COMPARISON CHARACTERIZATIONS OF Cr (III) AND Cr (VI) CONVERSION COATING ON ZINC ELECTROPLATING SUBSTRATE

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Abstract: *Some of characterizations of Cr (III) conversion coating have been compared with that of Cr (VI) conversion coating. The comparison was made on the base of conversion coating color, anticorrosion ability, and effect of drying temperature. The obtained results indicated that the color of Cr (VI) conversion coating was darker than that of Cr (III) conversion coating. However, the color of Cr (VI) conversion, more or less, depended on the drying temperature. The color of conversion coating the darkest if the drying temperature was at 50^{o}C. Moreover, the characterizations of Cr (VI) depended significantly on the drying temperature. The drying temperature had a significant effect on anticorrosion ability of Cr (VI) conversion coating, especially for samples dried at higher temperature than 110^{o}C. In contrast, the Cr (III) conversion coating showed more stable and insignificantly depended on drying temperatures. In addition, the surface of Cr (III) conversion samples was smooth, no crystalline structure. Conversion coating was layered fibrous. The Cr (III) sample had no crash while the Cr (VI) had. Hence, the obtained results indicated that Cr (III) conversion solution can creat the conversion coating which has anticorrosion ability, which can replace Cr (VI) based conversion coatings.*

Keywords: *Cr (III) conversion, Cr (VI) conversion, coating, zinc electrodeposited, anticorrosion.*

1. Introduction

Zinc plating is widely used to go against corrosion for steel due to the low cost and simple technology. However, the corrosion rate of zinc coating might be very high in a humid environment since zinc is a highly chemical reactive metal [1]. Therefore, a post-treatment is necessary to increase the lifetime of zinc coatings. One of the most popular methods was to use Cr (VI) conversion solution to create a thin conversion coating on the surface of zinc plating because of many advantages, such as high anticorrosion, self-healing ability, adversity color (white, rainbow color, black…), good adhesion with organic coating, simply engineering and low cost... However, the compound Cr(VI) has been convinced as a hazardous substance that may cause cancer. The content of Cr (VI) in conversion layer fluctuates from 5 - 400 mg/m^2 in the using process, the Cr (VI) compound would be dissolved and cause of pollution [2] [3].

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Hence, many other treatment methods have been presented with requirements to replace Cr(VI) based conversion coatings with safer treatments in which Cr (III) conversion coating is introduced and become popular in industrial practice [4] [5].

With the purpose to build a system of research and testing the conversion coating based on Cr (III) conversion solution, in this work, we would present the results of the comparison of characterizations of Cr (III) and Cr (VI) conversion coating on a zinc electrodeposited substrate.

2. Experimental

2.1. Materials

The chemical materials used including: NaOH, HNO_3 (both used pure grade (China)), iridescent Cr(III) conversion complex solution (containing: Cr^{3+} in type $Cr_2(SO_4)_3.6H_2O$ at 5g/L, complexion agent at 16g/L and pH at 1.5), Cr (VI) conversion solution UDYCRO 747 was purchased from Enthone. Zinc electroplating was fabricated according to the ENTHONE process. The components of zinc plating solution are $ZnCl_2$ (60g/L); NH_4Cl (250g/L); additive AZA (30ml/L) and AZB (1.5ml/L).

2.2. Sample preparation

Steel low carbon plates (100x50x1.2 mm) were degreased by immersing in UDYPREP-110EC (Enthone) with concentration of 60 g/L under 50-60^oC for 5-10 min. After that the samples were immersed in a solution containing HCl (10%), urotropin (3.5 g/L) at ambient temperature for 2-5 min.

The steels were industrially electro galvanized in plating bath with a solution of Enthone Company. The conditions were followed: cathodic current density of 2 A/dm^2; the zinc anode with a purity of 99.995%; rate of square anode/cathode of 2/1 and at ambient temperature for 30 min with the swinging cathode operation. Subsequently, the samples were rinsed with deionized water. Zinc coating had thickness of 12-13 μm

Immediately after the electro galvanizing step, the sample surface was activated in a 0.5% HNO_3 solution (pH = 1) for 3-5 s. Subsequently, the surface was passivated by either the following treatments green-colored Cr^{3+} based conversion treatment with parameters being 2-2.5 of pH, in 60 s or Cr (VI) conversion solution with parameter being 1,4-1,8 of pH during 30s in industrial immersion bath with mechanical stirring. Finally, the samples were rinsed in deionized water and dried in an oven at various temperatures for 30 min. All samples were stored in desiccators at ambient temperature in 48 h for stabilized samples.

2.3. Analysis

The general appearance of conversion coating was assessed after 48h for stabilizing samples. The corrosion resistance was evaluated by natural salt spray testing according JIS H 8502:1999 standard, which means by Q-Fog CCT 600 (USA) at Institute for Tropical Technology.

Morphology of conversion coating was obtained by HITACHI S-4800 Scaning electron microscopy.

Corrosion behavior of passive coating was determined by polarization method which means on Autolab Pgstat 30 using 3 electrodes with parameters were: 4.52 cm^2 of square sample, a platinum counter electrode, saturated calomel electrode as reference electrode, 2mV/s of scan rate, 3,5% NaCl solution, in presence of air.

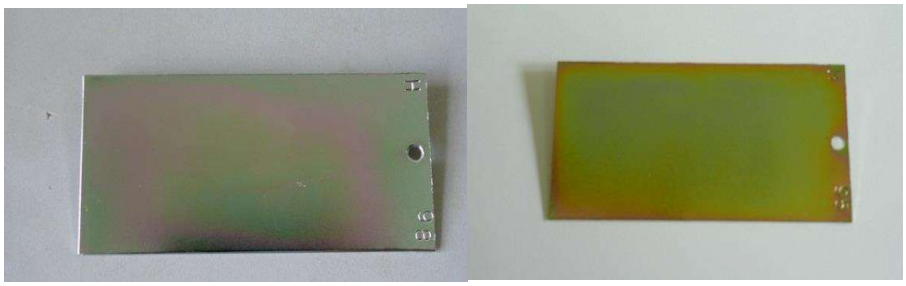
3. Results and discussions

3.1. The color of conversion coating

The appearances of conversion were obtained by either eyes and taking a photo. Table 1 presents the results of general appearance and color of conversion coating.

Table 1. *General appearance of conversion coatings*

From passive solution	***Notation***	***Appearance***
Iridescent Cr (III) conversion complex solution	C	Glossy surface, having the light rainbow color with main the color being pink and light green.
Cr (VI) conversion solution UDYCRO 747	747	Glossy surface, having the dark rainbow color with the main color being light blue and golden.



(C) (747)

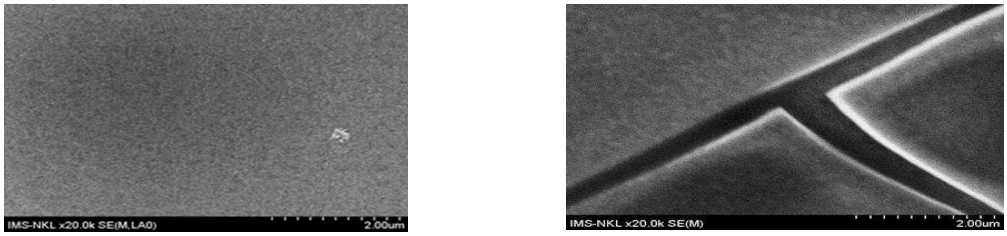
Figure 1. *The color of conversion coatings*

As can be seen from Table 1 and Fig.1: There was a significant difference in color between conversion coating from C conversion and 747 solution.

The color of conversion coatings from Cr (VI) conversion solution was darker than that of conversion coating from Cr (III) conversion solution.

3.2.Morphorlogy of conversion coating

Morphorlogy of conversion coating surfaces was displayed on Fig. 2.



a) C b) 747

Figure 2. *Mophorlogy of Cr(III) and Cr(VI)conversion coating surfaces*

From Fig. 2. It can be seen that both of conversion coating surfaces are smooth and do not show crystal.

For the Cr (III) conversion coating, the surface has no crash. In contrast, the surface of Cr (VI) conversion coating had some crash with about 200 nm in diameter. It may be due to the pull-push of conversion coating if the surface was dehydrated by drying process.

3.3. Effect of drying temperature and anticorrosion of conversion coating

3.3.1. Weight loss

The weight change of conversion coating in various temperatures of the drying process were shown in table 2.

Table 2. *The weight change of conversion coating in various temperatures*

Temp / Conversion coating	Weight loss (%)			
	50°C	80°C	110°C	210°C
747	9.7	14.3	23.6	28.4
C	8.6	11.4	17.1	24.3

As can be seen from table 2, the weight loss of conversion coating increased if the drying process temperature rises from 50 - 210°C. The weight of conversion coating dramatically reduced in the temperature range from 50 - 110°C. After that, it decreased slightly in the temperature range from 110 - 210°C in comparison with the previous period. The weight change is the cause of dehydration from conversion coating when the samples were dried. As a result, if the temperature was higher than 110°C, the amount of water in the conversion coating was insignificant.

3.3.2. Natural salt spray testing

The average time of white rust appear of conversion coatings were indicated on table 3. As can be seen from table 3: The highest anticorrosion of conversion coating depended on temperature in the drying process, at 80°C for Cr (III) and 50°C for Cr (VI).

If the drying temperature was higher than 110°C, the corrosion resistance substantially reduced. A standard example was Cr (VI) conversion coating. After the sample was dried at 210°C, the white rust appeared after 24h natural salt spray.

Table 3. *The time of white rust appear*

Drying temp. / Coating	The time of white rust appear on surface, hour			
	50°C	80°C	110°C	210°C
C	194	218	195	175
747	215	168	72	24

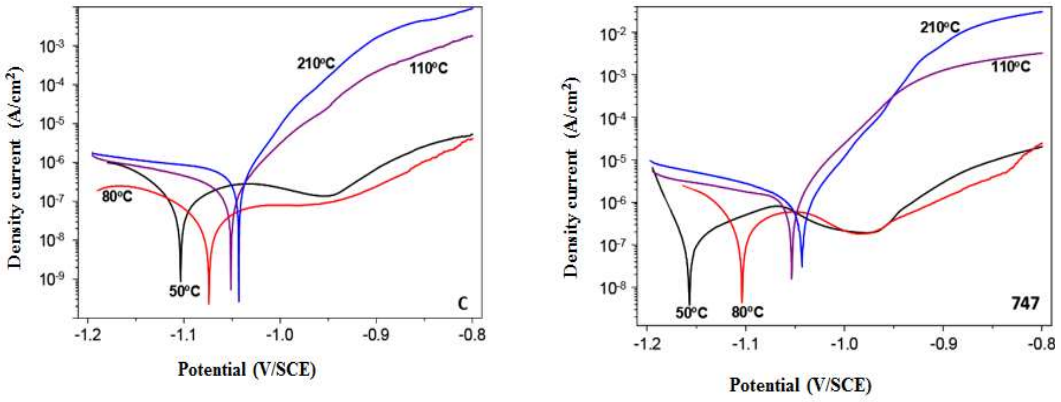
The obtained results indicated that the drying temperature had less effect on the Cr (III) conversion coating in comparison with on Cr (VI) conversion coating. The degradation of Cr (VI) conversion coating when increasing drying temperature might be

the cause of Cr (VI) change in conversion coating. If the drying temperature was higher than 50°C, the content of Cr (VI) dissolving might be changed or Cr (VI) could be converted to Cr (III) and thus reducing the anticorrosion ability.In the natural salt spraying process, it was obtained that the color of sample which dried at 50°C became lighter than initial sample. It is obvious that the amount of Cr (VI) in conversion coating, to some extent, dissolved. In contrast, the sample dried at higher temperatures, the color saw insignificant change during the natural salt spraying process.

3.3.3. The results of polarization measurement

The curves of dynamic polarization of conversion coating samples from Cr (III) and Cr (VI) conversion solutions would be illustrated in Fig. 3 and Fig. 4. The potential value, corrosion density current were shown in table 4.

For the conversion coating samples from Cr (III) conversion solution, current density reduced as follow arrange of drying temperature: 210°C; 110°C; 50°C; 80°C. These results also were suitable with the obtained results in table 3. The anticorrosion can be arranged as 50°C ~ 80°C > 110°C > 210°C.



a) b)

Figure 3. *Polarization curves of conversion coatings produced in a - Cr (III)and b - conversion solution with various drying temperatures*

Table 4. *E_{corr} and i_{corr} values of samples*

Conversion solution	Drying temp., °C	E_{corr}, mV/SCE	i_{corr}, A/cm^2
C	210	-1046	$5{,}87\times10^{-7}$
	110	-1053	$1{,}52\times10^{-7}$
	80	-1074	$3{,}35\times10^{-8}$
	50	-1104	$6{,}6\times10^{-8}$
747	210	-1044	$2{,}46\times10^{-6}$
	110	-1055	$3{,}19\times10^{-6}$
	80	-1074	$4{,}29\times10^{-7}$
	50	-1157	$1{,}94\times10^{-7}$

The current density values of two samples coatings by 747 solution and dried at 110 and 210°C were the highest. These results were compatible with the obtained results of natural salt spraying test.

The samples coatings by 747 solution and dried at 50°C having i_{corr} that is higher than that of sample coatings by C solution which was dried at 80°C (table 3). These results were compatible with the obtained results of natural salt spraying test.

However, the natural salt spraying results showed that the anticorrosion of samples coatings by 747 solution and dried at 50°C was better than that of the samples coatings by C solution and were dried at 50°C. It can be explained that the polarization measurement was determined at the initial. Moreover, this measurement was applied in a small square which may have disabilities while the natural salt spraying test was applied to all samples and some disabilities, more or less, had not effect on results.

4. Conclusion

The color of Cr (VI) conversion coating was darker than that of Cr (III) conversion coating.

The surface of passivated samples was smooth, with no crystalline structure. Conversion coating was layered and fibrous. The Cr (III) sample had no crash while the Cr (VI) had.

The drying temperature had a significant effect on anticorrosion ability of Cr (VI) conversion coating, especially for samples dried at higher temperature than 110°C. In contrast, the Cr (III) conversion coating showed more stable and insignificantly depended on drying temperatures.

The obtained results indicated that conversion Cr (III) solution fabricated can create the conversion coating which has anticorrosion ability as conversion from conversion Cr (VI) solution.

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