

Acrylic Resin Derivatives as Modifier for Potassium Silicate Binder in Zinc-Rich Coatings: Electrochemical Studies

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ABSTRACT

Water based inorganic alkali silicate binder of zinc rich primer was modified by adding acrylic resin derivatives. Several series of primer coatings were formulated by adding 5, 10 and 15 wt% of acrylic and acrylic/styrene copolymer to potassium silicate binder and used as binder in zinc rich coatings. The formulated primers were applied on low carbon steel plates and the corrosion protection properties of these primers were evaluated by electrochemical impedance spectroscopy (EIS), corrosion potential measurements, salt fog test and scanning electron microscope (SEM). The results indicated that the addition of 5% acrylic/styrene copolymer and/or 10% acrylic resin into the inorganic silicate binder led to improvement of corrosion protection performance of formulated primers. Prog. Color Colorants Coat. 7(2014), 213-225. © Institute for Color Science and Technology.

1. Introduction

Using zinc rich primers is a very efficient method for protecting steel structures against corrosion [1-7]. The waterborne inorganic zinc-rich coatings have been used because their environment friendliness and no volatile organic compound (VOC) contents. These coatings, after application on steel substrates, initially have a porous nature, so corrosive species permeate through the primer coating and reach to the steel/coating interface. The zinc particles scarify themselves to provide cathodic

protection of steel for a relatively short service time. As the exposure time increases, zinc corrosion products are formed and the nature of coating gradually converts to a barrier. Subsequently, reduction in cathodic protection and losing electrical contact between zinc particles themselves or zinc particles and the steel substrate is due to accumulation of zinc corrosion products that have poor electrical conductivity [4-7].

In zinc rich primers, the zinc pigment volume concentration (PVC) should be more than the critical

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PVC (CPVC) in order to give electrical conduction between the zinc particles as well as the zinc particles and the steel substrate to protect the underlying substrate against corrosion [7-10]. When the ratio of PVC to CPVC is greater than one, there is no sufficient vehicle to wet the zinc particles and substrate, resulting in poor mechanical properties of the coating such as adhesion, cohesion, flexibility, abrasion resistance, etc. Further, uniform dispersion of the zinc particles in these high PVC coatings is relatively hard [5, 11, 12].

Conventionally, alkali silicate salts and nano sized colloidal silica which can additionally contain a dissolved or dispersed organic resin or latex, has been used as modifier materials for providing an aqueous inorganic coating. In this respect, a number of patent applications thereon have been filed [13-16]. Modification of inorganic zinc coatings with small amounts of organic resins decreases the surface tension of the vehicle, hence increases the wettability of the vehicle. It has been reported that this type of alkali silicate binder modification improves the dispersion of the zinc pigments in the paint, cohesion of the film, adhesion to the substrate and corrosion resistance of the resultant coatings [17].

The aim of this work was to study the effect of modification of waterborne inorganic alkali silicate binder by adding of acrylic resins. The modified binder was used as binder for zinc rich primer and corrosion resistance properties of resultant coatings were studied.

The protective mechanisms of these coatings were examined by electrochemical method (EIS) and salt spray tests. In addition, an open-circuit potential change during immersion in NaCl electrolyte solution was analyzed.

2. Experimental

2.1. Materials and formulations

Commercial aqueous solutions of potassium silicate of 3.3/1 silica/alkali molar ratio were supplied by Iran silicate industries. For increasing the molar ratio of silica/alkali from 3.3/1 to 5.2/1, a 30% (w/w) colloidal acidic solution of nanosilica with particle size of about 10-20 nm (produced by Sharif Nano Pigment Company), were used. This binder was denoted as SI which was obtained by gradual adding and mixing of nanosilica solution in alkali silicate solution. The potassium silicate resin was modified by adding different amounts of commercial acrylic/styrene copolymer and acrylic emulsion polymers. The acrylic resin derivatives were supplied from Simab Resin Company (Tehran, IRAN). Typical properties of used acrylic and acrylic/styrene resins are shown in Table 1.

The modified binder solution were denoted as AS5, AS10, AS20 and A5, A10, A20 which contained 5, 10 and 20% acrylic/styrene copolymer and acrylic emulsion, respectively. Compositions of formulated coatings are shown in Table 2.

Table 1: Typical properties of used acrylic and acrylic/styrene resins.

Resin	Appearance	Type	Emulsifying system	Solids (%)	pH	T _g (°C)	Viscosity (cP)	MFFT (°C)
acrylic	milky white liquid	self-crosslink	nonionic	45 ± 1	2-3	-14	1000	<0
acrylic styrene	milky liquid	self-crosslink	anionic	47±1	6-8	-2	3000	0

Table 2: Specification of formulated coatings.

Coating code	Zinc dust content	Binder content	Used modifier organic resin	Organic resin/total resin
SI	90	10	-	-
AS5	90	10	acrylic/styrene	5%
AS10	90	10	acrylic/styrene	10%
AS20	90	10	acrylic/styrene	20%
A5	90	10	acrylic	5%
A10	90	10	acrylic	10%
A20	90	10	acrylic	20%

In the composition of zinc rich coatings, zinc dust with average particle diameters of 5 μm (fine) was supplied from Pars Zinc Dust Co (Tehran, Iran). This powder was added to the vehicles to prepare unmodified and modified zinc-rich paint. Zinc dust content was at the level of 90% by weight to ensure efficient electrical conduction between zinc particles and steel substrate and also achieve good protection.

2.2. Applying the primers

The used metallic substrate was carbon steel with dimensions of $15 \times 7 \times 0.2 \text{ cm}^3$. Before applying the coating, the metal surface was sandblasted according to SA 2 1/2 and for adjustment of viscosity, appropriate amounts of solvent (water) was added into the coating formulations. Prepared primers were immediately applied on blasted steel plates by air spray equipment. Two series of samples were prepared. The thickness of the obtained zinc-rich coatings was $50 \pm 5 \mu\text{m}$ for series 1 and 70 ± 5 for series 2 plates. Series 1 plates were used for EIS tests and series 2 plates were used for salt spray tests. Before beginning the tests, the coated plates were placed in laboratory atmosphere for seven days to ensure complete curing of binders.

2.3. Laboratory tests

The Electrochemical Impedance Spectroscopy (EIS) measurement was carried out in a 3.5% NaCl solution at room temperature, using Autolab PGSTAT 302N potentiostat/galvanostat (Autolab, Italy). Also, corrosion potential (E_{corr}) measurements were performed for confirmation of cathodic protection period. Polyvinyl chloride cylindrical tubes were fixed on each coated steel plate (to check repeatability). The exposed surface area of working electrode was 2 cm^2 .

FRA2 (frequency response analyzer) software (Eco Chemie B.V., Netherlands) was used to perform EIS measurements. All of the measurements were performed at open circuit potential at sinusoidal voltage amplitude equal to 10 mV over a frequency range of 10 MHz to 100 kHz at different immersion times. Electrochemical measurements were carried out in a three electrode cell. The reference electrode was a saturated Ag/AgCl electrode and platinum rod was used as counter electrode.

For evaluating the corrosion protection performance of the primers, the accelerated corrosion test in a salt

spray chamber (B.AZMA CTS- 114D, Iran) was conducted according to ASTM AS517-03. The samples were exposed to the NaCl fog for about 1500 h and were investigated for rusting on the areas with cutting, without cutting and blistering according to ASTM D1654-08, ASTM D610-01 and ASTM D714-02, respectively.

The scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy analysis studies were carried out using a SEM model VEGA3 XM (TESCAN, Czech Republic). The elementary compositions of the cross section were analyzed using energy dispersive X-ray (EDX) analysis.

The adhesion of the coating to the substrate was estimated using cross cut testing methods according to ASTM D 3359.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

Bode plots of the EIS spectra for different coatings obtained at various immersion times in 3.5 wt. % NaCl solutions are presented in Figures 1-7.

Figures 1, 4, 5 correspond with the model shown in Figure 8a. After 13 and 18 days of immersion time for AS and A series respectively, the Bode plots show two capacitive time constants.

Figures 2, 3, 6 and 7 relate to the model shown in Figure 8b. In the Figure 8, R_c corresponds to the charge transfer resistance processes taking place within the pores of coating and R_{ct} corresponds to the resistance of substrate/coating interface in the range of low frequencies. The impedance reduction for first few days is due to zinc particles activation, and then it increases because of reducing the active surface area due to zinc consumption and zinc corrosion products formation in the pores of the coatings. Spectra depression is related to the porous nature of the coatings [7,18].

Table 3 shows the EIS extracted parameters for AS series (samples modified with acrylic/styrene). The results indicate that the charge transfer resistance of AS10 (containing 10% of acrylic styrene) is higher than the others during 18 days of immersion time and showed better corrosion resistance than the other coatings. As mentioned in Table 3, from day 18 to 94 the charge transfer resistance of AS20 (containing 20% acrylic styrene) is a little more than AS10 and it seems that the corrosion product of AS20 is more stable than AS10.

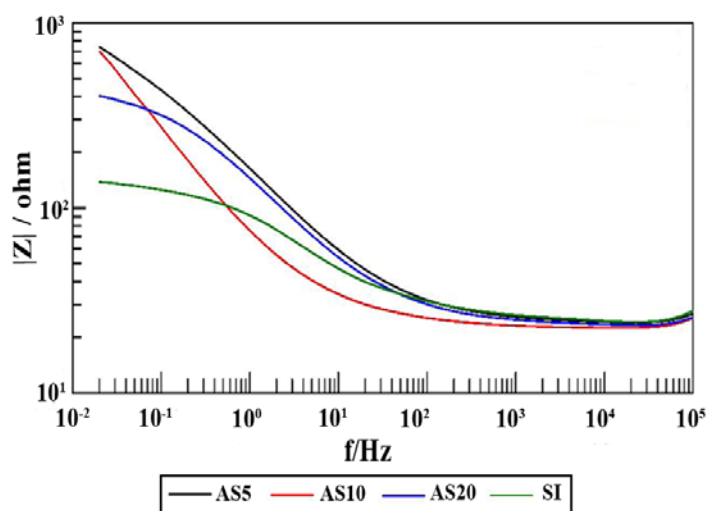


Figure 1: Bode plots of the EIS spectra for AS series after 1 day immersion in 3.5 wt.% NaCl solution.

Table 3: Parameters obtained from EIS spectra fitting for AS series.

Immersion time (days)	Coatings	R_{ct}	R_c
1	AS5	915.4	
	AS10	11431	
	AS20	448.9	
	SI	123.1	
18	AS5	384.6	396.9
	AS10	4667	1.033E4
	AS20	1516	2867
	SI	68.19	340.4
57	AS5	157.3	3821
	AS10	252.7	1.204E4
	AS20	614.9	1.346E4
	SI	300.5	4515
94	AS5	925.8	8806
	AS10	549.8	1.093E4
	AS20	2420	1.635E4
	SI	373.4	5141

Table 3 also shows that all of the AS series samples have extremely higher charge transfer resistance than SI series (containing no organic resin) and show better corrosion protection. This is related to the second mechanism of protection, formation and accumulation of corrosion product (barrier protection).

As depicted in Table 4, the EIS results of A series

(modified with acrylic) indicated that the charge transfer resistance of A5 sample (containing 5% of acrylic resin) is higher than the others in all immersion times. This means that the adding of 5% acrylic resin into the inorganic silicate binder improves corrosion prevention, but adding more than 5% did not improve corrosion prevention effectively.

Table 4: Parameters obtained from EIS spectra fitting for A series.

Immersion time (days)	Coatings	R_{ct}	R_c
1	A5	16967	
	A10	15531	
	A20	3850	
	SI	690	
5	A5	277.1	
	A10	246.9	
	A20	270.2	
	SI	189.7	
13	A5	65.32	1516
	A10	104.5	870.6
	A20	200.6	1042
	SI	64.71	817.3
57	A5	2268	7562
	A10	136.3	4208
	A20	229.2	2671
	SI	300.5	4515
94	A5	1416	1.17E4
	A10	160.5	5247
	A20	329.8	6311
	SI	373.4	5141

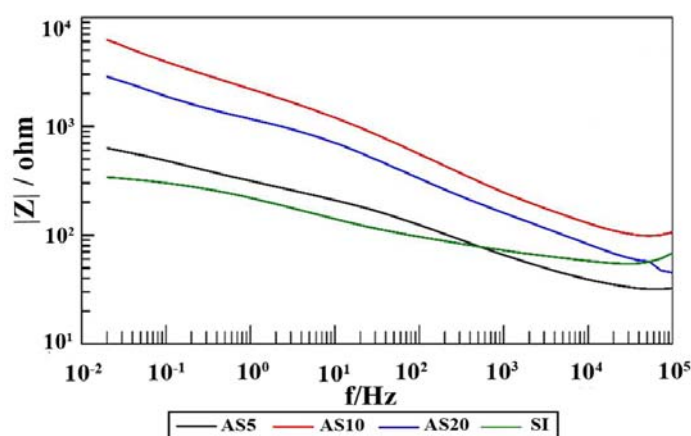


Figure 2: Bode plots of the EIS spectra for AS series after 18 days immersion in 3.5 wt.% NaCl solution.

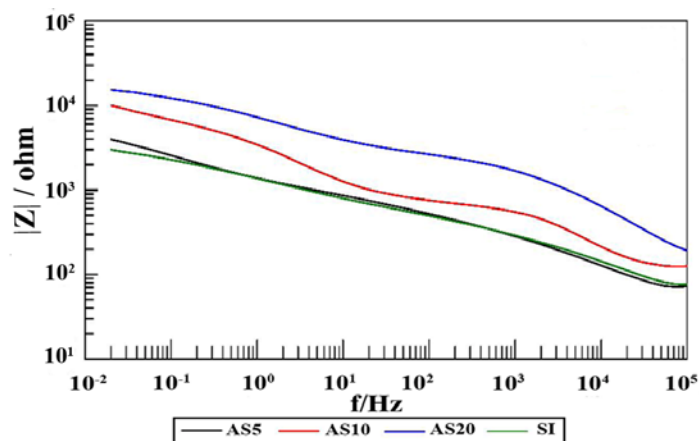


Figure 3: Bode plots of the EIS spectra for AS series after 94 days immersion in 3.5 wt.% NaCl solution.

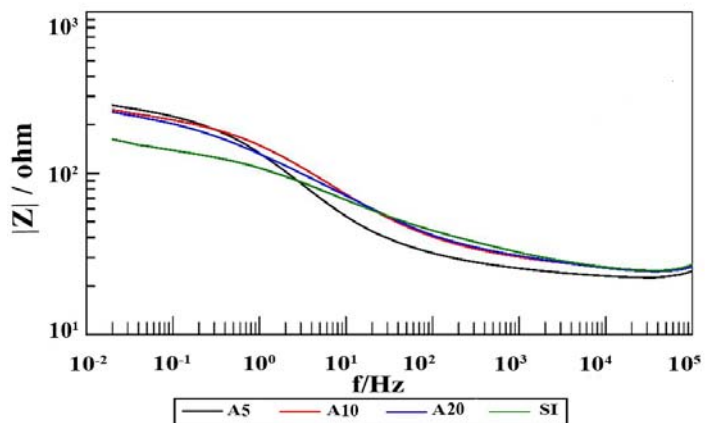


Figure 4: Bode plots of the EIS spectra for A series after 5 days immersion in 3.5 wt.% NaCl solution.

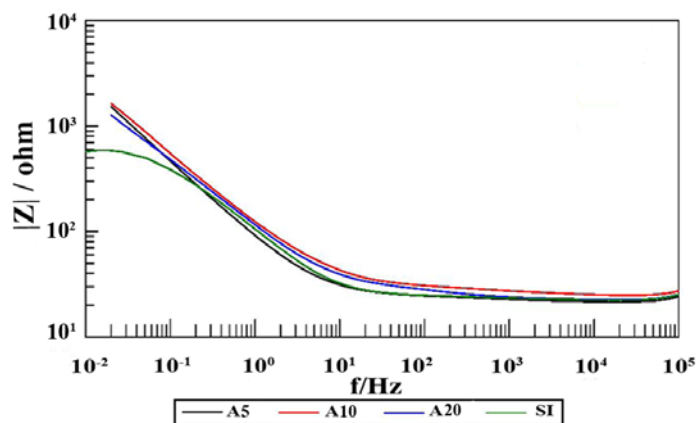


Figure 5: Bode plots of the EIS spectra for A series after 1 days immersion in 3.5 wt.% NaCl solution.

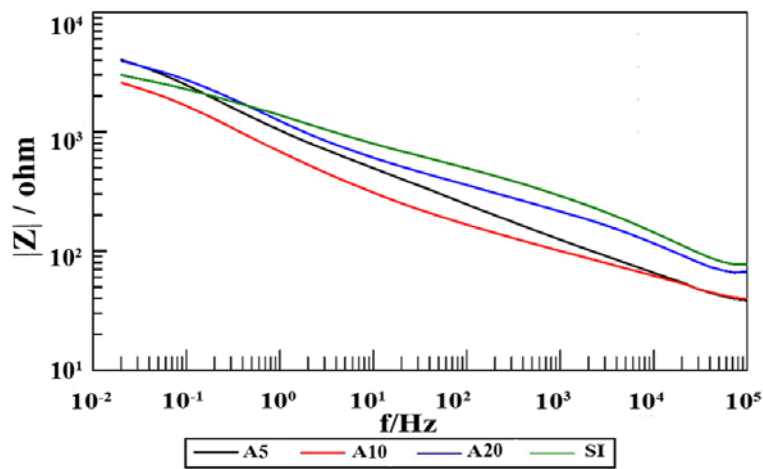


Figure 6: Bode plots of the EIS spectra for A series after 94 days immersion in 3.5 wt.% NaCl solution.

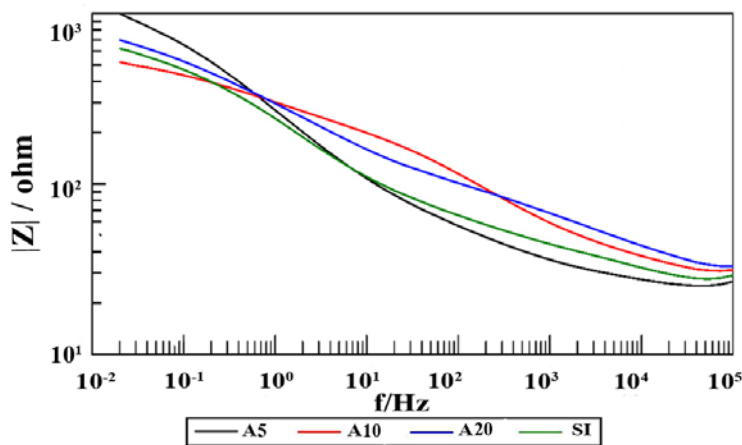


Figure 7: Bode plots of the EIS spectra for A series after 13 days immersion in 3.5 wt.% NaCl solution.

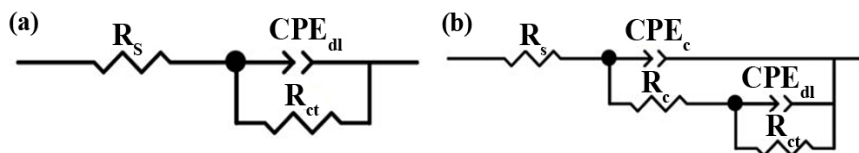


Figure 4: Equivalent circuits used for numerical fitting of the impedance plots obtained for (a) short immersion times and (b) long immersion times.

3.2. Corrosion potential (E_{corr}) measurements

In order to investigate the cathodic protection duration and electrochemical activity of the modified coatings, E_{corr} measurements were performed. Figure 9

shows the variation of corrosion potentials during immersion times for samples with different formulations exposed to 3.5 % NaCl electrolyte solution.

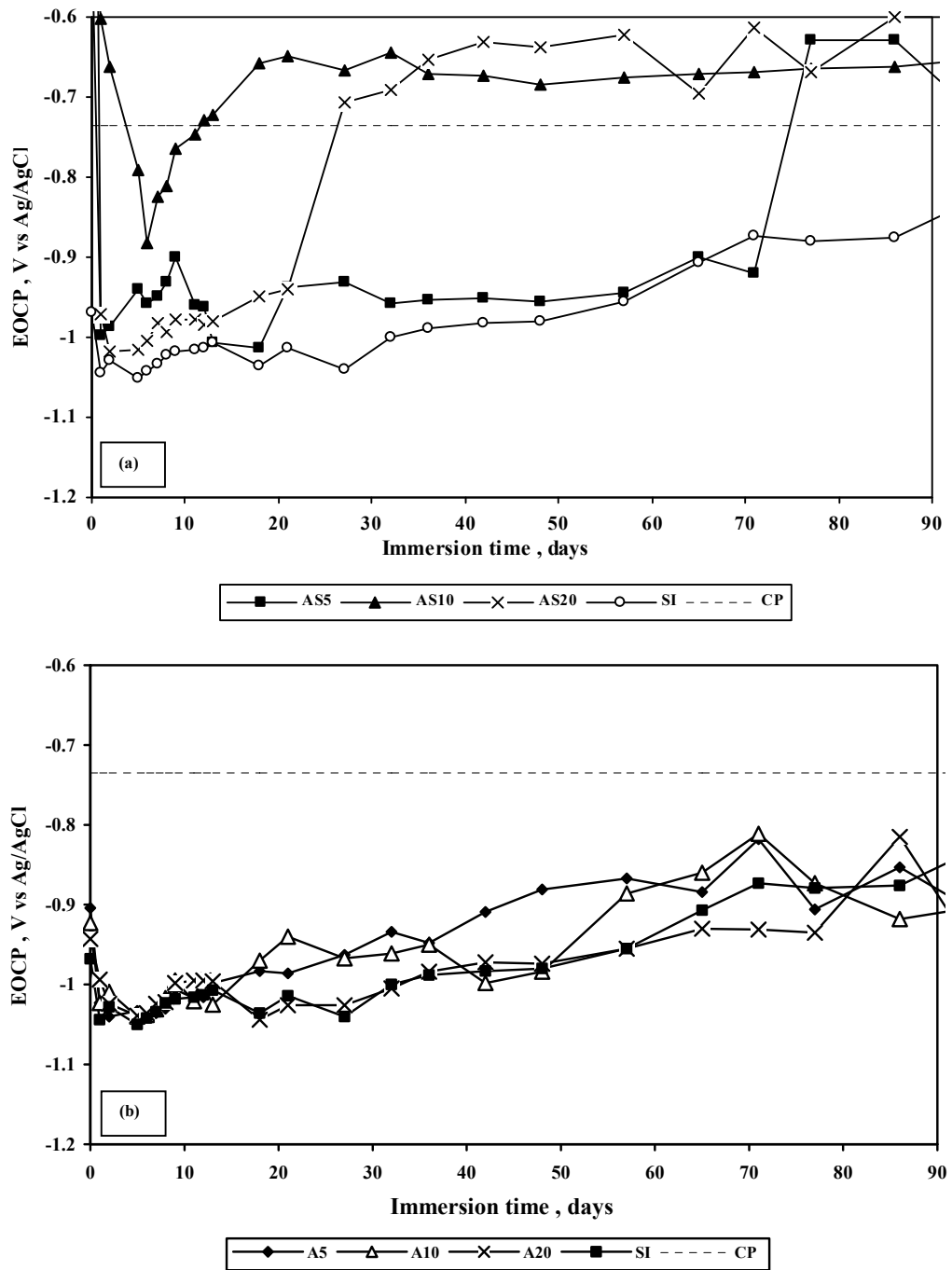


Figure 5: Variations in corrosion potential with time for (a) AS series and (b) A series.

It must be noted that the variation of E_{corr} values depends on the ratio of zinc to steel (active areas) [10]. According to the commonly accepted criterion to provide cathodic protection, E_{corr} value should remain lower than $-0.735 \text{ V(Ag/AgCl)}$ equivalent to -0.780 V(SCE) [19].

As shown in Figure 9, in both series at first, the corrosion potential shifted cathodically to negative values as a result of increasing Zn/Fe area ratio due to activating the zinc particles by reaction with the electrolyte. Then, the corrosion potential increased reaching to the potential over which cathodic protection is no longer efficient as the Zn/Fe area ratio decreases due to zinc corrosion and isolation of the zinc particles by the zinc corrosion products.

In the AS series, AS5 with 5% acrylic/styrene has longer cathodic protection duration than AS10 and AS20. AS5 has 77 days cathodic protection duration, but AS10 and AS20 have very short cathodic protection duration,

i.e. 12 and 27 days, respectively. The unmodified sample SI did not lose its cathodic protection during immersion time. This can be explained by the reduction in zinc pigments connections and stabilization of corrosion products as a result of high wettability of modified resin with acrylic/styrene. Figures 9 (a) and (b) show that in A series, none of the samples lost their cathodic protection during immersion time. It seems that A20 with 20% acrylic resin has a better cathodic protection than the others.

3.3. Salt-spray chamber test

The photographs of the samples during 1500 h exposure in the salt spray (fog) chamber are presented in Figure 10. After 1000 h (6weeks) of exposure in salty fog cabinet, some blistering but no rusting has been observed on the coatings. Using ASTM D610-01, the amount and distribution of visible surface rust were quantified.

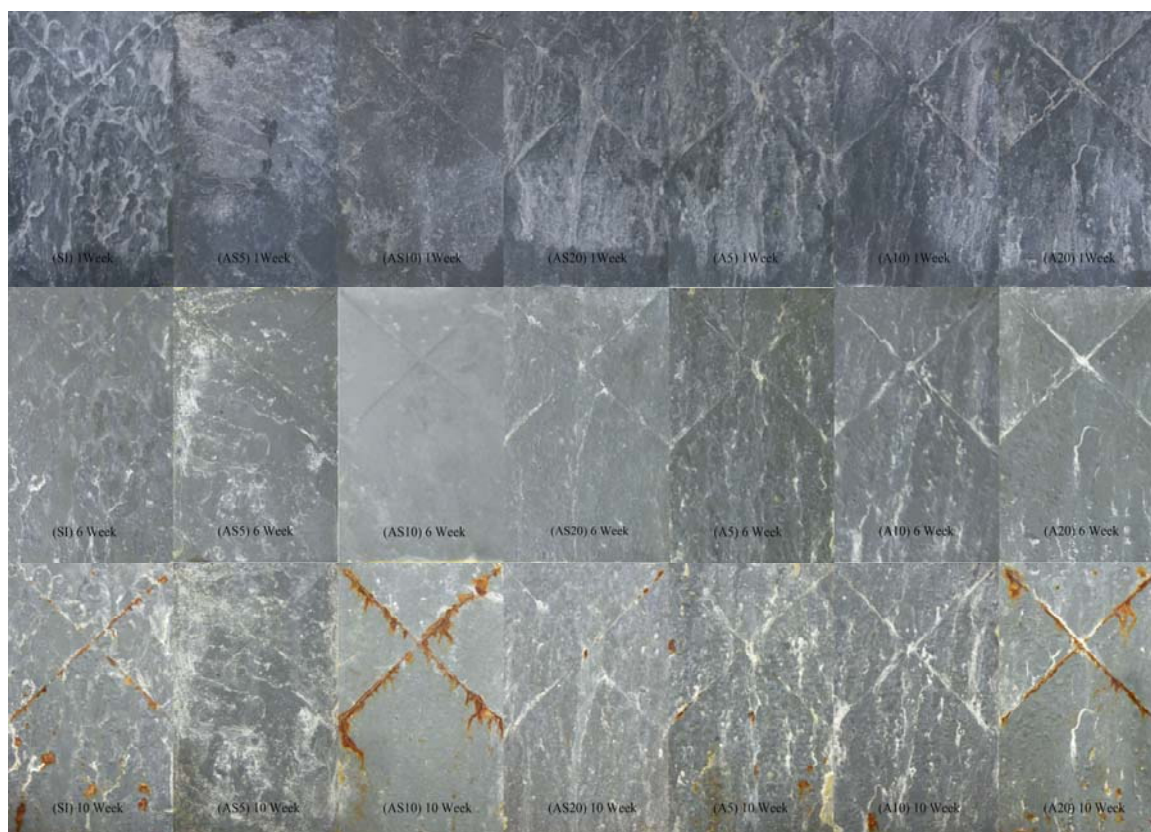


Figure 6: The photographs of the samples during 1500 h exposure in the salt spray (fog) chamber.

The degree of rusting corresponding to the areas without cutting was determined using rust grade of 0-10 where 0 indicates that greater than 50 percent of surface is rusted and 10 indicates that less than or equal to 0.01 percent of surface is rusted, followed by the type of rust distribution identified by *S* for spot, *G* for general, *P* for pinpoint or *H* for Hybrid. The results are displayed in Table 5.

According to this standard, all samples showed better corrosion resistance in areas without cutting than the unmodified sample (SI). Moreover, results of Table 5 allow concluding that series AS almost showed better anticorrosive function in areas without cutting than series A which is in agreement with EIS results. Rust creepage at scribed areas can be determined using ASTM D1654-08 by measuring overall width of the corrosion zone and width of the original scribe. Creep values reported in millimeters and rating numbers. All samples except AS10 and A20, showed better protective performance against rust creepage than unmodified sample. No signs of rust creepage at scribes of AS5 and A10 were observed after 1500 h exposure and they had the best performance. Using ASTM D714-02, we identified the size and density (frequency) of the blisters on the coatings.

The size of the blisters was identified by numbers from 10 to 0, in which No.10 represents no blistering. Nos. 8 and 2 represent the smallest and largest size blister, respectively. The frequency of blister occurrence was identified by some letters which come after the number of blister size. The greatest frequency of blister occurrence is showed with letter D (dense), whereas less dense blister is marked as MD (medium dense), M (medium) and F (few) [20]. The degree of blister on the

coating increases according to the following order AS5<A20<A10<AS10<AS20<SI<A5.

We also did this for areas near cutting of the coatings to obtain anticorrosion efficiencies [20]. The degree of blister in areas near cutting of coatings increases according to the following order A20<A10<AS10<AS20<SI<AS5<A5. Overall, the samples take the following order of salt spray resistance AS5>A10>AS20>A20>A5>AS10>SI.

The silicate binder provides different functions as: binding the zinc particles together, adhesion to steel substrate, cohesion (strength of the zinc rich coating), abrasion resistance and chemical resistance (except against hydrofluoric acid). However these binders have excellent resistance to radiation, including nuclear radiation and in the inert nature provides excellent weather resistance with no weather-related failure, such as chalking, cracking or other deterioration effects.

The enhancement of corrosion resistance of the modified binder coatings may be due to high wettability of modified binders which help to enhance coating adhesion to the substrate and increase the barrier properties of the coatings.

3.4. SEM observation

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis was used to study the structure of coating and the protective mechanism of the zinc pigment in the coating.

Figure 11(a) represents AS5 sample covered with the oxidation products (white corrosion) after 77 days exposure to 3.5 % NaCl solution. Sealing of the pores is necessary to secure the barrier protection of the substrate.

Table 5: Anticorrosive performance evaluation of the salt-spray tested paint coatings.

Coatings code	Blisters in paint area (ψ 1), ASTM D714	Blisters near section (ψ 2), ASTM D714	Primer corrosion in section (ψ 3), ASTM D1645	Primer corrosion in area (ψ 4), ASTM D610	Anticorrosion efficiency (α)
SI	2MD	2M	8(1mm)	5-G(3%)	38.75
AS5	6M	6MD	10(0)	9-S(0.03)	61.25
AS10	6MD	6M	6(3)	8-G(0.1)	46.25
AS20	4MD	4M	9(0.5)	9-G(0.03)	50.63
A5	4D	4MD	9(0.5)	7-G(0.3)	48.75
A10	6MD	6M	10(0)	7-S(0.3)	56.75
A20	2M	2F	7(2)	6-G(1)	50.63

EDX analysis of AS5 (which had the best cathodic protection duration in AS series) was performed after 77 days exposure to 3.5 % NaCl solution and results are given in Figure 11. No presence of iron was detected and the coating was provided satisfactory cathodic protection to the steel substrate.

3. 5. Adhesion measurement

In the case of the pull-off adhesion tests before exposure of coated sample to corrosive environment, it was observed that all the coatings have good adhesion to substrate and the coatings did not detached from the steel substrate.

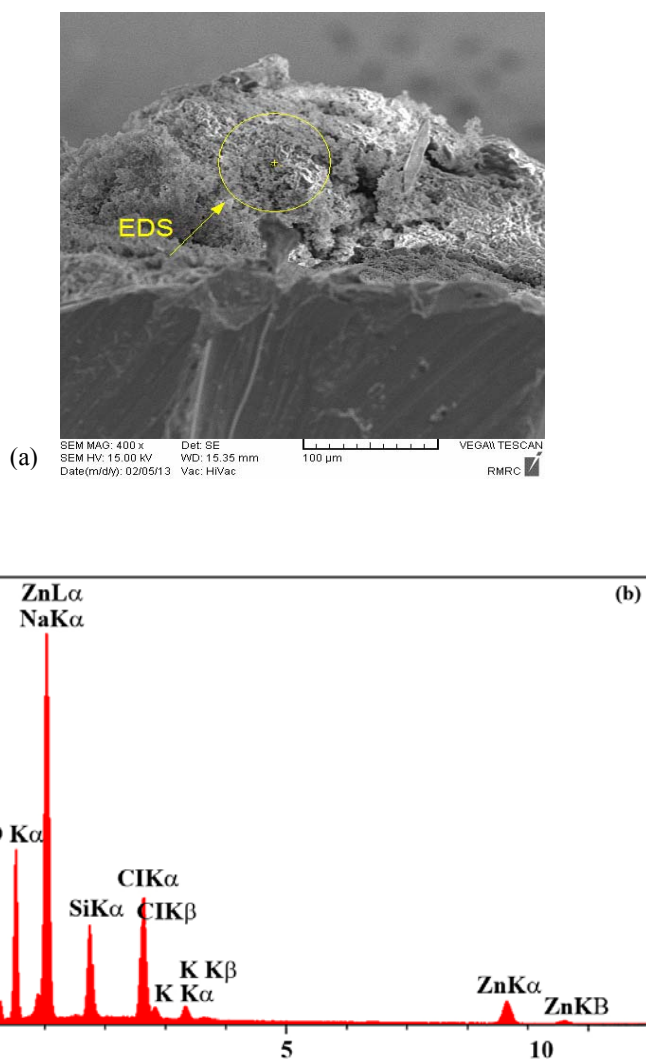


Figure 7: (a) SEM Image and corresponding (b) EDX spectrum of AS5 sample.

Table 6: Results of cross cut adhesion test.

Sample	AS5	AS10	AS20	A5	A10	A20	SI
Grade	5B	4B	4B	3B	5B	4B	3B

Table 6 shows the results of cross cut adhesion test after exposure to 1500hr salt spray; AS5 and A10 (modified) coatings have a stronger adherence to the substrate than the SI (unmodified) coating. The modified potassium silicate vehicle contains acrylic derivatives, which reduces the brittleness of the silicate coating and improves the adhesion indirectly. It seems that in the modified samples, the better flow and leveling properties of the modified samples were the reasons for forming better, continuous and compact coating films which provided a strong adhesion to the steel substrate.

4. Conclusions

Addition of 5, 10 and 20 wt% of acrylic and

acrylic/styrene copolymer, as binder modifier into the formulation of alkali silicate based zinc rich primer was studied. Electrochemical studies showed that the presence of water based acrylic derivatives in the formulations did not lead to the improvement of cathodic protection duration of the primers. Additionally, corrosion resistance and adhesion of coatings containing modified binder were improved due to the better sealing action of zinc corrosion products. Salt fog test results showed that the best results were achieved by introducing 5% acrylic/styrene copolymer and/or 10% acrylic resin as binder modifier into the coating formulations. Adhesion measurement tests showed that the adhesion of primers containing modified binder, in comparison with unmodified samples, was surprisingly increased.

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