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Improvement of Protective Properties of Top Coatings Applied on Zinc-Rich Primer by 3-Aminopropyl-Triethoxysilan and 2-(Benzothialylthio) Succinic acid

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Corrosion resistance of coating system consisting of zinc-rich primer (ZRP) and topcoat based on polyurethane resin with the presence of 3-aminopropyl-triethoxysilan (APS) and 2-(benzothialylthio) succinic acid (BSA) was studied by electrochemical impedance and wet adhesion. The interface metal/primer/topcoat was analyzed by scanning electronic microscopy. It was found that the presence of APS and BSA improved adhesion and barrier property of the topcoats.

Keywords *: electrochemical impedance, wet adhesion, zinc rich primer, topcoat*

1. Introduction

Primer heavily pigmented with zinc dust have used extensively in the last two decades for corrosion protection of steel structures in sea water environments.[1),2)] It is commonly accepted that two fundamental protection mechanisms operate in zinc-rich primer (ZRP): (i) the galvanic protection stage, which requires good electrical contact among the zinc particles themselves as well as between them and the steel substrate and (ii) the barrier-like behavior stage, which is reinforced by the amount and nature of zinc corrosion products leading to promotion of the formation of a dielectric surface film. The accumulation of zinc corrosion products that have poor electrical conductivity promotes the loss of electrical contact and diminishes the active surface area of the pigment. Subsequently, the galvanic action becomes less effective. As the exposure time increases, the deposition of inhibiting zinc compounds at the base of the coating pores followed by the sealing of the porous structure by the zinc corrosion products must undoubtedly occur to ensure long-term protection. Zinc-rich paints can be used as a single-coat shop primer for temporary protection and as primer in a multilayer coating system for long-term protection.

The aim of the present work is to improve of protection properties of topcoat used on zinc-rich primer by 3-Aminopropyl-triethoxysilan and (2-benzothiazolylthio) succinic acid. Corrosion resistance of coating was studied by impedance measurement during exposure time in 3% NaCl solution and the adhesion measurement during exposure to water (wet-adhesion).

2. Experimental

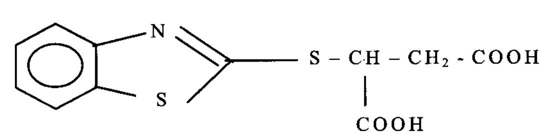
2.1 Materials

The carbon steel plates 15 x 10 x 0.2 cm were used as metallic substrate. The metal surface was polished by abrasive paper with roughness of 600 grades.

Zinc-rich primer prepared was based on Bayer polyurethane.

The topcoat used was polyurethane coating based on an acrylate resin and HDI curing agent obtained by Bayer. 3-Aminopropyl-triethoxysilan (APS) has been obtained by SIGMA-ALDRICH, its molecular structure is: $H_2N\ (CH_2)_3\ Si\ (OC_2H_5)_3$.

(2-benzothiazolylthio) succinic acid (BTS) has been obtained by CIBA, its molecular structure is:



The polished steel plates were degreased with toluene and coated with the ZRP, then the topcoat by using un spray gun. The film thickness was measured with electromagnetic gauze. The thickness measured of each paint layer was 40 ± 5 μm.

2.2 Electrochemical measurements

The working electrode was carbon steel panel coated. On each panel a cylindrical polyvinylchloride tube were fixed by using a silicon adhesive to get good adhesion to the coated substrate. The geometrical area for impedance measurements was 25 cm^2.

The auxiliary electrode was a platinum grid. A saturated calomel electrode (SCE) was used as reference, the electrolyte was 3% NaCl solution.

Impedance spectra were performed in the potentiostatic mode at the corrosion potential (E_{corr}) with the frequency range $10^{-3} \leq f \leq 10^5$ Hz during exposure in 3 % NaCl solution by using Autolab instrument. The data were processed by a Dell computer.

2.3 The adhesive measurements

The adhesion of coating exposed to water was measured by cross-cut tape test. The uncovered rear side of the sample was protected with a PVC adhesive film and the edges with an adhesive tape (Tesaband 4651). The samples were then immersed in distilled water at 25℃. The samples were drawn from the water and excess moisture before adhesion measurement.

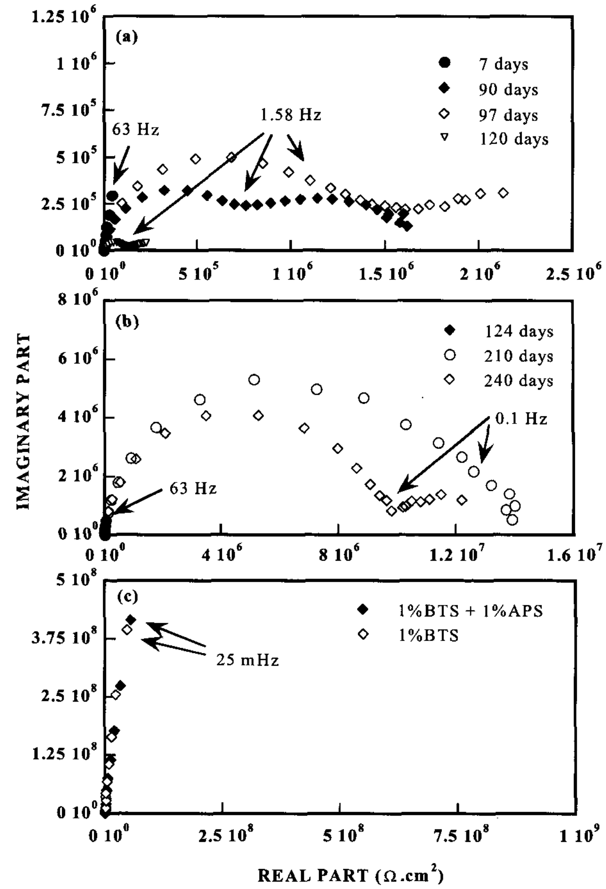


Fig. 1. Impedance diagram obtained after different immersion times in 3% NaCl solution for coating systems of ZRP and topcoat: (a) without additive; (b) with 1 % APS; (c) with 1 % BTS and 1 % BTS + 1 % APS after 240 days of immersion

3. Results and discussion

Fig. 1 illustrates the impedance diagrams obtained for three immersion times for coating systems of zinc rich primer and topcoat without additives, topcoat with additives: 1 % APS; 1 % BTS and 1 % APS + 1 % BTS.

For the coating system without additives it is observed that for a short immersion time of 7 days the impedance diagram presents only one capacitive arc, which indicates that the coating is intact. For immersion times of 90 and 97 days, a single Nyquist semi-circle is well determinated at high frequency, which is attributed to the coating film. The coating resistance determinated from impedance diagram characterizes the barrier properties of the coating.[3)] The size of loop at high frequency decreases when immersion time increases from 90 to 97 days and a second loop starts to appear at low frequencies after 90 days of immersion. This increase of size of HF loop cans be explained by the formation and accumulation of insoluble corrosion products of zinc particle, which blocks the film pores.[4)] After 97 days, HF loop decreases quickly with immersion time. A small blister is appeared at the exposure-coating surface after 90 days of immersion.

In the case of coating system with 1 % APS, it is observed that for immersion time of 124 days the impedance diagram presents capacitive behavior, which indicates that the coating is intact. Two Nyquist semi-circles was observed after 240 days of immersion while for coating system without additives two Nyquist semi-circle appeared after 97 days of immersion. These observations indicate that the coating system with 1 % APS gives higher protection then coating system without additives.

According to Paula Puomi et al.,[5)] the chemical interaction between the amino groups in the APS and the functional groups of the polyurethane coating was relatively strong, resulting in improved corrosion resistance. The formation of siloxane chains also can result in formation of interpenetration polymer networks with the paint polymer.[6)] In addition, when the electrolyte reach at the ZRP/ topcoat interface, there is also an interaction between silan and available hydroxyl groups of zinc particles. Both interactions have reinforced barrier properties of the coating system. These results show the good protection of coating achieved by the addition of small quantity of APS.

For coating system with 1 % BTS and 1 % BTS+1 % APS the impedance diagrams presents only one capacitive arc even after 240 days of immersion. This results show that for these both coating systems have excellent barrier properties. This result indicates that the presence of BTS has improved corrosion resistance of the coating. In addition, a good protection was obtained with the mixture of 1 % BTS + 1 %APS. This results can be explained by the adsorption of both APS and BTS on to ZRP which improved the ability of the coating to wet the surface and the formation of insoluble reaction products with zinc particles.

The coating capacitance was calculated from impedance diagrams.[7] Fig. 2 shows the dependence of the coating capacitance on immersion times.

It is observed that the coating capacitance of coating without additives is higher than coating capacitance of coating with additives. For immersion time less than 100 days, the coating capacitance of all coating systems were stable with immersion time. After 100 days of immersion the coating capacitance of coatings with additives were stable while the coating capacitance of the coating system without additive increased significantly. The increase of coating capacitance may be due to water uptake of the topcoat, which can be estimated by the equation of Brasher and Kinhsbury.[8]

This variation of coating capacitance with immersion time of coating systems containing 1% APS, 1% BTS and mixture 1% APS + 1% BTS demonstrates the excellent corrosion resistance of this coating systems, particularly for the systems containing 1% BTS and mixture 1% APS + 1% BTS.

Usually moisture reduces coating adhesion and also their protection against corrosion.[9] Beside impedance measurement the wet-adhesion of the coating systems was measured by the tape test during immersion time in water .[10] Fig. 3 represents the percentage of coating area detached measured during immersion time. For the coating system without additive, the area detached increased approximately linearly with time. After 15 weeks of exposure, its increase was slight.

For the coating system containing 1% APS, a fluctuation of area detached was observed for exposure time less than 140 days and after 140 days of exposure it remains stable at the rather lower values (20%). Promotive adhesive effect was observed in this case. The fluctuation may be due to reaction at ZRP/topcoat interface in presence of water. May be the quantity of APS compound was insufficient for the reaction can occur at total surface.

For the coating system containing 1% BTS, the area detached was zero during the first 28 days of immersion. This results indicate the good adhesion of coating system. After 28 days of immersion, the coating adhesion decreased. This adhesion decrease can be explained by accumulating of water at the interface.[11] However, after 56 days of immersion the area detached decreased to zero,

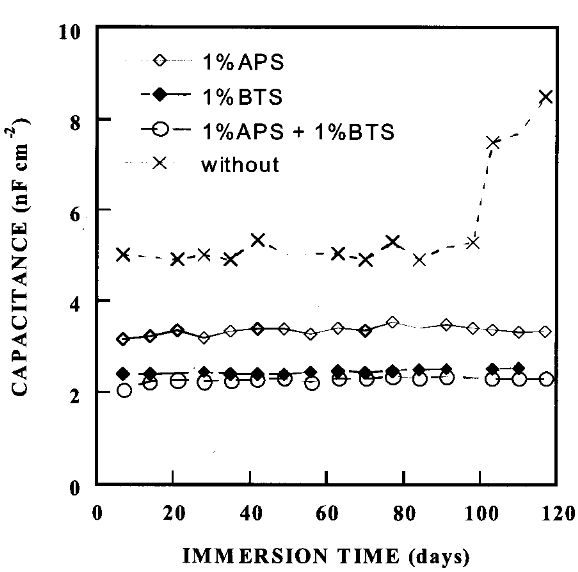


Fig. 2. Time dependence of the coating capacitance for ZRP panel coated by polyurethane coating without additives, polyurethane coating with 1% APS, with 1% BTS and with mixture 1% APS + 1% BTS

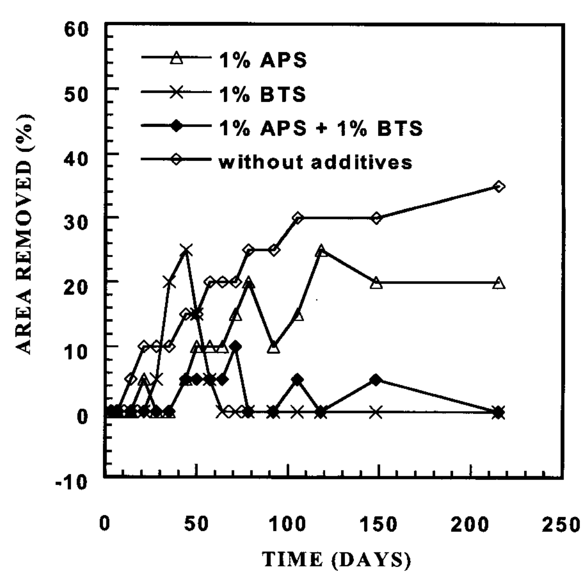
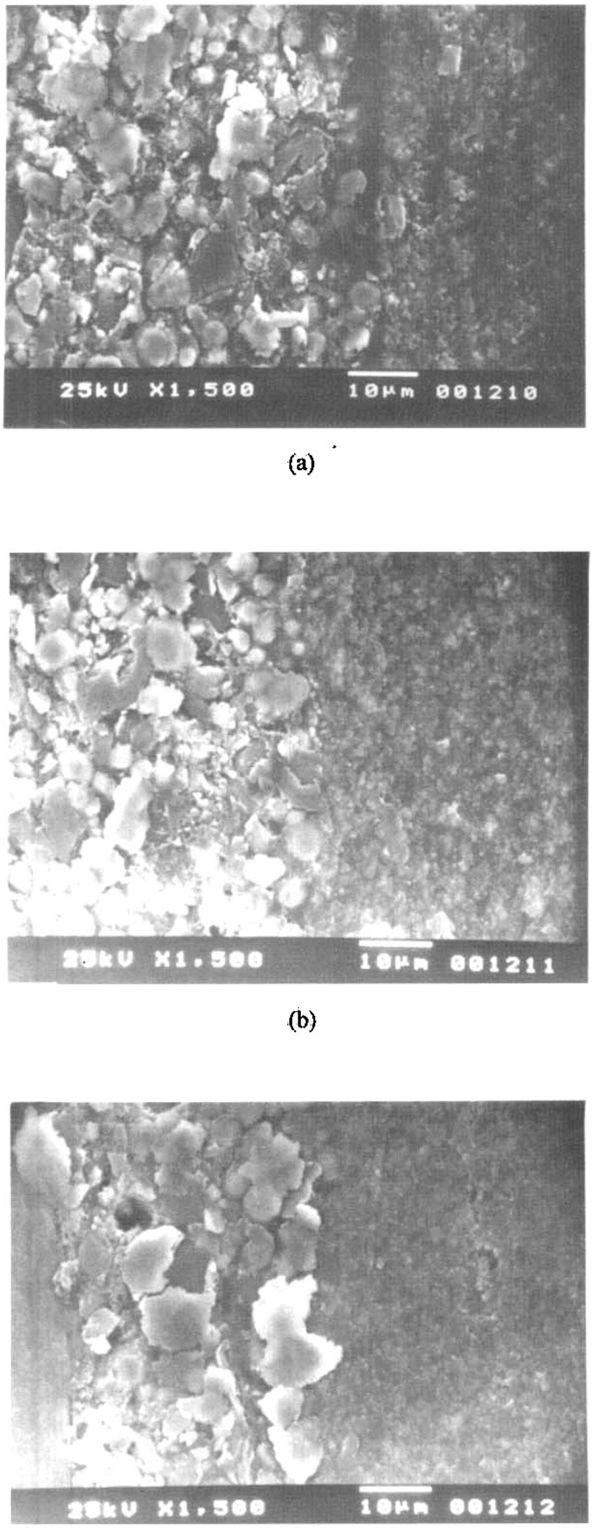


Fig. 3. Area detached of topcoat after tape test versus immersion time in water for ZRP panel coated by polyurethane coating, polyurethane coating with 1% APS, with 1% BTS and with mixture 1% APS + 1% BTS



(a)

(b)

(c)

Fig. 4. SEM cross-section photographs of the studied ZRP coated by (a) polyurethane coating, (b) polyurethane coating containing 1% APS, (c) polyurethane coating containing 1% BTS

which indicates the increase of coating adhesion.

For the coating system containing mixture 1% APS + 1% BTS, coating adhesion remained well to 42 days of exposure. For immersion time from 42 days to 70 days the coating adhesion decreased. By comparison with the coating containing BTS alone the coating adhesion was higher. After 70 days of immersion the area detached decreased with fluctuation. The fluctuation phenomenon may be due to the presence of APS compound. These results obtained were in agreement with those obtained by the electrochemical impedance measurements.

In order to understand the behavior of APS and BTS at the interface ZRP/topcoat the interface was analyze by scanning electronic microscopy. The SEM photographs of the cross-section of ZRP panel coated by polyurethane coating and by polyurethane coating containing APS and BTS after 30 days of exposure in 3% NaCl solution were shown in Fig. 4

For the coating without additive, a separation between ZRP layer and topcoat was clearly found. As reported in the literature,[12)] the formation of zinc hydroxychlorides in chloride medium will be predominate at the upper part of ZRP as well as at ZRP/topcoat interface. These corrosion products have caused an incompatibility between ZRP and topcoat layer during the exposure time in the electrolyte solution.

In contrast, for the paint systems containing APS and BTS, there was not the separation between ZRP layer and topcoat and a good compatibility at the interface was observed. These observations explained the good adhesion of coating system with the presence of APS and BTS.

4. Conclusions

The electrochemical impedance measurement was used to study the protective behavior of zinc-rich primer coated by polyurethane topcoat and polyurethane topcoat containing 3-aminopropyl-triethoxysilan and 2-(benzothialyl thio) succinic acid and their mixture.

These results indicate that the present of APS and BTS have improved significantly protective properties of topcoat. The mixture APS + BTS gave the better results caused by good compatibility bettwen themselves and with polyurethane binder.

Wet-adhesion measurements during exposure in water were also carried out. It was clearly shown that there was a significant improvement of coating adhesion in presence of BTS and mixture BTA + APS.

SEM cross-section analyzes of paint systems showed also a good compatibility at the ZRP/topcoat interface for the topcoat containing APS and BTS.

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