Unexpected Results from Corrosion Testing of Trivalent Passivates[1]

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Editor's Note: *The issues discussed in this article are timely and critically important. Some of our readers may find some of the results controversial. Accordingly, this article was carefully peer-reviewed by three longtime experts representing over a century of combined experience in the surface finishing industry. Though they shall remain anonymous, the consensus had no quarrel with the findings which follow.*

We expect strong opinions on the content of this article and invite all interested parties, whether in agreement or otherwise, to send comments to us (E-mail: editor@nasf.org; Subject line: P&SF Trivalent Passivates). We would especially appreciate comments based on experimental results, "real life" case histories and insight into specifying corporations and governments. They will be the subject of a Forum to be featured in P&SF early in 2008.

Finally, apologies to the authors are in order as, for reasons of cost reduction, we are unable to publish in color at this juncture. Therefore, the photos accompanying this article do not show the red-violet color indicating hexavalent chromium. However, we can certify that the darker shade in the black-and-white version is indeed red-violet in color in all photos printed here.

Trivalent passivates

Chromates for the post-plate protection of zinc-plated surfaces based on hexavalent chromium compounds were first patented in 1936.[2] They are commonly referred to as "conversion coatings," since the treating solution converts the zinc surface to a complex coating comprised of zinc chromate, trivalent chromium compounds and water in a hydrated gelatinous matrix. Most of the growth in conventional chromates took place after World War II. Formulae available in iridescent yellow, olive drab and blue-bright provided inexpensive improvement in the corrosion protection offered by zinc plating. Formulations incorporating silver salts provided black conversion coatings, but they were hardly inexpensive. Hexavalent chromium has established itself as an extraordinarily effective (as well as inexpensive) corrosion inhibitor when applied to zinc substrates.

Hexavalent chromium, though, has long been recognized as toxic as well as extremely hazardous (a strong oxidizer and corrosive) and carcinogenic. There has been a great deal of research and experimentation regarding post-plate passivates for zinc that do not use hexavalent chromium. The most commercially successful alternatives have been those based on trivalent chromium salts.

The earliest trivalent passivates were invented by Ken Bellinger and Gene Chapdelaine of Conversion Chemical Co. in Rockville, CT.[3,4,5] The commercial versions of these products, were based on urea nitrate.[6] Later versions used a mixture of sulfamic acid and sodium nitrate to generate nitric acid *in situ*. These formulations generally used chromium fluoride or chromium chloride as the source for trivalent chromium.

There are two general forms of trivalent passivates generally available in the marketplace. Formulae based on organic acids generally derive from the Klos patent,[7] which used trivalent chromium salts compounded with oxalic acid. Other commercial formulations are based on mineral acids and salts.

The first "thick film" trivalent passivate was that patented by Preikschat, *et al*.,[8,9] which uses trivalent chromium salts combined with an organic acid to produce a film that is claimed to be totally trivalent and from 100 to 900 nm thick. The commercial manifestations of these patents have given generally excellent performance in the ASTM B-117 Salt Spray Test. There is a general (but undocumented) perception that these "thick film" passivates function as a "barrier coating."

End of Life Vehicle Directives

Hexavalent chromium has long been recognized as hazardous, toxic and carcinogenic. The primary impetus for the reduction and/or elimination of hexavalent chromium has come from Europe, where the European Union has addressed the issue of the recycling and/or disposal of automobiles at the end of their useful lives.

The original directive (Directive 2000/53/EC of the European Parliament and of the Council of September 18, 2000 on End-of-Life Vehicles),[10] which was to take effect July 1, 2003, limited hexavalent chromium to 2.0 grams per vehicle, but only for the purpose of corrosion protection; all other uses were prohibited. Following the publication of the original directive was a period during which (1) there were no finishes that had been proven to meet the established automotive specifications without hexavalent chromium and (2) there was no agreement on an acceptable quantitative test for hexavalent chromium, a situation that still exists.[11]

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The current ELV directives became effective on July 1, 2006, although many manufacturers elected to put these requirements in place earlier, to compensate for the supply chain delay.

Annex II of the ELV directive was amended on June 27, 2002. The effective date was changed to July 1, 2007, and set forth the following changes relative to hexavalent chromium:[12]

> *"A maximum concentration value of up to 0.1% by weight and per homogeneous material, for . . . hexavalent chromium . . . shall be tolerated, provided (this substance is) . . . not intentionally introduced;*
>
> *"Intentionally introduced shall mean 'deliberately utilized in the formulation of a material or component where its continued presence is desired in the final product to provide a specific characteristic, appearance or quality'. . ."*

Annex II was further amended on September 20, 2005.[13] Under exemption item 13, corrosion preventive coatings related to fasteners used in chassis applications in the automotive industry are now exempt from the hexavalent chromium requirement until July 1, 2008.

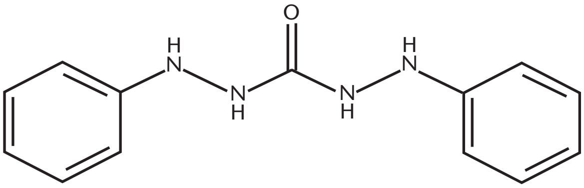
In fact, even though hexavalent chromium is prohibited, the EU provides no procedure for testing articles for hexavalent chromium to assure compliance with the directives.

Last year, Frank Altmayer of Scientific Control Laboratories wrote: "If, at any time in the future, the coating is found to contain excessive amounts of such banned substances, the metal finisher may be found liable for the cost of recall of the components."[14]

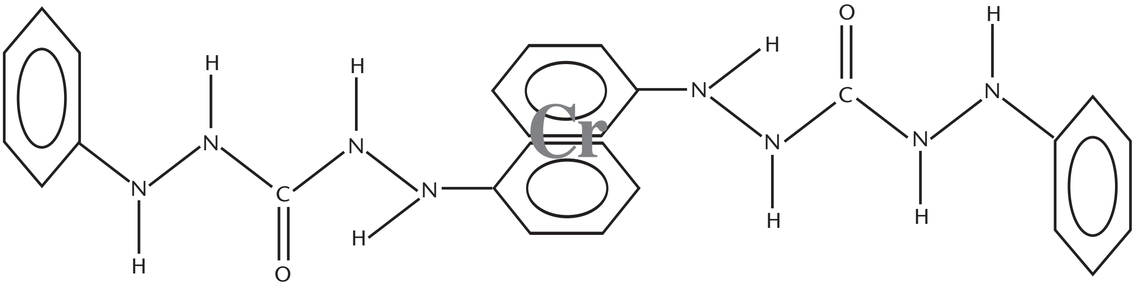
American zinc platers serving the automotive market have generally succeeded in complying with the requirements of the EU. Automotive companies have sought compliance on a world-wide basis. This has not been done without an increase in costs.

1,5 – Diphenylcarbazide[15-19]

Colorimetric testing has been the mainstay of testing for hexavalent chromium. 1,5-diphenylcarbazide (CAS 140-22-7) has the following structure:



Diphenylcarbazide forms a complex with hexavalent (and not trivalent) chromium at low pH values. The complex is generally accepted as having the following structure:



Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as mercury, molybdenum or vanadium, may be identified by its reaction with diphenylcarbazide in acid solution. The pH is typically reduced with sulfuric acid or phosphoric acid. This complex is **not** formed with trivalent chromium. The reaction is extremely sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. The hexavalent chromium reaction with diphenylcarbazide is generally free from interferences. However, certain cations may interfere if the hexavalent chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form colored complexes with the reagent. However, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not interfere. Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and the color does not normally interfere. To summarize: ***The 1,5-diphenylcarbazide test for hexavalent chromium in solution is accepted as a robust test generally free from interferences***.

Erlenmeyer flask showing the typical red-violet color of the complex formed between hexavalent chromium and 1,5-diphenylcarbazide. The sample on the left was prepared by diluting and acidifying the condensate from a commercial trivalent passivate obtained from the ASTM B-117 Salt Spray Test and treating the solution with 1,5-diphenylcarbazide at a reduced pH. The Erlenmeyer flask on the right illustrates the result obtained from a control sample that was unpassivated.

Unretouched photo illustrating the result obtained by placing a drop of diphenylcarbazide solution on the top of a trivalent passivated fastener and placing it in the salt spray cabinet for 24 hours. ***[Original color photo shows a purple color in the slightly darker shading within the center of the head (about half the diameter) - Ed.]***

Experimental details

We recently had the opportunity to investigate the behavior of trivalent passivates in the ASTM B-117 Salt Spray Test.[20]

The trivalent passivates used in this work were commercially available products sold by established manufacturers, both domestic and foreign. They included both conventional trivalent passivates and "thick film" passivates. All trivalent passivates gave the same general performance in the following tests, so there is no reason to disclose the names of the manufacturers of these products. All trivalent passivate treatments were conducted per the manufacturer's recommendations and were done on parts which were activated in 0.25% nitric acid. Articles passivated were primarily M10 machine screws (bolts) and washers. Deionized water was used for all tests. Passivated articles were rinsed after passivating.

Zachary Kennedy's test

A (trivalent) passivated article is placed in an operating ASTM B-117 Salt Spray Chamber with a drop of 1,5-diphenylcarbohydrazide test solution on the surface of the article. The test solution was prepared as follows:

> 0.4 grams of diphenylcarbazide was dissolved in a mixture of 20 mL acetone and 20 mL ethanol. After dissolution, 20 mL of 75% orthophosphoric acid solution and 20 mL of deionized water was added.[17] (This solution should be used within 8 hr.) All chemicals were reagent grade and were obtained from Sigma-Aldrich, Milwaukee, WI.

After 24 hr, the plated and passivated article is removed for inspection. The drop has turned reddish-violet, indicating the presence of hexavalent chromium.

Control test

The same test, with no passivate of any kind, showed no reddish-violet color.

An argument may be made that in this test, the presence of the test solution has created a chemical environment that is more amenable to the generation of hexavalent chromium from the trivalent passivates, and that, were it not for the test solution, no hexavalent chromium would be generated. The following test addresses that criticism.

Tom Rochester's test

A few (trivalent) passivated articles were placed above a crystallizing dish and the assembly introduced into the salt spray cabinet. After 24 hr, the condensate from the articles was diluted to 50 mL with deionized water, tested for hexavalent chromium by acidifying with 1.5 mL of 4.5M sulfuric acid and adding 1 mL of the following solution: [17]

> 0.50 grams of diphenylcarbazide was dissolved in 50 mL of acetone. While stirring, 50 mL of water was slowly added to this solution. All chemicals were reagent grade and were obtained from Sigma-Aldrich, Milwaukee, WI.

The characteristic red-violet color of the hexavalent chromium complex developed, indicating the presence of hexavalent chromium in the condensate from the trivalent passivated articles. (This test will be recognized as a variant of the GMW3034 test [18] or the ISO 3613 test. [17])

Control test

The same test, performed on zinc plated articles with no passivate of any kind, showed no reddish-violet color when the condensate was tested.

Discussion and interpretation of experimental results

This subject area is a true "hot button" issue for automotive manufacturers (particularly) as well as other companies selling to the European Union, which has formulated "End of Vehicle Life" restrictions on various substances.

In April 2002 the AESF Detroit Branch hosted its largest meeting in over 20 years when the subject was EU-generated automotive requirements for the elimination of hexavalent chromium.[21]

The experimental results we obtained were **unexpected** in that prevailing wisdom is that a strong oxidizer is required to oxidize trivalent chromium to the hexavalent form. For example, to test for the chromium concentration in trivalent passivates, the conventional test is to boil a sample with hydrogen peroxide and titrate with sodium thiosulfate.[22, 23] The aggressiveness of the oxidation required is construed as establishing that trivalent chromium is difficult to oxidize to the hexavalent chromium.

Kodama, in *Methods of Quantitative Analysis*,[19] mentions the following strong oxidizing agents as capable of oxidizing trivalent chromium to the hexavalent state: in alkaline solution Cl_2, Br_2, Na_2O_2 and H_2O_2; in acidic solution $KMnO_4$, $AgNO_3$, $(NH_4)_2S_2O_8$, PbO_2, Ag_2O_2, $KClO_3$, $KBrO_3$, or by fuming with $HClO_4$. These chemicals are all rightly considered strong oxidizing agents.

The general consensus is that these "trivalent passivates" function as barrier coatings and not as inhibitive coatings (as, for example, a conventional yellow chromate). But it seems highly improbable to the lead author that a coating that is less than 1000 nm thick, and more typically 200 to 400 nm thick,[8,9] is sufficiently thick to function as a barrier coating. We theorize that these coatings function (at least in the accelerated environment of a salt spray cabinet, although presumably in other environments as well) by providing trivalent chromium that is oxidized during the corrosion process to the hexavalent form.

The reaction

$$Cr^{+3} \leftrightarrow Cr^{+6} + 3e^{-}$$

is rightly considered an equilibrium reaction. Clearly in the environment of the salt spray cabinet there is sufficient oxidizing capability (presumably from atmospheric oxygen) to generate sufficient hexavalent chromium to render it detectable by the 1,5-diphenylcarbazide test.

Zinc metal is a strong reducing agent. The electromotive potentials would seem to indicate that the zinc would be preferentially oxidized to Zn^{+2} , but even if this happens, it is not sufficient to prevent the oxidation of Cr^{+3} to Cr^{+6}. Perhaps this is due to the strong inhibitive effect produced by hexavalent chromium.

False positives? – or not?

There have been a number of anecdotal reports of failure in the testing of trivalent passivates for hexavalent chromium. In the most common scenario, the parts delivered to the customer are tested for hexavalent chromium and determined to contain hexavalent chromium. The "blame" is then assigned to cross-contamination or from drag-in of oxidants into the passivating bath. Based on this research, another scenario is possible - the corrosion process has commenced, and with it, the generation of hexavalent chromium on the surface of the parts.

False negatives

The spot test for hexavalent chromium is capable of producing "false negatives," *i.e.*, indicating the absence of hexavalent chromium when it is in fact present. Zinc electroplated M10 machine screws were treated with a laboratory yellow chromate consisting of 0.4% w/v chromium trioxide (chromic acid) and 0.4% reagent grade salt in deionized water. They were rinsed and dried after this chromate conversion coating was applied. A tightly adherent yellow iridescent coating resulted. After 30 days a drop of the following solution:

> 0.4 grams of diphenylcarbazide was dissolved in a mixture of 20 mL acetone and 20 mL ethanol. After dissolution, 20 mL of 75% orthophosphoric acid solution and 20 mL of deionized water was added.[17] (This solution should be used within 8 hr.) All chemicals were reagent grade and were obtained from Sigma-Aldrich, Milwaukee WI.

was placed on the part. After one minute of contact, the solution on the article was inspected by blotting it with Whatman No. 40 filter paper. No reddish-violet color was evident, indicating (incorrectly) the absence of hexavalent chromium.

Conclusions

The authors believe that the European Union, the automobile manufacturers, their suppliers and metal finishers should determine whether trivalent passivates actually meet the requirements sought and the objectives of the directive.

Perhaps the metal finishing industry, the automotive industry and the European Union would be wise to eliminate the restriction on hexavalent chromium, which has provided highly effective, inexpensive corrosion protection for over fifty years. It would be simple to provide a broader exemption in Annex II for applications involving corrosion protection.

Even the European Union's consultant, Ökopol, said:[24]
"Because of the technical importance and the variety of application fields, a general ban of zinc and chromium chromates may not be appropriate."

Notes and references

1. ISO has argued against the use of the description "passivate." They set forth the position that "The application of very thin, colourless, practically invisible chromate conversion coatings is frequently called 'passivation,' while the application of thicker, coloured chromate conversion coatings is often called 'chromating.' The term passivation is not correct and is, therefore, not recommended." The International Material Data System (IMDS) refers to films containing hexavalent chromium as "chromate films" and films free from hexavalent chromium are referred to as "passivates." In the opinion of the authors, the term is descriptive as well as technically correct, and the term has found wide usage in the North American metal finishing industry.
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3. Where author Tom Rochester had the privilege to work from 1978 to 1984. Ken Bellinger had sold Conversion Chemical Company to 3M, who owned the facility in Rockville until 1983.
4. K.P. Bellinger & E.G. Chapdelaine, U.S. Patent 3,171,765 (1965).
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6. K.P. Bellinger, U.S. Patent 3,330,864 (1967).
7. K.P. Klos, U.S. Patent 5,368,655 (1994),
8. P. Preikschat, *et al*., U.S. Patent 6,287,704 (2001).
9. P. Preikschat, *et al*., U.S. Patent 6,946,201 (2005).
10. *Directive 2000/53/EC of the European Parliament and of the Council of September 18, 2000 on End-of-Life Vehicles, Official Journal of the European Communities L269 (21.10.2000)*. The complete text of ELV Directive 200/53/EC, passed on September 18, 2000, is available at the GMW 3059 website, http://www.gmw3059.com. There is also a great deal of additional information available from this site, including the annexes to this directive.
11. P. Wynn, "The End of Life Vehicle Directive and International Material Data System," *Products Finishing*, pp 58-63 (May 2003).
12. Commission Decision of 27 June 2002 amending Annex II of Directive 2000/53/EC of the Duropean Parliament and of the Council on end-of-life vehicles. This decision is available from the GMW 3059 website.
13. Council decision of 20 September 2005 amending Annex II of Directive 2000/53/EC of the European Parliament and of the Council on end-of-life vehicles. This decision is available from the GMW 3059 website.
14. F. Altmayer, "ELV, WEEE, RoHS and Hex-Chrome Testing," *Products Finishing*, pp 58-61 (August 2006).
15. *EPA Test for Hexavalent Chromium, Method 7196A*, available at www.epa.gov/sw-846/pdfs/7196a.pdf
16. M.S. Herrman, "Testing the Waters for Chromium," *J. Chemical Education*, **71** (4), 323 (1994).
17. *ISO 3613, Second Edition 2000-06-15*. Chromate conversion coatings on cadmium, aluminium-zinc alloys and zinc-aluminium alloys - test methods.
18. GMW 3034, *Absence of Hexavalent Chrome, Cr VI, in Coatings*, October 2006.
19. K. Kodama, *Methods of Quantitative Inorganic Analysis*, John Wiley & Sons, New York, NY (1994).

20. ASTM B117-07: *Standard Practice for Operating Salt Spray (Fog) Apparatus*, ASTM International, W. Conshohocken, PA, (2007).
21. J.H. Lindsay, “European Union ELV Directive: How Will It Impact the Automotive & Metal Finishing Industries?” *Plating & Surface Finishing*, **89** (6), 16 (2002).
22. *Chromiting Operating Data Sheet*, Continental Surface Treatment, Inc., Cleveland, OH, (08/29/2000 revision).
23. T.H. Irvine, *The Chemical Analysis of Electroplating Solutions*, Chemical Publishing Co., Inc., New York, NY, 1970; pp 12-19.
24. K. Sander, J. Lohse & U. Pirntke, *Heavy Metals in Vehicles – Final Report*, Ökopol – Institut fur Okologie und Politik GmbH Nernstweg 32-34 22765 Hamburg Germany.

Supplementary reading

F. Altmayer, “Testing Finished Parts for Hex Chrome” *Plating & Surface Finishing*, **91** (12), 20 (2004).

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