Trivalent Yellow Chromate

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The search for trivalent chromates complying with End of Life of Vehicle (ELV) and RoHS compliance from the European Union (EU) has emphasized trivalent chromates that are clear/blue and black. This has left the choice of yellow behind because of the challenges in achieving an acceptable color to the hexavalent yellow chromate and the performance of the trivalent clear/blue chromates salt spray corrosion resistance equals or exceeds hexavalent yellow chromate. Another challenge with the existing technology is that multiple dips are necessary to achieve the corrosion protection required for the yellow trivalent chromate processes. This paper will discuss two new processes available for the zinc electroplater; but before we go into the details of these two exciting new processes, let's review the facts regarding hexavalent yellow chromate.

What is hexavalent yellow zinc-chromate?

It is a blend of acids, catalysts and chromic acid which are formulated to produce an iridescent yellow finish. This finish has been a true work horse for the zinc metal finishing industry that typically achieves 72 to 144 hours salt spray. It is a thick film hexavalent chromate with self-healing characteristics which means that when the hexavalent yellow zinc-chromate film is scratched, the film does not lose its corrosion protection. This phenomenon occurs because the yellow chromate film is gelatinous, meaning it is soft and contains waters of hydration.

One challenge of the yellow hexavalent chromate is this: if you bring the yellow zinc-chromate film above 150°F (65°C), the gelatinous film dries out and cracks, becoming hard and losing its salt spray corrosion protection. A procedural challenge for the yellow hexavalent zinc-chromate finish is that some parts have to be baked to relieve the hydrogen that is absorbed during the zinc electroplating process. A typical baking cycle is 4 to 24 hr at 325 to 400°F. Therefore, the procedure for hexavalent yellow zinc chromate requires a zinc-plated part to be taken off the line, baked for hydrogen embrittlement and then placed back on the line to be chromated.

This paradigm of processing hexavalent yellow zinc-chromate as just described can be changed forever with a new approach, described here as process "A." The end user of yellow zinc-chromate finishes still wants the yellow color because of color identification and the fact that change is hard. To end users, a clear chromate always represented a chromate that will not last long in the field and will corrode quicker than the yellow one. The future of yellow hexavalent zinc-chromates is limited because of ELV, RoHS and the push to eliminate hexavalent chromium from metal finishing facilities.

A new approach to trivalent yellow chromating - process "A"

The color of this product is impossible to show in a grayscale picture, but based on experience to date, we have found that about one-half of the acid chloride zinc, alkaline non-cyanide zinc and zinc cyanide electroplaters accept the color of process "A." The color is iridescent yellow with a slight reddish-green hue. Some zinc electroplaters who do not accept the color object to it being too green. This has resulted in a process "B" for a trivalent chromate with a yellow color containing a reduced green cast. Color is always difficult to hit a home run for everyone, thus there are two processes for the zinc electroplater.

Process "A" bath parameters

- Composition:
    - Component A 3 vol%
    - Component B 2 vol%
    - Tap water 95 vol%
- pH 1.8, adjusted with ammonium hydroxide to raise the pH
- Temperature, 80 to 140°F
- Immersion time, 30 to 120 sec (60 sec optimum).
- Procedure

1. Zinc electroplate in acid chloride, alkaline non-cyanide or cyanide zinc plating processes to a minimum thickness of 0.0003".
2. Rinse the zinc plated part.
3. Bright dip using sulfuric acid 0.5 to 1.0 vol%.
   Note - Nitric acid bright dips can cause a poor yellow chromate film.
4. Rinse the sulfuric acid bright dip.
5. Apply process "A" trivalent yellow chromate.
6. Rinse process "A" trivalent yellow chromate.
7. Dry part in oven.
   Note - A hot oven at a temperature above 150°F can now be used.
8. Optional bake for hydrogen embrittlement.

ASTM B-117 salt spray corrosion results

Process "A" results on rack processed parts or Q-panels show an average 150 hr to 5% white corrosion. If these same parts are baked as for hydrogen embrittlement a minimum of 2 to 4 hr, the corrosion protection results in 300 hr to 5% white corrosion, effectively doubling the corrosion protection. The mechanism of this phenomenon is still being studied, but the theory suggests that the sites of the trivalent chromate, corrosion inhibitors and the coloring agents react to the heat to form a film that offers superior corrosion protection. What makes Process "A" different from other trivalent chromates is that the coloring agents have an additional benefit which will be discussed further in this paper.

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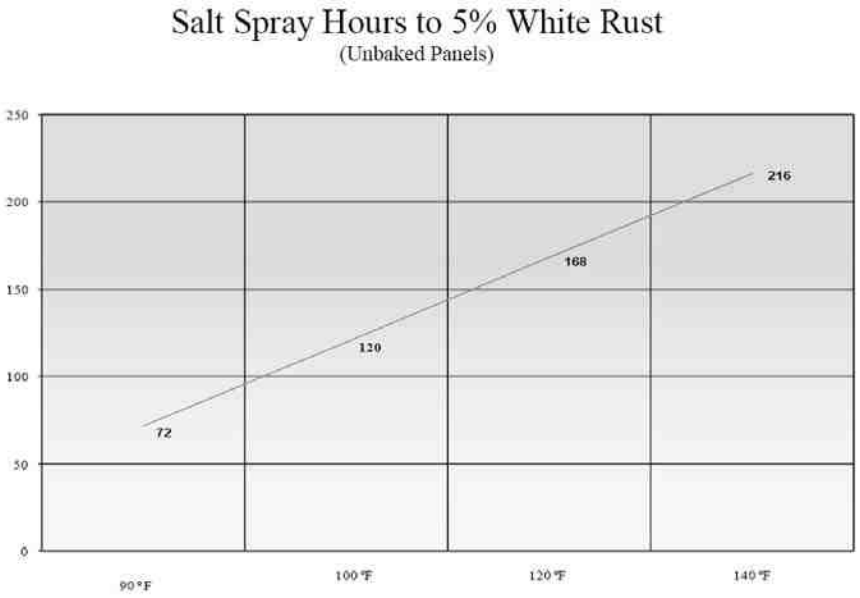


At lower temperatures, *e.g.*, 80°F, 24 to 72 hr salt spray resistance can be achieved. At 90 to 110°F, 48 to 120 hr of salt spray resistance is typical. At 115 to 140°F, 150 hr can be expected. The pH also plays an important role. The zinc electroplater needs to utilize a pH meter that is calibrated to 1.68 to obtain accurate pH readings. At a lower pH (1.0 to 1.6) less corrosion protection is realized. The pH range is 1.6 to 2.0 with 1.8 being optimum. To raise the pH use ammonium hydroxide and to lower it, use process "A" components A and B.

Red rust results with 0.0003" of zinc were 400 to 500 hr to red rust failure.

Color stability to ultraviolet (UV) light

Process "A" trivalent yellow chromate offers outstanding UV resistance to other dye trivalent chromates that fade in a matter of days in the sun. The color agent chemistry differs from the standard dyes offered today because it is more than organic dye chemistry. The coloring agents and the trivalent chemistry result in a technological breakthrough. The color fastness of process "A" chromates approach the results obtained with a standard hexavalent yellow chromate.

The first test was done with a UV fluorescence lamp at 300 to 400 nm for 500 hr. A zinc-plated panel of process "A" was compared to a zinc-plated panel of hexavalent yellow chromate. The results after 500 hr showed no fading with both the hexavalent and trivalent process "A," meaning that both finishes showed similar performance. Considering the different types of UV testing, the first test was more like a QUV test, a cyclic ultraviolet weathering test, at one UV wavelength.

With the initial testing done, a second test was done to process both "A" and "B" chromates and compared to the yellow hexavalent chromate. This test was performed by the Q-Lab Corporation, the manufacturer the Q-Panel and related coating exposure test equipment. The test selected was the Q-Sun test because it had a more real-life test. Specifically, it measured with more than one wavelength, including visible wavelengths to which all bright colors are sensitive. Q-SUN meets the requirements of ASTM G155 and consists of a xenon-arc test chamber. The sunlight spectrum ranges over wavelengths from 295 to 800 nm and the xenon arc duplicates that spectrum.

There are three elements that cause the fading of color and the degradation of coatings. Light, high temperature and moisture all play a role changing of color by the sun. Sometimes these elements will work by themselves and sometimes they work synergistically, just like zinc or nickel brightener components work together. For most coatings the short wavelengths will start the fading process. However, when working with dyes, longer wavelengths and visible light will initiate the color change. High temperature causes light fading to accelerate. This duplicates the hot sun in Cancun or the summer in the U.S. The final element is moisture and there are three components: dew, rain and humidity. Actually the morning dew is the most aggressive of all three causes of moisture being absorbed into the coating, because the dew is on the surface for a longer time, up to 8 to 12 hr. Rain has two mechanisms of causing fading in the sun. One would be exposing the coating to rain on a hot day, which causes thermal shock, as the cold rain will cool the hot metal down quickly. The second factor is that rain actually starts to mechanically erode the coating continuously, bringing fresh coating to the surface. For indoor applications, relative humidity plays a factor in the fading of color. The QUV and the Q-SUN test methods are relevant UV testing methods for trivalent yellow chromates. More can be learned about these tests by going to www.q-lab.com and asking for bulletin LU-8009, *QUV & Q-SUN: A Comparison of Two Effective Approaches to Accelerated Weathering and Light Stability Testing*.

One interesting fact is that the Q-SUN test after 100 hr is such a severe test that the yellow fades to a blue color on process "A" and "B" chromates. The hexavalent yellow process faded as well but it still showed some yellow. Therefore, more work is being done to develop a process that meets the Q-Sun test. In fact, Q-Lab states that this test is very challenging in developing stable yellow colors.

In addition to the excessive green color for some end users, process "A" does have two other challenges. The first one is cost. It can cost approximately ten times more for make-up costs than it does for hexavalent yellow chromates. The second is that it does not have the self-healing characteristics of hexavalent yellow zinc chromate. Nonetheless, if you are a rack zinc electroplater who bakes for hydrogen embrittlement, you have a huge cost savings in putting the parts on the line, which will negate the additional process "A" make-up cost.

Process "B" trivalent chromate

Process "B" resulted from trying to overcome the three challenges of process "A": (1) high make-up costs, (2) excessive and objectionable (to some users) green color and (3) scratch resistance resulting in loss of salt spray corrosion protection. We find that the make up costs for process "B" are 30 to 35% less than the make up costs of process "A." Some zinc electroplaters like the color better with process "B." For barrel plating, process "B" wins hands down as it produces a trivalent chromate film that offers moderate scratch resistance.

Process "B" bath aparameters

- Composition:
  - Component A 3 vol%
  - Component B 2 vol%
  - Tap water 95 vol%
- pH: make up - do not adjust pH
- Temperature, 80 to 140°F
- Immersion time, 30 to 300 sec (60 sec optimum).
- Procedure

1. Zinc electroplate in acid chloride, alkaline non-cyanide or cyanide zinc plating processes to a minimum thickness of 0.0003".

2. Rinse the zinc plated part.
3. Bright dip using sulfuric acid 0.5 to 1.0 vol%.
   Note - Nitric acid bright dips can cause a poor yellow chromate film.
4. Rinse the sulfuric acid bright dip.
5. Apply process "B" trivalent yellow chromate.
6. Rinse process "B" trivalent yellow chromate.
7. Dry part in oven.
   Note - A hot oven at a temperature above 150°F can now be used.
8. Optional bake for hydrogen embrittlement.

The salt spray results on parts and Q-Panels averaged 180 to 200 hr to 5% white rust and 400 to 500 hours to red rust with 0.3 mils thickness, according to ASTM B-117. Baking of process "B" finishes neither decreased nor increased the corrosion protection nor did the color of the film change during the baking process.

The zinc electroplater has two processes that can address the three current paradigms of (1) yellow trivalent chromate that wipes off with your finger, (2) the yellow color that disappears outdoors and (3) baking the part leads to color fading without no increase in salt spray corrosion resistance.

Comparative properties of the two trivalent yellow chromate processes

Property	Process "A"	Process "B"
Color	Yellow-green iridescence	Yellow iridescence
Corrosion protection	150 or 300 hr, if baked	180 to 200 hr
UV resistance	Yes	Slightly
Thickness nm@ 95% wt Zn	30 sec; 2057 nm	30 sec; 2092 nm
	60 sec; 3088 nm	60 sec; 2470 nm
Number of tanks	One	One
Bakable	Yes, with increased corrosion resistance	Yes, with no change of corrosion resistance
Cost	Most expensive	Least expensive
Scratch resistance	Slight	Moderate
Wipes Off With Thumb	No	No

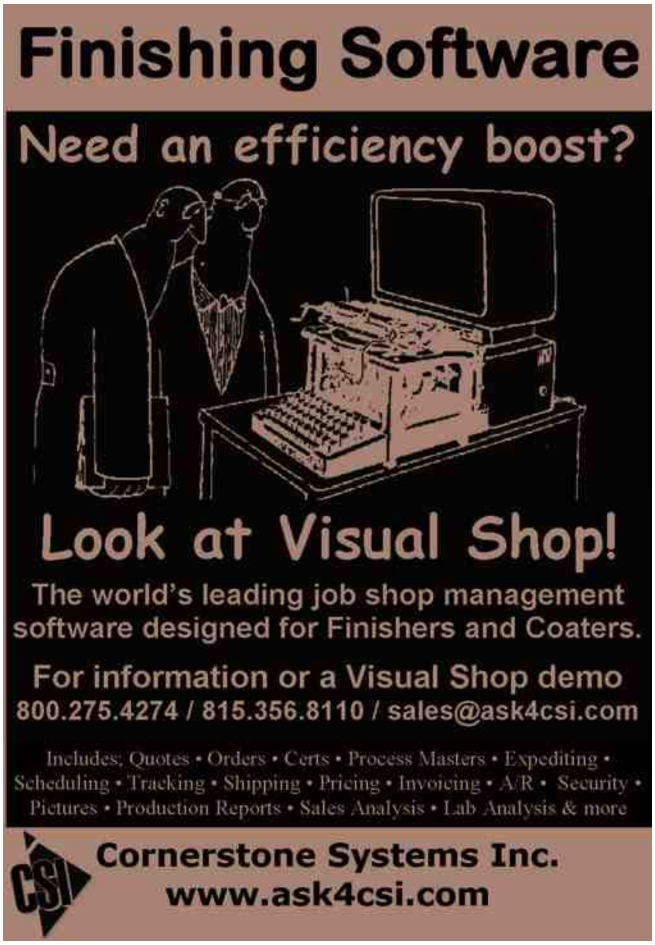
Conclusions

Processes "A" and "B" offer alternatives to hexavalent yellow chromate many advantages and few disadvantages. Today the zinc electroplater can take advantage of these benefits;

- Use of a single tank
- Labor cost savings of baking for hydrogen embrittlement
- Superior corrosion protection
- Does not wipe off
- UV-stable coloring system

About the Author

Eric Olander is President of EPi - Electrochemical Products Inc., of New Berlin, Wisconsin. He received a B.S. in Chemical Engineering from Iowa State University. He is a Past President of the AESF Milwaukee Branch AESF and a past member of the MFSA Board of Trustees. Mr. Olander has served of the SUR/FIN Steering Committee and the MFSA Membership Committee.



Answers to IQ Quiz #437

From page 9

1. An auxiliary cathode so placed as to divert to itself some current from portions of the work which would otherwise receive too high a current density.
2. A rigid conducting section, for carrying current to the anode and cathode bars.
3. Branched or irregular projections formed on a cathode during electrodeposition especially at edges and other high-current-density areas.
4. An acid solution used to remove oxides or other compounds from the surface of a metal by chemical or electrochemical action.
5. A cathode in a plating solution that is not used after plating, often used for removal or decomposition of impurities.