## **Finishers' Think Tank**



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## **Decorative Trichrome: How Goes It?**

Decorative trivalent chromium plating was perhaps the first big alternative developed to replace a standard plating process. Ever since the late 1920s, decorative chromium and hard chromium plating from chromic acid baths have been accepted plating operations. Over the years, nothing was developed to replace hard chromium plating on an equal basis. Electroless nickel can approach the hardness characteristics, after a specific post-bake treatment. However, hard chromium is still uniquely positioned, based on the deposit characteristics, thickness ranges and overall utility. Military, aerospace, aircraft, drilling equipment and the printing industry, are just some of the commercial applications best served by hard chromium.

The interest in decorative plating from a trivalent chromium-containing bath (as opposed to the traditional hexavalent) was probably sparked by the following basic chemical equations:

Cr(VI) + 6 electrons  $\rightarrow Cr$  metal

Cr(III) + 3 electrons  $\rightarrow Cr$  metal

The first equation requires six electrons for the reduction of the hexavalent chromium ion to metallic chromium.

The second equation requires three electrons for the reduction of the trivalent chromium ion to metallic chromium.

The difference in efficiency between both reactions (termed oxidation / reduction) is 2:1 in favor of the trivalent chromium reduction to the metallic state. Considering this difference, it was clear that several operating benefits could be achieved by switching from hexavalent decorative to decorative trivalent chromium plating. Perhaps the main benefit realized in plating is overall efficiency. Hexavalent chromium achieves 10 to 15% efficiency, based on the chromic acid-to-sulfate ratio and the catalyst system. Trivalent chromium readily doubles this to 30%. This is a big, important, industrially desired achievement.

Concurrent with process development, health and safety in the workplace became a critical issue. Clinical studies, coupled with personal exposure over time, confirmed a definite health risk to long term exposure to chromic acid solution and airborne mists. Hexavalent chromium was determined to be a carcinogen. This was, from a health and safety standpoint, a big reason to eliminate, where possible, hexavalent chromium compounds. This is another, perhaps bigger reason, to use trivalent chromium salts. Trivalent chromium compounds are not carcinogenic. In fact most multi-vitamin products contain trivalent chromium, essential for overall health.

Incidentally, the trend of replacing hexavalent chromium-containing processes continues today, and will for many tomorrows. For example, we have seen the installation of trivalent chromium passivates meeting RoHS and the newer REACH directives. Returning to trivalent chromium plating, these are some of the benefits achieved in the operation, as opposed to hexavalent:

- Production capacity can be doubled. More parts can be racked and with less space in between. Deposit throw and efficiency are markedly improved, where the nickel tank may become the limiting factor to production output.
- Chromium metal as Cr(III) in the bath ranges from 1 to 3 oz/gal (7.5 to 22.5 g/L). Post-plate rinsing is more effective, with less metal having to be waste treated. This compares to hexavalent chromium baths which typically contain 10 to 17 oz/gal (75 to 128 g/L) of chromium metal as Cr(VI), in a viscous, difficult-to-rinse solution.
- Shading, whitewash, and deposit burning are eliminated.
- Make-and-break electrical contact is no longer a problem. A rack can be lifted and inspected, then returned to continue

plating, similar to handling parts in a nickel bath.

- There is much less wasteful gassing. There are no corrosive mists, nor the requirement for a fume suppressant.
- Lead anodes are eliminated.
- AC ripple is no longer a critical factor. 5 to 10% ripple, similar to nickel, can be tolerated.
- Elimination of hexavalent chromium in waste treatment is realized. In most applications, simple alkaline precipitation of Cr(OH)<sub>3</sub> (trivalent chromium hydroxide) is all that is required, as part of the process.

Each of these examples does relate to cost savings, which can readily offset some rising costs in the current economic climate.

Commercially feasible decorative trivalent chromium plating was introduced in the early 1970s. Improvements and refinements have followed, most notably in the decade of the mid-1980s to 1990s. There are two main decorative baths in commercial use. These are referred to as the sulfate and chloride systems. The biggest initial problem associated with trivalent chromium plating was how to overcome the obvious oxidation of Cr(III) to Cr(VI) as an anode-recognized oxidation reaction. The unfortunate formation of Cr(VI) quickly resulted in problems such as darkened deposit color, lack of coverage and line shutdown. Introduction of reducing agents and related chemical purifiers helped, but only if extensive service and trained personnel spent quality time monitoring the process.

The next step in anode design was replacing carbon with lead. However, the lead anode was shielded from the actual plating bath. It was placed in a box containing a conductive solution of sulfuric acid, with the anode facing a semi-permeable membrane. Only hydrogen ions from water electrolysis inside the box could penetrate and pass through the membrane, migrating to the cathode, thus completing a plating circuit. This was a successful approach to eliminate the formation of Cr(VI). However, over extended time, some boxes in the field leaked, thus not accomplishing their intended purpose. There was also the initial capital expense of the membrane and the care needed not to damage it. The corrective action was to install anodes having a precious metal coating. By eliminating the box and membrane concept, the inert anode achieved a reasonable service life, greatly stabilizing the bath chemistry for continued quality plating. There was still the cost of the precious metal coating and the eventual requirement to re-coat the anode base material.

Improvements to stabilizers and purifiers have also enabled platers to operate a different base trivalent chromium chemistry bath, using carbon anodes. There was another attempt at isolating the anode from the trivalent chromium bath, but it was short lived, comprising the encasing of a carbon anode in a ceramic chamber.

We have detailed several excellent advantages to decorative trivalent chromium plating as opposed to the hexavalent chromium counterpart. Are there any disadvantages? Yes, and here, as I acknowledge, are the main ones:

**Thickness**. In the chromic acid-based systems, the deposit thickness is infinite (For the mathematicians, it follows the function,  $f(X) = x^2$ , as it relates to a parabolic graph.). Decorative trivalent chromium thickness is self limiting, approaching 30 millionths of an inch.

*Passivation*. Trivalent chromium solutions do not passivate thin or unplated steel surfaces (such as inside unplated tubing), as does chromic acid.

*Stripping.* Trivalent chromium solutions, as I am accustomed to, can't be cleanly stripped anodically in the electrocleaner. Rather, 30 to 50% hydrochloric acid is required for a clean, complete deposit stripping.

**Deposit color.** From my experience, trivalent chromium deposits range from slightly darker than hexavalent chromium to almost a pewter appearance. A big misnomer, as far as I am concerned, is the mistaken belief that trivalent chromium deposits can be a dead even match to the hexavalent chromium deposit color. From

my perspective, the crystalline deposit structures of both differ, and as such refract light differently. In addition, trivalent baths co-deposit organic additives.

Trivalent chromium baths seem to have been developed in a similar maintenance structure as for nickel baths. Trivalent chromium additives include a source of ready-to-plate metal, brighteners, stabilizers, buffers, wetting agents and purifiers. Normally, two additives are dosed per ampere hour. Wet analysis in conjunction with a Hull cell test typically comprise bath and deposit maintenance. Carbon filtration is important to minimize organic contamination. Dummy electrolysis or ion exchange is used to remove metallic contaminants.

Decorative trivalent chromium plating has advanced in reliability, understanding and process application. Acceptability has been across many consumer and industrial requirements. Health and safety issues make it a reasonable and wise selection. Trivalent chromium fits rather well into RoHS and REACH directives. The next big improvement in chromium plating would be commercially feasible hard chromium plating using trivalent chromium-based plating solutions. **PESF** 



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