Article written by Adam Blakeley, MacDermid Enthone

Adam Blakeley has been a technical service representative for MacDermid and MacDermid Enthone for the past five years. He recently obtained is Master Surface Finisher (MSF) designation and has written more than half a dozen articles for Products Finishing magazine. He specializes in crafting and designing exclusive classes for a variety of surface applicators in a diverse range of fields including zinc, decorative and hard chrome, bright and sulfamate nickel, electroless nickel, phosphating, and POP.

Tri-Chrome in Hard Chrome

Article Summary

This article seeks to demonstrate how tri-chrome build-up in hard chrome baths generates, how it affects the bath and deposit, how applicators can test for it, and how they can get rid of it.

Ways Tri-Chrome Builds Up in Hard Chrome Baths

In a basic hexavalent functional chromium (hard chrome) plating bath the anodes are insoluble, made most commonly of lead alloyed with tin (for corrosion resistance) and antimony (for rigidity). These anodes complete the electrical circuit and to deliver current to the parts being plated, but also to re-oxidize the trivalent chromium (tri-chrome or Cr+3) ion contaminants that form at the cathode during the deposition process back to the hexavalent state (Cr+6). Only 10-25% of the total current within this electrochemical plating cell is used to produce a metal deposit while the rest produces hydrogen gas, with a nominal percentage involved in tri-chrome (Cr+3) evolution.

Since tri-chrome is an inevitable contaminant in a hard chrome plating bath due to the reaction at the cathode it is not entirely feasible – nor recommended – to remove all traces of tri-chrome. It becomes problematic when it begins to exceed approximately 0.5-1 ounce per gallon (opg) or around 1-3% of the total chromic acid figure in an average hard chrome bath.

If chromium anodes were used instead of the leaded insoluble ones the dissolution rate would be at 100% efficiency and the ions created would be in the Cr+3 form instead of the Cr+6 form and would be therefore not produce a proper hard chrome deposit. The lead anodes require a certain amount of potential (voltage) to ensure the proper polarization effect, which favors the dissolution of lead and the formation of a thin, conductive, brown film of lead dioxide (PbO_2). The tin and antimony help the anode reach this polarization or partial passivation state, which causes oxygen to evolve and helps form the conductive film. The lead dioxide that forms not only transmits the proper quantity of current but also contributes a steady supply of oxygen, which helps to re-oxidize the Cr+3 to Cr+6. An improperly functioning electrode often develops an insulating yellow lead chromate film, indicating not only that the anode fails to transmit current but also that it cannot effectively oxidize the Cr+3. A lead dioxide film that is too thick and heavy can also lead to trouble. These are a couple common ways Cr+3 builds in the bath over time.

Failure to provide a secure connection of the anodes to the busbar rail will limit their ability to perform any of the aforementioned duties; therefore it is crucial to check the resistances within the electroplating system itself. A thorough inspection of the rectifiers and their internal circuitry for broken or malfunctioning diodes, thyristors, transformers, etc., and the bussing for tarnish, rust, and other voltage inhibiting impedances is paramount. Tong testers and volt-ohm meters are useful tools for this inspection. Anode to cathode ratios should be high – about 2-4:1 – to ensure multiple sites are available for Cr+3 oxidation.

Lastly, hex-chrome ions can be reduced to tri-chrome when they encounter organic contaminants generating from multiple sources and stages within the life of an electroplated part. Parts are manufactured, formed, cut, machined, and polished in an assortment of ways using an array of different chemical mixtures including lubricants, oils, fluids, buffing compounds, greases, and other organics that become highly problematic if dragged into the plating solution.

Organics are also used in the chemical pre-treatment tanks. Surfactants and other detergents in the soak, electro-cleaner, and even acid pickling solutions are used. These include sodium lauryl sulfate and butynediol, which – along with all other organics – can cause the deposit to become pitted, dull, or hazy all on their own, but can also act as a warning sign to the troubleshooter of the possibility of rising tri-chrome levels since these two components have a correlative connection. Proper cleaning methods and adequate rinsing will tend to forestall and obstruct excessive organic loading.

Stop-off lacquers, waxes, adhesives, tapes, and other maskant materials, especially the proprietary polymers and resins that contain xylene, naptha and PCE (perchloroethylene) among others, are organic too, and if introduced into the plating cell without being properly conditioned and tested can cause tri-chrome levels to rise due to their interaction with the hex-chrome ions. Organics can also be leached into the tank from tank linings, plastic piping, and other plastic components that degrade due to contact with the hot chromic acid constituents.

How Does the Tri-Chrome Impact Quality

Tri-chrome can wreak havoc on several properties and characteristics of a hard chrome deposit. Hard chrome baths are notoriously inefficient, but are even more so when dosed with Cr+3. Hard chrome baths, as previously mentioned, use 10-25% of the energy given effectively. The addition of high levels of tri-chrome and other metal contaminants can bring that incredibly

meager efficiency figure down even further. A 5% decrease in efficiency may not seem drastic, but when the average efficiencies are just over 17%, 5% counts for a 30% decrease in throughput, which can be a loss of an entire shift in some cases. Hex-chrome baths are also notorious for their poor coverage or inability to plate in the low current density (LCD) regions of parts, those areas furthest from the anode. This issue can be compounded significantly with the introduction of excess tri-chrome.

Burning in the high current density (HCD) regions of the part, which often manifests, manifests – depending on its severity – as exfoliation, often feels rough to the touch. The term burning was contrived because the deposit often appears as though a torch was applied to the inspected area. Nodulation and what has colloquially been termed "treeing" can occur as well, which is often a symptom of extreme burning in which the part neglects to produce a conventionally smooth deposit. It rather assembles and organizes together small nodules that stack on top of each other during the plating process, materializing into tree-like branches of metal often brought on by the influx of tri-chrome.

Macro-cracks are cracks visible to the unaided eye and often result in reduced corrosion and wear resistance, while micro-cracks are the desired crack type. A standard hard chrome, micro-cracked deposit should have approximately 800-1,000 cracks per linear inch, but macro-cracks have a density of only 1-50 cracks per linear inch due in large part to the introduction of tri-chrome.

Hard chrome deposits are some of the hardest deposits within the electroplating industry with figures as high as 850-1100 Vickers, but tri-chrome excesses can diminish that hardness figure considerably, tending to hurt both abrasion and wear resistance along with it.

Tri-chrome has also been responsible for poor adhesion due to its interference at the cathode and the bond formed between the substrate and the intended metallic deposit.

Methods for Testing Tri-Chrome

Three popular methods for determining tri-chrome levels in hex-chrome solutions are the titrimetric, visual and spectrophotometric methods.

Titrimetric analysis requires determining hex-chrome concentration of the hard chrome solution first and then repeating the same procedure once the tri-chrome has been oxidized using an oxidant like sodium peroxide. The analysis might show the chromic acid concentration at 35 oz/gal. Then, after adding the oxidant (peroxide) and boiling the solution, the second analysis might produce a chromic acid figure of 35.7 oz/gal, demonstrating that there was approximately 0.7 oz/gal of total tri-chrome in the solution that has now been converted to hex-chrome.

The visual method involves determining tri-chrome levels by color differentiation. A fresh hex-chrome solution exhibits a reddish-orange color when no tri-chrome is present. As the tri-chrome builds the bath becomes noticeably darker and browner. The change is not subtle, but rather quantifiable within a 5% accuracy range (which is on average a difference of + or - 0.03 opg). Test tube standards with an array of tri-chrome concentrations can be created in the lab using stock hard chrome solution by adding measured amounts of a reducing agent like sucrose (sugar) to form tri-chrome at predictable quantities.

Lastly, the spectrophotometric method measures the intensity of light beams as they relate to their color or wavelength. This method is essentially a more sophisticated and quantitative version of the visual method provided above, but removes the possibility for laboratory technician error and is, therefore, more accurate.

These tests are designed to inform hard-chrome applicators of any potential movement in tri-chrome levels. The discovery of tri-chrome growth would signal to the operator the need to ascertain the source of the build-up, whether organic accumulation, polarized anodes, or some other elusive phenomena.

Ways to Combat Tri-Chrome Build-Up

As tri-chrome and other metallic contaminants continue to build-up in the bath, an increase in the required amount of voltage to get the proper amperage will be greater. Many applicators increase both the chromic acid and catalyst figures to temporarily attenuate and mitigate the symptoms and issues caused by these contaminants. If using fluoride as a catalyst this might increase etching of the substrate; so this method needs to be used with prudence and discretion.

Reduction of the resistances in the plating cell from the rectifier, to the bussing, to the rack of parts can help abate and suppress the development of tri-chrome because it ensures the anodes are fully functional and thus able to oxidize the tri-chrome back to hex. Operators should certify and confirm all connections are tight and clean, taking care to regularly inspect the anodes for the correct brown color and level of thickness. Regularly scheduled cleaning and energizing sessions are needed for the anodes to be in proper working condition. Regular immersion of the anodes in appropriate acid or alkaline stripping solutions will adequately dissolve the improper films and removal of the anodes during idle periods to delay or prevent the development of these films is recommended.

Of course, keeping the bath free of organics generating from the manufacturing or cleaning areas or from the plastic elements and accessories used in the bath itself is crucial for stopping the advancement of tri-chrome.

Once tri-chrome develops to unacceptable levels the applicator can remove it via electrolysis or by dummying the solution at high cathode current densities (CCD) of 100-200 amps per square foot (ASF) with an anode current density (ACD) of 20-100 ASF, emphasizing the lower ASF over the higher one. Vigorous agitation and high temperatures (145 F) – provided the equipment can handle it – can increase the opportunities for oxidation.

Utilizing porous pot technology is a more controlled version of the electrolysis method. These ceramic membrane systems can remove tramp metals and oxidize tri-chrome ions back to hex-chrome provided the anode area is large and the temperature is high (140 F). During the process of electrolysis the chrome solution's cations (positively charged ions) are prompted to travel towards the leaded-mesh cathode through the <1 micron pores of the ceramic of the porous pot producing metal salts or hydroxides on the cathode film surface. The two anodes are placed adjacent to the walls of the pot on the outside and are responsible for converting the tri-chrome to hex due to their proximity and not any ionic attraction to the anodes themselves. The current will eventually drop as the cathode builds up with a coating of hydroxide metal salts. The anode to cathode ratio is often 30:1.

Electrodialysis uses a heavy-wall polyester membrane often immersed in the plating tank in the same way the porous pot is or, alternatively, in an auxiliary tank. Maintenance requirements are very similar. The electrochemical cells have an anolyte compartment containing the anode and a catholyte compartment for the cathode separated by an ion exchange membrane with a resin film versus a bead or powder as it is in other systems. $Cr+3$ is oxidized at the anodes to create chromic acid.

A small removal of the solution with an add back of the necessary hard-chrome constituents is always an option for any bath. If waste treatment can handle the extra gallonage then this is and always will be a last resort that should be considered for its simplicity and ease, but the cost of labor and treatment might outweigh the benefits.

Conclusion

Hard chrome solutions are incredibly resilient and robust plating solutions capable of handling large amounts of both organic and inorganic contamination beyond what a standard bath in any electroplating category could manage; however, there is a point at which the contamination will reach a fevered pitch at which time the applicator would notice major quality defects requiring immediate attention. To avoid responding reactively to the multiplication and accumulation of tri-chrome, precautionary measures and preventative maintenance (PM) activities must be instituted. Implementation of lab analyses and procedures using the visual, titrimetric or spectrophotometric methods is a start. An awareness and cognizance of those practices that encourage the evolution of trichrome, including organic contamination, plastic degradation, and anode conductivity, are pivotal to successful operation. It is far better to preemptively resist the formation of tri-chrome at every stage than to do nothing and allow the $Cr+3$ to emerge and accumulate. The time spent on prevention is almost always more efficient than fixing problems associated with efficiency, coverage, plating speed, burning, nodulation, macro-cracking, softness, adhesion, pitting, dullness, and haziness.