Corrosion Protection of Batch Galvanized Steels by Thin Silane Films with Corrosion Inhibitors

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Abstract

In this study it was demonstrated that galvanized steels can be protected by a thin silane film deposited from a water-based silane solution. This investigation revealed that the protective performance of the silane film was further enhanced by adding proper corrosion inhibitors. Two effective corrosion inhibitors, sodium meta vanadate and zinc phosphate, were incorporated in the above silane film. The anti-corrosion performance of these inhibitor-containing silane films on galvanized steels was studied using EIS and DC polarization measurements and a neutral salt spray test. The mechanism for the anti-corrosion effect of these two inhibitors was also discussed.

Keywords

Corrosion, batch galvanized steel, corrosion inhibitor, silane

1. Introduction

Galvanized steel provides excellent rust resistance and hence has been used in a wide range of applications. A compact protective layer, also called as "zinc patina", is formed on galvanized steel after exposure to the atmosphere for a long period of time, e.g., 2 years [1]. A freshly galvanized steel surface is sensitive to white rust and, therefore, needs an additional protective layer as a rust barrier before the patina layer is formed [2].

Chromate conversion treatments have been used to generate an effective passivation layer on galvalnized steel. These treatments convert the zinc surface to a surface layer containing a complex mixture of chromium compounds. The as-formed chromate conversion layer provides white rust resistance to galvanized steel. Even a scratched or damaged metal surface can be "self-healed" in that when in contact with water the hexavalent chromium ions can slowly leach out to form a protective film on top of the damaged areas. In recent years, the hexavalent chromium

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in chromate has been recognized as toxic and a health hazard. The use of this chromate compound has, therefore, been highly restricted by relevant regulations. A call for chromate replacement has thus arisen.

The search for chromate replacements has readily led researchers to the selection of trivalent chromium treatments due to their similar properties. Trivalent chromium films are similar to hexavalent types as far as the barrier effect of the coating except for the "self-healing effect". A comparison study has been reported [3]. It has been shown that all trivalent chromium products generally underperform the current hexavalent chromium products.

Silane treatments are one of the promising Cr-free treatments. This work was initiated by van Ooij and his co-workers in the early 1990s [4–7]. A thin silane film (typically less than 1 μm) has proven to be able to replace chromate conversion coatings on various metals without performance loss.

Silanes are a group of organic–inorganic silicon-based hybrids [8]. The silane molecule has a general formula $(OX)_3-Si-(CH_2)_n-Y$, where OX stands for a hydrolyzable group, typically methoxy, ethoxy and alkoxy, and Y stands for a non-hydrolyzable organofunctional group which is responsible for the paint adhesion to the metal surface such as amine, epoxy or isocyanate. When the silane is symmetrical about the organofunctional group Y, i.e., if there are two trialkoxy groups in the molecule, then they are called bis-silane which has the structure of $(OX)_3Si(CH_2)_nY(CH_2)_nSi(OX)_3$.

The formation of a silane film on metals involves two steps. The first step is the hydrolysis of the silane and the second step is condensation and formation of a silane film. The OX groups of the silane molecule hydrolyze to some degree, forming silanol groups (Si–OH). The silanol groups are hydrophilic and are readily adsorbed onto a clean metal surface, forming hydrogen bonds between the silanols and surface hydroxyls. Metallo-siloxane bonds (Me–O–Si) will form after condensation. At the same time, silanol groups will also crosslink with themselves to form hydrophobic siloxane (Si–O–Si) bonds. The former are responsible for excellent adhesion between the silane film and metals; the latter forming a hydrophobic silane film which is resistant to water penetration.

It has recently been reported that the corrosion protection performance of the silane film on metals can be further enhanced by introducing proper corrosion inhibitors into the silane film [9–11]. In this paper, we report the enhanced bare corrosion resistance of a thin silane film on batch galvanized steel by two effective corrosion inhibitors, i.e., sodium meta vanadate and zinc phosphate.

2. Experimental

2.1. Major Components in the Investigated Silane Systems

The major components in the investigated silane films are listed in Table 1. The corresponding silane solutions were made according to the following procedure. A 5 vol% silane mixture solution was prepared by adding 5 parts of the neat silane

Table 1.
Major components in the passivation formula used in this study

Component	Specific information	Function
Silane mixture	A mixture of aminosilane and vinylsilane in certain ratio	To form a hydrophobic silane layer
Resin	A polymeric resin, e.g., epoxy resin	To improve film formability
Corrosion inhibitor	Sodium meta vanadate and zinc phosphate	To enhance corrosion resistance of silane-treated galvanized steel

mixture into 95 parts of deionized water, followed by stir-mixing until the solution became clear. The resin was then added into the above silane solution. The solution was stirred until the resin was dispersed into the solution homogeneously. Two corrosion inhibitors, sodium meta vanandate (from Alfa Aesar) and zinc phosphate (from Rockwood Inc., Ward Hill, MA), were added into the above silane/resin mixture, in the range from 200 ppm to 1200 ppm based on the total silane solution.

2.2. Silane Treatment

Batch hot-dip galvalnized (HDG) steel panels (7 cm × 14 cm, from The Weert Group, The Netherlands) were immersed in a diluted (7 vol%) Okemclean® alkaline cleaner (Chemetall/Oakite, Providence, NJ) at 65°C for 4 min. The panels were then rinsed with tap water, followed by blow-air drying. The cleaned HDG panels were immersed in the above solutions for 10 s and were then dried at 100°C for 5 min.

2.3. Tests

2.3.1. Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were carried out on silane-treated HDG panels in a 0.6 M NaCl neutral solution, using an SR810 frequency response analyzer and a Gamry CMS 100 potentiostat. Impedance data were recorded at frequencies ranging from 10^{-2} to 10^5 Hz, with an alternating current voltage amplitude of ±10 mV. A commercial Saturated Calomel Electrode (SCE) served as the reference electrode, coupled with a graphite counter electrode. An area of 6.02 cm^2 of the specimen was exposed to the electrolyte during the measurement.

2.3.2. DC Polarization

These measurements were carried out on both silane treated and untreated HDG panels in a 0.6 M NaCl neutral solution. The panels to be tested were immersed in the electrolyte for 10 min to achieve a steady state before data acquisition. The reference and counter electrodes were commercial Saturated Calomel Electrode (SCE) and a platinum mesh, respectively. A range of $E_{corr} \pm 0.25$ V potential was applied on the panels, where E_{corr} is the equilibrium corrosion potential of the tested samples. The scan rate was 1 mV/s and the exposed sample area was 0.78 cm^2. Cor-

rosion rate, I_{corr} value, was obtained using Tafel analysis method. Tafel analysis is performed by extrapolating the linear portions of a log current versus potential plot back to their intersection. The value of either current at the intersection is I_{corr}.

2.3.3. Neutral Salt Spray Test (ASTM B117)

Salt spray test (SST) is an accelerated corrosion test that causes a corrosive attack to the coated metal substrate in order to test the corrosion protection performance of the coatings. In the salt spray chamber, metal panels are exposed to a 5% neutral salt fog at an angle of 45°. The chamber temperature is maintained at 35°C.

In this work, the corrosion performance of the silane-treated HDG panels before and after exposure to SST was quantitatively evaluated from EIS and DC polarization measurements. Two important parameters, low-frequency impedance (Z_{lf}) in EIS and corrosion rate (I_{corr}) in DC polarization measurements, were recorded. These have been recognized as an effective measure of the corrosion performance of the tested system, i.e., silane-treated HDG here [8].

The SST exposed panels were inspected periodically by EIS and DC polarization measurements at an interval of 1 day. The panels after EIS and DC testing were re-exposed to SST for another 24 h. This inspection was repeated for 3 consecutive days. The reason to select a 3-day SST exposure in this work is that the generally-accepted benchmark in the industry for bare corrosion protection of galvanized steel is less than 5% white rust after exposure to a salt spray test for 3 days, which is comparable to the behavior of chromate conversion treatments.

3. Results and Discussion

3.1. Corrosion Protection by a Silane Film with Sodium Meta Vanadate on Batch Galvanized Steel

3.1.1. DC Polarization Measurements

Figure 1 plots the I_{corr} values for silane-treated HDG treated with and without sodium meta vanadate, as a function of exposure time in a neutral salt spray test (SST). As is clearly seen in Fig. 1, the I_{corr} value for the untreated HDG (a dash-line curve in Fig. 1) rapidly increases with exposure time in SST, from the initial value (before exposure) less than 10–100 μA after 3 days in SST. The I_{corr} values for HDG are reduced to some extent after the silane treatment (without sodium meta vanadate). The suppression of I_{corr} is substantially enhanced after incorporating sodium meta vanadate into the silane film, as shown in Fig. 1, indicating that the corrosion activity of HDG can be reduced when combining sodium meta vanadate with the silane film.

In order to obtain the best anti-corrosion performance of silane/sodium meta vanadate system, the amount of sodium meta vanadate in the corresponding silane solution was optimized. Three levels of sodium meta vanadate were tested: 600 ppm, 1000 ppm and 1200 ppm in the corresponding silane solution. In Fig. 1, the I_{corr} values for all these three levels were reduced below 10 μA throughout the

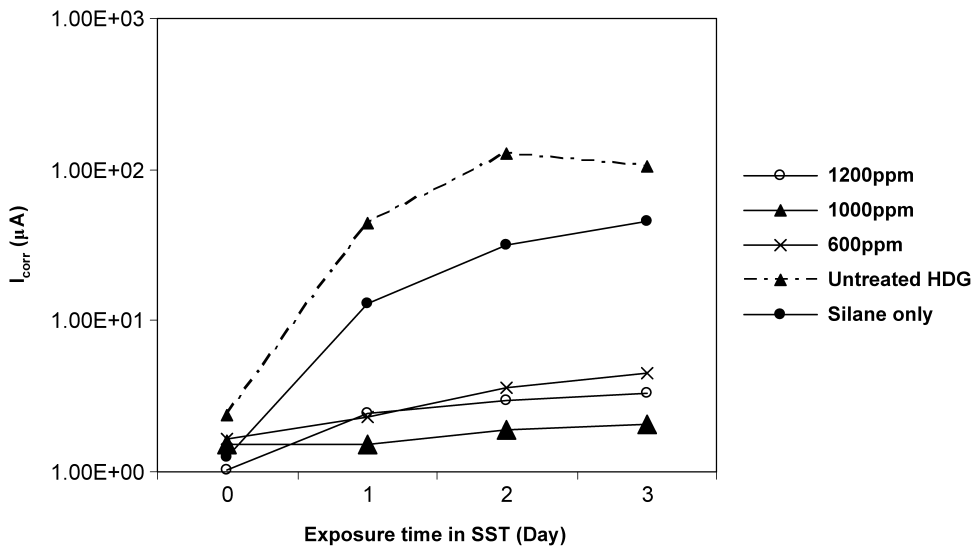


Figure 1. I_{corr} values for HDG treated without and with different contents of sodium meta vanadate-containing silane treatments, as a function of exposure time in neutral salt spray test.

entire test period, with the system with 1000 ppm sodium meta vanadate giving the lowest I_{corr} values. This indicates that the maximum inhibition power of sodium meta vanadate is achieved when the amount of sodium meta vanadate in the silane solution reaches 1000 ppm.

3.1.2. EIS Measurements

The anti-corrosion effect of sodium meta vandate in the above systems was further studied using EIS measurements in a 0.6 M neutral NaCl solution. It should be pointed out that in DC polarization tests, I_{corr} indicates the corrosion rate of the tested material. The higher the I_{corr} value is, the more the corrosion activity of the tested material. In the EIS study, the corrosion resistance of the tested system is measured and is reflected by low-frequency impedance values (Z_{lf}). The higher the Z_{lf} value is, the less the corrosion activity of the tested material. In this work, the impedance values at 0.02 Hz ($Z_{0.02Hz}$) were collected.

Figure 2 displays a plot of low-frequency impedance values at 0.02 Hz ($Z_{0.02Hz}$) for HDG treated with and without sodium meta vanadate-containing silane treatments, as a function of exposure time in the salt spray test. A similar trend is observed in Fig. 2: the $Z_{0.02Hz}$ value for HDG after a 3-day SST is improved by one order of magnitude for all silane treatments. The highest $Z_{0.02Hz}$ value (almost 2 orders of magnitude higher than the untreated one) is obtained for the system with 1000 ppm sodium meta vanadate. This confirms that the optimal level for sodium meta vanadate is 1000 ppm in terms of its maximum corrosion inhibition power, which is in good correlation with the result from the above DC test.

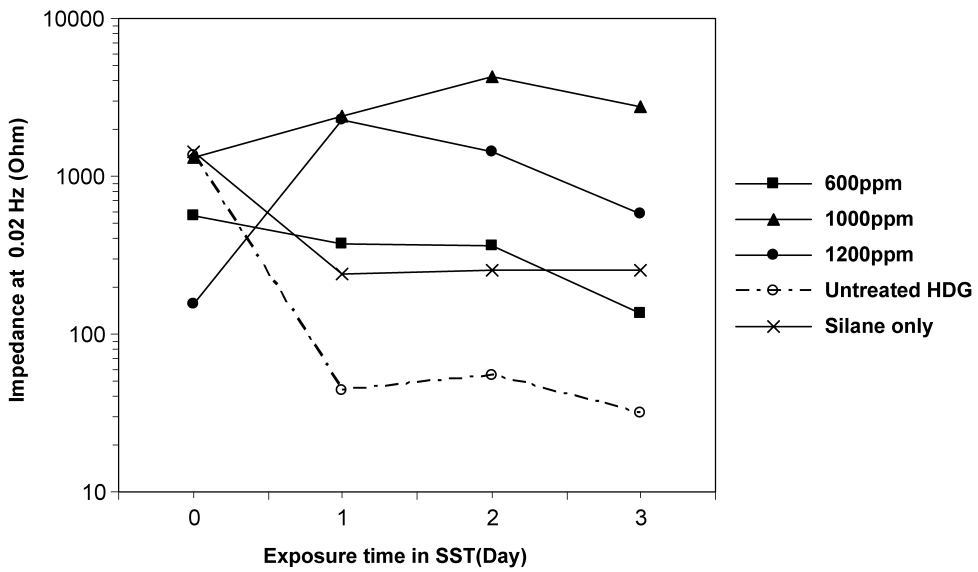


Figure 2. Low-frequency impedance values at 0.02 Hz ($Z_{0.02\text{Hz}}$) for HDG treated without and with different contents of sodium meta vanadate-containing silane treatments, as a function of exposure time in neutral salt spray test.

3.2. Corrosion Protection by a Silane Film with Zinc Phosphate on Batch Galvanized Steel

In addition to sodium meta vanadate, another effective corrosion inhibitor, zinc phosphate, was also studied and its anti-corrosion effect is discussed in the following sections.

3.2.1. DC Polarization Measurements

Figure 3 displays the I_{corr} values for HDG panels with and without zinc phosphate-containing silane treatments as a function of exposure time in the salt spray test. In general, the I_{corr} values for all silane-treated HDG are reduced to different extents during the 3-day exposure in SST, as compared to the untreated (dashed curve in Fig. 3). The reduction in the I_{corr} values for the silane film is further enhanced by the addition of zinc phosphate, with the zinc phosphate at the level of 1000 ppm giving the lowest I_{corr} value. This indicates that 1000 ppm zinc phosphate is the optimal level for its maximum corrosion inhibition power.

3.2.2. EIS Measurements

Figure 4 displays a plot of $Z_{0.02\text{Hz}}$ values for the silane-treated HDG with and without zinc phosphate as a function of exposure time in the salt spray test. A similar trend is again seen here: the silane film deposited from a silane solution with 1000 ppm zinc phosphate offers the greatest bare corrosion protection. This is evidenced by its highest $Z_{0.02\text{Hz}}$ values among all the treatments during the 3-day SST exposure. The $Z_{0.02\text{Hz}}$ value for the system with 1000 ppm zinc phosphate is

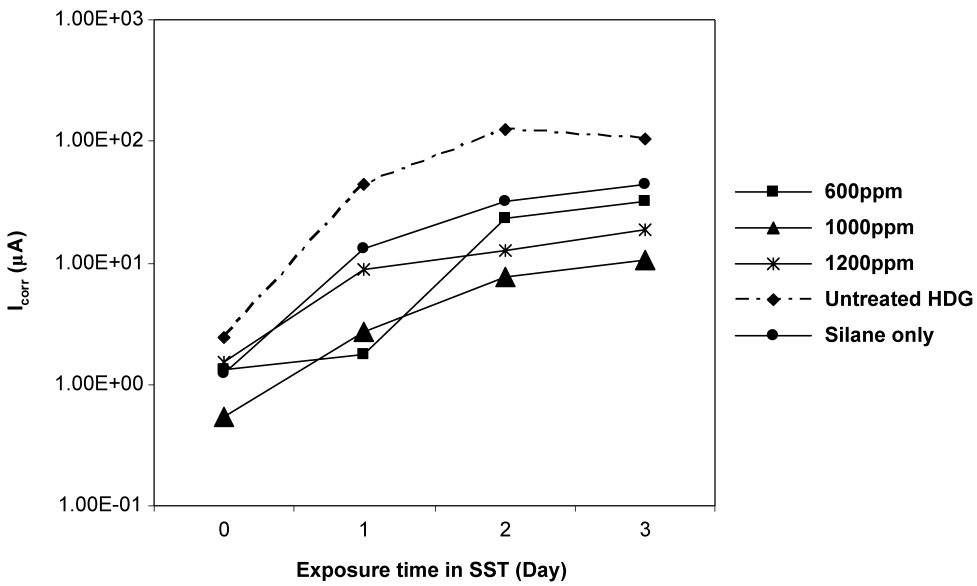


Figure 3. I_{corr} values for HDG treated without and with different contents of zinc phosphate-containing silane treatments, as a function of exposure time in neutral salt spray test.

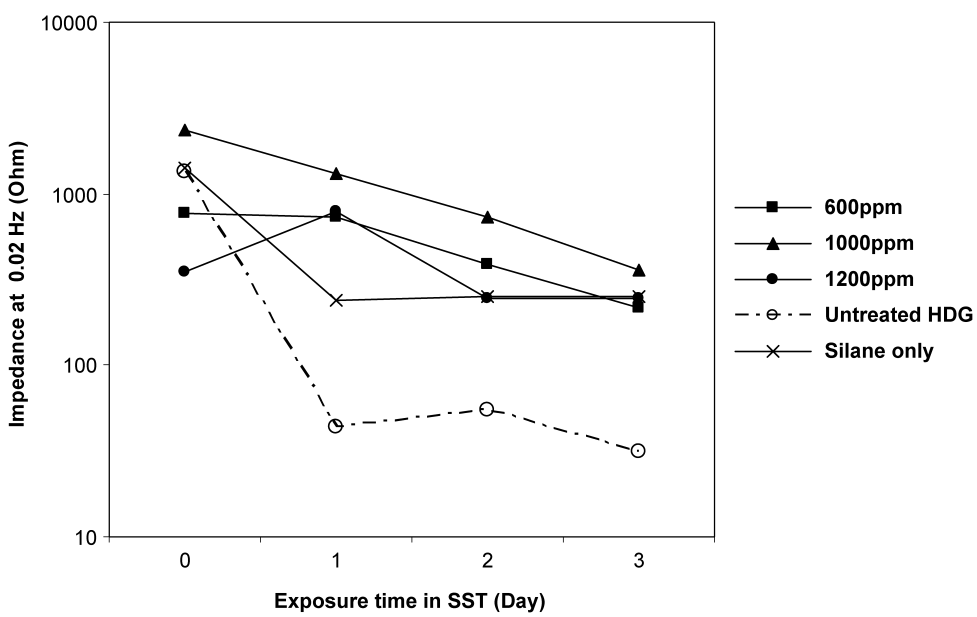


Figure 4. Low-frequency impedance values at 0.02 Hz ($Z_{0.02Hz}$) for HDG treated without and with different contents of zinc phosphate-containing silane treatments, as a function of exposure time in a neutral salt spray test.

approximately 2 orders of magnitude higher than that for the untreated and is always higher than the silane film without zinc phosphate during the entire exposure period.

3.3. Comparison of Anti-corrosion Capacities of Sodium Meta Vanadate and Zinc Phosphate in the Silane Films on HDG

Figure 5 compares the I_{corr} values for silane-treated HDG panels with different corrosion inhibitors, i.e., sodium meta vanadate and zinc phosphate at their optimal level (1000 ppm in their corresponding silane solutions). Clearly, both inhibitor-containing silane films outperform the untreated and the silane film without corrosion inhibitors. Furthermore, the silane film containing sodium meta vanadate suppresses the corrosion activity on HDG more effectively than zinc phosphate. The film with sodium meta vanadate exhibits the lowest I_{corr} values ($\sim$1 μA) during the entire test period, while the film with zinc phosphate has a slightly higher I_{corr} values but still lower than the silane film without inhibitors. It is also noticed that although the incorporation of zinc phosphate into the silane film in general leads to reduced I_{corr} values, an increasing trend for the I_{corr} values is still obvious in Fig. 5. Such trend, however, is not seen for sodium meta vanadate.

Figure 6 compares the $Z_{0.02\text{Hz}}$ values for the silane-treated HDG systems with the two corrosion inhibitors at their optimal level (i.e., 1000 ppm in their corresponding solutions), as a function of exposure time in SST. In general, higher $Z_{0.02\text{Hz}}$ values are obtained for all silane-treated HDG systems regardless of the addition of inhibitors, as compared to the untreated (the dashed line in Fig. 6) during the 3-day SST. The $Z_{0.02\text{Hz}}$ value for the silane-treated HDG without inhibitors

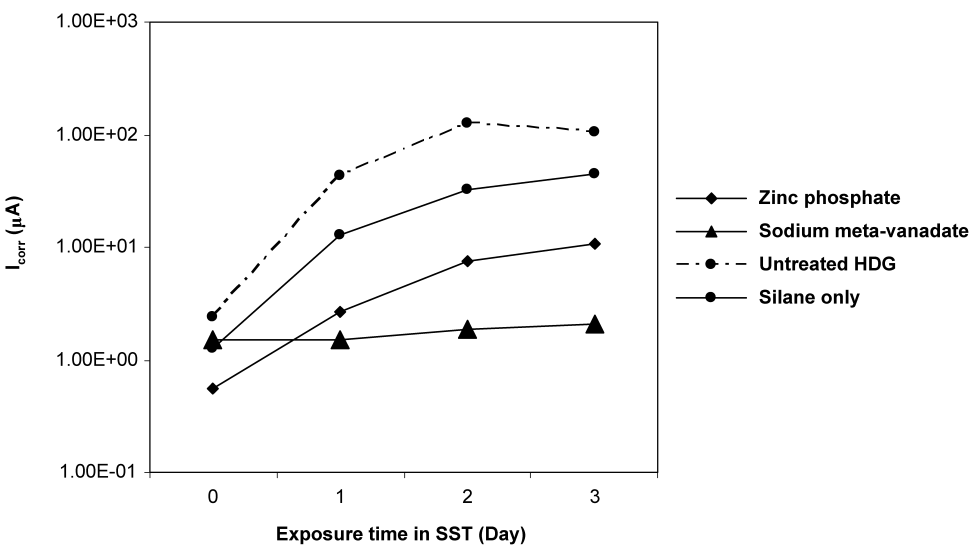


Figure 5. Comparison of I_{corr} values for inhibitor-containing silane films on HDG, measured in a 0.6 M NaCl solution, as a function of exposure time in a neutral salt spray test.

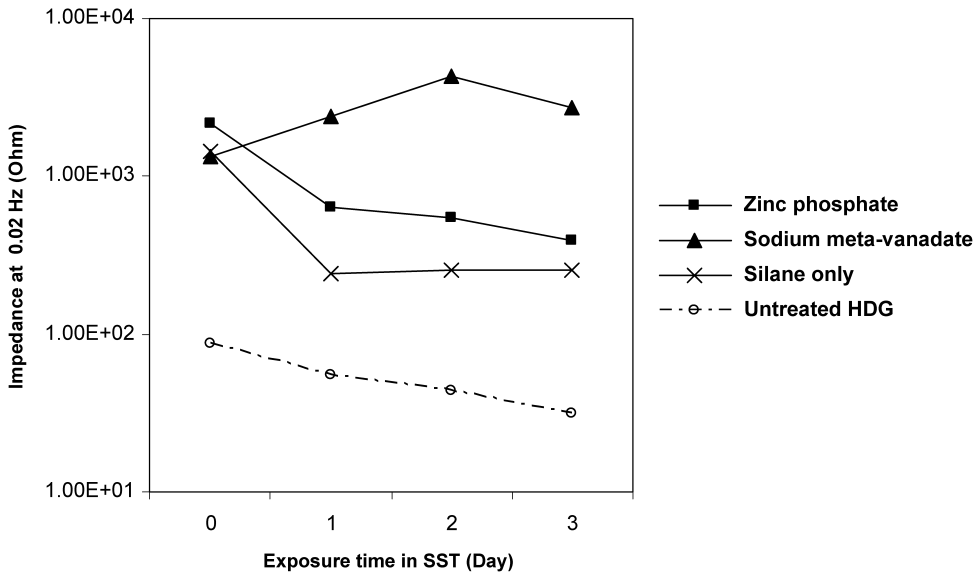


Figure 6. Comparison of low frequency impedance values at 0.02 Hz ($Z_{0.02\text{Hz}}$) for inhibitor-containing silane films on HDG, measured in a 0.6 M NaCl solution, as a function of exposure time in a neutral salt spray test.

(referred as "silane only" in Fig. 6) is more than 10^3 Ohm before the exposure (i.e., day 0). The $Z_{0.02\text{Hz}}$ value drops sharply to 5×10^2 Ohm after 1 day of exposure and becomes stable in the remaining exposure time period. This indicates that the inhibitor-free silane film has been saturated by the electrolyte (i.e., 0.6 NaCl solution) after one day of exposure. The $Z_{0.02\text{Hz}}$ value for the silane film with zinc phosphate also decreases after 1 day of exposure (referred as "zinc phosphate" in Fig. 6) and this decrease continues in the following days. After 3 days of exposure, a stable region is not yet reached for the zinc phosphate system, meaning that the system is still not saturated by the electrolyte. In other words, the water resistance of the system is somehow improved by adding zinc phosphate. In the case of sodium meta vanadate, the $Z_{0.02\text{Hz}}$ value gradually increases with time instead of showing a decreasing trend during the exposure. This phenomenon also indicates the water resistance of the system is largely improved by incorporating sodium meta vanadate.

3.4. Proposed Mechanisms for Bare Corrosion Protection of Galvanized Steel by Inhibitor-Containing Silane Films

Based on the previous work [7], an improvement in the water resistance of silane films can typically be achieved by the following two ways:

1. A further crosslinked silane film. When incorporating the two corrosion inhibitors into the silane solution, sodium meta vanadate largely and zinc phosphate partially dissolve into the silane solution. These dissolved ions from the

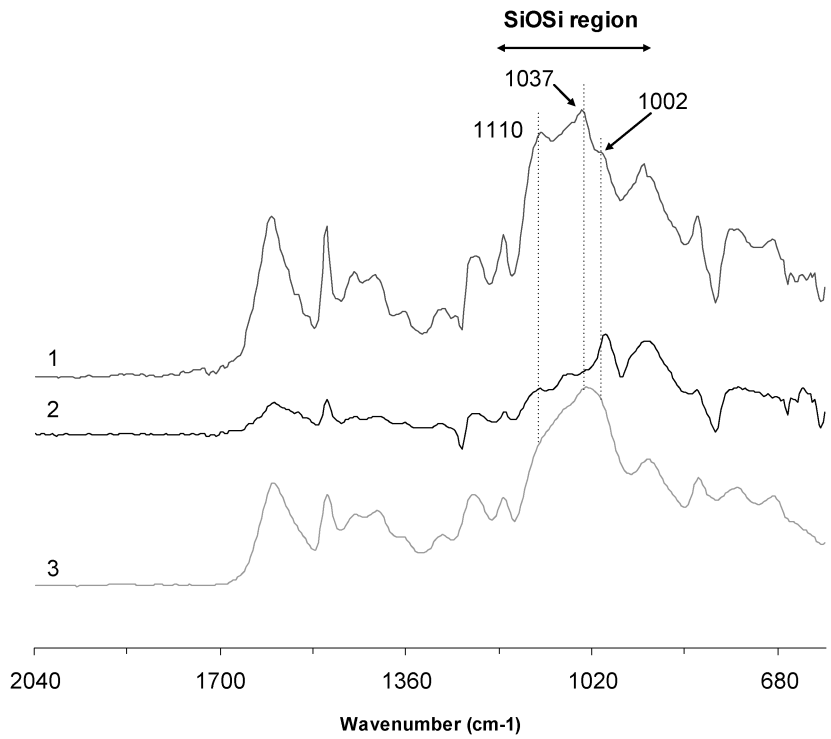
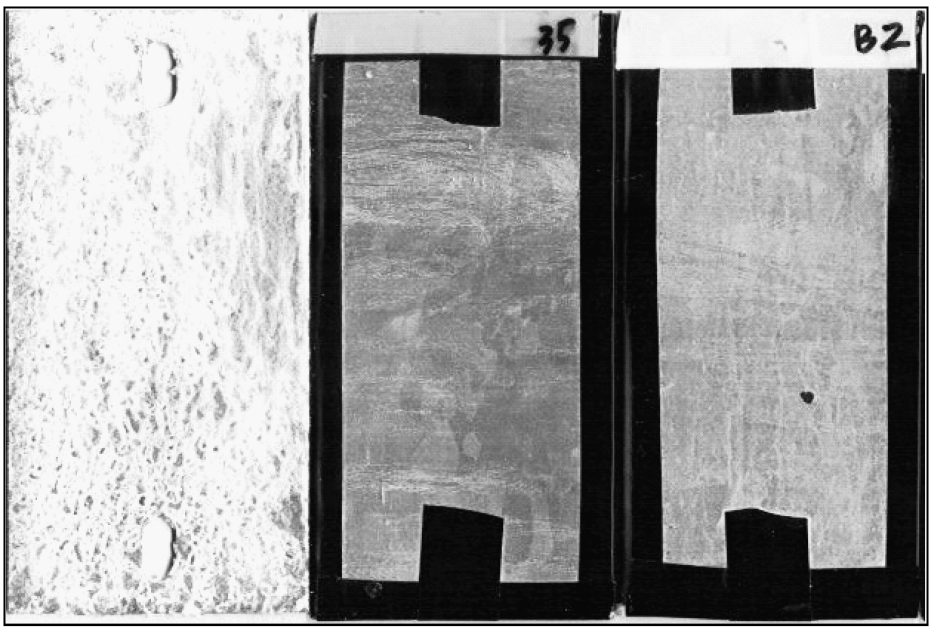


Figure 7. Comparison of FTIR-RA spectra of different silane films on HDG; (1) with sodium meta vanadate, (2) with zinc phosphate and (3) without corrosion inhibitors.

corrosion inhibitors may somehow induce more extensive crosslinking during the formation of the silane film, generating an extra number of hydrophobic siloxane bonds. As a result, the water resistance of the silane film further improved. Indeed, relevant evidence has been obtained in the recent IR characterization and is shown in Fig. 7. It is clearly seen in Fig. 7 that the peaks in the typical siloxane region (Si–O–Si) from 950 cm^{-1} to 1100 cm^{-1} [7] are strongly affected by the addition of the corrosion inhibitors, especially in the case of sodium meta vanadate. Si–O–Si peaks at 1100 cm^{-1}, 1037 cm^{-1} and 1002 cm^{-1} are stronger for the sodium meta vanadate (spectrum 1 in Fig. 7) than the system without corrosion inhibitors (spectrum 3 in Fig. 7). This evidence strongly supports the above theory.

2. Another possible mechanism is related to the formation of a water-resistant interfacial phase. This is also possible if both corrosion inhibitors in the silane film dissolve when the electrolyte penetrates into the film. The dissolved species in the electrolyte migrate to the metal surface and form a protective complex with metal oxides. This mechanism, however, needs to be further verified by other characterization tools.



(a) (b) (c)

Figure 8. Silane-treated HDG panels after neutral salt spray test. (a) Untreated HDG (24-h exposure, 100% white rust); (b) silane-treated HDG with sodium meta vanadate (1000 ppm) (72-h exposure, 0% white rust) and (c) silane-treated HDG with zinc phosphate (1000 ppm) (72-h exposure, 5% white rust).

Figure 8 shows the HDG panels with different treatments after the 3-day salt spray test. It is seen that the untreated HDG panel showed 100% white rust (i.e., heavily corroded) after only 24 h exposure to SST. The other two silane-treated panels with different corrosion inhibitors perform much better than the untreated even after 72 h exposure to SST. The one with sodium meta vanadate (Fig. 8b) shows no white rust at all, while the one with zinc phosphate (Fig. 8c) exhibits 5% white rust after the test.

4. Conclusions

The following conclusions can be drawn from this investigation:

- The corrosion protection performance of a thin silane film is much enhanced by both corrosion inhibitors: sodium meta vanadate and zinc phosphate.
- The silane films deposited from the silane solutions with 1000 ppm of the above individual inhibitors offer the best anti-corrosion performance on HDG.

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