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 -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 it corrosion protection. This phenomenon is because the yellow chromate film is gelatinous meaning it is soft and contains water of hydration. One challenge of the yellow hexavalent chromate is if you bring the yellow zinc-chromate film above 150 F (65C) the gelatinous film dries out and cracks, becoming hard and losing its salt spray corrosion protection. A procedure challenge for the yellow hexavalent zinc-chromate finish is some parts have to be baked to relieve the hydrogen that is absorbed during the zinc electroplating process. A typical baking cycle is 4-24 hours at 325-400F. Therefore, the procedure for hexavalent yellow zinc chromate requires a part that is zinc plated to be taken off the line, baked for hydrogen embrittlement and then placed back on the line to receive more chromating. This paradigm of processing hexavalent yellow zinc-chromate in the procedure described above will be changed forever with the 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 chrome from metal finishing facilities.

PROCESS " A" TRIVALENT YELLOW CHROMATE

The color of this product is difficult to show in a picture but based on the experience to date we have found that about one half of the acid chloride zinc, alkaline non cyanide zinc, and the zinc cyanide electroplaters accept the color of PROCESS A. The color is iridescent yellow with a slight red green hue. Some of zinc electroplaters that do not accept the color object to it being too green. This resulted in PROCESS B for a trivalent chromate with a yellow color containing less green in it. Color is always difficult to hit a home run for every one, thus there are two PROCESSES A and B for the zinc electroplater.

PROCESS" A" BATH PARAMETERS

Process "A" Component A	**3% by volume**
Process "A" Component B	**2% by volume**
Tap water	**95% by volume**

- **pH 1.8 adjust with ammonium hydroxide to raise the pH**
- **Temperature 80 -140F**
- **Immersion time 30-120 seconds 60 seconds optimum**

Process "A" Procedure

1. **Zinc Electroplate in acid chloride, alkaline non cyanide, and cyanide zinc plating processes to a minimum thickness of 0.0003".**
2. **Rinse the zinc plated part**
3. **Bright dip using sulfuric acid 0.5-1.0% by volume * 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 please note that a hot oven the results in a temperature above 150F can be used now.**
8. **Optional bake for hydrogen embrittlement**

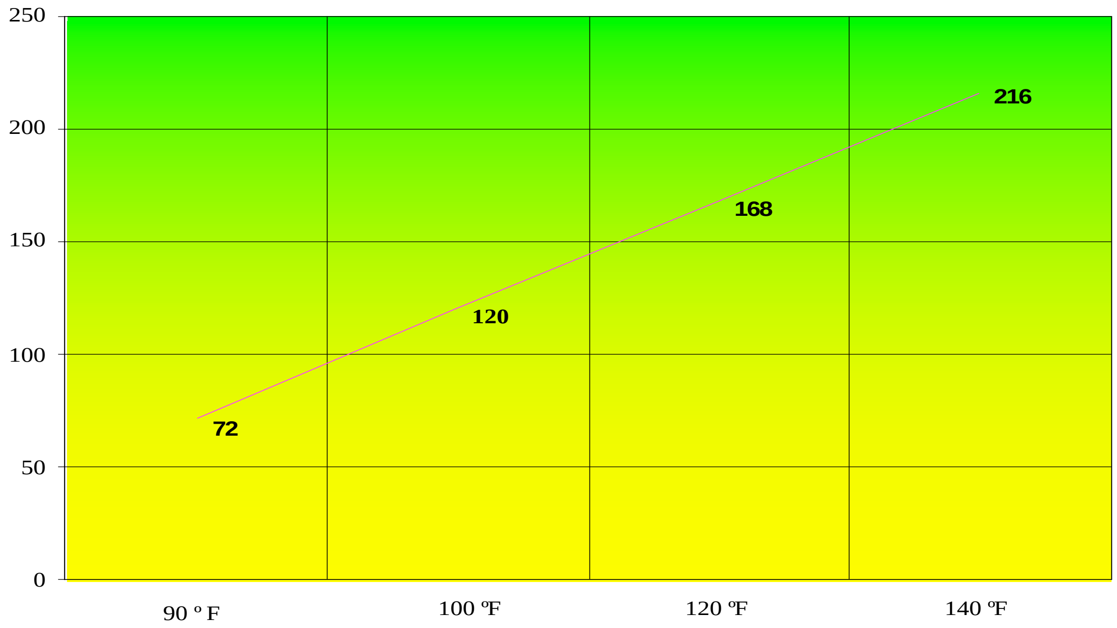
ASTM B-117 Salt Spray Corrosion Results

PROCESS "A" results on rack processed parts or Q-panels show on average 150 hours to 5% white corrosion. If these same parts are baked as for hydrogen embrittlement a minimum of 2-4 hours the corrosion protection results in 300 hours to 5% white corrosion. It actually doubles the corrosion protection! The mechanism of this phenomenon is still being studied, but the theory is 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? The color agents have an additional benefit which will be discussed further in this paper.

At lower temperatures 80 degrees F, you will achieve 24-72 hours salt spray. At 90-110 degrees F, you can achieve 48-120 hours salt spray. At 115-140 degrees F you achieve the 150 hours salt spray. The pH also plays an important factor. The zinc electroplater needs to utilize a pH meter that is calibrated to 1.68 to discover accurate pH readings. At a lower pH (1.0-1.6) you will get less corrosion protection. The pH range is 1.6-2.0 with 1.8 being optimum. To raise the pH use ammonium hydroxide and to lower it use PROCESS"A" component A and B.

Salt Spray Hour to 5% White Rust

(Unbaked Panels)



Red rust results with 0.0003” of zinc are hours to red rust failure.

COLOR STABILITY TO UV LIGHT

PROCESS “A” trivalent yellow chromate offers outstanding UV resistance to other dye trivalent chromate that fade in a matter of days in the sun. The color agents chemistry differs than the standard dyes offered today because it more than organic dye chemistry. The coloring agents and the trivalent chemistry result in a leap frog technology break through. The color fastness of PROCESS “A” approaches results of a standard hexavalent yellow chromate. The first test was done with a UV fluorescence lamp at 300-400 nm for 500 hours. A zinc plated panel of process “A” was compared to a zinc plated panel of hexavalent yellow chromate. The results after 500 hours were no fading with both the hexavalent and process “A”, meaning that Process “A” had similar performance to the hexavalent chromate process. Investing the different types of UV testing the first test was more like a QUV test at one UV wavelength. With the initial testing done, a second test was done to PROCESS “A” and “B” compared to the yellow hexavalent chromate. This test was performed by the Q-Lab Corporation who manufactures the Q-Panel and various coating exposure test equipment. The test selected was the Q-Sun test method because it has a more life-like test as it has more than one wavelength it is measuring (it includes visible wavelength to which all bright colors are sensitive). Q-

SUN meets ASTM G 155 and is a Xenon arc test chamber. The sunlight spectrum is many wavelengths from 295- 800nm 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 due to the sun. Sometimes these elements will work by themselves and sometimes they work synergistically, just like zinc or nickel brighter components work together. For most coatings the short wave light will start the fading process; but when you are working with dyes, longer wave and visible light will initiate the color change. High temperature causes the light fading to accelerate in the fading process. This duplicates the hot sun in Cancun or the summer in the US. 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 8-12 hours.. 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 with rain is it actually starts to mechanical 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 and you can learn more about the 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 hours is such a severe test that the yellow faded to a blue color on Process A and B. 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 this Q-Sun test. In fact Q- Lab states that this test is very challenging in developing stable yellow colors.

In addition to the too green color for some end users, PROCESS “A” does have other two challenges. The first one is cost. It can cost approximately ten times more for make up costs than hexavalent yellow. The second is that it does not have the self healing characteristics of hexavalent yellow zinc-chromate. If you are a rack zinc electroplater who bakes for hydrogen embrittlement and 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 in trying to overcome three challenges of the PROCESS “A”: (1) high make up costs, (2) color being too green and (3) scratch resistance resulting in loss of salt spray corrosion protection. We find that the make up costs for PROCESS “B” is 30-35% 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 PARAMETERS

Process “B” Component A	**3% by volume**
Process “B” Component B	**2% by volume**
Tap water	**95% by volume**

- **Make up do not adjust pH**
- **Temperature 80 -140F**
- **Immersion time 30 seconds- 5 minutes, 60 seconds optimum**

Process “B” Procedure

1. **Zinc Electroplate in acid chloride, alkaline non cyanide, and cyanide zinc plating processes to a minimum thickness of 0.0003”.**
2. **Rinse the zinc plated part**
3. **Bright dip using sulfuric acid 0.5-1.0% by volume * 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 please note that a hot oven the results in a temperature above 150F can be used now.**
8. **Optional bake for hydrogen embrittlement**

The resulting salt spray on parts and Q-Panel average 180-200 hours to 5% white rust and hours to red rust 0.3 mls of thickness ASTM B-117. Baking of PROCESS “B” did not decrease or increase 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 present three paradigms of (1) the yellow trivalent chromate that wipes off with your finger, (2) you put the part outside and the yellow color disappears and (3) you bake the part and the color fades without an increase in salt spray corrosion.

Conclusion

Benefit	Process “A”	Process “B”
Color	Yellow-Green Iridescence	Yellow Iridescence
Corrosion protection	150 hrs or 300 hrs, if baked	180 -200 hours
UV resistant	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 and increases corrosion resistance	Yes, but does not increase corrosion resistance
Cost	Most Expensive	Least Expensive
Scratch resistance	Slight	Moderate
Wipes Off With Thumb	No	No

Conclusion:

Process “A” and “B” offer great alternatives to hexavalent yellow chromate with great advantages and few slight disadvantages. Today the zinc electroplater can advantage of these benefits;

- One Tank
- Save labor cost of baking for hydrogen embrittlement
- Superior corrosion protection
- Does not wipe off
- UV stable coloring system