Corrosion Resistance and Blackening Mechanism of Trivalent Black Chromium Passivation Films

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Yuken America is a subsidiary of Yuken Industry, a manufacturer of a wide array of surface treatment chemicals. Yuken occupies over a 30% share of the trivalent black chromium process in the zinc plating corrosion resistance market in Japan, demonstrating the highest performance in acid/chloride applications.

Recently, the market has witnessed a dominant shift to trivalent chromium as an alternative to hexavalent chromium. We will discuss the high corrosion resistance mechanism of our trivalent black film and how the blackening reaction in the passivate film takes place. We will also detail the track record of our installations in the USA, as well as our future plans.

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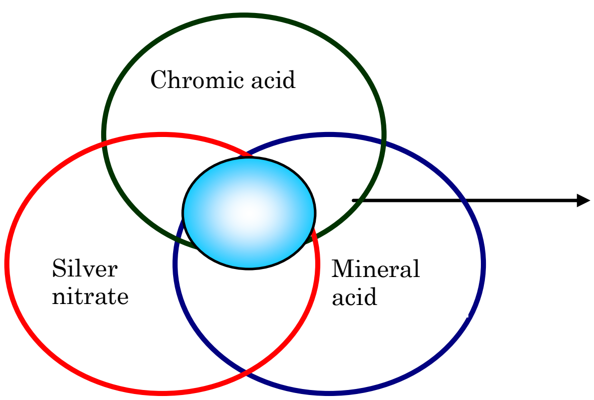
Preface

After the ELV directive was issued, trivalent chromium has been used as an alternative to hexavalent chromium for passivation film since 1998. The blue (clear) type has been consistently supplied, providing stable performance. In addition to the blue (clear) type, the black type is also currently available in the market to meet color requirements for part identification. Even though trivalent chromium black passivation films have been available since 2005, it is only recently that they can finally satisfy corrosion resistance requirements. As to development of the black color, it is still challenging to maintain the black color at a consistent level.

In this paper, we will discuss how our latest organic trivalent black passivation film with high corrosion resistance (referred to as the Latest Tri Black hereinafter) has been developed. We will also identify factors that make the film black and compare them with those of the hexavalent chromium.

Collaborative Interactions in Black Passivation Films

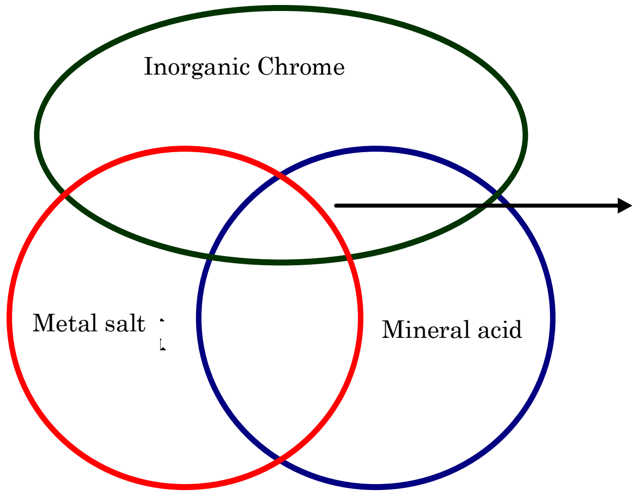
Hexavalent Chromium Black Passivation Film



Formation of hexavalent chromium black passivation

Silver oxide (AgO) makes the color black. Chromic acid and mineral acid play major roles to form passivation film with high level of corrosion resistance and rich black appearance.

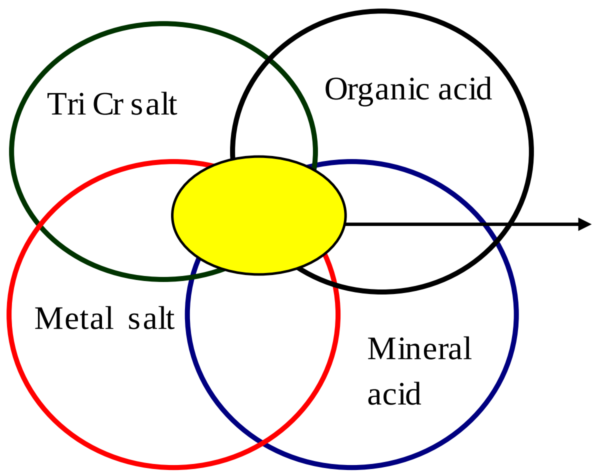
Trivalent Chromium Black Passivation Film (Inorganic Type)



The interaction of these three components does not create trivalent chromium black passivation film.

Even though trivalent chromium passivation film is developed, it does not turn black.

Trivalent Chromium Black Passivation Film (Organic Type)



Trivalent chromium black passivation film is formed.

Trivalent chromium passivation film is developed, and the color simultaneously goes black.

1. We prepared samples of the following solutions, and performed a trivalent chromium black passivation film evaluation to validate each film interaction.

1-1. Inorganic Chromium Only
1-2. Inorganic Chromium + Metallic Salt
1-3. Inorganic Chromium + Metallic Salt + Mineral Acid
1-4. Trivalent Chromium Salt + Organic Acid
1-5. Trivalent Chromium Salt + Organic Acid + Metallic Salt
1-6. Trivalent Chromium Salt + Organic Acid + Metallic Salt + Mineral Acid
1-7. Our Latest Organic Trivalent Chromium Black Passivation Process[*1] Only (referred to as Latest Tri Black hereinafter) (film was developed with newly made-up solution)
1-8. Latest Tri Black (Newly Made-up Solution) + Finish Coat
1-9. Latest Tri Black Only (Aged Solution)
1-10. Latest Tri Black (Aged Solution) + Finish Coat

Samples were made using each of the above solutions under the following conditions:

Process temperature:	40^0C
Process time:	60 sec.
pH:	2.20~2.30
Samples:	Plated with chloride zinc

2. Description of Validation Test
2-1. Film Analysis – XPS film element distribution analysis
X-ray Photoelectron Spectroscopy (JPS-9010MX) was used.

3. Film Analysis Results
3-1. Analysis of Difference in Film Quality between 1-1 through 1-3 and 1-4 through1-6
3-2. Analysis of Difference in Film Quality between 1-6 and 1-7
3-3. Analysis of Difference in Film Quality between Hexavalent Chromium Passivation Film and Trivalent Chromium Passivation Film

*1: METASU YFB, Yuken America, Novi MI

3-4. Effectiveness of Finish Coat

3-5. Effectiveness of Finish Coat (Comparison of Latest Tri Black Using New Solution and Aged Solution)

Considerations

3-1-1. Processed Sample External Appearance Comparison (Inorganic Type)

Inorganic Cr Only | Inorganic Cr +Metallic Salt | Inorganic Cr + Metallic Salt + Mineral Acid

3-1-2. Processed Sample External Appearance Comparison (Organic Type)

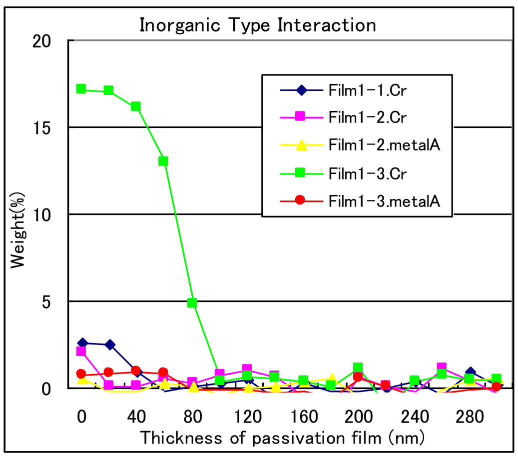
Tri Cr Salt + Organic Acid | Tri Cr Salt + Organic Acid + Metalic Salt | Tri Cr Salt + Organic Acid + Metalic Salt + Mineral Acid

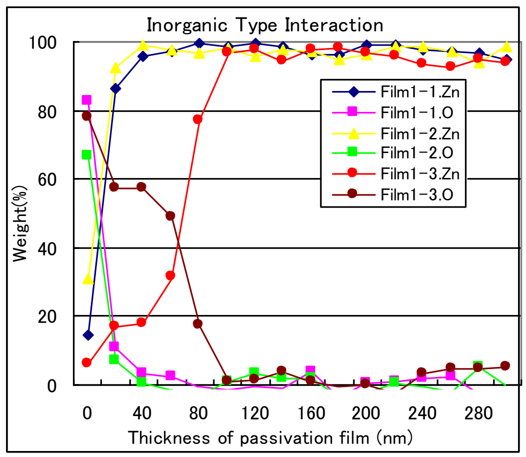
3-1-3. XPS Analysis (Inorganic Types: 1-1, 1-2 and 1-3)

XPS measurement principle: X rays are directed against the solid surface, and the emitted photoelectron energy and intensity are measured and calculated.

Graph compilation based on XPS analysis

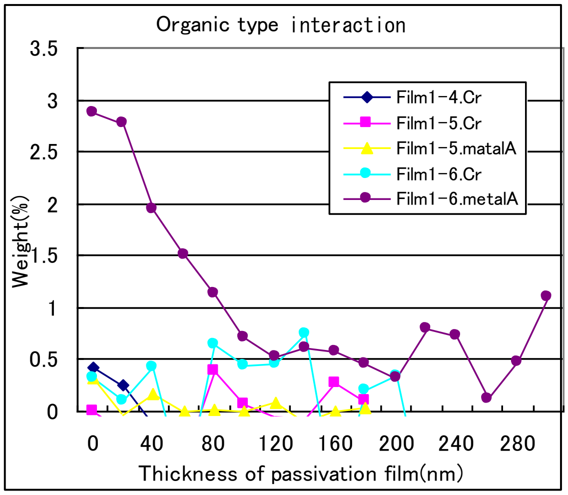
The ratio of the elements present in the solid surface is calculated using the intensity of photoelectrons emitted. By repeatedly etching and measuring the surface, the change in the element ratio in the depth direction is measured, as indicated in the graphs. The X axis shows the thickness of the passivation film. Zero indicates the surface of the passivation film. The number increases in the left-to-right direction, meaning that the passivation film is gradually etched in the depth direction.

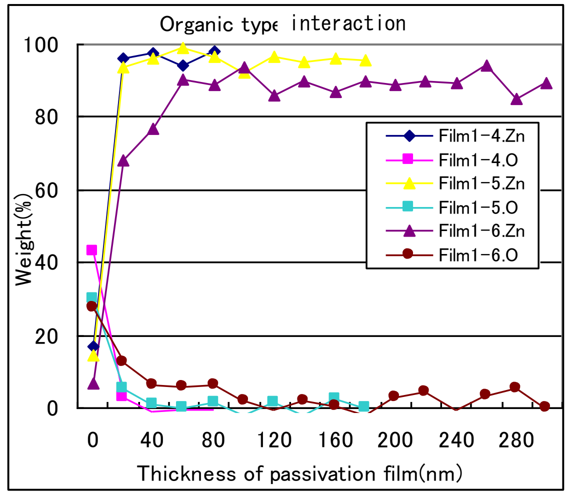




The differences in the inorganic films are described as follows. By adding mineral acid, the film thickness increased. This means that the weight % of the chromium and oxygen in the film increased, and the Zinc was also pushed down to the bottom portion from the top portion of the passivation film. We believe that under these conditions, Solution 1-3 (Inorganic chromium, metallic salt and mineral acid) developed approx. 60 to 80nm of passivation film with chromium and oxygen. Solutions 1-1 and 1-2 did not form a chromium film, and therefore had no capability for corrosion resistance.

3-1-4. XPS Analysis (Organic Types: 1-4, 1-5 and 1-6)

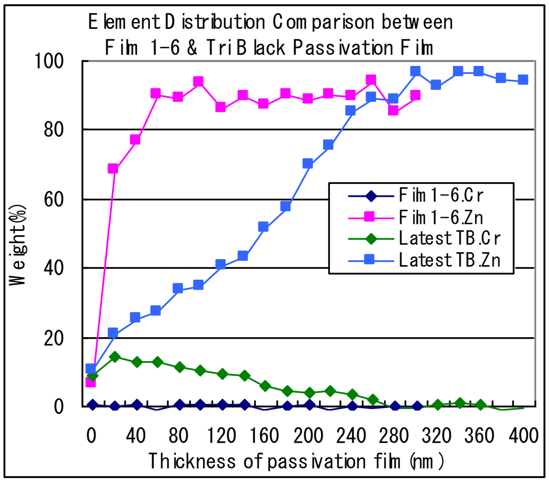


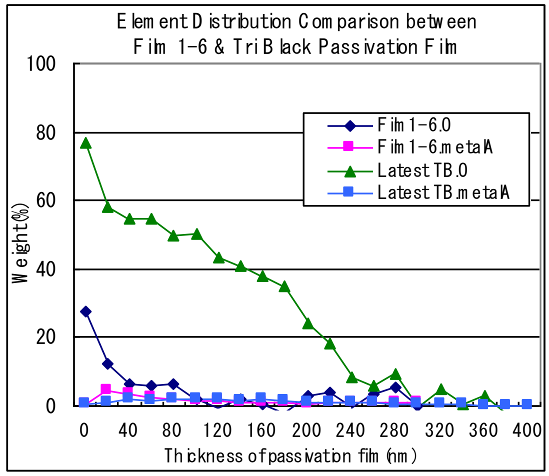


There was basically no difference in the organically developed passivation films. The element ratio of zinc and oxygen in the film formation did not fluctuate. There was also no difference in the chromium amount. The only difference that was observed among the films was in the Metal A content . Solution 1-6 developed a passivation film that was black, but the film created with Solution 1-6 should not be considered as a corrosion resistance film that includes chromium. Instead we can speculate that this film was black because Metal A was oxidized, thus turning the color black.

In terms of film development interactions, the inorganic film 1-3 was desirable because of the increased chromium film thickness. However, this increased film did not necessarily equate to high corrosion resistance. When Films 1-1 through 1-6 were evaluated for corrosion resistance, they showed no significant difference in their corrosion protection performance. In addition, it appears that it is neither metallic salt nor mineral acid but complexed (chelated) chromium that contributed toward turning the color black. Therefore, we believe that if corrosion resistance film can be developed using complexed (chelated) chromium, the formation of black corrosion resistance film can be achieved.

3-2-1. Difference between the Latest Tri Black and Film 1-6





Here are the differences between the Latest Tri Black Passivation Film and Film 1-6

(1) The thickness of the Latest Tri Black was approx. 10 times thicker than Film 1-6. When the thickness of Film 1-6 was at 40nm, the zinc amount in the film reached about 90%. The Latest Tri Black Film contained 90% zinc at 300nm.

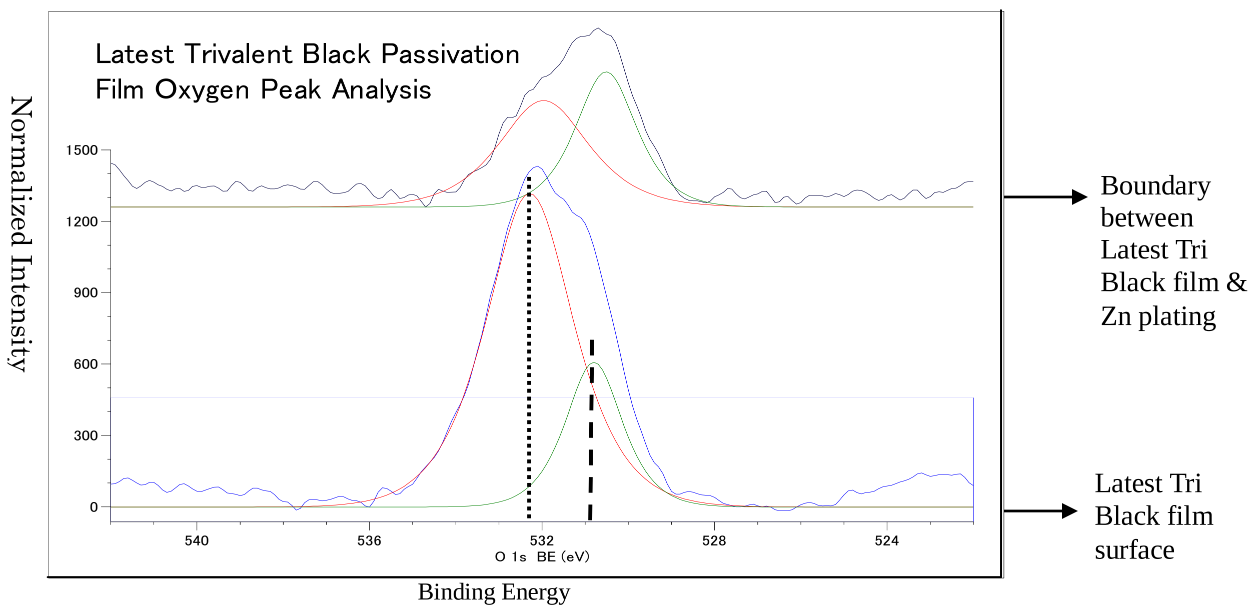
(2) The oxide layer of the Latest Tri Black was approx. 10 times thicker than Film 1-6. It was verified that the Latest Tri Black had an overwhelmingly high oxygen amount. However, further analysis is required to identify what was oxidized forming the oxide layer.

(3) The Chromium content in the Latest Tri Black was approx. 3 times higher than that of the inorganic films

The oxide layer is basically a type of passivation film. The oxide layer of the Latest Tri Black was 10 times thicker than those of Films 1-1 through 1-6. This leads us to believe that the corrosion resistance performance of the Latest Tri Black is also superior.
For the Latest Tri Black, the complexed (chelated) chromium solution is largely modified

from that of Film 1-6. As mentioned previously, Film 1-6 became black probably because Metal A was oxidized and turned black. Compared to this film, the Latest Tri Black had higher oxygen content. Therefore, it is highly possible that another element was oxidized, making the color black, and we sought to validate this hypothesis.

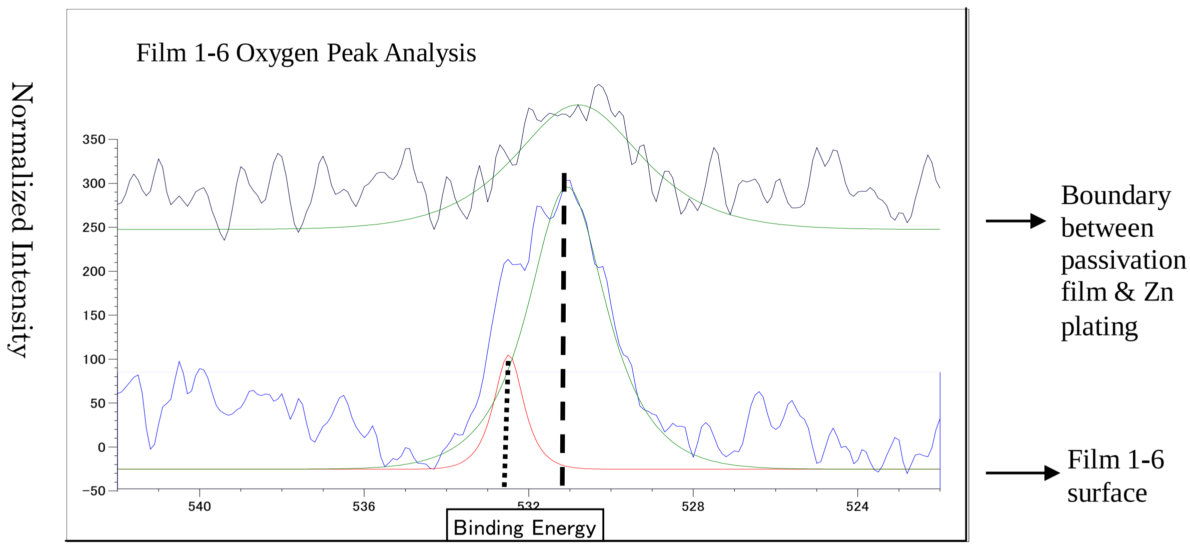
Reading of the following 2 graphs:
The energy of each element has a specific value. In addition, even the same element may slightly vary in value depending on peripheral bonding conditions. Using the energy value differences, we can estimate the chemical bonding conditions.
Energy values 528~ 534 show strong oxygen peaks, and this indicates that various types of oxygen combinations are present. Using these following graphs, we can determine what the oxygen peak is composed of, and which bonding is dominant.



There were two oxygen peaks in the Latest Tri Black film: one peak was near 532 ev and the other around 531ev. We confirmed that in the Latest Tri Black film surface the 532 ev peak was dominant, while the peak ratio changed at the Zn plating boundary.

The peak near 532 ev showed a film composed of trivalent chromium such as Cr (OH)3 and Na CrO2. There was also Cr (OH)3 at the peak near 531ev, but it was also verified that a Metal-A base oxide layer had developed mainly consisting A3O4 and A (OH)2.

The closer to the Zn plating boundary we went, the smaller the chromium layer peak we observed. However, we verified that the Metal A oxide layer showed almost the same peak at the boundary as at the surface of the Latest Tri Black film, and that the film was uniformly developed.

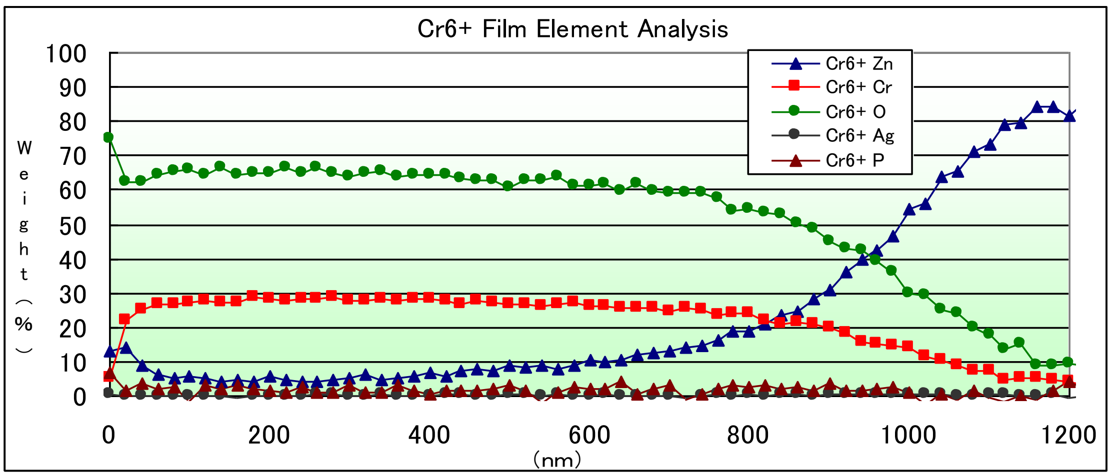


Compared to the Latest Tri Black, the oxygen peak ratio was reversed in Film 1-6. The reason why Film 1-6 did not work as a corrosion resistance film was because this film just had a thin trivalent chromium-base layer. We were also able to verify that the oxide layer near 531 ev was thick and a Metal A base, and that the black color of Film 1-6 resulted only from the metal oxide layer.

The peak neat 531 ev is very important in terms of the development of black color. As the Latest Tri Black film was thick and even, it also provided a non-transparent and smooth appearance. In addition, because the Latest Tri Black film also included a trivalent chromium base peak near 532 ev, we believe that a black film with high corrosion resistance performance was formed.

A complexed (chelated) chromium solution is very important for the appearance and corrosion resistance when trivalent chromium passivation film is developed. It certainly affects the general performance of the passivation film.

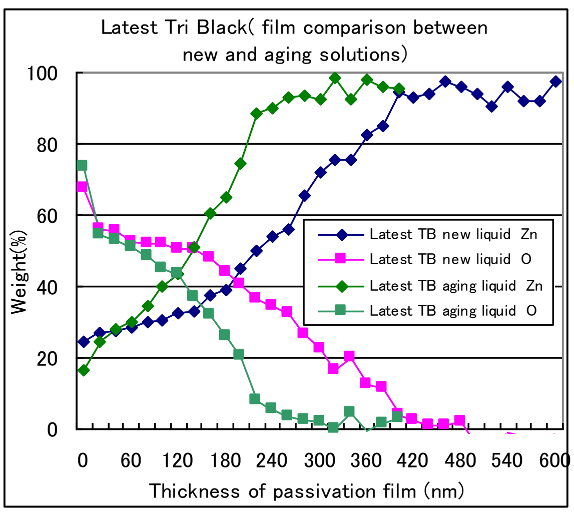
3-3-1 Difference between Trivalent and Hexavalent Chromium Passivation Films

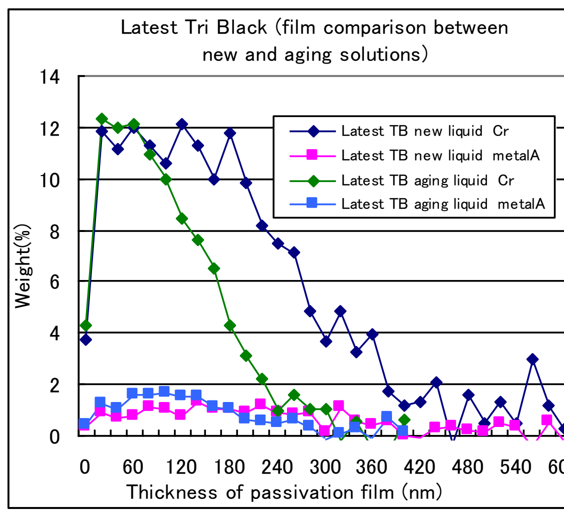


One of the characteristics of hexavalent black chromium is a thick film. The chromium content was approx. 30% and the oxide layer was also thick. Because of this thick film, the appearance looked as if the film were nicely coated. Therefore, in order to improve the rich black appearance of the Latest Trivalent Black film, a more advanced technology in developing thicker film is required.

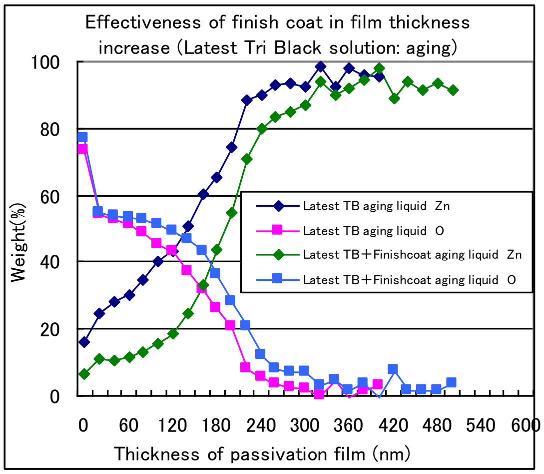
3-4-1 Effectiveness of Finish Coat (Comparison between New Solution and Aged Solution of the Latest Tri Black)

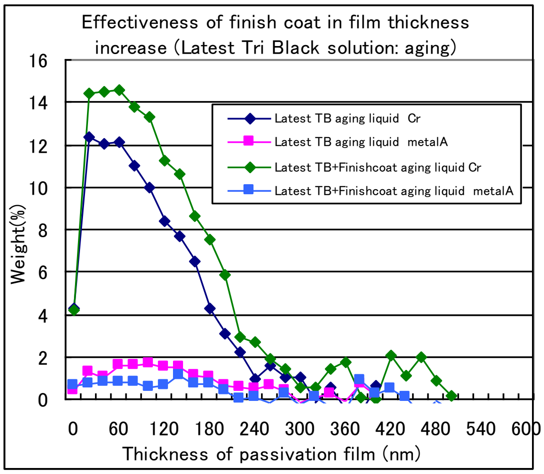
When the finish coat was applied to the Latest Tri Black film (developed from newly made-up solution), the corrosion resistance did not significantly improve (please refer to the SST photos). However, when the Latest Tri Black film was made from the aged solution containing 12 gram zinc/L, we confirmed that the finish coat over the Latest Tri Black film improved the corrosion resistance, as shown in the photos. Here we validated how the finish coat contributed to corrosion resistance performance when the Latest Tri Black solution was old.





As shown in the above graphs, we verified that the chromium content and the oxide layer in the passivation film itself decreased as the solution aged. Based on this fact, we concluded that the passivation film became thin, resulting in a decrease in the corrosion resistance performance.





There was no change in the oxygen content in the film (Latest Tri Black + finish coat). However, when the aged Tri Black solution was used with the finish coat, the Zn location was shifted to the Zn plating side from the top portion of the passivation film, indicating that the total film thickness increased. The finish coat is made with trivalent chromium, and this contributed to the increase in the total chromium volume in the film. Therefore, even though the old Latest Tri Black solution developed a thinner film, the finish coat was able to add the film thickness, maintaining the corrosion resistance performance to the level of the newly made-up Tri Black solution. In addition, the finish coat was also able to enrich the black appearance.

Conclusion

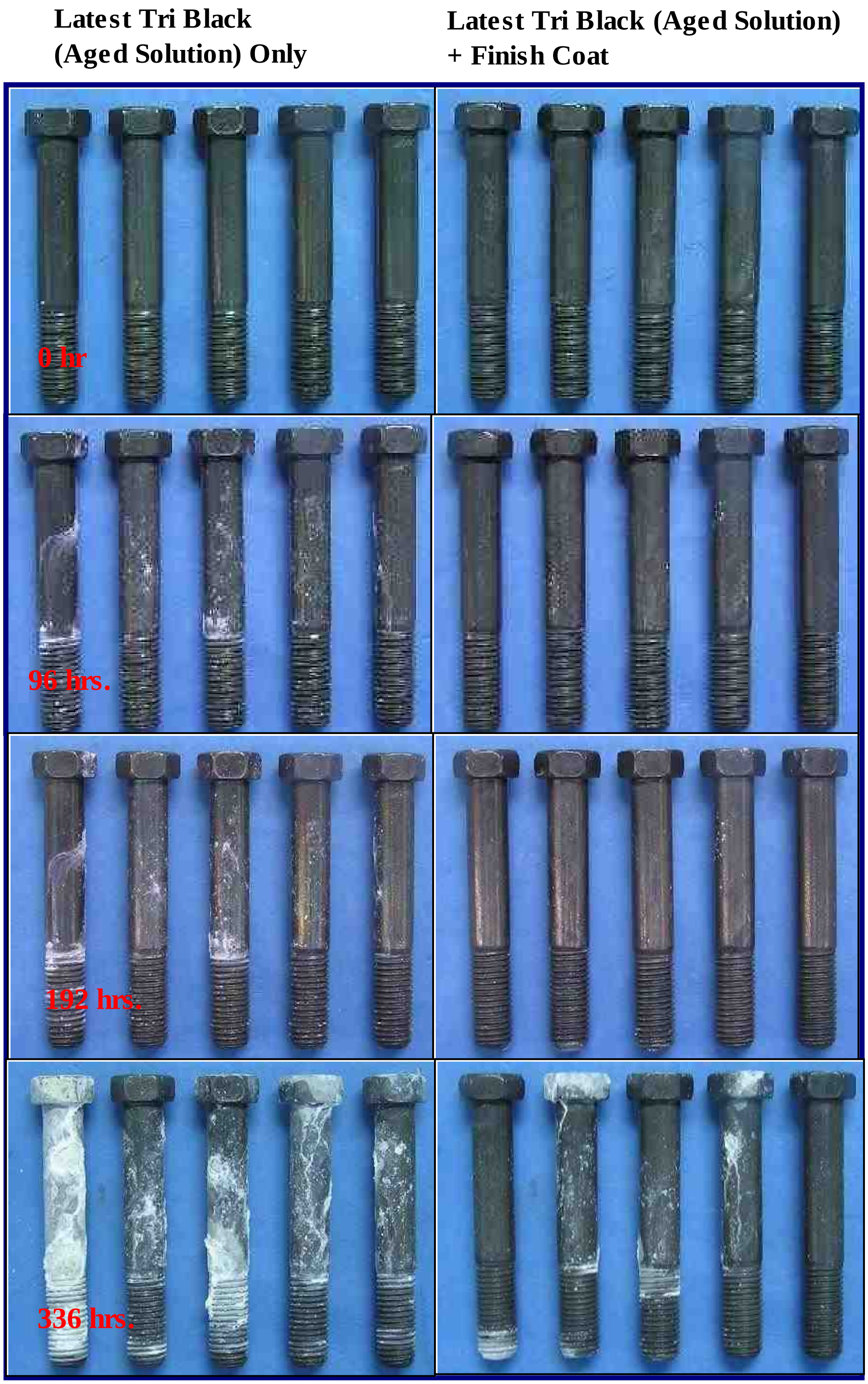
In order to develop a black passivation film with high corrosion resistance, the following factors are essential:

(1) Development of trivalent chromium salt and organic acid structure
This is an important factor to increase the thickness of the passivation film and to change the element ratio in the film.

(2) Increased thickness of the passivation film
Both oxygen and chromium amounts must be raised while the film thickness itself also needs to be increased.

- In reality, the application of the finish coat is very essential in the Latest Tri Black process. As the Latest Tri Black solution ages and the dissolved zinc content increases, the film becomes thinner and weaker. The black color also becomes paler and the corrosion resistance performance lowers. The use of the finish coat is a must to remedy this situation and maintain the rich black appearance and high corrosion resistance.

Salt Spray Test Result of the Latest Tri Black (New and Aged Solutions) with and without the Finish Coat


Latest Tri Black
(Aged Solution) Only
Latest Tri Black (Aged Solution)
+ Finish Coat
0 hr
96 hrs.
192 hrs.
336 hrs.

North American Market Observations

We would lastly like to point out the difference between job shops in USA and those in Japan.

The enormous sizes of process baths and large process volumes are overwhelming. We are seeing that job shops are handled differently in the USA from Japan. In Japan, chemical manufacturers directly contact job shops and provide technical support. In the USA, on the other hand, distributors generally follow up on issues and provide technical support. We are impressed with the high level of chemical knowledge that American distributors possess.

The way equipment is set up and used in the USA differs in many ways. In Japan, the elevator-type rack equipment is widely used, but we have seen belt-type rack equipment in several places in North America. In this setting, the immersion time difference between the top and the bottom portions of the hanger is large, making it difficult to optimize the reaction time. Chemical adjustments are sometimes challenging because of this.

Parts plated in the barrel are usually put into a basket and processed for the trivalent passivation reaction in Japan. In the USA, however, we see the barrel used in the plating continue to be used for the trivalent passivation process. Because there is a difference in the swing and agitation levels between these equipment types, we have learned that the standard process conditions for the Japanese market do not necessarily result in good parts in the USA. We strongly feel the need to establish those trivalent black passivation conditions suitable for the North American market.

Even though the quality of Japanese job shops is high on a global level, we have learned that the quality of the American counterparts is also comparable. We are excited about collaborating with American job shops who are willing to work hard to maintain high quality.

