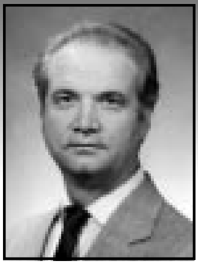

Advice & Counsel

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Training "Colombo"—Part XI
Carbonates & Cyanide Solutions

***Caution:** This article contains procedural information that may not be suitable in your specific case. Be sure to verify the suitability of the information provided in this article in the laboratory, and consult with the supplier of your plating solution chemicals and additives, or get professional advice before proceeding to treat your specific solution.*

Dear Advice & Counsel

My company operates a high-speed cyanide copper plating solution that is plating about as slow as molasses these days. The deposit looks fine, but the plating voltage is getting close to 10 volts. From what I have read, the problem is related to carbonate concentration, which is exceeding 20 oz/gal of potassium carbonate. I have tried to drop the carbonates by adding calcium hydroxide, but I'm not sure I added enough because there was almost no drop in concentration. What's the best way to go about this?

Signed,
Cy N. Eye

Dear Cy,

Because the "Training Colombo" series is on the subject of troubleshooting copper plating solutions, your letter is quite timely. One of the operational difficulties with cyanide plating solutions is that they tend to build up carbonates over time, and such buildup reduces conductivity (increasing the voltage required for plating as you observed). The net result is a high-speed plating solution operating at less than high speed.

Sources/Effects of Carbonates

Let's first discuss the role and source(s) of carbonates. Carbonates are powerful buffering agents in the pH range of 10.8–11.5, and are a necessary ingredient in strike solutions used for deposition over zinc die castings. Above pH 11.5, carbonates are unnecessary nuisances. The carbonates are formed by the following chemical/electrochemical reactions:[1]

1. Cyanide is oxidized on the surface of the anodes, if the anodes are polarized (maximum anode current density should be 4 A/dm^2 or 40 A/ft^2), if insoluble anodes are used or simply by exposure to the air (which is why you never want to air-agitate a cyanide plating solution). According to Crain,[2] the reactions are:

$$2KCN + O_2 \rightarrow 2KCNO$$
$$2KCNO + 2KOH + 2H_2O \rightarrow 2K_2CO_3 + 2NH_3$$

2. Carbonates are formed by the reaction between carbon dioxide from the air and either the hydroxide or water. In high-pH solutions:

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

In lower pH solutions (pH 10–10.8):

$$H_2O + CO_2 = H_2CO_3$$
$$H_2CO_3 + KCN \rightarrow KHCO_3 + HCN$$
$$KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O$$

3. Carbonates are formed by hydrolysis (reaction between cyanide and water) of cyanide.

$$KCN + 2H_2O \rightarrow HCOOK + NH_3$$
$$4HCOOK + 2KOH \rightarrow (KCOO)_2 + 2K_2CO_3 + 3H_2$$
$$(KCOO)_2 + 2KOH \rightarrow 2K_2CO_3 + H_2$$

According to Ref. 1, sodium carbonate should be maintained below 90 g/L (12 oz/gal) and potassium carbonate should be maintained below 120 g/L (16 oz/gal) to maintain optimum plating speed (efficiency).

Effect of high carbonate in high-efficiency solutions will reduce plating speed, reduce bright plating range and deliver larger grained (less ductile) deposits.

Lowering the Carbonate Content

A number of methods and reagents are in the literature, but the most common methods employed by platers are freezing (exposure to approximately 30° F for several hr) for sodium carbonate, and precipitation for potassium carbonate.

The precipitation method can be quite complicated, in that the addition of the precipitating compound almost always adds something you don't want or need. If you add calcium hydroxide, for example, you will increase the hydroxide content of the plating solution and must readjust the other ingredients to maintain the correct ratios. If you add calcium oxide, this increases the hydroxide as well. If you add calcium cyanide, this increases the free cyanide content, and so on.

Another problem to solve is the fact that all of the compounds that can be added to precipitate carbonates are not highly soluble in either water or in the plating solution. If you try to dissolve the compound and then add it to the plating solution, you end up diluting the plating solution far beyond normal concentrations. Last, the precipitated carbonate is quite voluminous (see Fig. 1), even if only a small fraction of the original carbonate concentration is removed.

All compounds mentioned in the literature are not readily available, so we tried some commonly available compounds on your solution:

- Calcium hydroxide
- Calcium nitrate
- Barium hydroxide

Fig. 1—Precipitated carbonate.

Fig. 2—Powdered barium nitrate added to the solution produces barium carbonate sludge.

- Barium nitrate
- Barium acetate

Each reagent was added in a theoretical concentration that would reduce the carbonates to 7.5 oz/gal. After treatment, a Hull cell panel was plated to verify the ability of the solution to produce an acceptable deposit under normal plating conditions, and to determine if the treatment affected the operating plating voltage.

Experimental Results:

Calcium Hydroxide

Calcium hydroxide was found to be ineffective at reducing the carbonate content of the solution. Because this compound is given the most mention as an effective way to precipitate carbonates, we were surprised at the result.

Calcium Nitrate

Calcium nitrate was found to be ineffective at reducing the carbonate content of the solution. It also eliminated the free caustic of the solution, lowering the pH to 11.0, and producing a plating solution that required high voltage to deliver “normal” current density in the Hull cell.

Barium Hydroxide

We found barium hydroxide to be ineffective at lowering the carbonate significantly, and the treated solution required high voltage to deliver normal current densities.

Barium Nitrate

Barium nitrate treatment reduced the carbonate content to the range of 9–10 oz/gal. The treated solution produced a good deposit, with normal (low) voltages for the current density applied.

Barium Acetate

Barium acetate treatment was found to be equally effective at reducing carbonates, but the treated solution operated at much higher voltage than would be desirable, although this was about 50 percent of the voltage of the “as-received” solution.

Optimum Treatment

The reagent of choice in this case was barium nitrate. However, this should not be construed to mean that barium nitrate will be the best choice in all cases of carbonate removal from cyanide solutions. The following is a description of the treatment we used:

1. To precipitate 7.5 oz/gal of potassium carbonate, it theoretically takes about 14 oz/gal of barium nitrate.

2. Barium nitrate is not highly soluble. Only about 11.6 oz will dissolve in a gal of water. The problem then becomes one of requiring so much water to dissolve the barium nitrate, that the plating solution will be diluted beyond desirable concentrations. We therefore decided to crush the barium nitrate into a fine powder and add it as a solid to the solution, using a high level of agitation. The reaction time should be at least four hr, preferably overnight.
3. The treatment produces a large amount of barium carbonate sludge (see photo). It can be settled in 4-8 hr, or pressure-filtered. The treatment can then be repeated to further lower the carbonates. However, at 8-10 oz/gal the carbonates should not be a hindrance to plating.
4. We were not able to reduce the carbonate by the theoretical amount. Multiple treatments, however, can be used to lower the carbonates to any desired level.
5. The treatment did not affect the concentration of the other ingredients in the plating solution.

Avoiding Carbonate Buildup

Because there is a large emphasis on pollution prevention these days and because treatment of carbonates produces a highly toxic waste (carbonate laced with cyanide), cyanide-based plating solutions should be operated in a manner to reduce the rate of carbonate buildup as much as possible. The following are “tips”:

1. Operate at as low a hydroxide concentration as possible.
2. Keep the tank covered when not in use. Crain found a 10-percent reduction in the buildup of carbonates simply by covering the tank when not in use. An idle, uncovered solution was found to increase in carbonate content at a rate of about 0.25 oz/gal per week!
3. Never air-agitate or propeller-agitate a cyanide plating solution. Air agitation can be expected to produce up to 1 oz/gal of carbonates per week of operating in a high-speed plating process. Crain found that prop mixers produced the same amount of carbonates as air agitation (presumably as a result of cavitation). Recirculating pump agitation (eductors can be used) reduced carbonate buildup rate by two-thirds.
4. Maintain anode current density below 40 ASF (4 ASD).
5. Maintain anode area by frequently checking your anode baskets and replenishing them.
6. Verify anode current density on each individual anode hook with a tong-meter.
7. Operate the plating solution at as low a temperature as possible. Crain found that a 50-percent drop in carbonate generation was obtained by dropping the temperature from 180° F to 160° F. P&SF

References

1. *Modern Electroplating,* Frederick A. Lowenheim, ed., John Wiley & Sons, Inc.
2. J.R. Crain, “Buildup and Control of Carbonates in Cyanide Copper Plating Solutions,” *Plating* (Jan. 1964) p. 31.