per solutions generally produce the opposite effect, especially on rougher surfaces; however, periodic current reversal (PR) cycles and/or pulse plating with some proprietary additives can provide significant leveling.

Cyanide Copper Plating Solutions Components

Copper cyanide, the source of copper in solution, is not soluble in water. It requires either sodium or potassium cyanide to form the soluble complexes to put it into solution. Further, an excess of the alkali metal cyanide, over the amount necessary to form the complexes, is needed for sound, good quality deposits and good anode corrosion. This excess amount is referred to as “free” cyanide or “uncomplexed” cyanide. Caustic soda (sodium hydroxide) or caustic potash (potassium hydroxide) is added to: (1) increase conductivity, (2) reduce electrochemical attack on steel anode containers or any wetted exposed steel, and (3) reduce the decomposition of cyanide. Caustic additions also have an influence on anode films. Rochelle salts or proprietary additives are commonly used. They provide a finer-grained copper deposit, as well as improving anode corrosion. In addition, they limit the effects of detrimental metallic impurities.

One other chemical found in cyanide copper plating solutions is the alkali metal carbonate. A small amount (2 to 4 oz/gal) is sometimes added to new solutions to provide solution buffering in the cathode film and improved conductivity. In any case, carbonates are formed naturally in the solution with time, due to the decomposition of cyanide and absorption of carbon dioxide from the air. (This is a strong argument against air agitation of the solution with in-plant air.) Eventually, with no drag-out losses, or by using poorly corroding copper anodes or insoluble anodes, or both, carbonates will build up to an excessive amount and have to be removed periodically. When making the choice of whether to use potassium or sodium salts, the plater should consider that potassium salts allow for plating at higher current densities and increase the throwing power (give more even plate distribution), but are more expensive than sodium salts. Additionally, because potassium carbonate is much more soluble than sodium carbonate, the freezing-out process for removing excess carbonate is only effective with sodium salts. Chemical precipitation with calcium salts, usually lime, is used for removal of excess carbonate from potassium salt-based solutions.

Copper strike solutions are used to ensure adhesion. The strike solution is a relatively dilute, low-efficiency solution with a high cyanide-to-copper ratio, thereby producing copious amounts of hydrogen gas. This provides an effective gas-scrubbing, final cleaning step while a thin layer of copper is being simultaneously deposited on the part. Strike tanks are usually smaller than the plating tank and, being good “cleaners”, they act as a sump for small amounts of work-borne dirt, buffing compounds, or other contaminants that are not always removed by the prior cleaning process. In this way, strike solutions protect the larger, higher metal content (and thus more expensive) cyanide plating solution. The smaller strike solution must be effectively filtered to reduce rough deposits. If severely contaminated, the strike solution is more economical to either treat or to destroy and dispose of. Strike solution alkalinity will vary depending on the base metal being plated. A strike solution to be used for zinc die castings, for example, would typically contain 2 to 3 oz/gal copper, 1.5 to 2.5 oz/gal free sodium cyanide, and 0.2 to 0.5 oz/gal caustic soda. A concentration of 2 to 4 oz/gal of Rochelle salts or an equivalent proprietary additive also helps. For applications involving steel, 2 oz/gal caustic can be used. For use over zincated aluminum, omit the caustic and lower the pH to 9.8 to 10.2 with sodium bicarbonate. Strike at a current density of 10 to 25 A/ft^2 for 2 to 3 min. at 110 to 120 °F, then transfer directly to the plating tank without a water rinse. Filter continuously to avoid roughness problems.

Formulations for copper plating solutions vary according to use. High speed solutions for rack plating contain 5 to 10 oz/gal copper (nominally about 6 oz/gal). Free cyanide is an important component and is maintained proportionally to the copper, usually at a 2:1 copper to “free” potassium cyanide ratio. Low free cyanide solutions give improved plating efficiency and higher speed; however, anode corrosion is reduced and deposits may be rough. Caustic potash (potassium hydroxide) at 2 to 4 oz/gal and Rochelle salts at 5 to 6 oz/gal make up the remainder of the basic bath. Anodes must corrode effectively to keep roughness and cyanide oxidation minimal. Proper anode current density range is important. If anodes are bagged, bag weave size is critical and the bagged anode area should be as large as possible.

For barrel plating, solutions vary in concentration from plant to plant. Some platers use high copper, up to 8 to 10 oz/gal. When barrel plating parts that nest or stick together excessively, higher free cyanide can be helpful; a 1.5:1 copper to free cyanide ratio may be used.

Proprietary additives are widely used in cyanide copper plating solutions. These additives improve the color, yield semi-bright or fully bright deposits, control the effects of various impurities, and improve anode corrosion. Brighteners may be metallic, organic, or mixtures. Generally, organic brighteners do not produce as bright a deposit, but after subsequent bright nickel plating, the deposit appears no different than the brighter deposits obtained from the use of metallic brighteners. Avoid addition of metallic brighteners when plating for carburizing stop-off uses as well as for some oxidizing post treatments.

Post Treatments

Fatigue strength is reduced by any hydrogen embrittlement that is introduced during the copper plating. To relieve hydrogen embrittlement when plating on hardened steel (Rockwell C35 or higher), parts are baked within 4 hr after the final plating operation at 191±14 °C (375±25 °F) for 24 hr. When copper deposits are to be treated with a chromate conversion coating, baking must be done before chromating. Baked parts may require a brief dip in 0.25 to 0.50 percent by vol. nitric acid to remove heat oxides before chromating. When copper plating is used as an undercoat, the deposit may require cleaning and activating before subsequent plating, in order to ensure adhesion.

Health Impact

Although copper is an essential element for health, excessive amounts can produce harmful effects. Exposure to the plated metal and exposure to the cyanide copper plating solution present very different situations. Copper metal in its plated form presents no unusual health problems. The current OSHA permissible exposure limit (PEL) in the workplace for copper dusts is 1 mg/m^3 averaged over an 8-hr shift. Dusts could result from dry grinding of copper plated goods; however, this may be an unusual possibility.

With regard to cyanide, the OSHA PEL is 5 mg/m^3 of air averaged over an 8-hr shift. Cyanide dust is possible when handling any of the cyanide salts, while making additions or making up new solutions.

Plated parts must be rinsed thoroughly to flush out any entrapped plating solution. Any contact of cyanide with acid is to be avoided, as it forms the very hazardous hydrocyanic gas (HCN). The LD$_{50}$ for rats is 10 mg of cyanide per kilogram of body weight of the test animal. People working with cyanide plating solutions should be thoroughly trained in their safe use.

Environmetal Status

Wastewater limits under EPA's Metal Finishing Regulations for copper are 3.38 mg/L for a single day and 2.07 mg/L as a monthly average. Total cyanide is 1.20 mg/L for a single day and 0.65 mg/L for a monthly average. These are the limits published as compliance requirements that went into effect July 15, 1986. Specific requirements as controlled by local regulations can be much more stringent; each facility must deal with local as well as state and federal requirements. One facility discharging into surface waters in Ohio is limited to 23 ppb (23 µg/L) as an average with a 35 ppb daily maximum. A Detroit facility, discharging into the city sewer system, has a pretreatment daily maximum 24-hr composite sample of 4.5 mg/L of copper and 2 mg/L of cyanide.

Copper-bearing sludges generated by platers must be disposed of in an EPA-approved manner. Recent changes in disposal regulations of metal-hydroxide sludges are coming into effect and require additional fixation to prevent re-dissolution. Platers have to keep up to date in this changing area.

Trends

The volume of copper plating has decreased in decorative applications with the reduction in the volume of plated automotive trim. Where copper is still specified on automotive parts, however, copper thickness requirements have been increased to give better protection on exterior parts. Some automotive specifications either require or suggest that a major portion of the copper plate thickness be from bright acid copper, and the use of cyanide copper continues to decrease. Cyanide copper used with periodic current reversal (PR) cycles, pulse plating, and non-metallic, non-sulfur brighteners has been used to provide equal protection with better plate thickness distribution, but it has not found significant usage in this case to date.

Plating with cyanide copper will continue with probably little change in volume until a suitable, and environmentally acceptable, system can replace it. The ability to plate an initial coating with good adhesion to light metal base materials and good throwing power and coverage in both rack and barrel plating applications are the key features of cyanide copper systems that continue to justify the safety measures required in its handling and the associated cyanide destruction and disposal costs.