

Silver Plating

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Applications

The largest application of silver plating lies in the holloware and flatware industry, where it functions as a durable decorative finish. Indeed, this use was covered by the first patent granted for silver electroplating in 1840. The solution formulation has remained practically unchanged since that time, but modern decorative silver plating solutions contain efficient chemical brighteners that have virtually eliminated the need for traditional mechanical polishing after plating.

Silver has excellent electrical conductivity, but its corrosion resistance is inferior to other precious metals such as gold. Nevertheless, silver is used as an economical coating on electrical connectors that are designed to operate at higher and less critical electrical loadings.

Recent innovations in techniques for bonding silicon chips has led to an increasing use of plated silver on semiconductor lead-frames. What was once the exclusive domain of gold is now dominated by silver. Gold is used only on the most sophisticated, high-reliability devices.

Perhaps the least recognized application of silver plating is as a bearing surface, most useful under conditions of high load in fluids of low lubricity (*e.g.*, kerosene pumps for jet engines).

Processes

Silver is plated from alkaline cyanide solutions almost exclusively. The metal is introduced as potassium silver cyanide, $\text{KAg}(\text{CN})_2$, which forms when silver anodes dissolve in potassium cyanide solution. Plating solutions usually contain between 10 to 40 g/L (1.3 to 5.3 oz/gal) silver metal and up to 120 g/L (16 oz/gal) free potassium cyanide. Potassium carbonate is added to improve conductivity; initial concentrations of about 15 g/L (2 oz/gal) will increase as a solution ages due to oxidation of cyanide, and reaction with CO_2 in air. When the carbonate level reaches 110 g/L (14.5 oz/gal), steps must be taken to remove the carbonates or the solution will need to be replaced with a new one.

Brighteners include organic compounds, frequently containing sulfur and trivalent antimony. The former, while being generally more difficult to control, do not significantly change the deposit hardness or electrical properties of pure silver. Antimony is easier to control by analysis, but increases both hardness and electrical resistance of the deposit. While SbIII is an effective brightener, SbV, its oxidation product, is not and care must be taken to control the concentration of the correct form. Antimony is also very current-density sensitive. For example, a process may produce 0.1 percent antimony in the deposit at 10 A/ft² but more than 1 percent Sb in the deposit at only 1 A/ft². As a result, black or brown spots develop on parts plated at low current densities.

Selenium is used as a grain refiner, particularly on electrical

or electronic components that do not require full brightness. This element is effective at concentrations below 5 mg/L (ppm) and its effectiveness increases as current density is increased.

Rack and barrel processes normally use silver anodes, and these should be of high purity (99 percent minimum) and possess the correct grain size. Trace anode impurities such as tellurium, bismuth or iron, or an anode grain size that is either too large or too small will cause uneven dissolution of the anode and introduce undissolved particles into the solution, resulting in rough deposits.

Cyanide silver plating solutions will form immersion silver deposits on any less noble metal immersed in them. This is true even though the parts enter the solution "live" (*i.e.*, with voltage applied to them from the rectifier). Immersion deposits cause poor adhesion of any subsequently applied electroplated layer. To avoid this result, a silver strike must be used from a solution with very low silver concentration (usually less than 5 g/L [0.6 oz/gal]) and high free cyanide (normally in excess of 75 g/L [10 oz/gal] as KCN). Parts should be plated at 5 to 15 A/ft² until completely covered with silver. Stainless steel anodes can be used in a silver strike solution so that the silver concentration does not increase.

Lead-frames are selectively plated with silver in specially designed high-speed plating machines. Current densities will depend on specifications and type of machine, but generally are between 350 A/ft² and 3500 A/ft². Platinum, platinized-titanium or platinized-tantalum wires or nozzles are used as anodes in these pieces of equipment.

Cyanide electrolytes tend to break down rapidly when high current densities are employed. Mildly alkaline, well-buffered solutions containing no free cyanide salts have been developed for this application. Silver is still introduced as $\text{KAg}(\text{CN})_2$ and concentrations of 65 to 82 g/L (8 to 10 troy oz/gal) are typical. Solution pH is normally 8.5 to 9.5, with conductivity being provided by potassium phosphate, potassium nitrate, or similar salts. Deposit thicknesses of 175 μm (4.5 μm) are routinely achieved in 1.5 to 5 seconds. All attempts to develop non-cyanide silver plating solutions have failed to provide a process that is as stable, reliable, and robust as the traditional one.

Post-plating

Silver will tarnish in time due to surface sulfide formation. Ornamental items can be coated with a clear lacquer. Recently introduced epoxy and acrylic materials applied electrophoretically are excellent. Naturally, these films cannot be used on components whose surface performs an electrical function.

Treating the silver cathodically in an alkaline chromate solution is sometimes employed for added protection. Slight

discoloration occurs, however, so this technique cannot be used on decorative articles.

Silver deposits on steel substrates that are susceptible to hydrogen embrittlement should be baked at 200 °C (395 °F) in a nitrogen atmosphere for at least 3 hr soon after plating. As part of the rinsing cycle, all silver plated parts should be immersed in water at least 90 °C (195 °F) for 2 min or longer. This procedure ensures removal of cyanide salts entrapped in the deposit. Failure to perform this hot water soak may result in patchy discoloration of the surface as salts "sweat out" at some later time.

Health Impact

The principal toxic materials involved in silver plating are potassium cyanide, silver cyanide, and potassium silver cyanide. When handling these salts, employ proper ventilation, use goggles, gloves, rubber boots and aprons, and a respirator if necessary. The threshold limit value (TLV) for silver is 5 mg/m³.

Environmental Status

Silver should be kept well below 5 mg/L (ppm) in wastewater and cyanide below 1 mg/L (ppm) when measured as free cyanide. However, it should be emphasized that all local, state and federal regulations must be adhered to in this regard.

Conventional treatment (alkaline chlorination to destroy cyanide followed by high-pH precipitation of metal hydroxides) is possible. It is usually economical to reclaim most of the precious metals from the drag-out and rinse systems before they reach the wastewater treatment plant.

Trends

Silver's unique white color will ensure that it will continue to be a fashionable finish for tableware. Minor improvements to the brightener systems may be possible, but the search for alternatives to the traditional cyanide plating solution appears to have been exhausted.

Silver will continue to be substituted for gold on semiconductor lead-frames until chip and wire bonding techniques are developed that require no precious metal at all.