

# Acid Sulfate & Pyrophosphate Copper Plating

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## Applications

Both acid sulfate and copper pyrophosphate copper plating solutions find use today in several areas. Acid sulfate solutions are the predominant copper plating solutions used in the printed circuit industry, although pyrophosphate solutions are specified by some Federal agencies where ductility of the deposit is of paramount importance. Recent advances in additive systems have resulted in comparable physical properties from acid sulfate solutions. Both solutions are also used in the plating-on-plastics industry after an electroless strike has been applied to the nonconductive surfaces.

Acid sulfate copper solutions are also used to plate steel wire, stainless steel cooking utensils and zinc die castings (after a cyanide copper strike). Pyrophosphate solutions are often used in electroforming applications and in the plating of zinc, aluminum, and steel die castings.

Pyrophosphate solutions are alkaline and are, therefore, less corrosive to plating equipment than acid sulfate. The deposit has excellent physical properties. The solutions have good throwing power, allowing surface-to-hole ratios of 1:1 to be achieved. Copper pyrophosphate solutions are, however, very difficult to control and are more difficult to waste treat than their acid sulfate counterparts.

Acid sulfate solutions are corrosive and must be used in equipment designed for them. With appropriate additives, they are easy to control, have good throwing power (surface-to-hole ratios close to 1:1 can be obtained) and are easily waste-treated.

## Processes

### Acid Sulfate Copper

Typical formulations for acid sulfate copper solutions are shown below:

#### General Purpose

Copper sulfate .....	25-40 oz/gal
Sulfuric acid .....	5-10 oz/gal
Chloride ion .....	30-60 ppm
Anode:Cathode ratio .....	1:1

#### High-Throw

Copper sulfate .....	8-12 oz/gal
Sulfuric acid .....	20-30 oz/gal
Chloride ion .....	30-60 ppm
Anode:Cathode ratio .....	2:1

As can be seen from the difference in the formulations, high-throw solutions result from increasing the conductivity of the solution by increasing the acid/metal ratio. The purpose of the chloride ion is to promote anode corrosion. Proprietary additives are normally employed to level and brighten the deposit, improve the throwing power and enhance the deposit's physical properties.

The solution is made up by adding the constituents to deionized water. Depending on the purity of the chemicals

used, the solution may then be carbon-treated to remove any organic contamination. Carbon treatment consists of treating the solution with both hydrogen peroxide and activated granular carbon. Details of this procedure may vary somewhat with the additive system being used and are available from the additive suppliers.

The purified solution is then pumped back into the plating tank, which has been loaded with cleaned anodes. Metallic impurities are then plated out by dummy plating at low current density (5 to 15 A/ft<sup>2</sup>) for 2-4 hours. The proprietary additives are then added per the recommendations of the additive supplier.

Acid sulfate solutions are operated at essentially room temperature. Burned deposits can result from low temperatures and dull plating and increased additive consumption from high temperatures. Most plating is done at 20-30 A/ft<sup>2</sup>. This will yield 1 mil (.001 in.) of plated copper in about 40-50 min. The solution operates at close to 100 percent current efficiency. Faster plating rates can be achieved with increased solution agitation, slight formulation modifications, and specialized equipment. Rectifiers must be specified to have less than 5 percent ripple. Excessive ripple will cause increased additive consumption and rough plating.

Air agitation is necessary and cathode agitation, either paddle or knife-edge, is recommended. Agitation air should be supplied from a blower with filtration and organic vapor removal, not from a compressor. Compressed air can introduce contaminants into the solution that will destroy its effectiveness.

Anodes for acid sulfate are either bar or nugget. If nuggets are used, titanium baskets are necessary. The copper anodes must be of high purity and must contain .02-.08 percent phosphorus. The phosphorus aids anode corrosion. The anodes must be cleaned prior to insertion into the solution. To prevent fines from the anodes from depositing on the cathode, anodes are usually bagged in napped polypropylene bags. In use, a dark black film will form on the anodes. This oxide film is necessary for good plating and, if disturbed, will cause increased additive consumption and rough plating.

Acid sulfate solutions should be continuously filtered through a 5-micron polypropylene filter to remove fines and other solid contaminants that may enter the solution. Filtration rate should be from 1 to 3 turnovers per hour.

The plating solution should be periodically analyzed to determine replenish requirements. Copper can be done by atomic absorption (AA) or by titration with EDTA, sulfuric acid by titration with a suitable base, and chloride by titration with silver nitrate. Additives are normally replenished on an ampere-hour basis per the recommendation of the supplier. Lately, more stringent requirements on the deposit have brought about more sophisticated analysis techniques for additives such as cyclic voltammetric stripping (CVS) or high performance liquid chromatography (HPLC). The use and interpretation of these methods will vary with the additive system used.



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 .....	7.0-8.0
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 oxygen-free 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 A/ft<sup>2</sup>.

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<sup>2</sup>). 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 ampere-hour 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. P&SF