Electroplating Processes*

Zinc Plating Processes

There are three different types of zinc plating processes: cyanide, alkaline non-cyanide (zincate) and acid chloride. If steel is coated with zinc, the zinc is more active (anodic) than the basis steel. In the presence of corrosive conditions, it is the zinc that corrodes anodically; the steel is cathodic and is protected. Even if small pores or discontinuities develop in the coating, the steel does not corrode for some time, until practically all the zinc has disappeared from the immediate neighborhood of the pore. Because the zinc "sacrifices" itself by corroding as it protects the steel, such coatings are often termed *sacrificial coatings.* Zinc is the most widely used coating metal for protecting steel from corrosion, although it has little purely decorative value.

Cyanide Zinc

In a typical cyanide zinc plating solution, the primary purpose of the sodium cyanide and the sodium hydroxide is to solubilize the insoluble cyanide zinc by forming soluble complex salts of zinc. Another function of sodium hydroxide is to provide good electrical conductivity to the plating solution. Most cyanide zinc baths are operated at room temperature.

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Cyanide zinc is insoluble in water. It combines chemically with sodium cyanide to form the soluble cyanide zinc complex salt. Cyanide zinc also reacts with sodium hydroxide to form a soluble complex hydroxy salt. Most zinc plating solutions are operated with proprietary brighteners, without which the deposits are dull gray. The concentration of the brightener must be controlled. The solutions are normally operated in the temperature range of 85 to 100°F. Elevated temperatures decompose the brighteners, which are relatively expensive. This applies to all types of zinc plating processes. Because of the drop off in cathode efficiency with increase in current density, good metal distribution is achieved.

Alkaline Non-cyanide Zinc

The alkaline non-cyanide solution is also high in pH, but it does not contain any cyanide. It has a soluble hydroxy complex ion of zinc without the cyanide complex salt. The process is somewhat more difficult to control and the deposits are not as bright. Brighteners are required. Without them, the deposits are dull gray and tend to be spongy. One of alkaline non-cyanide zinc's major advantages is ease of pollution control.

Acid Chloride Zinc

The most common acid zinc solution in use today is formulated with potassium chloride. The solution also contains boric acid to buffer or stabilize the pH. The pH is in the range of 4.5 to 5.5, and the bath is normally operated at room temperature. Without proprietary addition agents, however, the deposits are dull, powdery and relatively nonadherent. With the brightener, the deposits are very bright.

The process requires corrosion-resistant equipment and precautions must be taken to insure good rinsing of the plated parts. Otherwise, the entrapped chloride will form white corrosion products on the plated parts.

Copper

Copper Acid Sulfate

The acid sulfate electrolyte is easily prepared by dissolving copper sulfate in water and adding sulfuric acid, chloride and the addition agent as specified. A general purpose solution is used as an underplate for various parts, while a high throw formulation is used in printed wiring board manufacture. These solutions are operated at 24 to 32 °C (75 to 90 °F). Both air agitation and constant filtration are required.

The copper sulfate and sulfuric acid fulfill the function of enabling the electrolyte to transmit current in the pres-

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ence of the optimum quantity of cupric ions. Its concentration is carefully maintained at specified levels to enable the addition agent to perform its function.

The chloride ion also aids in the corrosion of the anodes. Special anodes containing small amounts of phosphorus (to promote smooth anode corrosion) are used. High rates of solution agitation, achieved by introducing low pressure air, are essential to produce bright deposits.

The ability of the acid copper to produce a deposit that is much smoother than the basis metal has great economical significance. Prior to this development, many of the bumpers for automobiles were given a relatively rough polish and then plated with acid copper, which was buffed to a high finish prior to plating with nickel and chromium. The cost of buffing was a major item in the overall cost of producing bumpers. In many cases, the cost of buffing has now been eliminated because of the ability of the copper to preferentially plate into the valleys of the polish marks, thereby producing a highly reflective surface without buffing.

Cyanide Copper

The chemistry of cyanide copper is similar to that of cyanide zinc. In this case, KCN or NaCN is used to solubilize the insoluble CuCN.

Zinc die castings are plated first with a cyanide copper strike followed by a heavy deposit from either a cyanide or an acid copper solution, then with nickel, and finally with a thin deposit of chromium. Attempting to plate the zinc die casting directly with nickel would result in attack of the zinc by the acidic nickel solution. The resulting nickel deposit (if any were obtained) would have no adhesion. The nickel solution does not attack the copper deposit.

Alkaline non-cyanide solutions for plating zinc die castings are currently in the pilot -plant stage, with a few dozen platers reporting success in certain applications. Full acceptance and proof of this substitute process are coming in the near future.

In the three cyanide copper formulations shown, the strike formulation is designed to yield a thin coating over most metal substrates without developing immersion deposits. The high-speed formulation delivers a high amount of thickness in a short period of time, while the "Rochelle" formulation is a hybrid of the strike and high-speed formulas, delivering some of the benefits of each.

Cyanide plating solutions usually contain either sodium hydroxide or potassium hydroxide to provide good electrical conductivity, stabilize the cyanide and to maintain the proper pH.

Additional sodium cyanide above the amount required to form the complex salt is always added. This is called "free" sodium cyanide. Free cyanide is essential for good anode corrosion. If the free cyanide is too low, the anodes become coated with copper oxide and they cease to dissolve. Note that these solutions are operated at elevated temperatures in order to obtain high rates of plating. Also, in some of the high-speed solutions, potassium salts are substituted for the sodium salts.

Copper Plating Processes:

- Acid
- Cyanide
- Fluoborate
- Pyrophosphate
- Alkaline Non-Cyanide

There are many plating solutions for deposition of copper. The most popular are the acid-sulfate and cyanide-based formulations.

Acid Copper

This shows the dramatic effect of the addition agent in producing a highly reflective bright deposit. In the absence of the addition agent, the deposit is dull and salmon in color. One of the unique features of the bright acid copper process is the ability to plate and fill in grooves occurring from polishing. Result: The deposit is smoother than the basis metal.

Cyanide Copper Formulations

	Strike	Rochelle	High Speed
CuCN	10	45	75
KCN	20	60	130
KOH	none	0-10	15-30
Rochelle Salt	none	45	Optional

K_2CO_3 (Not added) [illegible]

Operating Conditions

	Strike	Rochelle	High Speed
Thickness (mils)	0.1	0.5	>1.0
CCD, ASF	10-30	15-60	10-100
CCE, %	10-60	30-70	99+
Temp. (°F)	120-145	140-160	145-180

Three formulations for cyanide copper plating solutions.

Nickel Plating

Watts Nickel

The most common solution used today for nickel plating is the Watts formulation, which is produced with two sources of nickel ions. Small amounts of nickel chloride are added in conjunction with the nickel sulfate. The purpose of the nickel chloride is to improve anode corrosion. Boric acid in the solution stabilizes the pH, or reduces the rate at which the pH increases. The other important ingredient in the solution is the wetting agent, or anti-pitting agent. In the absence of the wetting agent, the liberated hydrogen gas bubbles cling to the surface of the part, leaving unplated areas under the gas bubbles that are readily visible when the parts are pulled out of the solution. In the presence of the wetting agents, the

Other Copper Plating Solutions

Pyrophosphate:
- Printed Wiring Boards
- Plating on Plastics
- Slightly Alkaline (pH 8-9)
- Waste Treatment Problems
- Finite Life
- Difficult Analytical Control
- High Throw

Fluoborate solutions:
- Highest Plating Speed
- Very Low pH (0.5-1.5)
- Expensive
- No Brighteners

Alkaline Non-Cyanide
- More Difficult to Operate
- 2-3 Times as Expensive

Other copper plating solutions that are in common use today. Pyrophosphate is almost exclusively used in the printed wiring board industry in specialized applications, where an acidic solution must be avoided. Fluoborate is used in very high-speed applications such as strip or wire plating, while alkaline non-cyanide is used in various applications where cyanide must be avoided, including decorative and as heat-treat stop-off on steel.

Anodes For Nickel Plating

[illegible]
- [illegible]

Cast/Rolled Carbon Depolarized
- pH 4.5 min. Bagging Recommended

Electrolytic (Pure Nickel)
- Require High Chloride Content

Sulfur Depolarized (0.02% S)
- Preferred, Bagging Still Recommended

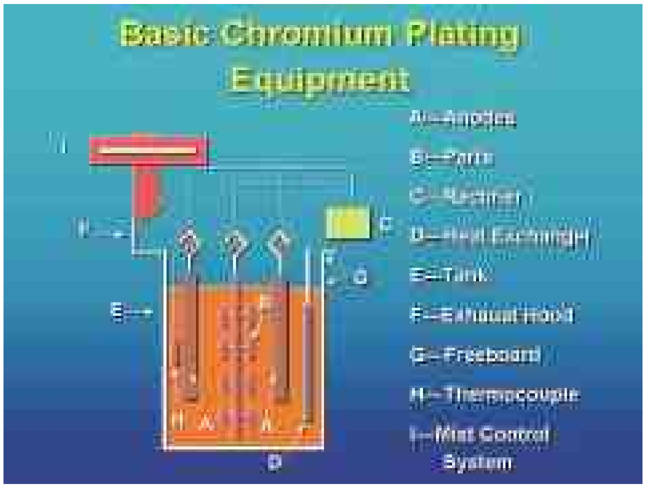
Inert
- C, Pt, Ti, SS (Non Chloride Only)

The use of perforated and expanded wire-mesh titanium anode baskets filled with nickel is the preferred method of satisfying anode requirements. Titanium is preferred because it does not dissolve. The anodes do *anodically dissolve at close to 100 percent efficiency. While several types of nickel anode materials are available, the round nickel anodes containing small amounts of sulfur to promote smooth anode corrosion are the most popular. Anode baskets are always surrounded by bags in order to minimize roughness on the plated parts.*

Decorative Properties of Chromium Plate

- Pleasing Blue-white Color
- High Reflectivity
- Excellent Tarnish Resistance
- Good Corrosion Resistance
- Good Wear Resistance
- Good Scratch Resistance

Chromium has an unusual combination of good properties. Its excellent tarnish resistance and good corrosion resistance are attributed to the presence of a thin, invisible oxide film (called a passive *film) on the surface. Chromium is very hard, which accounts for its good scratch and wear resistance.*



Basic Chromium Plating Equipment

A—Anodes
B—Parts
C—Rectifier
D—Heat Exchanger
E—Tank
F—Exhaust Hood
G—Freeboard
H—Thermocouple
I—Mist Control System

Illustration of the basic components of a chromium plating system.

gas bubbles are continuously released from the surface, and pitting of the deposit is avoided.

A pH of 3 to 4 is considered to be mildly acidic. The solutions are operated at elevated temperatures and at an average cathode current density of about 50 A/ft^2, which is quite high.

In decorative, bright metal plating, the Watts-type brightened solutions are used exclusively. For engineering applications, other solutions are also used. These include an all-chloride and a sulfamate solution. The latter is used extensively for electroforming, because it produces deposits with low stress.

Chromium

The oxide of chromium (CrO_3) is normally called *chromic acid,* which is a misnomer. CrO_3 does, however, become chromic acid when it is dissolved in water. The solution also contains small amounts of sulfuric acid. The preferred ratio of CrO_3 to sulfuric acid is approximately 100 to 1. In the absence of the sulfuric acid, the deposit contains oxides of chromium and is multi-colored, resembling a rainbow. Sometimes a mixture of sulfuric acid and a fluoride compound is used.

Because these are used in small amounts and very little is known regarding how they function, these additives are called *catalysts. A* considerable amount of current is required to deposit chromium.

Chromium Plating System

In a typical hexavalent chromium plating system (see illustration), the anodes (A) are made of a lead alloy, usually containing tin or antimony. The oxygen liberated on the surface of these anodes reoxidizes the trivalent chromium (Cr^{+3}) formed at the cathode to hexavalent chromium (Cr^{+6}). Chromium anodes would not be satisfactory.

The parts to be plated (B) are suspended in the plating solution from a plating rack, which is hung on the cathode bar, connected to the rectifier (C). The temperature of the solution must be controlled within a very narrow range (±2°F) for most decorative plating operations.

Large installations are normally equipped with an external heat exchanger (D), although in-tank heating is also common. Cooling is frequently required during operation because of the high wattage (amps x volts) employed. The solution is pumped from the tank through the heat exchanger and returned to the tank, while steam or coolant flows into the other side of the heat exchanger, controlled by the thermocouple (H).

The tank (E) is usually made of steel and lined with polyvinyl chloride sheet to prevent attack by the hot plating solution. The exhaust hood (F), which is connected to a scrubber, is essential to prevent the chromic acid mist from entering the atmosphere. Besides posing a very real health hazard to the employees, uncontrolled chromic acid spray can also contaminate adjacent plating tanks. In addition to the exhaust, fume suppressants are sometimes used to minimize chromic acid spray. The freeboard (G; distance from top of solution to lip of the tank) should be maintained at 6-12 inches to allow the use of fume suppressants and minimize emissions.

Decorative Chromium

Decorative chromium deposits generally are quite thin. A thickness of 0.25 mm (10 millionths of an inch) is equivalent to about 1/300 the diameter of a human hair. When the use environment changes (*e.g.*, from indoors to outdoors or to a marine environment), heavier deposits are applied on parts subjected to more severe exposure conditions.

Some typical parts that are plated with chromium as the final deposit include household appliances, plumbing fixtures, interior and exterior auto trim, and marine applications. Zinc parts are first plated with copper to protect them from attack when the parts are plated with nickel. Plastic parts are often chromium-plated for appearance and abrasion resistance properties. Chromium also reacts with oxygen to form a thin, invisible oxide layer that prevents further reaction with oxygen. Nickel is not satisfactory as a final finish because it reacts with oxygen in the air and turns to a milky-white appearance.

Decorative chromium can also be plated from a trivalent formulation. Such solutions have been available for more than 20 years, but are now becoming more popular because of regulatory requirements. Newer processes and control methods on the trivalent process have resulted in the production of decorative deposits that can match the appearance of deposits from a hexavalent solution. ***P&SF***

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*For enhanced learning, take a classroom course and benefit from the experience of the instructors. The Intro Course will be held March 21 & 22 in Nashville, TN, and on May 9 & 10 in Kansas City, MO. Details available from the Education Department (1-407-281-6441) or www.aesf.org (click on “Courses” but*ton.)