

Zinc Plating Using Mixed-Chloride Bath

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(received September 16, 2004; revised May 5, 2007; accepted May 15, 2007)

Abstract. Zinc electrodeposition from mixed ammonium chloride/potassium chloride bath was carried out and the influence of plating time on the rest potential, white rust and red rust was studied. The zinc plated mild steel specimens were divided into four categories: non-chromated, yellow-chromated, greenish-grey chromated and black-chromated zinc plated mild steel specimens. There is no effect of plating time on the rest potential. The time taken for white rust and red rust increased with increase in plating time. Black-chromated zinc plated mild steel specimens have maximum corrosion resistance. The abrasion resistance of yellow-chromated zinc plated mild steel specimens was very poor. The appearance and adhesion of the deposits were good.

Keywords: zinc electrodeposition, chromating, rest potential, white and red rust

Introduction

The durability of passivation in zinc electroplating has been studied using weak acid zinc bath free from cyanide and ammonia, and yellow and colourless passivating solutions for passivation process (Haque *et al.*, 2003a). Recently, colouring of electroplated zinc was reviewed (Haque *et al.*, 2003b).

A bath for bright blackening-passivation of electrodeposited zinc at room temperature was developed. The bath pH 0.5-1.2, contained chromic oxide 15-35 g/l, sodium hydrogen sulphate (monohydrate) 20-40 g/l, dihydrogen sodium phosphate dihydrate 5-15 g/l, silver nitrate 0.5-1.2 g/l and a film-forming agent. The technological conditions including post treatment were presented (Watanabe *et al.*, 1992).

Manufacture of zinc electroplated steel sheet involves electroplating a zinc underlay at a current density ≥ 60 A/dm² first in a zinc sulphate-based acidic bath containing sodium sulphate, potassium sulphate and/or ammonium sulphate and then a zinc overlay (≤ 1 g/m²) at a current density ≤ 50 A/dm² in a second zinc sulphate-based acidic bath. Optionally, the second bath may contain aluminum sulphate (Zeng, 1991).

The effect of quality and quantity of additives such as benzylideneacetone, ratio of zinc chloride to potassium chloride, concentration of chloride, cathodic current density, temperature, and impurities such as lead, cadmium, iron, and copper on the brighteners of electroplated zinc, and troubleshooting are discussed. A bath comprising zinc chloride 85-95 g/l and potassium chloride 210-230 g/l in spring and winter, boric acid 25-30 g/l any time during the year, cathodic

current density 2-4 A/dm² in spring and winter, electroplating temperature 15-30 °C in summer and autumn, 15-25 °C in spring and winter, and pH 5-6 any time of the year are suggested (Zhou and Wang, 1998).

The uniform electrochemical chromating of zinc-plated steel sheets involves dipping zinc plated steel sheet in a bath containing chromic oxide 15-200 g/l and sulphuric acid 0.05-1.5 ml/l for \geq half second without passing a current and then immediately carrying out an electrolysis at a current density 1-15 A/dm² in the same bath. In addition, the bath may contain zinc, nickel, cobalt, iron, lead, copper and/or manganese 0.01-5.0 g/l (Saito and Wada, 1991).

Zinc or zinc alloy is electroplated on more than one side of a steel sheet followed by electrochemical chromating on the zinc or zinc alloy plate. The chromate film comprises a metal layer and an oxide layer formed on the metal layer comprising chromium and nickel; the total amount of chromium and nickel is 3-1000 mg/m². The oxide layer comprises chromium oxide (3-100 mg/m² in terms of chromium), nickel oxide (1-50 mg/m² in terms of nickel), and silicon oxide (1-100 mg/m² in terms of silicon). The process involves using a chromating bath containing Cr⁶⁺ 5-75 g/l; Ni²⁺/total chromium = 0.05-0.8 (weight ratio), selenium oxide/total chromium = 0.3-3.0 (weight ratio), and contains one of 0.05-80 g/l sulphate, chloride, nitrate and fluoride ions; pH of the bath is 1.8-4.2. The current density in chromating is 2-40 A/dm² (Furuya *et al.*, 1992).

Materials and Methods

Chemicals. Zinc chloride (technical grade), Qingdao Sunchiment, China; ammonium chloride, Riedel-de Haën, Germany; chromium trioxide, OXYCHEM, USA; sulphuric

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acid, BDH, England; potassium dichromate, Riedel-de Haen, Germany; nitric acid, E-MERCK, Germany; hydrochloric acid, E-MERCK, Germany; nickel sulphate hexa-hydrate, INCO, Canada; maintenance 2222, DICO, Germany, wetting 1111, DICO, Germany. All other chemicals, ethanol, sodium silicate, potassium chloride, sodium hydroxide, sodium phosphate, copper sulphate were of laboratory grade or better and were used as received.

Preparation of plating bath. For the electrodeposition of zinc on mild steel, mixed ammonium/potassium chloride bath was used. The composition of this bath is given in Table 1. Bath was prepared from zinc chloride, ammonium chloride, and potassium chloride (Haque *et al.*, 2003a).

Cathode. The area of each mild steel article was 2×1 inch². Before plating, the article was polished, buffed, degreased with ethanol, electrolytically cleaned, rinsed, pickled and rinsed thoroughly. Then specimens were rinsed and pickled in 50% hydrochloric acid solution, again thoroughly rinsed and then immediately plated.

Anode. Zinc metal, electrolytic grade (99.9% pure), having dimensions 6×2.5 inch² were employed as anode. The surface of anode was covered with glass wool to avoid the residual zinc metal getting into the bath, formed due to non-uniform dissolution of zinc anode.

Zinc deposition. A home-made direct current power supply was used in all experiments. During experimental work, it was observed that the best zinc deposition was obtained at optimal conditions shown in Table 2.

Table 1. Composition of acid chloride bath

Chemicals	Concentrations
Zinc chloride	60 g/l
Potassium chloride	100 g/l
Ammonium chloride	40 g/l
^a Maintenance 2222	1ml/l
^b Wetting 1111	30 ml/l

a = primary brightener (proprietary formulation); b = wetting agent (proprietary formulation)

Table 2. Optimum plating parameters for zinc deposition

Plating voltage	0.6-0.75 V
pH	4-5
Temperature of the bath	30-40 °C
Time	5-30 min
Current density	3-3.5A/dm ²

Chromate coating on zinc deposited mild steel. After plating, the samples were rinsed with distilled water and immersed in the chromating solutions.

Yellow chromate. The golden yellow passive film was formed when zinc plated sample was dipped in the bath containing, chromic acid 50 g/l, potassium dichromate 30 g/l and sulphuric acid 2 ml/l, at pH 1.25, at 18-20 °C for one min.

Greenish gray chromate. Greenish gray passive film was formed when zinc plated sample was dipped in the bath containing, potassium, dichromate, 60 g/l, sulphuric acid 2.5 ml/l and nickel sulphate 80 g/l, at pH 1.25, at 18-20 °C for one min.

Black chromate. Black passive film was formed when zinc plated sample was dipped in a bath containing potassium dichromate, 60 g/l, sulphuric acid 2.5 ml/l and copper sulphate 40 g/l at pH 1.77, at 18-20 °C for one min.

Test methods for chromated film: Rest potential. Rest potential of yellow-chromated zinc deposited plates, greenish-gray-chromated zinc deposited plates, black-chromated zinc deposited plates and non-chromated zinc deposited plates were measured, respectively, versus mild steel electrode (specimen), platinum electrode, silver/silver chloride and chloride reference electrode in 5% potassium chloride solution.

Measurement of rest potential. Rest potential was measured by following procedure:

First, two non-plated mild steel plates were connected while immersed in 5% solution of potassium chloride; the rest potential was noted to be zero. Then the rest potential of non-chromated, yellow-chromated, greenish-gray-chromated and black-chromated plates was measured vs mild steel plate and platinum electrode. Rest potential was measured with the help of multimeter DT-830B. In each case, rest potential reading was noted immediately after closing the circuit, in an attempt to take instantaneous reading. Rest potential was also measured vs silver/ silver chloride reference electrode. In case of silver/ silver chloride reference electrode, two compartment cell was used. The solution in both compartments was 5% potassium chloride. The two compartments were connected through salt bridge containing saturated solution of potassium chloride. The rest potential was measured on digital pH meter PTI-15. Prior to taking the reading, the pH meter was calibrated. First reading was noted immediately after closing the circuit, a subsequent reading of the potential was noted after 10 sec.

Salt spray test. The plates were subjected to salt spray test (JIS 2007) for determining the time for white and red rust products.

Results and Discussion

Mild steel specimens were zinc electroplated using mixed ammonium chloride/potassium chloride bath. The zinc plated mild steel plates were divided into four categories; non-chromated, yellow-chromated, greenish-gray chromated and black-chromated.

The effect of plating time on the rest potential, and on white and red rust formation was studied.

It was noted that there was almost no effect of plating time and plating temperature on the rest potential and it was nearly the same for all the cases. Dispersion in the reading presumably arises from manual procedure used for recording the rest potential. The results are summarized in Table 3.

Combined cyclic corrosion test instrument model ISO-3-Cy-R was used for the purpose. The principale testing conditions for salt spray test are given in Table 4.

It was found that with the increase in the plating time, the time for white rust product also increased (Table 5). The time required for white rust product was minimum in the case of non-chromated zinc plated mild steel plates. The time for yellow-chromated zinc plated mild steel plate was more than non-chromated, but less than that for greenish-gray-chromated zinc plated mild steel plate. White corrosion resistance of greenish-gray-chromated zinc plated mild steel plate was almost twice that of yellow-chromated zinc plated mild steel plate. Maximum white corrosion resistance was observed for black-chromated zinc plated mild steel plate.

Similar results were obtained in the case of red rust product (Table 6). With the increase in the plating time, the time for red product also increased.

The time required for red rust product was minimum in the case of non-chromated zinc plated mild steel plates. The time for red rust product of yellow-chromated zinc plated mild steel

Table 3. Rest potential of chromated zinc plated mild steel plates measured vs reference electrode as a function of time of plating

	Plating time (min)	Mild steel plate (V)	Platinum electrode (V)	Ag/AgCl Cl ⁻ electrode	
				Measured immediately (mV)	After 10 sec (mV)
a	5	0.479	1.005	855.0	996.0
	10	0.504	0.975	895.0	985.0
	15	0.546	1.025	890.0	993.0
	20	0.537	1.0035	785.0	986.0
	25	0.502	1.021	920.0	999.0
	30	0.59	1.000	963.0	1023
b	5	0.571	1.008	904.0	999.0
	10	0.550	0.993	960.0	1008
	15	0.567	1.008	960.0	1008
	20	0.560	1.071	968.0	1008
	25	0.531	0.977	837.0	1003
	30	0.549	0.985	944.0	1017
c	5	0.555	0.937	912.0	1016
	10	0.536	1.038	765.0	1008
	15	0.572	1.068	887.0	1029
	20	0.579	0.968	906.0	1026
	25	0.582	0.997	875.0	1025
	30	0.556	0.995	974.0	1025
d	5	0.513	0.971	725.0	992.0
	10	0.505	0.953	794.0	991.0
	15	0.464	0.943	808.0	998.0
	20	0.542	0.955	838.0	983.0
	25	0.510	0.937	865.0	991.0

a = nonchromated; b = yellow-chromated; c = greenish-grey chromated; d = black chromated zinc plated mild steel plate

plate was more than non-chromated but less than greenish-gray-chromated zinc plated mild steel plate. Red corrosion resistance of greenish-gray-chromated zinc plated mild steel plate was almost twice that of yellow-chromated zinc plated mild steel plate. Maximum red corrosion resistance was observed for black-chromated zinc plated mild steel plate.

It appears that the most durable passivation (black-chromated) is observed when dichromate is used in conjunction with copper sulphate (Saito and Wada, 1991) that uses similar composition, but for electrochemical passivation. However, under our conditions, it is likely that copper salt is co-depos-

ited on the surface along the oxides of chromium with variable degree of hydration. Similarly when nickel sulphate is used, as in greenish-gray-chromated, the nickel salt (Furuya *et al.*, 1992) is deposited along the chromium-oxides.

Abrasion resistance of yellow-chromated zinc plated mild steel plates was found to be lesser than greenish gray and black-chromated zinc plated mild steel plates. Abrasion resistance was measured by abrading the plates with filter paper.

Conclusion

1. White and red corrosion resistance increases with increase in plating time.
2. The white corrosion resistivity increases in the following order: black-chromated > greenish-gray-chromated > yellow-chromated > non-chromated.
3. The red corrosion resistivity increases in the following order: black-chromated > greenish-gray-chromated > yellow-chromated > non-chromated.
4. Abrasion resistance of yellow-chromated zinc plated mild steel plates was found to be lesser than greenish gray and black-chromated zinc plated mild steel plates.
5. The appearance of deposits was good.

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Table 4. Principal testing condition of salt spray test

Parameter	Range during test
Density of sodium chloride solution, w/v %	4.0 - 6
pH	6 - 6.5
Compressed air pressure, kgf/cm ²	1.00 ± 0.01
Quantity of spray, ml/80 cm ² /h	1.0 to 2.0
Temperature of air saturator, °C	47 ± 1
Temperature of salt tank, °C	35 ± 1
Temperature of test room, °C	35 ± 1

Table 5. Effect of plating time on white rust products of (a) non-chromated, (b) yellow-chromated, (c) greenish-gray-chromated and (d) black-chromated zinc plated mild steel plates

Time of plating (min)	Time for white rust product (h)			
	a	b	c	d
5	12	18	40	62
10	13	19	43	64
15	15	20	45	65
20	16	22	47	68
25	17	24	49	70
30	18	26	50	72

Table 6. Effect of plating time on red rust products of (a) non-chromated, (b) yellow-chromated, (c) greenish-gray-chromated and (d) black-chromated zinc plated mild steel plates

Time of plating (min)	Time for white rust product (h)			
	a	b	c	d
5	32	43	76	102
10	33	44	73	104
15	35	45	75	105
20	36	47	77	108
25	37	49	79	110
30	38	51	80	112