

# The Characteristics of Cr-Free Coating Hot Dip Galvanized Sheet Steel

Jong-Gi Kim<sup>1,2,†</sup>, Man-Been Moon<sup>1</sup>, and Jeong-Mo Yun<sup>2</sup>

<sup>1</sup>Hyundai HYSKO, 313, Donggok-ri, Songsan-myeon, Dangjin-gun, Chungnam-do, Korea

<sup>2</sup>Chonbuk National University, 664-14, Deokjin-dong, Jeonju-city, Jeonbuk, Korea

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The greatest purpose of chromate treatment is to improve anti-corrosion by stabilizing a metal surface. Because metal surface forms a compound by absorbing oxygen or water in the air by being generally unstable, it is necessary to improve anti-corrosion of the metal by forming the metal surface with a stable film. When considering the economical efficiency and requirements together because the film of the metal surface treated with chromate has good anti-corrosion and the stability also in the air by being compact and strong, Chromate treatment has been used most up to the electronics industry from the auto industry. However, these days, because hexavalent chromium is both a toxic agent to be able to cause cancers and deadly poisonous environmental pollutant, the strong legal controls on its use is being imposed all over the world. Because of this reason, a new anti-corrosion method is being required. Also, by users' various demands, the passivations that have recently been developed require various characteristics such as conductivity, chemical resistance, alkali cleaning resistance as well as anti-corrosion. We could confirm the results such as excellent anti-corrosion compared to chromate, conductivity, chemical resistance and detergent resistance as the result of analysis of various characteristics of the galvanized sheet steels coated with Cr-Free solution developed in this research.

**Keywords** : HGI, Cr-free, Galvanized steel, corrosion

## 1. Introduction

The surface treatment consumables of cars, home appliances, aim at individualization, diversification, upgrading and high quality responding to the needs of life and amenity. We performed post-treatments such as phosphate treatment, chromate treatment, anti-fingerprint treatment to give good anti-corrosion, paintability and weldability to them after producing in the form of one-sided, both-sided or two-layer coating the steel coated with Zn, Zn-Ni and Al-Zn as the representative metal materials to meet these requirements. Because it materializes the excellent anti-corrosion and film-coated adhesion at a low cost, chromate treatment technology among these has been used widely as post-treatment technology of zinc and aluminum-treated steel.<sup>1,2)</sup> Chromate treatment shows excellent corrosion resistance by self-healing effect by hexavalent chromium contained in the film and chromate film's own barrier characteristics. But these post-treatments are the

main cause to increase both much waste water discharge and the cost of production.<sup>3)-8)</sup>

Because the soil and river contamination from the elution of hexavalent chromium contained in the products in the recycle and disposal of the automobiles and home appliances using the surface treated steel sheets is a problem while environmental problems are heightening attention, the legal controls on the specific things over the environment are being imposed, such as RoHS, ELV directives in EU,<sup>9)</sup> PRTR (Pollutant Release and Transfer Register) in Japan. In particular, because hexavalent chromium contained in the solution of chromate treatment is one of 4 heavy metals (Cr, Cd, Pb, Hg) of causing cancers in a human body and polluting the environment, various measures in the working environment and waste water treatment from it have been implemented.

We carried out the research regarding Cr-Free steel sheets with the characteristics of conductivity, chemical resistance, fingerprint resistance as well as anti-corrosion by using spray squeeze method in PGL(Pickled & Hot dip Galvanized Line)<sup>10),11)</sup>

<sup>†</sup> Corresponding author: hy720125@hysco.com

## 2. Experimental

### 2.1 Cr-Free solution preparation

The solution developed by our company was used as the Cr-Free solution for galvanized steel sheets. The developed solution produces the 1<sup>st</sup> solution that hydrolyzed it after adding to pure and ethanol mixtures the epoxy silane coupling agents and amino silane coupling agents which are the basic compounds to give the barrier and anti-corrosion with steel sheet. We produce the 2<sup>nd</sup> solution by stirring it for 30~60 minutes after melting in this the vanadium compound which is the substance to give anti-corrosion to the metal surface and phosphoric acid to carry out the function to adjust the adhesion and pH of the surface treatment solution, organic acid to play the role of stabilizing the solution after hydrolysis ends. After adding to this 2<sup>nd</sup> solution Ti-alkoxide, chelating agent, calcium phosphate compound and colloidal silica, we complete the solution of metal surface treatment by stirring it at normal temperature at more than 1500 rpm for 30~60 minutes. Here, Ti-alkoxide is added as the substance which plays the role of improving corrosion resistance, cross-linkage promotion and low temperature solidification, and chelating agent is added as the substance which plays the role of stabilizing the solution and reinforcing the corrosion resistance, and calcium phosphate compound is added as the substance which plays the role of improving the corrosion resistance. Also, colloidal silica is used as the substance to give barrier, anti-corrosion and anti-black patina.

### 2.2 Sample preparation

The sample used in this experiment was HGI(Hot Dip Galvanized Iron & Steel Strip) being mass-produced by our company, and the size was 75X150 mm. First of all, we prepared the solution of surf cleaner 3%(Nipsea Chemical Korea Co.) which is a degreasing agent, removed cleanly dust and oil stain of the specimen by conducting the dipping degreasing at 45 °C for 90 seconds, and removed the degreasing solution by washing it with the running water for 60 seconds. After spraying Cr-Free solution

on the sample made like this, squeezed Cr-Free solution by using a roll, and made the sample for evaluating the property. The coating weight of the coated Cr-Free solution was 350~400 mg/m<sup>2</sup>, the drying temperature was PMT(Peak Metal Temperature) 60 °C. The reason that we made the sample in the way like this is that the processing line to which we will apply the developed solution is the structure to produce Chromate/Cr-Free steel sheets by using a squeeze roll after spraying the solution.

The property of Cr-Free HGI produced like this was compared with that of Chromate(Cr coating weight 20~23 mg/m<sup>2</sup>)/Cr<sup>3+</sup> HGI.

Fig. 1 shows the structures of the post treatment hot dip galvanized steel sheets. The newly developed product has a nonresinous Cr-Free coated layer.

### 2.3 Evaluation method

We conducted the evaluation of corrosion resistance by salt spray test with 5%NaCl at 35 °C on the basis of the method stipulated in ASTM B117, evaluated the corrosion resistance by confirming white rust incidence with the passage of time. We evaluated anti-black patina, fingerprint resistance, chemical resistance, electrical conductivity according to Sony standards which are the major method to evaluate chemical coating hot dip galvanized steel sheet. In case of anti-black patina, we evaluated chrominance measurement, white color difference by using chrominance machine (KONICA MINOLTA SENSING, INC. CHROMA METER CR-400) after keeping it for 120 hours at humidity of 95% at temperature of 60 °C(2 methods of bare sample and pile up sample). In case of fingerprint resistance, we evaluated them by measuring the surface color changes before/after applying white vaseline on the surface.

In case of chemical resistance, we evaluated it after measuring the color difference on the surface before/after rubbing it 10 times by using MEK(Methyl Ethyl Ketone) which is a volatile solvent. Coating weight was measured with XRF by using the calibration curve from an inorganic element Si intensity from the coating thickness. In case of conductivity, we evaluated the surface resistance value

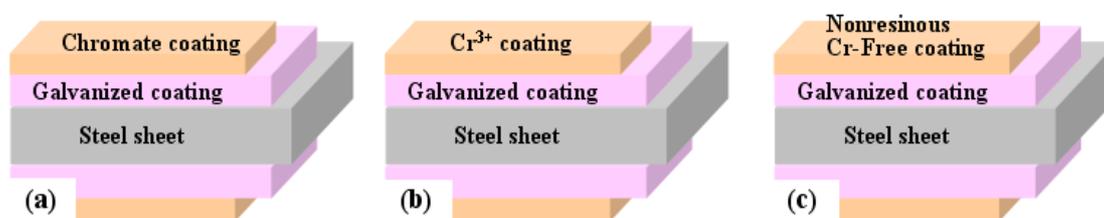


Fig. 1. Structures of various post treatment hot dip galvanized steel sheet Chromate coating(a), Cr<sup>3+</sup> coating(b), nonresinous Cr-Free coating(c).

by using 4 pin probe type Loresta-GP equipment. In case of poor conductivity, namely, the higher the surface resistance value is, the lower the electromagnetic shielding effects and the internal noise occurrence of electrical appliances gets, and other problems like weldability can occur. To evaluate alkali cleaning resistance, we evaluated salt spray test after dipping for 120 seconds under the condition of pH 12.2, 60 °C by using #543A(SAM YANG CHEMICAL INDUSTRY) which is a degreasing agent first of all.

#### 2.4 Paintability evaluation

To evaluate the paintability, we conducted Electro-deposition painting. In case of Electro-deposition painting, we prepared surfcleaner 3% solution, conducted dipping degreasing at 45 °C for 90 seconds, removed cleanly dust and oil stain of the specimen, and removed the degreasing agent by washing it with the running water for 60 seconds. We make phosphate formation be promoted by activating the surface after conducting it in 0.15% surface conditioning solution for 60 seconds. The conditions of phosphate concentration used for forming phosphate crystals on the surface in phosphate solution are total acidity of 20.3, free acidity of 0.9, 3.1 points of promotion degree, and make it react at 43 °C for 120 seconds. In case of the produced phosphate sample, electro-deposition painting is conducted after drying it by using air after washing the sample with the running water.

In case of electro-deposition pigments, we prepared the sample of electro-deposition painting of 15~20 um after making the voltage of 170 V for 70seconds at 25 °C after producing KED#2000P(DPIHOLDINGS Co.) and binder from the solid content of 20%. In case of the sample whose electro-deposition painting was completed, the final specimen was made by solidifying it at 160 °C for 15 minutes. Phosphate evaluation was performed by the coating weight measurement, and in case of phosphate coating weight we measured the weight differences before/after melting phosphate crystal by using chromic acid.

The thickness of electro-deposition film was measured by using Fischerscope, and in case of the 1<sup>st</sup> adhesion, we evaluated the film peeling by using 3 M tape after making 100 graduations at intervals of 1mm in the form of a checkerboard by using an Erichsen cross cutter. In case of water resistance adhesion, we conducted the adhesion evaluation after leaving it as it was in a thermostat bath of 40 °C for 20 days. In case of salt spray test (SST), we measured and compared the peeling width of electro-deposition painting after leaving it as it was for 480 hours by spraying 5% salt solution in the quantity of 1.6~1.9 ml per hour on the specimen of the electro-deposition painting on which scratched in 1 mm wide diagonally(at a 30 degree angle to the longitude of the specimen) to the specimen.

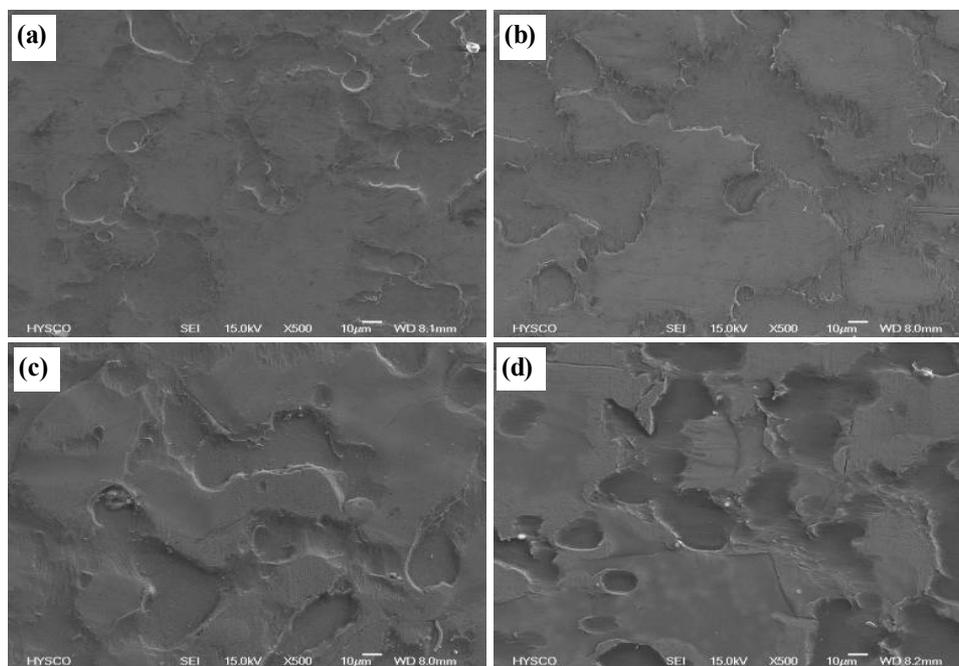


Fig. 2. Morphologies of as-received(a), Chromate(b), Cr<sup>3+</sup>(c), Cr-Free(d) HGI.

### 3. Results and discussion

Fig. 2 is SEM images of non-treatment specimens HGI, Chromate HGI, Cr-Free HGI, and there were no big differences externally.

Fig. 3 is the evaluation results of corrosion resistance using salt spray test, and the white rust occurrence area after 72 hours of Salt Spray Test was 20% in Chromate HGI, 30% in Cr<sup>3+</sup> HGI, 0% in Cr-Free HGI, and Chromate HGI showed the results of 50% in white rust occurrence area, Cr<sup>3+</sup> HGI showed 70%, Cr-Free HGI showed 15% when 96 hours passed after beginning the salt spray test. This is the results to show the fact that the developed Cr-Free HGI has an excellent corrosion resistance as compared to Chromate/Cr<sup>3+</sup> HGI.

Fig. 4 is the evaluation results of anti-black patina, and it shows that the less the whiteness differences get, the better the anti-black patina is. In case of bare sample, the whiteness difference of chromate HGI were smaller as compared to that of Cr<sup>3+</sup>/Cr-Free, and in case of stack, we could ascertain that the whiteness difference of Cr-Free HGI was little.

Fig. 5 is the evaluation results of conductivity, and we could ascertain that Chromate/Cr<sup>3+</sup>/Cr-Free HGI including the non-treatment specimen all had the excellent conductivity of the surface resistance values of less than 1 mΩ.

Fig. 6 is the evaluation results of chemical resistance,

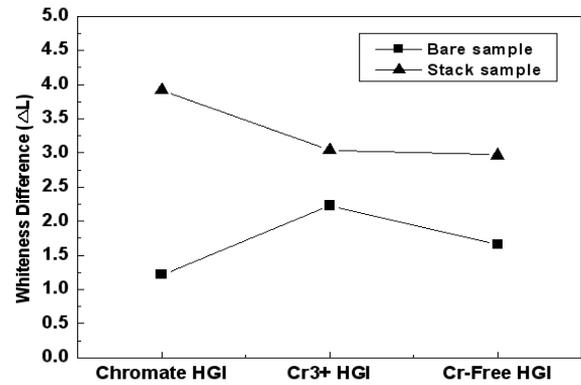


Fig. 4. The results of anti-black patina test.

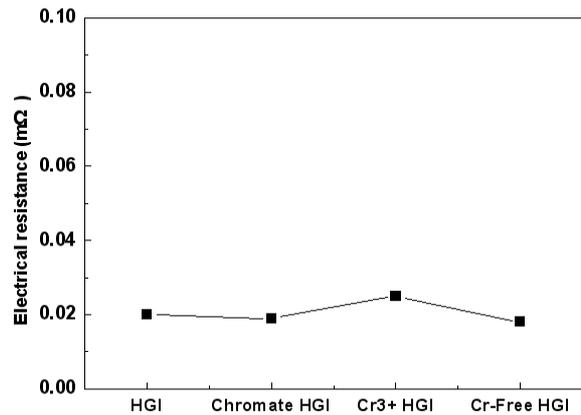


Fig. 5. Electrical resistance using Loresta-GP equipment.

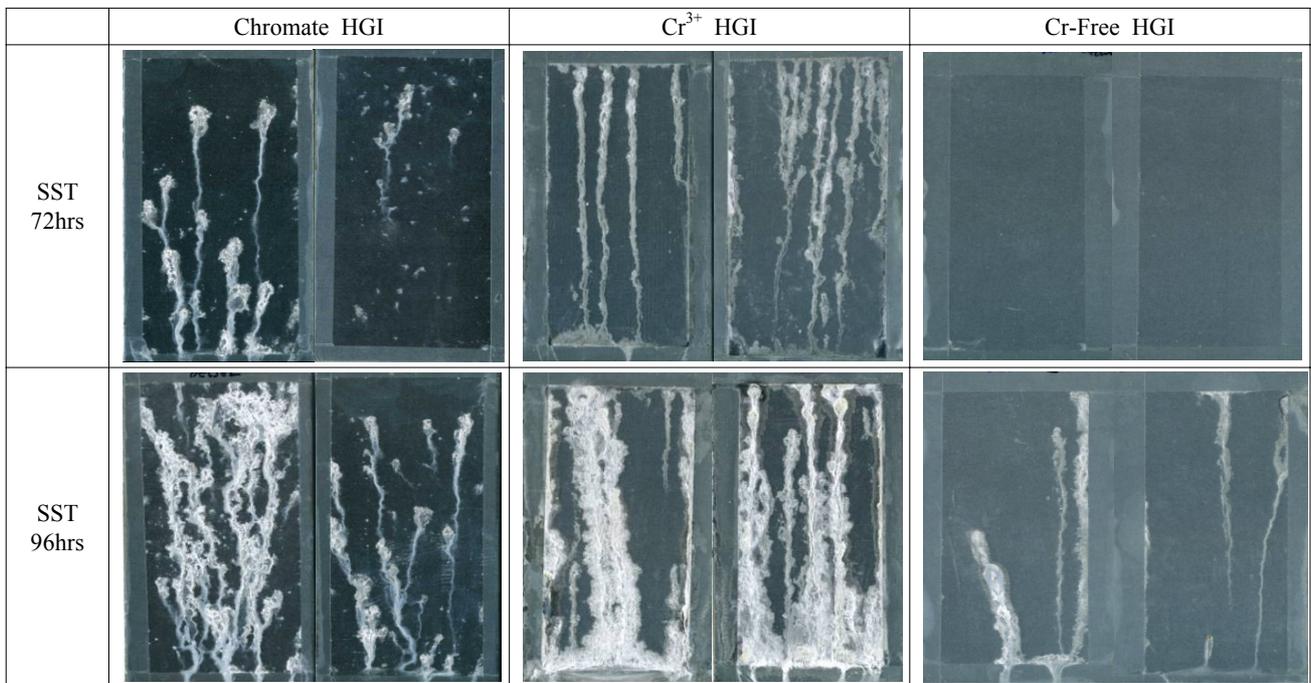


Fig. 3. Corrosion test results after 72, 96 hrs of Salt Spray Test.

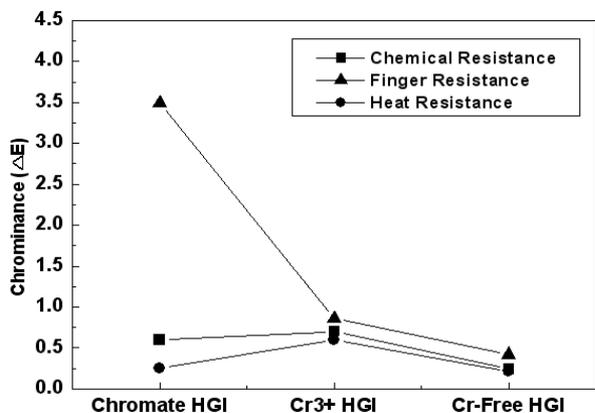


Fig. 6. The results of chemical resistance, fingerprint resistance & heat resistance test.

fingerprint resistance & heat resistance and we could ascertain that three post-treatment products (Chromate/Cr<sup>3+</sup>/Cr-Free HGI) all had the excellent chemical resistance, heat resistance. But evaluation results of fingerprint resistance, we could ascertain that two post-treatment products (Cr<sup>3+</sup>/Cr-Free HGI) had the excellent property.

Fig. 7 is the evaluation results of alkali cleaning resistance, and shows the best results as Cr-Free HGI white

rust occurrence area of less than 10% after 24 hours of salt spray test.

We could ascertain that phosphate coating weight of Chromate/Cr<sup>3+</sup>/Cr-Free HGI was deficient as compared to 2.5~5.0 g/m<sup>2</sup> of the standard coating weight, as 2.2, 1.6, 1.8 g/m<sup>2</sup>.

Fig. 8 is the evaluation results of electro-deposition painting adhesion, and three post-treatment products all show inferior results in case of water resistance adhesion after 480 hrs in 40 °C water(b), though three post-treatment products all were excellent as 100/100 in case of the results of the 1st adhesion(a).

Fig. 9 is the evaluation results of corrosion resistance of electro-deposition painting, and we could ascertain that membrane blister and separation occurred in all three post-treatment products.

Though getting the good appearance Cr-Free HGI after electro-deposition painting, they showed inferior results in case of water resistance adhesion and corrosion resistance of electro-deposition painting, and these things were caused by the effects of epoxy silane coupling agent of Cr-Free solution, amino silane coupling agent which play an important role in corrosion resistance, and additional researches on additives of Cr-Free solution are required to

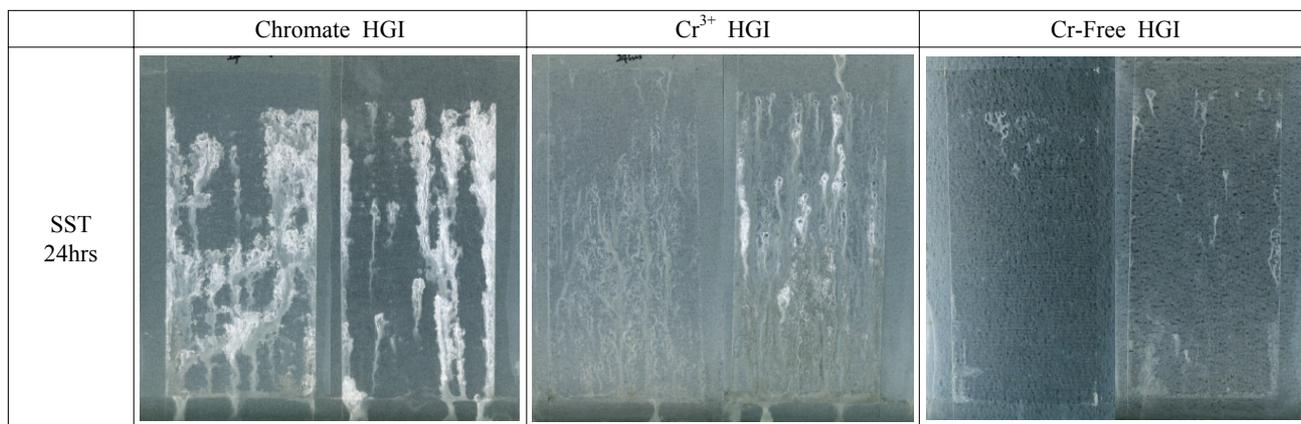


Fig. 7. Alkali cleaning resistance after 24 hrs of Salt Spray Test.

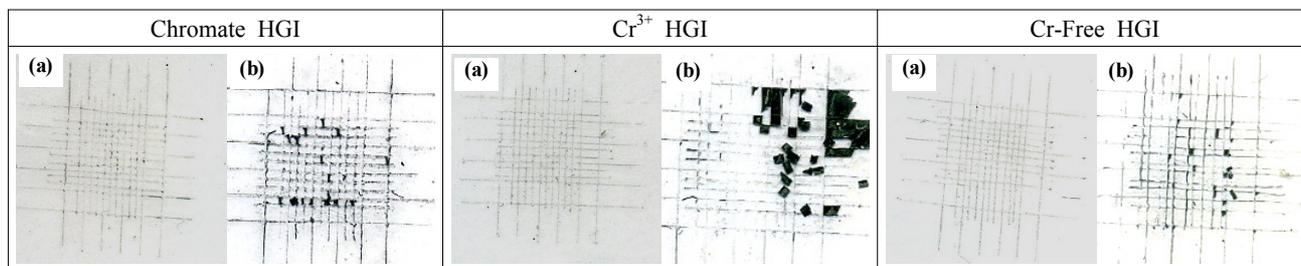


Fig. 8. Electro-deposition painting adhesion test peeling test at R.T(a), 40 °C water for 480 hrs(b).

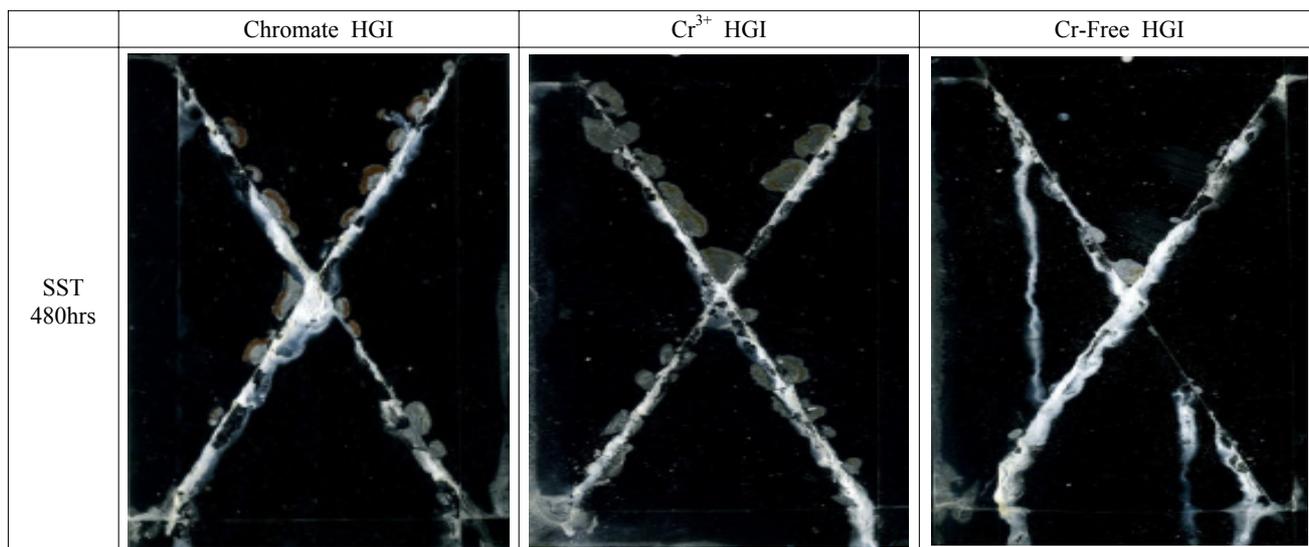


Fig. 9. Corrosion test results after 480hrs of Salt Spray Test.

secure the optimum electro-deposition painting of Cr-Free solution in the future.

#### 4. Conclusions

The developed Cr-Free solution for HGI showed the improvement of 1.5~3 times in corrosion resistance (white rust occurrence area basis) compared to the existing chromate/Cr<sup>3+</sup> HGI. Also, it showed anti-black patina, conductivity, chemical resistance, heat resistance of more than the same level, and improved excellently in anti-fingerprint, alkali cleaning resistance. It is required to study additionally in the future the properties to satisfy various users, such as securing the excellent anti-corrosion also after deep drawing like chromate, the general corrosion improvement to prevent white rust and red rust for a long time, the improvement of detergent resistance, chemical resistance for the application to various parts of home appliances and the security of the optimum electro-deposition painting through the study on the additives of Cr-Free solution.

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