# 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 l:l 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$^2$) 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$^2$. 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.