Alternatives to the Hexavalent Chromates: An Evolution of Trivalent Chromate Technologies*

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Fourth-generation trivalent chromate conversion coatings exhibit excellent corrosion resistance and self-healing properties, not unlike hexavalent chromate conversion coatings. These self-healing trivalent chromate conversion coatings incorporate chemically inert nanoparticles in the conversion coating. The nanoparticles add thickness and corrosion resistance to the chromate film. The migration of the nanoparticles into scratches in the conversion coating film produces the self-healing effect.

What surface coating technologies are available to fight against corrosion, now that hexavalent chromates are no longer available? Surface coatings increase service life with increased corrosion protection, aesthetic appeal and increased wear resistance. Zinc electroplate with chromate coatings are the low-cost, bulk-applied coatings that are widely specified. Electroplated zinc is given post-plating treatments consisting of chromate conversion coatings, topcoats and sealers. Until recently, these chromate conversion coatings and sealers contained the hexavalent chromium ion from either chromic acid or chromates.

The End of Life Vehicles (ELV) Directive (2000/53/EC) of the European Union mandated the replacement of hexavalent chromium by July 1, 2007 and has effectively ended the use of hexavalent chromium in the workplace, except for hard chromium plating.[1,2] The best alternative to hexavalent chromium is trivalent chromium for both chromate conversion coatings and for decorative chromium plating. Consequently, trivalent chromate conversion coatings are replacing conversion coatings containing hexavalent chromium. The process of replacing hexavalent chromium with trivalent chromium has a history going back to the 1970s.

First-generation trivalent chromates were mixtures that were similar in composition to hexavalent chromates, except that the oxidizing power was supplied by either hydrogen peroxide or by nitrates in place of chromic acid or chromate salts. These early trivalent chromates were used to produce a blue coating on alkaline non-cyanide zinc. The coatings were thin (~60 nm), powdery, and provided limited corrosion resistance. What corrosion resistance they did provide was often limited to the prevention of "finger staining," but not much more. Typical neutral salt spray test (NSST) resistance was 3 or 4 hr to 5% white rust.

Improvements that led to what are referred to as second-generation trivalent chromates, consisted of "more of the same." Higher concentrations, higher temperature and the use of fluoride extended the NSST corrosion resistance to perhaps as high as 24 hr to 5% white rust. The next step was the introduction of "thick film" trivalent passivates that relied on the introduction of weak organic acids into the formulations.[3] This innovation provided corrosion resistance of about 48 hr to 5% white rust in salt spray corrosion testing for films that were about 100 nm thick.

True third-generation trivalent chromates were improvements based on the introduction of transition metals and higher operating temperatures, which produced thick (~400 nm), green coatings with red/green iridescence.[4] The corrosion resistance provided by these "green" coatings was a quantum leap beyond what could heretofore be achieved. NSST results were in excess of 300 hr to 5% white rust. Another property of third-generation trivalent chromates is that they have little water of hydration in the film and are less affected by exposure to heat. Therefore, baking will not significantly degrade them.

Fourth-generation trivalent chromate films are also thick (~400 nm), but with a blue, slightly iridescent color. These films are also able to achieve over 300 hr in NSST to 5% white rust. A unique property of this fourth-generation trivalent chromate is that it exhibits self-healing properties, somewhat like the self-healing of hexavalent chromate films. The unique ability to self-heal is the result of incorporating nanoparticles in the formulations. These chemically inert particles spontaneously form a topcoat on the chromate, while the parts are being processed in the trivalent chromating solution.

These layers can be seen in Fig. 1, which illustrates the results of an analytical process called ion milling (sputtering), where the surface is bombarded with ionized argon to remove layers of the film. The revealed surface is then exposed to an electron beam that causes x-ray emission from Auger electron transitions in the excited atoms within the film.

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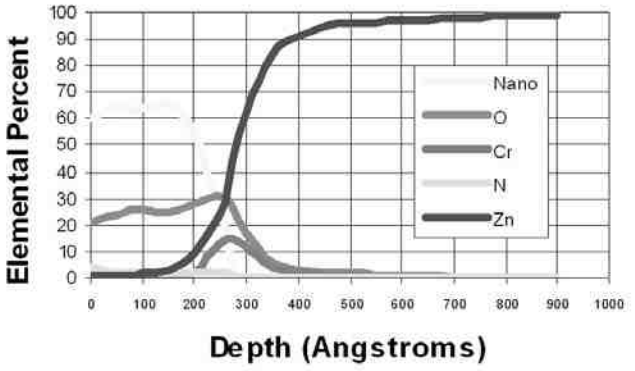

Figure 1—Ion milling of 4th generation trichromate film, using Auger detection.

As the sputtering proceeds, more and more layers of the film are peeled away, as illustrated in the figure. At the surface can be seen the presence of a spontaneously formed nanoparticle topcoat, followed by the actual chromate conversion coating which also contains nanoparticles. Finally, the milling process reaches the zinc surface. The total film thickness milled is about 400 nm. Fourth-generation trivalent chromates contain the nanoparticles in the chromating solution itself and are not a post-chromate topcoat.

The chromium-containing layer in this film is relatively thin for a chromate that achieves more than 300 hr in NSST testing and consequently contains much less trivalent chromium than third-generation films. Corrosion resistance of 600 hr to 5% white rust has been reported - twice what is achievable with yellow hexavalent chromates!

"Self-healing" is the property of chromate films which allows small imperfections or cracks in the film to be filled with more "chromate" from the chemicals already present in the chromate film and water from the environment; *i.e.*, the salt spray cabinet. In the case of hexavalent chromates, these "healing" chemicals include chromate ions that diffuse into scratches in the film and further react with zinc to repair the scratch with more chromate conversion coating.

Self-healing with nanoparticles is illustrated in Fig. 2. Here the nanoparticle coating can be seen filling a cut in the chromate film. Q-Panels with crosscuts have gone more than 300 hr in NSST without corrosion.

Fourth-generation chromates do not use organic acids, so waste treatment problems caused by complexed metals are avoided. These fourth-generation films are totally inorganic. Baking will not significantly degrade them.

Figure 3 shows the relationship between chromium concentration and NSST for a fourth-generation iridescent, trivalent chromate. Figure 4 shows the very important relationship between temperature and time to white rust. It can be seen that the optimum temperature is about 30°C, a significantly lower temperature than third-generation trivalent chromates. Therefore, fourth-generation trivalent chromates are considered to be "low temperature" chromates.

In Fig. 5 the effect of immersion time on corrosion in salt spray can be seen. It should be noted that most of the corrosion protection can be attributed to the first 20 sec of immersion at 30°C.

Figure 6 shows that for the best results in salt spray, the optimum pH is 2.0, with a fairly narrow range of operating pH from 1.8 to 2.2. At pH <1.8, the film is dissolving as well as forming, and at pH >2.2, the nanoparticles begin to fall out of solution before they can form a film.

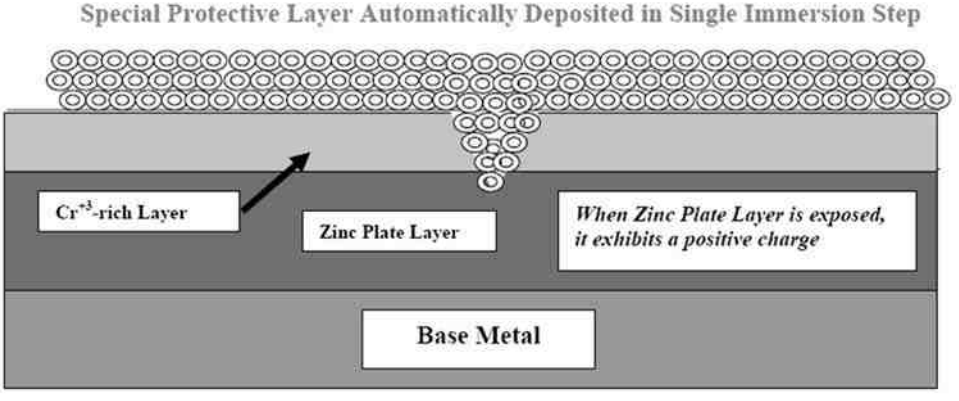

Figure 2—Self-healing illustration using nanoparticles to fill voids.

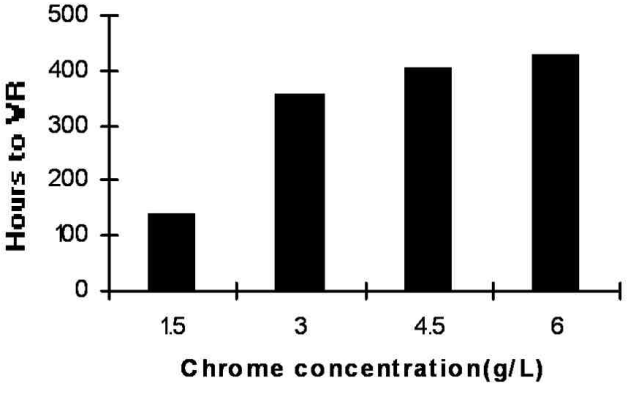

Figure 3—Corrosion resistance vs. chromium concentration.

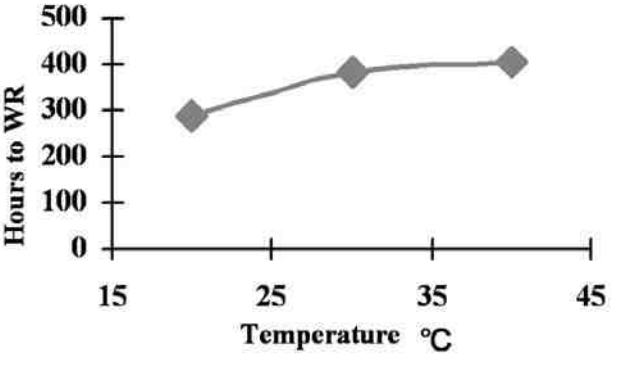

Figure 4—Corrosion resistance vs. operating temperature.

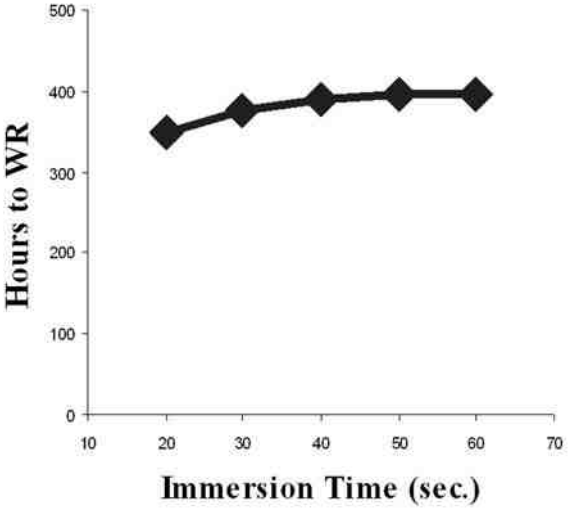

Figure 5—Corrosion resistance vs. immersion time.

Iron and zinc are the most significant contaminants in the chromating solution. Levels of iron can reach 300 ppm with no decrease in corrosion protection, whereas zinc can reach 20,000 ppm in these chromates with no detrimental effects. Iron will discolor (blacken) the film long before it reduces corrosion resistance.

Self-healing and low temperature operation are unique characteristics of fourth-generation trivalent chromates. As with all thick film trivalents, careful control of operating parameters is necessary to achieve the promised performance. This cannot be emphasized enough. Operating outside the recommended limits

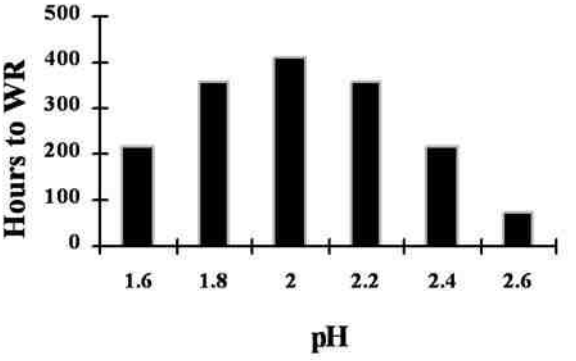

Figure 6—Corrosion resistance vs. operating pH.

in the operating instructions will result in poor performance, in terms of corrosion resistance, but can also cause the chromating solution to decompose. Therefore, there is a new learning curve for successful operation of fourth-generation trivalent chromates, requiring operators and vendors to work together to achieve optimum performance. ***P&SF***

References

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