

# Brass Plating

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## Applications

Brass plating is the most widely used form of alloy plating today. Its origins date as far back as the mid 1600s. Those early solutions were made by first dissolving solid brass in nitric acid and mixing with cyanide. Due to the obvious volatility of such a process, it was not until 1920 that electroplating began to be used as a viable alternative to solid brass. As an alloy of copper and zinc, brass electroplate can produce a pleasing deposit that can range in color from the popular yellow to green to red to white. Its versatility is unmatched in its ability to be used in conjunction with various post-treatments to produce a wide variety of final finishes. The greatest use of brass electrodeposits is as a decorative finish to produce an article that resembles solid brass. The major use is in hardware markets. There are also applications in the fastener, lighting and display fixture industries. Brass has its functional applications as well. It is used in special corrosion situations *i.e.*, marine hardware). Also, white brass has been used in the automotive industry as an intermediate layer on bumpers. Steel wire, which must be drawn, is coated with a brass deposit to utilize its lubricant action to allow the wire to pass through the drawing dies.

As was mentioned earlier, the greatest use of brass plating is decorative. Even this can be broken down into types of applications. One is the brass flash over nickel. The majority of square footage is plated in this manner. It is used to produce a bright finish with the brass color resembling a solid brass object. The other application is a heavy brass deposit, generally greater than 0.0002 in. in thickness. This is widely used in the hardware industry for its ability to be burnished, color buffed, brushed, or antique finished. Whatever the application, if brass is being used as a final finish, it must be coated with a protective film. This is generally a lacquer, but can also be a chromate or benzotriazole coating. Failure to use a protective film on the final brass deposit will result in tarnishing or discoloration of the surface due to rapid oxidation.

## Processes

Brass can be deposited by either rack or barrel operations. It is obvious that since brass is a soft metal, a rack operation will lend itself to brighter finishes, due to a lack of impingements created by the tumbling action of a plating barrel. Both operations can be adapted to the heavier deposits and subsequent post-treatments very well. Flash deposits form a fine-grained crystal structure. As the thickness of the deposit increases, the structure becomes less dense, and therefore duller in initial appearance. However, subsequent coloring or buffing operations will restore a significant amount of brightness.

A typical formulation of a rack brass plating solution contains 9 oz/gal copper cyanide, 2.6 oz/gal zinc cyanide, and 17 oz/gal sodium cyanide. The pH is maintained between 10.5 and 11.0. Temperature is generally 110 to 115 °F, with an average cathode current density of 5 to 10 A/ft<sup>2</sup>, which will produce a deposition rate of 0.0004 to 0.0005 in./hr.

Barrel plating solutions typically run more dilute and at a lower cathode efficiency. Constituents can run from 2.8 oz/gal copper cyanide, 1.2 oz/gal zinc cyanide, and 6.7 oz/gal sodium cyanide. In either rack or barrel plating, the copper-to-zinc ratio is generally held to about 4:1. This will aid in maintaining a good yellow brass color. Average cathode current densities for a barrel run from 1 to 4 A/ft<sup>2</sup> and will produce a deposition rate of approximately 0.00015 to 0.0002 in./hr.

Maintaining the copper-to-zinc ratio closely is important to consistent quality of the brass deposit. Copper metal exists in the solution as a cyanide complex. Cathode efficiency and plating rate depend primarily on the copper content. The zinc metal content can exist in the solution in many forms. It is the form of the zinc complex that determines the rate at which zinc deposits in the alloy. The color of the deposit is then affected by this plate-out rate of the zinc. Free cyanide and pH are factors in determining the zinc plate-out rate.

The free cyanide content is responsible for maintaining uniform copper and zinc deposits that will yield a uniform color across a wide current density range. When the free cyanide decreases, the result is an increase in cathode efficiency, which at a point will begin to create rough deposits. Low free cyanide will also cause polarization of the anodes and limit the current-carrying capacity of the solution. Conversely, as the free cyanide concentration increases, higher current densities will be allowed. However, too high of a free cyanide content will inhibit the deposition process. You will eventually reach a point where the content is high enough to inhibit the deposition process altogether, by stripping the brass as fast as it is plated.

In a brass plating solution, pH ranges from 10.0 to 11.5 and is generally controlled by ammonia and carbonate levels in the solution. As the pH level varies, so does the deposition potential of zinc, and therefore, the plate-out rate, which affects the color of the deposit. Ammonia is used for the main control of the color of the brass deposit. Its mechanism is twofold. First, the hydroxide group (OH) increases the pH, which will increase the plate-out rate of the zinc. Second, the ammonium group (NH<sub>4</sub>) complexes somewhat with the copper in the solution, creating an inhibiting effect on its deposition. Carbonates are both helpful and harmful in the plating solution. They are added in a new solution to aid in conductivity and form a buffer system. As the solution is electrolyzed, the sodium cyanide will break down to sodium carbonate at a rate of 2.16 lb of sodium carbonate for every pound of sodium cyanide consumed. When the carbonates reach 20 oz/gal in the solution, the efficiency of the solution will begin to be reduced. It is important to make the electrolysis of the cyanide the least preferred reaction. This is done by operating at maximum efficiency, so that the metal deposition is the preferred reaction. One needs to maintain good anode area and keep the anode current density under 10 A/ft<sup>2</sup>.

Other materials have been used in trace amounts in order to increase brightness and improve grain refinement. Metallic additives such as selenium, tellurium, lead, molybdenum, arsenic and bismuth will increase brightness. Organic addi-



tives, including quaternary amines, pyridine, substituted sugars and nonionic surfactants will affect both brightness and crystal structure. The use of tartrates and citrates will help prevent anode polarization and permit the use of higher current densities.

#### Post Treatments

As versatile as the brass deposit itself is, there are many more post treatments that may be applied. These treatments produce a range of final finishes from bright brass to colored effects. Regardless of the final finish desired, a post treatment step will be required because of the brass deposit's soft characteristics and affinity to tarnish easily. In the case of bright brass finishes, an anti-tarnish step is required. This is usually accomplished by applying a thin film by dipping the part in either a weak chromic acid or benzotriazole solution. This will produce a temporary protective coating, which will prevent tarnishing and discoloration until a subsequent lacquer can be applied.

Coloration of the brass deposit through a controlled oxidation process is commonly called "antique finishing." The purpose of this is to create a finish that resembles the natural aging process of the brass. Of course, due to refinements in the oxidation processes, the "aged" look has given way to a rich, deep tone that has become very popular in the furniture industry. The antiquing process has evolved from a difficult-to-control, luck-intensive art form into a consistent science. Originally, the brass was oxidized by dipping into a solution containing ammonia, sulfide, carbonate, hydroxide or chlo-

rates. This produced in consistent color, because the dipping solutions were very aggressive and control was nearly impossible. Later, a combination process using calcium polysulfide followed by sulfuric acid helped stabilize the color, but solution control is still a bit of an art. Most antique finishes today come from dip solutions containing selenious acid, molybdenum and copper. These solutions produce very uniform color, and variables in the process are limited to time, concentration and temperature. The color produced from these dipping solutions can range from a light brown to a near black. Following the antique dipping process, the parts generally will then go through either a brushing or highlighting step and relieve the parts of excess oxidation. This produces the rich, deep "antique look." As with the bright finishes, antique brass must receive a coat of lacquer to hold color and resist abrasion.

#### Health Impact

Due to the corrosion properties of brass, it is not recommended for food service applications. There are no other restrictions known for brass plating.

Care must be taken in the handling of copper, zinc and sodium cyanides in the preparation of brass plating solutions. Since cyanide can enter the body by inhalation, digestion and absorption, ventilation is required, as well as protective clothing during handling. Face shields, gloves, aprons, boots and respirators are strongly recommended. The threshold limit value (TLV) for cyanide is 5 mg/m<sup>3</sup>.

#### Environmental Status

Treatment requirements for brass plating operations can be fairly extensive. Wastewaters must first be chlorinated for the removal of cyanide. Once cyanide destruction is complete, high pH precipitation of copper and zinc metals into a hydroxide sludge is generally the practice. New standards adopted by EPA require a lime stabilization of this F006 classified waste to meet TCLP requirements for land disposal. Recycling of plating wastes is becoming a more viable alternative as new technology provides improved reclaiming processes.

Current EPA wastewater effluent standards for existing metal finishing sources discharging to a Publicly Owned Treatment Works (POTW) for copper are 3.38 mg/L for a single day and 2.07 mg/L monthly average. For zinc, the standards are 2.61 mg/L per day and 1.48 mg/L monthly average. For cyanide, 1.20 mg/L daily and 0.65 mg/L monthly. Many municipalities have more stringent requirements. You should contact state or local authorities to determine the appropriate standards for your area.

#### Trends

Brass electroplate continues to be the deposit of choice in the hardware and lighting industries. Alternatives to conventional cyanide brass plating solutions are an ongoing search. Some non-cyanide plating processes are being marketed but have received little acceptance. Electrolytically applied dyes and resins (E-coating) are potential substitutes. Although this is a relatively new technology, the finish is gaining some acceptance. At the present time, however, cost concerns, inability to adapt the process to bulk operations, and the fact that the finish cannot be oxidized or antiqued reduce its versatility, and therefore, will reduce its applications in the field. P&SF