Study chromium-free passivation coating on hot-dip galvanized steel sheet

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The chromic acid is often used on the metal surface treatment, but hexavalent chromium was considered as a carcinogen. In order to develop environmentally-friendly coating to replace chromating coating, A Tannic Acid-H_2TiF_6/KH792 silane coupling agent composite coating was prepared on hot-dip galvanized steel sheet to investigate the effect of such as PMT, pH and film thickness. The results showed on the coating structure and the corrosion resistance that PMT and film thickness has greater effect on the corrosion resistance, and the optimum operation condition is at pH = 4 and in the PMT range of 60-80 degree centigrade. The shows excellent corrosion resistance, anti-fingerprint property and paint-ability.

(Received October 22, 2014; accepted January 21, 2015)

Keywords: Hot-dip Galvanized Steel sheet, Anti-corrosion property, Environmentally protective coating

1. Introduction

Chromate conversion coatings have been widely applied on zinc-coated and galvanized steel in industry such as automobile, building structures and home appliances due to the excellent anti-corrosion and adhesion properties low cost and easiness to coat. However, chromating is liable to be avoided because consciousness of environmental conservation is recently intensified. The hexavalent chromium contained in the chromate conversion coating has direct detrimental influence on human bodies and pollutes the environment, Hexavalent Chrome (Cr, Cd, Pb, Hg) is considered carcinogenic and has been banned in many areas of the World, in particular, thanks to the European's "End of Life Vehicles Directive" (ELVD) and "Restriction of Hazardous Substances" (ROHS) [1-3].

Many substances has been reported to replace hexavalent chromium such as trivalent chromium, titanium, zirconium and molybdic acid. In addition, some organic compounds are also alternatives to hexavalent chromium conversion coating. One of the important characteristics required for these types of coatings is the ability to inhibit rust besides providing protection to the metal surfaces. Several papers have been written on the properties of tannic acid coatings on steel as an inhibitor. C.G. da Silva [4]. Reported the action of conversion based on a mixture of phosphoric acid and tannic acids using isopropyl and ter-butyl alcohol as solvents. The results showed that the tannic acid special network structure. The tannic acid was closely integrated with the single chain structure of silicasol and the two substances combined with the zinc layer to completely cut off from corrosive environment. Tannic acid and monolithic structure of silicasol are shown in Fig. 1, Fig. 2.

Funded by the 863 Project, the author conduct a research on the anti-corrosion property of hot-dip galvanized sheet coating of Tannic Acid- H_2TiF_6/KH792 silane coupling agent composite coat, focus on the microstructure of the coating, and the effect of the curing temperature and concentrations of pH on the corrosion resistance.

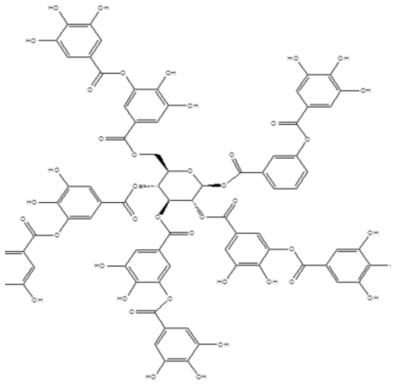


Fig. 1. Tannic acid monomer structure.

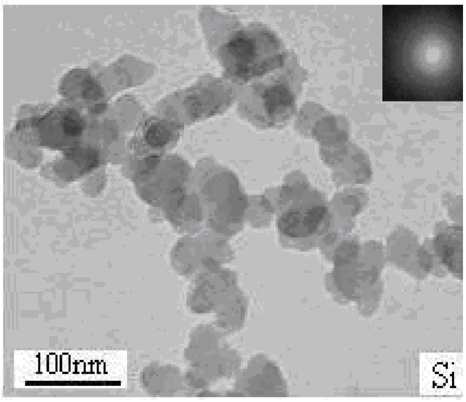


Fig. 2. Bright field electron micrographs and the selected area electron diffraction for KH792 silane coupling agent sol.

2. Experimental procedures

2.1 Base material and processing

Prepare the tannic acid solution with the concentration of 2% (w/w)~7% (w/w) was prepared at room temperature, A mixture of 0.2% (w/w) H_2TiF_6 and 15% (w/w)colloidal silica was added to it and stirred rapidly form a uniform phase and the pH value was controlled between 2~7. The effect of H_2TiF_6 here is to improve the corrosion resistance of the coating and to promote cross-linking between various components in the solution. Meanwhile, the silicon sol can improve the film-forming property of coating, lower curing temperature of galvanized coating layer and restrain the black patina and the corrosion of zinc coating.

The tested substructure were skin-passed hot dip galvanized steel sheets that are prepared on a continuous hot-dip production line, they were degreased and then rinsed in distilled water, followed by drying at 60 ℃ in an oven. The processed pre-hot dip galvanized sheet sample was put into the tannic acid / titanium composite solution with different pH (pH2 ~ 7) and soaked for 1s, then were dried for solidifying at different Peak Metal Temperature (20℃, 40℃, 60℃, 80℃ and 100℃). The range of film thickness is 580 ~ 620 mg/m^2. The specimens were sectioned into 75mm×150mm and the range, The industrially- product hot dip galvanized sheet with Cr (Ⅵ) passivation layer was selected to be the Contrast samples (see Table 1).

2.2 Test method

The microstructure of composition of the coating was evaluated by SEM (Ricoh JSM1600-LV), FT-IR (Nicolet Magna IR-560), UV-vis (SHIMADZU UV-2450) and EDAX energy spectrometer. The evaluation of anti-corrosion property was evaluated by neutral salt spray test with 5% (w/w) NaCl (GB/T 13448-92). The electrochemical action potential polarization curve and *Ep*-t curve was measured by Electrochemical Workstation (U.S. PAR352) at room temperature, with a scan rate of 0.5mv/s, and reference electrode of SCE. Test data were automatically recorded by the M352 software and calculated R_p, I_{corr} and E_{corr} were calculated [5-10].

Table 1. Film thickness of samples.

Trials	Film thickness/mg·m^{-2}	Surface treatment
1	73	Cr（Ⅵ)
2	582	tannic acid - H_2TiF_6/ KH792 silane coupling agent
3	607	tannic acid - H_2TiF_6/ KH792 silane coupling agent
4	624	tannic acid - H_2TiF_6/ KH792 silane coupling agent

3. Results and discussion

3.1 Coating microstructure and composition

The coated substrates are characterized by SEM, FT-IR and UV-vis as shown in Fig. 3~6.The morphologies of the tannic acid - H_2TiF_6 / KH792 silane coupling agent coating and the Cr (Ⅵ) coating are showed in Fig. 3. As the figures shown, tannic acid - H_2TiF_6 / KH792 silane coupling agent composite coating is evenly distributed and compactly covered on the surface of zinc layer, indicating that the coating has better covering property and adhesive performance. Because the tannic acid - H_2TiF_6/KH792 in the silane coupling agent system along with the sol particles, the organic molecules intertwined diffusion of

-Si-O- long chain in the sol, can enter into the cracks ,especially those with larger Gap (> 1μm) of surface layer to play the role of filling film, wherever the Cr (Ⅵ) passive film is crystalline grained, flake-shaped and uneven. Due to the accumulation of reaction product of chromic acid and zinc layer caused by no uniform Coating. Fig. 4 show the similar infrared spectra curve of standard tannin spectrogram，the strongest peak of the curves appearing in 3000-3500 cm-1,is produced by-OH stretching vibration. the peak appearing in 1500 cm-1 is produced by the result of bending vibration of C-C bond of a benzene ring The peak at 1710 cm-1 is formed form the C=O group stretching vibration. Fig. 5 shows the UV-visible spectrum of titanium ions which has the specific absorption at 505 nm. Fig. 6 shows a specific absorption peak of Si at 1.80 Kev in the EDAX energy spectrum. Form the above spectra, it is conclude that the substrate surface was covered with tannic acid and titanium coating and the composite coating has excellent coating properties.

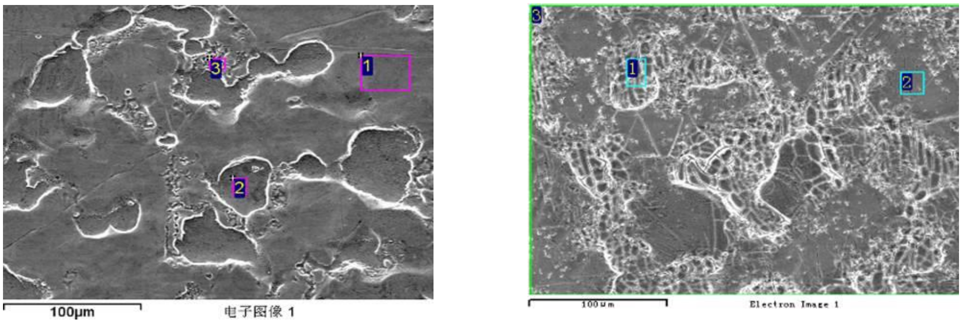


Fig. 3. Morphologies of as-received specimen of (a) Tannic acid- H_2TiF_6 / KH792 silane coupling agent coating (b) Cr（Ⅵ） coating GI.

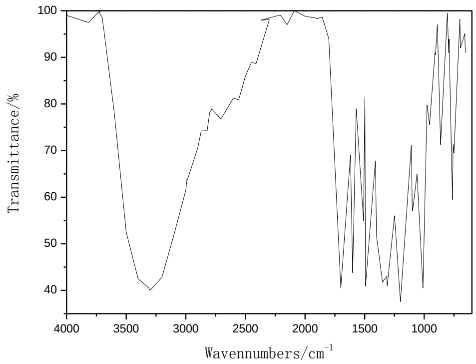


Fig. 4. FT-IR spectrum of Hot-dip galvanized steel sheet coated with tannic acid–H_2TiF_6/ KH792 silane coupling agent.

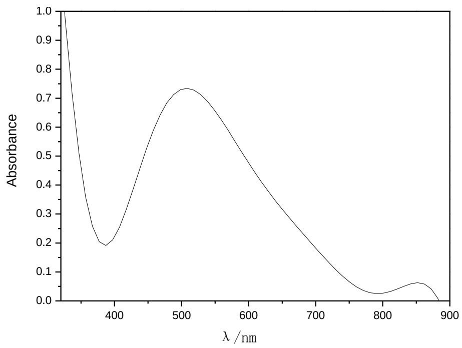


Fig. 5. UV-vis spectrum of Hot-dip galvanized steel sheet coated with tannic acid–H_2TiF_6/ KH792 silane coupling agent.

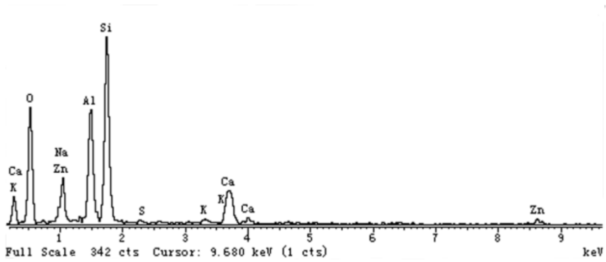


Fig. 6. EDAX results for Hot-dip galvanized steel sheet coated with tannic acid–H_2TiF_6/ KH792 silane coupling agent.

3.2Electrochemical research

The polarization curves of the coated samples are shown in Fig. 7. The potentiodynamic polarization parameters, such as R_p ,I_{corr} and E_{corr} are calculated by M352 Software, as shown in Table 2. The results show that the corrosion potential increases gradually with increasing film thickness, and the corrosion current *Icorr* shows a decreasing trend. This means that the corrosion potential is proportional to surface film thickness of the tannic acid-H_2TiF_6 / KH792 silane coupling agent on the hot galvanized steel sheets. When the thickness is greater than 600 mg/m_2, its E_{corr} is higher than that of the chromate passivation, whereas its I_{corr} is significantly lower than that of the chromate passivation film. That is to say, it has better corrosion resistance.

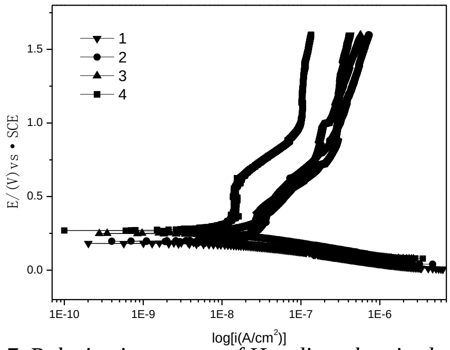


Fig. 7. Polarization curves of Hot-dip galvanized steel sheet with Tannic acid-H_2TiF_6/ KH792 silane coupling agent coating with different film thickness tested in 3.5g/l NaCl.

Table 2. Potentiodynamic polarization parameters for coating systems.

Sample number	*E(corr)*/ mV	*I(corr)*/A·cm^{-2}	*Rp*/Ohm·cm^{-2}
1	174.3	2.61×10^{-7}	4.39×10^{5}
2	184.1	3.88×10^{-7}	3.80×10^{5}
3	293.9	0.71×10^{-7}	8.14×10^{5}
4	410.5	9.30×10^{-8}	2.13×10^{6}

Fig. 8 The relationship between pitting potential and time（E_p-t）of samples with shows different coating thickness which were soaked soak in 3.5% NaCl saline solution for 24h,48h,72h or 96h, respectively. According to the curves, we can clearly see that the pitting potential has reached a high point value when the coating thickness is 600mg/m^2.

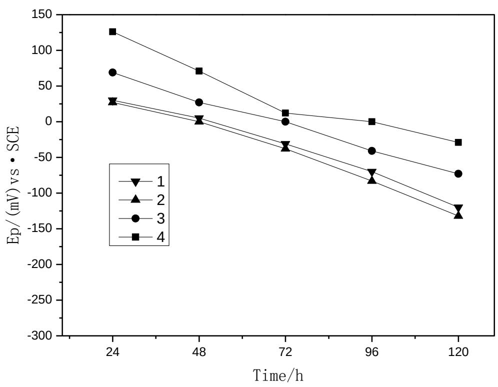


Fig. 8. Pitting potentials as a function of soaking time in 3.5% NaCl saline solution for sample with different film Thinckness coated with tannic acid-H_2TiF_6/ KH792 silane coupling agent compared with that of Cr(Ⅵ)-coated samples.

3.3 Corrosion resistance

Neutral salt spray test was used to evaluate the coating corrosion resistance of hot-dip galvanized steel sheet surface. As show in Fig. 9, it can be clearly seen that in the salt spray environment the time for white rust appeared to on the coating is longer when the pH value is 3 to 4, that means it has the best corrosion resistance. There is a tendency that the anti-corrosion property increases with increasing of the tannic acid amount. But after PH reaches 4, even if pH value of the solution is decreased, the time for while rust to appear on the sample surface will reduce.

Fig. 10 shows that the longest white rust time during salt spray test is obtained when curing temperature is 60-80. It means that the best anti-corrosion property could be achieved at the temperature range. However, the corrosion area on the composite coatings surface is less than ＜1% while that of Cr（Ⅵ）Passivation one reaches 3% after 96h NSST (seen in Fig 11). The above show that hot galvanized steel sheet surface coated with tannic acid-H_2TiF_6 / KH792 silane coupling agent coating has excellent corrosion resistance, which is comparable with hot dip galvanized sheet passivizing with Cr (Ⅵ).

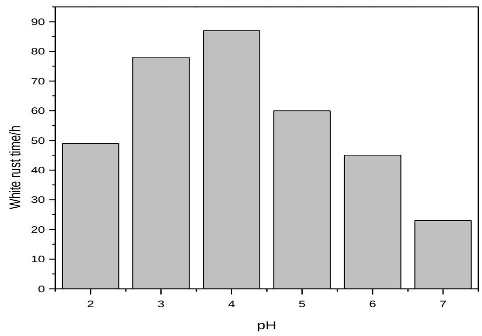


Fig. 9. Salt spray test results for coated Hot-dip galvanized steel substrates at different PH value (PMT =70℃).

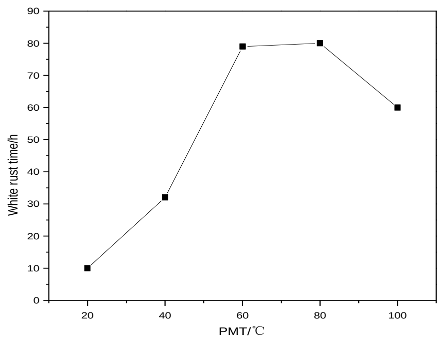


Fig. 10. Salt spray test for coated Hot-dip galvanized steel substrates cured at different PMT (pH =3).

Cr（VI）coating

tannin -H_2TiF_6/ KH792 silane coupling agent coating

Fig. 11. Corrosion test results after 96hrs of NSST.

3.4 Resistance to elevated temperature

The passivation film samples was put in ovens at 300 ℃ and baked for 20min. A Glossmeter made by BYK in Germany was used to evaluate the resistance to elevated temperature. As show in Fig. 12, the ⊿b is less than 1.2. Therefore, the passivation film has good resistance to elevated temperature.

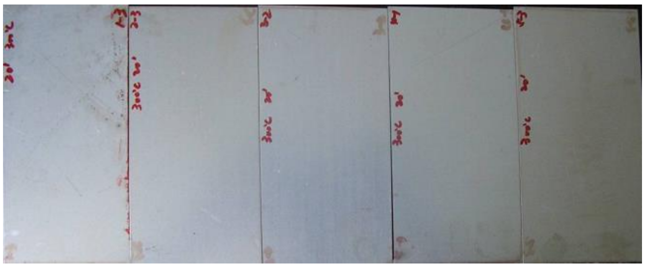


Fig. 12. The appearance of the passivation film after baking at elevated temperature.

3.5 Fingerprint resistant properties

The industry Vaseline was used to simulate the sweat pollution, colorimeter was used to measure the ⊿a, ⊿b and ⊿c value of the passivation film before or after spreading with Vaseline, then ⊿E was calculated by using formula $\Delta E = \sqrt{(\Delta a)^2 + (\Delta b)^2 + (\Delta c)^2}$ and it turned out to be less than 1.5. Therefore this passivation coating has a very good fingerprint-resistant performance.

3.6 Water resistance performance

The water resistance test is as follows a drop or a few drops of 100 ℃ water were dripped on the passivation layer, and let them dry in air. There is no white powdery substance found on the passivation coating. It is proved that the passivation film is not damaged by hot water immersion. That is to say, the passivation film has excellent water resistance performance.

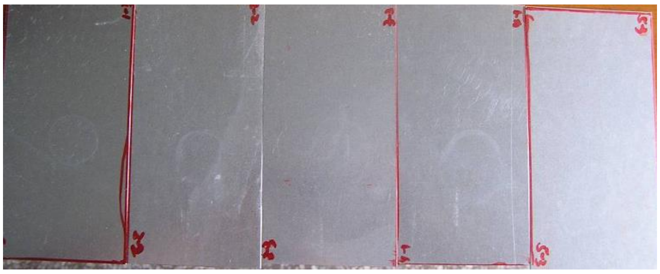
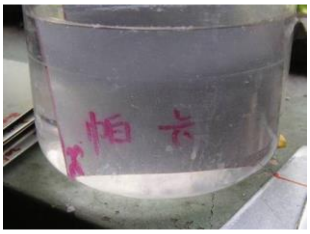


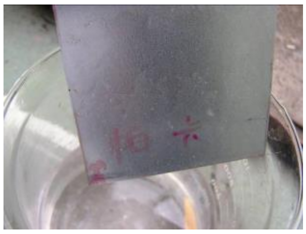
Fig. 13. Passive film coating samples and water resistance results.

3.7 Alkali resistance performance

The samples was immersed in 25 ℃, 5% NaOH solution to observe the changes on the passive film. The results are shown in Fig. 14. The results show that passive film began to locally exfoliate after immersion for 1min (as seen in Fig. b), and Passivation la4yer began to fall off entirely after 3min (as seen in Fig. c). It means that the passive film has good alkali resistance performance.



a) the moment when soaking begins



b) result after soaking for 1min

c) result after soaking for 3min

Fig. 14. Alkali resistance test.

4. Conclusions

1) In the tannic acid - H_2TiF_6/KH792 silane coupling agent system, due to the intertwined diffusion of -Si-O- long chain organic molecules in the sol, the sol particles can enter into the cracks of surface layer to play the role of filling film, to cover coating on the zinc coat surface uniformity and compactly.

2) Through the comparison of electrochemical test system on coated specimens, it was found that when the thickness of the tannic acid-H2TiF6 / KH792 silane coupling coating is greater than 600 mg/m^2, its E_{corr} and I_{corr} are better than those of conventional chromate passivation film.

3) When pH is 4, The curing temperature is between 60~80℃, and the film thickness is 600mg/m^2 (considering cost performance), the corrosion resisting property of the composite coating reaches or exceed that of the conventional Cr（Ⅵ）passivation coating.

4) A variety of performance test results show that the tannic acid-H_2TiF_6 / KH792 silane coupling agent composite coating has excellent resistance to fingerprint, resistance to elevated temperature performance, good water resistance and good alkali resistance.

Acknowledgement

One of the authors (Mr. Xu Zhefeng) gratefully acknowledges financial support from Ministry of Science and Technology of the People's Republic of China, through 863 Project (No.2009AA03Z529). The authors wish to acknowledge Prof. Yan Chuanwei, Institute of Metal Research, Chinese Academy of Sciences, for providing Electrochemical measurement system facility.

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