Acid Copper—Application & Keys to Consistency*

Written by Larry T. Rudolph & compiled by Dr. James H. Lindsay, AESF Fellow

"Many acid-copper applications utilize addition agents to produce special deposit characteristics. Historically, bright acid-copper has been used for its leveling properties on polished steel, for its improved corrosion resistance on die castings, for its wearability on rotogravure and for its elongation properties on electroplated plastics.

"Bright acid-copper exhibits exceptionally high leveling characteristics. On polished steel applications (such as on automobile [and truck] bumpers), it substantially reduces or eliminates intermediate buffing operations and permits the use of a coarser, final polishing step on the base steel prior to electroplating.

"Acid-copper electroplating applications are becoming more popular every day, especially in the field of plating on plastics. One of the greatest advantages of acid-copper is that it is the easiest solution to control and troubleshoot ... if it is handled correctly. A consistent and efficient maintenance program can prevent 95 percent of all acid-copper-related problems.

*Based on an original article from the "AES Update" series [*Plating*, **64**, 34 (December 1977)]

Applications & Advantages

"The application of bright acid-copper on die castings improves corrosion-resistance due to its excellent microthrowing power. Microthrowing allows the copper to fill in surface porosity that ordinarily would not be accomplished in a conventional zinc die-cast plating cycle (Fig. 1). The ability of acid-copper to cover a porous substrate, with or without buffing, also improves corrosion protection in a duplex-nickel system.

"Bright acid-copper is ideal material for rotogravure rolls because it produces a hard copper deposit, eliminates the presence of cleavage planes that crack under stress and offers easy etching characteristics.

"Thermal-cycle reliability of electroplated plastics can be achieved in part by the application of an acid-copper layer of suitable thickness, approximately [12.7 to 17.8 µm (5 to 7 mils)]. The elongation properties of copper allow it to serve as a cushion layer which compensates for differences in thermal expansion and contraction of plastic substrates. The leveling properties and brightness of the copper deposit smooth the etched surface of the plastic.

"Reduced costs for decorative finishes can be realized by using bright acid-copper for partial replacement of thick nickel deposits, due to the price difference of the anode materials. In addition, corrosion protection can be upgraded when a microporous [chromium] deposit is used in conjunction with copper.

Fig. 1—Cross-section of zinc die-casting segment shows micro-throwing power of bright acid-copper. The diameter of the pore (approximately 50 µm or 2 mils) has been filled completely by the acid-copper, leaving only a slight depression at the surface of the plate.

Precautionary Measures

"Prior to the application of acid-copper on zinc die-castings and steel, it is necessary to provide a barrier layer of some type on the parts. On steel, the barrier layer prevents immersion deposition in the low current-density area with subsequent flaking in the plating cycle and eliminates adhesion losses due to non-adherent, copper immersion deposits.

"Because of the acidic nature of the electrolyte and the inherent low-throw capabilities [in terms of macrothrow, not microthrow] of an acid-copper solution, certain part configurations and rack designs should be avoided. Die-cast parts with extreme blind holes are difficult to process. Rack contacts on critical machine-threaded areas should be avoided. The corrosive nature of acid-copper solution dictates that equipment be properly protected against chemical attack.

Servicing Problems

"Three problem categories exist in the servicing of bright acid-copper: chemical, physical and interrelated physical-chemical combinations. Maximum performance param-

Fig. 2—Effect of chloride content on acid-copper deposit quality. The optimum bright appearance at 50 ppm is lost if one operates above or below the proper range of 20 to 80 ppm of chloride ion.

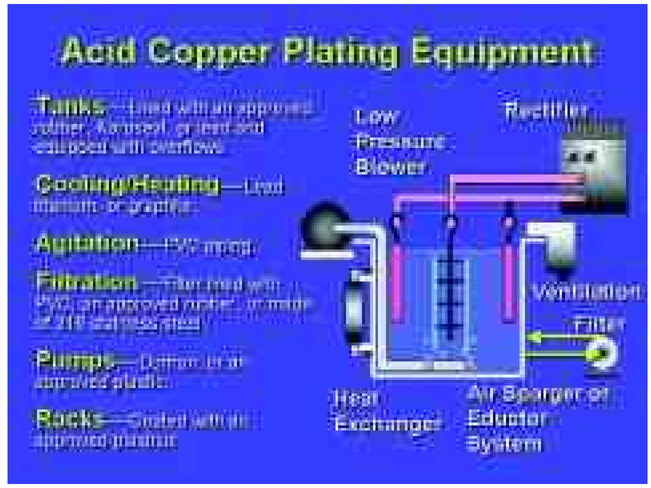

Fig. 3—Physical aspects of an acid-copper plating installation.

eters should reflect recommendations made by the supplier of proprietary addition agents.

Basic Chemical Problems

"Basic chemical problems involve the inorganic portions of electrolytes. It has been found that the ratio of sulfuric acid to copper sulfate effects copper distribution. A higher acid-to-metal content promotes distribution into low current-density areas, as evidenced in through-hole plating of printed-circuit boards. However, higher levels of sulfuric acid increase the tendency to "tree" or "burn" and give a somewhat softer deposit.

"High copper-sulfate content (more than 114 g/L or 30 oz/gal) tends to impair the function and/or solubility of some addition agents and causes the air-agitation lines to be susceptible to plugging from crystallized copper sulfate. Higher levels of copper sulfate are beneficial when insoluble, auxiliary anodes are used.

"A small quantity of chloride ion, in the 20-to-80 ppm range, provides a beneficial, synergistic effect in depositing copper. Quantities of chloride ion above or below this range can induce burning, striating, poor leveling and anode polarization [Fig. 2]. Drag-in of chloride ion from rinses or process tanks is the most common source for abnormal levels of chloride in acid-copper baths. Chloride levels in well-water sources should be checked before such water is used in a rinse. Chloride contamination has been traced back to faulty water seals on filter pumps used in acid-copper baths, and to employees who used well-water to clean salts off the anode rails.

Basic Physical Problems

"Basic physical problems in bright acid-copper operations involve bath filtration, anode bags, agitation and temperature, [so proper installation design is critical (Fig. 3)]. Adequate filtration of one-to-two turnovers of solution body per hour generally keeps the bath free of particulate matter. In all cases, the selection of filter media, powder or paper must be approved for use. Some types of paper and many available filter powders will selectively deplete some addition agents and result in loss of brightness and leveling.

"When using automatic filters, a filter-aid precoat may be required to give one micron retention or less. Also, an additional precoat of 3 to 6 g/L (4 to 8 oz/ 1000 gal) of carbon may be used to correct addition-agent unbalance or remove some organic contaminants.

"Proper selection of anode bags for a bright acid-copper bath is mandatory. Generally, a moderately tight-woven synthetic fabric napped on one side performs satisfactorily. The anode bag allows diffusion or interchange of copper-rich solution at the anodes with more dilute solution in the bath. The anode bag must, however, retain anode-generated fines which, if introduced into the bath, promote "stardusting" and are difficult to remove with simple filtration.

"Anode bags that excessively restrict solution-exchange become supersaturated inside. This causes copper-sulfate precipitation and anode polarization. Polarized anodes rapidly degrade addition agents and necessitate more frequent additions of copper sulfate. Polarized anodes cause parts to exhibit poor color, leveling and inferior electroplate distribution.

"Synthetic thread used to weave anode-bag cloth is commonly coated with a lubricant to facilitate weaving. These lubricants usually become organic contaminants in acid-copper baths. All anode bags should be pretreated to remove lubricants; a good pretreatment is a two percent sulfuric-acid leach followed by a soak in a dilute, acid-copper solution in a lined or plastic container.

"Modern, bright acid-copper systems are designed for optimum operation with good air agitation (Fig. 4). A clean source of low-pressure air (evenly distributed in a uniform pattern) allows plating at high current-densities without "burning." High-pressure air should not be used. In spite of the best efforts to filter high-pressure air, oil will be introduced into the plating solution with the air and will cause pitting and speckling. If black iron pipe is used in the air distribution system, it may be advisable to install in-line, final filters above each air header going into the tank to eliminate the introduction of small rust particles. Air intakes should be located in an area that is free of fumes, preferably outside away from solvent, cleaner or buffing and finishing compounds. The volume of air should be adequate to raise the solution 10 to 15 cm (4 to 6 in.) in height. Excessively violent air or poor rack design may result in "fish eye" pitting on the underside of shelf areas. Air leaks into pump chambers or intakes can cause very fine

Fig. 4—(Left) When electrolyte is operated with [low or no] air agitation, pronounced burning occurs in high current-density areas. The same solution quickly regains its wide operating range when air-agitation is used (Right).

bubbles, which do not disperse rapidly in plating solution and can cause pitting if trapped on the underside shelf areas.

"Anode area in the plating tank should be adjusted to fit the minimal current load on the tank. Good results can be obtained with an anode current-density of 2.2 to 3.2 A/dm^2 (23 to 35 A/ft^2). Excess anode area promotes sludge formation, which is build-up of wasted copper. A small anode area is conducive to polarization and necessitates more copper-sulfate additions and excessive use of addition agents. It may also trigger bipolarity.

Chemical-physical Problems

"Once the basic chemical and physical parameters have been put in order, attention can be directed to service problems of an interrelated chemical-physical nature.

"Opinions about the size, physical shape and phosphorus content of acid-copper anodes are numerous. In addition to having an anode 0.02 to 0.06 percent by weight phosphorus content, one must run an electrolytic test to determine sludging characteristics. Sludge generation does not always correlate to phosphorus content. Anode sludge promotes roughness in the copper deposit and results in wasted copper, plugged anode bags and high consumption of addition agents.

"Generally, acid-copper baths tolerate high levels of inorganic impurities. Some baths have been monitored with 40 g/L (5 oz/gal) of soluble zinc, 5 g/L (0.7 oz/gal) of nickel and 10 g/L (1.3 oz/gal) of iron.

"Soluble iron in an acid-copper bath chemically attacks the anodes and can cause excessive copper-sulfate levels in the bath. An installation with an exceptionally high drag-out or with many insoluble auxiliary anodes may find some economic advantage in generating copper sulfate in the plating bath. Iron contents of 1-10 g/L (0.13-1.3 oz/gal) have been used to compensate for high drag-out and to reduce copper sulfate additions when insoluble anodes are used. The use of insoluble auxiliary anodes selectively oxidizes organic addition agents. Under these conditions, recommendations from the supplier of the addition agents should be followed.

"During electrolysis of insoluble anodes in acid-copper, an excess of acidic hydrogen ion is generated. When the sulfuric-acid content reaches detrimental levels, the bath may be batch-treated with copper carbonate to lower the acid content.

Plating on Plastics

"An increasing demand for acid-copper is being realized in electroplating on plastics. With the introduction of more complex design of plastic parts, it is important to understand the basics of the preplate cycle as it relates to the electroplate cycle. Simple concepts such as the number of contacts and their placement can dramatically affect thickness values at check points.

"The length of current paths and their effect on bipolarity conditions on the same parts or on adjacent parts must be realized. Striations and poor adhesion of acid-copper can occur through a dependency of acid-copper on the preplate cycle.

"On plastics, a common complaint is "stardusting" or graininess. After the simple chemical and physical aspects of acid-copper have been put in order, investigation of the source prior to the acid-copper may be warranted. "Stardusting" and graininess have been legitimately traced back to etch residue, resin residue, precipitated particulate matter from the activator step, insolubles in the accelerator and auto-catalyzed precipitates from electroless copper and nickel.

Editor's note: The preceding article is based on the original piece written by Mr. Larry T. Rudolph for the AES Update series that ran in this journal in the late 1970s and early 1980s. The series, begun and coordinated by the late Dr. Donald Swalheim, and carried on by many others, brought practical information to the metal finisher. Further on in this issue is a very relevant article on the troubleshooting of decorative plated plastics systems by N. Mandich and D. Baudrand, which shows that much of the material here remains in play today. In some cases, words were altered [in brackets] for context. *P&SF*