface tension of the plating bath so that the hydrogen gas does not propel the chromium solution into the air when hydrogen bubbles break through the surface.

Testing the Chromium Deposit

Electrodeposited functional (hard) chromium deposits are covered in the U.S. by the following specifications: AMS-QQ-C-320, MIL-C-23422 and AMS 2406K, and ASTM b177-01. Many large companies also have their own specification documents.

For Hard Chrome, the most common test is one of thickness. Other requirements usually call for a smooth, bright, adherent deposit that is pit free. Sometimes specified is a minimum corrosion value, micro-hardness value, and/or wear characteristic.

Thickness is most commonly measured by a micrometer. For magnetic substrates (steel) several types of gauges are available which measure difference in the magnetic field and are calibrated for chromium deposit thickness.

"As Plated" Deposit Smoothness is an indicator of both how well the substrate material was prepared (functional chromium plating will magnify any base metal defects) and if plating was conducted at a proper current density and temperature for the particular chemistry utilized. For relative thin deposits, up to a few mils thickness, the "as plated" smoothness will be an indicator of corrosion resistance.

Smoother deposits exhibit better corrosion resistance than rougher deposits.

Brightness of the "as plated" deposit is an indicator that the proper plating conditions for the particular bath chemistry were used. There is a general correlation that the brighter the "as plated" deposit, the harder the deposit. There have been a few exceptions to this generalization reported. This quality indicator needs to be applied to the "as plated" deposit since all chromium deposits will appear bright following grinding. Also, Crack Free Chromium should be "mouse" gray in color.

Adhesion of chromium deposits to the substrate can only be tested by destructive means, usually by grinding through the deposit and into the base metal and then examining the substrate/chromium interface. A very good indicator of adhesion, however, is the lack of blisters in the deposit and the lack of deposit chipping upon grinding of the deposit to final size. Other tests are described in ASTM Standard B571.

Pits in a chromium deposit are almost always caused by one of two mechanisms. Either there is a surface defect such as a pit, a particulate, or a non-activated spot or there are particulates in the plating bath that adhere to the substrate at some point during the plating process. Usually pits

are visible to the naked eye or under low power magnification.

Minimum corrosion standards are sometimes specified, especially for deposits of less than one mil thickness. The most common test is the Neutral Salt Spray test (NSST) as specified by ASTM B177. The quality of corrosion resistance of a chromium deposit is significantly affected by substrate preparation, the type of plating bath utilized, deposit thickness, and post-treatment of the part such as grinding, honing and/or buffing.

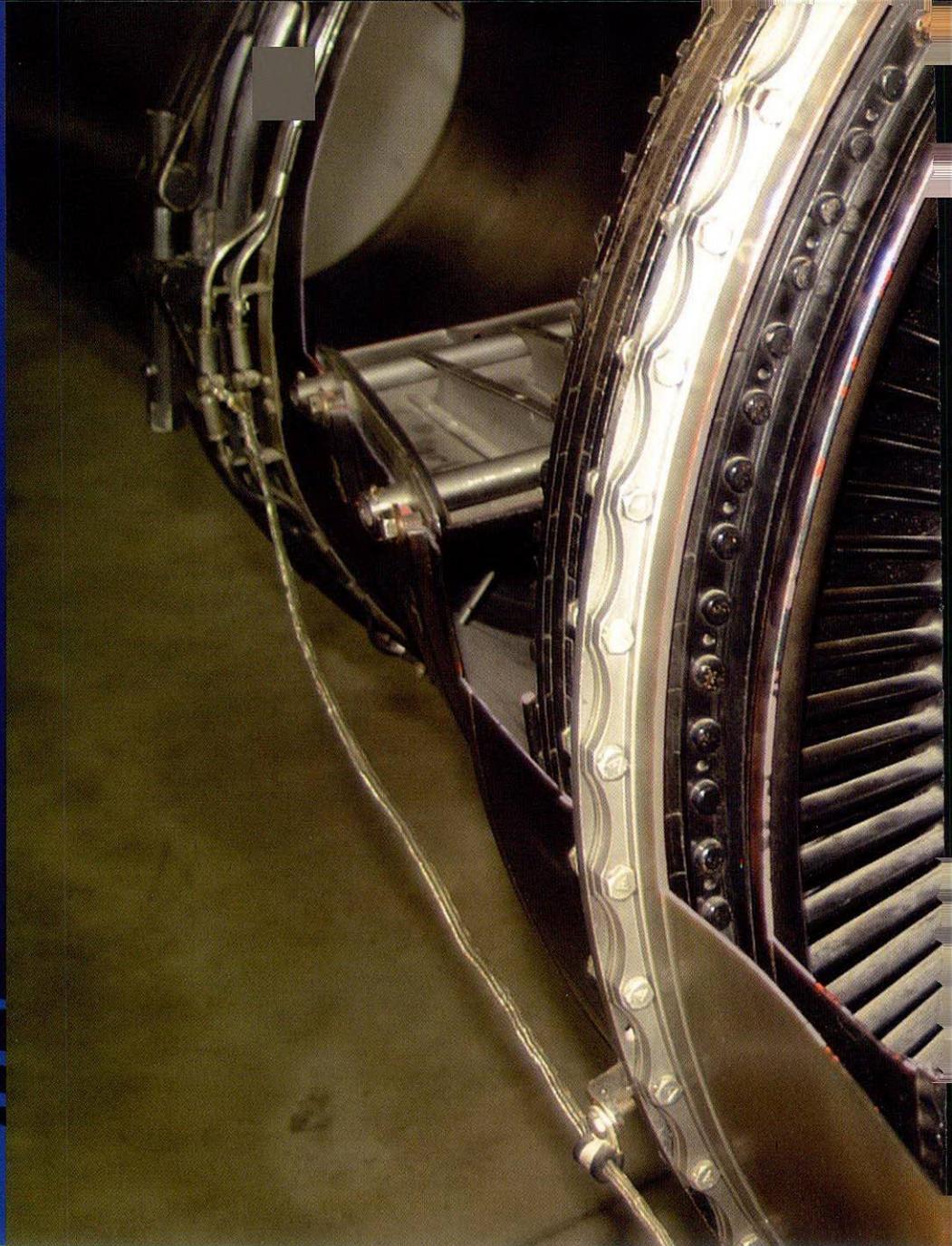
Deposit porosity is determined by the "ferroxyl test" which is described in AMS-QQ-C-320, Section 4.5.4.

The micro-hardness of bright deposits correlates well with wear properties. The usual minimum value is 850 Knoop (100 g load). Measurement of this property needs to be performed on cross-sections of the deposit in order to avoid obtaining false low readings due to substrate interferences. Usually a bright as plated deposit will have a hardness of at least 850 Knoop100.

Wear properties of a particular deposit can only be determined by destructive testing. The most common test is the Taber Abrader. Other tests include Falex and Pin on Disc.

5.

Activation/ Reactivation of various substrate materials

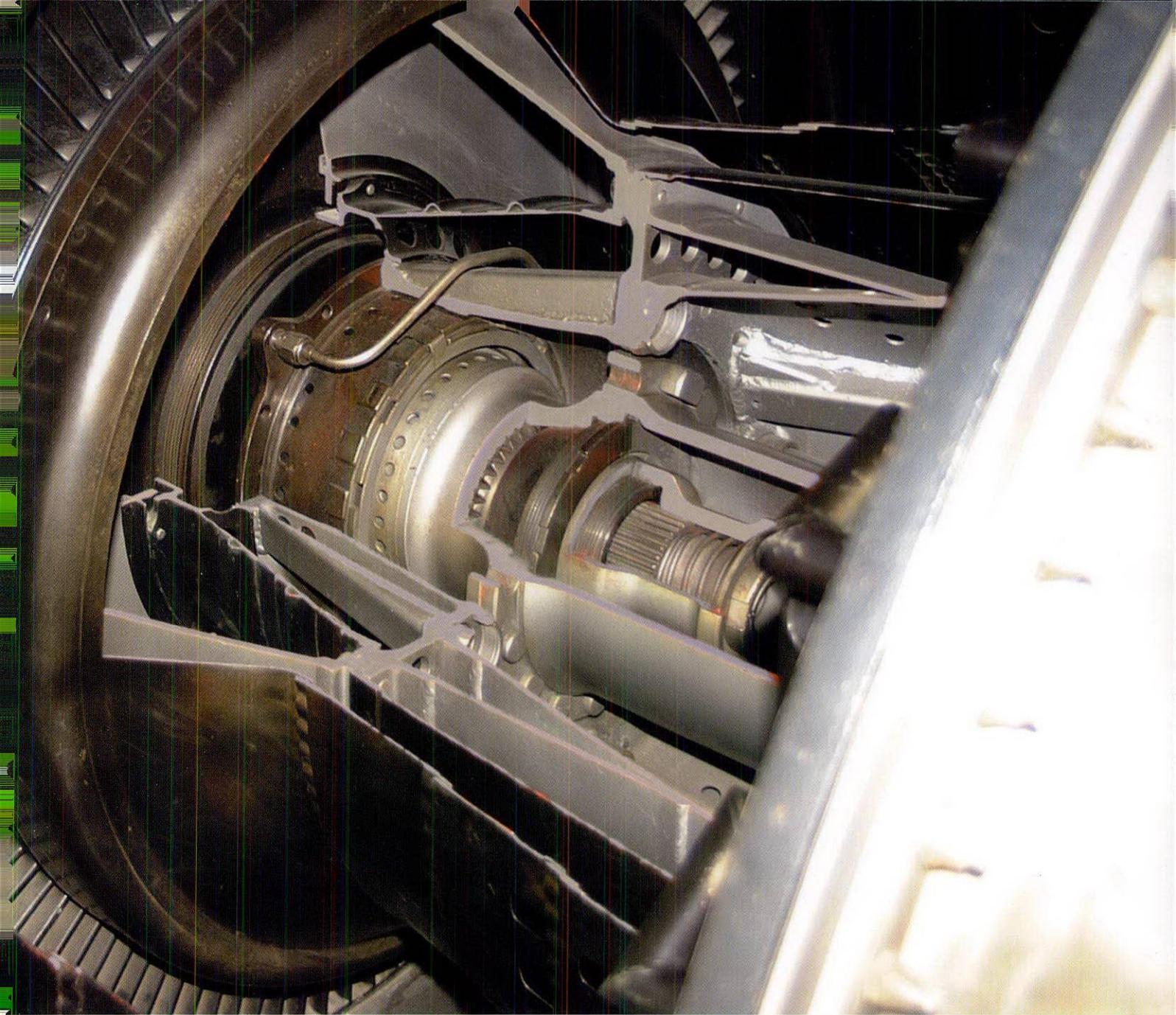


Mild Steel, Cast Iron, and High Carbon Steel

Hard chrome can be deposited on a very wide variety of base metals. The ideal pre-treatment cycle for activating parts to assure excellent adhesion and complete coverage varies greatly, depending upon the base metal. As a general rule, base metals that contain elements that readily passivate - such as nickel, chromium, tungsten, etc. - require acid activation and minimal or no reverse current activation in the plating tank when deposition is initiated. Similarly brass or copper parts are typically processed with minimal or no reverse current activation.

Most functional chromium is plated on steel substrates. While the type of alloy and the hardness may vary widely, the pretreatment cycle is usually one of cleaning in a soak or electrocleaner, anodic etching in chromic acid (frequently the plating bath) and then plating to thickness.

Anodic etching (frequently called “reverse etching”) refers to the practice of temporarily switching the polarity of the anode and cathode. This is done after pre-cleaning the parts of soils and oils. The main benefit of anodic etching is that it creates a microscopic roughening of the surface to be plated. This roughening



increases the number of active, physical sites where the plated deposit can contact the part to be plated, thereby increasing adhesion. Anodic etching may also remove damaged or loosely coherent substrate, thereby increasing the adhesion/cohesion of the substrate/coating system.

The carbon content of iron alloys is the key factor in determining the amount of reverse current activation that will produce optimum adhesion, without creating a heavy smut on the surface that will detract from proper performance. The higher the carbon content, the less the reverse current activation time. For example, cast iron parts seldom receive more than 10 to 15 seconds of reverse current activation, while a mild steel part may receive as much as 3 to 4 minutes.

Parts that have been hard chrome plated, but must be re-plated with an additional thickness of chromium require special consideration. The most common method is to allow the part (after it has been properly cleaned) to sit in the plating solution without any current until it has reached the approximate temperature of the plating bath. Once the part is at the bath temperature, current can be applied. But it must

be started as low as possible (say at about 10 to 20% of the normal current density) and then smoothly increased over several minutes to the final current density. The low current density washed the part in hydrogen to reduce any oxides on the surface to metal. This method is only recommended for plating additional chromium over chromium that has been deposited within the last few hours. Furthermore, it is only applicable where the hard chrome plate exhibited the proper adhesion and was free of pits and surface roughness. Otherwise the original deposit must be stripped or ground down and reverse etched prior to starting the plating again.

Nickel and Nickel Alloys (such as Inconel and 300 Stainless Steel)

These materials can be passivated by anodic treatments that make chromium adhesion difficult to obtain. Pre-treatments for these materials usually include a soak cleaner, followed by chromium plating. If the nickel or nickel alloy surface is old or has been heated or worked such that an oxide is present on the surface, then an activation step such as acid chloride or fluoride salt solution is necessary.

Aluminum

To plate adherent chromium onto aluminum, pre-treatment through a zincating process is required. This process consists of several steps that first etch the aluminum to obtain an active surface, and then applying an immersion zinc coating onto that "cleaned and deoxidized" surface. This process is best followed with a live lead entry into the chromium bath for plating. Also, as was mentioned previously, the nitrate ion is a serious poison for a chromium plating bath, so care must be taken to ensure adequate rinsing between the zincating operation and the chromium plating step.

Copper & Copper Alloys

These substrates, which are frequently found within the printing industry, should be cathodically or soak cleaned, rinsed well, then acid dipped in dilute hydrochloric acid to remove the copper oxide, rinsed well again, and chromium plated, preferably using a live lead entry.

*Specific plating cycles for the above materials, as well as other less common substrates, can be found in Durney, L. J., *Electroplating Engineering Handbook*, Fourth Edition, Van Nostrand Reinhold Company, New York (1984).*

6.

Glossary of Terms

Abrasive Blasting - A process for cleaning or finishing by means of an abrasive directed at high velocity against the work piece.

Activation - Elimination of a passive condition on a surface.

Addition Agent - A material added in small quantities to a solution to produce a desired effect. Also synonymous with "brightener."

Adhesion - The attractive force that exists between an electrodeposit or an electrochemical deposit and its substrate that can be measured as the force required to separate the deposit from the substrate.

Amorphous - Non-crystalline or without evidence of a regular structure.

Anode - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. In most instances it is the source of metal to be plated from the bath.

Anode Efficiency - The actual current efficiency of a specified anodic process compared to the theoretical value. The actual fraction of current used to dissolve metal from the anode compared to the theoretical amount as predicted by Faraday's Laws.

Autocatalytic Plating - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited. Often referred to as "electroless plating."

Barrel Plating - Electroplating or cleaning in which the work is processed in bulk in a rotating container (barrel).

Base Metal (or Substrate) - Material upon which processing is conducted or coatings are deposited. (It is not necessarily the material from which the part is constructed).

Blister - A dome-shaped imperfection or defect, resulting from loss of adhesion between a deposit and its substrate, or between various coatings where multiple layers of coatings are present.

Bright Dip - A solution used to produce a bright surface on a substrate by chemical immersion.

Bright Plating Range - The range of current densities within which a given plating solution produces a bright deposit.

Brightener - Another term for addition agent. A liquid or powdered material that, when added to a plating bath, improves the reflectivity or brightness of the deposits produced by the plating bath.

Brush Plating - A specialized method of plating, typically used for small scale applications, where an inert anode is surrounded by a pad, sponge, brush, or other device that will retain a volume of a concentrated solution containing a dissolved salt of the metal to be deposited. The anode/pad device is moved over the cathode during the plating operation in the area to be plated.

Buffing - The smoothing of a surface, accomplished by placing the surface to be finished against a rotating flexible wheel, to which fine abrasive particles have been applied in liquid, suspension, paste, or grease form.

Buffer - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.

Burnt Deposit - A rough, non-coherent or otherwise unsatisfactory deposit, typically produced by the application of an excessive high current density.

Bus Bar - The term used to describe the cables or conducting media – generally copper or aluminum stock – that transfers the current from the rectifier to the plating tank.

Carryover - See "Drag-in" defined on next page.

- CASS Test** - A special accelerated corrosion testing method using copper and acetic acid solution as the fog medium. It is most typically used to predict the corrosion protection of nickel/chrome, or copper/nickel/chrome electrodeposits. See ASTM Method B368.
- Cathode** - The part that is electroplated.
- Cathode Efficiency** - The actual amount of current used to deposit metal in a plating process, compared to the theoretical amount as predicted by Faraday's Laws.
- Chelate Compound** - A compound in which a metal is contained as an integral part of a ring structure and is not readily ionized.
- Cleaning** - The removal of grease or soil and other foreign materials from a surface using one or more chemical or electrochemical solutions.
- Alkaline Cleaning*—cleaning by means of an alkaline solution.
- Anodic or Reverse Cleaning*—electrolytic cleaning where the part is connected to the negative terminal of the rectifier.
- Cathodic or Direct Cleaning*—electrolytic cleaning where the part is connected to the positive terminal of the rectifier.
- Di-phase Cleaning*—cleaning by means of a solution that contains a solvent layer and an aqueous layer. Cleaning occurs by both solvent and emulsification actions.
- Soak Cleaning*—cleaning by chemical means without the use of current. Generally used to remove heavy oils and greases.
- Ultrasonic Cleaning*—cleaning by any chemical means aided by ultrasonic energy to speed up soil removal. Especially useful in the removal of buffing compounds.
- Spray Cleaning*—use of an alkaline cleaner that is sprayed onto the part(s) to be cleaned. The additional energy provided by the spraying operation accelerates the removal of soils, greases, and buffing compounds.
- Contact Plating** - Deposition of a metal by immersion of the work in a solution that is in contact with another metal.
- Corrodokote Test** - An accelerated corrosion test for electrodeposits using a special paste coating that is applied to parts before they are CASS salt spray tested. See ASTM Method B380.
- Corrosion** - Gradual dissolution or oxidation of a metal.
- Covering Power** - The ability of an electrodeposit to plate at very low current densities, such as in deep recesses or holes. (To be distinguished from Throwing Power.)
- Current Density** - The total current divided by the area to which the current is applied.
- Cathode Current Density*—the total current applied divided by the total area being plated.
- Anode Current Density*—the total current applied divided by the total anode area.
- Current Efficiency** - See Cathode Efficiency and Anode Efficiency.
- Degreasing** - The removal of grease and oils from a surface.
- Solvent Degreasing*—degreasing by immersion in liquid organic solvent.
- Vapor Degreasing*—degreasing by solvent vapors condensing on the parts being cleaned.
- Drag-In** - The water or solution that adheres to the objects from previous processing steps, and which is thereby introduced into a processing tank.
- Drag-Out** - The solution that adheres to articles when they are removed from a processing tank.
- Ductility** - The ability of a material to deform without fracturing.
- Dummy** - The term used to describe low current density plating done to remove metallic impurities from a plating bath.
- Duplex Plating or Duplex Deposit** - The term used to describe a multi-layer deposit that incorporates two layers with slightly different corrosion potential characteristics. The different layers are typically combined in a manner that allows one layer (the under-layer) to be sacrificial to the other layer (the top layer), thereby greatly improving the corrosion protection afforded, compared to that provided by a single layer of similar thickness.
- Electroless Plating** - A more commonly used term for Autocatalytic Plating.
- Electrolyte** - General term used to describe the processing bath, usually the plating bath.
- Electrolysis** - Process of causing chemical changes via the passage of current through an electrolyte.
- Electroplating** - The electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties, appearance, or dimensions different from those of the basis metal.

Electropolishing - Term used to describe the process of improving the appearance and surface condition of metallic substrates by applying a current to a chemical solution.

Etch - *Noun*—a roughened surface produced by a chemical or electrochemical means.
Verb—to unevenly dissolve a part of a surface or metal.

Faraday - The number of coulombs (96,490) required to deposit one chemical equivalent of a metal. The chemical equivalent value varies depending upon the metal being deposited.

Filter Aid - An inert, insoluble material, more or less finely divided, used as a filter medium, or to assist in filtration by preventing excessive packing of the filter cake.

Flash Plate - The application of a very thin electrodeposit, typically less than 2.54 microns (0.1 mil).

Flocculate - To aggregate into larger particles, to increase in size to the point where precipitation occurs.

Galvanic Protection - See Sacrificial Protection

Hard Chromium - Chromium plate for engineering, rather than decorative applications. Not necessarily harder than decorative chromium, but generally much thicker.

Hydrogen Embrittlement - Embrittlement of a metal or alloy caused by absorption of hydrogen typically during pickling, cleaning or plating operations.

Inert Anode - An anode that is insoluble in the electrolyte under the conditions prevailing in the electrolysis being performed. Typically used in plating baths where there is no convenient source of soluble metal an anode, such as chrome plating.

Karat - A measure of the fineness or purity of a gold deposit. One karat is equal to 1/24 part of pure gold; i.e., a 24 karat deposit is pure gold. Likewise, an 18 karat deposit is 18 parts of gold and 6 parts of another metal.

Mechanical Plating - The application of an adherent metallic coating on a substrate by impingement of finely divided solid particles of the coating to be applied onto the substrate. Alloy deposition is possible via mechanical plating. Also, plating occurs without any hydrogen embrittlement occurring.

Metal Distribution Ratio - The ratio of the thicknesses of metal deposited at two different current densities. Frequently used as a measure of the Throwing Power of an electrolyte.

Metal Turn Over (MTO) - The replacement of 100% of the original metal content of an electroless plating bath.

Microinch - One millionth of an inch, 0.000001 inches. (=0.001 mils)

Micron - One millionth of a meter, approximately one 25th of a mil. (25.4 microns = 1 mil)

Micro Throwing Power- The ability of an electrolyte to deposit metal in pores or very small recesses of substrates.

Mil - One thousandth of an inch (0.001 inches). (= 25.4 microns)

Oxidizing Agent - A compound that causes oxidation, thereby itself becoming reduced.

pH - The co-logarithm (negative logarithm) of the hydrogen ion activity. A measure of acidity (less than 7) or basicity (more than 7) of a solution.

Passivation or Passivity - The condition on a metal that retards its normal reaction in a specified environment. It is typically associated with the metal assuming an electrochemical potential more noble than its normal potential.

Peeling - The detachment or partial detachment of a deposited coating from the basis metal or undercoat layers.

Pickling - The removal of oxides or other compounds from the surface of a metal by chemical or electrochemical action.

Pit - A small depression or cavity in the surface of a part. It can be produced during manufacturing the part, during deposition, or by corrosion of the surface.

Polishing - See Buffing

Reducing Agent - A compound that causes chemical reduction, thereby itself becoming oxidized.

Regeneration - *Noun*—The replacement of 100% of the original metal content of an electroless plating bath.
Verb—The act of replenishing a processing bath in an attempt to restore optimum performance.

Resist - A material applied to a part of the surface of an article to prevent metal deposition on or metal removal from that area during chemical or electrochemical processes. Also called "masking."

Ripple - A measurement of the amount of AC current that is present in a DC current. Excessive ripple generally causes passive deposits or hazes in plated coatings. Ideally, ripple should be less than 5% for most plating applications.

RMS - A numerical reference to the smoothness of a surface. Literally, it refers to the Root Mean Square of the height difference between the microscopic peaks and valleys that are evident on a surface when it is viewed under sufficient magnification. The lower the number, the smoother the surface. In other words, the average distance from the tip of a peak to the bottom of an adjacent valley on a part with a 2 RMS finish, would be less than the equivalent distance on a part with a 16 RMS finish. RMS is typically measured with a profilometer, using vertical magnifications from 500x to 200,000x.

Robber - Term used to describe an auxiliary cathode placed near the part to be plated to divert current from concentrating in high current density areas, leading to heavy deposits in these areas.

Sacrificial Protection - The mechanism of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion (for example, zinc plating over a steel substrate). Also referred to as "Galvanic Protection."

Shelf Roughness - Roughness on surfaces of parts that face upward where solids have settled during a processing operation.

Shield - *Noun*—a nonconducting medium or panel used to alter the flow of current in an attempt to provide the most uniform cathode current density possible on the part being plated.

Verb—to alter the normal current distribution by placing a non-conducting medium in the path of the current in a manner that provides a more uniform overall current density on the part being plated.

Spontaneous Decomposition - See Triggering

Step Plating - Non-uniform thickness, striations, or skip-type plating. In electroplating operations this is generally evident in low current density areas, while in electroless plating operations it is typically evident on edges of parts and around holes or perforations in parts. Also referred to as "edge pullback" and/or "worm tracking."

Stray Current - Current that passes through paths other than the intended circuit, such as through heating coils, the plating tank, floor grating, hoist super-structures, etc.

Strike - *Noun*—a thin deposit applied to a substrate or other plated deposit to provide activation or protection from immersion plating. *Verb*—to apply such a coating by plating for a short time in a plating bath.

Strip - To remove a coating from the substrate or undercoat layer via chemical or electrochemical methods.

Substrate - The base metal to be plated.

Taber Abraser - An instrument used to characterize the wear properties of a substrate or plated finish. Test specimens are mounted to a small rotating turntable and subjected to the wearing action of two abrasive wheels, which are applied at a specific pressure, and which rotate in opposite directions. An important feature of the Taber Abraser is the all angles relative to the weave or grain of the material being tested.

Tarnish - Discoloration of a base metal or a plated coating, typically a darkening of the appearance of the basis or plated metal.

Thief - See Robber

Throwing Power - Term used to describe the uniformity of thickness of a plated coating. Electroless baths typically plate with 100% Throwing Power, i.e., the same thickness on all areas of a part in contact with the solution. Electroplating baths invariably exhibit greater thicknesses in high current density areas compared to low current density areas. See also Thickness Distribution Ratio.

Triggering - Spontaneous decomposition of an electroless plating bath, which is typically caused by excessively high concentration of reducing agents in the bath, or the introduction of solid contaminants, such as metal filings or other particles.

Troy Ounce - A unit in the Troy system of weights used for precious metals. Gold and other precious metals are typically measured in Troy ounces. (1 Troy ounce = 31.1035 grams)

Turnover - See Regeneration.

Water Break - The appearance of a discontinuous film of water on a surface, signifying non-uniform wetting and usually associated with the presence of surface contamination on parts.

Work (Plating) - The material being plated or otherwise finished.



Metal Finishing Suppliers' Association

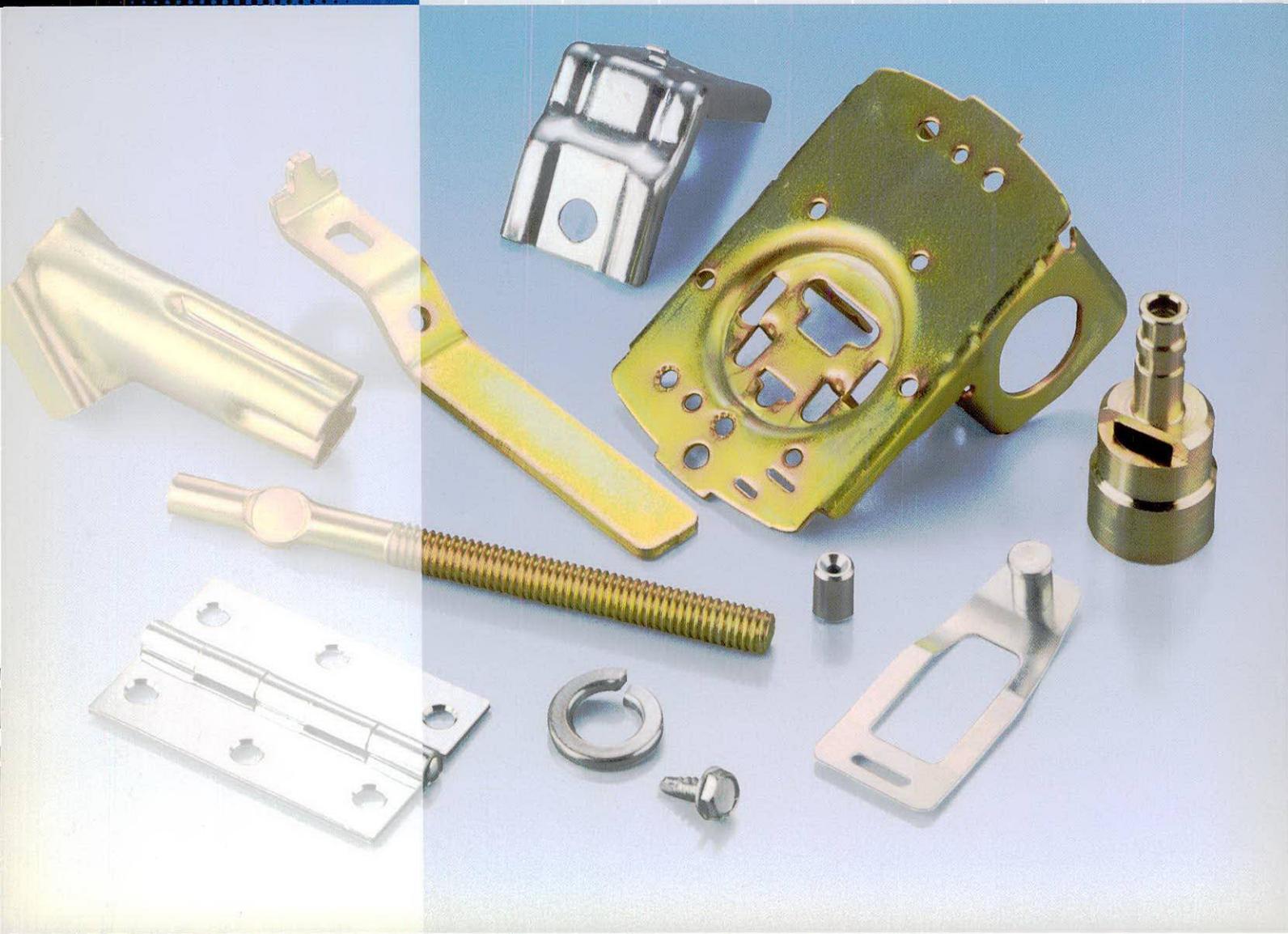
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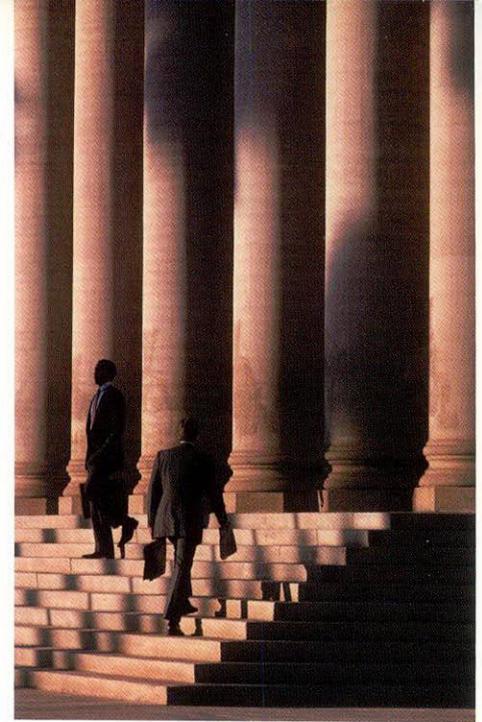
Quality Metal Finishing Guides

mfsa

Metal Finishing Suppliers' Association

Zinc, Zinc Alloy and Cadmium Coatings





Introduction

The Metal Finishing Suppliers' Association (MFSA) is a trade association of companies and individuals involved in supplying chemicals, equipment, technology, and solutions to the metal finishing industry. One of the association's primary objectives is to promote the interests and further the welfare of its members and their customers. MFSA also promotes the manufacturing of environmentally friendly products to safeguard the interests of the ultimate customer.

In 1960, MFSA initiated action to upgrade the durability of metal finishes. Known as the "Quality Metal Finishing Project" or QMF, this program was aimed at:

- 1) the promotion of technically sound specifications and standards in cooperation with interested trade and technical societies;
- 2) the provision of information to both producers and buyers of metal finished products;
- 3) the development of printed guides containing information on established standards and specifications, readily accessible for day to day use by the design engineer, the purchasing agent, and all those involved in the use of metal finished products.

Attribution

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Notice

The procedures included in this book are advisory only and their use by anyone is entirely voluntary. Reliance on any of the contents of this book for any purpose by anyone is at the sole risk of that person and neither the MFSA nor its members are responsible for any loss, claims or damage arising therefrom. A user of this book should consult a technically competent person to determine what procedure or material, whether included in this book or not, is appropriate for that user's application. By way of example only, the user will need to determine whether application problems or the environment to which the plated item will be exposed will require procedures different from those here set out, and will also have to determine what plating material is most appropriate for the user's application. In addition, the user is responsible for workplace safety, environmental protection, etc., and neither MFSA nor its members represent that use of the procedures or materials set out herein will be free from challenge. While the MFSA has made a determined effort to present state of the art plating technology and also to present the contents of this book accurately, it is almost inevitable that some errors may exist. While neither the MFSA nor its members accept responsibility or liability for such errors, the MFSA welcomes communications calling attention to any errors or commenting on the procedures described herein. Neither the MFSA nor its members have investigated any domestic or foreign patents. Accordingly, neither the MFSA nor its members are or will be responsible if use of any of the procedures or materials set out herein results in a patent infringement claim, suit, or liability.

Quality

As an association promoting the interest and welfare of the producers and customers of the metal finishing industry, MFSA realizes that everyone suffers loss when products are sold that are inadequately finished for the intended application. MFSA wishes to encourage the industry to develop and maintain high-quality standards needed to guarantee the expected or promised service of the unit.

Industry needs to know how a high-quality metal finish can be achieved, how to select proper specifications for a given application, and how to control the release of products to assure that they meet the needs of the customer. At the same time, management must be confident that this know-how is based on sound engineering principles and incorporates a reasonable margin of safety.

There have been significant developments of industrial standards for quality systems in the last few years that are applicable to metal finishing. These include:

- International Standards Organization; (ISO 9000; ISO 1456)
- American National Standards Institute/American Society for Quality Control; (ANSI/ASQC Q90)
- American Society for Testing and Materials; (ASTM B456)

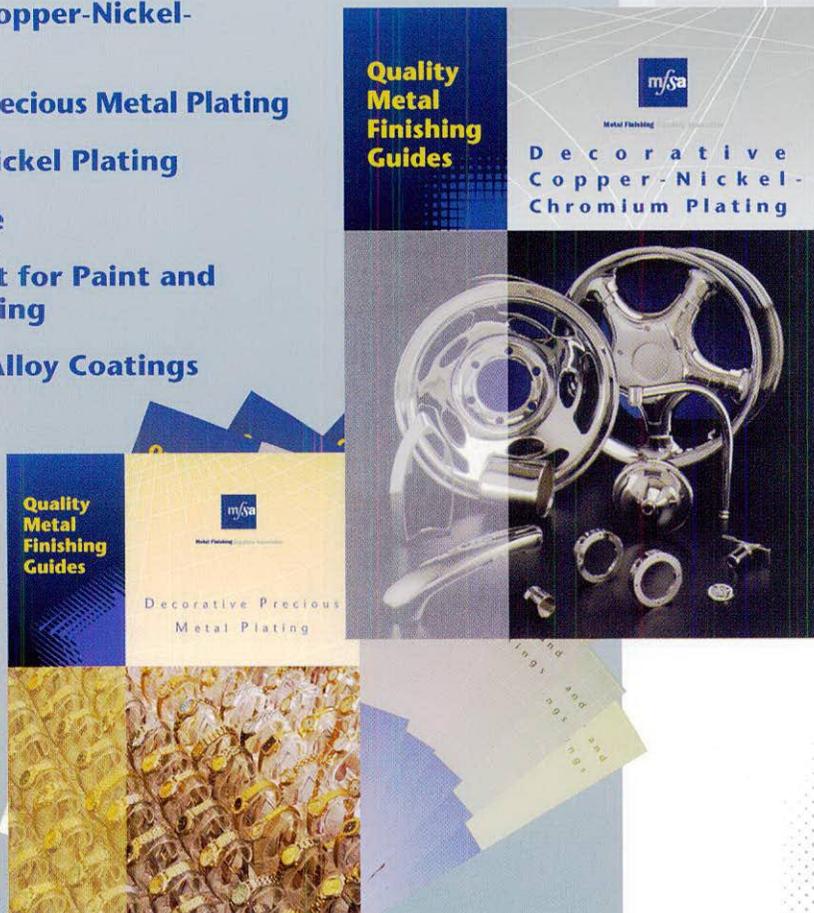
This manual will provide useful details on how to apply proven metal finishing engineering in your systems to help you maintain and improve your metal finishing quality.

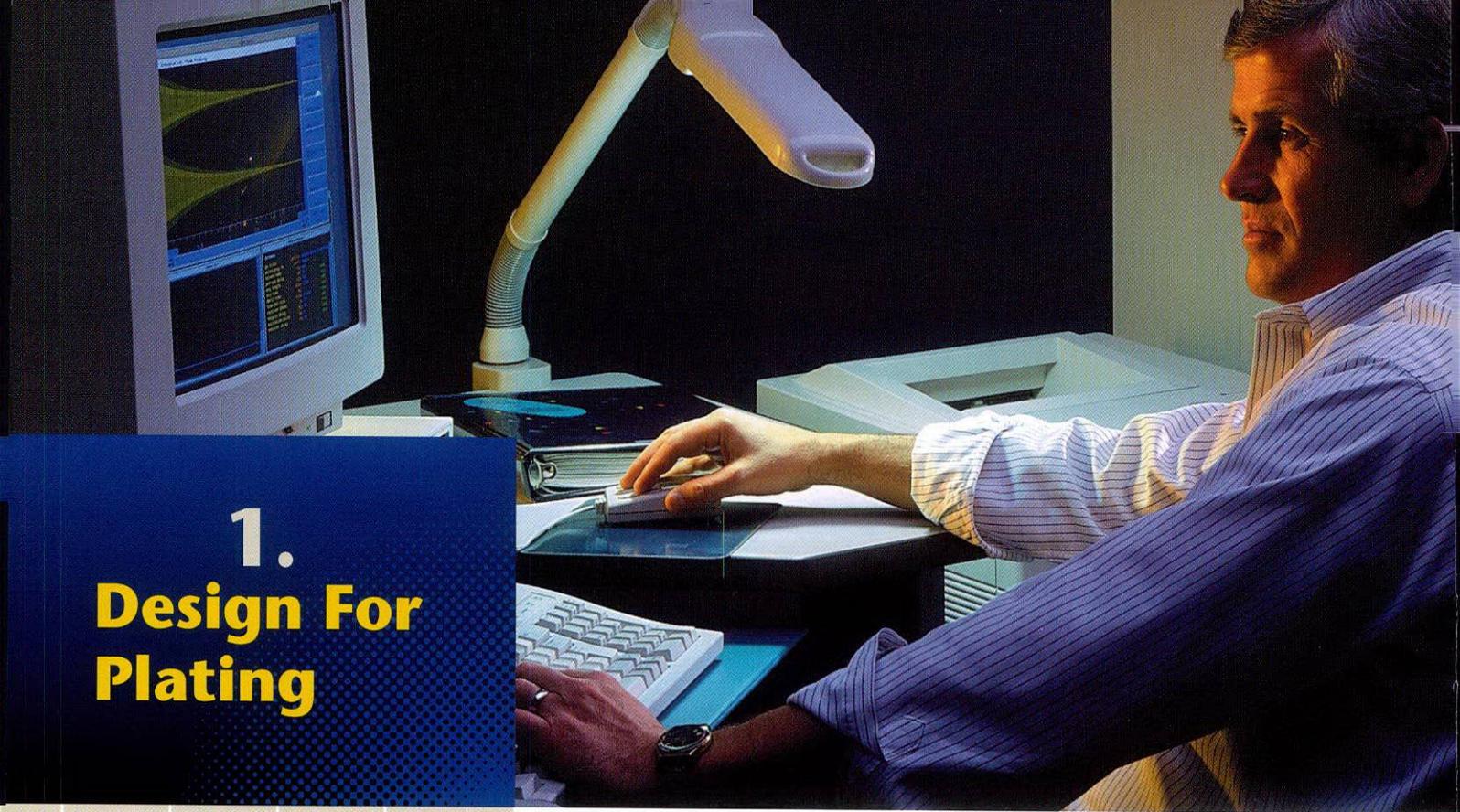
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Other QMF Guides:

- **Chemical Surface Preparation for Electroplated and Metallic Coatings**
- **Decorative Copper-Nickel-Chromium**
- **Decorative Precious Metal Plating**
- **Electroless Nickel Plating**
- **Hard Chrome**
- **Pretreatment for Paint and Powder Coating**
- **Tin and Tin Alloy Coatings**





1. Design For Plating

A program to improve and control the quality of a metal product should start at the desk of the designer. The metal finisher is restricted in what he or she can do by certain basic principles of mechanical finishing and of electroplating. The engineer should understand the limitations imposed by shape and size of components to facilitate quality finishing at an acceptable cost. The designer can exert as much influence on the quality attainable in finishing a part as can the electroplater. ASTM Standard B507 can provide the designer with helpful information.

Significant Surfaces

A most important term used in specifying metal finishes is “significant surfaces.” In most products the same standard of quality is not required over the entire surface. Instead, the quality specifications apply since compliance is expected only for the so-called “significant surfaces” defined by mutual agreement between the producer and purchaser as follows:

Significant surfaces are defined as those normally visible (directly or by reflection) that are essential to the appearance or serviceability of the article when assembled in normal position or which can be the source of corrosion products that deface visible surfaces on the assembled article. When necessary, the significant surfaces shall be the subject of agreement between purchaser and manufacturer and shall be indicated on the drawings of the parts or by the provision of suitably marked samples.

Design for Mechanical Finishing

Metal products that are to be coated are generally subjected to abrasive polishing with wheels or mass finishing techniques in preparation for the plating operations. This is done to aid in securing an attractive, uniform, mirror-like or satin appearance on the finished part. Mechanical finishing is an expensive operation. To reduce costs and assist the metal finisher in improving the appearance and quality of the product, the designer should consider certain rules applicable for parts requiring mechanical finishing:

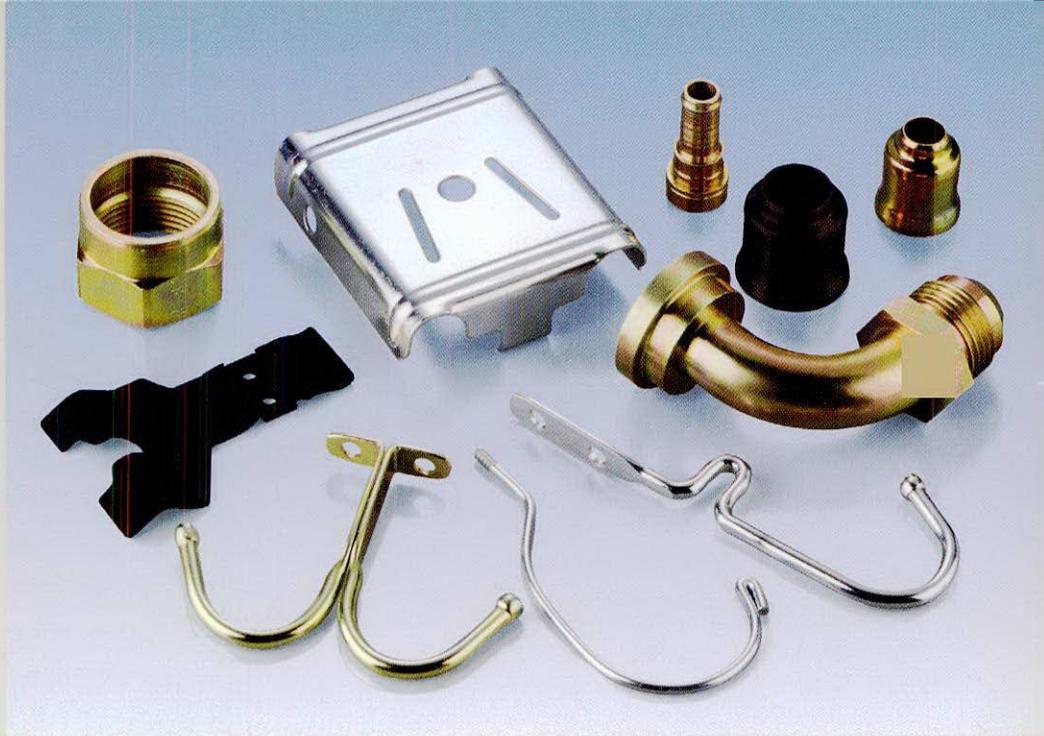
- Avoid blind holes, recesses and joint crevices which can retain polishing compounds and metal debris.
- Avoid intricate surface patterns which can be blurred by polishing operations.
- Significant surfaces should be exterior and reachable by ordinary polishing wheels or mass finishing media.
- Avoid sharp edges and protrusions which can cause excessive consumption of wheels or belts.

In small parts which are to be barrel processed, the above rules apply. This includes the requirement that the parts must be sturdy enough to withstand the multiple impacts of barrel rotation and will not entangle, causing damage or incomplete finishing. Whenever possible, small flat parts that tend to nest together should have ridges or dimples incorporated into their design to prevent such nesting.

Design for Racking, Draining, and Air Entrapment

Most metal parts weighing more than a few grams, or that require a high degree of surface brilliance, are not bulk plated in barrels, but are mounted on racks or fixtures for processing in cleaning and plating tanks. Design considerations relating to racked parts are described below.

- Consult the plating department to make certain that parts can be held securely on a plating rack with good electrical contact without masking a significant surface. Many difficult racking problems can be solved by minor design modification.
- Provide for good drainage of processing solutions from racked parts. Certain shapes tend to trap solution which then causes contamination by carry-over, possible corrosion of the part, and waste of materials. Carry-over aggravates the problem of waste disposal and adds excessive cost due to chemical losses. In design, avoid rolled edges, blind holes and spot-welded joints. Drain holes are especially helpful when they are included in the design of irregular shapes and tubular parts.
- Avoid shapes that can trap air on entry into processing tanks, if this air could block access of solution to areas requiring treatment. Wherever air can be trapped, hydrogen or oxygen gas may also accumulate during the cleaning or plating steps.



Design for Good Distribution of Electrodeposit Thickness

Simple shapes are always finished more uniformly and more economically than complex shapes. This is Rule Number One for the designer.

One of the most important factors that determines the quality of a coating is its thickness on significant surfaces. Fundamental laws of electrochemistry (current distribution), operate to prevent uniform deposition of an electrodeposited coating on a cathode of any practical shape and size. Portions of the work which are nearer to the anodes tend to receive a heavier deposit than those more distant from the anodes. Sharp edges or protrusions at all current densities tend to receive a disproportionate share of the current. The goal of the designer and the plater is to make thickness variations as small as possible. At the same time, it is appropriate to minimize the unnecessary waste of metal by excessive build-up on both

significant and non-significant areas. The same variation in plating thickness found on plated articles also typically exists when comparing parts plated on different areas of plating racks. For example, parts racked on the perimeter of fixtures tend to exhibit more thickness than parts from the center of fixtures.

It is possible to estimate metal distribution ratios from models or mock-ups, but there are also empirical rules. These can guide the designer to improved uniformity of thickness, hence improved quality with greater economy. These general principles and various sketches illustrate what has been learned from practical experience:

- Avoid concave or perfectly flat significant surfaces. Convex or crowned areas receive more uniform coatings. Use a 0.4 mm per 25.4mm (0.015 inch per inch) crown—minimum.

- Edges should be rounded to a radius of at least 0.4 mm (1/64 inch) and, preferably to 0.8 mm (1/32 inch).
- Re-entrant angles or corners should be filleted with a generous radius. Make sure radii are as large as possible.
- Avoid concave recesses, grooves, or slots with width less than one-half the depth.
- Minimize the number of blind holes because these must usually be exempted from minimum thickness requirements. Where necessary, limit their depth to 50% of their width. Avoid diameters less than 6 mm (7/32 inch.)
- Countersink threaded holes to minimize electroplate thickness build-up at their peripheries and to facilitate insertion of fasteners after plating.
- If fins or ribs are required, reduce their height and specify a generous radius, 1.6 mm (1/16 inch) at each base. Round off tips with radii of a least 1.6 mm (1/16 inch). Multiple parallel fins should have spacing between centers equal to four times the width of the fin. Broad hollow ribs are preferred over slender solid ones.
- Adopt recessed letters and insignias in preference to raised letters and insignias, but round-off edges and provide gentle contours.
- Integrated studs for fasteners should be shortened as much as possible and inside angles at each base should be rounded generously. Tips should be similarly rounded.
- Studs or bosses with hollow centers should be shortened as much as possible and angled 90 degrees from the major plane of the part. All bosses should face the same direction.
- Assist the plater by clearly marking significant surfaces on part drawings.

- Avoid use of a variety of different base metals on any one part to be plated. The contact of dissimilar metals may interfere with covering power or adhesion of the deposit due to galvanic action. It might also increase corrosion in service.

Design Features That Influence Electro-platability

The effect of the basic design of a product or component upon the effectiveness or durability of the plating used has been the subject of much study and research. Many

failures blamed on the plater can be attributed to the original design. A major contribution to the plating industry was made by the Zinc Institute, Inc. when it sponsored a design study by Battelle Memorial Institute to establish basic zinc die casting design principles; these findings are also applicable to other substrates.

The various shapes shown here provide the “dos and don’ts” of design configurations and their relationships to electroplating quality.

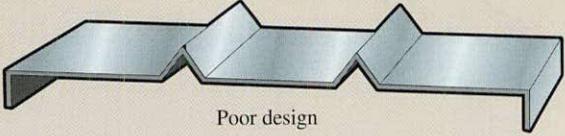
Feature	Influence On Electroplatability	Better Design
Flat-bottom grooves	Inside and outside angles should be rounded generously to minimize costs.	
V-shaped grooves	It is difficult to deposit corrosion resistant finishes in deep, V-shaped grooves. Shallow, rounded grooves are better.	
Fins	Increase plating time and costs for a specified minimum thickness and reduce the durability of the plated part.	
Ribs	Narrow ribs with sharp angles usually reduce electroplatability; 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.	
Concave recesses	Electroplatability is dependent upon dimensions.	
Deep scoops	Increase plating time and costs for a specified minimum thickness.	
Spearlike Juts	Buildup on jut will rob corners from their share of electroplate. Crown the base and round off all corners.	
Rings	Electroplatability is dependent upon dimensions. Round off corners and crown from center line, sloping towards both sides.	

The distribution of electroplate is indicated in an exaggerated fashion.

ROUND OFF HIGH SPOTS

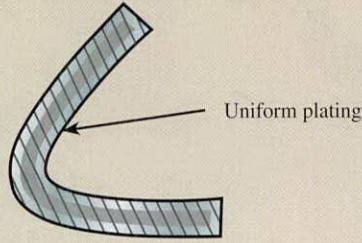


Good design

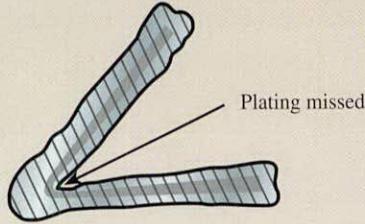


Poor design

AVOID SHARP INTERIOR ANGLES

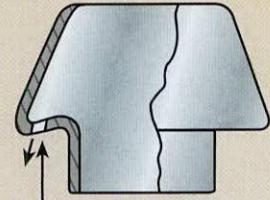


Uniform plating

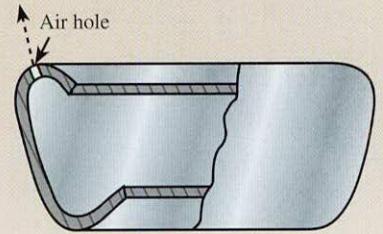


Plating missed

PLACE HOLES FOR DRAINING AND AIR ESCAPE



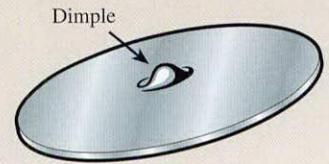
Drain hole



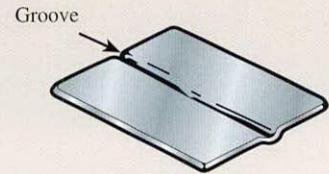
Air hole

Feature	Influence On Electroplatability	Better Design
Convex surfaces	Ideal shape. Easy to plate uniformly, especially where edges are rounded.	
Flat surfaces	Not as desirable as crowned surfaces. Use a 0.4mm/25.4mm (1/64 inch) crown to hide undulations caused by uneven buffing.	
Sharply angled edges	Undesirable. Reduced thickness at center areas and requires increased plating time for depositing a minimum thickness of durable electroplate. All edges should be rounded. (Edges that will contact painted surfaces should have a minimum radius of 0.8 mm [1/32 inch])	
Flanges	Large flanges with sharp inside angles should be avoided to minimize plating costs. Use a generous radius on inside angles and taper the abutment.	
Slots	Narrow, closely spaced slots and holes reduce electroplatability and cannot be properly plated with corrosion-protective nickel and chromium unless corners are rounded.	
Blind holes	Must usually be exempted from minimum-thickness requirements. Where necessary limit depth to 50% of width. Avoid diameters less than 6mm (7/32 inch).	
Sharply angled indentations	Increase plating time and costs for a specifically minimum thickness and reduce the durability of the plated part.	

AVOID STICKING WHEN BARREL PLATING



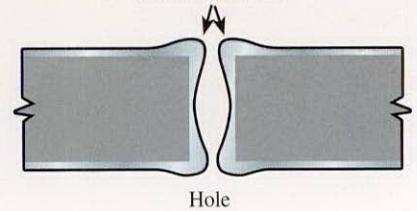
Dimple



Groove

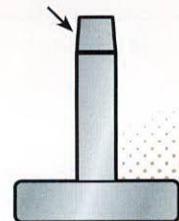
ALLOW FOR BUILDUP

Buildup reduces effective diameter



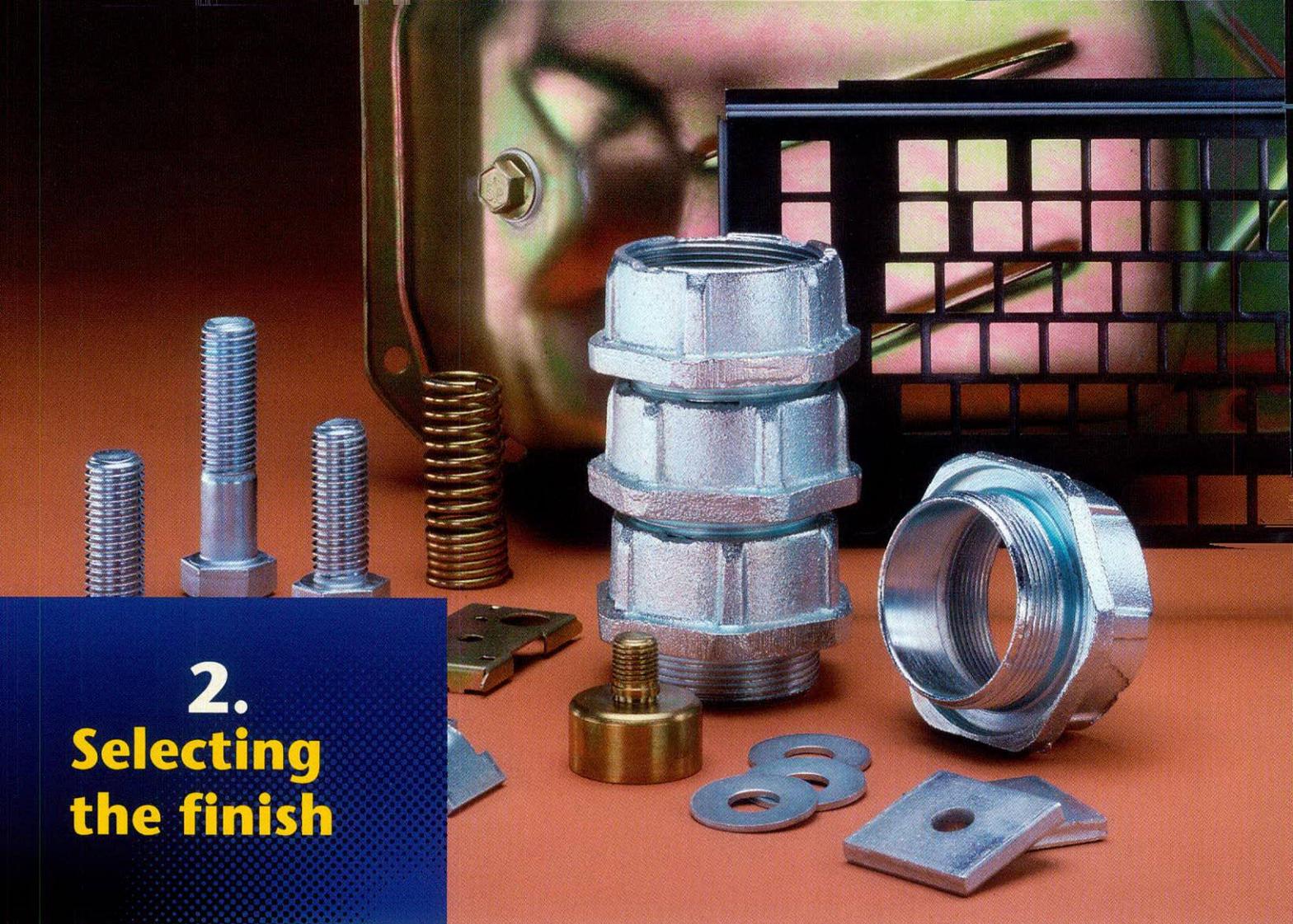
Hole

Tapered end to allow for buildup



Plug

The distribution of electroplate is indicated in an exaggerated fashion.



2. Selecting the finish

The designer should approach the problem of selecting a zinc, zinc alloy, or cadmium finish with a clear understanding of the requirements expected of the coating, the properties of the metal deposit, the properties of any film on the deposit and the service conditions the article will be expected to withstand. In most cases, pleasing appearance is an important factor regardless of function. A properly selected finish of high quality will have an acceptable appearance not only on the shelf, but also throughout the service life of the part.

Requirements of the Finish

Iron and steel surfaces rust readily even in mildly corrosive surroundings. The rust is not only unattractive, but also may interfere with mechanical functioning of a component or discolor materials that come in contact with it. Nearly all iron and steel structures or parts are therefore treated for rust prevention. Zinc, zinc alloy, and cadmium deposits afford excellent protection against rusting under most circumstances. The reason for applying these deposits may be classified as (a) to retard rusting; (b) to provide a pleasing appearance; (c) to serve in some functional capacity.

(a) Rust Prevention – The corrosion rates of zinc, zinc alloys and cadmium are much lower than those of steel in most atmospheres as well as in contact with water. In addition, the electrochemical relationships between each of these two metals and steel are such that rusting of the later is suppressed by galvanic action even where the coating is damaged or worn through.

(b) Appearance – In some applications zinc, zinc alloys, or cadmium coatings are used with the sole objective of providing a durable, pleasing appearance for the period of useful life of a steel part. Applications of this class have been greatly increased by the availability of bright zinc and cadmium deposits and the development of chromate conversion coatings and colored finishes.

(c) Functional Service – Zinc, zinc alloy, or cadmium may be deposited on steel components to serve functional purposes while retarding rusting. Examples of such uses are: 1) to improve solderability, to lower electrical contact resistance and to provide surface conductivity on electronic equipment, radio, computer, and television chassis; 2) to prevent discoloration of fabrics or other materials with which the plated coating may be in contact; 3) to prevent seizing of moving parts, bolts, nuts, and latches; 4) to provide maximum service life in high temperature environments.

Properties of the Metal

Although zinc, zinc alloys and cadmium are considered to be similar in their galvanic behavior to iron in most environments, they do differ in many of their physical deposit properties. These differences should be considered in selecting one coating versus another for a given application.

(a) Rust Retardation — The potential difference between cadmium and iron is usually less than that between zinc and iron. For this reason cadmium does not retard rusting over as large an area of exposed iron as does zinc. Zinc alloys exhibit even lower differences between themselves and iron. “Pinhole” corrosion of steel is occasionally observed to occur through pores in a cadmium coating. This suggests that the potentials of cadmium and iron may even be reversed in some environments. In the case of zinc-nickel alloy plating, there is a point where zinc-nickel is no longer sacrificial to iron due to potentials of high nickel content (above 15% by weight or more).

Exposure tests have shown conclusively that in industrial locations cadmium coatings fail more rapidly than do zinc coatings of equal thickness. Zinc alloy coatings of zinc-nickel, zinc-iron, tin-zinc, or zinc-cobalt will exceed the protective life of conventional zinc. In severe marine atmospheres, however, tin-zinc and cadmium are more effective than zinc in retarding rusting. The slower rate of corrosion of zinc and zinc alloy deposits in industrial atmospheres has been attributed to the fact that zinc corrosion products formed in such atmospheres are alkaline in character and of low solubility. Zinc alloy corrosion products are even more insoluble, and offer protection to the underlying metal plating. Zinc-cobalt shows greater ability to prevent the spread of red rust versus zinc-iron or plain zinc. The issue here may be the lower corrosion rate of the zinc-cobalt deposit. Cadmium corrosion products in industrial atmospheres are more soluble and tend to wash away. It is not clear why cadmium outperforms zinc in neutral salt spray testing and in pure marine atmospheres. The zinc corrosion products formed under these conditions are visible enough, but do not seem to be as protective.

(b) Corrosion Behavior — When zinc is stored in a humid, stagnant atmosphere, quantities of white, bulky corrosion products develop which are usually objectionable and may interfere with proper functioning of moving parts or cause seizure of threaded components. Cadmium as well as certain zinc alloy deposits weather differently and do not generate voluminous adherent corrosion products. Corrosion of this sort usually can be prevented or minimized by application of chromate conversion finishes.

(c) Solderability — Tin-zinc and cadmium coated steel can be soldered readily. This can be an important advantage in electronic and other electrical equipment.

(d) Toxicity — Cadmium corrosion products are both toxic and carcinogens. Hence cadmium should not be plated on articles which come in contact with foods or beverages. Cadmium vapors and oxide fumes are toxic, and should never be welded. Cadmium also poses a severe waste water treatment problem for the plater because of its toxicity. It is becoming increasingly expensive to legally discard cadmium waste products. Zinc salts are far less toxic. Although it is not advisable to use bare zinc deposits in contact with food, zinc coated wire with organic coatings have been used for many years in the manufacture of refrigerator shelves. Zinc and zinc alloy coatings may be welded safely if the fumes are removed by adequate ventilation.

(e) Electrical Properties — Cadmium and tin-zinc have a lower contact resistance than zinc. This, together with its ease of soldering, leads to its use on electronic apparatus. The lesser tendency of cadmium and tin-zinc to form bulky weathering products also is an advantage in electrical equipment, giving better surface conductivity and contact behavior.

(f) Whiskering — Zinc can exhibit whiskering or formation of dendritic crystal growth. Tin-zinc, zinc-cobalt, zinc-iron, and zinc-nickel alloys do not exhibit formation of these dendritic crystals.

(g) Hydrogen Embrittlement — High carbon and high strength steel having a hardness greater than Rockwell C35 are susceptible to embrittlement caused by absorption of hydrogen in the processing of the steel in machining, pickling, cathodic cleaning, or plating operations. Zinc, zinc alloys, and cadmium plating can cause this embrittlement on high strength steels used to make springs, lock washers, fasteners, and the like. The phenomenon of delayed cracking by hydrogen embrittlement has been studied by hundreds of workers, but is still not thoroughly understood. There is no general agreement on the appropriate pretreatment cycle for cleaning and plating such steels with zinc, zinc alloys or cadmium which will reliably avoid embrittlement. There is agreement that susceptible steel parts should be heated after machining, and after plating to reduce the danger of subsequent cracking. The baking should be done as soon as possible after electroplating, and before any supplementary chemical treatment of the electroplated surfaces. Baking at 191°C (375°F) for four or more hours is a widely used precaution suggested in ASTM B-242. However, the best time and temperature in some cases must be established experimentally. High efficiency alkaline and chloride plating processes, (which generate smaller amounts of hydrogen), enable a bright ductile deposit of zinc to be plated directly onto cast iron, malleable iron, or steel with greatly reduced possibility of inducing hydrogen embrittlement.

(h) Covering Castings — The phenomenon of “covering power” is defined as the ability to plate in deep recesses or low current density areas. Acid chloride zinc baths are routinely used to plate directly onto cast iron or high carbon steel components. Standard cadmium baths are generally superior to most zinc baths in their ability to effectively plate in recessed areas of a component.

(i) Formability — Cadmium, zinc, and certain zinc alloys may be deposited in a ductile form, although this is usually a function of thickness (higher thicknesses are usually less ductile). Steel coated with properly applied zinc, zinc alloy, or cadmium deposits can be formed, stamped, or drawn without damage.



3. Specifying the finish

Having selected either zinc, zinc alloy, or cadmium as the coating for a steel or iron component, and having decided whether or not a supplementary chromate finish is required, the designer must now specify the requirements of the system to assure its quality. High quality can be achieved by specifying the appropriate thickness for the application, adhesion, appearance and freedom of the base metal from embrittlement, together with appropriate tests agreed upon by the purchaser and the plater for assuring that these requirements have been met.

(a) Thickness — Atmospheric exposure tests in several countries have supported the generalization that the protective value of zinc, zinc alloy, or cadmium deposits is proportional to their thickness. That is, a steel part coated with 10 microns of zinc will be protected from rusting about twice as long as another part coated with 5 microns and exposed for the same time. Thickness is, therefore, a very important item in a quality specification.

Tables I, II, and III provide suggested thicknesses for high quality finishes on iron and steel. An attempt is made to define four classes of service conditions; mild, moderate, severe, and very severe. In case of doubt as to the severity of the planned application, one should specify the thickness for very severe service. It should be noted that the tables recognize some applications for very severe service. However, zinc and cadmium plated coatings at the heaviest thicknesses often give way to alternative zinc alloy deposits, hot dipped or mechanically applied coatings, metal spraying or other finishes.

Table I – Suggested Standards for Quality Zinc Coatings on Iron and Steel Products

Degree of Exposure	Minimum Thickness Microns (1)	Chromate Finish	Salt Spray Hours to White Corrosion (3)	Typical Applications
MILD – Exposure to indoor atmospheres with rare condensation & subjected to minimum wear or abrasion	5	None Clear Iridescent Yellow Black Olive Drab	- 12-24 72-96 72-96 150-300	Screws, nuts & bolts, wire goods, fasteners
MODERATE – Exposure mostly to dry indoor atmospheres, but subjected to occasional condensation, wear or abrasion	8	None Clear Iridescent Yellow Black Olive Drab	- 12-24 72-96 72-96 150-300	Tools, zipper pulls, shelves, machine parts
SEVERE – Exposure to condensation, perspiration, infrequent wetting by rain, cleaners	13	None Clear Iridescent Yellow Black Olive Drab	- 12-24 72-96 72-96 150-300	Tubular furniture, insect screens, window fittings, builders' hardware, washing machine parts, bicycle parts
VERY SEVERE (2) Exposure to bold atmospheric conditions & subject to frequent exposure to moisture, cleaners & saline solutions plus likely damage by denting, scratching or abrasive wear	25	None	-	Plumbing fixtures, pole line hardware

Chromate finishes are the first line of defense against corrosive attack on the plated coating and these thin films do an outstanding job of enhancing the total protective value of the metal coating. The chromate coatings serve to improve appearance of the plated coatings, retard staining and delay formation of white corrosion products which might interfere with functioning of a component. Once the chromate film is ruptured or breached, the protective value of the plated coating is employed. The thinner chromate finishes are specified when solderability and good electrical characteristics of cadmium coated electronic equipment must be maintained. Those treatments are also specified for service in which maintenance of appearance and long shelf life are the sole considerations as with thousands of varieties of hardware parts and wire goods.

25.4 Microns = 1.0 Mil.

- (1) Thickness of the coating after chromate treatment.
- (2) Although there exist some applications for heavy electro-deposited coatings for very severe service they are most usually satisfied by hot dipped or sprayed coatings.
- (3) ASTM B-201 specifies the protection afforded by the different chromate conversion coatings to the first sign of white salt corrosion of zinc.

Table II – Suggested Standards for Quality Cadmium Coatings on Iron and Steel Products

Degree of Exposure	Minimum Thickness Microns (1)	Chromate Finish	Salt Spray Hours to Cadmium Corrosion	Typical Applications
MILD – Exposure to indoor atmospheres with rare condensation & subjected to minimum wear or abrasion	5	None Clear Iridescent Yellow Olive Drab	- 12-24 96-120 150-250	Springs, lock washers, fasteners, tools, electronic & electrical parts
MODERATE – Exposure mostly to dry indoor atmospheres, but subjected to occasional condensation, wear or abrasion	8	None Clear Iridescent Yellow Olive Drab	- 12-24 96-120 150-250	TV & radio chassis, threaded parts, screws, bolts, radio parts, instruments
SEVERE – Exposure to condensation, perspiration, infrequent wetting by rain, cleaners	13	None Clear Iridescent Yellow Olive Drab	- 12-24 96-120 150-250	Washing machine parts, military hardware, electronic parts for tropical service
VERY SEVERE (2) Exposure to bold atmospheric conditions & subject to frequent exposure to moisture, cleaners & saline solutions plus likely damage by denting, scratching or abrasive wear	25	None Clear Iridescent Yellow Olive Drab	- 12-24 96-120 150-250	

25.4 Microns = 1.0 Mil.

- (1) Thickness of the coating after chromate treatment.

Table III – Suggested Standards for Quality Zinc Alloys

	Deposit/Chromate	Hrs to White Corrosion	Hrs to Red Corrosion
Zinc	Yellow	100	300
Zinc-Cobalt (0.5%)	Yellow	250	500
Zinc-Cobalt (0.5%)	Black	200	500
Zinc-Nickel (8%)	Yellow	400	1000+
Zinc-Nickel (12%)	Yellow	1000	1500+
Zinc-Iron (0.5%)	Black	300	800+
Zinc-Tin (70%)	Yellow	100	1500+

Table IV – Published Specifications for Zinc Coatings on Steel

Sponsor	Specification	Class or Type	Minimum Thickness (microns)
ASTM	B-633	Fe/Zn – 25 Very Severe	25.4
		Fe/Zn – 12 Severe	12.7
		Fe/Zn – 8 Moderate	8
		Fe/Zn – 5 Mild	
Federal (1)	QQ-Z-325a	1	25.4
		2	12.7
		3	5.08
	FF-B-561a	Lag bolts	5.08
	FF-H-106a	Locks, door trim	12.7
	FF-H-111a	Shelf & misc hardware	12.7
	FF-H-116c	Hinges	12.7
	WW-T-806b	Electrical metal tubing	20.3
WW-P-541b	Plumbing fixtures	27.4	
Military	MIL-F-14072	Ground Signal Equipment-I	12.5
		Ground Signal Equipment-II	12.5

25.4 Microns = 1.0 Mil.

(1) In recent years, the Federal specifications have deferred to the ASTM specifications for zinc.

- ASTM B 840 is the standard specification for electrodeposited coatings for zinc cobalt alloy deposits
- ASTM B 841 is the standard specification for electrodeposited coatings for zinc nickel alloy deposits
- ASTM B 842 is the standard specification for electrodeposited coatings for zinc iron alloy deposits

The thickness standards suggested by MFSA in Tables I and II include grades suitable for all uses. In Tables IV and V some of the specifications for zinc and cadmium coatings published by other organizations are listed. Yellow Chromate is a hexavalent type.

(b) Protective Value — As indicated earlier, specifying a minimum thickness of a zinc, zinc alloy, or cadmium deposit is the best way to guarantee protective value of high quality. Some buyers require additional performance in the standard salt spray test as another acceptance requirement. Assuming equivalent thicknesses, cadmium will typically outperform zinc coatings in salt spray testing. In actual exposure tests, cadmium deposits on steel usually show a superiority over zinc in marine atmospheres. Correlating performance in a salt spray chamber to actual performance in the field is difficult.

A different test that is becoming increasingly popular in the automotive industry is a cyclic test. In this test, the component parts are subjected to a cycle of salt fog and humidity dictated by the specifier. Some designers feel that this test offers a more “real world” meaning to the tests.

(c) Adhesion — The coating must remain adherent to the basis metal when subjected to bending, cutting, or grinding. There is no accepted standard of adhesion and these tests can only be considered qualitative. In high quality plating the adhesion of the metallic coatings is so good that in any destructive test the bond between the basis metal does not fail at the interface. Adhesion testing of plated coatings is specified in ASTM B-571.

Table V - Published Specifications for Cadmium Coatings on Steel

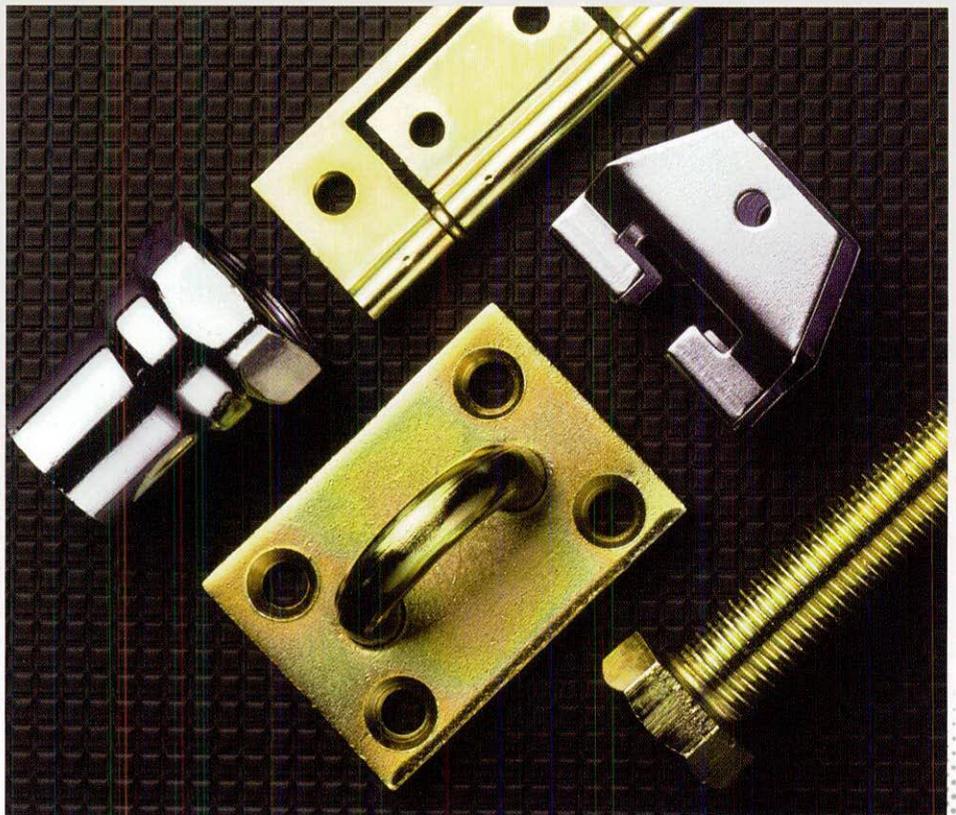
Sponsor	Specification	Class or Type	Minimum Thickness (microns)	
ASTM	B-766	25	25.4	
		12	12.7	
		8	8	
		5		
Federal (1)	QQ-P-416B	1	12.7	
		2	7.6	
		3	5.1	
		FF-B-561a	Lag bolts	5.1
		FF-H-106a	Locks, door trim	3.8
		FF-H-111a	Shelf & misc. hardware	3.8
Military	MIL-F-14072	I	12.7	
		II	7.6	

25.4 Microns = 1.0 Mil.

(d) Appearance — Appearance cannot be readily specified because it involves factors which are not easily assessed such as brightness, roughness, uniformity of color, and freedom from blisters, pits and other surface defects. It is suggested that samples be prepared which are acceptable to both the plater and the purchaser as standards of quality in appearance. For chromated finishes the general appearance is automatically specified when the type of finish is selected. However, if the requirement of color is critical, use of standard samples for comparison is suggested.

(e) Hydrogen Embrittlement — All high strength steel parts with hardness greater than Rockwell C35 are susceptible to embrittlement caused by absorption of hydrogen during the processing of the steel or in pickling, cleaning, or electroplating operations. Cathodic cleaning should be avoided if possible in favor of anodic cleaning and activating. To avoid possible failure of such components on the shelf or in service due to delayed cracking, it should be noted that they shall be heated within 1 – 2 hours after plating for 3 – 4 hours at 191 – 205°C (375 – 400°F) or as described in ASTM B242.

If immunity from hydrogen embrittlement is a paramount requirement, coating high strength steel parts by mechanical plating should be considered because no hydrogen is introduced into the steel during the plating process itself. It should be noted that the use of this process for the purpose of controlling hydrogen embrittlement to a minimum must recognize the possible embrittling effects of any machining, cleaning, and pretreatment procedures. Please see the section on Mechanical Plating and Galvanizing found in this guide.



Blue bright and yellow chromates enhance zinc plating.

4.

Testing the finish

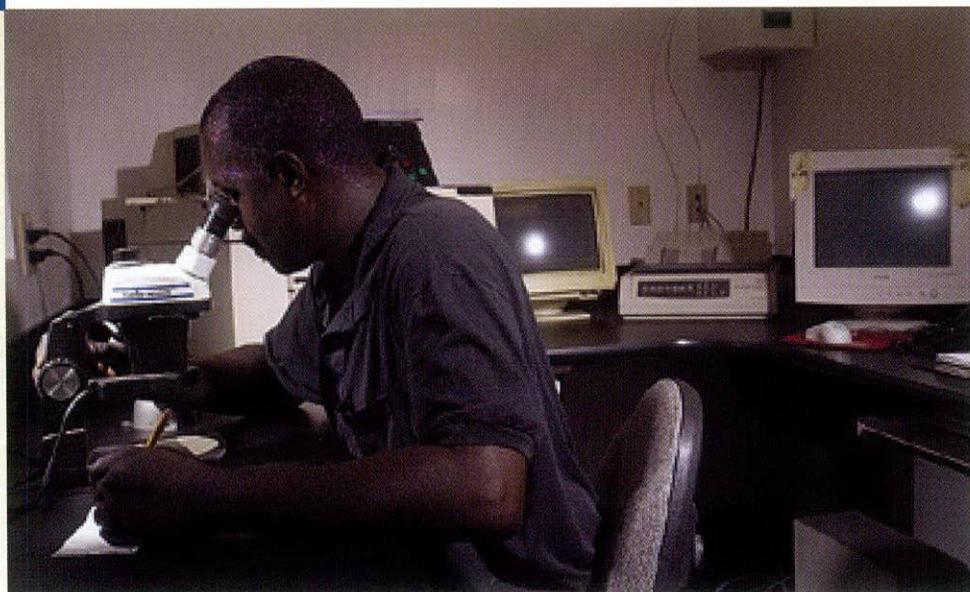
Thickness

There is no practical method of measuring the thickness of chromate conversion coatings, although electrical impedance measurements are useful in characterizing the coatings. The appearance of such finishes itself is an index of relative thickness because the olive drab films are known to be thicker than the clear finishes, while the iridescent yellow films are of an intermediate thickness. For the metal coatings there are several methods to test for thickness, some being destructive of the part tested.

(a) X-Ray Thickness Method – In this method, x-rays produced by an x-ray tube are focused on the area to be tested and the radiation emitted from that surface is measured. The radiation measured is secondary emissions from the interaction of the x-rays with the coating and substrate. This method is described in ASTM B568. The emissions measured are specific for each metal. Among the characteristics of this method are:

- No physical contact with the measured surface is required, thereby protecting that surface.
- Extremely small areas may be measured.
- Since the emissions are specific for each metal, alloy compositions may be determined. However, zinc alloys that contain small amounts of alloying elements (such as zinc-cobalt and zinc-iron) may be difficult to measure for alloy content.

(b) Microscopic Method – The part under test is cut on a plane perpendicular to a significant surface and is mounted for metallographic examination. The cross-section is polished and etched to contrast the plated coating with the basis metal. The thickness is then measured optically with a microscope at a magnification great enough to permit measurements of thickness with an accuracy of plus or minus one micron, or one percent of the coating thickness, whichever is greater. The method is obviously destructive. Because of the skill required by the operator and the time involved, it is not ordinarily used for production testing. Where there is disagreement in thickness measured by other methods, the microscopic is generally accepted as the referee test. This method is described in ASTM B487.



Microscopic thickness examination

(c) Coulometric Methods — Instruments are available which determine the thickness of zinc and cadmium coatings on steel automatically by recording the number of ampere minutes or coulombs required for a controlled anodic current to dissolve the coating from a small, well defined area on the surface. Although the test destroys the coating, it is rapid and simple. This method is described in ASTM B504.

(d) Magnetic Methods — Since zinc, cadmium and most zinc alloys are non-magnetic, while iron and steel are magnetic, it is possible to determine the thickness of these coatings by commercially available instruments which employ the magnetic field principle. This method is described in ASTM B499. It should be noted that the high nickel (12-15%) alloy is not recommended for test by magnetic means.

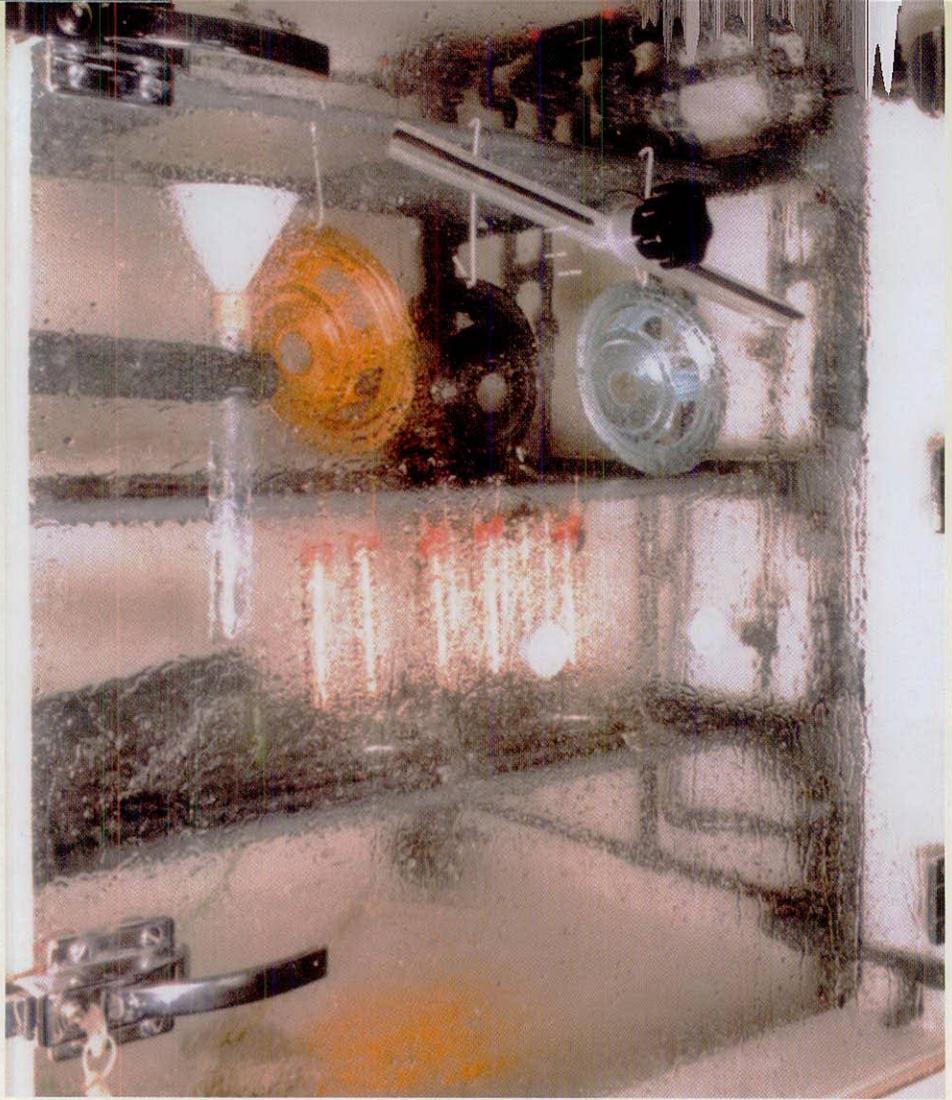
Instruments are available that measure the force necessary to detach a small magnet from the surface of the finished part. Other instruments utilize the reluctance of magnetic flux passing through the coating and basis metal to measure the thickness. Both types of instruments are calibrated against standards of known thickness. The tests are non-destructive and rapid.

(e) Destructive Methods

— Dropping and jet tests destroy the coating, but not the part. They determine thickness by measuring the time required for penetration through the coating to the basis metal by the action of a steady stream of drops or a jet of a corrosive solution. Reproducibility of plus or minus 5% may be achieved. The solution is chosen so as to provide a constant rate of attack on the coating. ASTM B555 specifies the uses of a chromic acid/sulfuric acid solution for drop testing zinc and cadmium coatings on steel substrates.

(f) Weight Loss on Stripping

— A test commonly used to determine average thickness of zinc or cadmium deposits over the entire surface of a part depends upon measuring the loss of weight of the part after subjecting the coating to chemical stripping. From the area of the surface and density of the deposit, thickness can be calculated. The method is destructive, not rapid and does not determine local thickness. It does find use in determining the thickness of small, barrel plated parts.



Steel parts are tested by simulating corrosive environments.

Protective Value

(a) CCCT (Compound Cyclic Corrosion Test)

- (1) This test is comprised of a series of tests, usually consisting of neutral salt fog/spray, hot air blowing on parts, and high humidity.
- (2) The specifier can specify exactly which cycle is most meaningful. Some use an 8-hour cycle comprised of 4 hours salt fog, then 2 hours hot air blowing on the parts, then 2 hours high humidity. The cycle is repeated again and again until white corrosion and then red corrosion (failure) is observed and recorded.
- (3) Some specifiers use a cycle that takes 24 hours to complete. For them that cycle is most meaningful. Most would agree that it appears to be more of a “real world” approach to corrosion testing, since the ASTM B117 test only uses salt fog. In the real world, parts are exposed to varying degrees of salt corrosion, dry hot air, or high humidity.
- (4) The specification will typically detail how many “cycles” the tested parts must complete to pass.

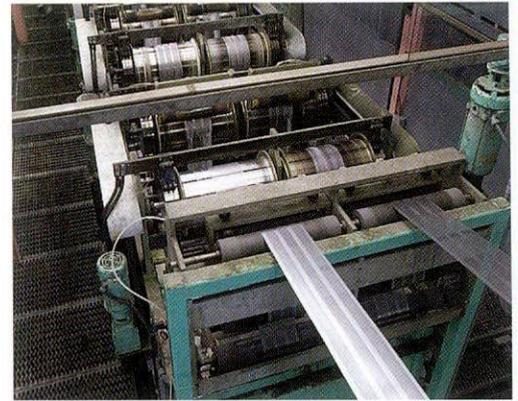
(b) Salt Spray Test

The salt spray test has been used to assess the protective value of zinc and cadmium coatings. However, the results do not correlate with any given service exposure. At best the test is only able to distinguish very poor from very good coatings by picking out bare areas or other areas where the coating is very thin. Although ASTM does not recommend the salt spray test for determining the protective value of zinc or cadmium coatings, the procedure is described in ASTM B117. Most purchasers do use the salt spray test to assess the quality of chromate treatments on zinc, zinc alloy and cadmium by specifying the number of hours to appearance of white corrosion products on a significant surface. ASTM B201, “Standard Practice for Testing Chromate Coatings on Zinc and Cadmium Surfaces,” is applicable and suggested performance is indicated in Tables I, II, and III.

(c) Lead Acetate Spot Test

The presence of clear chromate finishes is often hard to detect visually. On zinc or cadmium coatings such films can be detected by spot testing with a drop of solution containing 5% lead acetate in water. The time elapsed to the appearance of a colored spot is compared with the time required for a spot to appear on an unchromated coating. There is no valid correlation with the salt spray test.

5. Suggested Bath Formulations



Reel-to-reel continuous strip zinc plating line

Advantages:

Relatively even distribution of thickness.
Deposit is alloy-rich in low current density areas.
Easier to maintain than acid cobalt baths.
Deposits can be blackened with a non-silver based chromate.
Deposits are more ductile than from acid cobalt baths.

Disadvantages:

Deposits not as brilliant as those from acid cobalt baths.
Does not deposit well on cast iron or heat-treated steels.

Advantages:

Accepts chromate conversion coatings.
Faster plating rate than alkaline bath; economy of production plating.
Easy to maintain.
Excellent Kesternich test results.

Disadvantages:

Alloy difficult to control in deposit. (Variables such as temperature, agitation, metal concentration, will affect the alloy composition of the deposit.)
Deposit may experience more brittleness than alkaline technology.
Edge buildup (dog boning) will be evident in the deposit.

Advantages:

Cost— Price to plate this alloy will be closer to conventional zinc plating than other alloys.
Accepts a chromate conversion coating.
Can blacken with a non-silver based chromate.

Disadvantages:

Temperature resistance of chromated deposit is poor without a topcoat.
Excess iron may lead to delayed blistering.

1. ZINC COBALT (ALKALINE) 0.5% in deposit

Zinc Oxide (Low Lead)	10 – 15 Grams/Liter (1.3 – 2.0 oz/gal)
Sodium Hydroxide (Rayon Grade)	120 – 135 Grams/Liter (16 – 18 oz/gal)
Cobalt (usually added as a proprietary)	50-100 ppm
Organic Additive(s)	Per supplier recommendation
Temperature	20 – 40°C (68 – 104°F)
Cathode Current Density	0.5 – 5.0 Amps/Dm ²
Anodes	Steel (with the use of a generation tank off-line)

2. ZINC COBALT (ACID) 0.5% in deposit

	Potassium Formulation	Mixed Bath Formulation
Zinc Chloride	60 – 90 Grams/Liter (8 – 12 oz/gal)	55 – 90 Grams/Liter (7.3-12 oz/gal)
Potassium Chloride	150 – 200 Grams/Liter (20 – 26.7 oz/gal)	70 – 150 Grams/Liter (9.3 – 20 oz/gal)
Ammonium Chloride		45 – 70 Grams/Liter (6.0 – 9.3 oz/gal)
Cobalt (usually added as a proprietary)		20 – 100 ppm
Boric Acid	20 – 30 Grams/Liter (2.7 – 4.0 oz/gal)	20 – 30 Grams/Liter (2.7 – 4.0 oz/gal)
pH	5 – 6	5 – 6
Temperature	20 – 40°C (68 – 104°F)	20 – 40°C (68 – 104°F)
Cathode Current Density	1.0 – 4.0 Amps/Dm ² (10 – 40 Amps/Ft ²)	1.0 – 4.0 Amps/Dm ² (10 – 40 Amps/Ft ²)
Anodes	Zinc	Zinc

3. ALKALINE ZINC-IRON PLATING 0.5% in deposit

	Typical Bath Concentration
Zinc (Metal)	10 – 25 Grams/Liter (1.3 – 3.3 oz/gal)
Iron (usually added as a proprietary)	50 – 350 ppm
Caustic Soda	120 – 150 Grams/Liter (16 – 20 oz/gal)
Temperature	18 – 30°C (70 – 90°F)
Cathode Current Density	0.5 – 5.0 Amps/Dm ² (5 – 50 Amps/Ft ²)
Anodes	Steel (with the use of a galvanic generation tank off-line)

4. ACID ZINC-NICKEL PLATING BATH (5 – 7% in deposit)

	Rack	Barrel
Zinc Chloride	75 Grams/Liter (10 oz/gal)	70 Grams/Liter (9.2 oz/gal)
Nickel Chloride	100 Grams/Liter (13.3 oz/gal)	100 Grams/Liter (13.3 oz/gal)
Ammonium Chloride	230 Grams/Liter (30.7 oz/gal)	230 Grams/Liter (30.7 oz/gal)
pH	5.2 – 5.5	5.2 – 5.5
Proprietary Additives	Per supplier recommendation for grain refinement	
Temperature	45– 55°C (113 – 130°F)	45 – 55°C (113 – 130°F)
Cathode Current Density	0.1 – 4.0 Amps/Dm ² (1 – 40 A/Ft ²)	0.05 – 3.0 Amps/Dm ² (1 – 40 A/Ft ²)
Anodes	Pure Zinc Nickel (usually added as a proprietary)	

Advantages:

Plating speed is faster than alkaline formulations, allowing barrel plating at faster deposition speeds. Best formulation for reel-to-reel strip plating.

Accepts chromate conversion coatings.

Disadvantages:

Will experience edge build-up (dog bone).

Deposit is typically more brittle than alkaline deposits.

May be more difficult to chromate than alkaline deposits.

Dual Rectification.

5. ALKALINE ZINC-NICKEL (5 – 9% Nickel)

Zinc	6.0 – 12.0 Grams/Liter (0.8 – 1.6 oz/gal)
Nickel	1.3 – 1.8 Grams/Liter (1,300 – 1,800 ppm)
Caustic Soda (Rayon Grade)	112.0 – 140.0 Grams/Liter (15 – 19 oz/gal)
Proprietary Additives	Per supplier's recommendation
Temperature	23 – 26°C (73 – 80°F)
Cathode Current Density	1.0 – 10.0 Amps/Dm ² (10 – 100 Amps/Ft ²)
Anode Current Density	5.0 – 9.0 Amps/Dm ² (10 – 100 Amps/Ft ²)
Anodes	Nickel or nickel plated steel (with use of a galvanic generation tank off-line)

Advantages of the 5 – 9% Alloy:

Excellent resistance to temperature during service life.

Excellent corrosion resistance to either salt spray testing or cyclic testing.

Ease of operation.

Accepts a variety of chromate conversion coatings.

Deposit is ductile enough to allow post-plate bending.

Disadvantages of the 5 – 9% Alloy:

Poor resistance to Kesternich Testing (wet sulfur dioxide).

Barrel has slower plating speed than acid formulation.

6. ALKALINE ZINC-NICKEL (12 – 15% NICKEL)

Zinc	6.0 – 12 Grams/Liter (0.8 – 1.6 oz/gal)
Nickel	1.3 – 1.8 Grams/Liter (1,300 – 1,800 ppm)
Caustic Soda (Rayon Grade)	112 – 140 Grams/Liter (15 – 19 oz/gal)
Proprietary Additives	Per Supplier's Recommendation
Temperature	26 – 30°C (79 – 86°F)
Cathode Current Density	2 – 5 Amps/Dm ² (20 – 50 Amps/Ft ²)
Anode Current Density	3 – 7 Amps/Dm ² (30 – 70 Amps/Ft ²)
Anodes	Nickel or nickel plated steel (with use of a galvanic generation tank off-line)

Advantages of the 12 – 15% Alloy:

High corrosion protection of the Zn-Ni alloys.

Harder deposit than other zinc alloys (360 – 410 Vickers).

Accepts a variety of chromates, including a non-silver black.

Does not dog bone or build up on edges of work.

Has highest in-service heat resistance of ZnNi alloys.

Nickel alloy uniform at all times.

Disadvantages of the 12 – 15% Alloy:

Efficiency of bath may be lower than the 5 – 9% ZnNi bath.

Longer plating time to reach desired thickness.

Higher nickel means slightly more brittle deposit.

Higher cost to plate than 5 – 9% ZnNi bath.

Usage:

Currently specified in Europe & South America.

Expect to see specifications develop in the United States as requirements for better heat resistant coating evolve.



Freshly plated closures are emptied from a finishing barrel.

Advantages:

Soft, lubricious deposit (13 – 17 Vickers).
Best Kesternich Test results of all alloy plating.
Readily accepts a chromate conversion coating.
True sacrificial protection of steel parts.
Solderable.
Good conductivity, used for grounding bolts.
Easy bath to operate.
No whiskering. Dendritic crystal growth in 600 days.
No "tin pest" observed in low temperature surroundings.
Thickness & alloy may be tested with an X-ray thickness tester.
Deposit may be bent, formed, squashed without losing appreciable corrosion protection.

Disadvantages:

Deposit not suited for high temperature service.
Suggested plated thickness 10 microns (0.0004 inch).
Higher cost than the other zinc alloys.

7. TIN-ZINC ALLOY 70-75% in deposit

Acid Bath

Similar in formulation to bright acid tin plating baths. Tin & zinc do not co-deposit at the lower pH range. Zinc can be expected to deposit in a very low percentage. Protection is considered to be from barrier rather than sacrificial reasons.

Alkaline Non-Cyanide Bath

Tin	45 Grams/Liter (6 oz/gal)
Zinc	6 Grams/Liter (0.8 oz/gal)
Caustic Potash	7.5 Grams/Liter (1.0 oz/gal)
Anodes	75% Tin, 25% Zinc (must be filmed before each plating session) OR Stainless Steel Anodes

Operating Temperature	60 – 71°C (140 – 160°F)
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High temperature bath, produces good deposits that will accept a chromate conversion coating.

Neutral pH Bath

	Rack	Barrel
Tin	20 Grams/Liter (2.7 oz/gal)	20 Grams/Liter (2.6 oz/gal)
Zinc	8 Grams/Liter (1.1 oz/gal)	15 Grams Liter (2.0 oz/gal)
Organic Additives	Per supplier recommendation	
pH	6.0 – 7.0	6.0 – 7.0
Cathode Current Density	1.5 – 2.0 Amps/Dm ² (15 – 20 A/Ft ²)	0.5 – 1.0 Amps/Dm ² (5 – 10 A/Ft ²)
Anode Current Density	0.6 – 1.1 Amps/Dm ² (5 – 10 A/Ft ²)	0.6 – 1.1 Amps/Dm ² (5 – 10 A/Ft ²)
Temperature	21 – 27°C (70 – 80°F)	21 – 27°C (70 – 80°F)
Anodes	75% Tin, 25% Zinc	75% Tin, 25% Zinc

6. Conversion Coatings, Passivates

Even though zinc and cadmium are excellent rust retarders, the surface of steel coated with these metals does not remain bright and stain-free in service. To avoid staining and delay the formation of white corrosion products during storage or in service indoors, practically all zinc, zinc alloy and cadmium coated steel manufactured today is given a thin protective film using one of the available chromate conversion coating processes. There are four classes of chromate films in general use on cadmium and zinc coatings: clear (single dip or leached), iridescent yellow, black, and olive drab. The thickness of the finish increases in the same order, the olive drab being relatively thicker than the others.



Chromate conversion coatings

The zinc alloy deposits each have their own types of chromates as follows:

	Iridescent Yellow	Black	Bronze	Blue or Clear
Zinc-Nickel (5 – 9% Nickel)	x	x	x	
Zinc-Nickel (12 – 15% Nickel)	x	x		x
Zinc-Iron (0.4 – 0.8% Iron)	x	x		x
Zinc-cobalt (0.4 – 0.6% Cobalt)	x	x		x
Tin-Zinc (70 – 75% Tin)	x			

The class of conversion coating selected depends upon the kind of service condition to be met and the properties desired in the finish.

(a) Corrosion Protection – The protective value of a chromate finish increases with increasing thickness. In a salt spray test such as ASTM B-117, bare electrodeposited zinc will show white corrosion products in less than one hour. The same parts, given an olive drab finishing can withstand more than 150 hours exposure before showing white corrosion products. Zinc alloys may go much higher than that before showing any white products. The protection afforded is particularly valuable in retarding white corrosion under highly humid storage conditions in stagnant air. When used as a base for paint or other organic coatings, the chromate coating is extremely beneficial because it forms a barrier to lateral corrosion and undercutting of the topcoat. Applications include auto components, washing machines, refrigerator parts, military hardware, and equipment intended for tropical service.

Trivalent chromium processes for developing a chromium containing film on zinc and cadmium are available, although they are typically limited to blue to slightly iridescent chromates. The film produced is used similarly as a base for organic finishes and gives improved corrosion resistance to the final product when used in this fashion. The corrosion protection afforded by the film alone is generally not equivalent to that which is provided from a hexavalent chromate process. The exception to that is the high build clears but the color will be clear to slightly iridescent.

(b) Decorative Value – The use of chromate finishes permits a wide choice of surface appearances. The chrome-like brilliance of bright zinc or cadmium can be preserved for extended periods of time indoors by application of a clear or bleached chromate finish. Further protection can be provided by a clear lacquer coating. Tubular furniture and business machines are typical examples.

The thicker finishes offer a variety of color ranging from yellow through iridescent yellow to bronze, black, and olive drab. Further choice of colors is possible through application of organic dyes. Some of these are readily absorbed by the chromate finishes to give reds, blues, and greens and blacks which are sufficiently color-fast for indoor service. The primary purpose for use of dyes is color coding of similar parts.

The chromate finishes are also used to reduce tarnishing and finger-marking and thus improve the shelf life of hardware and appliance parts.

(c) Electrical Properties – The electrical resistance of the chromate finishes varies with the film thickness; i.e., the thinner the film, the lower the resistance. Although the electrical resistance of chromate conversion coatings can be measured, the results are insignificant enough in many cases that chromates can be considered to be conductors. In many applications their protective value can be utilized without losing the advantages of low contact resistance and good surface conductivity of cadmium plated steel. Many electronic, electrical and aircraft components are treated this way.

(d) Solderability – Soldering with rosin fluxes is possible on tin-zinc plated surfaces with yellow iridescent chromate finishes, or cadmium plated surfaces treated with clear chromate finishes. However, clear bright coatings on zinc deposits and colored finishes on both zinc and cadmium usually, but not always, must be removed in the area of the soldering joint. Applications of clear chromate finishes on plated parts for soldering are typified by electronic equipment, business machines, and telecommunications equipment.

(e) Abrasion Resistance – Most chromate conversion coatings form a relatively hard film which can withstand a moderate amount of wear and handling. The coating does retain entrapped water (approximately 20% by weight), which enables the coating to “self heal” or flow back into a scratched area. Trivalent passivates do not exhibit this “self healing trait so a topcoat is usually required to add abrasion resistance. It is possible to fold form chromated surfaces with smooth dies without appreciably damaging the finish.

(f) Thermal Resistance – Chromated zinc-nickel alloys stand out as the best sacrificial deposits for withstanding heat and high temperature service. This characteristic is very important in the automobile industry where parts routinely encounter high under the hood temperatures.

Hexavalent Chrome-Free Passivation

Table (1) – Current Automotive Standards as of Aug 2001

(Subject to change)

8 – 9 μ zinc plating with hex-chrome free passivation and sealer (optional)
NSS test requirements per ASTM B-117

Auto Maker	Hrs – White Corrosion	Hrs – Red Corrosion	Heat Treatment Required	Conditions
GM 3044				
Clear/Blue/Black	120	240	May be specified	150° C/1 hr
Yellow-Irid	120	360		150° C/1 hr
Ford WSS –M12P17B1/B3				
Clear/Silver white	96	384	No	120° C / 4 hrs
Clear/Silver white	72	360	Yes	
Daimler Chrysler PS 1207 – R				
Iridescent – Rack	200		May be specified	
Iridescent – Barrel	160			
Iridescent – Rack No sealer	120			
Iridescent – Barrel No sealer	100			

(a) New requirements

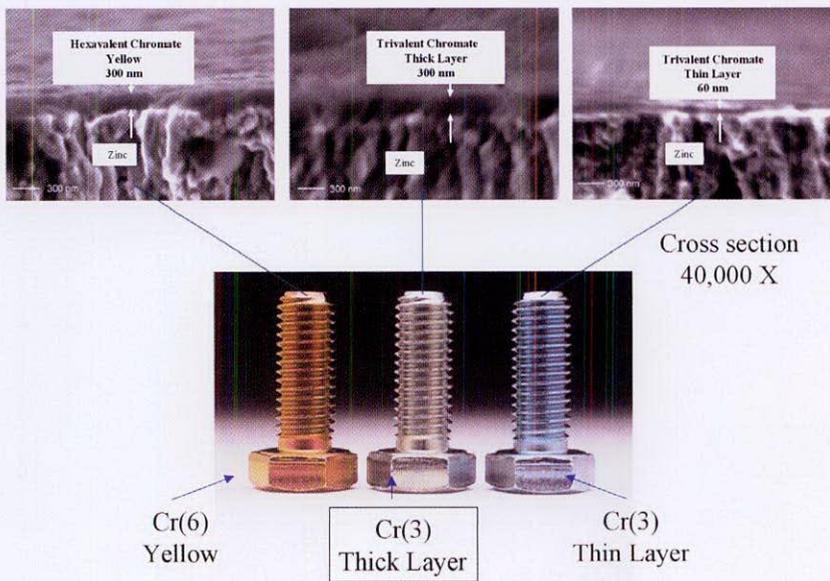
Recent ELV directives mandate that 85% by weight of discarded vehicles must be recycled, while restricting handling of toxic or hazardous materials in discarded components. One such material is leachable hexavalent chrome, used extensively in passivation of zinc and zinc alloy plating. Being a carcinogen, it is to be eliminated from these coatings. Implementation deadline is currently set for 2007. Current automotive industry new requirements and specifications for passivation free of hexavalent chrome is shown in Table (1)

(b) Film properties

Substitute passivation processes based on trivalent chrome are currently commercially available. Cr(3)-based compounds are environmentally safer, and are used extensively in many industries such as wood preservatives, paint and in dyes manufacturing. Depending on operating conditions of these new solutions, thin, light blue layers, or thick light green iridescent conversion coatings can be obtained. The latter replace conventional yellow iridescent Cr(6)-based passivation and has an equal average layer thickness of 300 – 350 nm. Fig (1). By comparison, the thin layers range from 50 to 80 nm and offer lower corrosion resistance for light duty applications.

Unlike Cr(6) passivation, Cr(3) conversion coating solutions can be operated in a range of concentrations and temperatures. Table (2), on the following page, compares typical operating parameters of these solutions and the corresponding passivation films produced on zinc plate.

Fig (1) Passivation Film Thickness



(c) Corrosion resistance — The corrosion resistance of these new coatings is generally equal or better than that obtained with conventional chromates, although they have a reduced self-healing property Fig (2). Upon severe mechanical damage or scratching of the film, there are no soluble Cr(6) compounds capable of dissolution in the surrounding moisture to fill or mend the scratched areas, thus leading to reduced corrosion protection. Although Cr(3) thick layer passivation films are harder and more scratch resistant, care must be exercised when barrel plating components with sharp edges. It is recommended that the passivation step be carried out in baskets or under controlled handling conditions. Sealers and top coats are used to enhance resistance to mechanical damage.

Field applications show that Cr(3) passivation is equally effective on zinc alloys. Fig (3) shows resistance to first white corrosion in NSS testing for various alloys to thermal treatment.

Table (2)

Parameters	Cr(6) Yellow Passivation	Cr(3) Thin Layer Passivation	Cr(3) Thick Layer Passivation
Make up	0.5 – 1.5%	2 – 8% v/v	10 – 13% v/v
pH	0.5 – 1.5	1.8 – 2.4	1.6 – 2.2
Temperature	20 – 25° C	20 – 25° C	55 – 56° C
Time	30 - 45 Sec	30 – 60 Sec	30 – 60 Sec
Agitation	Mechanical or air	Mechanical or air	Mechanical or air
Activation	Dil. acid	Dil. nitric or sulfuric	Dil. nitric or sulfuric acid
Film color	Yellow iridescent	Blue bright iridescent	Light green hue
Film thickness, nm	300 - 350	60 - 80	100 - 200

Fig (2.)- NSS Comparison Cr(6) vs. Cr(3) Passivation on Zinc

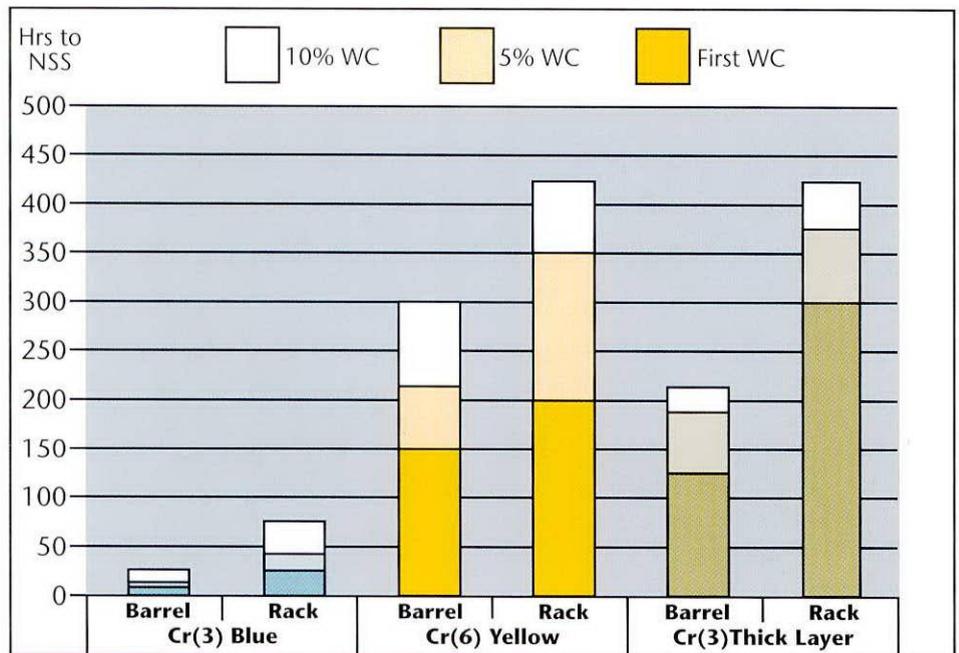


Fig (3.)

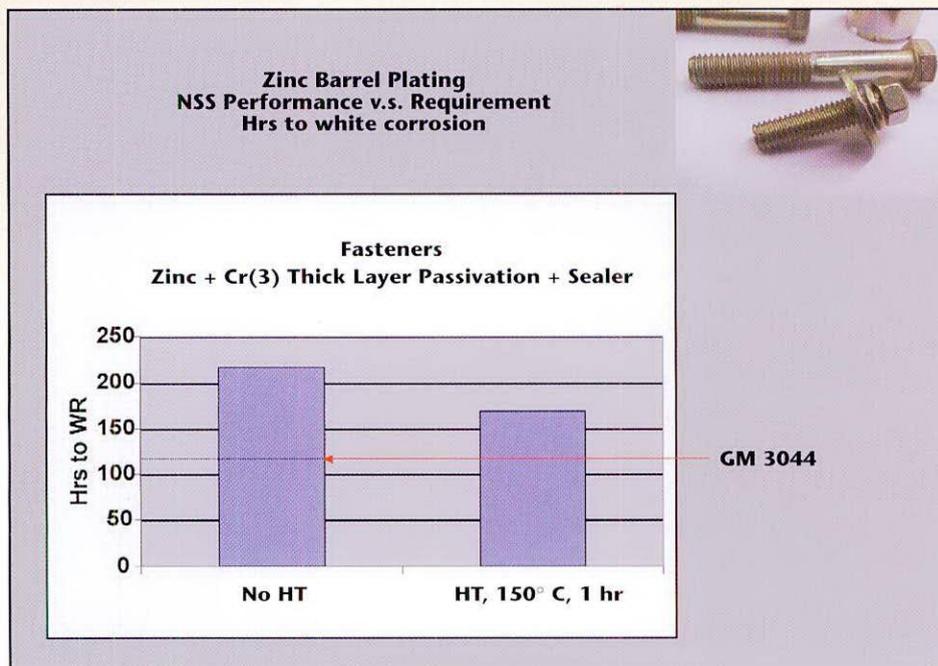
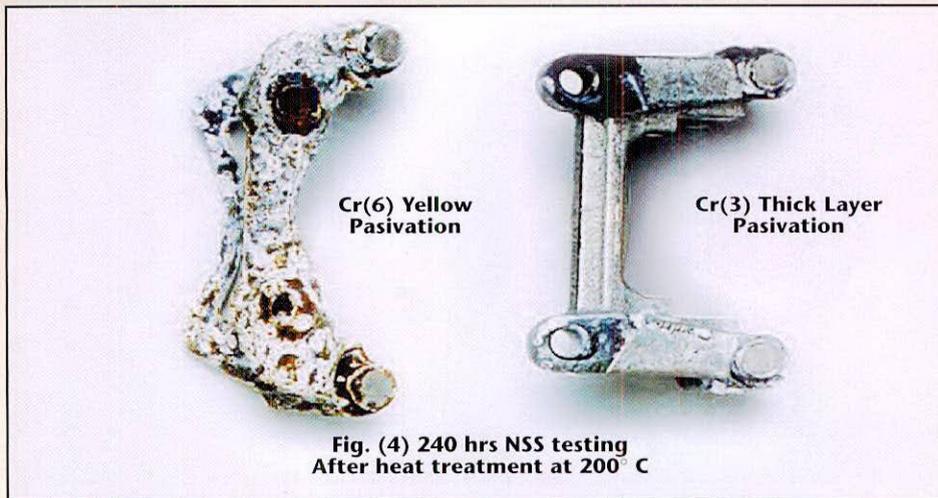
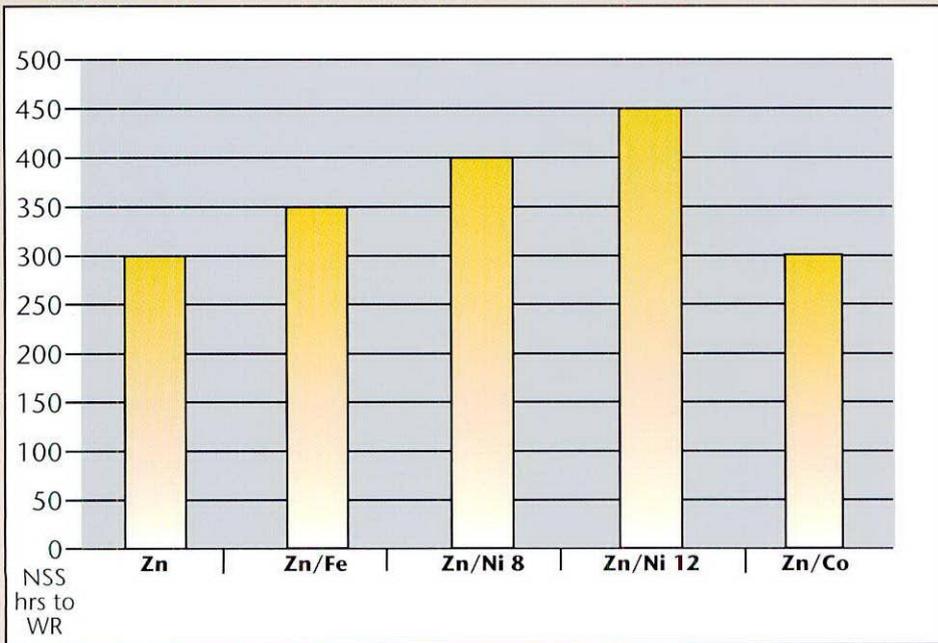


Fig (5)

(d) Thermal resistance

An important advantage of Cr(3) based passivation is its resistance to high temperatures. Exposure to 200°C for up to 8 hrs reduces its corrosion resistance only marginally. By contrast, Cr (6)-type passivation loses most of its corrosion resistance if exposed to 60 – 65°C for a short time. Fig. (4)

Many new automotive specifications require heating parts with Cr(6)-free passivation to 120°C to 150°C for 1hr and up to 24 hrs prior to NSS testing. Commercially available Cr(3) based passivation meets these requirements.

(e) Post passivation treatment

Trivalent chrome passivation should be considered in the context of a total system, which may include an optional post treatment to provide additional film properties. Post passivation may include one or more of the following treatments:

1 – Sealers

These are types of products that react with the conversion coating film, and result in more durable resistant finishes. Examples are silicates applied at room or elevated temperatures. They will leach out a small portion of the passivation film and leave a protective layer of silicate reaction products on the surface. Other types of sealers may contain phosphates, silanes and transition metals, as well as organic components.

2 – Top Coats

These may be organic lacquers, polymers, lubricants, waxes, oils and oil emulsions with suspended particles and coloring dyes. They may be applied by immersion, spray or dip-spinning and may be used to provide specific torque-tension properties.

A top coat used commercially contains zinc or aluminum flakes to provide protection against galvanic corrosion between the fasteners and magnesium or aluminum surfaces.

3 – Integrated sealer-lubricants

These are combined solutions of sealers and lubricant additives designed to provide desired levels of coefficient of friction along with specified corrosion resistance. They are primarily geared to threaded components.

Sealers and top coats increase the overall protection value in barrel applications as well as resistance

7. Seals

To enhance the properties of the final coating, an extra post treatment step after passivation of zinc or zinc alloy deposits can be applied. Sometimes bronze, brass or copper deposits (with or without passivation) are also sealed. Sealing is a process where soluble salts or oxides are encapsulated or converted to form an insoluble top coating with new characteristics. Seals are applied to enhance the following properties:

Functional Properties

- Enhanced corrosion resistance of zinc based coatings to white and red rust.
- Constant surface friction: Controlled total friction for mounting fasteners or extra low friction for wood screws and ease of packaging and storage.
- Thermal shock resistance for mounting parts in environments with elevated temperatures such as motor compartments.
- Improved solderability.
- Enhanced resistance to contact corrosion when parts are in contact with aluminum or magnesium-based alloy castings.

Decorative aspects

- Inclusion of pigments can affect color tone.
- Enhanced gloss, uniform color without iridescence.

Environmental

- Seals can be applied on chrome free coatings for some indoor applications.
- Sealing uses fully water-based chemistry without the need of post rinsing (no wastewater, low oxygen demand.)
- Sealed coatings encapsulate chromium salts in many cases; during drying the majority of hexavalent chrome is reduced to trivalent chromium when an organic seal is used.



Stages within the system: zinc plated (top)
yellow passivated (center),
pigment sealed (bottom).

Economic aspects

- Market demands are fulfilled for several properties at once (multifunctional coating.)
- Acceptable price increase (only 0.1 – 2.0 mm thick coatings are obtained.)
- Easy implementation in existing lines: rack, barrel, & dip-spin installations.

Seal Types

Polymer seals can have different types of functional groups such as acrylic, urethane, polyester or amine. Although these polymers are water based, sometimes a significant amount of solvent is used. Polymeric seals have a wide use as a decorative (glossy) topcoat, but tend to lose corrosion resistance once the coating is physically damaged.

Wax seals can result in coatings with very low friction which can prevent mechanical damage during transport or packaging. Depending on the viscosity, wax seal coatings can be applied very thinly to avoid any dimensional change of the parts.

Inorganic seals are based on silica, silicate or other silicon derivatives. Due to the high alkalinity of these baths, compatible passivation coatings need to be used. The inorganic seal is a secondary conversion coating, converting the original chromate coating into a silicate passivation layer. Bath life of these seals can be limited by drag-in of diluted chromium solution.

Pigmented seals are expensive because of the high pigment load or dye needed to give full coverage when the seal is applied as a thin coating. Thick coatings tend to cause problems on sharp edges where the pigment is drawn inward (edge flight) or can cause run and sag defects to appear.

Depending on the type of topcoat, very different ways of seal application are used. The simplest way of sealing is to dip the plated parts in a container that contains the sealing solution. This method can be used in rack or barrel installations, but has the disadvantage in that the rack or barrel itself needs cleaning to remove excessive seal. Wax-based seals are removed from the equipment by returning the rack or barrel through the soak cleaning cycle. In this way zinc plated & sealed contact points can be stripped in the acid pickling solution. Because wax and polymer emulsion based seals tend to cross-link very fast in acid solutions, it is mandatory to run the equipment through the cleaners first to guarantee optimal electrical contact on the contact points or dangles.

Table VI: Coating characteristics of different seals on yellow passivated (acid) zinc deposits

Effect	Polymer Seal	Wax Seal	Inorganic Seal	Pigmented (black seal)
Neutral salt spray test (hours to first white corrosion)	220	270	260	210
Corrosion barrier	++	+++	+++	++
Self heating effect	-	+++	-	++
Resistance against mechanical damage	+	+++	+	+
Friction coefficient	0.25 – 0.35	0.14 or 0.09	0.20 – 0.40	0.25 – 0.35
Low price	++	+(+)	+++	-
Ease of operation	+++	++	+	+++
Stability	++	++	+	+++
Easy to use	+	++	++	+
Uniformity	+++	+++	++	+
Covering/hiding power	+	+	-	+++
Gloss	+++	+(+)	++	+++
Teardrop	++	++	+	-
Safety	++	++(+)	+	++
Ease of waste treatment	++	+++	+++	+
Appearance	pale gold	pale gold	iridescent light green	glossy black (pale edges)
Temperature resistance (1 hour @ 120° C)	++	+++	++	++

(1) When used over the appropriate chromate conversion coating.
Ratings= +++ Best; ++ Next Best; +Least Best

When pigmented seals are used, higher viscosities are needed to obtain sufficient coverage. In this case a dip procedure can cause many problems, due to higher thickness and less uniform spread of the pigmented seal. Cleaning the plating equipment is also a major problem. The higher viscosity in a dip process will also lead to optically unattractive side effects such as running & sagging of the coating. Therefore, in mass production of barrel operations the use of a thinner coating applied in 2 – 3 dip spin cycles is commonly used. For many rack operations, spraying the coating is often utilized. Finally, the drying time also

needs to be extended to obtain a dry to the touch coating.

Implementing seal technology requires good coordination between the existing situation at the electroplater, the available product package, the specifications put forward by the end user and local environmental regulation. The use of seals provides the possibility to fulfill multiple specifications in different fields and should return the extra investment by producing products with superior quality.

8. Mechanical Plating & Galvanizing



Process Advantages:

- Freedom from hydrogen embrittlement.
- Ability to deposit a wide range of metals.
- Ability to apply a wide range of thicknesses.
- Low energy consumption.
- Simple waste treatment.
- No baking required.
- More uniformity of coating compared to hot dip galvanizing.

Process Disadvantages:

- Coatings not as smooth or bright as electroplating.
- Glass beads can be entrapped in certain parts.
- At low end commercial thickness, can be higher cost than plating.
- Size/weight limit of parts due to potential damage during tumbling.

Process description:

A physical tumbling plating method for coating ferrous metals, copper, lead, stainless steel, and castings. The process applies a malleable, metallic, corrosion resistant coating of zinc, cadmium, tin, copper and certain alloys in lined rotating tumbling barrels. In an acid environment, metal dusts are “cold-welded” or impacted onto the part substrate with the use of glass beads as the impacting force. Proprietary chemicals are used to clean and prepare the part surface for an adherent bond and uniform thickness of the metal dust.

Mechanical Zinc

Thickness:	3.8 – 17.5 um(plating)	20 – 100 um(galvanizing)
pH:	1.0 – 2.5	
Temperature:	18 – 25°C (64 – 77°F)	
Typical cycle:	Surface Preparation	5 minutes
	Copper flash	4 minutes
	Accelerator agent	3 minutes
	Zinc seed	5 minutes
	Zinc additions	20 – 30 minutes

9.

Glossary of Terms

Abrasive Blasting - A process for cleaning or finishing by means of an abrasive directed at high velocity against the work piece.

Activation - Elimination of a passive condition on a surface.

Addition Agent - A material added in small quantities to a solution to produce a desired effect. Also synonymous with "brightener."

Adhesion - The attractive force that exists between an electrodeposit or an electrochemical deposit and its substrate that can be measured as the force required to separate the deposit from the substrate.

Amorphous - Non-crystalline or without evidence of a regular structure.

Anode - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. In most instances it is the source of metal to be plated from the bath.

Anode Efficiency - The actual current efficiency of a specified anodic process compared to the theoretical value. The actual fraction of current used to dissolve metal from the anode compared to the theoretical amount as predicted by Faraday's Laws.

Autocatalytic Plating - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited. Often referred to as "electroless plating."

Barrel Plating - Electroplating or cleaning in which the work is processed in bulk in a rotating container (barrel).

Base Metal (or Substrate) - Material upon which processing is conducted or coatings are deposited. (It is not necessarily the material from which the part is constructed).

Blister - A dome-shaped imperfection or defect, resulting from loss of adhesion between a deposit and its substrate, or between various coatings where multiple layers of coatings are present.

Bright Dip - A solution used to produce a bright surface on a substrate by chemical immersion.

Bright Plating Range - The range of current densities within which a given plating solution produces a bright deposit.

Brightener - Another term for addition agent. A liquid or powdered material that, when added to a plating bath, improves the reflectivity or brightness of the deposits produced by the plating bath.

Brush Plating - A specialized method of plating, typically used for small scale applications, where an inert anode is surrounded by a pad, sponge, brush, or other device that will retain a volume of a concentrated solution containing a dissolved salt of the metal to be deposited. The anode/pad device is moved over the cathode during the plating operation in the area to be plated.

Buffing - The smoothing of a surface, accomplished by placing the surface to be finished against a rotating flexible wheel, to which fine abrasive particles have been applied in liquid, suspension, paste, or grease form.

Buffer - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.

Burnt Deposit - A rough, non-coherent or otherwise unsatisfactory deposit, typically produced by the application of an excessive high current density.

Bus Bar - The term used to describe the cables or conducting media – generally copper or aluminum stock – that transfers the current from the rectifier to the plating tank.

Carryover - See "Drag-in" defined on next page.

CASS Test - A special accelerated corrosion testing method using copper and acetic acid solution as the fog medium. It is most typically used to predict the corrosion protection of nickel/chrome, or copper/nickel/chrome electrodeposits. See ASTM Method B368.

Cathode - The part that is electroplated.

Cathode Efficiency - The actual amount of current used to deposit metal in a plating process, compared to the theoretical amount as predicted by Faraday's Laws.

Chelate Compound - A compound in which a metal is contained as an integral part of a ring structure and is not readily ionized.

Cleaning - The removal of grease or soil and other foreign materials from a surface using one or more chemical or electrochemical solutions.

Alkaline Cleaning—cleaning by means of an alkaline solution.

Anodic or Reverse Cleaning—electrolytic cleaning where the part is connected to the negative terminal of the rectifier.

Cathodic or Direct Cleaning—electrolytic cleaning where the part is connected to the positive terminal of the rectifier.

Di-phase Cleaning—cleaning by means of a solution that contains a solvent layer and an aqueous layer. Cleaning occurs by both solvent and emulsification actions.

Soak Cleaning—cleaning by chemical means without the use of current. Generally used to remove heavy oils and greases.

Ultrasonic Cleaning—cleaning by any chemical means aided by ultrasonic energy to speed up soil removal. Especially useful in the removal of buffing compounds.

Spray Cleaning—use of an alkaline cleaner that is sprayed onto the part(s) to be cleaned. The additional energy provided by the spraying operation accelerates the removal of soils, greases, and buffing compounds.

Contact Plating - Deposition of a metal by immersion of the work in a solution that is in contact with another metal.

Corrodokote Test - An accelerated corrosion test for electrodeposits using a special paste coating that is applied to parts before they are CASS salt spray tested. See ASTM Method B380.

Corrosion - Gradual dissolution or oxidation of a metal.

Covering Power - The ability of an electrodeposit to plate at very low current densities, such as in deep recesses or holes. (To be distinguished from Throwing Power.)

Current Density - The total current divided by the area to which the current is applied.

Cathode Current Density—the total current applied divided by the total area being plated.

Anode Current Density—the total current applied divided by the total anode area.

Current Efficiency - See Cathode Efficiency and Anode Efficiency.

Degreasing - The removal of grease and oils from a surface.

Solvent Degreasing—degreasing by immersion in liquid organic solvent.

Vapor Degreasing—degreasing by solvent vapors condensing on the parts being cleaned.

Drag-In - The water or solution that adheres to the objects from previous processing steps, and which is thereby introduced into a processing tank.

Drag-Out - The solution that adheres to articles when they are removed from a processing tank.

Ductility - The ability of a material to deform without fracturing.

Dummy - The term used to describe low current density plating done to remove metallic impurities from a plating bath.

Duplex Plating or Duplex Deposit - The term used to describe a multi-layer deposit that incorporates two layers with slightly different corrosion potential characteristics. The different layers are typically combined in a manner that allows one layer (the under-layer) to be sacrificial to the other layer (the top layer), thereby greatly improving the corrosion protection afforded, compared to that provided by a single layer of similar thickness.

Electroless Plating - A more commonly used term for Autocatalytic Plating.

Electrolyte - General term used to describe the processing bath, usually the plating bath.

Electrolysis - Process of causing chemical changes via the passage of current through an electrolyte.

Electroplating - The electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties, appearance, or dimensions different from those of the basis metal.

Electropolishing - Term used to describe the process of improving the appearance and surface condition of metallic substrates by applying a current to a chemical solution.

Etch - *Noun*—a roughened surface produced by a chemical or electrochemical means.
Verb—to unevenly dissolve a part of a surface or metal.

Faraday - The number of coulombs (96,490) required to deposit one chemical equivalent of a metal. The chemical equivalent value varies depending upon the metal being deposited.

Filter Aid - An inert, insoluble material, more or less finely divided, used as a filter medium, or to assist in filtration by preventing excessive packing of the filter cake.

Flash Plate - The application of a very thin electrodeposit, typically less than 2.54 microns (0.1 mil).

Flocculate - To aggregate into larger particles, to increase in size to the point where precipitation occurs.

Galvanic Protection - See “Sacrificial Protection” defined on next page.

Hard Chromium - Chromium plate for engineering, rather than decorative applications. Not necessarily harder than decorative chromium, but generally much thicker.

Hydrogen Embrittlement - Embrittlement of a metal or alloy caused by absorption of hydrogen typically during pickling, cleaning or plating operations.

Inert Anode - An anode that is insoluble in the electrolyte under the conditions prevailing in the electrolysis being performed. Typically used in plating baths where there is no convenient source of soluble metal an anode, such as chrome plating.

Karat - A measure of the fineness or purity of a gold deposit. One karat is equal to 1/24 part of pure gold; i.e., a 24 karat deposit is pure gold. Likewise, an 18 karat deposit is 18 parts of gold and 6 parts of another metal.

Masking - See “Resist” defined on next page.

Mechanical Plating - The application of an adherent metallic coating on a substrate by impingement of finely divided solid particles of the coating to be applied onto the substrate. Alloy deposition is possible via mechanical plating. Also, plating occurs without any hydrogen embrittlement occurring.

Metal Distribution Ratio - The ratio of the thicknesses of metal deposited at two different current densities. Frequently used as a measure of the Throwing Power of an electrolyte.

Metal Turn Over (MTO) - The replacement of 100% of the original nickel metal content of an electroless plating bath.

Microinch - One millionth of an inch, 0.000001 inches. (=0.001 mils)

Micron - One millionth of a meter, approximately one 25th of a mil. (25.4 microns = 1 mil)

Micro Throwing Power- The ability of an electrolyte to deposit metal in pores or very small recesses of substrates.

Mil - One thousandth of an inch (0.001 inches). (= 25.4 microns)

Oxidizing Agent - A compound that causes oxidation, thereby itself becoming reduced.

pH - The co-logarithm (negative logarithm) of the hydrogen ion activity. A measure of acidity (less than 7) or basicity (more than 7) of a solution.

Passivation or Passivity - The condition on a metal that retards its normal reaction in a specified environment. It is typically associated with the metal assuming an electrochemical potential more noble than its normal potential.

Peeling - The detachment or partial detachment of a deposited coating from the basis metal or undercoat layers.

Pickling - The removal of oxides or other compounds from the surface of a metal by chemical or electrochemical action.

Pit - A small depression or cavity in the surface of a part. It can be produced during manufacturing the part, during deposition, or by corrosion of the surface.

Polishing - See “Buffing”.

Reducing Agent - A compound that causes chemical reduction, thereby itself becoming oxidized.

Regeneration - *Noun*—The replacement of 100% of the original metal content of an electroless plating bath.
Verb—The act of replenishing a processing bath in an attempt to restore optimum performance.

- Resist** - A material applied to a part of the surface of an article to prevent metal deposition on or metal removal from that area during chemical or electrochemical processes. Also called "masking."
- Ripple** - A measurement of the amount of AC current that is present in a DC current. Excessive ripple generally causes passive deposits or hazes in plated coatings. Ideally, ripple should be less than 5% for most plating applications.
- RMS** - A numerical reference to the smoothness of a surface. Literally, it refers to the Root Mean Square of the height difference between the microscopic peaks and valleys that are evident on a surface when it is viewed under sufficient magnification. The lower the number, the smoother the surface. In other words, the average distance from the tip of a peak to the bottom of an adjacent valley on a part with a surface with a 2 RMS finish, would be less than the equivalent distance on a part with a 16 RMS finish. RMS is typically measured with a profilometer, using vertical magnifications from 500x to 200,000x.
- Robber** - Term used to describe an auxiliary cathode placed near the part to be plated to divert current from concentrating in high current density areas, leading to heavy deposits in these areas.
- Sacrificial Protection** - The mechanism of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion (for example, zinc plating over a steel substrate). Also referred to as "Galvanic Protection."
- Shelf Roughness** - Roughness on surfaces of parts that face upward where solids have settled during a processing operation.
- Shield** - *Noun*—a nonconducting medium or panel used to alter the flow of current in an attempt to provide the most uniform cathode current density possible on the part being plated.
Verb—to alter the normal current distribution by placing a non-conducting medium in the path of the current in a manner that provides a more uniform overall current density on the part being plated.
- Spontaneous Decomposition** - See "Triggering."
- Step Plating** - Non-uniform thickness, striations, or skip-type plating. In electroplating operations this is generally evident in low current density areas, while in electroless plating operations it is typically evident on edges of parts and around holes or perforations in parts. Also referred to as "edge pullback" and/or "worm tracking."
- Stray Current** - Current that passes through paths other than the intended circuit, such as through heating coils, the plating tank, floor grating, hoist super-structures, etc.
- Strike** - *Noun*—a thin deposit applied to a substrate or other plated deposit to provide activation or protection from immersion plating.
Verb—to apply such a coating by plating for a short time in a plating bath.
- Strip** - To remove a coating from the substrate or undercoat layer via chemical or electrochemical methods.
- Substrate** - The base metal to be plated.
- Taber Abraser** - An instrument used to characterize the wear properties of a substrate or plated finish. Test specimens are mounted to a small rotating turntable and subjected to the wearing action of two abrasive wheels, which are applied at a specific pressure, and which rotate in opposite directions. An important feature of the Taber Abraser is the all angles relative to the weave or grain of the material being tested.
- Tarnish** - Discoloration of a base metal or a plated coating, typically a darkening of the appearance of the basis or plated metal.
- Thief** - See "Robber."
- Throwing Power** - Term used to describe the uniformity of thickness of a plated coating. Electroless baths typically plate with 100% Throwing Power, i.e., the same thickness on all areas of a part in contact with the solution. Electroplating baths invariably exhibit greater thicknesses in high current density areas compared to low current density areas. See also Thickness Distribution Ratio.
- Triggering** - Spontaneous decomposition of an electroless plating bath, which is typically caused by excessively high concentration of reducing agents in the bath, or the introduction of solid contaminants, such as metal filings or other particles.
- Troy Ounce** - A unit in the Troy system of weights used for precious metals. Gold and other precious metals are typically measured in Troy ounces. (1 Troy ounce = 31.1035 grams)
- Turnover** - See "Regeneration."
- Water Break** - The appearance of a discontinuous film of water on a surface, signifying non-uniform wetting and usually associated with the presence of surface contamination on parts.
- Work (Plating)** - The material being plated or otherwise finished.



Metal Finishing Suppliers' Association

www.mfsa.org

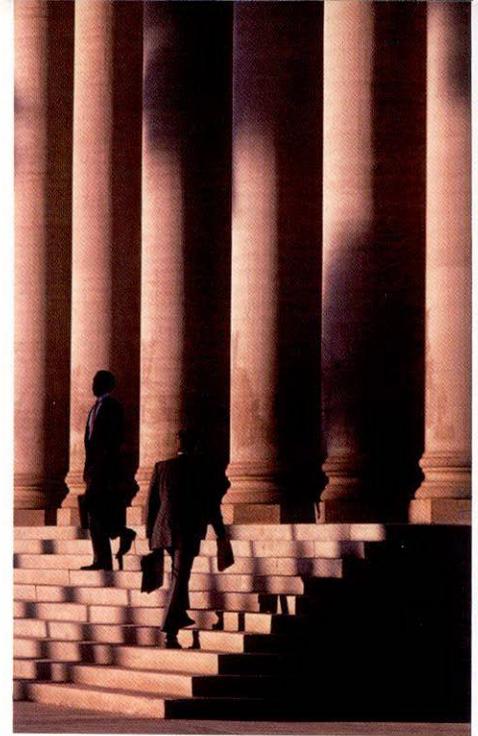
Quality Metal Finishing Guides



Metal Finishing Suppliers' Association

Decorative Copper-Nickel- Chromium Plating





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Introduction

The Metal Finishing Suppliers' Association (MFSA) is a trade association of companies and individuals involved in supplying chemicals, equipment, technology, and solutions to the surface finishing industry. One of the association's primary objectives is to promote the interests and further the welfare of its members and their customers while safeguarding the interests of the ultimate customer.

In 1960, MFSA initiated action to upgrade the durability of metal finishes. Known as the "Quality Metal Finishing Project" or QMF, this program was aimed at:

- 1) the promotion of technically sound specifications and standards in cooperation with interested trade and technical societies;
- 2) the provision of information to both producers and buyers of metal finished products;
- 3) the development of printed guides containing information on established standards and specifications, readily accessible for day-to-day use by the design engineer, the purchasing agent, and all those involved in the use of metal finished products.

Notice

The procedures included in this book are advisory only and their use by anyone is entirely voluntary. Reliance on any of the contents of this book for any purpose by anyone is at the sole risk of that person and neither the MFSA nor its members are responsible for any loss, claim or damage arising therefrom. A user of this book should consult a technically competent person to determine what procedure or material, whether included in this book or not, is appropriate for that user's application. By way of example only, the user will need to determine whether application problems or the environment to which the plated item will be exposed will require procedures different from those here set out, and will also have to determine what plating material is most appropriate for the user's application. In addition, the user is responsible for workplace safety, environmental protection, etc., and neither MFSA nor its members represent that use of the procedures or materials set out herein will be free from challenge. While the MFSA has made a determined effort to present state of the art plating technology and also to present the contents of this book accurately, it is almost inevitable that some errors may exist. While neither the MFSA nor its members accept responsibility or liability for such errors, the MFSA welcomes communications calling attention to any errors or commenting on the procedures described herein. Neither the MFSA nor its members have investigated any domestic or foreign patents. Accordingly, neither the MFSA nor its members are or will be responsible if use of any of the procedures or materials set out herein results in a patent infringement claim, suit, or liability. Updated and reprinted 2004.

Quality

As an association promoting the interest and welfare of the producers and customers of the metal finishing industry, MFSA realizes that everyone suffers loss when products are sold that are inadequately finished for the intended application. MFSA wishes to encourage the industry to develop and maintain high-quality standards needed to guarantee the expected or promised service of the unit.

The industry needs to know how a high-quality metal finish can be achieved, how to select proper specifications for a given application, and how to control the release of products to assure that they meet the needs of the customer. At the same time, management must be confident that this know-how is based on sound engineering principles and incorporates a reasonable margin of safety.

There have been significant developments of standards for quality systems in the last few years that are applicable to metal finishing. These include:

- International Standards Organization; (ISO 9000; ISO 1456)
- American National Standards Institute/American Society for Quality Control; (ANSI/ASQC Q90)
- American Society for Testing and Materials; (ASTM B456)

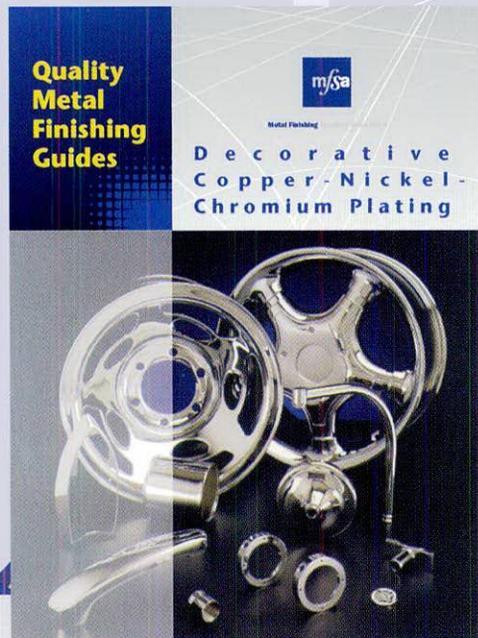
This manual will provide useful details on how to apply proven metal finishing engineering in your systems to help you maintain and improve your metal finishing quality.

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Other QMF Guides:

- **Chemical Surface Preparation for Electroplated and Metallic Coatings**
- **Decorative Precious Metal Plating**
- **Electroless Nickel Plating**
- **Hard Chrome**
- **Pretreatment for Paint and Powder Coatings**
- **Tin and Tin Alloy Coatings**
- **Zinc, Zinc Alloy and Cadmium Coatings**





1. Design For Plating

A program to improve and control the quality of a metal product should start at the desk of the designer. The metal finisher is restricted in what he or she can do by certain basic principles of mechanical finishing and of electroplating. The engineer should understand the limitations imposed by shape and size of components to facilitate quality finishing at an acceptable cost. The designer can exert as much influence on the quality attainable in finishing a part as can the electroplater. ASTM Standard B507 can provide the designer with helpful information.

Significant Surfaces

A most important term used in specifying metal finishes is "significant surfaces." In most products the same standard of quality is not required over the entire surface. Instead, the quality specifications apply since compliance is expected only for the so-called "significant surfaces" defined by mutual agreement between the producer and purchaser as follows:

Significant surfaces are defined as those normally visible (directly or by reflection) that are essential to the appearance or serviceability of the article when assembled in normal position or which can be the source of corrosion products that deface visible surfaces on the assembled article. When necessary, the significant surfaces shall be the subject of agreement between purchaser and manufacturer and shall be indicated on the drawings of the parts or by the provision of suitably marked samples.

Design for Mechanical Finishing

Metal products that are to be coated are generally subjected to abrasive polishing with wheels or mass finishing techniques in preparation for the plating operations. This is done to aid in securing an attractive, uniform, mirror-like or satin appearance on the finished part. Mechanical finishing is an expensive operation. To reduce costs and assist the metal finisher in improving the appearance and quality of the product, the designer should consider certain rules applicable for parts requiring mechanical finishing:

- Avoid blind holes, recesses and joint crevices which can retain polishing compounds and metal debris.
- Avoid intricate surface patterns which will be blurred by polishing operations.
- Significant surfaces should be exterior and reachable by ordinary polishing wheels or mass finishing media.
- Avoid sharp edges and protrusions which cause excessive consumption of wheels or belts.

In small parts which are to be barrel processed, the above rules apply. This includes the requirement that the parts must be sturdy enough to withstand the multiple impacts of barrel rotation and will not entangle, causing damage or incomplete finishing. Whenever possible, small flat parts that tend to nest together should have ridges or dimples incorporated into their design to prevent such nesting.

Design for Racking, Draining, and Air Entrapment

Most metal parts weighing more than a few grams, or that require a high degree of surface brilliance, are not bulk plated in barrels, but are mounted on racks or fixtures for processing in cleaning and plating tanks. Design considerations relating to racked parts are described below.

- Consult the plating department to make certain that parts can be held securely on a plating rack with good electrical contact without masking a significant surface. Many difficult racking problems can be solved by minor design modification.
- Provide for good drainage of processing solutions from racked parts. Certain shapes tend to trap solution which then causes contamination by carry-over, possible corrosion of the part, and waste of materials. Carry-over aggravates the problem of waste disposal and adds excessive cost due to chemical losses. In design, avoid rolled edges, blind holes and spot-welded joints. Drain holes are especially helpful when they are included in the design of irregular shapes and tubular parts.
- Avoid shapes that can trap air on entry into processing tanks, if this air could block access of solution to areas requiring treatment. Wherever air can be trapped, hydrogen or oxygen gas



may also accumulate during the cleaning or plating steps.

Design for Good Distribution of Electrodeposit Thickness

Simple shapes are always finished more uniformly and more economically than complex shapes. This is Rule Number One for the designer.

One of the most important factors that determines the quality of a coating is its thickness on significant surfaces. Fundamental laws of electrochemistry (current distribution), operate to prevent uniform deposition of an electrodeposited coating on a cathode of any practical shape and size. Portions of

the work which are nearer to the anodes tend to receive a heavier deposit than those more distant from the anodes. Sharp edges or protrusions at all current densities tend to receive a disproportionate share of the current. The goal of the designer and the plater is to make thickness variations as small as possible. At the same time, it is appropriate to minimize the unnecessary waste of metal by excessive build-up on both significant and non-significant areas. The same variation in plating thickness found on plated articles also typically exists when comparing parts plated on different areas of plating racks. For example, parts racked on the perimeter of fixtures tend to exhibit more thickness than parts from the center of fixtures.

It is possible to estimate metal distribution ratios from models or mock-ups, but there are also empirical rules. These can guide the designer to improved uniformity of thickness, hence improved quality with greater economy. These general principles and various sketches illustrate what has been learned from practical experience:

- Avoid concave or perfectly flat significant surfaces. Convex or crowned areas receive more uniform coatings. Use a 0.4 mm per 25.4mm (0.015 inch per inch) crown-minimum.



- Edges should be rounded to a radius of at least 0.4 mm (1/64 inch) and, preferably to 0.8 mm (1/32 inch).
- Re-entrant angles or corners should be filleted with a generous radius. Make sure radii are as large as possible.
- Avoid concave recesses, grooves, or slots with width less than one-half the depth.
- Minimize the number of blind holes because these must usually be exempted from minimum thickness requirements. Where necessary, limit their depth to 50% of their width. Avoid diameters less than 6 mm (7/32 inch.)
- Countersink threaded holes to minimize electroplate thickness build-up at their peripheries and to facilitate insertion of fasteners after plating.
- If fins or ribs are required, reduce their height and specify a generous radius, 1.6 mm (1/16 inch) at each base. Round off tips with radii of a least 1.6 mm (1/16 inch). Multiple parallel fins should have spacing between centers equal to four times the width of the fin. Broad hollow ribs are preferred over slender solid ones.
- Adopt recessed letters and insignias in preference to raised letters and insignias, but round-off edges and provide gentle contours.
- Integrated studs for fasteners should be shortened as much as possible and inside angles at each base should be rounded generously. Tips should be similarly rounded.
- Studs or bosses with hollow centers should be shortened as much as possible and angled 90 degrees from the major plane of the part. All bosses should face the same direction.
- Assist the plater by clearly marking significant surfaces on part drawings.

- Avoid use of a variety of different base metals on any one part to be plated. The contact of dissimilar metals may interfere with covering power or adhesion of the deposit due to galvanic action. It might also increase corrosion in service.

Design Features That Influence Electro-platability

The effect of the basic design of a product or component upon the effectiveness or durability of the plating used has been the subject of much study and research. Many

failures blamed on the plater can be attributed to the original design. A major contribution to the plating industry was made by the Zinc Institute, Inc. when it sponsored a design study by Battelle Memorial Institute to establish basic zinc die casting design principles; these findings are also applicable to other substrates.

The various shapes shown here provide the “dos and don’ts” of design configurations and their relationships to electroplating quality.

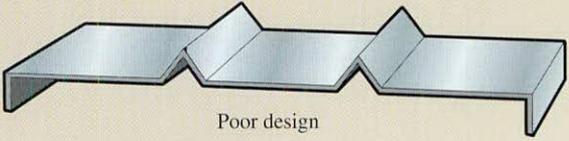
Feature	Influence On Electroplatability	Better Design
Flat-bottom grooves	Inside and outside angles should be rounded generously to minimize costs.	
V-shaped grooves	Deep, V-shaped grooves cannot be satisfactorily plated with corrosion protective nickel and chromium and should be avoided. Shallow, rounded grooves are better.	
Fins	Increase plating time and costs for a specified minimum thickness and reduce the durability of the plated part.	
Ribs	Narrow ribs with sharp angles usually reduce electroplatability; 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.	
Concave recesses	Electroplatability is dependent upon dimensions.	
Deep scoops	Increase plating time and costs for a specified minimum thickness.	
Spearlike Juts	Buildup on jut will rob corners from their share of electroplate. Crown the base and round off all corners.	
Rings	Electroplatability is dependent upon dimensions. Round off corners and crown from center line, sloping towards both sides.	

The distribution of electroplate is indicated in an exaggerated fashion.

ROUND OFF HIGH SPOTS

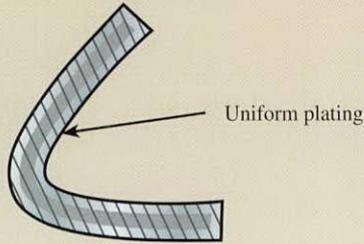


Good design

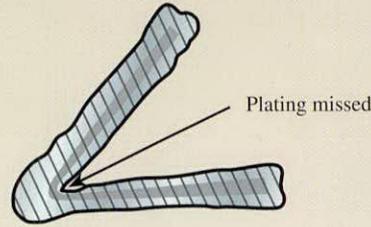


Poor design

AVOID SHARP INTERIOR ANGLES

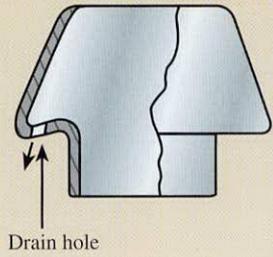


Uniform plating

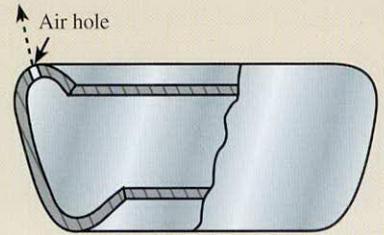


Plating missed

PLACE HOLES FOR DRAINING AND AIR ESCAPE



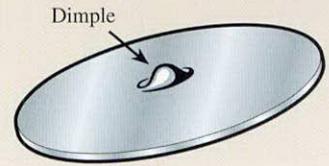
Drain hole



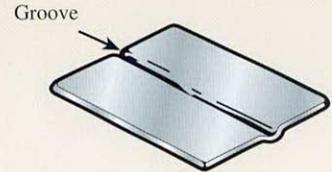
Air hole

Feature	Influence On Electroplatability	Better Design
Convex surfaces	Ideal shape. Easy to plate uniformly, especially where edges are rounded.	
Flat surfaces	Not as desirable as crowned surfaces. Use a 0.4mm/25.4mm (1/64 inch) crown to hide undulations caused by uneven buffing.	
Sharply angled edges	Undesirable. Reduced thickness at center areas and requires increased plating time for depositing a minimum thickness of durable electroplate. All edges should be rounded. (Edges that will contact painted surfaces should have a minimum radius of 0.8 mm [1/32 inch])	
Flanges	Large flanges with sharp inside angles should be avoided to minimize plating costs. Use a generous radius on inside angles and taper the abutment.	
Slots	Narrow, closely spaced slots and holes reduce electroplatability and cannot be properly plated with corrosion-protective nickel and chromium unless corners are rounded.	
Blind holes	Must usually be exempted from minimum-thickness requirements. Where necessary limit depth to 50% of width. Avoid diameters less than 6mm (7/32 inch).	
Sharply angled indentations	Increase plating time and costs for a specifically minimum thickness and reduce the durability of the plated part.	

AVOID STICKING WHEN BARREL PLATING



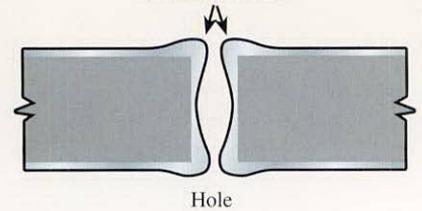
Dimple



Groove

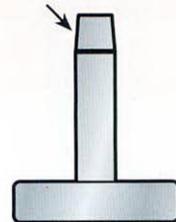
ALLOW FOR BUILDUP

Buildup reduces effective diameter



Hole

Tapered end to allow for buildup



Plug

The distribution of electroplate is indicated in an exaggerated fashion.

2. Selecting the finish

The designer should approach the problem of selecting the proper copper/nickel/chromium or nickel/chromium finish with a clear understanding of the requirements imposed on the plated product, the properties of the individual metals of the coating system and the service conditions to be satisfied. A properly selected decorative finish of high quality should be expected to perform acceptably throughout the service life of the product.



Requirements of the Finish

(a) Appearance

While appearance standards vary, the usual requirements are characterized by deposits that have high reflectivity and are free of pits, clouds, and surface roughness. When such finishes are required, there are a variety of suitable copper/nickel or nickel undercoats that meet this need. Similarly, functional decorative applications (e.g. flashlights, floodlights, electrical heaters, and instruments) which require a high luster and mirror-like surface can be satisfied more economically by such finishes, as compared to precious metal coatings. Satin and brushed surface effects can be produced for more subdued finishes. In-contrast with bright or satin coatings, non-reflective black oxide chromium or nickel can be deposited for various lustrous surface applications.

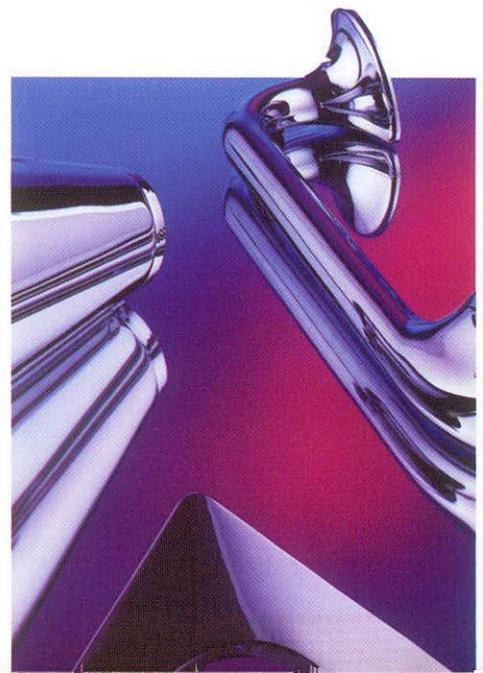
(b) Corrosion Behavior

To satisfy the prime requirement of maintaining an acceptable appearance, a decorative coating necessarily must effectively resist deterioration of itself and protect the basis metal from corroding. There are a multitude of finishes which can protect a basis metal from rusting or tarnishing, including paints, lacquers, and sprayed or vapor-deposited metal coatings. However, where a durable bright

metallic finish is desired, the choice is limited. Chromium provides a top coating with excellent resistance to tarnish in atmospheric exposure. The copper/ nickel or nickel undercoat provides the proper foundation for the lustrous chromium finish and the protection of the underlying steel, plastic, aluminum, zinc, stainless steel, or other basis material from corrosion.

(c) Wear and Abrasion

If the part must resist cleaning and handling or abrasive wear, copper/nickel/chromium or nickel/chromium finishes are usually specified in preference to softer metallic and organic coatings.



Coating Metals Considerations

(a) Rust Retardation

There are two classes of plated coatings that differ by mechanism in their ability to retard rusting or other corrosion of the base metal. The distinction arises from the different electrochemical relationships between the coating and the basis metal when a corrosive enters a pore or other discontinuity in the coating.

If the finish is anodic to the basis metal when exposed to a corrosive medium, then corrosion of the basis metal will be inhibited. This is the way in which zinc and cadmium and other anodic coatings retard the rusting of steel.

The other class of finishes, represented by copper/nickel/chromium and nickel/chromium coatings, are called cathodic coatings. They show an opposite electrochemical behavior, since copper, nickel and chromium are generally cathodic to common basis metals. Such finishes actually tend to promote galvanic corrosion when only a few pores or cracks are present in the coating.

It is obvious that cathodic coatings must resist corrosive attack which could create pores or pits extending to the basis metal. From outdoor exposure tests it has long been known that thickness is a prime factor of quality of copper/nickel/chromium and nickel/chromium finishes. In general, the thicker the coating the longer the basis metal is protected. However, it was found that just increasing the nickel thickness up to 50-75microns (two or three mils) did not keep pace over the years with increasing severity of some outdoor urban environments, nor was it economical. Then it was discovered that multiple layers of nickel of differing composition gave superior protection without increasing the total nickel thickness. These, together with modifications to the chromium plate, provided the means for a spectacular improvement in protective value while maintaining the appearance.

(b) Chromium

Chromium offers good corrosion resistance and abrasion resistance in the family of commonly plated metals. Thin chromium coatings over suitable undercoats provide excellent decorative systems. Furthermore, special chromium types can be deposited over copper/nickel or nickel undercoats so that the overall corrosion protective value of the system is increased.

Corrosion protection can be improved by the use of special types of chromium coatings. The useful life of the finish can be extended by the use of microporous or microcracked chromium. These invisible pores or cracks may be achieved by employing one of several process techniques. Methods to produce microporous chromium are explained under (c) Nickel, page 10. Two methods are commonly used to produce microcracked chromium. A highly stressed nickel deposit in-between the bright nickel and the chromium micro cracks the chromium when stressed relieved by mild heating. The second method is to use one or two specially formulated chromium processes that produce micro cracks as plated. Double chromium deposits usually have a visible blue haze. Chromium deposited from a trivalent bath is inherently microporous up to 0.6 microns, so no additional treatment is required to produce micro-discontinuous chromium. Corrosion resistance is significantly increased by microdiscontinuous chromium. This improvement is particularly beneficial in such applications as automotive and marine hardware.

Chromium may be deposited from baths with the metal in either the hexavalent or trivalent state. The hexavalent or Cr+6 uses chromic acid as its source

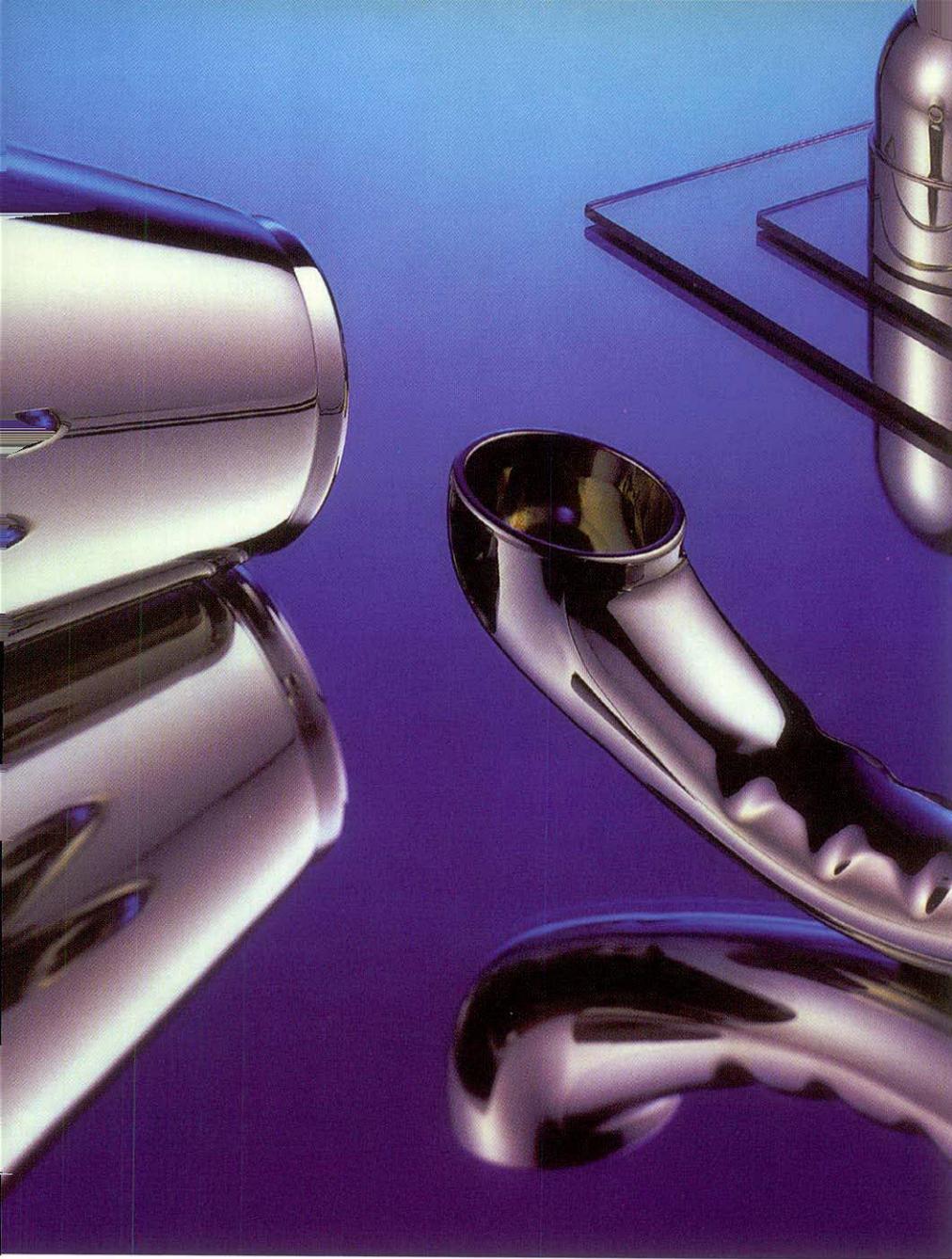
for metal, along with sulfates for control. There are proprietary catalysts used to improve efficiency and covering power. Hexavalent chromium has been identified as a carcinogen and several regulatory agencies have tightened its emission controls.

Trivalent chromium, or Cr+3 processes, use chromium sulfate or chloride as the source of metal. There are currently several processes available worldwide using this technology. Special additives along with proprietary anode designs are used to prevent the oxidation of the trivalent chromium to hexavalent at the anode.

Trivalent chromium technologies eliminated many of the deficiencies associated with hexavalent chromium plating such as high current density burns, white wash, poor throw, and high sensitivity to current interruptions. In addition, waste treatment is greatly simplified. Since trivalent chromium is not classified as a carcinogen, it is much safer and meets emission standards without the need for expensive emission control devices such as fume scrubbers.

Alloys, primarily containing tin, cobalt, and/or nickel, are being used as replacements for chromium primarily because they can be barrel plated. Small, hard-to-rack parts can be economically bulk plated with an alloy over bright nickel and then used on the same assembly with larger, rack-plated parts containing bright nickel under hexavalent chromium, trivalent chromium or alloy deposits.





(c) Nickel

The function of nickel is to provide a tough, durable, and ductile undercoat. Nickel protects the basis metal from corrosion and, in combination with the chromium top coat, results in a lasting decorative finish. Nickel levels micro-roughness in the basis metal providing a smoother, brighter finish. With increased leveling in the nickel, the need for other expensive substrate preparation work is reduced.

In double-layer nickel undercoats for chromium finishes, the metal immediately under the chromium is bright nickel containing small amounts of sulfur (e.g. more than 0.04 mass %) while the layer under that is semi-bright nickel, essentially free of sulfur. In any galvanic electrolytic cell set up with the chromium, the bright nickel reacts anodically to the purer semi-bright nickel. When microscopic corrosion penetrates through the chromium and bright nickel layers, galvanic action between the semi-bright and bright nickel layers tends to cause the microscopic pit to spread laterally in the outer bright nickel layer. The net effect is to retard penetration toward the basis metal, hence, to lengthen the

useful life of the coating. The negative effect is that as the lateral corrosion increases, the resulting surface pits may decrease the reflectivity of the corroded finish.

The potential difference between the semi and bright nickel layers can be measured by the Simultaneous Thickness and Electrode Potential test method (ASTM B764). S.T.E.P. potentials between 100 and 200 millivolts are typically specified. The higher the S.T.E.P. value, the more lateral corrosion occurs in the bright nickel layer before the semi-bright nickel layer is penetrated. This extends the time before basis metal corrosion, but increases the rate of deterioration of the appearance.

The same galvanic corrosion system can be further enhanced by the use of three layers of nickel of different sulfur contents. In this case, a high potential nickel strike layer (high sulfur in the nickel) is deposited between the semi and bright nickel. This strike acts as a sacrificial deposit to both these layers. The illustration on Page 17 shows this structure over copper plated aluminum. Such a system retards the corrosion penetration toward the basis metal. When a high potential nickel strike is utilized, the S.T.E.P. between the semi-bright and bright nickel layers is sometimes decreased to improve the appearance after corrosion commences without a loss in basis metal corrosion protection.

A nickel strike electrodeposited between the bright nickel and chromium deposits is more frequently used than the high potential nickel strike. This layer performs two important functions. Co-deposited with inert particles, it produces micro-pores in hexavalent chromium deposits increasing the basis metal corrosion protection. It is also used without particles under trivalent chromium and some chromium replacements to increase basis metal corrosion protection. This strike must be less active (more noble) than the bright nickel preceding it as measured by the S.T.E.P. Test. Depositing this strike with the proper S.T.E.P. and thickness, the above-mentioned negative effect on the loss of reflectivity due to the formation of surface pits during corrosion can be delayed and minimized. The galvanic action between this strike and the bright nickel deposit forces the corrosion under the strike into the bright nickel deposit. This minimizes the diameter of the surface pits in the noble nickel strike and chromium deposit thus retarding the loss of reflectivity.

(d) Nickel-iron

Bright nickel-iron alloy coatings containing up to 50% iron are sometimes used as an economical substitute for single layer bright nickel deposits for mild or moderate service conditions. Low-current density chromium coverage is sometimes better on nickel-iron deposits than on bright nickel deposits even though the nickel-iron deposits are generally more active. The appearance of the more active nickel-iron deposit will deteriorate faster because of the larger surface pits which will form when corroded. Care must be exercised when choosing the alloy composition. An iron content exceeding 15-30% can result in significant surfaces staining (iron rust appearance) in moderate or severe service conditions. The exact level of iron in the deposit at which staining starts is subject to debate.

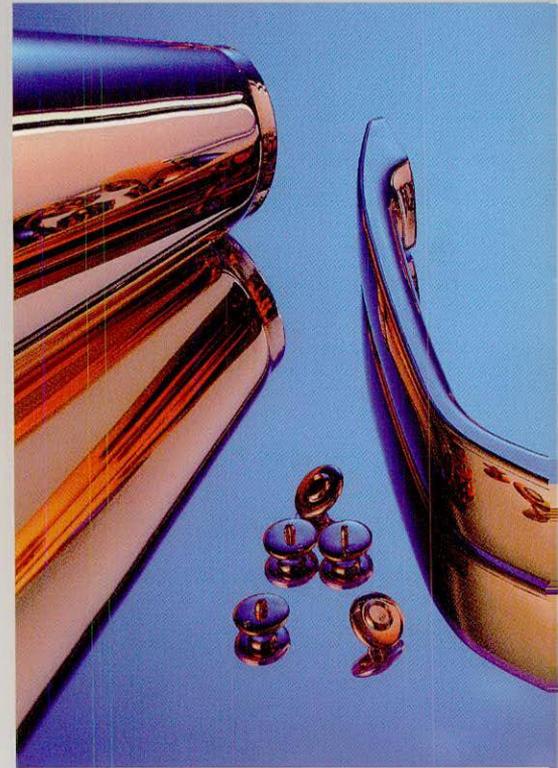
Nickel-iron coatings are generally more ductile than bright nickel deposits, are more easily replated, and cover better with chromium.

It is generally not recommended to use trivalent chromium or hexavalent chromium with high pore counts (unless a pore sealant is also used) over nickel-iron alloy deposits with greater than 10% iron, due to the poor after-corrosion appearance usually obtained.

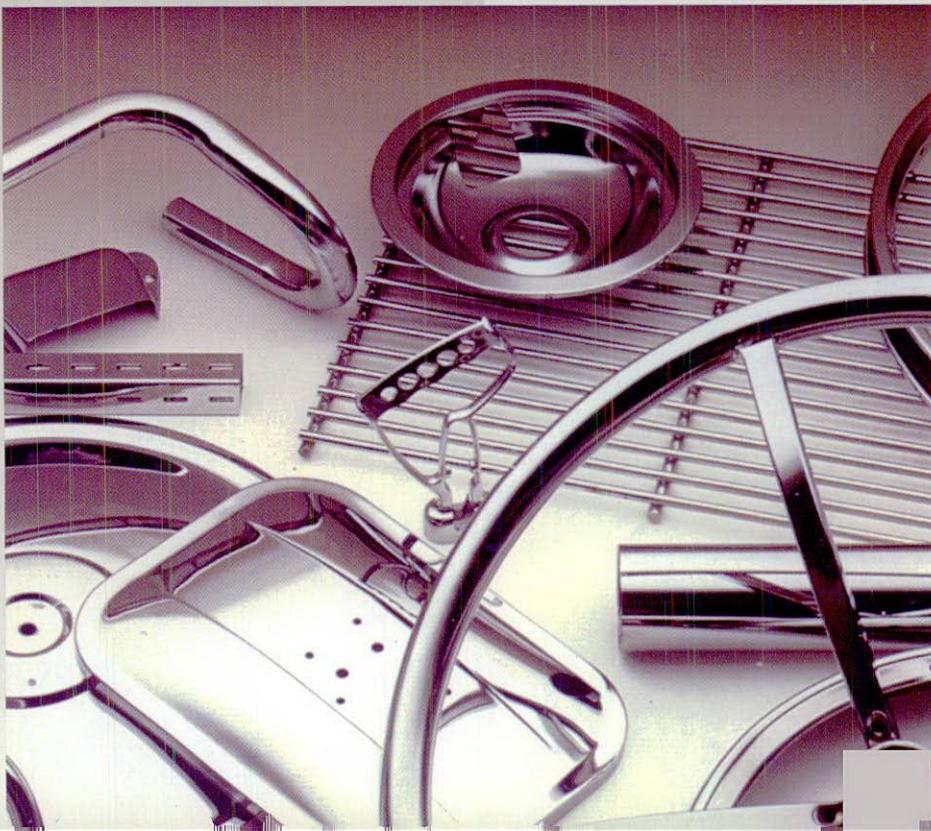
(e) Copper Undercoat

Nickel/chromium coatings may be deposited over a copper undercoat. ASTM specification B456 has been established for copper/nickel/chromium coatings over steel, zinc, aluminum, and plastic substrates. Conventional or micro-discontinuous chromium may be used. Alkaline copper coatings, generally cyanide, are first plated on zinc die castings to protect the active zinc from attack by the subsequent acid copper or nickel processing.

As with nickel deposition, leveling copper processes can be used to upgrade the basis metal finish, and thus contribute to an overall improvement in the appearance of the final chromium finish. The excellent buffability of copper permits obtaining a high luster finish, and buffed copper coatings are employed when buffing costs can be justified. Ductile copper plate improves the apparent ductility of overlying nickel-chromium coatings. Bright leveling acid copper plate can minimize the undesirable effect of basis metal porosity by filling and bridging pores and also because of its superior micro-throwing power. Acid copper deposits are currently being used on some zinc die castings following a thin protective copper plate deposited from a cyanide bath.



In recent years, the development of a non-cyanide alkaline copper strike may sometimes allow the copper cyanide strike to be replaced with a copper strike and copper plating system that is free of cyanides; but cyanide copper is still the preferred process for zinc die castings. The absence of immersion copper which leads to poor adhesion must be established prior to using non-cyanide copper strikes.



(f) Other Specialty Finishes

A number of modified finishes based on copper, nickel, or chromium can produce specialty finishes.

• Satin Nickel

Satin nickel processes have the ability to produce deposits that range from a coarse texture resembling etched aluminum to a very fine texture resembling pearl. This satin deposit is achieved by producing a controlled micro-pitted deposit.

• Antiqued and relieved copper plating

In antiqued and relieved copper processes, the copper plate is colored brown, black or green by immersion in sulfur based or other proprietary antiquing baths. The converted surface can then be relieved mechanically by light buffing or mass finishing then optionally sealed with a clear organic top coat. Examples of such applications are electrical fixtures, hardware, and clothing accessories.

• Decorative black nickel

In decorative black nickel processes, nickel is plated and then it is oxidized by either a dip or by electroplating of an alloy of nickel such as nickel-tin, nickel-zinc, and other available combinations. There are also proprietary black pure nickels that can be applied directly and which can be subsequently relieved. Typical applications of this process are luggage hardware, rivets and screws.

• Black chromium

Black chromium is produced by using proprietary hexavalent or trivalent chromium plating formulations. The process and equipment are similar to those for bright chromium plating. Solar collectors, furniture, and some camera components, as well as other specialty decorative black finishes are plated by this process.

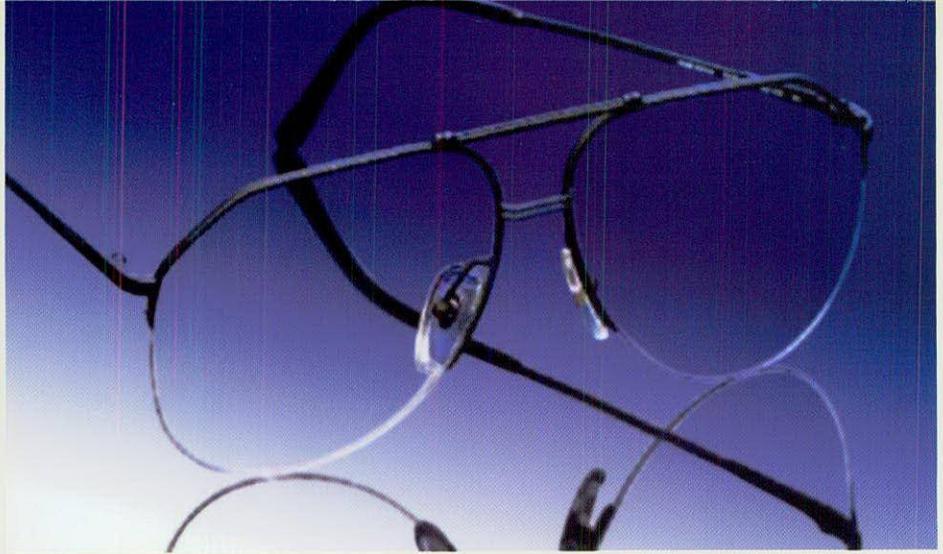


(g) Formability

Although basis metals with bright nickel/chromium finishes have been successfully drawn, stamped and otherwise formed, the bright nickel/chromium layer is relatively brittle. The best way to withstand forming operations is to plate the workpiece with a very ductile Watts or sulfamate nickel layer that is polished and /or buffed to obtain the desired finish and then plated with a thin, micro-discontinuous chromium deposit. An alternative method that is less expensive and time consuming includes the use of micro-discontinuous chromium over the bright nickel coating. This tends to relieve the hydrogen embrittlement in the nickel layer, thereby improving formability.

The most economical and simplest method is to substitute decorative nickel-iron for bright nickel (Note the discussion on the properties of these deposits above). These coatings are more ductile, especially after chromium plating, which in some cases allows the plated parts to be formed or bent without having to resort to the use of special procedures or additional plating baths. This should only be done when the high corrosion protection offered by pure nickel is not required.

3. Specifying the finish



Type and Thickness

The Type of copper, nickel or chromium, designated by their respective chemical symbols (Cu, Ni, and Cr), specify the deposit's required chemical and physical properties. The combination of the Type of deposits with their respective Thickness constitute the Classification Number required for each Service Condition; see Tables I, II, III and IV. A variety of multiple-layer decorative finishes have been developed. Most are superior in protecting the substrate from corrosion than single-layer bright nickel covered by chromium.

Having selected copper/nickel/chromium or nickel/chromium as the coating system for a steel, plastic, aluminum, stainless steel, copper and copper alloys, zinc or other substrate, the designer must now specify the Type, Thickness and other characteristics desired in the coating. High quality can be obtained by properly specifying the Types and Thickness of layers to be applied. The designer must specify the appearance of the layer's finished surface to determine the protective value of the final part. The required performance tests such as adhesion and ductility should also be specified. For specific subjects, refer to the Annual Book of ASTM Standards, Volume 02.05, which covers Electrodeposited Coatings.

Explanation of Tables I - IV

(1) Service Conditions

Depending upon the customer, there are four or five service conditions which define the environment to which the plated part may be exposed as a function of the substrate.

(2) Classification

The classification letters shown in the tables indicate the type of deposit to be provided. The classifications of nickel are designated:

- b** - Nickel deposited in the fully bright condition.
- p** - Dull or semi-bright nickel containing less than 0.005 mass % sulfur (Note: 0.005 mass % sulfur is essentially a sulfur-free deposit). Polishing/buffing is required to give full brightness.
- d** - Double-layer or triple-layer nickel coating of which the bottom layer contains less than 0.005 mass % sulfur and the top layer contains more than 0.04 mass % sulfur. The low sulfur layer should be from 60% to 80% of the total nickel thickness. If there are three layers, the intermediate one shall contain not less than 0.15 mass % sulfur and shall not exceed 10% of the total nickel thickness.

There is no restriction on the type of chromium used, except that one is not permitted to buff the chromium deposit. There are no restrictions on how the microporous and microcracked deposits are produced. The deposits must meet the following classifications:

- r** - Regular (i.e., conventional) chromium. This deposit is non-microdiscontinuous.
- mc** - Microcracked chromium having more than 300 cracks per linear cm. (750/in.) in any direction over significant surfaces. The cracks shall be invisible to the unaided eye.
- mp** - Microporous hexavalent and trivalent chromium containing a minimum of 10,000 pores per sq. cm. (65000/sq. in.). the pores shall be invisible to the unaided eye.

Table I
Recommended Standards For Quality Nickel/Chromium Finishes On Steel, Iron and Zinc Products

Service Conditions	Classification		Minimum Thickness In Microns		Typical Applications
	Ni	Cr	Nickel	Chromium	
SC 1 MILD Exposure indoor in normally warm, dry atmospheres; coating subject to minimum wear or abrasion	b	r	10	0.13	Toaster bodies, rotisseries, waffle makers, oven doors and liners, interior auto hardware, trim for major appliances, hairdryers, fans, inexpensive utensils, coat & luggage racks, standing ashtrays, interior trash receptacles, inexpensive light fixtures
SC 2 MODERATE Exposure indoors in places where condensation of moisture may occur: for example, in kitchens and bathrooms.	b	r	20	0.25	Steel & Iron: Stove tops; oven liners; home, office and school furniture; bar stools; golf club shafts. Zinc Alloys: bathroom accessories; cabinet hardware
	b	mc	15	0.25	
	b	mp	15	0.25	
SC 3 SEVERE Exposure which is likely to include occasional or frequent wetting by rain, dew, or possibly strong cleaners and saline solutions	d	mc	25	0.25	Patio, porch and lawn furniture; fixtures; bicycles; scooters; wagons; hospital furniture, fixtures and cabinets
	d	mp	25	0.25	
SC 4 VERY SEVERE Service conditions which include likely damage from denting, scratching or abrasive wear in addition to corrosive media.	d	mc	30	0.25	Minimum requirements for auto bumpers, grilles, hub caps and lower body trim; light housings
	d	mp	30	0.25	
SC 5 EXTENDED-VERY SEVERE Service conditions which include likely damage from denting, scratching or abrasive wear in addition to exposure to corrosive environments where long-time protection of the substrate is required.	d	mc	35	0.25	Minimum requirements for extended protection for auto bumpers, grilles, hub caps and lower body trim; light housings.
	d	mp	35	0.25	

Note: 5 micrometers copper is required on zinc and zinc alloys prior to nickel-chromium. 15 micrometers copper may be used on steel for service conditions 3 through 5. If copper is used, the total nickel thickness can be reduced by 5 micrometers. Adapted from ASTM Standard B456

Table II
Recommended Standards For Quality Nickel/Chromium Finishes On Copper and Copper Alloys

Service Condition	Classification		Minimum Thickness In Microns		Typical Applications
	Ni	Cr	Nickel	Chromium	
SC 1 MILD Exposure indoor in normally warm, dry atmospheres; coating subject to minimum wear or abrasion	b	r	5	0.13	Toaster bodies and similar appliances; oven doors and liners; interior auto hardware; trim for major appliances; receptacles; light fixtures
SC 2 MODERATE Exposure indoors in places where condensation of moisture may occur: for example, in kitchens and bathrooms.	b	r	15	0.25	Plumbing fixtures; bathroom accessories; hinges; light fixtures; flashlights; spot lights
	b	mc	10	0.25	
	b	mp	10	0.25	
SC 3 SEVERE Exposure which is likely to include occasional or frequent wetting by rain, dew, or possibly strong cleaners and saline solutions.	d	mc	20	0.25	Patio, porch and lawn furniture and light fixtures; bicycles; hospital and laboratory fixtures
	d	mp	20	0.25	
	b	r	30	0.25	
	b	mc	25	0.25	
	b	mp	25	0.25	
SC 4 VERY SEVERE Service conditions which include likely damage from denting, scratching or abrasive wear in addition to corrosive media.	d	mc	25	0.25	Boat fittings; auto trim, hub caps and lower body trim
	d	mp	25	0.25	

25.4 Micrometers = 1.0 Mil. Adapted from ASTM Standard B456

Table III
Recommended Standards For Quality Nickel/Chromium Finishes On Platable Plastic Products

Service Conditions	Classification		Minimum Thickness In Microns			Typical Applications
	Ni	Cr	Cu	Ni	Cr	
SC 1 MILD Exposure indoor in normally warm, dry atmospheres; coating subject to minimum wear or abrasion	b	r	15	7	0.25	
SC 2 MODERATE Exposure indoors in places where condensation of moisture may occur:	b	r	15	15	0.25	Kitchens and bathrooms
	b	mc	15	10	0.25	
	b	mp	15	10	0.25	
SC 3 SEVERE Exposure which is likely to include occasional or frequent wetting by rain, dew, or possibly strong cleaners and saline solutions	d	r	15	25	0.25	Porch and lawn furniture; bicycles and perambulator parts, hospital furniture and fixtures
	d	mc	15	20	0.25	
	d	mp	15	20	0.25	
SC 4 VERY SEVERE Service conditions which include likely damage from denting, scratching or abrasive wear in addition to corrosive environments	d	r	15	30	0.25	Exterior components of automobiles and boat fittings in salt water service
	d	mc	15	25	0.25	
	d	mp	15	25	0.25	
SC 5 EXTENDED-VERY SEVERE Service conditions which include likely damage from denting, scratching or abrasive wear in addition to exposure to corrosive environments where long-time protection of the substrate is required.	d	mc	15	30	0.25	Exterior components of automobiles
	d	mp	15	30	0.25	

Adapted from ASTM Standard B604

(3) Use of Copper

Copper undercoats are preferred for deposits on plastic, zinc die castings and aluminum where it protects these materials from acid solutions during subsequent acidic plating steps. It also improves the durability of the coating system when there is a significant difference in the thermal expansion between the substrate, such as aluminum and plastic and the plated deposits. Copper is sometimes specified for steel to improve part appearance and to cover up corrosion-enhancing surface defects. Copper thicknesses are not substitutable for any part of the specified nickel thickness.

(4) Typical Application

The lists of typical applications will help the designer or purchaser select a suitable coating specification when not certain of the service conditions to be met. In case of doubt as to the severity of a planned application, a classification should be specified suitable for the next more severe type of service condition.

Protective Value

The problem of specifying performance of decorative coatings involving copper/nickel/chromium and nickel/chromium composites has intrigued the metal finishing industry continually since the early 1900s. The factors controlling corrosion are so numerous that

the only valid test is exposure of parts to actual service conditions over the life of the part.

In recent years, several accelerated corrosion tests have been developed which have shown some correlation with the performance of copper/nickel/chromium and nickel/chromium coated parts in moderate and severe outdoor urban and outdoor seacoast service. There is copious data available to support the specification of the number of hours of resistance to these accelerated corrosion tests, as shown in Table IV, as a measure of minimum acceptable quality in coatings intended for a given type of service. The tests themselves are described under the heading "Testing the Finish."

Table IV
Accelerated Test Requirements For Copper/Nickel/Chromium Coatings

Basis Material	Service Condition	Corrosion Test (Duration In-Hours)	
		CASS ²	CORRODKOTE ³
Steel, Zinc Alloy, Copper or Copper Alloy ¹	SC 1 Mild –	–	–
	SC 2 Moderate	8	4
	SC 3 Severe	16	16
	SC 4 Very Severe	22	32 ⁴
	SC 5 Extended – Very Severe	66	–
Plastic ⁵	SC 1 Mild	–	–
	SC 2 Moderate	8	–
	SC 3 Severe	16	–
	SC 4 Very Severe	32 ⁴	–
	SC 5 Extended - Very Severe	48 ⁶	–

¹ ASTM B465

² ASTM B368

³ ASTM B380

⁴ Two 16 hour Cycles

⁵ ASTM B604

⁶ Three 16 hour Cycles

Cyclic corrosion tests involving cycles of heat, humidity, spray, etc. are beginning to be used in an attempt to better simulate natural environmental corrosion. The existing tests have not been standardized at this time, but individual companies do specify them.

The conventional salt spray test, ASTM B117 which was instituted in 1914, has been generally discredited as an accelerated corrosion test for these decorative coatings largely because of lack of reproducibility of results and questionable correlation with service. It is recognized, however, that the test is still used in some segments of the plating industry because it can serve as an inspection tool to reveal gross defects in the coating and bare areas. It is mainly classified as a porosity test.

Adhesion

Adhesion can be specified for each aspect of composite coatings: coating adherence to the basis metal, separate composite layers to each other, and the performance of the finished part to adhesion tests described under the heading "Testing the Finish."

Appearance

Appearance cannot be readily specified because it involves factors such as brightness, roughness and uniformity of color which are not easily addressed objectively. Location and extent of surface defects may influence acceptability. It is suggested that samples be prepared which are acceptable to both manufacturer and purchaser as standards of quality in appearance.

Ductility

If the product is to be used in such a way that the coating will be formed or deformed in service it may be desirable to specify ductility requirements. ASTM Specification B456 calls for a minimum of 67% ductility for semi-bright, a minimum of 11% for bright (ASTM B490), and a minimum 8% elongation for copper deposits. Meeting these minimum levels of ductility also reduces or eliminates cracking due to thermal expansion in service.

4. Testing the finish

There are several methods for measuring the thickness of copper/nickel/chromium and nickel/chromium coatings, some being destructive of the part tested and others not. Most only measure a small area of the part and so thickness measurements are often made at several specified set-points or at different current density areas.

(1) Microscopical Method

The part under test is cut on a plane perpendicular to an area being measured and is mounted for metallographic examination. The cross-section is polished and etched to contrast the plated coating with the basis metal. The thickness is then measured with an optical microscope at a magnification great enough to permit measurements of thickness with an accuracy of plus or minus one micrometer (0.00004 inch) or ten percent of the coating thickness, whichever is greater. Thicknesses below one micrometer are too thin for this method.

The method is obviously destructive, time consuming and requires a high level of skill and experience by the operator. Despite these disadvantages, it is used to some extent for production testing. When there is disagreement in thickness measured by other methods, the microscopical method is often selected as the referee test. This method has been accepted by ASTM as described in ASTM Standard B487.

(2) Magnetic Methods

Since the magnetic properties of the basis metal and the various layers of finishes differ, it is possible to use these differences to determine the total thickness of coatings. To use ASTM Standard B499, the coating being measured must be non-magnetic and plated over a magnetic surface. Instruments are available that measure the force necessary to detach a small magnet from the surface of the finished part. Other instruments utilize the reluctance of a magnetic flux passing through the coating and basis metal to measure the thickness. Both are easy and rapid to operate. They are calibrated against standards of known thickness. The tests are non-destructive. Results are within 10 percent of the true thickness. These instruments cannot measure the thickness of nickel if there is an undercoat of copper present.

ASTM Method B530 describes a magnetic test method for coatings on magnetic and nonmagnetic substrates. As described in these standards, only the appropriate method must be used for the deposits and substrate being tested.

The Seven Stages Of Zinc Diecast Plating

Stage 1:
Blank zinc diecasting



Stage 2:
Ground or polished



Stage 3:
Copper strike plated



Stage 4:
Bright copper plated



Stage 5:
Semi-bright nickel plated



Stage 6:
Bright nickel plated



Stage 7:
Bright chromium plated



(3) Coulometric Method

The Coulometric method is also known as the electrochemical or anodic solution stripping method. It depends upon measuring the number of ampere-minutes or coulombs required for a controlled anodic current to dissolve a coating from a small fixed area of the surface. The test is destructive. Instruments are available which record the current flow automatically so that they are simple and fast to operate. Coating thickness of chromium (greater than 0.075 micrometers), and nickel and copper (between 0.75 and 50 micrometers) can generally be determined by these instruments. ASTM Standard B504 provides some particulars on this method.

(4) S.T.E.P. Test

The S.T.E.P. method is useful to simultaneously determine both the thickness and electrode potential of individual nickel layers in multi-layer nickel deposits. The S.T.E.P. (Simultaneous Thickness and Electrode Potential) Test method is based upon the Coulometric Method and is destructive. As each nickel layer is stripped under a constant direct current, a different voltage (electrode potential) is measured. This potential is determined by comparison to a standard electrode.

The main function of this test is to monitor these variables on production parts. These measurements can also be used to indicate the corrosion protection offered by the overall system, ASTM Method B764 describes this test in detail. Commercial equipment is available and requires minimal experience.

(5) X-Ray Spectrometry

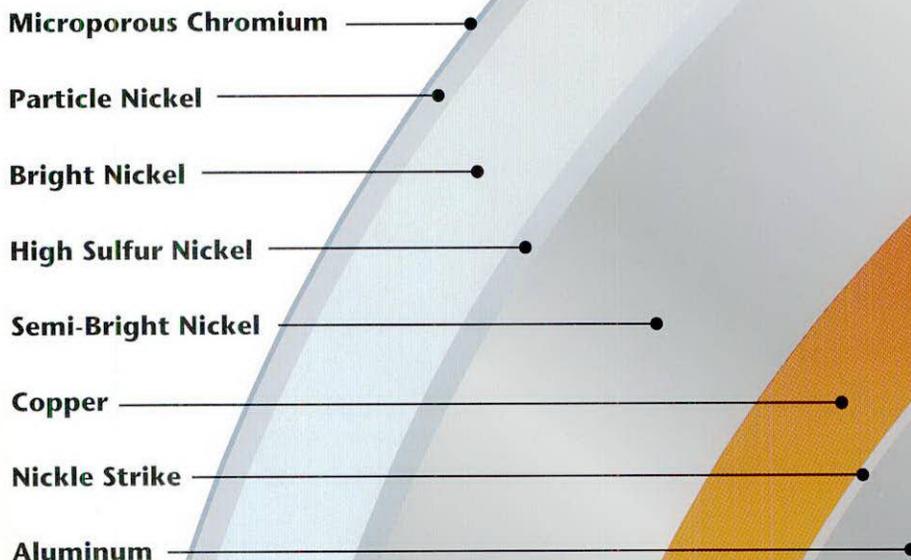
By the use of X-Rays, the Spectrometry method measures the mass of the coating per unit area, which can also be expressed in units of linear thickness provided that the density of the coating is known. Equipment is available for this easy-to-operate, non-destructive method. Depending upon the instrument and the metals being measured, the accuracy decreases as the thickness increases. Known standards are used to calibrate the instrument. ASTM B568 describes this method.

(6) Spot Test Method for Chromium

Like other chemical methods, the Spot Test for chromium thickness is destructive. A circular spot on the surface is exposed to a drop of hydrochloric acid solution which attacks the chromium at a known rate. The time required for penetration through the chromium layer is a measure of the thickness. Precision of up to plus or minus 20 percent can be achieved. Details of the test method are given in ASTM Standard B556.

(7) Weight Loss on Stripping

It is often possible to strip or dissolve a coating, chemically or anodically, without appreciable dissolution of the basis metal. By weighing the specimen before and after the stripping and estimating its surface area, the average thickness of the coating can be calculated. Sometimes, the entire sample, basis metal and coatings, is dissolved and the solution analyzed for nickel, chromium, copper and the ingredients of the basis metal. Again, the average thickness is what is obtained from the calculations. This method will not indicate significant surfaces with insufficient coating thicknesses. This method is often used in testing the quality of the finish on small barrel-plated parts. It is also used on other parts in which surface roughness, lack of accessibility, and other restricting factors make thickness measurements impractical by other methods.



Protective Value

The accelerated corrosion tests specified in Table IV are a means of controlling the continuity and quality of copper/nickel/ chromium coating, but the duration of such tests does not have a linear value with the service life of the finished article. Generally, the deterioration of the appearance of the deposit's surface is greater after these tests than typically observed in natural corrosive environments. Passing accelerated corrosion tests at the plating plant level helps to assure consistent quality parts. Details of the test methods are found in the corresponding ASTM Standards. The designer and purchasing agent need only know the general methods employed which can be briefly described as follows:

The CASS Test, ASTM Standard B368, involves exposure to a fog of droplets of five percent sodium chloride solution containing enough acetic acid to maintain a pH in the acidic range of 3.1 to 3.3. The droplets also contain a small amount of cupric chloride to accelerate corrosion.

The Corrodokote test, ASTM Standard B380, is conducted by applying a slurry of corrosive salts and kaolin to the significant surfaces of the specimen, allowing the slurry to dry, and then exposing the slurry-coated part to a highly humid atmosphere for a specified period of time.

After subjecting an article to the corrosion test for the specified time, it is examined for evidence of corrosion of the basis metal or blistering of the coating and appearance of the corrosion site. It is up to the plater and the purchaser to determine which test to use and what constitutes failure after accelerated corrosion testing. These corrosion tests were developed to give a relative measurement of the protection of the basis metal and are not reliable for predicting surface appearance after use. The extent to which such surface alteration will be tolerated is again subject to agreement between purchaser and manufacturer.

Two other accelerated corrosion tests that are still found in the older literature, but which are no longer considered useful for most decorative parts are the Neutral Salt Spray Test, ASTM B117 and the Acetic Acid-Salt Spray Test. The latter test had an ASTM number of B287 but is now included in the general salt spray standard ASTM G85. It is still used in the plumbing industry and others.

Adhesion

There is no accepted quantitative standard test for adhesion. Qualitative tests are suggested in ASTM Standard B571. A bend test involves repeated flexing or deformation of the plated parts until fracture occurs. Any separation of the layers or coating constitutes failure. In the file test a piece is cut out of the part with a saw, then a coarse file is applied to the cut edge of the coating so as to attempt to raise or separate it. There is also a quenching test in which the finished article is heated in an oven to an elevated temperature and then is quenched in cold water: if no test method is specified, pick the one that most closely simulates the possible adhesion failure mode for the part during actual service. Another test that is gaining popularity is the so-called "reverse saw" test where parts are cut with a band saw, and the area immediately adjacent to the cut is examined for chip-back.

Ductility

ASTM provides two recommended practices for evaluating ductility. ASTM B489, used for copper deposits, describes a procedure that consists of bending a narrow strip cut from a metal plated article over a mandrel. An elongation measurement is obtained from the smallest diameter mandrel that does not cause the deposit to fracture. When the shape is such that a suitable specimen cannot be cut from the plated part, a test panel may be prepared from an appropriate basis metal or plastic, with the same coating system in the same baths.

ASTM B490 is suitable only for evaluation of deposits having low ductility, such as nickel. It describes a procedure for measuring the ductility of electrodeposited foils obtained from the actual plating solutions. The recommended practice consists of measuring the bend of a foil held between the jaws of a micrometer; these are closed until fractures or cracks appear. This is the typical method used for decorative electrodeposited nickel deposits.

Microdiscontinuity

For enhanced corrosion protection with the same nickel thickness, microporous and microcracked chromium is used instead of standard, conventional, or "non-porous" chromium deposits. Several methods are available producing equivalent results. Microdiscontinuity is invisible to the unaided eye and so must be tested. ASTM B456 contains the most established method, the Dubpernell Test. This test enlarges the sites by plating copper only into the pores and cracks so that they can be visible under 100 to 200x magnification. A newer method used by the automotive industry and others is also described in ASTM B456. It involves corroding the part for the number of hours in CASS as specified by the Service Condition of the part or the purchaser, typically 22 to 44 hours. After CASS, the chromium is stripped and the surface pits in the underlying nickel deposit are observed at 100 to 200x magnification. The surface pits are classified as "active sites" in which corrosion took place through the pores in the micro discontinuous chromium deposit.

5.

Copper/Nickel/ Chromium Finishes On Other Substrates

Aluminum Alloys

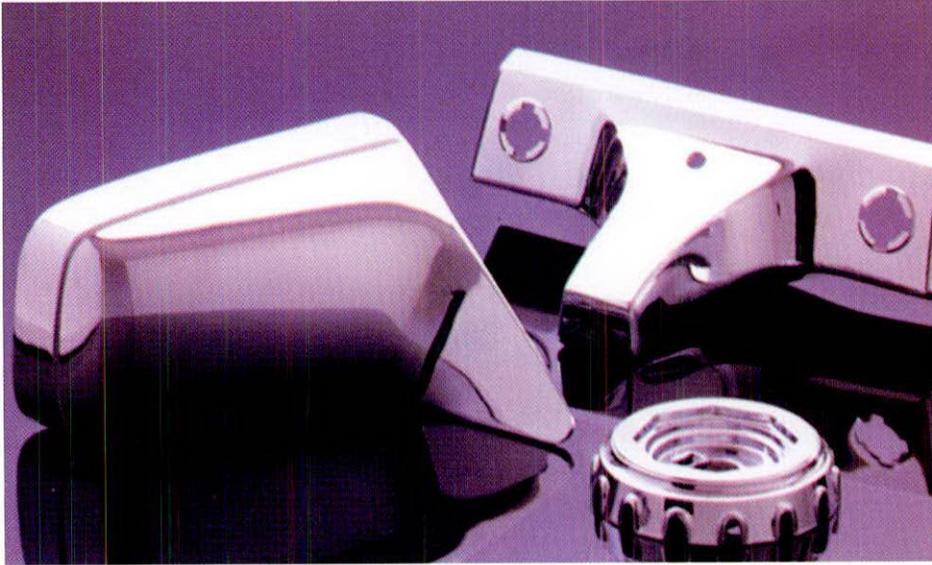
Aluminum usually requires special conditioning treatments to remove the natural oxides and alloying surface elements prior to plating. The most critical steps in plating on aluminum alloys are those relating to surface preparation.

A typical sequence consists of oil, grease, and buffing compound removal, followed by removal of the surface oxide layer. The oxide layer is heavier and chemically more resistant on heat treated alloys. The choice of acid deoxidizers versus alkaline etchants earlier in the cycle may depend on the extent of this oxide layer. Alkaline etching following degreasing is often used to remove extrusion or machining lines and other surface imperfections. Depending on the alloy composition, smut develops on the surface after etching. The choice of desmutter is based on the type of aluminum alloy processed.

A thin layer of oxide redevelops on the surface soon after desmutting and will affect adhesion when plated. This oxide must be replaced by thin metallic coatings applied by immersion. Single or double zincates and stannates are typical of such coatings.

Recent developments include modified alloy zincates which incorporate small amounts of nickel, iron, and/or copper in addition to zinc. These modified alloy zincates are more dilute and less viscous than conventional zincates. They produce fine, dense crystalline alloy zincate layers that typically improve adhesion of subsequent coatings.

A bronze strike is applied to a stannate treated surface. Whereas strikes of either Watts-based nickel, copper, electroless nickel, or sulfamate nickel is applied following the zincate. A double zincate should be used where adhesion and corrosion protection is important. After striking, normal electroplating procedures may be followed. ASTM B456 specifies types and thicknesses of copper, nickel and chromium coatings on aluminum alloys.



Plastics

Plastics and some other non-conductors can be finished by electroplating operations once the article is made conductive. The electroplate type can be selected as the user desires.

Among the plastic substrates which have been successfully electroplated in production are acrylonitrile butadiene styrene (ABS), ABS alloyed with polycarbonate (PC), polyphenylene oxide, polypropylene, polysulfone and nylon. The substrates most widely used today are ABS and ABS/PC. The plastics mentioned all require different preparatory techniques.

The "preplate" operations prepare the plastic surface for electroplating. Several proprietary and non-proprietary techniques, with and without electroless nickel or copper, are available to provide a conductive layer on the plastic for subsequent electroplating. ASTM B727 covers the preparation of plastics for electroplating. ASTM B604 covers the thickness of the deposit required for different service conditions that the finished plastic part will experience in use.

The electroplated layers on metallized plastic substrates are essentially the same as plated on metal substrates. While plastic substrates do not corrode in the same manner as metal, the galvanic relationships of the electroplated layers in the coating are the same whether the substrate is metal or plastic. Therefore, when an article is exposed to corrosive atmospheres, the electroplate structure is selected to withstand corrosion penetration.

When plating plastics, there is one layer that must be given special consideration; that is the copper electroplate. Copper plating serves two primary functions:

- 1) It effectively levels the etched, microroughened surface.
- 2) Its ductility serves as a cushion to absorb the temperature induced movement between the plastic and the metallic coating.

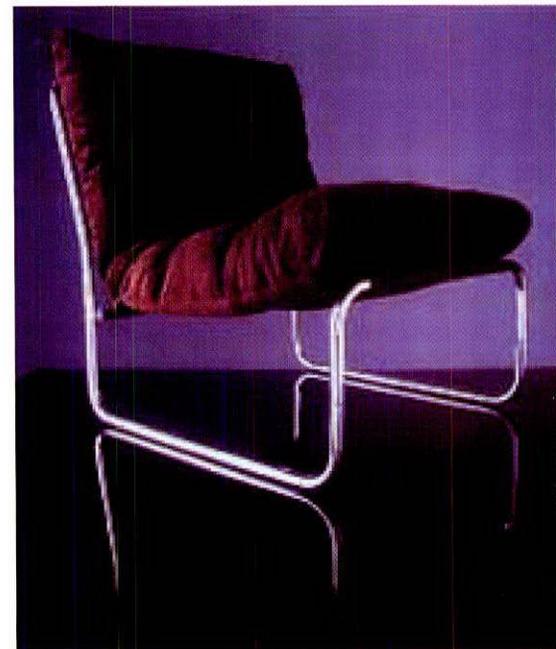
Generally, 12 to 25 micrometers (0.0005 to 0.001 inch) of copper is deposited. The copper electroplating bath must provide a leveled and ductile deposit. ASTM Standard B504 covers measurements of thickness of metallic coatings on non-metallic substrates.

Stainless Steel

Austenitic and ferritic stainless steels can be electroplated with decorative nickel and chromium to provide improved appearance and corrosion protection. Surface oils and buffing compounds are removed by hot alkaline soaks and electrocleaners similar to those used for mild steels. An anodically electrified acid is used to remove surface oxides and, in conjunction with a Woods nickel strike, provides acceptable adhesion. ASTM B254 covers the preparation of and electroplating on stainless steel. ASTM Standard B571 describes typical adhesion tests that must be met. The subsequent bright nickel layer is of sufficient thickness to provide the desired appearance. Microdiscontinuous chromium is required for severe service conditions to prevent the formation of large pits during corrosion. ASTM B456 covers the required thickness of the electrodeposits for different service conditions that the part will experience in use.

Zinc Die Cast

Parts made with zinc substrates can be electroplated to be used in all the same service conditions as steel substrate parts. ASTM B252 covers the preparation of zinc for electroplating. ASTM B456 covers the thickness of the electrodeposits required for each service condition.



6. Glossary of Terms

Abrasive Blasting - A process for cleaning or finishing by means of an abrasive directed at high velocity against the work piece.

Activation - Elimination of a passive condition on a surface.

Addition Agent - A material added in small quantities to a solution to produce a desired effect. Also synonymous with "brightener."

Adhesion - The attractive force that exists between an electrodeposit or an electrochemical deposit and its substrate that can be measured as the force required to separate the deposit from the substrate.

Amorphous - Non-crystalline or without evidence of a regular structure.

Anode - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. In most instances it is the source of metal to be plated from the bath.

Anode Efficiency - The actual current efficiency of a specified anodic process compared to the theoretical value. The actual fraction of current used to dissolve metal from the anode compared to the theoretical amount as predicted by Faraday's Laws.

Autocatalytic Plating - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited. Often referred to as "electroless plating."

Barrel Plating - Electroplating or cleaning in which the work is processed in bulk in a rotating container (barrel).

Base Metal (or Substrate) - Material upon which processing is conducted or coatings are deposited. (It is not necessarily the material from which the part is constructed).

Blister - A dome-shaped imperfection or defect, resulting from loss of adhesion between a deposit and its substrate, or between various coatings where multiple layers of coatings are present.

Bright Dip - A solution used to produce a bright surface on a substrate by chemical immersion.

Bright Plating Range - The range of current densities within which a given plating solution produces a bright deposit.

Brightener - Another term for addition agent. A liquid or powdered material that, when added to a plating bath, improves the reflectivity or brightness of the deposits produced by the plating bath.

Brush Plating - A specialized method of plating, typically used for small scale applications, where an inert anode is surrounded by a pad, sponge, brush, or other device that will retain a volume of a concentrated solution containing a dissolved salt of the metal to be deposited. The anode/pad device is moved over the cathode during the plating operation in the area to be plated.

Buffing - The smoothing of a surface, accomplished by placing the surface to be finished against a rotating flexible wheel, to which fine abrasive particles have been applied in liquid, suspension, paste, or grease form.

Buffer - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.

Burnt Deposit - A rough, non-coherent or otherwise unsatisfactory deposit, typically produced by the application of an excessive high current density.

Bus Bar - The term used to describe the cables or conducting media – generally copper or aluminum stock – that transfers the current from the rectifier to the plating tank.

Carryover - See "Drag-in" defined on next page.

- CASS Test** - A special accelerated corrosion testing method using copper and acetic acid solution as the fog medium. It is most typically used to predict the corrosion protection of nickel/chrome, or copper/nickel/chrome electrodeposits. See ASTM Method B368.
- Cathode** - The part that is electroplated.
- Cathode Efficiency** - The actual amount of current used to deposit metal in a plating process, compared to the theoretical amount as predicted by Faraday's Laws.
- Chelate Compound** - A compound in which a metal is contained as an integral part of a ring structure and is not readily ionized.
- Cleaning** - The removal of grease or soil and other foreign materials from a surface using one or more chemical or electrochemical solutions.
- Alkaline Cleaning*—cleaning by means of an alkaline solution.
- Anodic or Reverse Cleaning*—electrolytic cleaning where the part is connected to the negative terminal of the rectifier.
- Cathodic or Direct Cleaning*—electrolytic cleaning where the part is connected to the positive terminal of the rectifier.
- Di-phase Cleaning*—cleaning by means of a solution that contains a solvent layer and an aqueous layer. Cleaning occurs by both solvent and emulsification actions.
- Soak Cleaning*—cleaning by chemical means without the use of current. Generally used to remove heavy oils and greases.
- Ultrasonic Cleaning*—cleaning by any chemical means aided by ultrasonic energy to speed up soil removal. Especially useful in the removal of buffing compounds.
- Spray Cleaning*—use of an alkaline cleaner that is sprayed onto the part(s) to be cleaned. The additional energy provided by the spraying operation accelerates the removal of soils, greases, and buffing compounds.
- Contact Plating** - Deposition of a metal by immersion of the work in a solution that is in contact with another metal.
- Corrodokote Test** - An accelerated corrosion test for electrodeposits using a special paste coating that is applied to parts before they are CASS salt spray tested. See ASTM Method B380.
- Corrosion** - Gradual dissolution or oxidation of a metal.
- Covering Power** - The ability of an electrodeposit to plate at very low current densities, such as in deep recesses or holes. (To be distinguished from Throwing Power.)
- Current Density** - The total current divided by the area to which the current is applied.
- Cathode Current Density*—the total current applied divided by the total area being plated.
- Anode Current Density*—the total current applied divided by the total anode area.
- Current Efficiency** - See Cathode Efficiency and Anode Efficiency.
- Degreasing** - The removal of grease and oils from a surface.
- Solvent Degreasing*—degreasing by immersion in liquid organic solvent.
- Vapor Degreasing*—degreasing by solvent vapors condensing on the parts being cleaned.
- Drag-In** - The water or solution that adheres to the objects from previous processing steps, and which is thereby introduced into a processing tank.
- Drag-Out** - The solution that adheres to articles when they are removed from a processing tank.
- Ductility** - The ability of a material to deform without fracturing.
- Dummy** - The term used to describe low current density plating done to remove metallic impurities from a plating bath.
- Duplex Plating or Duplex Deposit** - The term used to describe a multi-layer deposit that incorporates two layers with slightly different corrosion potential characteristics. The different layers are typically combined in a manner that allows one layer (the under-layer) to be sacrificial to the other layer (the top layer), thereby greatly improving the corrosion protection afforded, compared to that provided by a single layer of similar thickness.
- Electroless Plating** - A more commonly used term for Autocatalytic Plating.
- Electrolyte** - General term used to describe the processing bath, usually the plating bath.
- Electrolysis** - Process of causing chemical changes via the passage of current through an electrolyte.
- Electroplating** - The electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties, appearance, or dimensions different from those of the basis metal.

Electropolishing - Term used to describe the process of improving the appearance and surface condition of metallic substrates by applying a current to a chemical solution.

Etch - *Noun*—a roughened surface produced by a chemical or electrochemical means.
Verb—to unevenly dissolve a part of a surface or metal.

Faraday - The number of coulombs (96,490) required to deposit one chemical equivalent of a metal. The chemical equivalent value varies depending upon the metal being deposited.

Filter Aid - An inert, insoluble material, more or less finely divided, used as a filter medium, or to assist in filtration by preventing excessive packing of the filter cake.

Flash Plate - The application of a very thin electrodeposit, typically less than 2.54 microns (0.1 mil).

Flocculate - To aggregate into larger particles, to increase in size to the point where precipitation occurs.

Galvanic Protection - See Sacrificial Protection

Hard Chromium - Chromium plate for engineering, rather than decorative applications. Not necessarily harder than decorative chromium, but generally much thicker.

Hydrogen Embrittlement - Embrittlement of a metal or alloy caused by absorption of hydrogen typically during pickling, cleaning or plating operations.

Inert Anode - An anode that is insoluble in the electrolyte under the conditions prevailing in the electrolysis being performed. Typically used in plating baths where there is no convenient source of soluble metal an anode, such as chrome plating.

Karat - A measure of the fineness or purity of a gold deposit. One karat is equal to 1/24 part of pure gold; i.e., a 24 karat deposit is pure gold. Likewise, an 18 karat deposit is 18 parts of gold and 6 parts of another metal.

Mechanical Plating - The application of an adherent metallic coating on a substrate by impingement of finely divided solid particles of the coating to be applied onto the substrate. Alloy deposition is possible via mechanical plating. Also, plating occurs without any hydrogen embrittlement occurring.

Metal Distribution Ratio - The ratio of the thicknesses of metal deposited at two different current densities. Frequently used as a measure of the Throwing Power of an electrolyte.

Metal Turn Over (MTO) - The replacement of 100% of the original metal content of an electroless plating bath.

Microinch - One millionth of an inch, 0.000001 inches. (=0.001 mils)

Micron - One millionth of a meter, approximately one 25th of a mil. (25.4 microns = 1 mil)

Micro Throwing Power- The ability of an electrolyte to deposit metal in pores or very small recesses of substrates.

Mil - One thousandth of an inch (0.001 inches). (= 25.4 microns)

Oxidizing Agent - A compound that causes oxidation, thereby itself becoming reduced.

pH - The co-logarithm (negative logarithm) of the hydrogen ion activity. A measure of acidity (less than 7) or basicity (more than 7) of a solution.

Passivation or Passivity - The condition on a metal that retards its normal reaction in a specified environment. It is typically associated with the metal assuming an electrochemical potential more noble than its normal potential.

Peeling - The detachment or partial detachment of a deposited coating from the basis metal or undercoat layers.

Pickling - The removal of oxides or other compounds from the surface of a metal by chemical or electrochemical action.

Pit - A small depression or cavity in the surface of a part. It can be produced during manufacturing the part, during deposition, or by corrosion of the surface.

Polishing - See Buffing

Reducing Agent - A compound that causes chemical reduction, thereby itself becoming oxidized.

Regeneration - *Noun*—The replacement of 100% of the original metal content of an electroless plating bath.
Verb—The act of replenishing a processing bath in an attempt to restore optimum performance.

- Resist** - A material applied to a part of the surface of an article to prevent metal deposition on or metal removal from that area during chemical or electrochemical processes. Also called "masking."
- Ripple** - A measurement of the amount of AC current that is present in a DC current. Excessive ripple generally causes passive deposits or hazes in plated coatings. Ideally, ripple should be less than 5% for most plating applications.
- RMS** - A numerical reference to the smoothness of a surface. Literally, it refers to the Root Mean Square of the height difference between the microscopic peaks and valleys that are evident on a surface when it is viewed under sufficient magnification. The lower the number, the smoother the surface. In other words, the average distance from the tip of a peak to the bottom of an adjacent valley on a part with a surface with a 2 RMS finish, would be less than the equivalent distance on a part with a 16 RMS finish. RMS is typically measured with a profilometer, using vertical magnifications from 500x to 200,000x.
- Robber** - Term used to describe an auxiliary cathode placed near the part to be plated to divert current from concentrating in high current density areas, leading to heavy deposits in these areas.
- Sacrificial Protection** - The mechanism of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion (for example, zinc plating over a steel substrate). Also referred to as "Galvanic Protection."
- Shelf Roughness** - Roughness on surfaces of parts that face upward where solids have settled during a processing operation.
- Shield** - *Noun*—a nonconducting medium or panel used to alter the flow of current in an attempt to provide the most uniform cathode current density possible on the part being plated.
Verb—to alter the normal current distribution by placing a non-conducting medium in the path of the current in a manner that provides a more uniform overall current density on the part being plated.
- Spontaneous Decomposition** - See Triggering
- Step Plating** - Non-uniform thickness, striations, or skip-type plating. In electroplating operations this is generally evident in low current density areas, while in electroless plating operations it is typically evident on edges of parts and around holes or perforations in parts. Also referred to as "edge pullback" and/or "worm tracking."
- Stray Current** - Current that passes through paths other than the intended circuit, such as through heating coils, the plating tank, floor grating, hoist super-structures, etc.
- Strike** - *Noun*—a thin deposit applied to a substrate or other plated deposit to provide activation or protection from immersion plating.
Verb—to apply such a coating by plating for a short time in a plating bath.
- Strip** - To remove a coating from the substrate or undercoat layer via chemical or electrochemical methods.
- Substrate** - The base metal to be plated.
- Taber Abraser** - An instrument used to characterize the wear properties of a substrate or plated finish. Test specimens are mounted to a small rotating turntable and subjected to the wearing action of two abrasive wheels, which are applied at a specific pressure, and which rotate in opposite directions. An important feature of the Taber Abraser is the all angles relative to the weave or grain of the material being tested.
- Tarnish** - Discoloration of a base metal or a plated coating, typically a darkening of the appearance of the basis or plated metal.
- Thief** - See Robber
- Throwing Power** - Term used to describe the uniformity of thickness of a plated coating. Electroless baths typically plate with 100% Throwing Power, i.e., the same thickness on all areas of a part in contact with the solution. Electroplating baths invariably exhibit greater thicknesses in high current density areas compared to low current density areas. See also Thickness Distribution Ratio.
- Triggering** - Spontaneous decomposition of an electroless plating bath, which is typically caused by excessively high concentration of reducing agents in the bath, or the introduction of solid contaminants, such as metal filings or other particles.
- Troy Ounce** - A unit in the Troy system of weights used for precious metals. Gold and other precious metals are typically measured in Troy ounces. (1 Troy ounce = 31.1035 grams)
- Turnover** - See Regeneration.
- Water Break** - The appearance of a discontinuous film of water on a surface, signifying non-uniform wetting and usually associated with the presence of surface contamination on parts.
- Work (Plating)** - The material being plated or otherwise finished.



Metal Finishing Suppliers' Association

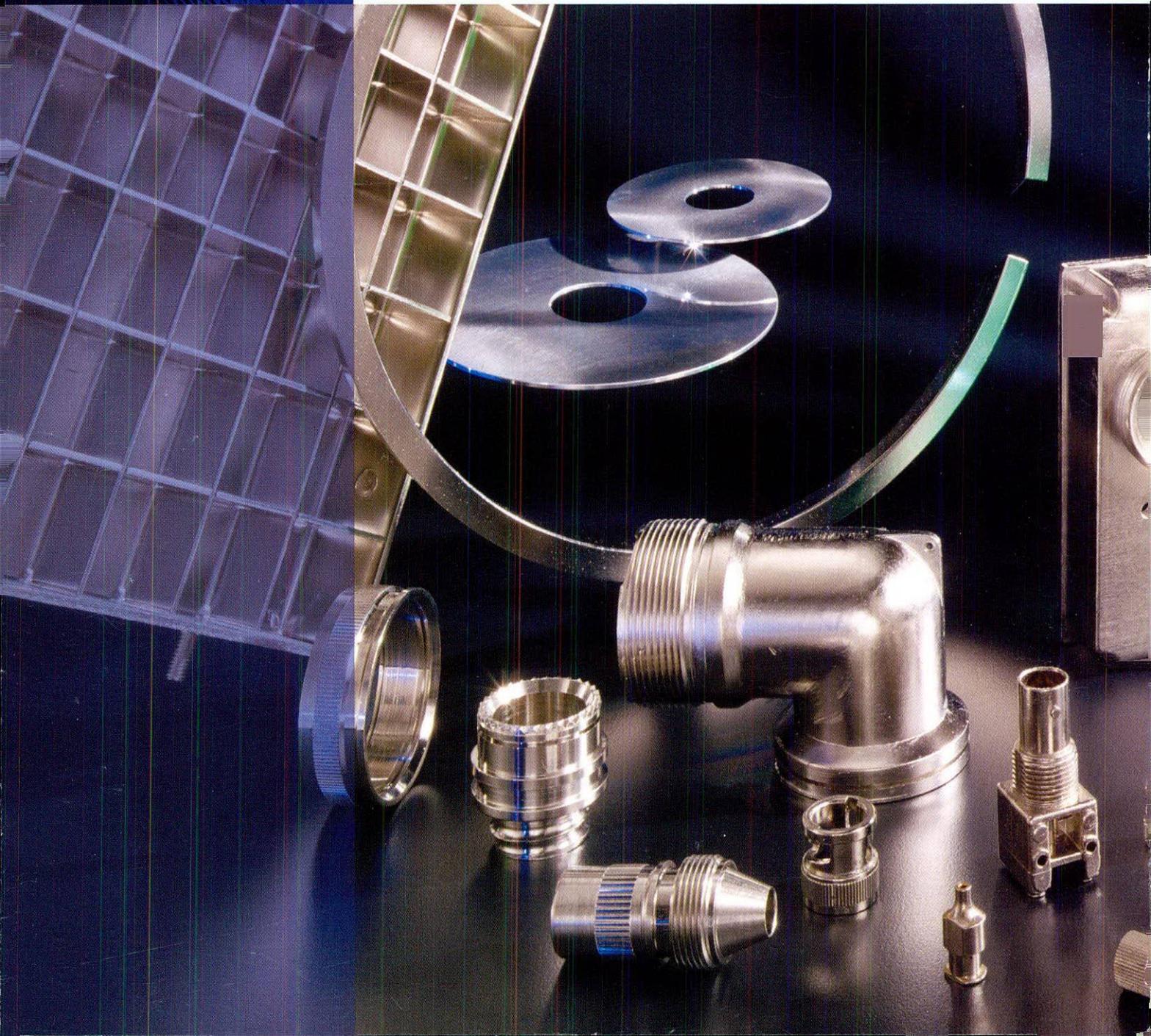
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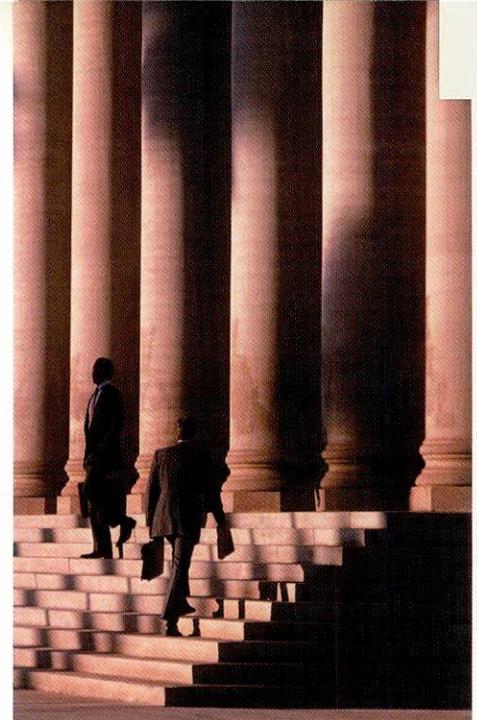
Quality Metal Finishing Guides



Metal Finishing Suppliers' Association

E l e c t r o l e s s N i c k e l





Introduction

The Metal Finishing Suppliers' Association (MFSA) is a trade association of companies and individuals involved in supplying chemicals, equipment, technology, and solutions to the surface finishing industry. One of the association's primary objectives is to promote the interests and further the welfare of its members and their customers while safeguarding the interests of the ultimate customer.

In 1960, MFSA initiated action to upgrade the durability of metal finishes. Known as the "Quality Metal Finishing Project" or QMF, this program was aimed at:

- 1) the promotion of technically sound specifications and standards in cooperation with interested trade and technical societies;
- 2) the provision of information to both producers and buyers of metal finished products;
- 3) the development of printed guides containing information on established standards and specifications, readily accessible for day-to-day use by the design engineer, the purchasing agent, and all those involved in the use of metal finished products.

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Quality

As an association promoting the interest and welfare of the producers and customers of the metal finishing industry, MFSA realizes that everyone suffers loss when products are sold that are inadequately finished for the intended application. MFSA wishes to encourage the industry to develop and maintain high-quality standards needed to guarantee the expected or promised service of the unit.

The industry needs to know how a high-quality metal finish can be achieved, how to select proper specifications for a given application, and how to control the release of products to assure that they meet the needs of the customer. At the same time, management must be confident that this know-how is based on sound engineering principles and incorporates a reasonable margin of safety.

There have been significant developments of standards for quality systems in the last few years that are applicable to metal finishing. These include:

- International Standards Organization; (ISO 9000; ISO 1456)
- American National Standards Institute/American Society for Quality Control; (ANSI/ASQC Q90)
- American Society for Testing and Materials; (ASTM B456)

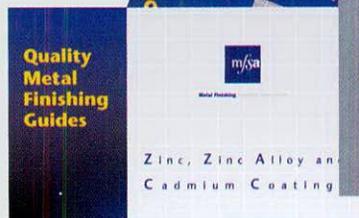
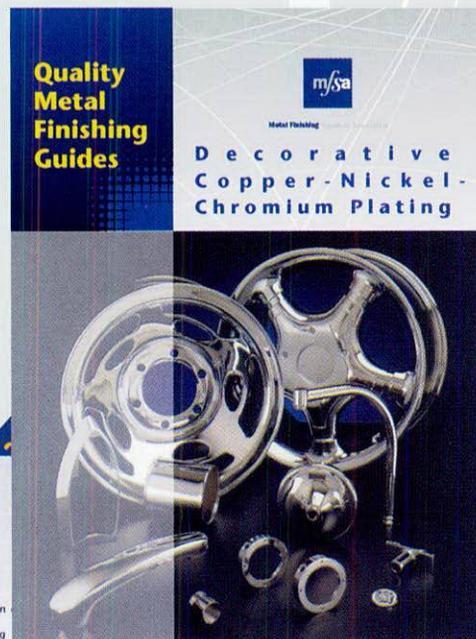
This manual will provide useful details on how to apply proven metal finishing engineering in your systems to help you maintain and improve your metal finishing quality.

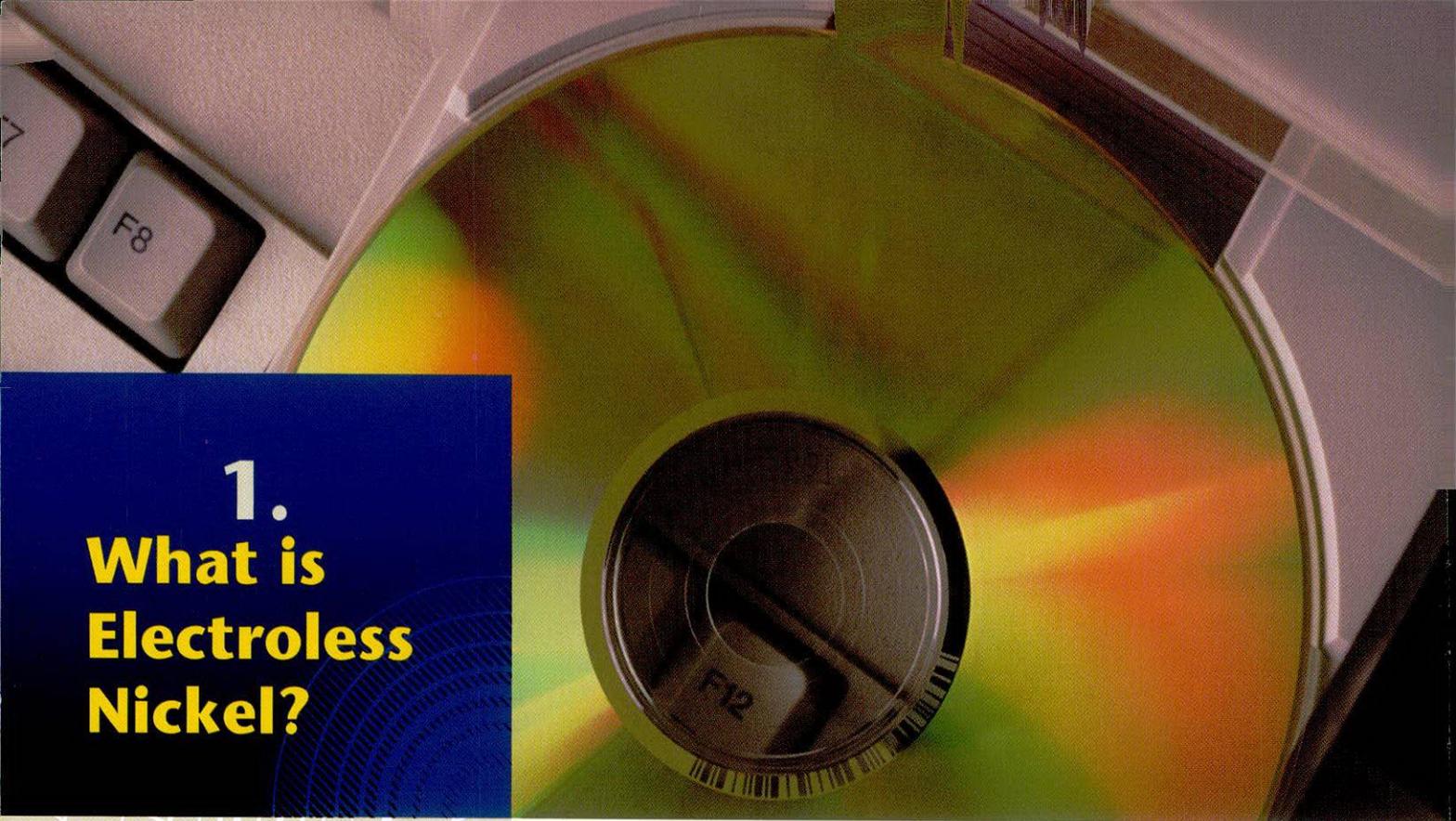
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- **Chemical Surface Preparation for Electroplated and Metallic Coatings**
- **Decorative Copper-Nickel-Chromium Plating**
- **Decorative Precious Metal Plating**
- **Hard Chrome**
- **Pretreatment for Paint and Powder Coatings.**
- **Tin and Tin Alloy Coatings**
- **Zinc, Zinc Alloy and Cadmium Coatings**





1. What is Electroless Nickel?

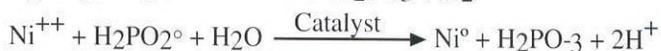
This guide is concerned with autocatalytic nickel plating, commonly referred to as electroless nickel plating. In contrast with electroplating, electroless nickel (EN) plating does not require rectifiers, electrical current or anodes. Deposition occurs in an aqueous solution containing metal ions, a reducing agent, complexing and buffering agents and stabilizers. Chemical reactions on the surface of the part being plated cause deposition of a nickel alloy.

Since all surfaces wetted by the electroless nickel solution have the same plating rate, the deposit thickness is quite uniform. This unique property of EN makes it possible to coat internal surfaces of pipes, valves and other parts. Such uniformity of deposit thickness is difficult, if not impossible, to achieve by any other metal finishing method.

The discovery of electroless plating is credited to Brenner and Riddell in the 1940s. Today EN has grown into a very substantial segment of the metal products finishing industry.

This guide seeks to provide the reader with a more through understanding of the process. The guide includes descriptions of deposit properties, equipment required, process applicability, and test procedures to the end that a high quality EN deposit can be achieved and maintained.

The chemical reactions that occur when using sodium hypophosphite as the reducing agent in electroless nickel plating are as follows:



An electroless nickel coating is a dense alloy of nickel and phosphorus. The amount of phosphorus co-deposited can range from less than 4% to 13%, depending upon bath formulation, operating pH, and bath age. The deposition process is autocatalytic; i.e., once a primary layer of nickel has formed on the substrate, that layer and each subsequent layer become the catalyst that causes the above reactions to continue. Thus, very thick coatings can be applied, provided that the ingredients in the plating bath are replenished in an orderly manner. In general, commercial practice, thickness range from 2.5 to 125 microns (0.1 mil to 5 mils), but in some salvage operations, 750 micron (30 mil) deposits are not uncommon.

Electroless nickel deposits are functional coatings and are rarely used for decorative purposes only. The primary criteria for using electroless nickel generally falls within the following categories:

- 1) Corrosion resistance.
- 2) Wear resistance.
- 3) Hardness.
- 4) Lubricity.
- 5) Solderability and bondability.
- 6) Uniformity of deposit regardless of geometries.
- 7) Nonmagnetic properties of high-phosphorus nickel alloy.

These items will be discussed at greater length in the "Properties" section of this guide

In the early years, platers encountered many problems with electroless nickel because of poor formulations, inferior equipment, misapplications and a general misunderstanding of the process and the deposit. In the first decade and a half of its existence, electroless nickel plating had an aura of "black magic" attached to it. Modern bath formulations, however, use only the purest grades of chemicals, delicately balanced and blended to give the processor plating baths with long life, exceptional stability, consistent plating rates, self-maintaining pH and most importantly, reproducible quality. In addition, advancements in tank design, filtration systems, heating and agitation have virtually eliminated the problems that plagued the user years ago.

Furthermore, in the past decade, advancements have been made in autocatalytic nickel plating solutions. Reducing agents other than sodium hypophosphite are used for special applications; composites of nickel with diamond particles, silicon carbide, and PTFE are available; and ternary alloys may be applied. Also, baths have been formulated to yield specific results; i.e., high corrosion resistance, brightness, high plating rate, improved ductility, and low levels of magnetic response. Today, chemistries that utilize extended life strategies are becoming more common. Some of these extended life



approaches include sulfate free formulations, those based upon nickel hypophosphite, or those that utilize membrane technology to reduce the build-up of objectionable reaction products in the bath.

It has taken many years of hard work and cooperative effort by the suppliers and users to arrive at the present state of the art.

2. Types of Electroless Nickel

All electroless nickel coatings are not the same. Different types have been developed to provide special properties, depending on the end-use requirement. Table I lists deposit characteristics and suggests suitable EN types or systems.

Nickel-phosphorous Baths

Acid nickel phosphorus -

Deposits from these baths can be identified by phosphorus content that, in turn, determines deposit properties. 4-5% = Low-phosphorus; 6-9% = Mid-phosphorus; 10-13% = High-phosphorus. Low-phosphorus deposits offer improved hardness and wear characteristics, higher temperature resistance, and increased corrosion resistance in alkaline environments. Mid-phosphorus coatings are bright and aesthetically pleasing and have good hardness and wear resistance, along with moderate corrosion resistance. High-phosphorus coatings provide very high corrosion resistance and a complete lack of magnetic response.

Alkaline nickel-phosphorus -

These baths plate at relatively low temperatures (24-60° C, 75-140° F), making them suitable for plating on plastics and other nonconductive materials, or for use on zincated aluminum. In addition, because of the low phosphorus content deposited (3-4%), they offer enhanced solderability and bondability, especially in electronic applications.



Nickel-boron Baths

Low boron, nickel-boron

coatings (less than 1% B) - reduced with amine boranes, are most often used in electronic applications to provide high electrical conductivity, good solderability and good ultrasonic bonding characteristics. Deposits with higher levels of boron (2-3%) have high hardness values and better wear resistance than other coatings. In addition, the melting point of nickel-boron alloys is higher than that of nickel-phosphorus coatings. The only major disadvantage is that the chemical cost of amine borane reduced coatings is five to 10 times that of nickel-phosphorus deposits.

Sodium borohydride reduced nickel-boron

plating solutions deposit higher levels of boron (3-5%) than amine borane baths and are usually co-alloyed with thallium. These coatings provide exceptionally high hardness and wear resistance, usually equal to hard chromium.

Lead-free, Cadmium-free formulations have been introduced by several suppliers of proprietary electroless nickel processes to meet the requirements of the End of Life Vehicle (ELV) Initiative created by the European Union (EU). These systems generally offer similar operating features as “conventional” electroless processes, including plating rate, deposit hardness, bath life, brightness, and corrosion resistance.

Polyalloys

Several electroless nickel plating solutions produce deposits having three or four elements. These include nickel-cobalt-phosphorus; nickel-iron-phosphorus; nickel-tungsten-phosphorus; nickel-rhenium-phosphorus; nickel-molybdenum-boron; nickel-tungsten-boron; and others.

Each of the above is designed to maximize qualities such as corrosion resistance, hardness, high-temperature resistance, electrical properties and magnetic or nonmagnetic characteristics.

Composite Coatings

Co-depositing hard particulate matter with the nickel-phosphorus alloy can further enhance the excellent wear resistance of electroless nickel. Usually, particles of silicon carbide (4,500 VHN) or synthetic diamonds (10,000 VHN) are used in this process. A uniform dispersion of particles (20 to 30% by volume) is held in place in the deposit

by the nickel-phosphorus matrix. These deposits are very brittle and require a sound substrate to prevent cracking in use. Composites containing silicon carbide (SiC) are most often used in mold and die applications. Those containing diamonds have found use in textile and cutting tool applications.

The co-deposition of PTFE particles in an electroless nickel coating can significantly improve its lubricity and release properties. These coatings typically contain 15 to 25% (by volume) PTFE particles and can provide coefficients of friction nearly as low as solid Teflon[®] or dry film lubricants.

Table I
Electroless Nickel Coating Most Suitable For Specific Deposit Characteristics

Characteristic Desired	Most Suitable Electroless Nickel Coating
Wear resistance	<ol style="list-style-type: none"> 1. Composite coatings with Silicon Carbide (SiC) or diamonds 2. Nickel-boron, with 3% or more B and 3% or more TI 3. Nickel-phosphorus, with 11% or more P, heat treated 4. Nickel-phosphorus, with 35% P
Corrosion resistance	<ol style="list-style-type: none"> 1. Nickel-phosphorus, with 11% or more P
Hardness	<ol style="list-style-type: none"> 1. Composite coatings with SiC or diamonds 2. Nickel-boron, with 3% or more B and 3% or more TI 3. Nickel-phosphorus, with 10% or more P, heat treated 4. Nickel-phosphorus, with 3-5% P
Ductility	<ol style="list-style-type: none"> 1. Nickel-phosphorus, with 11% or more P 2. Nickel-phosphorus, with 2% or less phosphorus
Lubricity	<ol style="list-style-type: none"> 1. Composite coatings with Teflon[®] 2. Nickel-phosphorus
Chemical resistance	<ol style="list-style-type: none"> 1. Nickel-phosphorus, with 11% or more P
Solderability and bonding	<ol style="list-style-type: none"> 1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
Non-magnetic response	<ol style="list-style-type: none"> 1. Nickel-phosphorus, with 11% or more P
Electrical conductivity	<ol style="list-style-type: none"> 1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
Electrical resistivity	<ol style="list-style-type: none"> 1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
Precious metal replacement	<ol style="list-style-type: none"> 1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
High temperature resistance	<ol style="list-style-type: none"> 1. Nickel-boron 2. Nickel-phosphorus
Brightness or pleasing appearance	<ol style="list-style-type: none"> 1. Nickel-phosphorus, with 6-9% P, brightened

Selection depends on the severity of the requirements and on the economics of the application.

3. Applications of Electroless Nickel

Table II
Electroless Nickel Applications

Application	Base Metal	Deposit-Mils Approx.	REASON FOR USE									
			Wear Resistance	Corrosion Resistance	Repair & Salvage	Fretting Resistance	Release Properties	Weldability	Solderability	Base for Electroplating	Infinite Throw	Thickness Control
Automotive												
Heat Sinks	Al	.4		x					x		x	
Pistons	Fe	.6	x	x								
Engine Bearings	Al		x	x								
Hose Couplings	Fe	.2	x									
Gears & Gear Assemblies	Fe	0.4-1.0									x	x
Aircraft												
Engine Overhaul	Fe	1.0+	x	x	x						x	x
Struts	S/S	1.0-2.0			x							x
Landing Gear	Fe	1.0+	x	x	x							
Hydraulics	Fe	1.0+										
Propellers	Fe	1.0+	x	x	x							
Hinges	Fe	.4	x							x		
Tape Guides	Al	.2	x									
Engine Mounts	4130 4140	1.0-2.0	x	x								x
Turbine Parts	Fe	1.0-2.0										x
Gyro Parts	Fe	0.5-1.0	x									
Chemical Equipment												
Tanks	Steel & SS	2.0-5.0		x								
Pumps	Steel & SS	2.0-5.0	x	x								
Filters	Steel & SS	2.0-5.0	x	x								
Heat Exchangers	Steel & SS	2.0-5.0		x								
Spray Nozzles	Fe/Cu	0.3-1.0	x	x							x	x
Tubing	Cu/Al Fe/SS	0.5-2.0	x	x							x	x
Railroad												
Diesel Shafts	Fe	1.0+	x		x	x					x	x
Electrical Motors												
Variable Speed Shafts	Fe	0.5+	x		x							x
Rotor Blades, Starter Rings	Fe/Al	0.5-5.0	x	x								
Printing Rolls	Fe/Cu	0.8-1.5	x	x								x

Electroless nickel coatings have many unusual properties, which make them very useful in a broad range of functional applications. Most applications take advantage of the hardness, lubricity, corrosion resistance, electrical and magnetic properties of electroless nickel, as well as its ability to cover complex geometries and internal as well as external surfaces. Table II lists many of the common applications and indicates which properties of EN are of value in each of these applications.

4. Properties of Electroless Nickel

It is the superior properties of electroless nickel coatings that caused the rapid expansion of its use. No other coating has the combination of properties offered by electroless nickel.

Corrosion Resistance and Corrosion Protection

One of the most common reasons for using of electroless nickel coatings in functional applications is its excellent corrosion resistance. In the very corrosive conditions encountered in drilling and producing oil wells, for example, electroless nickel has shown its ability to withstand the combination of corrosive chemicals and abrasion.

The alloy content of the EN deposit influences its performance in most environments. Phosphorus alloys typically provide better protection than boron-reduced coatings. In hot, highly alkaline solutions, low-phosphorus deposits are more corrosion resistant than high-phosphorus alloys. However, in most other chemical environments, high-phosphorus alloys provide superior corrosion resistance.



Density

The density of EN coatings declines with increasing phosphorus content. An electroless nickel deposit containing 3% phosphorus has a density of 8.5 g/cm^3 , while that of a deposit with 11% phosphorus has a density of 7.75 g/cm^3 . These values are lower than those of pure metallurgical nickel (8.91 g/cm^3).

Coefficient of Thermal Expansion

The coefficient of thermal expansion of a deposit containing 8 to 9% phosphorus is about $13 \times 10^{-6}/^\circ \text{C}$. This compares to values for electrodeposited nickel of 14 to $17 \times 10^{-6}/^\circ \text{C}$.

Thermal Conductivity

The thermal conductivity of an electroless nickel deposit containing 8 to 9% phosphorus is 0.0105 to $0.0135 \text{ cal/cm/sec}/^\circ \text{C}$. Electrodeposited nickel has a value of 0.19 to $0.26 \text{ cal/cm/sec}/^\circ \text{C}$.

Melting Temperature

The final melting temperatures of electroless nickel deposits vary widely, depending upon the amount of phosphorus alloyed in the deposit. The initial melting point is about 890°C (1630°F) for all deposits. This temperature corresponds to the eutectic point for nickel phosphorus.

Magnetism

Electroless nickel deposits containing greater than 8% phosphorus are considered to be essentially nonmagnetic as plated. The coercivity of 8.6% and 7.0% phosphorus content deposits has been reported at 1.4 oersteds and 2.0 oersteds, respectively. A 3.5% phosphorus content deposit produces a magnetic coating of 30 oersteds. When the phosphorus content is increased to 11%, the deposit is completely nonmagnetic.

Coating thickness measurements with devices that rely on the nonmagnetic characteristic of the coating become inaccurate, if phosphorus content is below 8%.

Heat treatment of electroless nickel at temperatures over about 270° C (520° F) will increase the magnetism of the deposit. Even deposits that are completely non-magnetic as plated, will become highly magnetic when heat-treated above 330° C (625° F). At these temperatures amorphous solid solutions of phosphorus in nickel decompose to form nickel phosphide (Ni₃P) and magnetic nickel.

Electrical Resistivity

The electrical resistivity of EN deposits also varies with their phosphorus content. That of pure metallurgical nickel has a value of 6.05 microhm-cm. Electroless nickel deposits containing 6 to 7 percent phosphorus have resistivities between about 52 to 68 microhm-cm. The resistivity of a deposit containing 2.2% phosphorus is 30 microhm-cm, while that of a deposit with 13% phosphorus is 110 microhm-cm.

Heat-treating electroless nickel reduces its electrical resistivity. Beginning at about 270° C (520° F), heat-treating decreases electrical resistivity due to the precipitation of nickel phosphide in the coating. The resistivity of an electroless nickel deposit with 7% phosphorus, heat treated to 600° C (1100° F), was reduced from 72 to 20 microhm-cm.

Solderability/Weldability

Electroless nickel-phosphorus alloys are easily soldered with a highly active acid flux. Soldering without a flux or with mildly active fluxes can be more difficult if the parts are allowed to form oxides by extended exposure to the atmosphere. The heat processing of electroless nickel plated parts can make soldering very difficult, unless a highly active acid flux is used.

Welding of electroless nickel deposits is not commonly done. The dissolution of phosphorus in the weld can produce low melting point compounds and “hot cracks” and disintegration of the weld.

Adhesion

Excellent adhesion of electroless nickel deposits can be achieved on a wide range of substrates, including steel, aluminum, copper and copper alloys. Typical bond strengths reported for electroless nickel on iron and copper alloys range from 340 to 410 MPa (50 to 60,000 psi). The bond strength on light metals, such as aluminum, tends to be lower, in the range of 100 to 240 MPa (15 to 35,000 psi).

Low-temperature heat treatment is commonly employed to improve adhesion of EN on all metals, particularly on light metals such as aluminum or titanium. During this heat treatment, diffusion can occur between the atoms of the coating and the substrate.

Surface preparation and activation are two of the most important factors for producing excellent adhesion.

Thickness

Electroless nickel can be deposited to produce a wide range of coating thicknesses, with uniformity and minimum variation from point to point. This uniformity can be maintained in plating both large and small parts, and on components that are fairly complex, and with recessed areas. Electroplating of such parts, on the other hand, would produce thickness variation and possible voids in the plating, when coating holes and inside diameters. The range of thicknesses for electroless nickel in commercial applications is 2.5 to 125 µm (0.1 to 5 mils), although deposits as thick as 1000 µm (40 mils) have been reported. The typical plating rate of most baths is 7.5 to 20 µm/hr (0.3 to 0.8 mil/hr).

The majority of commercial applications, except those involving corrosive service or heavy buildup of worn parts, utilize a thickness between 2.5 and 25 µm (0.1 and 1.0 mil). Thicknesses of 25 to 75 µm (1.0 to 3.0 mils) are common for corrosive service, while deposit thicknesses above 75 µm (3.0 mils) are typical of repair and rework applications. Deposition of coatings greater than 75 µm (3.0 mils) requires more careful attention to process control to avoid roughness and pitting.

Brightness

The brightness and reflectivity of electroless nickel can vary significantly, depending on the specific formulation. The reflectivity of the deposit is also affected by the surface finish of the substrate. Thus, a very bright electroless deposit may appear dull if the substrate is rough.

The appearance of most electroless nickel coatings is similar to that of electrodeposited nickel.

5. Good EN Plating Practice

Achieving the full potential of electroless nickel plating requires that the finisher pay attention to the original metallurgical surface condition before beginning to put the part in an electroless nickel processing line. In a similar fashion, the part must be cleaned properly; the right equipment must be available for precleaning the parts and for operating the electroless nickel plating solution; the solution best able to produce the required properties must be used; the finisher must recognize the common processing problems and be able to correct them; and the finisher must know how to heat treat and provide other postplate treatments required to achieve certain properties. The following sections elaborate on the metallurgy and process methods important in producing sound deposits.

Substrate Effects

Substrate surface smoothness influences the protective value of electroless nickel deposits. The smoother the surface to be plated, the better the quality of the final electroless nickel deposits and the better the corrosion resistance the coating provides.

Fabricating operations such as rolling, stamping, casting, shearing, lapping, drawing, machining, and grit blasting can cause defects in the basis metal before it enters the electroless nickel process line. Inclusions in the substrate metal may cause the part to be hard to clean and not easily wetted. This will make uniform coverage with electroless nickel difficult, even when thick deposits are applied. In addition, pores in the substrate can entrap preplate chemicals that then "bleed out" during the plating cycle, causing inferior electroless nickel deposits at those sites.

When it is necessary to electroless-nickel plate substrates with surface defects, the quality of plate can sometimes be improved by alternating hot and cold rinses during the preplate cycle, operating the plating bath in a manner that produces a slower than normal plating rate, increasing the rate of agitation, and lowering the plating bath surface tension with an approved wetting agent.

Preparation of Metals for Electroless Nickel Plating

The importance of cleaning and activating metal surfaces prior to electroless nickel plating cannot be over-emphasized. Many of the problems thought to be caused by improper electroless nickel plating are actually caused by failure to clean and pretreat surfaces adequately. Here are recommended preplate steps for each of the metals commonly plated with electroless nickel. To optimize the performance of the preplate line, proper temperature and concentration must be maintained. Filtration of the preplate chemicals will reduce the chance of drag-in of particulate matter.

Steel

- 1) Soak clean.
- 2) Rinse(s).
- 3) Electroclean - anodic or periodic reverse.
- 4) Rinse(s).
- 5) Acid dip - 10% sulfuric acid or 30% hydrochloric acid.
- 6) Rinse(s).
- 7) Electroclean - anodic or periodic reverse.
- 8) Rinse(s).
- 9) Electroless nickel plate.

Copper

- 1) Soak clean.
- 2) Rinse(s).
- 3) Electroclean.
- 4) Rinse(s).
- 5) Acid dip - 10% sulfuric acid or 30% hydrochloric acid.
- 6) Rinse(s).
- 7) Apply direct current, momentarily, to initiate deposition or utilize an electrolytic strike.
- 8) Electroless nickel plate.

Aluminum

Single-zincate process:

- 1) Non-etch soak clean.
- 2) Rinse(s).
- 3) Alkaline or acid etch.
- 4) Rinse(s).
- 5) Desmut.*
- 6) Rinse(s).
- 7) Zincate.
- 8) Rinse(s).
- 9) Electroless nickel plate.

Double-zincate process:

- 1) Non-etch soak clean.
- 2) Rinse(s).
- 3) Alkaline or acid etch.
- 4) Rinse(s).
- 5) Desmut.*
- 6) Rinse(s).
- 7) Zincate - long immersion.
- 8) Rinse(s).
- 9) Strip in 50% v/v nitric acid.
- 10) Rinse(s).
- 11) Zincate - short immersion.
- 12) Rinse(s).
- 13) Electroless nickel plate.

*Desmut in 50 % nitric acid, or 50% nitric acid plus 15% sulfuric acid, or 50% nitric acid plus 25% sulfuric acid plus 1 lb/gal ammonium bifluoride.

Equipment

Tanks - The most basic item in a line for plating electroless nickel is a clean polypropylene or stainless steel tank of a known and calibrated capacity. With stainless steel, either Type 304 or 316 grade is acceptable. If a stainless steel tank is used, a small anodic charge (say, 2 volts) should be applied to prevent EN deposition onto the tank.

Before a plating tank is used, a dilute caustic solution heated to 50° C (120° F) should be pumped into the tank and allowed to leach out impurities. After the caustic has been drained out and the tank has been rinsed, a 30 percent solution of nitric acid should be pumped in and recirculated through the tank, heaters, filters and accessory equipment to passivate these surfaces. The nitric acid solution should be left in the tank overnight to completely passivate the equipment. After use, the nitric acid solution should be pumped to a holding tank and saved for future maintenance.

Excellent rinsing is imperative following each passivation period. A small amount of ammonia added to the rinse water and pumped through the system is necessary to neutralize residual acidity.

Nitrate contamination of electroless nickel solutions will cause slow plating rates and produce deposits having lower than normal phosphorous contents. Such contamination most often occurs after the tank has been passivated with nitric acid and the tank, piping, and associated equipment are improperly rinsed with water.

Also, ion selective papers are available that allow the present of nitrates to be determined in both the plating bath, and in the make-up water in concentrations as low as 10-500 mg/L (ppm).

Filters - For most EN tanks, polypropylene, felt filter bags are preferred. For tanks of 570 liters (150 gallons) or less, cartridge type filter units may also be used. Both bags and cartridges can be purchased in appropriate sizes, and can be connected to a distribution manifold. The filtration rate should be equal to a minimum of ten tank volumes per hour.

Before new filters are used they should be thoroughly rinsed with warm, deionized water to remove sizing compounds. After they have been used, polypropylene filter bags may be stripped in nitric acid to remove nickel residue and reused. After stripping, they should be rinsed in deionized water, containing a small amount of ammonia, to neutralize any remaining nitric acid. Periodic laundering of these bags is advisable to remove dirt. This dirt will cause more rapid plate-out of the filters, and deplete nickel from the bath.

Racks, Barrels - Racks should be designed to provide for good drainage of processing solutions from racked parts. Certain shapes tend to entrap solution, which causes contamination of subsequent solutions by carry-over or drag-in. Rack coatings should also be carefully selected and maintained to avoid disbonding and pockets, which are another source of contamination. The holes in plating barrels should be large enough to provide rapid transfer of process solutions, but small enough to prevent parts from falling out of the barrel into the plating bath.

Bath Makeup, Replenishment and Operation - A proprietary electroless nickel product is a blend of many ingredients carefully balanced to provide long bath life and consistent, reproducible quality deposits. It is important that the user follow the supplier's instructions to not disturb this balance. The following is a list of important points for operating an EN plating solution.

- 1) The tank volume should be known to properly makeup and replenish a bath.
Tank volume (liters) = length (m) x depth (m) x width (m) x 1,000
[Tank volume (gallons) = length (in.) x depth (in.) x width (in.) 231]
- 2) Deionized water should be used to makeup and replenish a bath.
- 3) The bath temperature should be controlled within $\pm 0.5^\circ\text{C}$ ($\pm 1^\circ\text{F}$).
- 4) The solution should be filtered at a

rate of ten tank volumes per hour through polypropylene bags or cartridges.

- 5) The makeup and replenishment solutions should be used according to the supplier's instructions.
- 6) The replenishment containers should be well marked.
- 7) The bath pH should be maintained within ± 0.1 pH units.
- 8) An analysis, replenishment and operations log should be maintained.
- 9) Standardized reagents should be used for analysis.
- 10) The bath should not be allowed to become too depleted before an addition. "Shocking the bath" with a large volume of replenishment additions should be avoided.
- 11) The working solution volume should be maintained at a constant level, especially before analysis.
- 12) Racks, hooks, or barrels used for cadmium, chromium, lead, solder, tin, or zinc plating should not be used in the electroless nickel solution.
- 13) The bath should not be heated for extended periods of time without being used.
- 14) The chemical balance of the bath should not be upset by unauthorized additions by a "creative" operator.
- 15) The bath should not be used beyond its normal life.

Chemicals - The chemicals required to makeup a new electroless nickel bath should be carefully measured and mixed according to their manufacturer's instructions. The bath's pH should be measured using a pH meter, and adjusted to its suggested working range. The tank's normal operating level should be marked on the tank wall for later observation. When calculating the tank's volume, care should be taken to allow for the solution contained in the pump, filter, and in pipes outside the tank.

Once the volume has been adjusted to bring the bath to its correct concentration, a sample should be taken and reserved for a lab standard for nickel titrations. A graph should be made of Ni concentration versus the volume (mls) of EDTA used in titrations. The graph will allow rapid determination of bath strength during production hours, and avoid calculations where errors might occur. The bath is now ready to be brought to its recommended operating temperature and used in production.

Periodic nickel titrations and replenishment of nickel and reducer chemicals is necessary to maintain the bath at its proper operating condition with a normal plating rate. It is not necessary to replenish the bath every time it is titrated, unless it is out of its recommended working range. Generally, operating with a nickel concentration less than 85 percent of optimum will reduce the plating rate and slow production.

The bath's pH can also have a large effect on the bath's operation and on the deposit's quality. The pH should be checked frequently and adjusted with neutralizer when necessary. Although most proprietary baths will maintain pH within the recommended range with their normal replenishment additions, complex parts can cause excessive "drag-in" and pH variations. With parts of this type, the pH should be checked and adjusted continuously. Drag-in may also affect bath operation and deposit quality and should be minimized.

Records - Good record keeping of analytical results and replenishments is very important to maintaining proper control and coating quality. Automatic analyzer/controller systems are available which will maintain the solution chemistry without manual additions and will keep complete bath records. However, these controllers should also be calibrated and standardized periodically.

Plating Thickness - A good way to determine plating thickness and deposition rates is to measure the thickness of plated coupons or panels. Coupons of known consistent thickness may be hung on racks carrying parts. Periodically, a panel may be removed from the rack and the coating's thickness measured. Parts being plated with the coupon will have the same thickness. Also, the deposition rate of the bath can be calculated from the thickness and the time that the coupon was plated. A properly processed panel of a similar substrate metal can also be used to test the deposit's adhesion.

Tank Size - Usually it is more economical to have several different sizes of electroless nickel plating tanks, rather than to process all of the work through one large tank. Not only is it more expensive to heat and maintain larger tanks, but plating only a few parts in a large volume of solution can degrade an EN bath by causing an imbalance of ingredients, especially the reducing agent.

EN solutions should not be heated unless they are to be used. If a bath is continuously heated and not used, or if only a few small parts are to be plated at a time, the bath will be degraded and deposition rates will fall, for the reason mentioned in the above paragraph.

Filtration - EN plating solutions should be continuously filtered to remove particulates and degradation products. The pump and filter should be capable of circulating the solution at a rate equivalent of 10 times the solution volume each hour. For example, a 375 liter (100 gallon) tank should have a filter and circulation pump capable of providing a flow rate of 3,750 liters per hour (1,000 gallons per hour, or approximately 16 gallons per minute).

Agitation - Good agitation is necessary for EN solutions. Mechanical agitation is usually practical only for small tanks. Most EN baths are best agitated with air from an oil-free blower. Good air agitation will eliminate many roughness and gas-pitting problems. It can also eliminate the need for periodic movement of parts hung in the bath. Better solution changeover will also be produced in barrel plating.

Care must be taken in plating shapes that can trap air or hydrogen. Pockets of these gases can prevent plating solution from reaching the part and can result in incomplete or no plating.

Rinsing - Good rinsing is mandatory for high quality plating. Air-agitated, counter-flowed rinses after all preplate processes are best. Where practical, spray rinses are also very effective. All rinse tanks should have overflows along their entire length to skim the whole surface of the tank continuously. Rinses should be kept at or near room temperature. Very cold rinses will "set-up" certain cleaners on the part surface rather than remove them. Finally, a two-second dip in a rinse tank is not enough; rinsing should be thorough and

should remove all of the process solution on the part's surface before the part is placed in the next tank.

Passivation and Cleaning - Some users of electroless nickel use one tank of electroless nickel solution day after day. Even though an adequately filtered bath usually may last through this punishment, its performance and that of its deposit will suffer. Daily transfer of the solution and cleaning of its tank is preferable.

Electroless nickel tanks are best set up in pairs. One is operated one day and one the next. A 30 percent (by volume) nitric acid solution should be left overnight in the previously used tank to remove any particulate matter or EN deposits and to passivate the tank walls, heaters and other equipment. This procedure should be followed even when the tank is free of EN deposits. While the solution in the second tank is being heated and the first load of parts is being prepared, the nitric acid solution should be pumped to a storage tank and the cleaned tank properly rinsed. This will give the plater a clean, spare tank to use with his working tank.

If for some reason the solution has to be drained immediately, it can be pumped to the clean tank, the heater turned on, and production may continue. This happens sometimes when a part is dropped, or when a bath has started to decompose and must be filtered quickly. Another reason for daily transfer, even



when a high filtration rate is used, is that the geometry of a tank does not allow every bit of solution to be filtered, no matter how many times per hour the bath is turned over. Even with daily transfers and nitric acid exposure, polypropylene tanks or liners should last three to five years.

Transfer and passivation may seem to be a complicated procedure, but if practiced daily, it is a fast and inexpensive one. It will eliminate costly downtime and loss of baths by plate-out or decomposition.

6. Post Treatments

Heat Treatment

Heat treatment is frequently used to improve a coating's adhesion, or to modify its properties for a particular application. As a result of heat treatment, hardness, corrosion resistance, wear resistance, ductility and internal stress, fatigue resistance, magnetic susceptibility, and other properties of the deposit can be affected.

Figure 1 shows the effect of different heat treatment temperatures on the microhardness of different EN coatings. Figure 2 shows their effect on Falex wear resistance. (Additional details are provided in the "Deposit Properties" section of this booklet.)

Figure 1

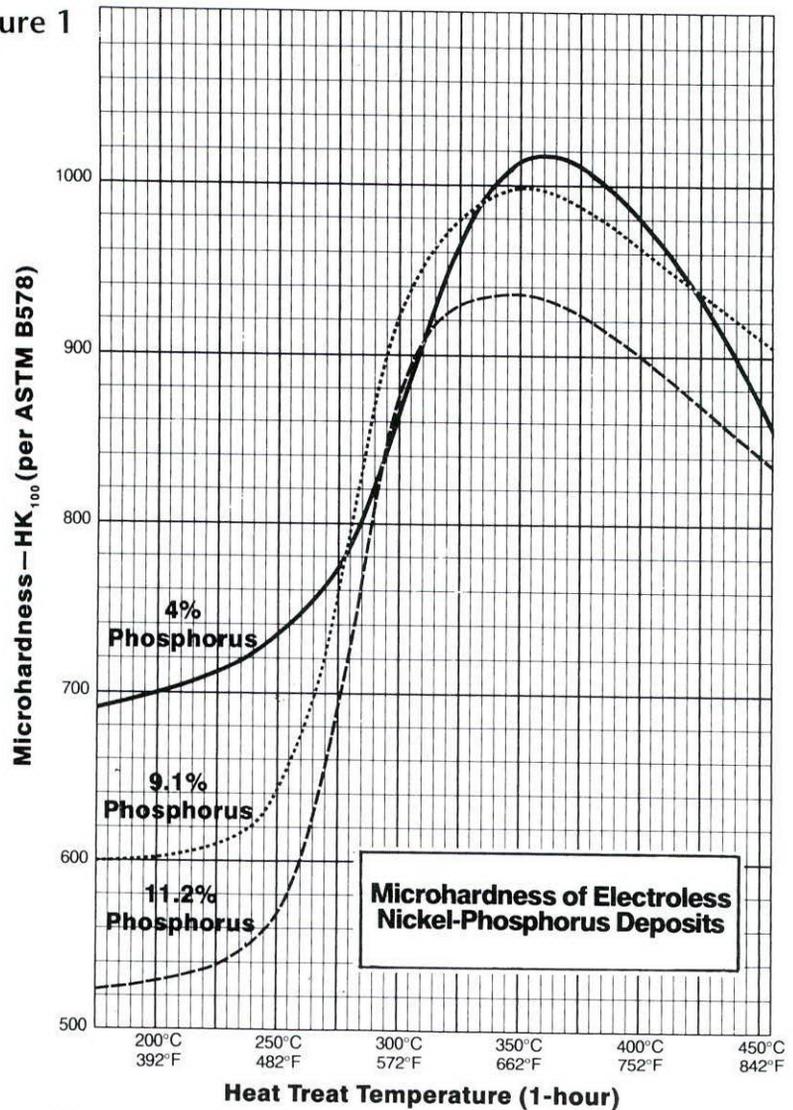
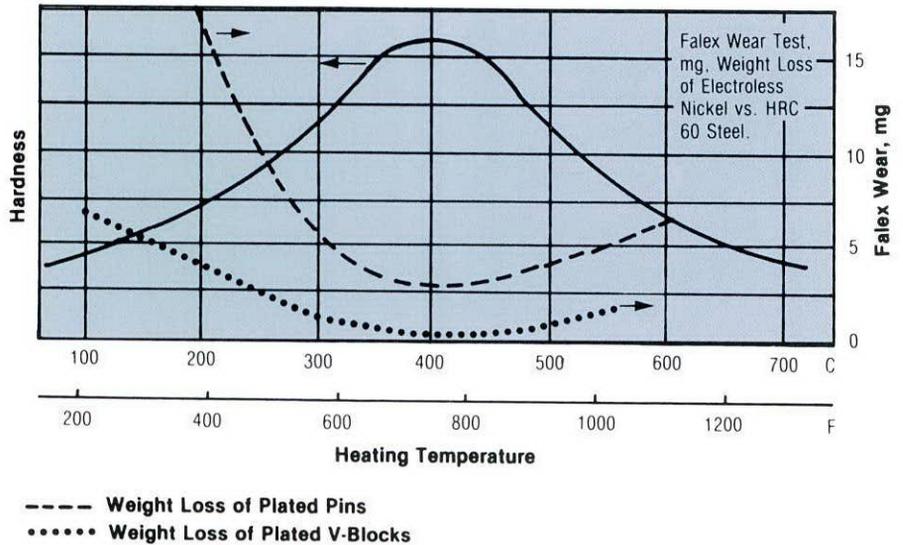


Figure 2



Heat treatment is normally performed at temperatures of 260 to 400° C (500 to 750° F) for 30 minutes to several hours. Heating at 350 to 400° C (660 to 750° F) produces maximum hardness. Commercial treatments are oftentimes conducted at lower temperatures for longer time periods. The most common temperatures are 290 to 340° C (550 to 650° F) for periods up to twelve hours. Heat treatment at temperatures above 260°

C (500° F) will cause nickel phosphide to precipitate within the deposit and will change the physical, mechanical and protective properties of EN coatings. Heat treatment at temperatures above 260° C (500° F) will reduce the strength and ductility of EN coatings. It will also severely degrade their corrosion resistance and protective ability.

Heat-treating should be carried out in an inert atmosphere such as nitrogen or vacuum to minimize oxidation. If a coating is heated to more than 260° C (500° F) in air, its surface will become highly discolored.

Coatings

Warm chromic acid or proprietary chromating solutions are sometimes used to passivate EN coatings after plating and to help protect the substrate from corrosive attack. Dry-to-touch oils may also be used to compensate for base metal porosity and to increase corrosion resistance.

Table III
Faulty Deposits - Possible Causes, Suggested Remedies

Problems	Possible Causes	Suggested Remedies
1) Skip plating, poor coverage, pullback and frosted edges.	<ul style="list-style-type: none"> a) Improper cleaning b) Improper activating c) Improper rinsing d) Metallic contamination e) Organic contamination f) Too much air agitation 	<ul style="list-style-type: none"> a) Temperature should be checked, as well as the purity and concentration of the cleaner, edge and other pretreatment solutions. b) Activators should be checked. Some metals and alloys, such as leaded steels, brasses, copper, aluminum, and magnesium, require special preparation. c) Rinse temperature and rinsing time should be checked. Too long a time in a rinse may cause an oxide film to form; too short a time may not remove residual films. Rinses must be kept clean. d) Bath should be dummied, or discarded and replaced. e) Bath should be cooled, carbon treated and filtered. Rinses should be checked for residual drag-in. f) Air agitation should be reduced.
2) Roughness in deposit	<ul style="list-style-type: none"> a) Contamination from solid particles, i.e., dust, loose nickel, or metal chips b) Turbidity of solution c) Heavy or too rapid EN solution replenishment while work is being plated d) Contaminated makeup water e) Localized over-heating f) Particles of metal or soil on work g) Contaminated filter cartridges, liners, or bags h) Only one side of work affected i) High Sodium phosphate concentration 	<ul style="list-style-type: none"> a) Solution should be filtered through 5 micron cartridges at high flow rates. b) May be result of high pH, which aids in formation of metallic hydroxides. The pH should be checked and adjusted. Complexers may be added. c) Solution replenishment should be made slowly and the solution mixed thoroughly. Additions should be made in an area as far away from work as possible. d) Quality of water should be checked. Water may require carbon treatment and filtration. e) Air agitation should be checked or temperature adjusted. De-rated heaters should be used. f) Cleaning and rinsing should be improved. g) Liners should be leached prior to makeup. Filters should be changed. h) Agitation around work should be increased. Work rod or solution agitation should be provided. i) All or part of the solution should be discarded.

7.

Causes of faulty deposits

Some common problems in electroless nickel plating, possible causes of the problems, and suggested remedies are contained in Table III.

Table III (continued)
Faulty Deposits - Possible Causes, Suggested Remedies

Problems	Possible Causes	Suggested Remedies
3) Streaks in deposit.	<ul style="list-style-type: none"> a) Gas streaks from position of work b) Silicate drag-in c) Poor rinsing d) Improper cleaning e) High concentration of metals f) Organic contamination g) Poor agitation h) Low surface area i) Low reducer content j) Too much agitation k) Too much complexer 	<ul style="list-style-type: none"> a) Either solution or work rod agitation should be provided. Work should be repositioned periodically. Agitation should be increased. b) Non-silicated cleaners should be used. Rinsing should be improved. c) Process cycle should be checked, rinsing improved d) Cleaning and/or rinsing should be improved. e) Bath should be dummed to remove metals. Bath may have to be discarded and replaced with new solution. f) Bath should be carbon treated and filtered, or discarded and replaced with new solution. g) Air agitation should be increased, or a different air pattern developed. h) Surface area should be increased to recommended range. i) Reducer should be checked and adjusted. j) Agitation should be reduced. k) Complexer should be reduced.
4) Pitting	<ul style="list-style-type: none"> a) Heavy metal contamination b) Ethylene glycol contamination from jacketed tank c) Basis metal pitted d) Organic contamination e) Improper cleaning f) Excessive bath activity g) Copious evolution of hydrogen h) Low complexer concentration i) Improper reducer concentration 	<ul style="list-style-type: none"> a) Bath should be dummed, or discarded and replaced. b) Bath should be discarded and replaced. Ethylene glycol must be kept from bath. c) Basis metal should be checked after each step in the cycle d) Bath should be cooled, carbon treated and filtered. e) Cleaning and rinsing should be improved. f) pH should be lowered. g) Surface area being plated should be reduced. Reducing agent concentration should be checked and adjusted. If the plating of tank walls and equipment is causing the problem, it may be necessary to clean the tank and other processing equipment. h) Complexer should be added in small increments. i) Bath should be analyzed and adjusted.
5) Dull or matte deposit	<ul style="list-style-type: none"> a) Organic contamination b) Improper cleaning c) Bath very old (more than 15 regenerations) d) High or low pH e) Bath imbalance f) Poor quality substrate g) Low temperature h) Excessive brightener drag-out i) Metallic contamination j) Low reducer concentration k) Low nickel content 	<ul style="list-style-type: none"> a) Bath should be cooled, carbon treated, and filtered. b) Cleaning should be improved. Electrocleaning may be required. c) Bath should be discarded and new bath prepared. d) pH should be adjusted with acid or alkali. e) Nickel and reducer should be checked and bath adjusted. f) Substrate should be improved. g) Temperature should be adjusted. h) Solution chemistry should be balanced. i) Bath should be dummed onto a large surface. j) Reducer should be added. k) Nickel should be added.

Table III (continued)
Faulty Deposits - Possible Causes, Suggested Remedies

Problems	Possible Causes	Suggested Remedies
6) Poor adhesion	<ul style="list-style-type: none"> a) Metal contamination b) Improper surface preparation c) Improper zincating of aluminum d) Reoxidation e) Drag-in of acid inhibitors f) Organic contamination g) Improper heat treatment h) Quality of alloy 	<ul style="list-style-type: none"> a) Bath should be dummied or discarded. b) Cleaning and rinsing should be improved. c) Concentration of zincate, processing time should be checked. d) Transfer times should be reduced. e) Uninhibited acid should be used; rinsing improved f) Bath should be carbon treated and filtered. g) Heating time and temperature should be corrected. h) Alloy quality should be checked.
7) Frosted deposits	<ul style="list-style-type: none"> a) Low work load b) Metallic contamination 	<ul style="list-style-type: none"> a) Work load should be increased. b) Bath should be dummied or discarded and replaced.
8) Step plating	<ul style="list-style-type: none"> a) Metallic contamination b) Certain alloys that contain lead c) Bath imbalance 	<ul style="list-style-type: none"> a) Bath should be dummied or discarded and replaced. b) A copper or nickel strike should be used prior to plating, followed by galvanic activation for copper. c) Bath should be analyzed and adjusted.
9) Laminar deposits	<ul style="list-style-type: none"> a) Poor temperature, pH and/or bath control 	<ul style="list-style-type: none"> a) Uniform temperature, pH and bath control must be maintained.
10) Poor wear resistance	<ul style="list-style-type: none"> a) Low heat-treatment temperature and/or short time b) Low phosphorus content 	<ul style="list-style-type: none"> a) Temperature and time cycle should be adjusted. b) Phosphorous content should be increased by lowering pH and temperature. Bath should be analyzed and chemical balance restored.
11) Poor corrosion and/or chemical resistance	<ul style="list-style-type: none"> a) Low phosphorus content. b) Metallic contamination. c) Poor bath control 	<ul style="list-style-type: none"> a) Phosphorus content should be increased by lowering pH and increasing reducer concentration. b) Bath should be dummied or discarded and replaced. c) Uniform temperature should be maintained, pH and replenishment controlled.
12) Dark to black deposits	<ul style="list-style-type: none"> a) High stabilizer content b) Metallic contamination c) Bath imbalance d) Poor activation e) Organic contamination f) Improper surface preparation g) Inadequate rinse h) High work load i) Low work load j) Low reducing agent k) Low metal concentration 	<ul style="list-style-type: none"> a) Bath should be dummied or diluted. b) Bath should be dummied or diluted c) Bath should be analyzed and adjusted d) Reactivate e) Bath should be carbon treated and filtered f) Cleaning, pickling and rinse cycles should be improved. g) Rinsing should be improved. h) Work load should be reduced. i) Work load should be increased. j) Reducing agent should be increased. k) Metal content of the bath should be increased.
13) Blistering	<ul style="list-style-type: none"> a) Inadequate surface preparation b) Improper zincating of aluminum c) Organic contamination d) Metallic contamination e) Improper pH f) Improper heat treatment 	<ul style="list-style-type: none"> a) Cleaning, pickling, and rinsing should be improved. b) Concentration of zincate, processing time should be checked. c) Bath should be carbon treated and filtered. d) Bath should be dummied or discarded and replaced. e) pH should be checked and adjusted. f) Heat treating temperature and time should be checked and corrected.

8.

Stripping Electroless Nickel

Modern techniques for electroless nickel plating have greatly reduced the need for stripping of unsatisfactory deposits. However, defective new coatings or older worn coatings in need of rejuvenation may occasionally require stripping and replacement.

Electroless nickel deposits can be difficult to remove because they are highly resistant to chemical attack. Further, steel is the most common basis metal for electroless nickel coatings, and can be easily attacked by many stripping solutions. Contact the manufacturer of the EN process for specific recommendations for the optimum stripping solution to be used for a given situation.

Cleaning and Activation

Cleaning and activation of the electroless nickel surface is necessary before stripping can begin. Components that have seen severe service may require rigorous cleaning to remove organic soils, carbonaceous deposits, and other incrustations. Thorough cleaning by solvent cleaning, alkaline soak and electrocleaning is recommended.

Electroless nickel deposits that have aged or have been heat-treated should be activated by acid immersion between the cleaning and stripping cycles. Inhibited hydrochloric acid (30 to 50% by volume), mixed acids (40% by volume hydrochloric acid and 10% by volume sulfuric acid), or proprietary acid salts may be used for activation.

Stripping Solutions

Electroless nickel deposits are usually stripped by immersing them in aqueous chemical solutions. Electrolytic stripping is not commonly used to strip electroless nickel coatings.

There are two types of immersion strippers: alkaline and acidic. Alkaline solutions usually contain nitro-organic compounds as oxidizers and either amino compounds or cyanide as complexers and are suitable stripping electroless nickel deposits from steel and low alloy substrates. For maximum bath life and safety, alkaline cyanide strippers should not be operated at temperatures greater than 60° C (140° F). Non-cyanide strippers are more stable than the cyanide type, and may be operated at temperatures up to 95° C (200° F). Proprietary processes of this type are available with inhibitors that permit the solutions to strip deposits from copper and copper alloys.

Solutions of nitric acid (40 to 50% by volume) are recommended for stripping electroless nickel from aluminum and aluminum alloys and from most stainless steels and high alloy steels.

Stripping Bath Operation

Concentration - Proprietary electroless nickel stripping solutions must be made up at the concentrations recommended by the supplier. Overly concentrated solutions may cause etching of the basis metal. Conversely, dilute solutions may reduce the rate of stripping and cause solution depletion and inadequate inhibition.

When immersion nickel strippers become saturated with dissolved metal, they should be discarded in accordance with pertinent regulations. The stripping rate of these strippers declines as the concentration of dissolved metal rises. Thus, it is usually cheaper to dispose of a bath that has become saturated with metal than to try to prolong bath life by chemical replenishment.

Temperature - Electroless nickel strippers are designed to operate within specific temperature ranges. Temperature control, therefore, is of paramount importance for good stripping results.

Agitation - Agitation is recommended for most electroless nickel stripping solutions. Agitation keeps fresh stripping solution moving past the work surface and increases the rate of stripping. It also removes air or gas bubbles from the parts' surfaces that may result in non-uniform stripping and prevents localized depletion of the stripper chemicals. Agitation also prevents overheating of stripping solutions near heating devices.

Equipment - The importance of equipment specifications relating to electroless nickel stripping cannot be overstated. Specifications must take into account. Tanks and their components should be:

- a) resistance to chemical attack
- b) suitable for use at high temperatures
- c) designed to minimize safety and health hazards

The depth of the vessel containing the stripper solution must be at least 30 cm (12 inches) greater than the parts being stripped to allow for sludge accumulation. Heating and/or cooling coils and the parts to be stripped must be electrically insulated from the tank. All other equipment, such as mechanical agitators and temperature sensors, should also be insulated to prevent stray currents from entering the tank.

Substrate Metallurgy - Mechanical work (machining, drawing, stamping, etc.), heat treatment, or operating conditions can all result in deformation of a substrate, which can promote pitting and etching during stripping. Coupling of two or more metals in one substrate (such as brazed components) can also lead to localized attack of the less noble metal (usually near the interface between the two metals). These substrates should be handled and observed carefully during stripping.

Once all of the electroless deposit has been removed, localized attack of substrate may begin. Thus, the course of the stripping action must be monitored, and the components should be removed from the solution as soon as the electroless nickel deposit has been completely removed from the parts.

Stripping Rate - Typical stripping rates are 10 to 15 $\mu\text{m}/\text{hour}$ (0.4 to 0.6 mil/hour) except for very high phosphorus alloyed deposits and certain heat-treated or aged deposits. These will strip at a rate of 5 to 10 $\mu\text{m}/\text{hour}$ (0.2 to 0.4 mil/hour).

9.

Specifications and Tests for Electroless Nickel Plate

There are a number of specifications and test methods commonly used to judge the quality of electroless nickel coatings. The tests mentioned here do not cover all possible physical properties, but do cover those normally of interest to users of electroless nickel: hardness, thickness, porosity, corrosion resistance, solderability, and phosphorous content. A number of the tests are those developed by the American Society for Testing and Materials (ASTM).

Hardness

Hardness may be determined by the method outlined in ASTM B578 "Microhardness of Electroplated Coatings", using a 100-gram load and a deposit thickness of 75 microns (3 mils), unless otherwise specified.

Thickness

Thickness of deposits may be determined by microscopically examining a cross-section, by beta backscatter methods, or by x-ray fluorescence. The deposit thickness can also be measured by using a micrometer before and after processing the article, or a test specimen. Magnetic test methods may be used, but are affected by the magnetism of deposits containing less than 9% phosphorus. Electroless nickel calibration standards containing the same phosphorus content as the coating being tested must be used.

The microscopic examination of the cross-section of the article to be tested should be in accordance with ASTM B478 "Standard Methods for Measurements of Metal and Oxide Coating Thicknesses by Microscopic Examination of a Cross-Section." Deposits on metals that have an atomic number less than 18, or greater than 40, can be measured by the use of a beta backscatter device. This test should be in accordance with ASTM B567 "Standard Method for Measurement of Coating Thickness by the Beta-backscatter Principle."

ASTM B659 "Standard Guide for Measuring Thickness of Metallic and Organic Coatings," illustrates the use of beta backscatter, coulometric, eddy current and magnetic methods of measurement. Some methods are sensitive to alloy composition.

Porosity

Plated parts may be inspected for pits and porosity by a number of methods.

Ferroxyl test - This test is for use with EN on steel and iron basis metals.

Prepare a test solution by mixing 25 grams of potassium ferricyanide and 15 grams of sodium chloride in one liter of deionized water. Clean the article and immerse in test solution for thirty seconds. Blue spots visible on the surface indicate pore sites.

Alizarin test - This test for deposits on aluminum alloys is performed by wiping a test specimen with a 10% by weight sodium hydroxide solution. After three minutes, rinse and apply the solution of alizarin sulfonate. After four minutes, apply glacial acetic acid until the violet color disappears. Red spots indicate pore sites. The alizarin sulfonate solution is prepared by dissolving 1.5 grams of methyl cellulose in 90 milliliters of boiling deionized water, to which, after cooling, a solution of 0.1 gram of alizarin sulfonic acid, dissolved in five milliliters of ethanol, is added.

Hydrochloric acid spot test - This test is for deposits on aluminum alloys.

It is performed by immersing the plated article into a solution of 50% by volume hydrochloric acid at room temperature for two minutes. Hydrogen evolution or black spots on the surface indicate pore sites.

Five percent neutral salt spray test - This test may be used on all alloys and should be in accordance with ASTM Standard B117, "Method of Salt Spray (fog testing)."

Electrochemical pitting test -

This test also can be used on any basis material, in accordance with ASTM G-61, "Standard Practice for Conducting Cyclic Potentio-dynamic Polarization Measurements for Localized Corrosion."

Corrosion

Corrosion test methods may be used to determine the corrosion rate of the deposit in various environments. The immersion weight loss test is performed on all types of basis materials, in accordance with ASTM G1, "Standard Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens."

Electrochemical test methods also can be used on all types of basis materials, in accordance with the following methods: ASTM G3, "Standard Recommended Practice for Electrochemical Measurements and Corrosion Testing;" ASTM G5, "Standard Recommended Practice for Standard Reference Methods for Making Potentiostatic and Potentio-dynamic Anodic Polarization Measurement;" ASTM G59, "Standard Practice for Conducting Potentio-dynamic Polarization Resistant Measurement."

Solderability

A solderability test may be performed by heating a plated article to 230° C (450° F) and applying a 60-40 tin-lead solder to the plated article. This solder should wet the surface, indicating that the deposit is solderable.

Other Tests

Other tests are available for electroless nickel-phosphorous deposits and they should be agreed upon between the end-user and the applicator of the coatings.

10.

Glossary of Terms

Abrasive Blasting - A process for cleaning or finishing by means of an abrasive directed at high velocity against the work piece.

Activation - Elimination of a passive condition on a surface.

Addition Agent - A material added in small quantities to a solution to produce a desired effect. Also synonymous with "brightener."

Adhesion - The attractive force that exists between an electrodeposit or an electrochemical deposit and its substrate that can be measured as the force required to separate the deposit from the substrate.

Amorphous - Non-crystalline or without evidence of a regular structure.

Anode - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. In most instances it is the source of metal to be plated from the bath.

Anode Efficiency - The actual current efficiency of a specified anodic process compared to the theoretical value. The actual fraction of current used to dissolve metal from the anode compared to the theoretical amount as predicted by Faraday's Laws.

Autocatalytic Plating - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited. Often referred to as "electroless plating."

Barrel Plating - Electroplating or cleaning in which the work is processed in bulk in a rotating container (barrel).

Base Metal (or Substrate) - Material upon which processing is conducted or coatings are deposited. (It is not necessarily the material from which the part is constructed).

Blister - A dome-shaped imperfection or defect, resulting from loss of adhesion between a deposit and its substrate, or between various coatings where multiple layers of coatings are present.

Bright Dip - A solution used to produce a bright surface on a substrate by chemical immersion.

Bright Plating Range - The range of current densities within which a given plating solution produces a bright deposit.

Brightener - Another term for addition agent. A liquid or powdered material that, when added to a plating bath, improves the reflectivity or brightness of the deposits produced by the plating bath.

Brush Plating - A specialized method of plating, typically used for small scale applications, where an inert anode is surrounded by a pad, sponge, brush, or other device that will retain a volume of a concentrated solution containing a dissolved salt of the metal to be deposited. The anode/pad device is moved over the cathode during the plating operation in the area to be plated.

Buffing - The smoothing of a surface, accomplished by placing the surface to be finished against a rotating flexible wheel, to which fine abrasive particles have been applied in liquid, suspension, paste, or grease form.

Buffer - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.

Burnt Deposit - A rough, non-coherent or otherwise unsatisfactory deposit, typically produced by the application of an excessive high current density.

Bus Bar - The term used to describe the cables or conducting media – generally copper or aluminum stock – that transfers the current from the rectifier to the plating tank.

Carryover - See Drag in.

CASS Test - A special accelerated corrosion testing method using copper and acetic acid solution as the fog medium. It is most typically used to predict the corrosion protection of nickel/chrome, or copper/nickel/chrome electrodeposits. See ASTM Method B368.

Cathode - The part that is electroplated.

Cathode Efficiency - The actual amount of current used to deposit metal in a plating process, compared to the theoretical amount as predicted by Faraday's Laws.

Chelate Compound - A compound in which a metal is contained as an integral part of a ring structure and is not readily ionized.

Cleaning - The removal of grease or soil and other foreign materials from a surface using one or more chemical or electrochemical solutions.

Alkaline Cleaning—cleaning by means of an alkaline solution.

Anodic or Reverse Cleaning—electrolytic cleaning where the part is connected to the negative terminal of the rectifier.

Cathodic or Direct Cleaning—electrolytic cleaning where the part is connected to the positive terminal of the rectifier.

Di-phase Cleaning—cleaning by means of a solution that contains a solvent layer and an aqueous layer. Cleaning occurs by both solvent and emulsification actions.

Soak Cleaning—cleaning by chemical means without the use of current. Generally used to remove heavy oils and greases.

Ultrasonic Cleaning—cleaning by any chemical means aided by ultrasonic energy to speed up soil removal. Especially useful in the removal of buffing compounds.

Spray Cleaning—use of an alkaline cleaner that is sprayed onto the part(s) to be cleaned. The additional energy provided by the spraying operation accelerates the removal of soils, greases, and buffing compounds.

Contact Plating - Deposition of a metal by immersion of the work in a solution that is in contact with another metal.

Corrodokote Test - An accelerated corrosion test for electrodeposits using a special paste coating that is applied to parts before they are CASS salt spray tested. See ASTM Method B380.

Corrosion - Gradual dissolution or oxidation of a metal.

Covering Power - The ability of an electrodeposit to plate at very low current densities, such as in deep recesses or holes. (To be distinguished from Throwing Power.)

Current Density - The total current divided by the area to which the current is applied.

Cathode Current Density—the total current applied divided by the total area being plated.

Anode Current Density—the total current applied divided by the total anode area.

Current Efficiency - See Cathode Efficiency and Anode Efficiency.

Degreasing - The removal of grease and oils from a surface.

Solvent Degreasing—degreasing by immersion in liquid organic solvent.

Vapor Degreasing—degreasing by solvent vapors condensing on the parts being cleaned.

Drag-In - The water or solution that adheres to the objects from previous processing steps, and which is thereby introduced into a processing tank.

Drag-Out - The solution that adheres to articles when they are removed from a processing tank.

Ductility - The ability of a material to deform without fracturing.

Dummy - The term used to describe low current density plating done to remove metallic impurities from a plating bath.

Duplex Plating or Duplex Deposit - The term used to describe a multi-layer deposit that incorporates two layers with slightly different corrosion potential characteristics. The different layers are typically combined in a manner that allows one layer (the under-layer) to be sacrificial to the other layer (the top layer), thereby greatly improving the corrosion protection afforded, compared to that provided by a single layer of similar thickness.

Electroless Plating - A more commonly used term for Autocatalytic Plating.

Electrolyte - General term used to describe the processing bath, usually the plating bath.

Electrolysis - Process of causing chemical changes via the passage of current through an electrolyte.

Electroplating - The electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties, appearance, or dimensions different from those of the basis metal.

Electropolishing - Term used to describe the process of improving the appearance and surface condition of metallic substrates by applying a current to a chemical solution.

Etch - *Noun*—a roughened surface produced by a chemical or electrochemical means.
Verb—to unevenly dissolve a part of a surface or metal.

Faraday - The number of coulombs (96,490) required to deposit one chemical equivalent of a metal. The chemical equivalent value varies depending upon the metal being deposited.

Filter Aid - An inert, insoluble material, more or less finely divided, used as a filter medium, or to assist in filtration by preventing excessive packing of the filter cake.

Flash Plate - The application of a very thin electrodeposit, typically less than 2.54 microns (0.1 mil).

Flocculate - To aggregate into larger particles, to increase in size to the point where precipitation occurs.

Galvanic Protection - See Sacrificial Protection

Hard Chromium - Chromium plate for engineering, rather than decorative applications. Not necessarily harder than decorative chromium, but generally much thicker.

Hydrogen Embrittlement - Embrittlement of a metal or alloy caused by absorption of hydrogen typically during pickling, cleaning or plating operations.

Inert Anode - An anode that is insoluble in the electrolyte under the conditions prevailing in the electrolysis being performed. Typically used in plating baths where there is no convenient source of soluble metal an anode, such as chrome plating.

Karat - A measure of the fineness or purity of a gold deposit. One karat is equal to 1/24 part of pure gold; i.e., a 24 karat deposit is pure gold. Likewise, an 18 karat deposit is 18 parts of gold and 6 parts of another metal.

Mechanical Plating - The application of an adherent metallic coating on a substrate by impingement of finely divided solid particles of the coating to be applied onto the substrate. Alloy deposition is possible via mechanical plating. Also, plating occurs without any hydrogen embrittlement occurring.

Metal Distribution Ratio - The ratio of the thicknesses of metal deposited at two different current densities. Frequently used as a measure of the Throwing Power of an electrolyte.

Metal Turn Over (MTO) - The replacement of 100% of the original nickel metal content of an electroless plating bath.

Microinch - One millionth of an inch, 0.000001 inches. (=0.001 mils)

Micron - One millionth of a meter, approximately one 25th of a mil. (25.4 microns = 1 mil)

Micro Throwing Power- The ability of an electrolyte to deposit metal in pores or very small recesses of substrates.

Mil - One thousandth of an inch (0.001 inches). (= 25.4 microns)

Oxidizing Agent - A compound that causes oxidation, thereby itself becoming reduced.

pH - The co-logarithm (negative logarithm) of the hydrogen ion activity. A measure of acidity (less than 7) or basicity (more than 7) of a solution.

Passivation or Passivity - The condition on a metal that retards its normal reaction in a specified environment. It is typically associated with the metal assuming an electrochemical potential more noble than its normal potential.

Peeling - The detachment or partial detachment of a deposited coating from the basis metal or undercoat layers.

Pickling - The removal of oxides or other compounds from the surface of a metal by chemical or electrochemical action.

Pit - A small depression or cavity in the surface of a part. It can be produced during manufacturing the part, during deposition, or by corrosion of the surface.

Polishing - See Buffing

Reducing Agent - A compound that causes chemical reduction, thereby itself becoming oxidized.

Regeneration - *Noun*—The replacement of 100% of the original metal content of an electroless plating bath.
Verb—The act of replenishing a processing bath in an attempt to restore optimum performance.

Resist - A material applied to a part of the surface of an article to prevent metal deposition on or metal removal from that area during chemical or electrochemical processes. Also called "masking."

Ripple - A measurement of the amount of AC current that is present in a DC current. Excessive ripple generally causes passive deposits or hazes in plated coatings. Ideally, ripple should be less than 5% for most plating applications.

RMS - A numerical reference to the smoothness of a surface. Literally, it refers to the Root Mean Square of the height difference between the microscopic peaks and valleys that are evident on a surface when it is viewed under sufficient magnification. The lower the number, the smoother the surface. In other words, the average distance from the tip of a peak to the bottom of an adjacent valley on a part with a surface with a 2 RMS finish, would be less than the equivalent distance on a part with a 16 RMS finish. RMS is typically measured with a profilometer, using vertical magnifications from 500x to 200,000x.

Robber - Term used to describe an auxiliary cathode placed near the part to be plated to divert current from concentrating in high current density areas, leading to heavy deposits in these areas.

Sacrificial Protection - The mechanism of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion (for example, zinc plating over a steel substrate). Also referred to as "Galvanic Protection."

Shelf Roughness - Roughness on surfaces of parts that face upward where solids have settled during a processing operation.

Shield - *Noun*—a nonconducting medium or panel used to alter the flow of current in an attempt to provide the most uniform cathode current density possible on the part being plated.

Verb—to alter the normal current distribution by placing a non-conducting medium in the path of the current in a manner that provides a more uniform overall current density on the part being plated.

Spontaneous Decomposition - See Triggering

Step Plating - Non-uniform thickness, striations, or skip-type plating. In electroplating operations this is generally evident in low current density areas, while in electroless plating operations it is typically evident on edges of parts and around holes or perforations in parts. Also referred to as "edge pullback" and/or "worm tracking."

Stray Current - Current that passes through paths other than the intended circuit, such as through heating coils, the plating tank, floor grating, hoist super-structures, etc.

Strike - *Noun*—a thin deposit applied to a substrate or other plated deposit to provide activation or protection from immersion plating. *Verb*—to apply such a coating by plating for a short time in a plating bath.

Strip - To remove a coating from the substrate or undercoat layer via chemical or electrochemical methods.

Substrate - The base metal to be plated.

Taber Abraser - An instrument used to characterize the wear properties of a substrate or plated finish. Test specimens are mounted to a small rotating turntable and subjected to the wearing action of two abrasive wheels, which are applied at a specific pressure, and which rotate in opposite directions. An important feature of the Taber Abraser is the all angles relative to the weave or grain of the material being tested.

Tarnish - Discoloration of a base metal or a plated coating, typically a darkening of the appearance of the basis or plated metal.

Thief - See Robber

Throwing Power - Term used to describe the uniformity of thickness of a plated coating. Electroless baths typically plate with 100% Throwing Power, i.e., the same thickness on all areas of a part in contact with the solution. Electroplating baths invariably exhibit greater thicknesses in high current density areas compared to low current density areas. See also Thickness Distribution Ratio.

Triggering - Spontaneous decomposition of an electroless plating bath, which is typically caused by excessively high concentration of reducing agents in the bath, or the introduction of solid contaminants, such as metal filings or other particles.

Troy Ounce - A unit in the Troy system of weights used for precious metals. Gold and other precious metals are typically measured in Troy ounces. (1 Troy ounce = 31.1035 grams)

Turnover - See Regeneration.

Water Break - The appearance of a discontinuous film of water on a surface, signifying non-uniform wetting and usually associated with the presence of surface contamination on parts.

Work (Plating) - The material being plated or otherwise finished.



Metal Finishing Suppliers' Association

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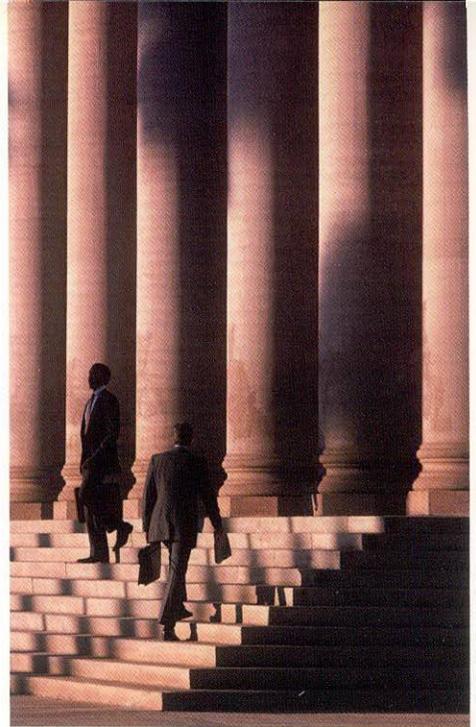
Quality Metal Finishing Guides



Metal Finishing Suppliers' Association

D e c o r a t i v e P r e c i o u s M e t a l P l a t i n g





Introduction

The Metal Finishing Suppliers' Association (MFSA) is a trade association of companies and individuals involved in supplying chemicals, equipment, technology, and solutions to the metal finishing industry. One of the association's primary objectives is to promote the interests and further the welfare of its members and their customers. MFSA also promotes the manufacturing of environmentally friendly products to safeguard the interests of the ultimate customer. In 1960, MFSA initiated action to upgrade the durability of metal finishes. Known as the "Quality Metal Finishing Project" or QMF, this program was aimed at:

- 1) the promotion of technically sound specifications and standards in cooperation with interested trade and technical societies;
- 2) the provision of information to both producers and buyers of metal finished projects;
- 3) the development of printed guides containing information on established standards and specifications, readily accessible for day to day use by the design engineer, the purchasing agent, and all those involved in the use of metal finished products.

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Quality

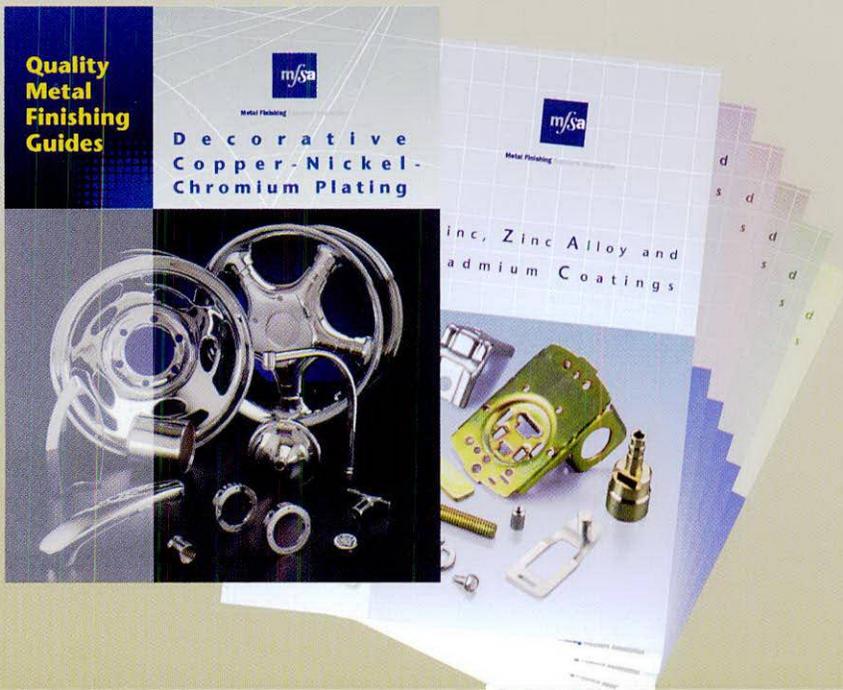
As an association promoting the interest and welfare of the producers and customers of the metal finishing industry, MFSA realizes that everyone suffers loss when products are sold that are inadequately finished for the intended application. MFSA wishes to encourage the industry to develop and maintain high-quality standards needed to guarantee the expected or promised service of the unit.

The industry needs to know how a high-quality metal finish can be achieved, how to select proper specifications for a given application, and how to control the release of products to assure that they meet the needs of the customer. At the same time, management must be confident that this know-how is based on sound engineering principles and incorporates a reasonable margin of safety.

There have been significant developments of industrial standards for quality systems in the last few years that are applicable to metal finishing. These include the International Standard Organization (ISO) 9000 Standard and American National Standards Institute/American Society for Quality Control (ANSI/ASQC) Q90 Standard. This manual will provide useful details on how to apply proven metal finishing engineering in your systems to help you maintain and improve your metal finishing quality.

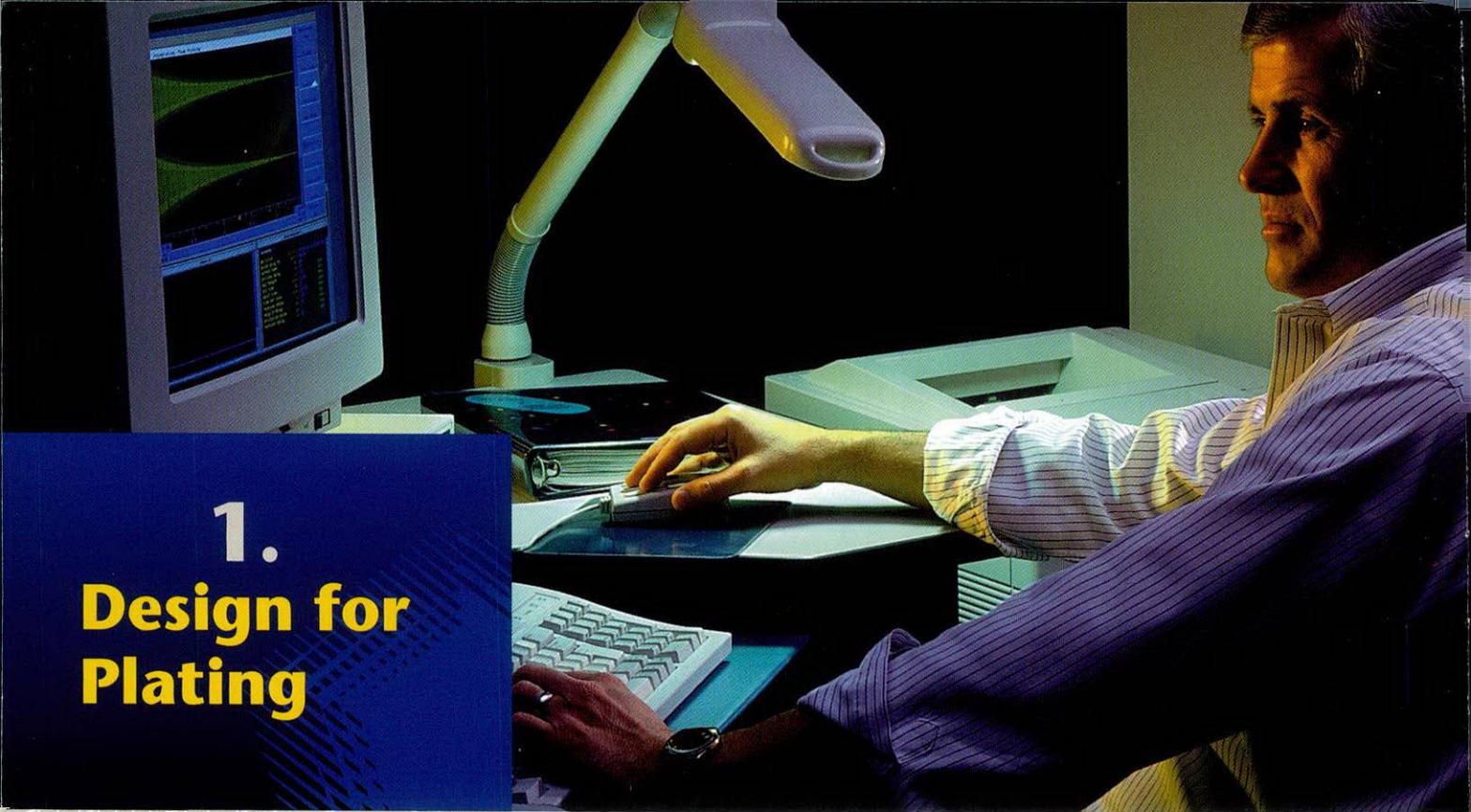
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- **Chemical Surface Preparation for Electroplated and Metallic Coatings**
- **Decorative Copper-Nickel-Chromium**
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1. Design for Plating

A program to improve and control the quality of a metal product should start at the desk of the designer. The metal finisher is restricted in what he or she can do by certain basic principles of mechanical finishing and of electroplating. The engineer should understand the limitations imposed by shape and size of components to facilitate quality finishing at an acceptable cost. The designer can exert as much influence on the quality attainable in finishing a part as can the electroplater. ASTM Standard B507 can provide the designer with helpful information.

Significant Surfaces

An important term used in specifying metal finishes is "significant surfaces." In most products the same standard of quality is not required over every square inch of surface. Instead, the quality specifications apply and compliance is expected only for the so-called "significant surfaces" defined by mutual agreement between the producer and purchaser as follows:

Significant surfaces are defined as those normally visible (directly or by reflection) that are essential to the appearance or serviceability of the article when assembled in normal position or which can be the source of corrosion products that deface visible surfaces on the assembled article. When necessary, the significant surfaces shall be the subject of agreement between purchaser and manufacturer and shall be indicated on the drawings of the parts or by the provision of suitably marked samples.

Design for Mechanical Finishing

Metal products that are to be coated with copper/nickel/decorative precious metal or substrates using non-nickel plating processes followed by the decorative precious metal finish are generally subjected to abrasive polishing with wheels or mass finishing techniques in preparation for the plating operations. This is to be done to aid in securing an attractive, uniform, mirror-like or satin appearance on the finished part. Mechanical finishing is an expensive operation. To reduce costs and assist the metal finisher in improving the appearance and quality of the product, the designer should consider certain rules applicable for parts requiring mechanical finishing.

- Avoid blind holes, recesses and joint crevices that can retain polishing compounds and metal debris.
- Avoid intricate surface patterns, which will be blurred in polishing.
- Significant surfaces should be exterior, reachable by ordinary polishing wheels or mass finishing media.
- Avoid sharp edges and protrusions, which cause excessive consumption of wheels.

In small parts, which are to be barrel processed, the above rules apply. This includes the requirement that the parts must be sturdy enough to withstand the multiple impacts of barrel rotation and will not entangle causing damage or incomplete finishing. Small flat parts, which tend to nest together, should be provided with ridges or dimples to prevent such nesting.

Design for Racking, Draining, and Air Entrapment

Most metal parts weighing more than a few ounces or that require a high degree of surface finish or a jewelry finish, are not plated in bulk in barrels but are mounted on racks for processing in cleaning and electroplating tanks. Design considerations relating to racked parts are described below.

- Consult the plating department to make certain that parts can be held securely on a plating rack with good electrical contact without masking a significant surface. Many difficult racking problems can be solved by design modification.
- Provide for good drainage of processing solutions from racked parts. Certain shapes tend to trap solution, which then causes contamination by carry-over, possible corrosion of the part and waste of materials. Carry-over aggravates the problem of waste disposal and adds excessive cost due to chemical losses. In design, avoid rolled edges, blind holes, and spot-welded joints. Drain holes are especially important in irregular shapes and tubular parts.
- Avoid shapes that can trap air on entry into processing tanks if this air could block access of solution to areas requiring treatment. Wherever air can be trapped, hydrogen or oxygen gas may also accumulate during the cleaning or plating step.

Design for Good Distribution of Electrodeposit

Experience and cost accounting show that simple shapes are always finished more uniformly and more economically than complex shapes. This rule is Number One for the designer.

One of the most important factors determining the quality of a coating is its thickness on significant surfaces. Fundamental laws of electrochemistry (current distribution) operate to prevent uniform deposition of an electro-deposited coating on a cathode of any practical shape and size. Portions of the work, which are nearer to the anodes, tend to receive a heavier deposit. Sharp edges or protrusions at all current densities tend to steal a disproportionate share of the current. The goal of the designer and the plater is to make thickness variations as small as possible. At the same time, uneconomical waste of metal by excessive build-up of both non-significant areas must be avoided. The same difference in plated thickness found within a plated article also exists from piece to piece on the rack of plated parts due to both cost sensitivity from overplating and the lack of adequate corrosion in underplated areas.

It is possible to estimate metal distribution ratios from models or mock-ups, but there are also empirical rules. These can guide the designer to improved uniformity of thickness, hence, improved quality with greater economy. These general principles and various sketches illustrate what has been learned from practical experience:

- Avoid concave or perfectly flat significant surfaces. Convex or crowned areas receive more uniform coatings. Use a 0.4 mm per 25.4 mm (0.015 inch per inch) crown-minimum.
- Edges should be rounded to a radius of at least 0.4 mm (1/64 inch) preferable 0.8 mm (1/32 inch).
- Re-entrant angles or corners should be filleted with a generous radius. Make sure radii are as large as possible.
- Avoid concave recesses, grooves, or slots with width less than one-half the depth.

- Minimize the number of blind holes because these must usually be exempted from minimum thickness requirements. Where necessary, limit their depth to 50% of their width. Avoid diameters less than 6 mm (7/32 inch).
- Countersink threaded holes to minimize electroplate thickness at their peripheries and facilitate insertion of fasteners after plating.
- If fins or ribs are required, reduce their height and specify a generous radius, 1.6 mm (1/16 inch) at each base. Round off tips with radii of at least 1.6 mm (1/16 inch). Multiple parallel fins should have spacing between centers equal to four times the width of the fin. Broad hollow ribs are preferred over slender solid ones.
- Adopt recessed in preference to raised letters and insignia but round off edges and provide gentle contours.
- Integrated studs for fasteners should be shortened as much as possible and inside angles at each base should be rounded generously. Tips should be similarly rounded.
- Studs or bosses with hollow centers should be shortened as much as possible and angled 90 degrees from the major plane of the part. All bosses should face the same direction.
- Assist the plater by clearly marking significant surfaces in part drawings.
- Avoid use of a variety of basis metals in any one part to be plated. The contact of dissimilar metals may interfere by galvanic action with covering power or with adhesion of the deposit.

2. Influence on Electroplatability

Design Features That Influence Electroplatability

The effect of the basic design of a product or component upon the effectiveness or durability of the plating used has been the subject of much study and research. Many failures for which the plater has been blamed can be attributed to the original design.

A major contribution to the plating industry was made by the Zinc Institute, Inc., when it sponsored a

design study by Battelle Memorial Institute, which has resulted in the establishment of basic design principles to be applied to zinc die castings. The principles can be applied to other substrates.

The various shapes shown here provide the “dos and don’ts” of design configurations and their relationship to electroplating quality.

Feature	Influence On Electroplatability	Better Design
Convex surfaces	Ideal shape. Easy to plate uniformly, especially where edges are rounded.	
Flat surfaces	Not as desirable as crowned surfaces. Use a 0.4mm/25.4mm (1/64 inch) crown to hide undulations caused by uneven buffing.	
Sharply angled edges	Undesirable. Reduced thickness at center areas and requires increased plating time for depositing a minimum thickness of durable electroplate. All edges should be rounded. (Edges that will contact painted surfaces should have a minimum radius of 0.8 mm [1/32 inch])	
Flanges	Large flanges with sharp inside angles should be avoided to minimize plating costs. Use a generous radius on inside angles and taper the abutment.	
Slots	Narrow, closely spaced slots and holes reduce electroplatability and cannot be properly plated with corrosion-protective nickel and chromium unless corners are rounded.	
Blind holes	Must usually be exempted from minimum-thickness requirements. Where necessary limit depth to 50% of width. Avoid diameters less than 6mm (7/32 inch).	
Sharply angled indentations	Increase plating time and costs for a specifically minimum thickness and reduce the durability of the plated part.	

The distribution of electroplate is indicated in an exaggerated fashion.

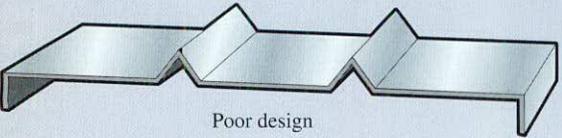
ROUND OFF HIGH SPOTS

AVOID SHARP INTERIOR ANGLES

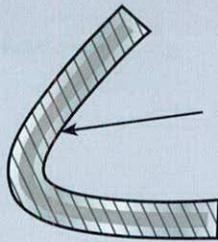
PLACE HOLES FOR DRAINING AND AIR ESCAPE



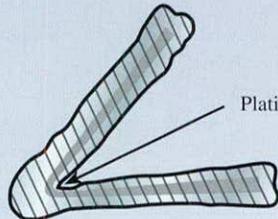
Good design



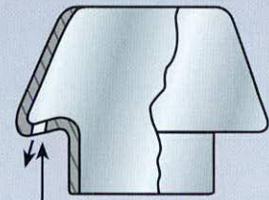
Poor design



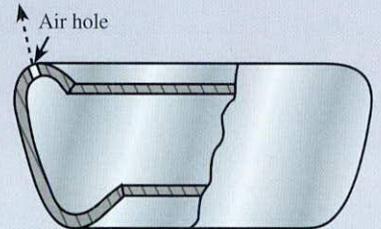
Uniform plating



Plating missed



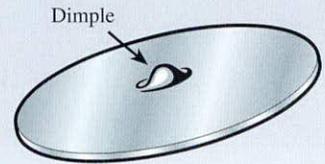
Drain hole



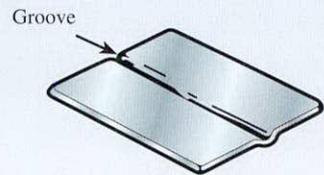
Air hole

Feature	Influence On Electroplatability	Better Design
Flat-bottom grooves	Inside and outside angles should be rounded generously to minimize costs.	
V-shaped grooves	Deep, V-shaped grooves cannot be satisfactorily plated with corrosion protective nickel and chromium and should be avoided. Shallow, rounded grooves are better.	
Fins	Increase plating time and costs for a specified minimum thickness and reduce the durability of the plated part.	
Ribs	Narrow ribs with sharp angles usually reduce electroplatability; 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.	
Concave recesses	Electroplatability is dependent upon dimensions.	
Scoops	Increase plating time and costs for a specified minimum thickness.	
Juts	Buildup on jut will rob corners from their share of electroplate. Crown the base and round off all corners.	
Flanges	Electroplatability is dependent upon dimensions. Round off corners and crown from center line, sloping towards both sides.	

AVOID STICKING WHEN BARREL PLATING



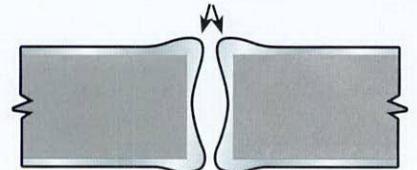
Dimple



Groove

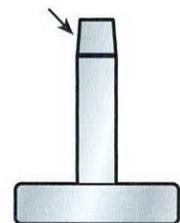
ALLOW FOR BUILDUP

Buildup reduces effective diameter



Hole

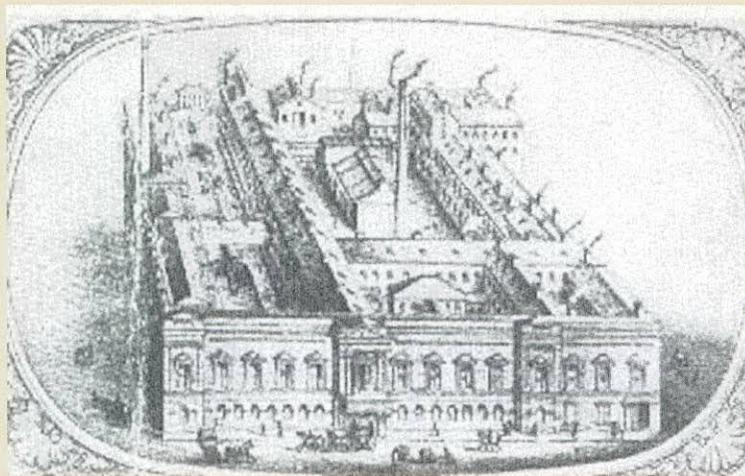
Tapered end to allow for buildup



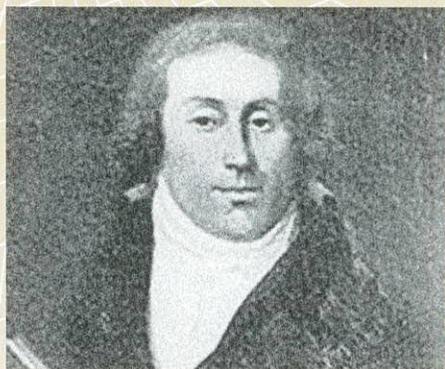
Plug

The distribution of electroplate is indicated in an exaggerated fashion.

3. Historical Perspective



Elkington Works in Birmingham, England



Luigi V. Brugnatelli

The history of the deposition of precious metals can be traced to Luigi V. Brugnatelli, who probably first performed his electrodeposition of gold around 1800 using the Voltaic Pile as discovered by his friend, Allisandro Votla. However, an insult from Napolean Bonaparte caused Brugnatelli to confine the publication of his works to his own journal, which effectively caused the loss of this information for almost 40 years.

John Wright, from Birmingham, England, found that potassium cyanide was a suitable electrolyte for gold and silver electroplating. His work, combine with that of the Elkington cousins and other developments by Barratt, resulted in the issue of several patents in 1840. These discoveries and patents are the foundation of modern gold and silver plating.

This alliance, and its discoveries, was almost certainly precipitated by the invention of copper electroplating (referred to as electroforming and electrotyping in the literature) developed in the latter part of 1838, early 1839. This led to the adaptation of galvanic current for the deposition of gold and silver.

Gold and silver plating proceeded at a fast pace. By 1842, Elkington and Mason had a successful silverware manufacturing facility where George Elkington used the new gold electroplating processes to make spectacle frames, pen nibs, etc. of such quality and low cost that he dominated the entire trade in Birmingham. Charles Christoffle (license of Elkington), in France, had overnight commercial success with his electroplating company producing hollowware and flatware for the government and society of France. He provided the table settings for the official receptions of Napoleon III.

It was in Russia that the first large scale electroplating of copper, silver, and gold took place. Hundreds, perhaps thousands, of statues, icons and other religious artifacts, as well as numerous copper plates for cathedral domes, were gold plated. One cathedral dome alone required almost 500 kilograms (about 16,000 troy ounces) and appears to be the first specification plating. Two parts from every 100 were checked by strip and weigh methods; if both parts failed to meet the specification, the entire batch was rejected.

From that time on, the gold and silver plating industry in Europe and the United States grew in size with practically no new developments. The passing of the Victorian grand object d'art relegated gold plating to faux jewelry, spectacle frames and other inexpensive novelties, and silver plating to the flatware and hollowware industries. Much of the technology used to plate large items, heavy deposits and massive electroforms was lost. This quiescent period lasted almost 80 years, for it was not until World War II and the advances in electronics industries that interest was renewed in gold electroplating (with the exception of the Providence, RI and NY areas). It was not until the 1950s that the electrodepositing fine grained, uniform, thick gold plate occurred. Non-cyanide gold electrolytes were introduced during the late 1960s. Chemical developments since have provided plating solutions that show improved performance in the areas of deposition speed, throwing power, covering power, distribution, and a variety of colors.

4.

Preparation for Electroplating

Many of the items that are precious metal plated are first surface finished by means of mechanical polishing or mass finishing.

As with all electroplating operations, the first step after any polishing operation is to clean and activate the basis metal so proper adhesion and defect-free appearance of the finished part may be achieved.

Since the introduction and adoption of the Montreal Protocol, the gradual phasing out of CFCs and other ozone depleting chemicals has resulted in the virtual elimination of degreasing by means of chloro and/or fluoro carbon type solvents.

Cleaning, degreasing and activation are carried out in aqueous cleaning solutions, using various alkalis, surface active agents, detergents, chelators, saponifiers and emulsifiers. Activation of the surfaces to be plated is usually provided by either dilute mineral acids or by dry acid salt solutions.

After cleaning, most of the items that will finally receive their noble metal top-coat are electroplated with copper and/or nickel in order to achieve the fully bright or satin finished appearance.

5.

Copper Electroplating

ACID COPPER DEPOSITION

- Decorative, bright, high-leveling for rack or barrel
- Electroforming, rotogravure and other functional coatings
- High-speed functional for wire, strip and rods
- Electronic copper (ductile, high-throw baths)
- Acid copper strike undercoat for plastics
- Electrowinning and electrorefining of copper

ALKALINE COPPER DEPOSITION

- Alkaline, cyanide-free copper for rack barrel
- Alkaline, cyanide copper deposition
- Alkaline, cyanide copper strike undercoat

All but the cyanide copper baths deposit from a divalent copper ion, taking twice as many ampere hours to deposit the same amount of copper. However, since the acid copper baths and some of the alkaline baths are able to operate at higher cathode current densities, the negative aspect can be easily removed.

All the types of alkaline copper baths use some type of complex ion in order to tie-up the copper ion and prevent it from precipitating out. This complex typically can be cyanide, tartrates, pyrophosphates, or phosphonates. Acid copper, on the other hand, deposits right out of a plain copper ion, whether the anion in the bath is sulfate, fluoborate, or other. Acid copper is also the process, due to the additives used, which can level out imperfections and scratches in the substrate. Therefore, it is often recognized that acid copper is the preferred deposit for decorative applications.

A copper strike puts on a barrier copper coating that allows subsequent deposits to go on trouble-free. In the case of plastics, the strike increases the thickness of the electroless coatings, allowing for conductivity and stability under higher voltages. A copper strike is essential for the subsequent acid copper plating of zinc-based die castings and tin based castings.

A wide range of functional or decorative copper electrodeposition processes are presently available. The copper to be used is defined by regulatory laws, the speed needed, the rate used and appearance requirements. The general types of copper electrodeposition used at the present time are:

6. Decorative Nickel



Introduction

Decorative bright nickel electro-deposits are often used as an undercoat for precious metal coatings. Nickel undercoats provide brightness to improve reflectivity and leveling to smooth out surface defects. They also improve corrosion resistance, reduce porosity and can act as a diffusion barrier to prevent the base metal from migrating into the precious metal top-coat.

Today's bright nickel processes are vastly superior to earlier processes. Current nickel processes provide outstanding leveling characteristics and excellent physical properties. Most employ a WATTS electrolyte that can be modified to satisfy specific plating requirements. For example, a high chloride WATTS type bath is employed where plating speed is important; a low chloride WATTS is more suitable for applications that require excellent ductility and low stress. Typical basic formulations are shown in the chart.

Watts Bath

Nickel Sulfate	40.0 ounces/gallon
Nickel Chloride	8.0 ounces/gallon
Boric Acid	5.5 ounces/gallon

High Chloride

Nickel Sulfate	8.0 ounces/gallon
Nickel Chloride	30.0 ounces/gallon
Boric Acid	5.5 ounces/gallon

Low Temperature or Mixed Bath

Nickel Sulfate	35.0 ounces/gallon
Nickel Chloride	15.0 ounces/gallon
Boric Acid	6.0 ounces/gallon

Addition Agents

The brightness and leveling of bright nickel deposits are, perhaps, the most desirable properties for the jewelry industry. Organic addition agents are used to provide these characteristics. The additive systems are usually a combination of ingredients called Primary and Secondary Addition agents. These ingredients work synergistically to provide very bright deposits that can substantially smooth out surface defects common to the base metal, thereby providing a brilliant surface that is substantially free of surface defects. Supplier recommendations must be carefully followed to provide optimum performance.

Anionic surfactants are often used in bright nickel baths to emulsify oils and prevent pitting. They can be measured by monitoring the surface tension of the nickel-plating bath. Low-foaming wetting agents are used in air-agitation baths and reduce surface tension to about 40 dynes/cm. Since cathode agitation baths have a greater tendency to pit because of higher organic loading and less agitation than air-agitated baths, higher foaming surfactants with greater wetting properties are used. The surface tension of these baths is generally less than 35 dynes/cm.

Agitation

Agitation is very important with respect to plating speed, as well as brightness and leveling. The greater the agitation, the faster a bright nickel bath will plate and level out surface defects. Cathode rod agitation is often used when bright nickel plating for jewelry and other applications, while air agitation would provide faster speed and better leveling, it is normally not used when precious metal plating is the final finish. This is because most jewelry is not positively racked (held rigid) and the violent agitation would knock parts off the racks and into the plating tank.

Equipment

Bright nickel baths require tanks that are polypropylene or steel lined with approved rubber or Koroseal. Anodes are generally electrolytic squares or sulfur depolarized rounds that are placed in titanium baskets. Rolled carbon bars can also be used. All anodes must be bagged with either laundered cotton or a synthetic, such as polypropylene or Dynel, to prevent roughness. Air agitation is distributed through a properly designed sparger and supplied by a low-pressure blower. Mechanical agitation is generally supplied by moving the cathode bar back and forth. Heating coils, utilizing steam or electricity, are required to maintain proper operating temperature and are generally made of titanium, tantalum, or Teflon*. Filters are generally used to remove particulate matter and prevent roughness. Normally, the filters are packed with activated carbon to remove organic degradation products, oils or impurities that have dragged down the plating line. It is extremely important that your plating supplier approve all materials.



Decorative Satin, Antique, and Black Nickels

Black nickel plating solutions provide a distinctive finish suitable for a wide variety of articles. Any black finish, ranging from matte to a brilliant luster, can be obtained. Matte (or satin) finishes have been developed that allow for controlled, but different, shades to be plated out of the same rack or barrel bath. A unique look is obtained by gold plating these finishes and they have been found suitable for industrial and military instruments, cameras, microscopes and binocular parts. Articles requiring lustrous finishes include tubular furniture, plumbing fixtures, buttons and trophies. Often these surfaces can be mechanically relieved to provide highly desirable antique finishes suitable for casket hardware, jewelry, buckles and lamps. The substrate on which the black nickel coating is applied, (e.g., copper, zinc, nickel, etc.) can alter the appearance of the antique finish.

Corrosion resistance of black nickel coatings is generally poor, so a clear coating is either sprayed or applied electrophoretically to the piece. The clear coating prevents tarnish and base metal deterioration. In cases where the application of a clear coating is impractical, light oil can be applied to the significant surfaces with a soft cloth.

Black coatings can be achieved by chemical or electrolytic treatment of a dull or bright nickel surface or by plating a black coating directly from a proprietary electrolyte. In the latter case, addition agents and/or post treatments are used to intensify the blackness. Different shades of blackness can be achieved, ranging from a warm, slightly dark metallic finish to a jet-black deposit.

Processes that provide black coatings directly from a plating tank utilize the same equipment as other decorative processes. Likewise, the articles are cleaned and prepared in exactly the same manner. Lined tanks are required. Heaters, air spargers, anodes and bags should be used according to the recommendations of the specific supplier of the process. Reputable plating suppliers will also recommend specific cycles that are suitable for the user's specific needs.

7. Nickel Contact Dermatitis



In Europe and the Far East, the use of nickel in components that come into contact with the skin, or that are inserted into the human body, has undergone a strict review and is now controlled by strict legislation particularly for the EEC Countries (European Economic Community). In October of 1994, the European Council of Research Ministers adopted Directive 94/27/EC, a supplement to the 1976 Directive 76/759/EEC, limiting the use of nickel. The implementation of this Directive has been slow but it is in effect. The Directive needs to then be adopted by each member of the European Community. Once this is done, approximately 6 months later a prohibition of import and manufacturing would take effect.

Directive 94/27/EEC, requires that nickel may not be used as an undercoat and products not conforming to the directive be marked accordingly.

- Post assemblies that are inserted into pierced ears or other human body parts, unless the nickel content is less than 0.05%.
- In products intended to come into direct contact with the skin, e.g., earrings, necklaces, bracelets, anklets, snaps, fasteners, zippers, etc., if the rate of release is more than 0.5 micrograms per cm² per week.
- In products such as those that have a non-nickel coating (a lacquer or heavy gold electroplate for example) whose rate of nickel release will not exceed 0.5 micrograms per cm² per week for a period of at least two years of normal wear.

The legislation calls out specific tests and control methods for determining the quantity of nickel released in order to be able to comply with this EEC directive. The tests range from soaking the plated article in artificial human sweat followed by testing for nickel using specified wear testing equipment and then testing for nickel along the wear track.

Most of the EEC member countries individually passed legislation conforming to the EEC directive during 2000 providing local manufacturers 6 months to bring their individual manufacturing specifications into line with the law.

It is recommended that any manufacturer of these products, many of which are plated with decorative precious metals, especially those manufacturers who export their goods to Europe, will need to:

- (a) Carefully review the Directive, and
- (b) Consider alternatives to the use of nickel and undercoat to the precious metal.

*Note: Legislation exists limiting the use of nickel in Denmark, Germany, and Sweden.

8. Non-Nickel Alternatives

The most obvious alternative to nickel is acid copper. Acid copper can provide equal brightness and leveling to that obtained from bright nickel solutions when rack plating. Acid copper can also provide a suitable satin or matte surface for those applications. Recent developments have vastly improved the performance of barrel acid copper plating providing similar performance to (barrel) nickel plating.

The most common precious metals plated, namely gold and silver, will migrate into copper. It is, therefore, necessary to plate a barrier layer that will retard or prevent this migration. These barrier layers are either palladium, palladium/cobalt alloy, yellow bronze, white bronze or a combination, such as yellow bronze plus palladium.

Yellow Bronze and White Bronze

Both these processes are deposited from high, free cyanide plating solutions and offer options to the electroplater because of the alloy deposited. Traditionally, bronze plating used ammonia to maintain good color and soluble alloy anodes. Modern alloy baths contain alternate complexors and, therefore, do not require the use of ammonia and, for better control, utilize full additive systems and inert stainless steel or graphite anodes. More stable than earlier generation processes, these modern formulations can be non-magnetic, antiallergenic, and some can be non-tarnishing – thus they have been used as replacements for silver or palladium (besides nickel) for a combination of cost and functional reasons. Typical bath formulations are shown in the table below.

BRONZE PLATING SOLUTIONS		
	Yellow	White
Copper g/l	15 to 36	12 to 18
Tin g/l	5 to 9	10 to 16
Zinc g/l	—	2 to 5
Free Cyanide g/l	35 to 58	45 to 60
Temperature	100 to 120°F	110 to 130°F
pH	12.0 to 13.5	11.0 to 12.0
Current Density	20 to 50 ASF	10 to 50 ASF
Alloy Composition		
Copper	72 to 88%	54 to 65%
Tin	12 to 28%	25 to 40%
Zinc	—	0 to 10%

Palladium and Palladium Alloys

Palladium and palladium alloys, notably palladium-nickel and palladium-cobalt, are used in the jewelry industry and other decorative precious metal applications. Low porosity and bright white deposits are used to enhance the appeal of many decorative items.

Deposits of pure palladium and palladium-cobalt are used as barrier layers between bright acid copper deposits and gold deposits in the production of non-nickel containing products. A deposit thickness of 7 to 10 microinches (0.175 to 0.25 microns) will greatly limit the migration of gold into the copper electroplate and vice versa. Palladium and palladium alloys are used as final white finishes. The color of the deposits obtained is bright white and is often used as a rhodium replacement. For decorative applications, palladium and its alloys can be deposited from ammoniacal systems in which palladium is present as an amine complex. Other complexing systems are also used when specific deposit properties are required.

Since ammoniacal solutions will readily tarnish copper, copper alloys and nickel, and copper contamination in quite small quantities will cause darkening of the deposit, it is good plating practice to strike the work prior to plating with palladium and/or palladium alloy processes. Typical formulations are shown in the Table below.

	Palladium	Palladium Nickel	Palladium Cobalt
Palladium g/l	2-15	1.5 to 6	2 to 6
Nickel g/l	—	0.3 to 3.0	—
Cobalt g/l	—	—	0.0 to 3.0
Ammonium Salt	60 to 100	60 to 100	60 to 100
pH	7.5 to 8.5	7.5 to 8.5	7.5 to 8.5
Temperature(°F)	75 to 120°	85 to 100°	85 to 100°
Current Density	10 to 25	10 to 25	10 to 25
Alloy Composition			
Palladium	100%	60 to 90%	75 to 90%
Nickel	—	10 to 40%	—
Cobalt	—	—	10 to 25%

9. Gold Plating



Today's decorative gold plating processes are applied to a very diverse range of consumer products. Typically, plated items include watch cases and bands, plumbing fixtures, writing instruments, jewelry, eyeglass frames, cigarette lighters, fashion accessories, and lighting fixtures. Deposit thickness will vary with the specifications and application.



Watch cases, watch bands, and writing instruments are often plated to thickness of 2 to 5 microns (80 to 200 microinches). The watch industry often uses duplex gold by first applying a thick deposit of alloy gold, typically in the range of 12 to 16 karat, followed by a hard acid gold deposit of up to 0.5 microns (20 microinches). This final layer of gold also provides the final color.

Plumbing, bathroom and kitchen accessories usually fall into two segments. Those that are plated with gold thicknesses ranging from 0.5 microns minimum to 3 microns or more (20 microinches to 120 microinches) and marketed to the luxury markets. The other segment utilizes flash deposits of 0.075 to 0.125 microns (3 to 5 microinches), followed by a topcoat, either clear powder coat or electrophoretically applied lacquers.

Fashion jewelry typically uses deposits ranging in thickness from a flash of 0.075 microns to 2.5 microns or more (3 to 100 microinches) of hard gold deposit. The requirements for most other industries are similar.

The gold deposits for these diverse applications are obtained from chemistries which are segmented into four (4) types, as follows.

Hard Acid Gold

Hard acid gold is defined as the premier gold plating process. First developed in the early 1950s. These processes, based on potassium gold cyanide and operating at pH values as low as 3.5, are able to produce a multitude of basic color standards, and include the full range of Hamilton colors.

The deposit purity, as plated, ranges from 90 to 99%. The deposits also exhibit excellent wear resistance, durability, and color stability. The hardness and brightness of the deposits is obtained from the inclusion of various metal complexes in the plating solution matrix. These metals, (cobalt, nickel, indium, and others), either individually or in combination, are co-deposited with the gold provide a ranges of colors. Typical formulations are reviewed in Table 1.

Table 1: HARD ACID GOLD SYSTEMS

Constituent	Concentration g/l
Gold	2 to 10
Conducting Salt	60 to 150
pH 3.2 to 4.4	
Temperature	70 to 120°F
Nickel Complexed	0 to 10
Cobalt Complexed	0 to 8
Indium Complexed	0 to 1
Iron Complexed	0 to 3

In the late 1980's, further development provided for the inclusion of organic additives within the solution matrix. These additives offered lower gold concentration, increases the brightness range, extended the current density range, and improved productivity. Other benefits of these organic additives are improved distribution, enhancement of the color and richness of the deposits. These hard acid gold systems enjoy now, and are expected to enjoy for the foreseeable future, a predominant share of the decorative gold plating market.

Alkaline Non-Cyanide Gold

The major discovery of this unique chemistry during the 1950s resulted in the development of cyanide-free sulfite system offering outstanding benefits in metal distribution, ductility, electroforming, and the ability to build brightness. These systems contain gold sulfite, free sulfite, complexing agents, stabilizing agents and color additives; offer an excellent range of colors as indicated in Table 2, and were well received by the optical frame industry. Cyanide-free sulfite systems are particularly attractive to the European optical frame industry, where pink color rolled gold eyeglass frames are very fashionable.

**Table 2: CYANIDE-FREE SULFITE SYSTEMS
COLOR ADDITIVES**

Color	Metals Additives
Green	Cadmium, Silver, Zinc
Pink-Red	Copper
Pale Yellow-Grey	Palladium
Champagne	Palladium
Pale Yellow-White	Nickel

These non-cyanide systems produce thick, ductile deposits that are extremely useful in high build and electroforming applications. Typical formulations are shown in Table 3.

**Table 3: CYANIDE-FREE SULFATE SYSTEMS
TYPICAL FORMULATIONS**

Constituent	Concentration g/l
Gold	10
Metal	Complex 5
Stabilizer	15
Free Sulfate	50
Complexor	5+
pH	9 to 10
Temperature	95 to 130°F
Current Density	10 Amps./sq. ft.

Alkaline Cyanide Gold

Alkaline cyanide gold systems originated in 1840 and have been associated with having the widest color range. More than 600 shades were plated in the 1930s and 1940s. The formulations, based on potassium gold cyanide or potassium auri-cyanide, free potassium cyanide and coloring additives, are extremely versatile, offering flash coats, thin and thick deposits, allow deposits often used in duplex gold systems, and electro-forming. However, as improvements have been made in other systems, the future use for alkaline cyanide gold will mostly be limited to alloys, duplex systems, and electroforming. Typical formulations are shown in Tables 4 and 5.

Table 4: FLASH GOLD PLATE

Gold as Potassium	g/l
Gold (I and II) Cyanide	0.8 to 6
Free Potassium Cyanide	2 to 15
Di Potassium Phosphate	2 to 25
Metal Coloring Additives	.025 to 3.0
pH	10 to 12.5
Temperature	140 to 160°F
Current Density	10 to 50
COLORING ADDITIVES	
Green to White	Silver, Tin Zinc, Cadmium
Yellow to White	Nickel
Pink to Red	Copper, nickel

Table 5: HEAVY GOLD PLATE

	g/l
Gold (as gold potassium cyanide)	8 to 20
Silver & Silver Potassium Cyanide (For bright deposits)	0.3 to 2
Potassium Cyanide	15 to 100
pH	12 to 12.5
Temperature	60 to 80°F
Current Density	
Rack Amps./Sq. Ft.	3 to 8
Barrel Amps./Sq. Ft.	1 to 2

Table 6: NEUTRAL CYANIDE GOLD PROCESSES

	g/l
Gold (as gold Potassium Cyanide)	0.75 to 2.0
Conducting Salt	15 to 30
Complexor	6 to 10
pH	6.5 to 7.5
Temperature	110 to 140°F
Current Density Amps./Sq. Ft.	10
COLOR ADDITIVES	
Yellow to White	Nickel
Green	Silver
Red	Copper
Pink	Nickel/Copper

Alloy Gold Plating

Similar formulations to those shown in Table 5 are utilized to produce low karat alloy gold electrodeposits ranging from 12 karat to 23 karat (50% to 98 % of gold in deposit). Alloying metals are usually silver, nickel, copper and cadmium. The free cyanide content of these alkaline solution formulations is often relatively low.

These processes are used as a final finish such as white gold, or as part of a duplex system as a method of producing thicker deposits at lower cost. Typical duplex systems are used by the watch case industry, where alloy gold is used as an undercoat, followed by at least one micron (40 microinches) of hard acid gold of the desired color.

Neutral Cyanide Gold

Alkaline gold systems are modified to provide more accurate control of the complexed alloy systems by using alternate chelating agents in place of free cyanide. For example, a typical formulation may use complexors like EDTA. As these solutions operate at or near a pH of 7.0, they are designated as neutral cyanide gold processes. These processes are designed for ease of operation and for use in flash operations only. Typical formulations are shown below in Table 6.

Standards

Classifications are set by international agencies worldwide. In the United States, the Federal Trade Commission classifies gold deposits by thickness.

Gold Flash, Gold Wash and Gold Tone refer to gold deposits that are less than 7 microinches (0.175 microns) in thickness. Gold Electroplate or Gold Electroplated refers to gold electro-deposits of at least 7 microinches (0.175 microns or more) minimum.

To carry Heavy Gold Electroplate or Heavy Gold Electroplated designation, the deposit must be at least 10 karat in fineness and be 100 microinches (2.5 microns) in thickness. If the gold is produced from a specific process, this may also be stated, for example, as Heavy Gold Electroplate (x karat) or Heavy Gold Electroplate (x process). If products are to be exported to overseas markets, the relevant local standards should be used, i.e., the ISO Standards in Europe.

10. Gilding

Gilding, or the art of coating metals and non-metals with gold, is indeed an ancient art. This art was certainly practiced by the Egyptians as can be seen by the artifacts recovered from the Tombs of the Valley of Kings. Cleopatra was reported to have the beams of her palace gilded with gold. There is some evidence to show that gilding was practiced by Babylonians. Broaches and pins of gilt have been found on the site believed to be that upon which Babylon sat.

Arab artisans gilded copper and silver by the mercury amalgam method (vermeil). This method involves the application of a coating of mercury and then burnishing on a layer of gold leaf. In the mid-nineteenth century, many items including spectacle frames, candelabra and the dome of the cathedral church of St. Isaac's in St. Petersburg, were gilt by this very dangerous method, often resulting in death and/or severe disability of the artisan. It is reported that some 60 craftsmen died from the resultant mercury poisoning from the gilding of the cathedral dome of St. Isaac's.

During the eighteenth and early nineteenth century, large amounts of "water gilding" was carried out using dilute solutions of gold chloride. G. R. Elkington improved this process and was issued patents for developing an immersion gold (or gilt) bath based on gold chloride neutralized with potassium bicarbonate. Elkington's process was vastly superior to traditional water gilding and approached the quality on non-metallic substrates of wood or plaster religious artifacts.



St. Isaac's Cathedral, St. Petersburg

11. Brush Plating

The anode, usually non-soluble, is encased in a porous material such as felt. The porous pen or brush is dipped into the specially formulated plating solution. The pen or brush is then applied to the surface of the part to be plated (the cathode) using a brushing action. In large applications rollers, similar to paint rollers, are employed. Perhaps one of the most spectacular examples in North America of brush plating is the Slovak Cathedral of the Transfiguration just north of Toronto, Canada. The copper domes of this cathedral, including the orbs, crosses and other fixtures, were all brush plated with gold. The effect is both dramatic and spectacular. Other examples include the elevator doors of the MGM in Las Vegas, Nevada and the independent man atop the Rhode Island State House.

Other precious metals can be, and often are, brush plated. These include silver, for spot repair of silver plated hollowware; Rhodium, providing a bright white finish in recesses of jewelry and Ruthenium, for contrast.



Brush plating is the modern equivalent of gilding. The general principle of brush plating is to connect the work to the negative side of the D.C. power source – a battery, a small or larger rectifier, or even a portable D.C. generator.



12. Silver Plating



Silver electroplating is as old as the plating industry itself, first patented and produced in 1840 (British Patent 8447 in 1840) by the Elkington cousins. The basic electrolyte has changed little since then. The only developments until recently (for decorative applications) has been that of grain refiners and brighteners, as today's metal deposits are required to be bright in order to reduce or eliminate the cost of polishing. Typical formulations are given the following chart.

Constituent	Concentration g/l (oz./gal.)		
	I	II	III
Silver (metal)	5 to 40 (0.6 to 5.5)	5 to 40 (0.6 to 5.5)	4.50 to 120 (1 to 14)
Potassium Cyanide (free)	16 to 130 (2 to 18)		45 to 160 (5.5 to 20)
Sodium Cyanide (free)		16 to 110 (2 to 15)	
Potassium Carbonate	15 to 90 (2 to 6)		16 to 80 (2 to 10)
Sodium Carbonate		15 to 45 (2 to 3)	
Potassium Hydroxide	2 to 6 (.25 to .75)		4 to 30 (0.5 to 4)
Temperature°F	68 to 86°	68 to 76°	100 to 120°
Current Density ASF`	1 to 40	5 to 15	5 to 100

The plating solution is best made using potassium silver cyanide in high purity from supply houses and readily soluble. This material has a silver content of $54.0\% \pm 0.2\%$. Silver cyanide is also available with a silver content of about 80% it is not soluble in water. While considered pure, its purity is often less than that of silver potassium cyanide. The use of the silver potassium cyanide salt eliminates the possible source of impurities which may affect the performance of the operating bath.

As is common with all alkaline precious metal solutions, immersion coatings on less noble metal surfaces are a common occurrence. This will cause poor adhesion. It is, therefore, desirable to apply a silver strike in order to minimize or eliminate this effect. Typical strike formulations are shown on the following table.

Constituent	For Ferrous Metal	For Non-Ferrous Metal	
		I	II
Silver (metal)	1.5 to 2.5 g/l	1.5 to 2.5 g/l	1.5 to 2.5 g/l
Potassium Silver Cyanide	1.5 to 3.0 g/l	5 to 8 g/l	1 to 2 g/l
Sodium Cyanide	60 to 90 g/l		60 to 90 g/l
Potassium Cyanide			20 to 30 g/l
Potassium Hydroxide			18 to 22 g/l

Rinsing the work between silver striking and silver plating is not required.

Non-cyanide solutions are now being used primarily for electronic and functional applications. However, as research continues, fully bright, decorative processes will be available in the not too distant future.

13. Rhodium Plating

Of the platinum group metals, rhodium has found wide acceptance in decorative precious metals applications. Rhodium

has several desirable properties – it's brilliant white color, high reflectivity, and hardness which make it very popular with the jewelry and faux jewelry industries.

Rhodium can provide excellent tarnish protection for sterling silver and silver plated flatware and hollowware from quite thin deposits.

Typically, rhodium electroplate is deposited on precious and faux jewelry, sterling and silver-plate to a thickness of 0.05 to 0.125 microns (2 to 5 microinches). This thickness of rhodium is produced in about 20 to 60 seconds from phosphate, sulfate or phosphate-sulfate baths.

Typical formulations are shown below.

	Phosphate	Sulfate	Phosphate/Sulfate
Rhodium g/l	1.5 to 2.0	1.3 to 2.0	1.5 to 3.0
Phosphoric Acid Pure	40 to 80		
Sulfuric Acid Pure		25 to 80	20 to 80
Temperature C	20 to 50°	20 to 50°	20 to 60°
Agitation	None-Moderate	None-Moderate	Moderate
Current Density	20 to 100	20 to 100	

14. Platinum Plating

The electrodeposition of platinum is not as well established as that of rhodium. The recent surge in demand for platinum and platinum finishes for the jewelry industries will result in the platinum processes becoming more established. Recent development eliminating stress, solution

polarization, anode polarization, and porosity have led to the ability to electroform this valuable metal.

15. Ruthenium Plating

Electroplated ruthenium is gaining acceptance in the jewelry, giftware and other industries. It has a unique dark finish varying in shade from a distinctive gray through to black.

Deposits of electroplated ruthenium are the hardest of all the platinum group metals.

The electroforming of precious jewelry is gaining wide acceptance worldwide. Gold can be electroformed from cyanide alloy solutions, providing karat deposits ranging from 10 karat to 24 karat. Typically, the alloys deposited are gold/silver alloys or gold/copper/cadmium alloys. The use of the computer and sophisticated chemical control has permitted the mass production of quality karat jewelry.

Silver requires simple equipment and many items are electroformed in silver, ranging from jewelry to statuettes.

As previously mentioned, platinum is now being electroformed from relatively simple equipment but with very close control of the solution chemistry and operating conditions.

16. Electroforming

17.

Glossary of Terms

Abrasive Blasting - A process for cleaning or finishing by means of an abrasive directed at high velocity against the work piece.

Activation - Elimination of a passive condition on a surface.

Addition Agent - A material added in small quantities to a solution to produce a desired effect. Also synonymous with "brightener."

Adhesion - The attractive force that exists between an electrodeposit or an electrochemical deposit and its substrate that can be measured as the force required to separate the deposit from the substrate.

Amorphous - Non-crystalline or without evidence of a regular structure.

Anode - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. In most instances it is the source of metal to be plated from the bath.

Anode Efficiency - The actual current efficiency of a specified anodic process compared to the theoretical value. The actual fraction of current used to dissolve metal from the anode compared to the theoretical amount as predicted by Faraday's Laws.

Autocatalytic Plating - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited. Often referred to as "electroless plating."

Barrel Plating - Electroplating or cleaning in which the work is processed in bulk in a rotating container (barrel).

Base Metal (or Substrate) - Material upon which processing is conducted or coatings are deposited. (It is not necessarily the material from which the part is constructed).

Blister - A dome-shaped imperfection or defect, resulting from loss of adhesion between a deposit and its substrate, or between various coatings where multiple layers of coatings are present.

Bright Dip - A solution used to produce a bright surface on a substrate by chemical immersion.

Bright Plating Range - The range of current densities within which a given plating solution produces a bright deposit.

Brightener - Another term for addition agent. A liquid or powdered material that when added to a plating bath, improves the reflectivity or brightness of the deposits produced by the plating bath.

Brush Plating - A specialized method of plating, typically used for small scale applications, where an inert anode is surrounded by a pad, sponge, brush, or other device that will retain a volume of a concentrated solution containing a dissolved salt of the metal to be deposited. The anode/pad device is moved over the cathode during the plating operation in the area to be plated.

Buffing - The smoothing of a surface, accomplished by placing the surface to be finished against a rotating flexible wheel, to which fine abrasive particles have been applied in liquid, suspension, paste, or grease form.

Buffer - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.

Burnt Deposit - A rough, non-coherent or otherwise unsatisfactory deposit, typically produced by the application of an excessive high current density.

Bus Bar - The term used to describe the cables or conducting media – generally copper or aluminum stock – that transfers the current from the rectifier to the plating tank.

Carryover - See Drag in.

CASS Test - A special accelerated corrosion testing method using copper and acetic acid solution as the test medium. It is most typically used to predict the corrosion protection of nickel/chrome, or copper/nickel/chrome electrodeposits. See ASTM Method B368.

Cathode - The part that is electroplated.

Cathode Efficiency - The actual amount of current used to deposit metal in a plating process, compared to the theoretical amount as predicted by Faraday's Laws.

Chelate Compound - A compound in which a metal is contained as an integral part of a ring structure and is not readily ionized.

Cleaning - The removal of grease or soil and other foreign materials from a surface using one or more chemical or electrochemical solutions.

Alkaline Cleaning—cleaning by means of an alkaline solution.

Anodic or Reverse Cleaning—electrolytic cleaning where the part is connected to the negative terminal of the rectifier.

Cathodic or Direct Cleaning—electrolytic cleaning where the part is connected to the positive terminal of the rectifier.

Di-phase Cleaning—cleaning by means of a solution that contains a solvent layer and an aqueous layer. Cleaning occurs by both solvent and emulsification actions.

Soak Cleaning—cleaning by chemical means without the use of current. Generally used to remove heavy oils and greases.

Ultrasonic Cleaning—cleaning by any chemical means aided by ultrasonic energy to speed up soil removal. Especially useful in the removal of buffing compounds.

Spray Cleaning—use of an alkaline cleaner that is sprayed onto the part(s) to be cleaned. The additional energy provided by the spraying operation accelerates the removal of soils, greases, and buffing compounds.

Contact Plating - Deposition of a metal by immersion of the work in a solution that is in contact with another metal.

Corrodkote Test - An accelerated corrosion test for electrodeposits using a special paste coating that is applied to parts before they are CASS salt spray tested. See ASTM Method B380.

Corrosion - Gradual dissolution or oxidation of a metal.

Covering Power - The ability of an electrodeposit to plate at very low current densities, such as in deep recesses or holes. (To be distinguished from Throwing Power.)

Current Density - The total current divided by the area to which the current is applied.

Cathode Current Density—the total current applied divided by the total area being plated.

Anode Current Density—the total current applied divided by the total anode area.

Current Efficiency - See Cathode Efficiency and Anode Efficiency.

Degreasing - The removal of grease and oils from a surface.

Solvent Degreasing—degreasing by immersion in liquid organic solvent.

Vapor Degreasing—degreasing by solvent vapors condensing on the parts being cleaned.

Drag-In - The water or solution that adheres to the objects from previous processing steps, and which is thereby introduced into a processing tank.

Drag-Out - The solution that adheres to articles when they are removed from a processing tank.

Ductility - The ability of a material to deform without fracturing.

Low Current Density Plating - The term used to describe low current density plating done to remove metallic impurities from a plating bath.

Plating or Duplex Deposit - The term used to describe a multi-layer deposit that incorporates two layers with distinctly different corrosion potential characteristics. The different layers are typically combined in a manner that allows the more noble layer (the under-layer) to be sacrificial to the other layer (the top layer), thereby greatly improving the corrosion protection afforded, compared to that provided by a single layer of similar thickness.

Electroless Plating - A more commonly used term for Autocatalytic Plating.

Electrolyte - General term used to describe the processing bath, usually the plating bath.

Electrolysis - Process of causing chemical changes via the passage of current through an electrolyte.

Electroplating - The electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties, appearance, or dimensions different from those of the basis metal.

Electropolishing - Term used to describe the process of improving the appearance and surface condition of metallic substrates by applying a current to a chemical solution.

Etch - *Noun*—a roughened surface produced by a chemical or electrochemical means.
Verb—to unevenly dissolve a part of a surface or metal.

Faraday - The number of coulombs (96,490) required to deposit one chemical equivalent of a metal. The chemical equivalent value varies depending upon the metal being deposited.

Filter Aid - An inert, insoluble material, more or less finely divided, used as a filter medium, or to assist in filtration by preventing excessive packing of the filter cake.

Flash Plate - The application of a very thin electrodeposit, typically less than 2.54 microns (0.1 mil).

Flocculate - To aggregate into larger particles, to increase in size to the point where precipitation occurs.

Galvanic Protection - See Sacrificial Protection

Hard Chromium - Chromium plate for engineering, rather than decorative applications. Not necessarily harder than decorative chromium, but generally much thicker.

Hydrogen Embrittlement - Embrittlement of a metal or alloy caused by absorption of hydrogen typically during pickling, cleaning or plating operations.

Inert Anode - An anode that is insoluble in the electrolyte under the conditions prevailing in the electrolysis being performed. Typically used in plating baths where there is no convenient source of soluble metal an anode, such as chrome plating.

Karat - A measure of the fineness or purity of a gold deposit. One karat is equal to 1/24 part of pure gold; i.e., a 24 karat deposit is pure gold. Likewise, an 18 karat deposit is 18 parts of gold and 6 parts of another metal.

Mechanical Plating - The application of an adherent metallic coating on a substrate by impingement of finely divided solid particles of the coating to be applied onto the substrate. Alloy deposition is possible via mechanical plating. Also, plating occurs without any hydrogen embrittlement occurring.

Metal Distribution Ratio - The ratio of the thicknesses of metal deposited at two different current densities. Frequently used as a measure of the Throwing Power of an electrolyte.

Metal Turn Over (MTO) - The replacement of 100% of the original nickel metal content of an electroless plating bath.

Microinch - One millionth of an inch, 0.000001 inches. (=0.001 mils)

Micron - One millionth of a meter, approximately one 25th of a mil. (25.4 microns = 1 mil)

Micro Throwing Power- The ability of an electrolyte to deposit metal in pores or very small recesses of substrates.

Mil - One thousandth of an inch (0.001 inches). (= 25.4 microns)

Oxidizing Agent - A compound that causes oxidation, thereby itself becoming reduced.

pH - The co-logarithm (negative logarithm) of the hydrogen ion activity. A measure of acidity (less than 7) or basicity (more than 7) of a solution.

Passivation or Passivity - The condition on a metal that retards its normal reaction in a specified environment. It is typically associated with the metal assuming an electrochemical potential more noble than its normal potential.

Peeling - The detachment or partial detachment of a deposited coating from the basis metal or undercoat layers.

Pickling - The removal of oxides or other compounds from the surface of a metal by chemical or electrochemical action.

Pit - A small depression or cavity in the surface of a part. It can be produced during manufacturing the part, during deposition or by corrosion of the surface.

Polishing - See Buffing

Reducing Agent - A compound that causes chemical reduction, thereby itself becoming oxidized.

Regeneration - *Noun*—The replacement of 100% of the original metal content of an electroless plating bath.
Verb—The act of replenishing a processing bath in an attempt to restore optimum performance.

Resist - A material applied to a part of the surface of an article to prevent metal deposition on or metal removal from that area during chemical or electrochemical processes. Also called "masking."

Ripple - A measurement of the amount of AC current that is present in a DC current. Excessive ripple generally causes passive deposits or hazes in plated coatings. Ideally, ripple should be less than 5% for most plating applications.

RMS - A numerical reference to the smoothness of a surface. Literally, it refers to the Root Mean Square of the height difference between the microscopic peaks and valleys that are evident on a surface when it is viewed under sufficient magnification. The lower the number, the smoother the surface. In other words, the average distance from the tip of a peak to the bottom of an adjacent valley on a part with a 2 RMS finish, would be less than the equivalent distance on a part with a 16 RMS finish. RMS is typically measured with a profilometer, using vertical magnifications from 500x to 200,000x.

Robber - Term used to describe an auxiliary cathode placed near the part to be plated to divert current from concentrating in high current density areas, leading to heavy deposits in these areas.

Sacrificial Protection - The mechanism of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion (for example, zinc plating over a steel substrate). Also referred to as "Galvanic Protection."

Shelf Roughness - Roughness on surfaces of parts that face upward where solids have settled during a processing operation.

Shield - *Noun*—a nonconducting medium or panel used to alter the flow of current in an attempt to provide the most uniform cathode current density possible on the part being plated.

Verb—to alter the normal current distribution by placing a non-conducting medium in the path of the current in a manner that provides a more uniform overall current density on the part being plated.

Spontaneous Decomposition - See Triggering

Step Plating - Non-uniform thickness, striations, or skip-type plating. In electroplating operations this is generally evident in low current density areas, while in electroless plating operations it is typically evident on edges of parts and around holes or perforations in parts. Also referred to as "edge pullback" and/or "worm tracking."

Stray Current - Current that passes through paths other than the intended circuit, such as through heating coils, the plating tank, floor grating, hoist super-structures, etc.

Strike - *Noun*—a thin deposit applied to a substrate or other plated deposit to provide activation or protection from immersion plating. *Verb*—to apply such a coating by plating for a short time in a plating bath.

Strip - To remove a coating from the substrate or undercoat layer via chemical or electrochemical methods.

Substrate - The base metal to be plated.

Taber Abraser - An instrument used to characterize the wear properties of a substrate or plated finish. Test specimens are mounted to a small rotating turntable and subjected to the wearing action of two abrasive wheels, which are applied at a specific pressure, and which rotate in opposite directions. An important feature of the Taber Abraser is the all angles relative to the weave or grain of the material being tested.

Tarnish - Discoloration of a base metal or a plated coating, typically a darkening of the appearance of the basis or plated metal.

Thief - See Robber

Throwing Power - Term used to describe the uniformity of thickness of a plated coating. Electroless baths typically plate with 100% Throwing Power, i.e., the same thickness on all areas of a part in contact with the solution. Electroplating baths invariably exhibit greater thicknesses in high current density areas compared to low current density areas. See also Thickness Distribution Ratio.

Tramming - Spontaneous decomposition of an electroless plating bath, which is typically caused by excessively high concentration of reducing agents in the bath, or the introduction of solid contaminants, such as metal filings or other particles.

Troy Ounce - A unit in the Troy system of weights used for precious metals. Gold and other precious metals are typically measured in Troy ounces. (1 Troy ounce = 31.1035 grams)

Turnover - See Regeneration.

Water Break - The appearance of a discontinuous film of water on a surface, signifying non-uniform wetting and usually associated with the presence of surface contamination on parts.

Work (Plating) - The material being plated or otherwise finished.



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