Alkaline Cyanide-Free Copper Process for Functional and Decorative Plating

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Copper plating is the building block plating process for many products. This paper includes a brief review of a variety of copper plating processes, with emphasis on the newest technology – alkaline non-cyanide copper. Alkaline non-cyanide copper has found its niche as a method to eliminate cyanide. Platers who use cyanide copper can switch to it to meet goals in EPA's Common Sense Initiative because it eliminates the treatment of cyanide and cyanide waste. A discussion on the characteristics of alkaline non-cyanide plating will be included.

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Introduction

Copper plating is the base building block in plating chrome-plated bumpers to printed circuit boards. There are four types of copper plating – acid copper, alkaline non-cyanide copper, alkaline cyanide copper, and electroless copper. The acid copper process offers a high degree of leveling (microthrow). Acid copper is used for printed circuit boards and decorative applications. The alkaline non-cyanide process is replacing cyanide copper for strike and plate applications. Cyanide copper, a workhorse for the plating industry, cleans the substrate while being plated, has a large operating window, and is easy to use. The alkaline non-cyanide copper and the cyanide copper do not level like acid copper (macrothrow). Electroless copper is an autocatalytic immersion copper process that is utilized on plastics and printed circuit boards. In the search for a copper plating process that eliminates cyanide copper process which then will meet the EPA's Common Sense Initiative (CSI), the choice process is alkaline non-cyanide copper process.

Alkaline non-cyanide copper processes include copper pyrophosphate chemistries and propriety alkaline non-cyanide copper chemistries.

Pyrophosphate chemistry is still used today. There are the standard formulas found in the metal finishing handbooks and proprietary modified pyrophosphate baths. Some of the pyrophosphate baths use ammonium hydroxide as a brightener. The result of using ammonia is waste treatment challenges. Pyrophosphate chemistry limitations include adhesion concerns on some substrate and a breakdown product called orthophosphate. The orthophosphate is formed from the hydrolis of the pyrophosphate into orthophosphate (see equation 1 below).

$$P_2O_7^{-4} + H_20 \rightarrow 2HP0_4^{-2}$$

At 40-60 grams/liter of orthophosphate, the plating bath will have to be diluted or dumped. At this level of orthophosphate, bath performance is greatly affected – banded copper plated deposits, loss of ductility, and throwing power.

Electrochemistry

Alkaline non-cyanide copper, pyrophosphate copper, and electroless processes plate copper from the divalent state (see equation 2 below).

Equation 2

$$Cu\ (Complexor) \rightarrow Cu^{++} + Complexor$$
$$Cu^{++} \rightarrow Cu^{o}$$

Cyanide copper processes plate from the monovalent state (see equation 3 below)

Equation 3

$$Na_2\ Cu\ (CN)_3 \rightarrow 2Na^{+} + Cu\ (CN)_3^{-2}$$
$$Cu\ (CN)_3^{-2} \rightarrow Cu^{+} + 3\ CN$$
$$Cu^{+} \rightarrow Cu^{0}$$

It has been difficult to replace cyanide in alkaline copper plating baths because of the need for a high metal compound concentration while maintaining a low metal ion concentration in the bath. The high metal compound concentration furnishes a reservoir for the copper throughout the solution and also stops polarization of the anodes as they are dissolved. On the other hand, a low metal ion concentration is required to produce small crystals at the cathode to produce a bright plate. A low metal ion concentration also increases coverage and throwing power. A high metal compound concentration with a low copper ion concentration in a bath is accomplished with a common anion such as sulfate with sulfuric acid and copper sulfate in an acid copper plating bath, and with cyanide in alkaline baths with copper cyanide and sodium cyanide. With cyanide as a common anion in the bath, the bath can contain an excess of cyanide to control anode corrosion and cathode efficiency. In addition, cyanide breaks down into relatively harmless by-products of ammonia and carbonate, which are not detrimental to the operation of the bath. That is, the carbonates are not really detrimental until they reach a concentration of 16 ounces or more per gallon of the bath. In searching for a common anion to replace cyanide as a complexer, it has been an important consideration to find a common anion which does not break down into undesirable by-products and at the same time does not have a

negative effect on present waste treatment operations. Therefore, strong chelators such as EDTA and NTA cannot be used.

A non-cyanide alkaline copper plating bath has been developed and is being used in heavy production for over 6 years with excellent success. The bath will plate directly on iron and steel, brass and copper, zincated aluminum, diecast zinc, stainless steel and white metal castings in both rack and barrel operations. The process consists of a liquid concentrate which contains the copper and all the chemistry required in the process. The liquid concentrate is used at a volume of 40 to 60% in D.I. or soft water to charge the bath initially. Thereafter, only one primary addition agent, the electrolyte, is used to maintain the bath as the copper is dissolved from the anodes. In addition, there is a high current density booster additive. A bath charged at 40% by volume will have a copper concentration of 1 ounce per gallon. The bath can be operated very successfully at this level of copper, but there are instances where a faster plating speed is desired in which the anodes are dissolved until a concentration of 1.5 to 2 ounces per gallon of copper is reached. It is very important that the electrolyte additive be added on a daily basis while the copper anodes are being dissolved. Once the preferred level of copper is determined for a particular installation, the anode area and anode current density required to maintain the optimum copper concentration in the bath are determined.

The pH of the bath is monitored and will increase as the bath is used. When the pH exceeds 10, it is reduced by adding dilute sulfuric acid. The bath has proven to be easy to use and maintain with only the copper metal and pH being monitored.

Bath Operation

Copper Metal	1.0 to 2.0 oz/gal.
pH	9 to 10
Temperature	100 to 150°F
Anode C.D.	10 to 15 ASF
Voltage, Rack	1 - 6
Voltage, Barrel	12 - 18
Agitation	Vigorous air
Filtration	Continuous with carbon pack
Copper Anodes	OFHC CDA 101
Anode Baskets	Titanium
Heating	Stainless Steel and Titanium elements
Tank	Plastic or lined steel
Ventilation	None required

With the non-cyanide copper, a single bath can be used to replace cyanide strike and plate baths. The bath is very stable and does not require periodic dumping and recharging as is common with pyrophosphate baths. In addition, the process does not require an auxiliary dummy tank or special expensive ceramic anodes for operation.

The alkaline non-cyanide baths being sold at the present time contain a lower concentration of copper metal than the typical cyanide copper baths. However, this is an advantage as it reduces the copper loading in waste treatment.

The anode and cathode efficiencies of the alkaline non-cyanide copper baths are 100%. Typically the alkaline non-cyanide copper baths do not plate as fast as cyanide baths, but at approximately 75% of the speed. The conventional cyanide copper bath contains monovalent copper; whereas, the present non-cyanide alkaline copper baths contain divalent copper.

The non-cyanide alkaline copper plating bath is being used successfully as a strike prior to bright nickel plating, tin plating, solder plating and acid copper plating. In addition, it has been used as a finish in itself for hardware and lamp fixture parts which are usually antiqued or oxidized. The copper plate has proven to be an outstanding heat treat stop-off finish.

Deposit characteristics include outstanding throw and coverage, which are superior to the conventional cyanide bath. The plate will have excellent micro-throw with very uniform distribution in the LCD areas. The deposit is fine grained and smooth which is required for decorative purposes while being dense and ductile and non-porous which makes it ideal as a strike bath. There is no out-gassing, making the plate ideal for brazing operations.

A review of the benefits of a non-cyanide alkaline copper plating bath would include:

- Eliminating the inherent dangers of cyanide in the workplace and improving employee health and safety.
- Eliminating the concern for catastrophic accidental acidification of cyanide.
- No carbonates to be treated
- No carbonate sludge containing cyanide to be treated or waste hauled.
- No cyanide in F006 sludges.
- No danger of cyanide if a fire occurs in a plant.
- Reduces waste treatment costs for destroying cyanide.
- Eliminates the use of hazardous chlorine and sodium hypochlorite to treat cyanide
- Accidental drag-in of non-cyanide alkaline copper plating solution poses no toxic problems with the subsequent acid copper solutions.
- Reduces fire and liability insurance premiums.
- Easily installed in existing plating lines.
- One bath serves as both a strike and plate bath.

Bath Contaminants

Organic Contamination - remove with batch carbon treatment. Sometimes hydrogen peroxide is added to remove the organics.

Iron - Can absorb up to 2000 ppm iron. Remove the iron through high current density dummy plating.

Lead - Can absorb up to 50 ppm of lead. Remove with high current density dummy plating.

Calcium - Will destroy the copper - complexor bond and more complexing product is necessary. Switching to DI or softened water alleviates this problem.

Chrome - Up to 10-15 ppm limit. Chrome reducer does work, but use sparingly.

Plating on Aluminum

One of the applications of plating alkaline non-cyanide copper is plating onto a zincated aluminum surface with this copper process. A typical plating process for aluminum can include approximately seventeen steps - cleaning to copper plating.

Table 1
Plating Aluminum Cycle

1. Soak clean	10. Cold water rinse
2. Cold water rinse	11. Nitric acid strip
3. Deoxidize	12. Cold water rinse
4. Cold water rinse	13. Non-cyanide zincate
5. Etch	14. Cold water rinse
6. Cold water rinse	15. Non-cyanide alkaline copper strike
7. De-smut	
8. Cold water rinse	
9. Non-cyanide zincate	16. Cold water rinse
	17. Acid copper or nickel plate

Plating aluminum requires more steps than other substrates such as steel, brass and zinc diecast. The main reason for more steps is that copper cannot be directly plated onto aluminum. It needs the proper pre-plate cycle to be successful. To determine the pre-plate process, the aluminum alloy, type of aluminum - casting or extrusion, and existing condition of aluminum - stamping, polished/buff, or machined must be known before the pre-plate cycle can be determined. With alkaline non-cyanide processes available, metal finishers can now use non-cyanide zincates creating an entire non-cyanide process for aluminum. With recent development of new non-cyanide zincates, they meet or exceed cyanide-based zincates in performance.

Another application for the non-cyanide process is the replacement of stannate process for aluminum and the cyanide bronze. The non-cyanide zincate will directly replace the stannate process. The typical stannate process is an immersion alkaline tin process - sometimes electroplated tin. The non-cyanide zincate process costs less to use versus the stannate process because of its ease of use and wider operation window and cost of zinc versus tin.

The zincate process utilized to ASTM B-253-68 (1) will meet the service condition specification adhesion and corrosion of the SAE J207 (2) specification. The stannate process is losing favor to the zincate process with the need to eliminate cyanide since the typical stannate process uses a cyanide bronze process. The manufacturers (platers) of aluminum bus bar are investigating alternatives to the stannate process. Included in the alternatives is zincated

aluminum with the alkaline non-cyanide copper process.

Conclusions on Plating on Aluminum

Platers of aluminum have a new environmentally friendly process for plating aluminum without the use of any cyanide zincate or cyanide copper plate. The key to the process is the alkaline non-cyanide copper. The proprietary alkaline non-cyanide copper process has better throw than the cyanide process, low copper metal concentration, more stable chemistry than copper pyrophosphate chemistry, and reduces waste treatment costs eliminating chlorine/bleach from the waste treatment area.

References

1. ASTM B-253-68 *Preparation of and Electroplating on Aluminum Alloys by Zincate Process.*

2. Society of Automotive Engineers, *Electroplating of Nickel and Chromium on Metal Parts – Automotive Ornamentation and Hardware* SAE J207 February 1985