

## Durability of Passivation in Zinc Electroplating

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**Summary:** The durability of passivation in zinc electroplating has been studied using weak acid zinc bath free from cyanide and ammonia for zinc plating, and yellow and noncolored passivating solutions for passivation process. At the running voltage of 1.1 V, amperage of 1 A, pH 5-5.4, and at room temperature, best plating results were obtained from the zinc bath. The plated sample was washed in distilled water and then dipped in dilute HNO<sub>3</sub> for two seconds to make zinc plated surface active toward accepting final passivating film. The sample was then dipped in passivating solutions; chromate film developed on the zinc surface, which protected it against corrosion as well as gave it an attractive appearance. It was found that yellow passivation at dipping time of one minute and at room temperature with the passivating solution composition of CrO<sub>3</sub> 50 g/L, H<sub>2</sub>SO<sub>4</sub> 1 ml/L, HNO<sub>3</sub> 3 ml/L gives best corrosion resistance but weak abrasion resistance, while on the other hand colorless passivating solution comprising CrO<sub>3</sub> 2 g/L, KF 4 g/L and HNO<sub>3</sub> 3 ml/L gives good abrasion resistance with weak corrosion resistance.

### Introduction

Zinc is a bluish-white, lustrous metal, which is hard, crystalline, brittle and electronegative to iron. For the bright zinc plating, cyanide, acid and zincate baths are most commonly used these days [1]. Most of the zinc platings are followed by chromating in order to improve the corrosion resistance of the zinc platings themselves [2]. In recent years chromate free passivates were developed to avoid the use of hexavalent chromium which is now designated as a Class 1 carcinogen [3]. Composition of low-toxicity solution for colorless-bluish, black, yellow-iridescent passivation of electrochemically zinc and zinc alloy deposits and conditions of the passivation process were presented [4-7].

Results of X-ray photoelectron spectroscopy and Auger electron spectroscopy showed that all these passive films were composed of CrO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Zn(OH)<sub>2</sub>, ZnO and minor quantities of H<sub>2</sub>O [8]. Iron and chromium are present in passive film as Fe<sub>3+</sub> and Cr<sub>3+</sub> respectively, and oxygen exists in both metal-O and metal-OH bonds in the passive film [9]. The technology for the passivation and factors influencing the passivation were described [10]. Some rare earth elements were added to improve the corrosion resistance of zinc electroplates [11]. Modification of a conversion-passivating layer on zinc by layers of ZnCrO<sub>4</sub> succeeds in significantly improving the

corrosion resistance both of the non-heat-treated surface as well as the heat-treated surface [12].

Plan of work consisted of: (a) preparation of mild steel specimens, (b) deposition of metallic zinc through electroplating on the specimens, followed by chromating of zinc coats. Finally chromated zinc films were subjected to various tests.

### Results and Discussion

During practical work it was observed that the mild steel samples corroded very fast in the open atmosphere. To protect mild steel from corrosion and rust, zinc coatings are generally employed. Since zinc shows susceptibility to corrosion in humid environment, it is necessary to resort to its chromating. During Hull cell experiments it was observed that best zinc plating layer was obtained at optimal conditions, as shown in table 2, along with concentrations of the additives (table 1). It was observed that by increasing the thickness of zinc coating the rusting hours of mild steel also increased. It took 24 rusting hours at 5 microns and 180 rusting hours at 32 microns as shown in table 3, while the thickness of coating layer depended upon the plating duration. But a heavy thick layer changed the physical properties of mild steel. It was observed that

thickness of zinc plating layer in the range of 15–20 microns served all the purposes. Different chromating processes were studied on zinc plated layer i.e. colorless, rainbow and yellow, which had different end results.

Table 1: Composition of zinc plating bath

Reagents	Concentrations
Zinc Chloride	50 g/L
Boric Acid	20 g/L
Potassium Chloride	250 g/L
Brightener Lunacid, Rsh, Kn888	6 ml/L
Secondary Brightener, Lunacid, Rsh, Kn888020	30 ml/L

Table 2: Plating parameters for zinc plating

	Range	Optimal Conditions
Applied Voltage, V	3.0-5.0	3.8
Plating Voltage, V	.8-1.4	1.1
pH of The Bath	5.0-5.4	5.2
Temperature Of The Bath, °C	30-35	32
Plating Duration, Minutes	5-40	15
Current Density, A/dm <sup>2</sup>	3-5	4

Since age hardening was also necessary for the chromate film, the salt spray test of the chromate film was performed more than 24 hours after the chromating. The corrosion resistances of with and without passivated zinc plating samples, during salt spray experiments, at different thicknesses are given in table 3. It was observed that resistance against the generation of red rust corresponded to zinc-coat thicknesses of 27, 15 and 12 microns, respectively, in case of colorless, rainbow and yellow passivations. Though the chromate film was very thin, 0.07-0.3 microns, the white corrosion product of zinc was not generated by a salt spray test of 60, 84, 108 hours for colorless, rainbow and yellow chromate films respectively as shown in the figure 1.

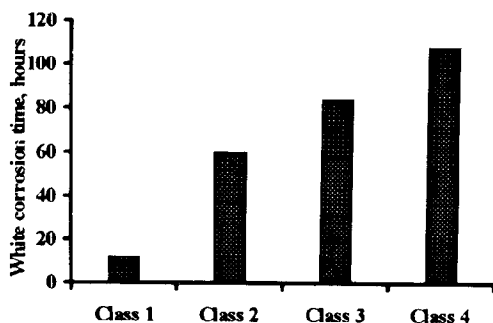


Fig. 1: White corrosion resistance of different chromate-treated and without chromate-treated zinc plated mild steel samples

The thinner colorless chromate film was less resistive against the corrosion in salt spray chamber; it showed only 132 rusting hours at optimum plating thickness, 17 microns. It was observed that when the film was excessively thick and yellow, it took 204 hours for the generation of red rust at 17 microns but it had weak abrasion resistance. In case of rainbow film the rusting hours were very close to that of yellow passivation; almost 192 hours at 17 microns, but it had better abrasion resistance than yellow film. It was observed that the appropriate thickness in rainbow film was judged by the appearance of the medium color tones of yellow, red and reddish-green. It was observed that at the optimum plating thickness, yellow passivation was most durable and had maximum corrosion resistance as compared to rainbow and colorless passivations, shown in figure 2.

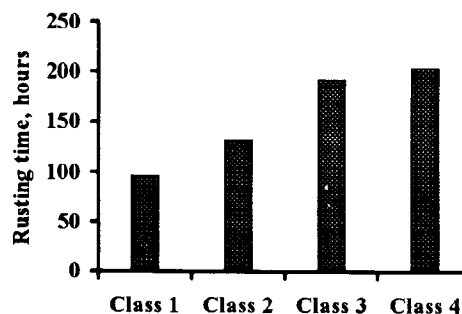


Fig. 2: Red rust resistance of different chromate-treated and without chromate-treated zinc plated mild steel samples

Chromating was mostly performed at room temperature, but in order to keep the proper quality of the coating, it was desirable to set the temperature within the range of 30–40°C, the higher temperature was better for both the brightness and the coloration. The dipping time ranges from a few seconds to several seconds. Furthermore, the film was not formed during dipping and was formed when the sample was held in the air, therefore, the adjustment of time for keeping in the air was important. In the case of colorless passivation, the film got thicker in proportion to the dipping time, the chemical polishing was greater in solution of low pH, and therefore, the brightness was better, whereas the film formation was faster when the pH was high.

Higher the concentration of the hexavalent Cr, the stronger was the chemical polishing power with

better brightness, but more difficult it was for the coating to stick. The greater the hexavalent chromium contents in the developed film, the better the corrosion resistance. Clear chromating solution contained less hexavalent chromium so that the developed film has low corrosion resistance.

Table 3: Corrosion resistance of with and without passivated zinc plating, using salt spray test

Class type	Plating duration minutes	Plating thickness microns	Hours Required for the Generation of white corrosion product	Hours Required for the generation of red corrosion product
Class 1	5	6	12	24
(without chromate film)	10	11	12	60
Plates	15	17	12	96
	20	23	12	120
No 1-18	25	27	12	144
Class 2	30	32	12	188
(with colorless chromate film)	5	6	60	72
Plates	10	11	60	96
	15	17	60	132
No 19-36	20	23	60	156
Class 3	25	27	60	180
(with rainbow chromate film)	30	32	60	216
Plates				
No 37-54				
Class 4	5	6	108	132
(with yellow chromate film)	10	11	108	168
Plates	15	17	108	204
	20	23	108	252
No 55-72	25	27	108	276
	30	32	108	324

Sulfate ions (added as  $H_2SO_4$ ) in the chromate solution act as catalyst, promoting the film formation with a certain amount of the hexavalent chromium. The nitric acid acts as a polishing agent, but it made the surface passive when it was added beyond a certain ratio against the chromic acid, making the chromating impossible. It also acted as a catalyst for the colorless or low concentration solution. However since even the slightly excessive addition of nitric acid beyond the recommended amount was likely to cause the chromate film to peel away easily, it should be successively supplied since it was gradually consumed by dissolving the zinc.

The trivalent chromium gradually accumulated together with the zinc when the solution

aged. Some 3-15 g/L of the trivalent chromium was needed in the yellow and rainbow passivation for film formation, and a certain quantity in the colorless solution.

The drying method of chromate film greatly influenced its corrosion resistance, the latter being the best when chromate film dried at 50-60°C for 30 minutes. When dried over 100°C, larger cracks appeared on the chromate film, the color faded out and the corrosion resistance deteriorated. The film dried at room temperature had high water content. Consequently it was soft, showed hygroscopic character and low corrosion resistance.

## Experimental

### a) Chemicals

The chemicals  $CrO_3$ ,  $H_2SO_4$ ,  $ZnCl_2$ , were of laboratory grade and as supplied by OXYCHEM, USA; BDH, England; and Qingdao Sunchemint, China, respectively. Other chemicals were technical grade and were used as received.

### b) Zinc plating on mild steel samples

*Plating bath:* In all experimental work, acid zinc bath, free from ammonia and cyanide was used to electrodeposit zinc on the mild steel samples due to decreased hazard effects as compared to cyanide bath. The composition of the bath is described in table 1. German made zinc brightener was used to develop luster on zinc plated steel sheet which was composed of basic brightener like sodium benzoate, sodium salt of sulphited and sulphated alkylphenol ethoxylate and top brightener like benzylidene acetone and surfactant like polyethylene glycol. The concentration of additives and plating conditions were adjusted by performing Hull cell test, employing the common American version [13].

Mild steel specimen of geometric area  $2 \times 1 \text{ in}^2$  was used as cathode. The surfaces of cathode were polished carefully with the emery paper of grade (00) to obtain smooth and even faces of the cathode for good experimental results. Zinc metal of electrolytic grade, 99.9% purity, having dimensions  $6 \times 2.5 \text{ in}^2$  was used as anode. The surfaces of anodes were covered with nylon cloth bags to avoid any oxide developed at anode from entering the plating bath.

Before plating different pre-plating processes, pickling and electrolytic cleaning, were performed for preparation of the substrate to obtain better

plating results. A home-built D.C. power supply was used for the experiments to provide variable D.C. voltage and amperage in the range of 0-10 V and 0-10 A respectively. The applied voltage was controlled by regulator attached to the power supply. The electrodes were connected to the current source and dipped in the electrolyte in a glass container. During experiments, current was measured by an analog ammeter (model Mo-65, Tokyo Japan) connected in series with the circuit and voltage was measured by digital multimeter (TES 2201) connected in parallel with the circuit.

After pre-plating processes the sample was dipped in 30% HCl solution (for about a minute) to make the surface active towards plating. Then sample was dipped in the plating bath and D.C. voltage, 3.8 V, was applied across the electrodes; as a result zinc ions from the solution were deposited on the sample, at the same time anodes started to corrode and transferred zinc ions to the solution. Bath agitation was carried out by moving the specimen continuously to achieve smooth deposition. After the deposition process, sample was rinsed in running water.

Zinc plating was done on 72 mild steel samples by using same conditions as described in table 1. These samples were further divided into four classes, while each class contained 18 plated samples. All the 18 samples of class 1 were preserved as such and other classes were further treated.

#### c) Passivation of zinc plating

After zinc-plating, the plated samples of class 2, 3 and 4 were dipped in 2-3% diluted nitric acid one by one and then passivated these immediately by using following different chromating solutions. The concentrations of passivate solutions were fixed after trial in the varied concentration range of the concerned chemicals.

#### c-1 Colorless chromate

Class 2 (plates 19-36) was passivated in colorless or bluish chromate solution. The colorless passive film was formed when zinc-plated sample was dipped in a bath containing  $\text{CrO}_3$  3-5 g/L, KF 4-5 g/L and concentrated  $\text{HNO}_3$  2-4 ml/L, at pH 2.0 for 3-5 seconds at room temperature.

#### c-2 Rainbow chromate

Class 3, (plates 37-54), was passivated in rainbow passivation. This color passivation was

obtained by dipping the plated sample in a bath containing  $\text{CrO}_3$  20-30 g/L, concentrated  $\text{HNO}_3$  5-6 ml/L and concentrated  $\text{H}_2\text{SO}_4$  1.0-1.5 ml/L; room temperature and pH 3.0, for 30-45 seconds.

#### c-3 Yellow chromate

Class 4, (plates 55-72), was passivated in yellow chromate solution. The yellow color passivation was carried out in a bath comprising  $\text{CrO}_3$  40-60 g/L, concentrated  $\text{H}_2\text{SO}_4$  0.8-1.0 ml/L and concentrated  $\text{HNO}_3$  3-4 ml/L; passivation time of 1-1.5 minutes, pH 3.5-3.8, and room temperature were other experimental conditions. The sample itself was agitated for stirring purposes.

#### d) Test methods of passivation film

Salt spray test [14], was used for corrosion resistance, principal testing conditions are given in table 4, while magnetic thickness measuring instrument was used to measure the thickness of zinc plated layer [15].

Table 4: Principal testing conditions

Parameter	Range during test
Density of sodium chloride solution, W/V %	4.0 To 6.0
pH	6.5 To 7.2
Compressed air Pressure, Kg/cm <sup>2</sup>	1.00 ± 0.01
Quantity of spray, ml/80 cm <sup>2</sup> /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

Initial density of sodium chloride solution, W/V 4% and pH 6.5

#### Conclusions

1. Medium thickness, 15~20 microns, is best layer for protecting steel parts with final coat of chromate film. It has little effect on physical properties of steel.

2. Hexavalent chromium ions in chromating solution have great effect on corrosion resistance and coloration of passivation layer.

3. Dipping time in chromating solution depends upon the required thickness of passivate film, but it should be up to certain limits.

4. Drying process is required at 50~60°C for chromate passivating film. Baking the film at higher temperature causes rapid elimination of water which leaves behind cracks on the surface.

5. Yellow passivation of zinc plated sample has higher corrosion resistance tendency than colorless or rainbow passivation.

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