

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

By William Eckles and Rob Frischauf, Taskem, Inc.

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 (ELVs) Directive (2000/53/EC) of the European Union mandated the replacement of hexavalent chrome by July 1, 2007 and has effectively ended the use of

hexavalent chrome in the work place, except for hard chrome plating.^{1,2} The best alternative to hex-chrome is trivalent chromium for both chromate conversion coatings and for decorative chrome plating. Consequently, trivalent chromate conversion coatings are replacing conversion coatings containing hex-chrome. This process of replacing hex-chrome with trivalent chrome 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 provide 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 hours to 5% white rust.

Improvements that lead 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 hours to 5% white rust.

The next step was the introduction of “thick film” trivalent passivates that relied upon the introduction of weak organic acids into the formulations.³ This innovation provided corrosion resistance of about 48 hours 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 (~400nm), 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 hours 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 (~400nm), but with a blue, slightly iridescent color. These films are also able to achieve over 300 hours 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 nano-particles 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 Figure 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.

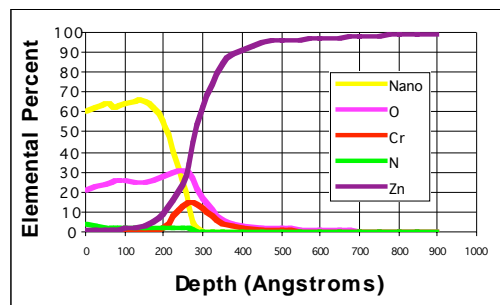


Figure 1. Ion milling of 4th generation trichromate film, using Auger detection.

As the sputtering proceeds, more and more layers of the film are peeled away, as illustrated in Figure 1. At the surface can be seen the presence of a spontaneously formed nano-particle topcoat, followed by the actual chromate conversion coating, that also contains nano-particles. Finally, the milling process reaches the zinc surface. The total film thickness milled is about 400 nm. Fourth generation trivalent chromates contain the nano-particles in the chromating solution and are not a post-chromate topcoat.

The chrome-containing layer in this film is relatively thin for a chromate that achieves more than 300 hours in NSST testing, and consequently contains much less trivalent chromium than third generation films. Corrosion resistance of 600 hours 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 ion that diffuse into scratches in the film and further react with zinc to repair the scratch with more chromate conversion coating.

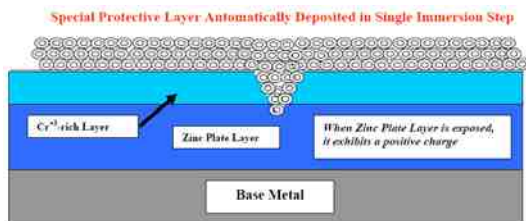


Figure 2. Self-healing illustration using nanoparticles to fill voids.

Self-healing with nano-particles is illustrated in Figure 2. Here the nano-particle coating can be seen filling a cut in the chromate film. Q-Panels with crosscuts have gone more than 300 hours 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.

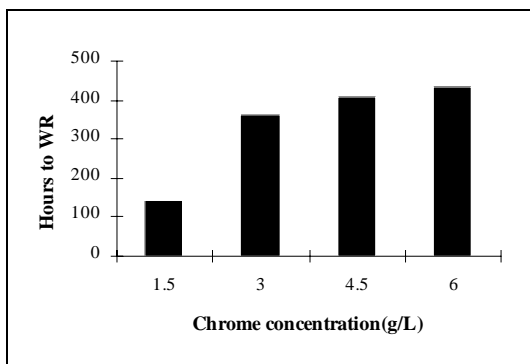


Figure 3. Corrosion resistance vs. chrome concentration.

Figure 3 shows the relationship between chrome 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 noticed that the optimum temperature is about 30 degrees centigrade, a significantly lower temperature than third generation trivalent chromates. Therefore, fourth generation trivalent chromates are considered “low temperature”.

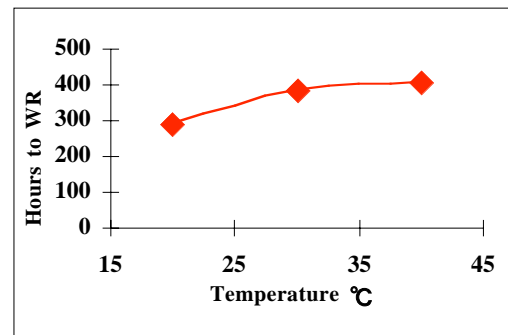


Figure 4. Corrosion resistance vs. operating temperature.

In Figure 5 the effect of immersion time on corrosion in salts spray can be seen. It should be noted that most of the corrosion protection can be attributed to the first 20 seconds of immersion at 30 degrees.

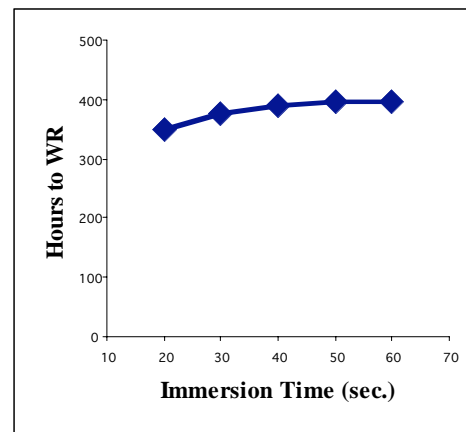


Figure 5. Corrosion resistance vs. immersion time

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 nano-particles begin to fall out of solution before they can form a film.

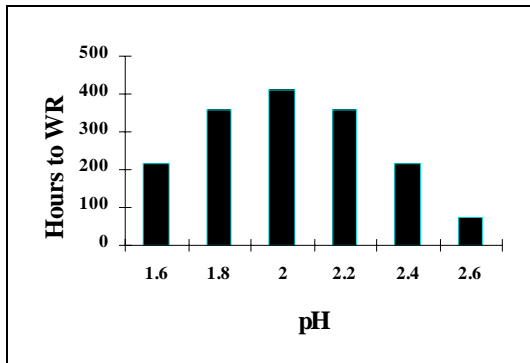


Figure 6. Corrosion resistance vs. operating pH.

Iron and zinc are the most significant contaminants in the chromating solution. Levels of iron can reach 300 ppm without any decrease in corrosion protection, whereas zinc can reach 20,000 ppm in these chromates without any 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 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.

References:

1. The Environment Agency, 2006, www.environmentagency.gov.uk
2. Directive 2002/95/EC of the European Parliament and Council.
3. Klos, US Patent 5,368,655; 1994.
4. Preikschat, et al, US Patent 6,946,201.