The Acid Copper Alternative

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The price of nickel had been steadily increasing this year, actually surpassing $32/lb a few months ago. The recent price trend has seen it sort of level off in the $13 to $17/lb range. By comparison, the "good old days" pricing of below $6/lb seem so long ago, but actually occurred within the past five years. Thus, nickel plating has become quite an expensive proposition. Attention to detail, with respect to plating current densities, plating times, thicknesses, bath maintenance, optimizing chemistry - all combine to leave critical room for deviation. Failure to meet any specific plating objective or operating parameters significantly adds to the overall plating cost. There is very little margin for error. The consequence is to erode what profit margin exists. Perhaps it would be beneficial to plate less nickel and yet meet the overall plating requirements and service characteristics for processed parts. One way to accomplish this is to plate a rapidly leveling, bright nickel deposit. Known systems, referred to as the "hot" or "pyridine" based proprietary brighteners, readily deposit mirror bright and highly reflective nickel. The overall benefit is to reduce nickel deposit thickness significantly while providing the required aesthetic characteristics. Corrosion protection or wear resistance, if important, may be compromised. If this is important, improved base metal protection can be achieved by plating a sufficient undercoating of copper. For many plating requirements, such as automotive finishes, this is very critical to obtaining the required wear resistance and meeting test parameters (CASS, salt spray, etc . . .).

In today's pricing structure of metals, the consideration of copper as a suitable primary deposit can reasonably supplant nickel plating thicknesses. Although copper metal prices have also risen, these average about one-fourth those of nickel metal. This certainly makes the extended use of or introduction of copper plating as more attractive, specifically for economic sense. Acid copper plating develops a deposit with the following beneficial characteristics: very bright, highly leveling, ductile and soft, readily buffed. Aside from ferrous and zinc metals, which require a cyanide or alkaline copper deposit before acid copper, the acid copper can be plated directly on to brass and copper substrates. The application of acid copper may ease the "pain" of the nickel plating cost.

Let us consider an example of what a savings in nickel deposition can relate to when a portion of it can be replaced with copper. Consider nickel metal at $17/lb and copper metal at $5/lb. For every 100 lb of nickel metal plated, the cost of depleted anode metal would be $1,700. Replacing 25% of the nickel plated with copper results in a saving of $425 of nickel, while depositing in its place, $125 of copper. Overall, the cost savings in total metal deposited versus just all nickel is $300 or 17.7%. There are other factors that can be compared, such as consumption of brighteners and additives, and power requirements. On average, approximately one gallon of nickel brightener may be consumed for every 8,000 amp-hours. Conversely, one gallon of acid copper brightener may be consumed for every 25,000 amp-hours.

Based on data at 100% cathode efficiency, the deposition rate for nickel is 0.039 ounces per amp-hour and for copper it is 0.042 ounces per amp-hour.

From this perspective let us review the basics of acid copper plating.

The bright acid copper plating process is relatively simple to make up and maintain. Sulfuric acid is an important component constituent. This makes the bath a corrosive solution. All the safety precautions, handling and use of proper equipment must be adhered to. The following information provides the basic concentrations and general operating parameters.

Temperature control is very important. Too low may result in some copper sulfate precipitation. Too high will consume more of the organic additives and by itself can dull the deposit.

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Bath chemistry

Constituent	Optimum	Range
Copper Sulfate*	28 oz/gal (210 g/L)	27 - 30 oz/gal (202.5 - 225 g/L)
Sulfuric Acid	8 oz/gal (60 g/L)	7 - 9 oz/gal (52.5 - 67.5 g/L)
Sulfuric Acid	3.2 vol%	3.2 - 4.2 vol%
Chloride Ion	70 ppm (70 mg/L)	30 - 150 ppm (30 - 150 mg/L)
* Copper Sulfate Pentahydrate (liquid concentrate or crystals)		

Operating parameters

Requirement	Ranges
Temperature	75 - 90°F (24 - 32°C)
Cathode CD	10 - 90 A/ft^2 (1.0 - 9.0 A/dm^2)
Anode CD	5 - 20 A/ft^2 (0.5 - 2.0 A/dm^2)
Voltage	2 - 9 V
Anode to cathode area ratio	2:1
Agitation	Low pressure air blower (oil free)
Filtration	Continuous, 1 - 2 turnovers/hour

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Editor's Note:
We would like to mention that Mr. Dini is having so much fun providing these columns that he is churning them out at a rate faster than we can publish them on a monthly basis. Indeed, he has created a blog at http://myblogscience.blogspot.com. If you wish to see more of Mr. Dini's provocative works that might not have appeared in Plating & Surface Finishing*, check it out.*

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Agitation is also very important to prevent burning and rough deposits. It also permits the use of higher current densities and contributes to fine grained, bright deposits.

Note: The information provided here relates to bright acid copper rack plating of most consumer and automotive goods. The other types of related processes for printing applications - rotogravure and textile, along with electroforming - are not referenced in this review.

The copper anodes required should contain 0.025 to 0.06% phosphorus. Anode baskets are titanium. Napped polypropylene or Dynel anode bags are recommended.

About the bath constituents

Copper sulfate is the secondary source of metal in the plating bath. As in most plating baths, maintaining the copper sulfate above the minimum concentration is required to prevent high current density burning and lower plating rates, as well as poor deposit leveling. Higher concentrations result in harmful precipitation of copper sulfate on the tank equipment, especially coating the anode baskets and deposit roughness.

Sulfuric acid provides the solution conductivity, thereby lowering the voltage required for any current density. Higher concentrations of sulfuric acid promote high current density burning and passive anodes.

Chloride, in conjunction with the organic brightener / leveling additives, prevents deposit burning, dullness, poor leveling and restricted plating current density ranges.

The organic additives consist of proprietary blends that control deposit: grain refinement, brightness, leveling, anti-burn and prevent low current density skip plating.

Analytical control

Wet analysis procedures are commonly used. The copper sulfate is titrated per the iodine - thiosulfate couple method. Sulfuric acid is determined by the acid neutralization titration with sodium hydroxide. Chloride is usually analyzed by a few different methods. In one, the sample is made cloudy by the addition of silver nitrate and the % transmittance of light is measured. Its logarithmic value is then determined, and the concentration is extrapolated on a Beer's Law graph. In another method, the sample is made cloudy by the silver nitrate addition, and then titrated to clarity with mercuric nitrate. Because of the severe restrictions on handling and disposing of mercury containing solutions, this method is not now as widely used.

A Hull cell test normally provides an excellent determination of the deposit characteristics, especially highlighting any defects due to a bath out of balance condition.

Based on specific finishing applications, the possibility of replacing some of the nickel deposit may be an appropriate method for overall cost savings. Back in the 1970s the emergence of nickel-iron alloy baths was somewhat popular during a period of higher nickel prices. Going back a bit farther to the good old days of 1969, the average price of nickel was $1.14/lb. It just goes to show that problems and opportunities do go hand in hand. *P&SF*