Deposit properties are also periodically checked and today are the most commonly used basis for deciding when to carbon treat a solution to remove organic contamination.

Pyrophosphate Copper

Typical pyrophosphate formulations are shown below:

General Purpose

Copper	3-5 oz/gal
Pyrophosphate	20-33 oz gal
Weight Ratio—	-
Pyrophosphate:Copper	
Ammonia	0.1-0.4 oz/gal
Nitrate	0.6-1.3 oz/gal
Oxalate	2.0-4.0 oz/gal

Printed Circuit Applications

Copper	3.6-4.4 oz/gal
Pyrophosphate	21-33 oz/gal
Weight Ratio—	-
Pyrophosphate:Copper	7.0-8.0 oz/gal
Ammonia	0.1-0.4 oz/gal
Nitrate	0.6-1.3 oz/gal
Oxalate	2.0-4.0 oz/gal
Proprietary Additives	As required

The formulation for printed circuit applications is more tightly controlled than the corresponding general purpose solution.

Copper is present as a pyrophosphate complex and is replenished via anode corrosion. Occasional addition of the complex may be necessary to keep the solution within limits. The excess pyrophosphate is required to solubilize the copper and increase solution conductivity. Ammonia is added to improve deposit uniformity and brightness and aid anode corrosion. The nitrate reduces polarization at higher current densities and the oxalate is a buffer. For most printed circuit applications, proprietary additives are used to enhance physical properties.

Pyrophosphate solutions are operated between 120 and 140 °F. Higher temperatures increase maximum current density and improve solution conductivity. The pH range is 8.2-8.8 and is kept in range through the addition of pyrophosphoric acid or potassium hydroxide. Low pH will precipitate copper pyrophosphate while high pH will cause precipitation of copper hydroxide.

Both formulations are operated with vigorous air agitation to obtain the required brightness and uniformity. As in acid sulfate, agitation air must be supplied by a blower rather than an air compressor.

Anode-to-cathode ratios should be at least 1.2 to ensure uniform copper dissolution. Anodes are generally oxygenfree high conductivity (OFHC) copper. A copper pyrophosphate plating solution forms ortho- phosphate by hydrolysis. This hydrolysis increases with increasing temperature. When the concentration of orthophosphate in the solution reaches 100 grams per liter, the solution must be diluted or discarded.

Solution makeup proceeds similarly to the procedure described earlier for acid copper sulfate. The dummy plate to remove metallic impurities is done at $3-5 \text{ A/ft}^2$.

The operating solution should be filtered through 5 micron filters at a rate of 1-3 turnovers per hour to remove solid contaminants.

Pyrophosphate solutions can be operated at a wide range of current densities (10-80 A/ft^2). The range for an acceptable

deposit is determined by the solution formulation and the cell geometry. Throwing power and current efficiency drop sharply with increasing current density.

Periodic solution analysis must be performed and can be done in a straightforward manner. Copper is measured either by atomic absorption (AA), titration, or by electrochemical techniques. Pyrophosphate is determined by titration. Ammonia, which is replenished by the addition of ammonium hydroxide, is analyzed by the Kjeldahl distillation method.

The key to successful operation of a copper pyrophosphate solution is in the control of the additives. Pyrophosphate solutions are considerably more sensitive to organic contamination than are acid copper sulfate solutions and, therefore, the additives must be more closely controlled. More frequent carbon treatment is also necessary with pyrophosphate solutions. The CVS method of additive analysis mentioned in the acid copper sulfate section was originally developed to control additives in pyrophosphate solutions. The technique, which is too complex for discussion here, is widely in use today to determine additive concentration in both types of plating solutions. The ease of analysis, but not necessarily interpretation, permits frequent additive analysis and additions and yields better control. Additives for copper pyrophosphate baths are often added both on a time and amperehour basis, with adjustments being made every few hours based on CVS analysis.

Health Impact

Neither acid sulfate nor pyrophosphate copper plating solutions, their constituents, nor their deposits are particularly toxic or noxious. Both solutions should be properly ventilated to protect operating personnel, and normal storage and handling precautions should be observed with the constituents.

Environmental Status

Copper is the only constituent of these plating solutions that is controlled by the EPA. As with most other controlled metals, the allowable discharge limits have fallen sharply in recent years. Most POTWs require a ppm in the effluent stream. In most shops the plating solution and its associated rinses are but one of many processes that contribute copper to the waste stream. Routine waste treatment by pH adjustment and clarification, ion exchange, or membrane technology has proven successful in meeting these requirements. Sludge from plating shops is classified as F006 waste and is affected by the land ban legislation of August 8, 1988. Stabilization of copper bearing sludge is required.

Trends

Acid copper sulfate continues to be the solution of choice, where choice is allowed, in printed circuit shops today. With increasing trends toward more complex, surface-mount boards, the demand for circuit uniformity and higher aspect ratio holes has sparked considerable attention to additive control and research. The industry has recently observed the introduction of several full-build electroless copper solutions with superior physical properties. Although the electroless solutions are still considerably more expensive than their electrolytic counterparts, there are designs in existence that cannot be manufactured with today's electrolytic technology. Since this trend is likely to continue, suppliers are seeking new additives and control methods to improve deposit uniformity and throwing power.