Shop Talk

Eliminating Problems
In Cyanide Copper Plating

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You may be wondering why, in the year 2002, we would be reprinting this practical article on cyanide copper plating. Unlike zinc plating, there hasn't been an easy alkaline substitute for cyanide copper. There are still specifications that call for throw characteristics that cannot be supplied by acid copper. It is interesting to look at cyanide copper plating, which is still around in significant volume. If nothing else, the value of the venerable Hull Cell stands out.

High efficiency baths are used in applications such as zinc diecastings, in which high plating speed, good throwing power and brightness are very important. A thorough knowledge of the basic principles is essential to insure success and to avoid problems that cause rejects.

Copper is present in the bath, as complex cyanide ions. Baths can be prepared by slurrying copper cyanide in water and then adding either sodium cyanide or potassium cyanide. Good mixing is required when the operation is carried out on a large scale, since the reaction rate is relatively slow. Because of this, platers may experience problems in making maintenance additions. Unless good agitation is provided, the salts settle to the bottom. That's why your analytical department may be correct when it reports essentially no change in the copper content after you have made a maintenance addition.

Many platers prefer to use the complex salts for make-up and maintenance because they dissolve very readily. Additional sodium cyanide or potassium cyanide is always added to provide "free" or excess cyanide. Alkali is also necessary for good bath conductivity and anode corrosion.

Now let's examine the electrochemistry of the process (Fig. 1). In a cyanide copper bath, copper has a valence of +1. All of the copper is essentially tied up as the $Cu(CN)_3^=$ anion. For all practical purposes, there are no "free" cuprous ions. During plating, the electrons neutralize the single positive charge on the copper in the complex to form metallic copper. The process operates at close to 100 per cent electrode efficiencies.

Agitation is Important

Why is agitation so important in high efficiency baths? There are several reasons, as far as electrochemistry is concerned. You will note by the equation in Fig. 1 that as we deposit copper, free cyanide is liberated on the surface of
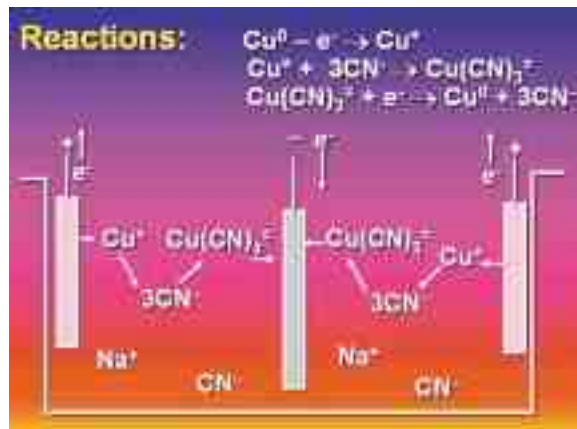

Fig. 1—Electrochemistry of cyanide copper.

the part. If the excess cyanide is not mixed with the rest of the bath, hydrogen will co-deposit with the copper. Unlike cyanide zinc plating, the deposits are coarse-grained and burned when hydrogen is co-deposited. The charge on the cyanide complex is negative. This means that the complex will migrate toward the anode instead of the cathode where it is needed to replenish the copper removed during plating.

Agitation is also very important for good anode corrosion. Each cuprous ion requires three cyanide ions to form the complex salt. Basically, we have to move the excess cyanide from the surface of the parts to the anode in order to prevent anode polarization, particularly if the bath is being operated at relatively high current densities. We can not rely solely on diffusion.

Plating Speed

If you are faced with increasing thickness of copper to meet specifications, there are several factors to consider. Let's assume you are operating a sodium-formulated bath. You have much to gain by incorporating potassium as well.

A special technique was used in photographing the Hull Cell panels in Fig. 2. A copper wire mesh screen was placed in back of the artwork and lighted to reflect an image of the screen in the panel. When bright copper plated panels are photographed without the screen, the deposits appear dark and almost black.

The Hull Cell panels were plated at 2.0 A from baths containing 45 g/L (7.0 oz/gal) of copper with the temperature maintained at 82°C (180°F). A Hull Cell agitator was also used to move the solution across the face of the
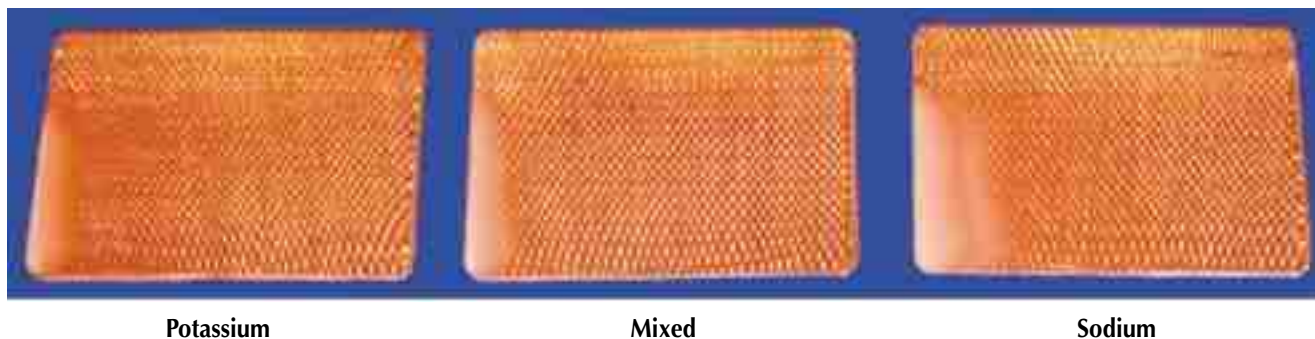
Potassium **Mixed** **Sodium**

Figure 2—Hull Cell panels showing effect of sodium and potassium (all panels run at @A, 10 min with periodic reverse at 10 to 1).

panels. The bright plating range of the panel on the left (made from a potassium-formulated bath) is appreciably higher than the plating range of the sodium bath shown on the right. The panel in the center was plated from a mixed bath containing equal molar amounts of sodium and potassium. The plating range is very similar to the potassium bath. Although not evident from the photograph, the deposits from the baths containing potassium are also brighter in appearance.

Now, obviously, we are not suggesting you discard your present bath. The most economical method of introducing potassium is to substitute potassium hydroxide for sodium hydroxide in maintaining alkali. The benefits to be gained soon become apparent, especially if you also substitute the potassium complex salt for the sodium complex salt of copper in maintaining the bath. After achieving the desired increase in plating speed, you may continue to have success by relying on the additions of potassium hydroxide as the sole source of potassium.

Plating range is also influenced by temperature. For example, the burned range at 82°C (180°F) extends down to about 8.5 A/dm^2 (80 A/ft^2). At 71°C (160°F), the burned range extends to about 6.0 A/dm^2 (55 A/ft^2). If you are only relying on cathode bar movement to move the solution, you can achieve a substantial increase in plating speed by installing air agitation. Circulation by means of pumps is far less effective. The brightness of the deposits also increases with effective agitation.

Brightness of Deposits

High efficiency baths are normally operated with proprietary additives. Besides agitation and the presence of potassium to improve the brightness, another technique used quite extensively is current interruption (Fig. 3).

The purpose of interrupting the current for a short period is to allow time for agitation to replenish the depleted cathode film. The panel on the right was plated for 10 sec, the current interrupted for 1.0 sec and the cycle repeated. Current interruption has several beneficial effects. Under normal conditions, copper deposits from cyanide baths are columnar in structure. The final surface usually is not quite as smooth as the basis metal. Current interruption produces a random type structure with some degree of leveling. If you are not satisfied with the brightness of your deposits, try experimenting with current interruption.

Particle Roughness

Particle roughness probably represents the greatest single problem in high efficiency cyanide copper plating. It can be very serious in plating thick deposits (18 to 25 μm; 0.7 to 1 mil). If you are having difficulties, you should carefully analyze all factors which can contribute to the problem. These include (1) portions of anodes suspended above the electrolyte, (2) oxide inclusions in the anodes, (3) poor anode contact, (4) drag-in on parts, (5) "shelf" areas, (6) location of circulating pipes, (7) anode spacing and (8) stray currents.

The presence of copper oxide is disastrous. Malfunctioning of the anodes is the source of copper oxide. If copper oxide is allowed to form on the anodes, it will usually flake off and circulate in the bath. It is relatively insoluble, low in density and tends not to settle. Upon physical contact with the parts being plated, it is immediately reduced to metallic copper, which becomes attached to the surface. This is just the beginning of the problem. You now have a high current density area and the rate of growth can be astronomical. The "shelf" area on parts, in particular, can resemble coarse sandpaper in appearance.

It takes a mere trace of copper oxide to cause serious problems and the only solution is to eliminate the source. Use high quality anodes and make sure that all anodes are making electrical contact with the bus bars. In extreme cases, the anodes will completely polarize and turn black. Also, if some of the anodes are not completely submerged, the exposed surfaces oxidize to form copper oxide. Some platers bag the anodes to minimize the problem.

If the anode current density is too low, the anodes form sludge and generate copper particles. These particles will tend to settle on the "shelf" areas, especially if the parts are relatively close to the anodes. Drag-in of metal particles on mechanically polished parts will also cause roughness. Magnetized steel particles are also in the disastrous category.

Another factor frequently neglected is the location of the circulation pipes from the filter. If the pipes are close to the bottom surface of the tank, the solution circulation pattern will sweep settled particles from the bottom and distribute them throughout the bath. A spacing of 15 to 22 cm (6 to 8 in.) should be allowed to minimize this source of particles.
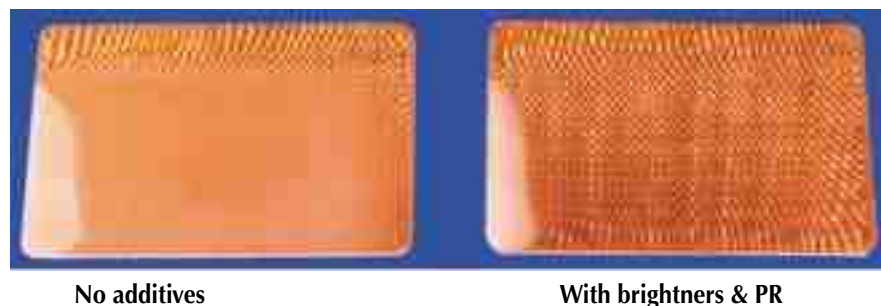

No additives **With brightners & PR**

Figure 3—Effect of proprietary additives (brighteners).

Contaminants

High efficiency baths, in general, are quite sensitive to organic contaminants originating from the cleaner. This contaminant collects in the copper "strike" bath and finally builds up in the high efficiency bath. You can readily establish by Hull Cell tests, the sensitivity of your plating bath to incremental additions of the cleaner. Obviously, you can not continue to operate with the degree of contamination shown in Fig. 4.

The only solution for removing the contaminants is carbon treatment. The most effective method is to treat the bath first with hydrogen peroxide. A normal addition is 130 mL /100L (500mL / 100 gal) of 35 per cent hydrogen peroxide. The peroxide must be diluted with about seven parts of water before adding it to the bath. The purpose of the peroxide is to oxidize the organic contaminants to more insoluble compounds, which are more readily absorbed by activated carbon. A normal addition of carbon is 0.5 kg/ 100 L (4 lb/ 100 gal).

If organic contamination is a serious problem, we suggest you change your operation in order to avoid the problem. We recommend you provide a separate filter on the strike, which will permit you to carbon treat the bath continuously. This does not require a high capacity filter, since the volume is not large.

We recommend that you follow the method outlined here in carbon treating the high efficiency bath. Although you may have eliminated drag-in of contamination from the "strike," brightener decomposition products may also be harmful. A small amount of carbon is added to the filter, and after operating several days (usually one week), additional carbon is applied. Normally, an addition equivalent to 75 g/100 L (10 oz/100 gal) is sufficient. This operation is repeated until the filter is cleaned and recharged. By following this practice, excessive amounts of brightener are not removed by the carbon and the necessity for shutdowns to batch treat are avoided.

Metal Contaminants

If your deposits resemble brass in appearance in the low current density range, you have zinc contamination, a common problem in plating zinc diecastings. Failure to remove the diecastings which fall off the racks is the problem. Bipolar circuits are created and the diecastings dissolve electrochemically, as well as chemically. It is good practice to rake the bottom of the tank daily. The bath is "dummy" electrolyzed at low current densities to remove the zinc.

Another common contaminant is chromic acid. The effects are observed at concentrations as low as 1 ppm (0.001 g/L or 0.0001 oz/gal). You will initially observe dullness in the high current den-

Cleaner contamination   After carbon/peroxide treatment

Figure 4—Effect of proprietary cleaner contamination.

sity range and, as the concentration increases, the deposits will blister (Fig. 5). Special precautions must be taken in conducting Hull Cell tests. The brass panels should be immersed in the bath for a period of 15 to 30 sec before applying the current. This allows time for the hexavalent chromium to passivate the surface.

Reducing agents and proprietary additives containing reducing agents are used to treat the bath. The reduced form of chromium Cr(III) is not detrimental in the bath. We also recommend that you treat the copper "strike" bath in order to reduce drag-in to the high efficiency bath.

Pitting

Pitting normally is not a problem in air-agitated baths. It is, however, common in "still" baths where cathode rod agitation is employed. In such cases, small quantities of proprietary wetting agents must be used to prevent hydrogen bubbles, which cause pitting, from sticking to the surface of the parts being plated.

Skip Plate

Most plating operations encounter, from time to time, a phenomenon called "skip plate" or "ledging." This condition is always found in the very low current density areas of the plated parts. The defects normally are not covered by subsequent nickel deposits. It appears as a mottled deposit and the thickness drops abruptly, leaving a "ledge." The cause is not known. We do know, however, that the condition is associated with the copper metal content and "free" cyanide levels in the plating bath. The standard cure for "skip plate" is simply to increase the "free" cyanide in the bath in 3.8 g/L (0.5 oz/gal) increments until the problem disappears. Usually only one addition is required. Most platers soon learn by experience where to maintain the "free" cyanide in order to avoid the problem. *P&SF*
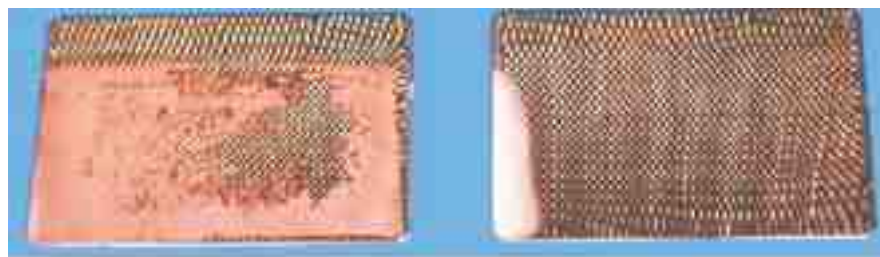
5 ppm Cr(VI)—before and after treatment

Figure 5 - Effect of hexavalent chromium.