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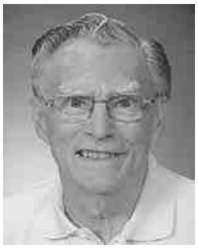

Copper Plating:
Part I

Atomic number 29
Atomic weight 63.546
Melting point 1356.15°K (1083°C; 1981.4°F)
Ionization energy 745.5 kJ/mol
Density 8.933 g/cm^3
Oxidation states +1 and +2,
Electron shell configuration $1s^2 \cdot 2s^2 \cdot 2p^6 \cdot 3s^2 \cdot 3p^6 \cdot 3d^{10} \cdot 4s^1$

Why copper plate? Copper plated onto any metal serves as a protective layer, not in the sense of corrosion protection, although it does add to corrosion protection, but as a layer that lowers stress and provides a crystal orientation favorable to the start of subsequent plated layers. The first layer deposited onto a metal substrate tends to follow the crystal structure of the surface material, then changes to the characteristic structure of the metal being deposited, in this case, copper. The resulting stress is very high in the transition zone. Since copper is very ductile, the stress induced by the different structure of the basis metal is borne by the copper interface. This reduces the overall stress from subsequent plated deposit. Hydrogen embrittlement is also lowered somewhat when cyanide or pyrophosphate copper plating is used.

History

The name **copper** comes from the Latin word *cuprum*, which means "from the Isle of Cyprus."

Archaeological evidence suggests that people have been using copper for at least 12,000 years. 7,000 years ago the Romans got their copper from the island of Cyprus. Today copper is found in the United States, Chile, Zambia, Zaire, Peru and Canada. (I read another paper that told about the use of copper 1,800 years ago in Mesopotamia. It is possible and likely that immersion (chemical replacement) plating took place very early in history.)

The first authentic recorded use of copper plating by electrodeposition is ascribed to Henry Bessemer, better known as a pioneer in steel manufacture. In 1831 Bessemer plated castings of insects, frogs and plants by immersing them in copper sulfate solution on a zinc tray. Electroplating with an external source of electricity followed quickly in 1836.

Early on copper was used for electrotyping and reproducing other metallic shapes and non-metallic shapes. In 1840, J Wright, a Birmingham surgeon, developed the first cyanide plating solution, for both copper and silver electroplating. Elkington patented them in the same year.

Bright acid copper plating began about 1940 by Phillips and Clifton using thiourea and molasses. Later, the Dayton Bright Copper Co. used acetylthiourea and sulfonated substituted thioureas. Udylite used a hydantoin and mercaptans sulfonated by propane sulfone. Complex amino dyestuff was used in conjunction with a colloidal aromatic amine to produce bright leveling acid copper deposits. Today there are similar compounds used for brightening and leveling.

Characteristics of popular copper plating solutions

Cyanide copper

Cyanide copper plating solutions are best for throwing power and covering power, as long as the free cyanide is not too high or too low (Range: 1.5 to 2.0 oz/gal; 11.2 to 15.0 g/L). Lower free cyanide results in higher efficiency and faster plating, but less throwing power. To lower the free cyanide, add copper cyanide. One oz/gal of copper cyanide will lower the free sodium cyanide by 1.1 oz/gallon. One oz/gal of copper cyanide will lower the free potassium cyanide by 1.45 oz/gal. Higher free cyanide (2.0 to 2.25 oz/gal; 15.0 to 16.8 g/L) results in better throwing power but less efficiency. Very high free cyanide (3.5 to 4.0 oz/gal; 26.2 to 30.0 g/L) results in slow plating rate or no plating at all. Cyanide copper plating solutions are easy to operate and forgiving of less-than-perfect cleaning. Cyanide copper strikes are used prior to copper plating to provide a good clean surface for the copper plating solution to do its best job. Strikes are necessary when plating over steel and zinc die-castings to prevent immersion (non-adherent) plating. Copper strike solutions are formulated to have lower copper and higher cyanide and, for zinc die-castings, a pH less than 12. For steel, 1.0 to 2.0 oz/gal (7.5 to 15.0 g/L) sodium hydroxide added to in the solution.

Acid copper

Sulfuric acid copper plating solutions provide rapid deposition and less throwing power as compared with cyanide copper and pyrophosphate copper solutions. Acid copper can be made to level and be very bright. Additions agents help microthrowing power when used for through-hole plating on printed circuit boards and for plated plastics prior to bright nickel and chromium. The solution is easy to use and maintain. The chloride content is the only critical ingredient that must be controlled, between 40 and 70 ppm. Therefore it is not wise to use hydrochloric acid prior to acid copper plating. Addition agents are available for leveling, brightening and "high throw" formulations that consist of a lower copper content and higher sulfuric acid. A cyanide or alkaline non-cyanide copper strike is required when plating onto steel, aluminum or zinc die-castings.

Methansulfonic acid

Another type of acid copper uses methanesulfonic acid. These solutions are similar to sulfuric acid copper but the acid is mild by comparison, making it somewhat safer to use. The process allows a rapid deposition rate and with additions agents, the deposit can be level and bright.

Fluoboric acid

This acid copper solution provides the opportunity to use even higher current densities than most other formulations, producing very high deposition rates. Higher rates are reported over acid sulfate and methanesulfonic acid copper plating systems. The deposit characteristics are similar to acid-sulfate copper and methanesulfonic acid systems. However, fluorides are toxic and dangerous. Extreme care must be used in dealing with fluoboric acid systems even though it is a weak acid. Fluorides can be easily absorbed through the skin.

Pyrophosphate copper

Pyrophosphate copper plating solutions provide good throwing power (not as good as cyanide copper) and are used for printed circuit boards and applications where cyanide copper or acid copper should not be used. There are formulations that can be used as a copper strike, going into the solution with a live cathode. There is a risk of an immersion copper coating if the aforementioned step is not used, and that will lead to poor adhesion.

New alkaline non-cyanide formulations

The newer non-cyanide alkaline baths introduced in 1991 are claimed to have the ability to plate directly onto steel, zinc, aluminum and white metal with no danger of immersion deposition. The solution can be used as a copper strike, replacing cyanide strikes on steel and zinc die-castings prior to other copper plating solutions or used alone for thick deposits. The operating conditions are: 0.8 to 1.8 oz/gal (6.0 to 13.5 g/L) copper; pH 9 to 10; temperature, 110 to 140°F (43 to 60°C); current density, 5.0 to 30.0 A/ft^2 (0.53 to 3.23 A/dm^2); air agitation and OFHC anodes. This non-cyanide solution is sensitive to impurities such as lead, silver and iron. Lead and silver impurities are removed by dummy plating at 0.5 A/ft^2 (0.05 A/dm^2). Organic contamination is removed by peroxide and carbon treatment. Surface preparation is critical when compared with cyanide copper. Cyanide copper solution will clean many oils and other soils whereas acid, pyrophosphate and other non-cyanide solutions will not clean. The waste treatment procedure uses calcium chloride followed by filtration.

Uses for copper plating

Among the many uses of copper plating are:

- Stop off for heat-treating
- Electroforming such as molds, records, CDs, wave-guides and art objects
- Make non-conductors conductive.
- Electronics applications, including trench filling, via filling, circuits, printed circuits, through-hole plating, pattern plating and additive circuits
- Coating steel wire
- Continuous strip plating
- Electrical devices
- EMI and RFI shielding
- Plating on steel for buffing
- Plating zinc die-castings
- Undercoat for nickel plating and pennies.

I am sure there are more uses for copper plating. What have I missed?

Troubleshooting Cyanide Copper Plating Solutions

Do's and don'ts

Do:

1. Use a filter. A filter is essential for good copper plating. Continuous filtering with occasional pump out and filter back
2. Have a storage tank equal to, or somewhat larger than the size of the plating solution tank.
3. Use steel hooks for anodes (Never Monel).
4. Control solution by frequent analysis.
5. Provide cover for the tank. Keep dust out of the plating solution.
6. Provide adequate cleaning of parts to be plated. Keep buffing compounds, oils and other soils out of the solution.
7. Remove fallen parts from the bottom tank every day.
8. Provide good temperature control.

Don't:

1. Install polishing or buffing or blasting equipment in the immediate area, preferably not even in the same room or building.
2. Use or try to plate anything that has silicone lubricants on it. Don't use silicone in the same building. Silicones are difficult or impossible to remove in the cleaning process.
3. Forget that cyanide is poison. And use proper waste treatment methods.

Additional Notes:

1 ounce of copper cyanide requires 1.1 oz of sodium cyanide, and 1 oz of copper cyanide requires 1.45 oz of potassium cyanide to form the proper complex without adding any free cyanide.

To lower the free cyanide by 1.0 oz/gal, add 0.9 oz/gal copper cyanide. Or add 0.7 oz/gal copper cyanide to lower the free *potassium* cyanide by 1.0 oz/gal.

Rochelle salt is a great help in keeping the anodes working properly. Also proprietary additions equivalent to Rochelle salts work well. ***P&SF***

The preceding column was adapted from an online article written by Mr. Baudrand for the Technical Library in the website Plateworld - A Directory of Surface Finishing Suppliers & Plating Shops, www.plateworld.com – Ed.

Troubleshooting Chart – Cyanide Copper

CAUSE	REMEDY
Rough deposits:	
Low free cyanide	Adjust to proper amount (1.5 oz/gal; 11.2 g/L).
Insufficient cleaning	Inspect cleaned parts be sure all compound is removed from recessed areas, threads and holes.
Dust or foreign matter	Filter the solution.
Drag-over of acids or cleaners	Improve cleaning.
Precipitated salts from hard water	Use treated water.
Organic contamination	Add wetting agent (surfactant). Treat with hydrogen peroxide. Carbon treat and filter.
Polarized Anodes:	
Low Temperature	Adjust temperature controller.
Low free cyanide	Add cyanide.
Organic contamination	Carbon treat and filter.
Zinc Contamination (deposit has brassy look)	Dummy plate at low CD, 2 to 3 A/ft^2. Add anodes, preferably OFHC.
Low copper metal content	Add copper cyanide along with the appropriate amount of cyanide.
Chromium contamination	Treat with sodium hydrosulfite, ¼ oz/100 gal copper plating solution. Repeat if necessary
Pitting	Add surfactant (wetting agent). Chromium contamination, see above.
Difficulty buffing copper	Free cyanide too low, add cyanide. Organic contamination, see above. Low or unbalanced addition agents. See above under “Pitting.” See above under “Roughness.”
Burning:	
High free cyanide	Add copper cyanide.
Low temperature	Raise temperature. Increase agitation. Lower current density. Adjust anode-to-cathode distance to 6”.
Low copper content	Add copper cyanide with additional cyanide.
Low agitation	Increase agitation.
Low caustic content	Add sodium or potassium hydroxide.
Organic contamination	Treat as above.
Unbalanced addition agents	Contact manufacturer.
Low Cathode efficiency:	
High free cyanide	Add copper cyanide.
Copper metal too low	Add copper cyanide.
Chromium contamination	See above, under “Polarized anodes.”
Plate peeling:	
Chromium contamination	See above, under “Polarized anodes.”
Insufficient cleaning	Improve cleaning cycle.
Contaminated rinses	Use clean rinse water.