Plating & Surface Finishing Retrospective

Originally contributed by Ronald Kornosky
Compiled by Dr. James H. Lindsay, AESF Fellow

Based on an original article from the early *Finishers Think Tank* series
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Fickle black oxide

Q: We've been using the same black oxide bath on steel for more than six years. Occasionally, we experience a problem where the bath will quit blackening in the middle of a run. Temperature adjustment, better cleaning and long immersion times don't help. Neither does pickling, recleaning, adding more salts . . . even cursing! Usually, the next morning the bath starts working normally again. The problem sometimes occurs every other day, and sometimes not for months. What's wrong?

A: A black oxide bath is used to give a true iron oxide (Fe_3O_4) over steel. Most of the baths operate at about 149°C (300°F) and use of an accurate thermometer is necessary. A mercury-filled glass thermometer is very good [if you can find one in 2006]. The baths also contain some water, the concentration of which must be controlled. Without water additions, you may end up with an insoluble rock in your tank. Usually, this problem shows up as interference colors (not black) on the work surface. Even shades of red rust may occur.

Most proprietary products have ingredients to control the color, refine the grain of the deposits and monitor the rate of blackening. One of these additives could dissociate with excessive heat to the point of stopping the bath, and only by cooling and reheating would the bath work normally again. I would look into possible overheating and better temperature control for your answer.

Another possibility, according to Walter Schwartz of The Enequist Chemical Co., Brooklyn, NY, is that the bath is accumulating iron and/or copper. Sodium cyanide has been used as an addition to black oxide baths to help correct the problem of iron accumulation. Other complexing materials also are available from supply companies.

Mr. Schwartz adds, "An alternate means of removing the iron is to transfer the blackening solution to a separate storage tank and dilute it to approximately half strength. The iron will precipitate out at this point as iron hydroxide. The clarified solution can then be transferred back into the oxide tank and brought back to operating strength with fresh salts. Copper, if present, can be removed at the same time by adding sodium sulfide to the oxide bath. The sodium sulfide is dissolved in water and added at the rate of approximately 0.12 g/L (1.0 lb/1000 gal) of the previously diluted black oxide bath. If this procedure is utilized, the oxide tank should concurrently be cleaned of sludge, dirt, dropped parts, etc. The clear diluted solution can be used to replenish the reconstituted black oxide solution."

Small blind holes

Q: I'm sending you some blocks (Fig. 1) that we chloride zinc plate. One has been cut in half to show you the blind holes that are giving us so much trouble. We do excessive rinsing, hot and cold, use air agitation and apply a lubricating oil on the last step. Solution still runs out of the block, causing part rejection. Any ideas?

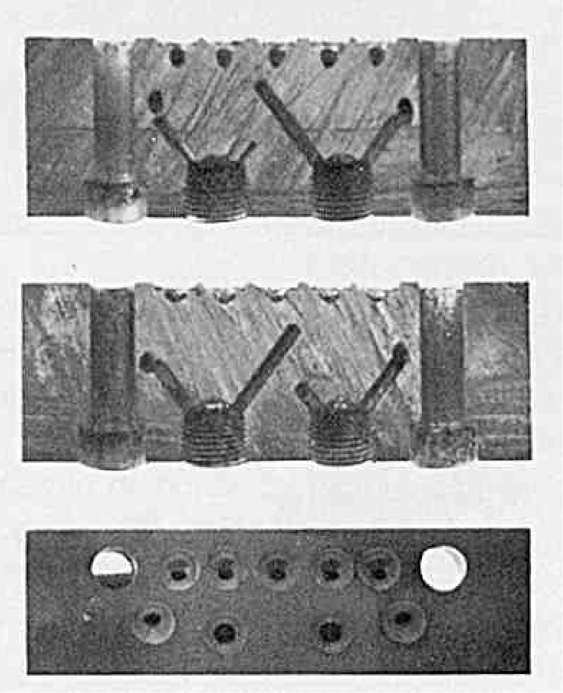


Figure 1—Block with blind holes; at bottom is a surface view; the top and middle photos show a cross-section of the same part cut in half. Part is about 1.25 × 4.0 cm.

A: This is a tough one. Since you've already tried hot and cold water rinses and air agitation, perhaps an ultrasonic rinse, although expensive, may help to remove contaminants. An extended drying time to evaporate all the liquid in the holes may help too.

John Laurilliard of SPS Technologies, Jenkintown, PA, also took a look at your parts. Here's what he says: "We found that only two of the small holes at the bottom of the tapped holes are actually blind. All the other small holes exit through a larger hole. The route was determined by pumping ethyl alcohol solvent from a plastic squeeze bottle through each hole and observing the exit point. Only two holes, one in each of the threaded holes, were blind.

"As Mr. Kornosky has indicated, the standard practice of alternate rinsing in hot and cold water will normally suffice if the diameter of the holes is not so small that capillary action prevents free drainage of trapped solution. An evaporation technique using elevated temperature or vacuum will remove water but may leave the salts behind. These will later absorb moisture from the air and 'bloom.'

"Mechanical removal may help you. Parts could be stacked in a spinner basket and centrifuged to remove the solution. A second or even a third subsequent cold water rinse followed by additional spinning may be necessary.

"Another technique involves rinsing parts in either methyl or ethyl alcohol, which are miscible in all proportions with water. Several such rinses may be necessary to totally remove the water. Displacement methods may also be helpful. Water displacement can be accomplished using Freon solvents. The high density and low surface tension of Freon TF solvent and a hydrophobic surfactant enhance water separation.

"If all the above fail, you may be forced to use a direct selective-rinsing technique. You will have to construct a small-diameter rinsing device. Two hypodermic needles soldered to a piece of copper tubing and fitted to a trigger hose nozzle work well for rinsing out blind holes. The parts should be unracked after the final rinse, the blind holes rinsed using hypodermic needles and, finally, the entire part rerinsed to wash off the solution that emerges from the blind holes. A similar device may be used to blowout and dry the blind holes with compressed air." Mr. Laurilliard concludes.

As a final thought, perhaps you should check with the part designer. A rule of thumb would be to limit blind holes to 50% of their diameter, and avoid blind holes with a diameter of less than 0.56 cm ($^{7}/_{32}$ in). Not only is rinsing a problem when holes are too small, electrodeposition becomes a difficult practice in these spots. Quality products require quality design! Without this, the type of problem you have is bound to occur.

Removing trivalent chromium

Q: What suggestions do you have for removing trivalent chromium from hard chromium plating solutions?

A: The first thing you need to do is use an excess of anode area from the start. Make sure each anode is passing current and is not insulated by an insoluble lead chromate. A light yellow film of lead peroxide on the surface is normal, but scale buildup is not. Hard chromium plating on hollow parts or those with large surface areas does present a problem with trivalent chromium buildup and dissolved heavy metals like iron.

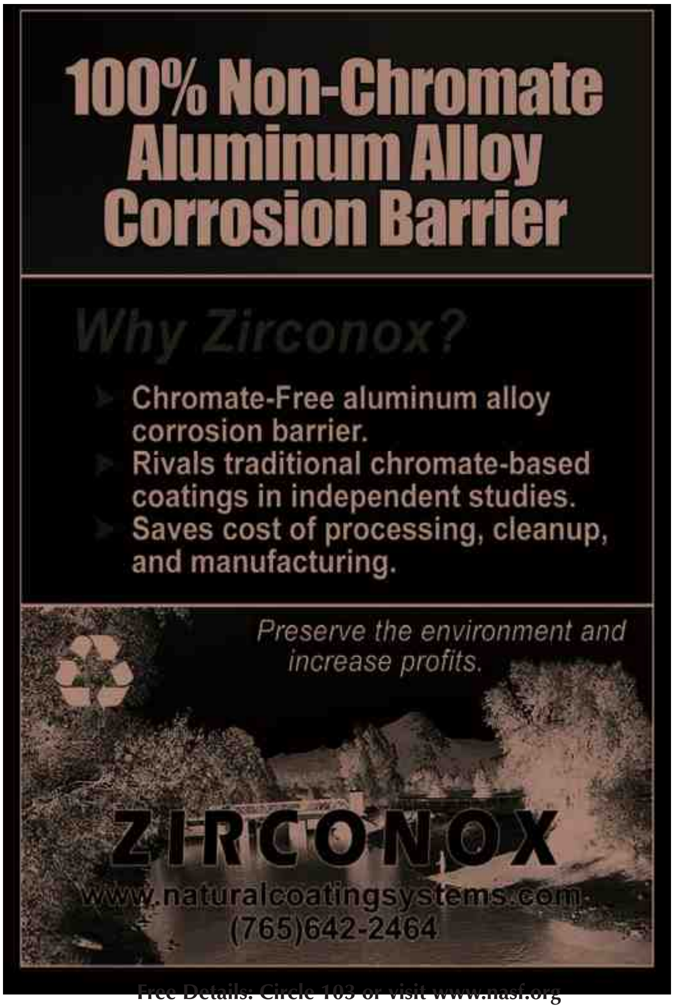
A popular method of removing trivalent chromium and iron from chromium plating solutions is to use an oxidation-resistant, stable cation-exchange resin, reports Dr. E. J. Seyb of M& T Chemicals, Rahway, NJ. Both trivalent chromium and ferric iron are present as cations and are removed by the resin while the chromic acid anion passes through the exchanger. The resin will last longer if the bath concentration is reduced to 100 g/L or less for treatment. Regeneration of the resin should be done with dilute sulfuric acid and care should be taken to assure that the resin is rinsed free of sulfate afterwards, Dr. Seyb explains.

Another method is to dummy the bath during normal downtime using an extremely small cathode area. With this arrangement, only a small amount of chromium is deposited and the anode area is then capable of converting the trivalent chromium to the hexavalent state again. This also can be done in a small overflow tank on the side so that the process is continuous. Analysis is needed to measure the rate of oxidation.

Still another procedure employs a stone-type porous cup. The cup is filled with dilute sulfuric acid and a lead cathode is inserted. Oxidation of trivalent chromium still takes place at the anode area, but some trivalent chromium and dissolved iron find their way into the sulfuric acid, and therefore can be removed. A minor problem is that some sulfate diffuses into the bath, so that sulfate analysis should be performed to keep the balance.

A more recent advancement deals with electromigration principles. A specialized membrane is used with current in a separate cell to enable trivalent chromium to pass through the membrane and concentrate it in a small volume for removal from the bath. ***P&SF***

The edited preceding article is based on material compiled by Mr. Ronald Kornosky, then of Hager Hinge Co., in Montgomery, AL, as part of the Finishers Think Tank series, which began its long run in this journal 26 years ago. It dealt with everyday production plating problems, many of which are still encountered in the opening years of the 21st century. As we have often said, much has changed ... but not that much. The reader may benefit both from the information here and the historical perspective as well. For many, it is fascinating to see the analysis required to troubleshoot problems that might be second nature today. In some cases here, words were altered for context.



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