Study on environment-friendly passivation for hot-dip galvanized steel with high corrosion resistance

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Abstract. In order to improve the corrosion resistance of hot-dip galvanized steel, experimental study developed a new trivalent chromium passivation film with high corrosion resistant. The preparation method of passivation coating with high corrosion resistant was that the CrO₃ was reduced to trivalent chromium by sufficient organic compound with reduction, then added colloidal SiO₂, the matter containing radical phosphate and other substances after reaction completely. The passivation coating did not contain hexavalent chromium, and can meet the requirement of RoHs directive, so the film on hot-dip galvanized steel after passivation was environment-friendly. After coated on the hot-dip galvanized steel, the coating could be fast drying at 100 °C about 10s to 20s. The film was uniform, and did not appear floating, falling and other abnormal phenomenon, so that the passivation coating had good coating performance. The passivation reaction of the new trivalent chromium coating on the hot-dip galvanized steel was compound processes of electrochemical reaction, precipitation reaction and physical deposition. The passivation film produced no corrosion basically after 120h in the neutral salt spray test according to the Chinese national standards GB/T10125 and corroded area is less than 5% after 216 h, thus the corrosion resistance of the passivation film was excellent. In addition, the film has excellent heat resistance and fingerprint resistance, so it can meet the requirements of the user.

1. Introduction
The hot-dip galvanized steel has been widely used in household appliances, automobiles, Building and other industrial fields owing to its excellent mechanical properties. The GI appear corrosion easily in the moist environment, so the hot-dip galvanized steel need to be treated with passivation [1-2]. At present, the passivation coating for the hot-dip galvanized steel contain the trivalent chromium passivation, the hexavalent chromate passivation and the chromate-free passivation. The hexavalent chromate passivation has some advantages, such as simple process, good adhesion, high corrosion resistance, self-repaired ability. But because the hexavalent chromate that is a carcinogen has serious harm to the human body and the environment, it is mainly used for the construction. The toxicity of trivalent chromium is only one percent of hexavalent chromate, the passivation mechanism [3-4] is clear, and the corrosion resistance of the trivalent chromium passivation film after proper closed treatment [5], has been more than six chromium passivation, so the trivalent chromium passivation is mainly used in some field of household appliances. The chromium-free passivation technology [6] has been researched at home and
abroad. But no matter how the development of chromate-free passivation, it was unable to reach the standard of chromate passivation. With the corrosion resistance of the hot-dip galvanized steel the user required is more and more high as the expansion of the market, the distance between users and factories increased and the deterioration of the global environment. One user required the corrosion area of the hot-dip galvanized steel in NSST/200h is less than or equal to 10% that the hexavalent chromate and chromium-free passivation were far short of this requirement. Therefore, this paper study a new trivalent chromium passivation coating with high corrosion resistance for the hot-dip galvanized steel, then discuss the surface quality, performance of the coating, and the film-forming mechanism.

2. Experimental

Preparation of passivation coating. First of all, make up the solution contained trivalent chromium. The CrO$_3$ as oxidant and the organic acid reaction react in acidic solution. In order to make hexavalent chromate completely translate into trivalent chromium, the organic acid must be excess and the reaction time was at least five hours. Secondly, add an appropriate amount of deionized water into the trivalent chromium solution in order to make the content of chromium appropriate, then add SiO$_2$ colloid, phosphoric substances, surface active agent and so on. At last, stir evenly.

The passivation treatment. The substrate is the oiled the hot-dip galvanized steel without passivation treatment produced by Panzhihua iron and Steel Group Company, that is DX51D+Z and the Specifications for that is 600mm*100mm*0.8mm. The technological process of former processing is: polish (to the edge burr) skim washing - dip galvanized steel after cleaning was coated by the trivalent chromium passivation coating used the US RSD4# scraping stick, then dried and cured in the BYK gradient oven about 10s to 20s at the temperature of 100°C.

The new passivation coating did not contain hexavalent chromium, and can meet the requirement of RoHS directive, so the film on hot-dip galvanized steel after passivation was environment-friendly. Do not print page numbers: each sheet toward the middle near the bottom (outside the typing area) should be numbered with a soft pencil.

Performance test.

1) The corrosion resistance of the passivation film. Usually the neutral salt spray tests could be used. Test conditions and methods accorded to the GB/T10125, and the test instrument is the YWX/Q-020 salt fog corrosion test box. In the test, made the NaCl solution with a concentration of 50 g/L and pH value of 6.5 as corrosion material, the temperature was Set in 33~37 ℃, specimen was placed with the vertical direction about 15° to 25°. Then spray Continuously for 120h and 216h, and observated the white rust percentage of the specimen surface.

2) The microstructure and composition of the passivation film. The microstructure of was observed by JSM-5600LV scanning electron microscope (SEM), and the composition of the coating was analyzed by the energy dispersive spectroscopy (EDS).

3) The heat resistance of the passivation film. Bake the sample in the hot blast stove at 300 ℃for 20 minutes. And measure the color value of the sample by BYK color difference meter before and after baking, then determine the heat resistance according to the value of ΔE derived from the formula ΔE = (∆L$^2$+∆a$^2$+∆b$^2$)$^{1/2}$.

4) The fingerprint resistance of the passivation film. Coat some Vaseline on the specimen surface with a clean soft cloth. And measure the color value of the sample by BYK color difference meter before and after coating, then determine the heat resistance according to the value of ΔE derived from the formula ΔE = (∆L$^2$+∆a$^2$+∆b$^3$)$^{1/2}$.

3. Results and Discussion

3.1 The film-forming mechanism.
The microstructure of the passivation film on the hot-dip galvanized steel was shown in Fig. 1, and the composition is shown in Fig. 2. Thus, the passivation film on the hot-dip galvanized steel is a transparent
film, no undesirable phenomena such as flooding and falling, and the film is uniform and compact. The main components of the passivation film is O, Si, P, Cr and Zn that consist with the passivation coating.

![Fig. 1 The microstructure of the passivation film](Image)

![Fig. 2 The composition of the passivation film](Image)

The surface morphology of the passivation film half of which was soaked in 5%NaOH for 10 min is shown in Fig.3, and the composition is shown in Table 1. The film has been completely dissolved after being soaked by 5% NaOH from Fig.3 and table 1. And the passivating film soaked in water for 1h did not change significantly. So the main component of the film can be dissolved by NaOH solution, but not by water. Color of the passivation film was light green, and the main component of trivalent chromium coating contain Cr$^{3+}$, H$_2$PO$_4^-$, the organic acid and SiO$_2$, and the coating is highly acidic, so can infer that the main component of the passivation film is CrPO$_4$.3H$_2$O and the film may contain a small amount of CrPO$_4$ and CrPO$_4$.2H$_2$O. In addition, the film also contain Zn$_3$(PO$_4$)$_2$ and ZnHPO$_4$, because the Zn on the hot-dip galvanized steel sheet would react with the trivalent chromium coating.

![Fig. 3 The microstructure of the passivation film after being soaked by 5%NaOH](Image)
Table 1 The composition after being soaked by 5%NaOH%

| Area | O  | Si  | P   | Cr  | Zn  |
|------|----|-----|-----|-----|-----|
| 1    | 28.34 | 2.08 | 6.93 | 2.29 | 60.36 |
| 2    | 3.41  | -   | -   | -   | 96.59 |
| 3    | 4.38  | -   | -   | -   | 95.62 |
| 4    | 25.31 | 2.04 | 6.74 | 1.91 | 64.00 |

It follows that the passivation reaction of trivalent chromium coating on the hot-dip galvanized steel were compound processes of electrochemical reaction, precipitation reaction and physical deposition.

In the passivation coating, there is the ionization equilibrium shown in equation (1).

\[ \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+ \quad \text{(1)} \]

In the film-forming process, the first of all, the electrochemical reactions were started, the anodic reaction was shown in equation (2) and cathodic reaction was shown in equation (3). Then the pH value of the interface reaction increased with large consumption of H⁺ of the cathode region, and the ionization in equation (1) turn to the right continuously, then PO_4^{3-} increase constantly, so many precipitation reaction take place. The reaction was shown in equation (4), (5), (6).

\[ \text{Zn} - 2\text{e} \rightarrow \text{Zn}^{2+} \quad \text{(2)} \]
\[ 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2 \quad \text{(3)} \]
\[ \text{Cr}^{3+} + \text{PO}_4^{3-} \rightarrow \text{CrPO}_4 \quad \text{(4)} \]
\[ 3\text{Zn}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Zn}_3(\text{PO}_4)_2 \quad \text{(5)} \]
\[ \text{Zn}^{3+} + \text{HPO}_4^{2-} \rightarrow \text{ZnHPO}_4 \quad \text{(6)} \]

In the drying and curing process, CrPO₄ will continue to lose crystal water, thus CrPO₂·3H₂O, Zn₃(PO₄)₂, ZnHPO₄ together constitute the skeleton of the passivating film. Also in the curing process, the SiO₂ occur cross-linking reaction by -OH and -O bond, and form network structure though the covalent bonds about Si-O-Si and O-Si-O, then cover the fill in the skeleton of the passivating film. Due to sealing effect of SiO₂, the passivation film is very dense.

3.2 The Properties of Passivation film

The corrosion resistance. The passivation film with high corrosion resistance can be combined tightly with the hot-dip galvanized steel due to formation of chemical reactions, so that the passivation film is dense and uniform, which can effectively block the hot-dip galvanized steel react with water and oxygen in the air, thus prevents the hot-dip galvanized steel corrosion occur. The corrosion resistance of passivation film the was shown in Fig. 4. In the Fig. 4, the passivation film had no corrosion basically after NSST/120h, and the area of corrosion only 2% after NSST/216h. At present, the corrosion resistance of all passivation films is required that the corrosion area in NSST/72h are less than 5%, so this film has excellent corrosion resistance.

![Fig. 4 The corrosion resistance](image-url)

The heat resistance. In order to ensure the film on the hot-dip galvanized steel not come into being color change when single-sided coating and baking, The passivation film must has good heat resistance. Experimental study show that the film has excellent heat resistance when the ΔE< 4. The results are shown in Fig. 5 and Table 2. Thus, the passivating film with high corrosion resistance after baking did
not appear obvious discoloration and the $\Delta E$ were less than 3. Because this passivating film is mainly inorganic, containing only a small amount of organic components. Therefore, it has very excellent heat resistance.

![Fig.5 The heat resistance](image_url)

| Samples | $\Delta L$ | $\Delta a$ | $\Delta b$ | $\Delta E$ |
|---------|-----------|-----------|-----------|-----------|
| 1       | -1.53     | 0.29      | 2.54      | 2.98      |
| 2       | -0.78     | 0.22      | 2.37      | 2.50      |
| 3       | -1.22     | 0.25      | 2.23      | 2.56      |

The fingerprint resistance. In order to avoid the operator stay fingerprints on the surface of part that can affect coating adhesion or appearance quality in the parts production process, user require the film on the hot-dip galvanized steel has the fingerprint resistance. Experimental research shows the film has excellent fingerprint resistant when $\Delta E < 1$. The result are shown in Table 3. Thus, the film with high corrosion resistance has excellent fingerprint resistance.

| Samples | $\Delta L$ | $\Delta a$ | $\Delta b$ | $\Delta E$ |
|---------|-----------|-----------|-----------|-----------|
| 1       | 0.07      | -0.04     | -0.06     | 0.10      |
| 2       | -0.34     | -0.10     | -0.01     | 0.35      |
| 3       | -0.38     | 0.04      | -0.01     | 0.38      |

4. Conclusions

(1) The preparation method of the new trivalent chromium passivation coating was that the CrO$_3$ was reduced to trivalent chromium by sufficient organic compound with reduction, then added colloidal SiO$_2$, the matter containing radical phosphate and other substances after reaction completely.

(2) The new coating could be fast drying at 100 °C in 10s to 20s. The film is uniform and compact, and did not appear floating and falling or other abnormal phenomenon. The film can meet the requirement of RoHS directive, so was environment-friendly.

(3) The passivation reaction of the new trivalent chromium coating on the hot-dip galvanized steel was compound processes of electrochemical reaction, precipitation reaction and physical deposition.

(4) The new passivation film on the hot-dip galvanized steel produced no corrosion basically after 120h in the neutral salt spray test and corroded area is 2% after 216 h. So this film has excellent corrosion resistance. In addition, the new film with high corrosion resistance has excellent heat resistance and fingerprint resistance.

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