Advice & Counsel



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Training "Colombo"-Part X Acid Copper (continued)

Columnist's Note: This is a continuation of last month's article, "Acid Copper." The letter requesting advice concerned a company that plates zinc diecastings and had a problem with blisters. They also asked for guidance on analyzing chloride in the solution. Please refer to the December issue of P&SF for further review.

Function of Ingredients

Copper Sulfate

Copper sulfate is the source of the metal which is plated out on the work. It is important that the concentration of copper sulfate be maintained within the recommended limits. In bright, high leveling applications, the copper should not be allowed to decrease below 20 oz/gal. Such concentrations may cause burning or dull deposits at high current density areas. In printed wiring board applications, the copper content is intentionally lowered to around 10 oz/gal (75 g/L), as the sulfuric acid is increased, in order to obtain almost perfect throwing power (thickness in drilled holes equals thickness on top of laminate).

High concentration of copper sulfate is not a problem until the concentration exceeds 40 oz/gal. At concentrations above 40 oz/gal, the anode bags may be coated with copper sulfate crystals and the anodes may no longer properly dissolve. The plating may look fine, however.

SulfuricAcid

The sulfuric acid provides conductivity and aids in the dissolution of the anodes. The sulfuric acid varies in concentration depending upon the application. For the type of work being done, he needs a high degree of leveling and brightness, more than throwing power. Printed wiring board manufacturers, in contrast, need a high degree of throwing power, and leveling is unnecessary. Therefore, for this type of application, keep the acid much lower in concentration than a PWB facility.

For high leveling/high brightness applications, concentrations of sulfuric acid higher than 13.5 oz/gal can produce high-current-density area burning and anode passivation (resulting in depletion of copper from the solution). Concentrations below 8 oz/ gal can result in high plating voltages, slow plating speed and dull deposits in low-current-density areas.

It is not likely that normal operation of the plating solution will result in high sulfuric acid concentration. This problem usually results from a mistake in making an addition. It is therefore always an excellent idea to divide any addition in half and see the result (or have the solution reanalyzed) before adding the second half.

Chloride Ion (CI-)

The chloride ion promotes anode corrosion, but concentrations above 150 mg/L can produce dull deposits, reduce leveling and passivate the anodes. Concentrations below 50 mg/ L can cause rough or striated deposits and step plating in high current density areas, but this depends to a large degree on the additives used. In the rotogravure industry, for example, the acid copper solutions are operated with about 3-5 mg/L of chloride, as the controlled hardness of the copper deposit is most important.



Microscopic cross section, 400X, blistered nickel-silver electroplate over zinc diecasting caused by inadequate copper strike.

High Chloride Concentration

If the chloride concentration is too high, brightness and leveling of the deposit fall off and may be restored by excessive additions of brightener. How much chloride is too high depends upon the formulation of the additives. Some additive systems can tolerate up to 150 mg/L of chloride. When the chloride concentration exceeds 150 ppm, high current density patterns or dullness may result. At still higher concentrations, a whitish film forms on the anodes and causes excessive anode polarization. Visual inspection of the anodes will indicate the relative concentration of chloride ions. If chlorides are normal, the anodes will appear black in color. A white or gray anode film indicates an excess of chloride ion.

Brightener/Additives

Numerous additives for improving hardness, brightness, leveling, grain size and, in the case of electroforming, reduction in tendency to deposit "trees" at high-current-density areas, have been developed and are available.



Chart for determining chloride, courtesy of Donald Sales & Mfg.

Always add just enough additive to get the job done. Operating at too high additive concentration over a long period of time will result in organic contamination, which will require carbon treatment.

In many additive systems, a ratio between various additives should be maintained. This ratio should be monitored using analytical methods or a Hull cell. Inorganic Impurities

The copper sulfate electrolyte has good tolerance toward many ionic impurities due its high acid concentrations. For instance metals such as nickel, cobalt, zinc and iron will tend to build up in solution rather than plate-out with the copper. These following contaminants may cause trouble:

Aluminum (dull deposits above 50 ppm) Antimony (brittle deposit above 20-100 ppm)

Calcium (rough deposit, above 100 ppm) Iron or nickel (reduced conductivity and throw above 1000 ppm)

Tin (dark deposit above 50 ppm) Chromium (dull deposit above 100-1000 ppm)

Zinc (brassy deposit in low current density areas above 2,000 ppm).

Because copper is a noble metal, removal of metallic contaminants is not easily accomplished. If maximum metallic contaminant concentrations are reached or exceeded, there is no easy method for their removal, and the plating solution will have to be replaced or diluted.

Organic Impurities

Organic impurities in copper sulfate electrolytes are often more of a problem than inorganic impurities. They can influence the appearance of the plating, yielding dull deposits in low current density areas. If a Hull cell panel is dull in the low current density area and then is brighter after a brief carbon treatment of the Hull cell solution (after addition of additives at normal concentrations), the problem may be organic contamination.

The most common source of organic contamination is breakdown of organic additives, and contact with unsuitable rubber or plastic hardware. Organics are typically removed by treatment with activated carbon. In severe cases, a hydrogen peroxide treatment may also be required.

Maintenance & Control

Under normal operating conditions, the sulfate bath should require very

little adjustment. In some operations, where loss of solution by drag-out is small, there may be a slow increase in copper concentration. This may require occasional dilution. Monitoring needed is for copper sulfate, sulfuric acid and chloride ion content. A simple method of control is achieved by the use of a hydrometer. For each degree Baume' below 20°, add 12 lb of copper sulfate and 30 fluid oz of sulfuric acid to a 150gallon tank. If an ampere-hour meter is installed on the rectifier, some additive additions can be made based on the readings of the meter. Otherwise, such additions can be based on recordkeeping (amperes times hours logged for all parts plated) or by using a Hull cell.

Analytic procedures for copper and sulfuric are easily performed, and are

not covered here. However, you asked about an easy procedure for chloride, and we came across one:*

Chloride Content-Visual Method

- 1. Place 75 mL sample in a 100 mL graduated beaker that has been rinsed thoroughly with DI water and then dried.
- 2. Add 5 mL of concentrated nitric acid, mix well.
- 3. Add 1 mL of 0.1 N silver nitrate, mix well.
- 4. Place an empty graduated beaker over a sheet of newspaper containing standard newsprint.
- 5. Pour the solution from step 3 into the beaker until the newsprint is unreadable. Measure the mL of solution poured into the beaker.
- 6. Determine the chloride content using the accompanying graph.

An instrumental method I have used for many years is:

Chloride Content-

Spectrophotometric Method

- 1. To each of two stoppered, glass 25mL volumetric flasks, identified arbitrarily as A and B, add 5mL of sample.
- 2. Add 5 mL of concentrated nitric acid to each flask.
- 3. Add 10 mL ethylene glycol to each flask, and swirl to mix.
- 4. Add 1 mL of 0.1 N silver nitrate to only one of the flasks. The solution in this flask will be used for the absorbance reading of the sample. The solution in the flask that does not contain silver nitrate will be used to set the spectrophotometer to zero.
- 5. Dilute both flasks to volume, then stopper and mix well. Wait between 5 and 15 min (no more than 15).
- 6. Set the spectrophotometer to zero absorbance at a wavelength of 440 nm, using the sample that did not have silver nitrate added to it.
- 7. Measure the absorbance of the sample that did have silver nitrate added to it at a wavelength of 440 nm.
- 8. Calculate the chloride concentration, in mg/L, by multiplying the absorbance reading from step 5 by 152.

Example: If the absorbance is 0.244, the chloride concentration = 0.244 x 152 = 37.1 mg/L (ppm). PRSF

^{*} Donald Sales & Mfg. Co., Menomonee Falls, WI.