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Corrosion performance of zinc chromate (hexa:tri Cr) complex compound coating on zinc-coated components

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Abstract

Zinc chromate complex compound is a thin coating formed through a passivation process produced by a chemical or electrochemical treatment of a metallic surface that gives a superficial layer. This layer which is actually a compound of the metal gives corrosion protection and has a profound influence on the properties of the coating. The chromate film was produced from chromating liquid which consists of three different chemical compositions comprising of chromic ions (hexa & tri Cr) and acids. The zinc plated steel sheet were then immersed in the solution and approximately 0.5-3.0 μm thick chromate film was formed on the metal sheet surface. It was found that pH value and immersion time have a significant effect on the corrosion resistance of the chromate layer. The microstructure analysis and corrosion rating in accordance to BS/ISO was conducted. The chemical reaction of the phenomena was also discussed. The newly blended formulation gives the best corrosion performance in comparison with a proprietary product used commercially.

1 Introduction

Chromate films are chemical conversion coatings. The substrate metal participates in the coating reaction and becomes a component of the coating and it has a profound influence on the properties of the coating. The solutions for chromating are acidic [1].

In the coating operation a number of concurrent chemical reactions occur with changing ionic balance and imbalances of resulting concentration and relative

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proportion of active ingredients, such as the chromate and sulphate or fluoride ion concentration, which may affect coating ability [2].

The basic protective function of chromate conversion coating (CCC) is the evolution of chromate ions into a humid environment, which due to their inhibiting properties, protect zinc against corrosion in the damaged areas of CCC [3]. The course of CCC formation involves oxidation of the metal ions to the solution and evolution of hydrogen. The reaction taking place during chromating are as follows:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \quad (1)$$

$$3H_2 + 2Na_2Cr_2O_7 \rightarrow 2Cr(OH)_3 + 2Na_2CrO_4 \quad (2)$$

$$2Cr(OH)_3 + Na_2CrO_4 \rightarrow Cr(OH)_3CrO_4 + 2NaOH \quad (3)$$

The CCC are formed because the metal surface dissolves to a small extent, causing a pH rise at the surface-liquid interface. This result in the precipitation of a thin complex chromium-metal gel on the surface, composed of hexavalent and trivalent chromium and the coated metal itself. The solubility decreases as the coating loses water and as oxidation proceeds, the solubility reaches an optimum for most purposes after at least two days ageing under warm and dry conditions. Excessive dessication by over exposure to high temperatures leads to total insolubilation and, what is worst, to film cracking [4,5].

The colour and thickness of CCC vary with conditions of chromating, and particularly composition, pH, temperature of bath and time of treatment (immersion). Treatment times, whether by spray or dip, are relatively short, ranging from a few seconds for zinc and to a maximum of five minutes for aluminium. Most solutions operate at or near room temperature [1]. The most important factor, decisive for the formation of chromate coatings is the pH of the chromating solutions [6].

Zinc and cadmium electroplates are among the metals commercially chromated. CCC improve corrosion resistance and appearance of metals and adhesion of organic top coat. About a half of the world consumption of zinc (> 4 million tons) is used for making protective coatings [7].

The aim of this work is to develop a chromate coating which can withstand severe deformation processes and its solution that is stable over a wide range of pH without affecting its aesthetic, corrosion resistance and mechanical properties.

2 Procedure

The substrates used were low-carbon steel sheets. They were zinc electroplated in a zinc alkaline bath to a coating of about 10μm before finally being chromated to about 0.5 –3.0 μm in three different solutions. Solutions C1 and C11, were formulated by the investigator and the other was Solution L, an established proprietary product. Solution C1 constitute a mixture of Cr^{+6} and Cr^{+3} at a ratio

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of 1.5 to 2.0, 1-20 g/l H_2SO_4, 1-20 g/l HNO_3, 1-20 ml/l 10%NaOH and C11 with the presence of 1-10% of Si oil. The parameters under study were pH, between the range of 0.8 to 2.0, and dipping time, between the range of 5 to 20 seconds with mechanical agitation. The chromate bath and drying temperature were at ambient and 53 °C respectively. These were in accordance to normal industrial practices. The specimens were then subjected to salt spray test (ASTM B-117), bend test, adhesion test (ASTM B 201-80/89), standard industrial cross-hatch test (ASTM D 3359-87) and surface defect analysis (BS 5466 Part 6: 1982).

3 Testing

To determine the film corrosion resistivity, the salt spray test as specified in ASTM B-117 was conducted on the chromated zinc electroplated components. The weight loss, percentage corroded area and surface topography analysis were carried out.

3.1 Salt spray test.

The salt spray test was conducted by using a media of 5%NaCl atomised at a flowrate of 10ml per 80cm^2 per hour. The humidity was kept at 95-100% RH with temperature of 35 °C and pressure at 20 psi. The pH was maintained in the range of 6.9-7.0 for six hours.

4 Results and Discussion

It was observed that the CCC from solutions C1 and C11 were formed even as low as pH 0.8, but the CCC from proprietary solution L was not stable below pH value of 1.8 where no chromate film formed on the sheet as indicated in Table 1. The zinc chromate layer is as shown in Figure 1.

4.1 Corrosion test

Table 1 shows the total weight loss for each specimen from solutions C1, C11& L.

From the overall weight loss and percentage corroded area analysis, the corrosion performance of CCC from C11 solution was the best. The effective operating range parameters were an immersion time between 5 to 10 seconds and the pH value from 1.5 to 2.0.

Table 1: Weight loss ($x10^{-4}$ g) in Salt-Spray Test for Solutions C1, C11 & L

pH	Immersion time(sec)	C1 (x 10^{-4}g)	C11 (x 10^{-4}g)	L (x 10^{-4}g)
0.8	10	35	32	*
	15	24	22	*
	20	22	44	*
1.2	5	28	45	*
	10	21	24	*
	15	21	57	*
	20	29	29	*
1.5	5	27	23	50
	10	25	27	47
	15	21	25	60
	20	39	20	55
1.8	5	31	17	28
	10	46	17	31
	15	28	51	30
	20	35	41	12
2	5	34	17	12
	10	37	12	31
	15	34	25	26
	20	27	21	23

Table 2 shows the percentage corroded area after 6 hours of salt spray test.

Table 2 : Corrosion rating for solutions C1, C11 & L

pH	Immersion time (sec)	C1	C11	L
0.8	5	3	4	*
	10	4	2	*
	15	6	1	*
	20	4	8	*
1.2	5	4	1	*
	10	6	1	*
	15	6	1	*
	20	7	3	*
1.5	5	6	5	*
	10	7	1	*
	15	8	1	*
	20	4	8	*
1.8	5	5	8	5
	10	7	9	8
	15	7	2	5
	20	8	8	4
2	5	4	8	5
	10	8	7	5
	15	6	6	5
	20	6	3	3

* no chromating (Legend : 1-10 , 1 = worse corroded & 10 = not corroded)

Figure 1 shows the intact adhesion of the complex zinc chromate layer on zinc coated steel component.

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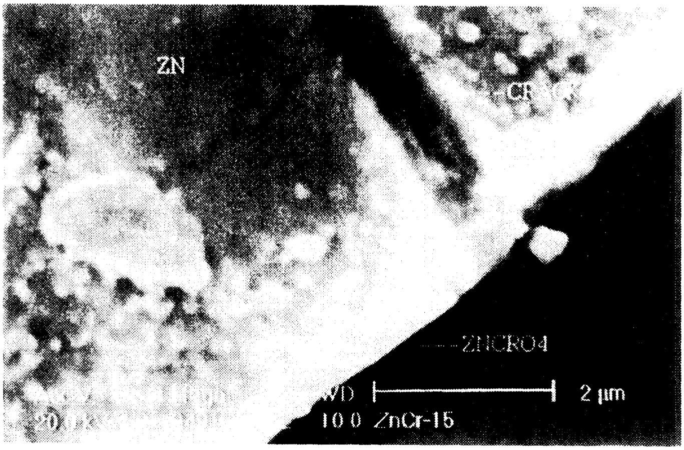
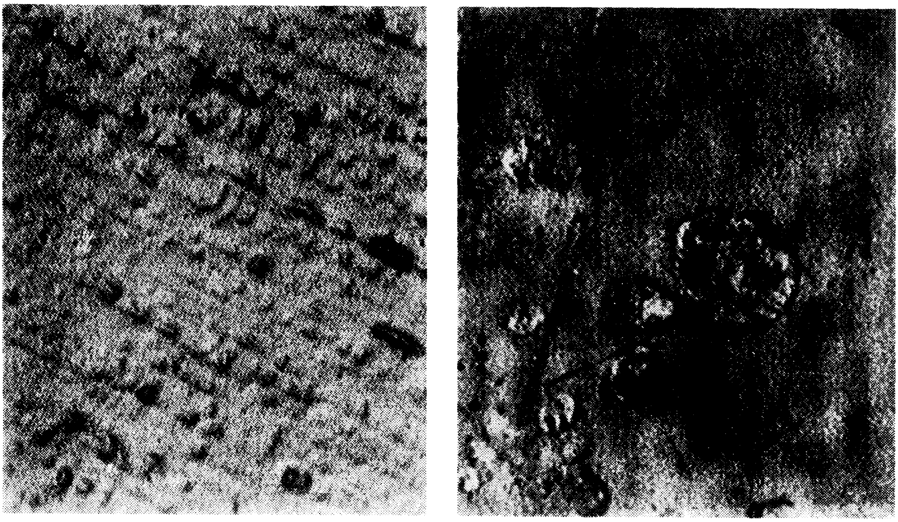


Figure 1: Zinc chromate layer (x 9491)

Figure 2 shows the surface topography of the CCC before and after salt spray test. It shows the unstable patches of zinc chromate layer that has deteriorated.



Before After

Figure 2: Surface Topography before and after salt spray test (x100)

Figure 3 shows that C11 has the least weight loss. This shows that the presence trivalent chromium in the chromating solution improves the corrosion resistance of the CCC compared to the commercial solution that is of hexavalent base. It also suggest that the silicon oil probably has a stabilizing effect on the reaction at the chromate solution and zinc surface interface where by the pH value might be stabilize.

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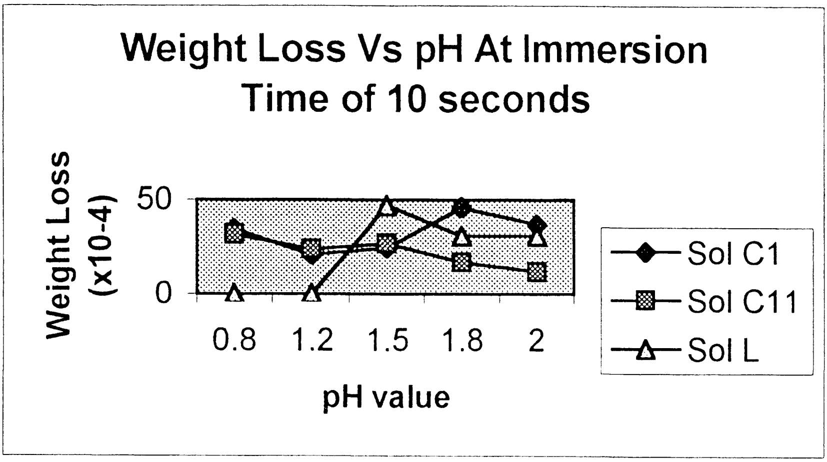

Figure 3: Weight loss ($x10^{-4}$g) vs pH at immersion time of 10 seconds

5 Conclusions

1. Solutions C1 and C11 give a broader effective range of operating parameters such as pH from 0.8 to 2.0 and immersion time of 5 to 20 seconds.

2. Solution C11 gives the best surface topography and excellent corrosion resistivity.

3. More utilisation of trivalent chromium which is more easier to treat and thus environmentally friendly.

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