Trivalent Yellow Chromate New Discoveries & an Answer to Plating & Surface Finishing October 2007 article on the Diphenylcarbazide Controversy

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Last year I made a presentation at Sur/Fin 2007 in Cleveland on two yellow trivalent chromates discussing the high corrosion resistance and the UV resistance of the trivalent yellow chromates. Since that time much more R & D has been done with new discoveries. Also there has been some controversy regarding trivalent chromates and what happens during ASTM-B117 salt spray. Tom Rochester wrote an article in the October, 2007 Plating & Surface Finishing magazine. The discussion included research using the diphenylcarbazide indicator before and after salt spray on trivalent chromate zinc plated surfaces. The before salt spray exhibited no hexavalent chrome, while after salt spray showed some positive indication of hexavalent chrome. First, I will discuss the diphenylcarbazide results using our trivalent yellow and blue chromates. Second, I will present the discoveries of the trivalent yellow chromate R & D.

Diphenylcarbazide Controversy

First, we utilized an ISO 3613:2000 (E), Chromate conversion coatings on zinc, cadmium, aluminum-zinc alloys and zinc-aluminum alloys-Test Method. This method involves four different types of test methods for hexavalent chromate: Section 5.2 Test uses one drop of diphenylcarbaizde to the chromated zinc surface, Section 5.5 Test for the presence of hexavalent chromium in both colourless and coloured coatings (uses 1-5 drops of diphenylcarbazide), Section 5.6 Test: Determination of hexavalent chromium content of coloured chromate coatings (Spectrophotometer), and Section 5.7 Test which is similar to 5.6 using a ICP to determine total chrome section. We tested all of our blue and yellow trivalent chromates utilizing Section 5.6 and Section 5.5 test methods. These results are shown in Table 1. The results were negative for hexavalent chromium using test method Section 5.6.

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Subject	Hexavalent Chromium Analysis of Exposure Samples		

TABLE 1 Chemical Analysis Results

Sample 10	Conditions of Exposure	Hexavalent Chromium
Collection sample from chamber prior to exposure	N/A	Negative
Process D Blue	(1)	Negative
Process B Yellow	(1)	Negative
Process C Yellow	(1)	Negative
Process A Yellow	(1)	Negative
Process D Blue	(2)	Negative
Process B Yellow	(2)	Negative
Process C Yellow	(2)	Negative
Process A Yellow	(2)	Negative
Process D Blue	(3)	Negative
Process B Yellow	(3)	Negative
Process C Yellow	(3)	Negative
Process A Yellow	(3)	Negative
Collection sample from chamber after exposure	N/A	Negative
Process D Blue	(4)	Negative
Process B Yellow	(4)	Negative
Process C Yellow	(4)	Negative
Process A Yellow	(4)	Negative

Analysis completed using Ultraviolet-Visible Spectroscopy of extraction solution.
A negative result indicates <0.005 weight percent hexavalent chromium.

(1) sample panels tested as received.
(2) sample panels tested at first sign of white corrosion after exposure to salt spray per ASTM B117.
(3) sample panels tested after considerable white corrosion as per EPI discretion after exposure to salt spray per ASTM B117.
(4) sample panels tested after 523 hours exposure to the humidity chamber per ASTM 02247.

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The diphenylcarbazide drop test method utilized was section 5.5. This test uses 1-5 drops of the diphenylcarbazide reagent (3.3 Test Solution C). The formula for this test solution is: dissolve 0.4 g of diphenylcarbazide in a mixture of 20 ml acetone and 20 ml ethanol (96%). After dissolution, add 20 ml of 75% orthophosphoric acid solution and 20 ml of distilled water. Prepare this solution not more than 8 hours prior to use. The trivalent blue and yellow chromates tested utilizing test methods 5.5 were negative for hexavalent chrome.

During the test we used a dedicated salt spray chamber that had been verified that there was no hexavalent chrome. The initial test in the salt spray chamber showed < 0.1 ppm of total chrome. The after salt spray test in the salt spray chamber showed < 0.1 ppm of total chrome. Therefore, no chromium was dissolved into the salt solution. There is one theory that during the salt spray test the trivalent chrome converts to hexavalent chrome because of the salt solution and the temperature. Since we could not find an increase in total chrome after salt spray this indicates that the salt solution does not change the trivalent to hexavalent chrome. Another test utilized was a humidity test ASTM-2247 to see if water versus a salt solution was the source of the change in trivalent to hexavalent chromium. The humidity results were negative as well. Therefore, this means that the salts spray test ASTM B-117 or the humidity test ASTM-2247 do not cause the trivalent to go to hexavalent. Another interesting fact I learned about salt spray cabinets is that cooling water is utilized for keeping the temperature constant. The lab that conducted the test recently expanded and moved their salt spray chambers. When they drained the cooling water they found that the cooling water contained hexavalent chrome. Check your salt spray cabinets so that your cooling water is not leaking into your cabinet. Also when we did our tests we did not test any hexavalent chromate panels at the same time. I recommend that if you use a salt spray cabinet for trivalent chromates do not test hexavalent chromates as they can skew your results for corrosion and the diphenylcarbazide test. If you use an outside lab to verify your salt spray results then you need to verify that the salt spray chamber is free from hexavalent chrome.

One possible explanation for the positive hexavalent results using diphenylcarbazide is that there are some materials that do interfere with the diphenylcarbazide test. The EPA has a test method 7196A that is used for Chromium, Hexavalent (Colorimetric).

1.0 Scope and Application
  1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Section 3.0 Interferences below).
  1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.
2.0 Summary of Method
  2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red- violet color of unknown composition is produced. The reaction is very sensitive, the absorbency index per gram atom of chromium being produced being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540nm.
3.0 Interferences
  3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain

substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200mg/liter of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in the concentrations greater than 1 mg/liter may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

The EPA 7196A test method is for hexavalent chrome for acidified liquid solutions and these interferences may correlate to testing zinc plated steel with trivalent chromates. The diphenylcarbazide test is a colorimetric test. It may not be the best test for testing trivalent chromates because there could be additional interferences besides those mentioned in EPA method 7196A.

Another factor to consider is using a test method that is for liquids and not a dry surface. What is the resulting pH of the surface? What if the zinc deposit is high in iron? What if some other type of metallic interference occurs? What if there are other interferences that have not even been discovered yet? Do we have the answer to why the diphenylcarbazide reacts the way it does? No. We do offer another test method for hexavalent chrome using the ISO 3613:2000 (E) section 5.6 test methods that produces excellent results that are repeatable and that are based on a spectrophotometer, not a colorimetric method. ISO section 3613:2000 (E) section 5.2 and 5.5 have test reagents (3.1 and 3.3 respectively) for using the diphenylcarbazide test. When using the diphenylcarbazide drop test method make sure that you utilize the appropriate reagent. Also presented in the test method are the reagents, how you make them up, plus shelf life of the diphenypcarbazide. Reagent solutions shelf life are 4-8 hours, except 3.1 Test Solution A which has a shelf life of several months.

Conclusions:

1) Verify your trivalent chromate using the ISO 3613:2000 (E) section 5.6 spectrophotometer method.
2) Dedicate a salt spray cabinet for trivalent chromates. Check your salt spray cabinet cooling water to see if it contains hexavalent chrome. If so, make sure that it is not leaking into your salt spray cabinet.
3) Ask your trivalent chromate/sealer supplier if there are potential interferences such as molybdenum, mercury, iron, and/or vanadium in its formulation.
4) Information based on the test methods indicates that there are trivalent chromates that will meet the challenge in the October, 2007 Plating & Surface Finishing article.

Trivalent Yellow Discoveries

Since the last paper, we have been working on three improvements based on customer challenges. The first of these three challenges is color. Approximately 50% of the potential customers want a yellow-red hue instead of the yellow-green hue we have presently. When you look at your traditional acid chloride zinc process with a hexavalent yellow chromate, you will see both types of hues that are yellow-red and yellow-green, depending on how you hold the part in the light and what type of light you use to look at the part. Today, we have yellow-red hue trivalent chromate for the zinc metal finisher. The second challenge is to increase the UV resistance of the trivalent yellow chromate. One of the existing formulas has offered some UV resistance when performing UV and QUV tests while other trivalent yellows fade in a matter of days while in the sun. The last paper had a discussion on the different types of testing for color stability. QUV/UV tests are our standard for measuring the UV resistance. The third challenge is to improve the corrosion resistance even though our existing two yellow trivalent chromates offer excellent corrosion protection: one that goes to 150-200 hours and the other that offers 150 hours salt spray to 5% white corrosion. One can be baked retaining its color and actually increasing in the salt spray corrosion up to 300 hours.

The first challenge presented by the potential users is the color of the trivalent yellow. In last year's paper I discussed the fact that there are two potential colors out there. One is the yellow-green hue and the other is the yellow-red hue. The first product we talked about was the yellow-green formula. We found that about 50% of potential users liked this color. The other 50% said it was too green. Thus, we started working on a version that had the same properties, but a different color. We also benchmarked against other existing colors. We discovered a rainbow of colors out there that included gold to orange. The other challenge in developing a system is finding one that does not rub off with your fingers and the color has staying power. Recently we have developed a yellow-red version for those who like it red.

The second challenge last year was the QUV resistance of a trivalent yellow. I have also heard this concern with trivalent black chromate. We have started a study with different coloring agents that have improved the color stability of the product. The existing yellow trivalent chromate is 1000 QUV or about 500 hours of UV. After that testing we find that the color goes to a slightly violet color (about 40-60% of its original yellow color). It is subjective on how much color change occurs because there are not any standards to date. The new coloring agents we have found extended the color stability. We noticed less fading than the original yellow trivalent, as the improvement resulted in a faded color that is to a yellow and not the violet color. The change in color is 20-30% when using 500 hours UV. We have actually found that straight UV testing is faster because the UV light is on all the time. The QUV testing is light and dark with some moisture to simulate the dew of the morning. More work is necessary on the QUV/UV testing, but we do have an improvement since last year. Once the QUV/UV testing is completed we will conduct further testing using actual outdoor exposure in Florida.

The final challenge resulted in a new discovery that could change trivalent yellow standards. Through our research we have a new product that offers outstanding ASTM B-117 salt spray resistance. The results of plating 0.3 mls of acid chloride zinc and alkaline non cyanide plating are as follows using ASTM B-117.

First signs of white rust	300 hours
To 5% white rust	600-700 hours
To red rust	800-900 hours

A recently completed field test of fasteners in a barrel application of cyanide zinc resulted in passing 120 hours (no white rust). Please note that the testing did not proceed any further because the specification had been met. Prior to using this latest formula we attempted using one of last year's formulas and it achieved 70-80 hours salt spray.

The longer salt spray hours result in a leap frog change and a new paradigm. The new paradigm is that traditional zinc plating can now achieve salt spray hours of some zinc alloy plating processes without the using the zinc alloy. What this means to the zinc metal finisher is cost savings and also a process that easily adapts to existing metal finishing lines. This latest process only needs one tank to run. No sealer or topcoat tank is required. Let's look at the process parameters.

		Optimum
Part A	4-6% by volume	5%
Part B	1-3% by volume	2%
Water		93%
Temperature	80-130°F	115°F
Immersion Time	30-120 seconds	90 seconds
pH	1.6-2.2	1.8

Use ammonium hydroxide to raise pH. Use 10% nitric acid to lower the pH

Plating Procedure:

1) Zinc Plate parts to 0.0003" of zinc from acid chloride, alkaline non cyanide and cyanide zinc process.
2) Cold Water Rinse
3) Sulfuric Acid Dip 0.1% by volume (do not use nitric acid)
4) Cold Water Rinse
5) Process in Trivalent Yellow to the parameters of above
6) Cold Water Rinse
7) Dry Off oven and/or bake for hydrogen embrittlement

Another new fact with this latest trivalent yellow is it offers scratch resistance. We have implemented a test procedure that is similar to organic coating/paint. The Q-panel is painted, the edges are taped, and then an X is cut across the painted film. During the salt spray test they are not looking for white corrosion like in zinc plating. They are looking for creeping corrosion. The X that is cut into the paint film simulates what happens to when you get a scratch on a painted surface. The other trivalent yellow processes achieve white creeping corrosion of 24-48 hours. With the latest trivalent yellow first signs of white creeping corrosion occurred in 200 hours. This is exciting news for the zinc metal finisher, especially barrel users. The end user is excited about this because it overcomes the challenge of the self healing properties of a yellow hexavalent chromate. Why is this occurring? This is not a thick film trivalent chromate and does not have self healing properties. But we have discovered a synergistic affect of chemistries resulting in a new technology.

We conclude that the latest exciting development offers the following benefits:

1) Outstanding Salt Spray Hours
   300 hours to first sign of white rust
   600 hours to 5% white corrosion
   800 hours to red rust
2) Single Dip Process
3) Can be baked without losing corrosion resistance
4) Scratch resistance (white creeping corrosion)
5) Alternatives to replace zinc alloy plating
6) Works with all types of zinc plating acid chloride, alkaline non cyanide and cyanide

References

ISO 3613 Second Edition Second Edition 2000-06-15 Chromate conversion coatings on zinc, cadmium, aluminum-zinc alloys and zinc-aluminum alloys – Test Method Licensed to Stork Technimet New Berlin, WI

Method 7196A CHROMIUM, HEXAVALENT (COLORMETRIC) www.epa.gov