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Effect on temporary protection and adhesion promoter of silane nanofilms applied on electro-galvanized steel

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ABSTRACT

In this paper, the effectiveness of γ-mercaptopropyltrimethoxysilane (MTMO) films as temporary corrosion protection and adhesion promoter on electro-galvanized steel was studied. The films were synthesized from hydrolyzed MTMO with ethanol or methanol, applied by immersion on electro-galvanized steel and cured under different conditions. The porosity of the coating was evaluated by cyclic voltammetry, the corrosion behavior by polarization curves and the protection degree by exposure in the humidity and prohesion chambers. The films were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). From the obtained experimental results, it was concluded that this protection is markedly affected by the coating curing conditions and the alcohol used in the hydrolysis. MTMO is a good temporary protector against electro-galvanized steel corrosion in high humidity environment but it is less effective in environments containing aggressive ions such as Cl^- and SO_4^{-2}.

In a second stage, pretreated samples were coated with an alkyd anticorrosive paint and exposed to the salt spray chamber. Dry adhesion tests as well as SEM and EDS studies were also done in order to know the nature of the disbonding fails (adhesion or cohesion).

1. Introduction

The electro-galvanized steel is used in a wide range of consumer goods. It can be painted for aesthetic reasons or due to consumer demand. The combination of paint and galvanized steel is known as duplex system and has a synergistic effect because its useful service life is greater than the sum of the galvanized steel or painted steel systems considered separately [1–3].

After applying the zinc coating on the steel substrate, the surface is very active, so, in order to prevent the formation of zinc oxides and hydroxides during storage and until the product is put in service a pretreatment is applied. In most cases, the galvanized steel will be painted, demanding the pretreatment to be a suitable adhesion promoter. Although direct correlation between adhesion strength and corrosion protection seems not to exist, the maintenance of some adhesion level is necessary for preventing corrosion progress or at least to delay the access of aggressive species to metal substrate and the diffusion along the metal/coating interface [4,5]. The most efficient pretreatments used as corrosion temporary protection and/or adhesion promoters of galvanized steel are based on Cr (VI) and zinc phosphate [6]. However, the high toxicity and carcinogenic nature of the Cr(VI) creates the necessity to look for new environmental-friendly alternatives as replacement [7–11]. In this sense, pretreatments with functionalized silane solutions rise as an alternative because they are not toxic and can form a protective barrier on the metal. The protection capacity of this barrier depends not only on the film thickness and porosity but also on the silane nature [12–17]. Although silane films do not provide the self-healing effect afforded by the Cr(VI) ions, these properties can be given by the addition of anticorrosive ions such as cerium [18–23]. Also, silanes films are harder, more resistant to erosion and show good thermal stability.

In general, the silane is hydrolyzed before its application to the substrate in order to form silanol groups, Fig. 1a. Silane adheres to the metal substrate by covalent bonds resulting from the reaction between the silanol formed during the hydrolysis and the oxides-hydroxides groups present on the metal surface, Fig. 1b [18,22,24,25].

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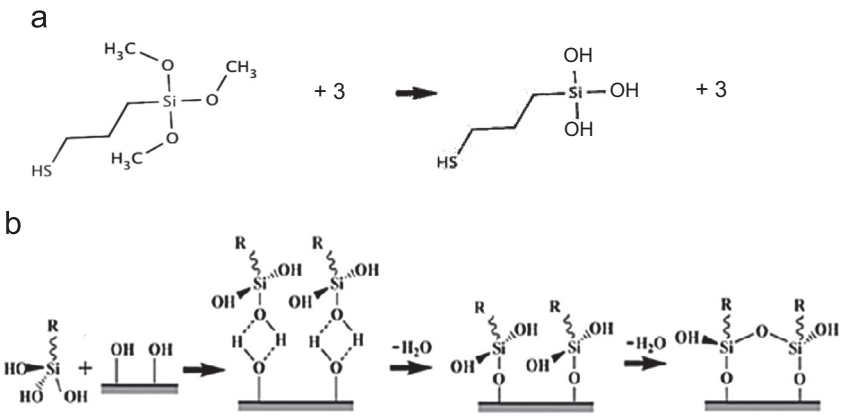

Fig. 1. a) Hydrolysis of MTMO; and b) Adhesion mechanism of the silane to the metal substrate.

The aim of this work was to evaluate the use of methanol or ethanol as a component of the hydrolysis solvent and to study the time and temperature influence of the curing process on the final silane film properties.

The porosity of the obtained films was evaluated by cyclic voltammetry (CV), the protective performance by polarization curves and by exposure tests in humidity and prohesion chambers (HC and PC, respectively). In these cases, the corrosion degree was evaluated as a function of the exposure time. Finally, the film morphology and composition were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). For comparison purpose uncoated electro-galvanized steel sheets (EG) were also tested.

In a second stage, silane pretreated samples coated with alkyd paint were exposed to the salt spray chamber (SSC) to evaluate the corrosion behavior of duplex systems. Dry adhesion was assessed and, after the corrosion test, the area underneath the removed paint was observed by SEM and studied by EDS to know the nature of the failure (adhesion or cohesion).

2. Experimental details

2.1. Zinc electrodeposition

SAE 1010 steel coupons (40 mm x 80 mm x 0,7 mm) were electrochemically cleaned in 20% (w/v) NaOH at 30 A/dm^2 for 20 s at 22 ± 1 °C, pickled with 30% (w/v) HCl solution at the same temperature, and washed with distilled water. After cleaning and pickling, the samples were electro-galvanized in acid (pH=2) Zn_2SO_4 electrolyte (90 g/L of Zn^{+2}) at 40 A/dm^2 for 20 s giving a uniform 7 μm zinc coating, determined by gravimetry.

2.2. Sol–gel pretreatment

2.2.1. Methanol/water solvent mixture

The silane suspension was prepared by dissolving two volumes of MTMO in three volumes of methanol/water solution (1.5/1 v/v) [26]. pH of the methanol/water solution was previously adjusted to 4 with acetic acid. The suspension was stirred at 22 ± 1 °C for 1 h in order to complete the dissolution process [25]. After reaction, a tenfold dilution with the same methanol/water solution was done [26]. The final concentration of MTMO was 4% v/v.

Finally, some electro-galvanized steel sheets were immersed in the solution for 1 min. The samples were then distributed in three groups to be cured in an oven at different conditions: (a) 80 ± 2 °C for 10 min; (b) 100 ± 2 °C for 10 min, and (c) 20 °C for 2 days.

Table 1
Processes of silane application, curing conditions and samples identification.

Hydrolysis solvent	Curing conditions		Sample code	Painted sample code
	Temperature (ºC)	Time		
Methanol/water	20	2 days	M2	PM2
	80	10 min	M8	PM8
	100	10 min	M10	PE10
Ethanol/ water	20	2 days	E2	PE2
	80	10 min	E8	PE8
	100	10 min	E10	PE10
Control coupons (electro-galvanized steel)	–	–	EG	PEG

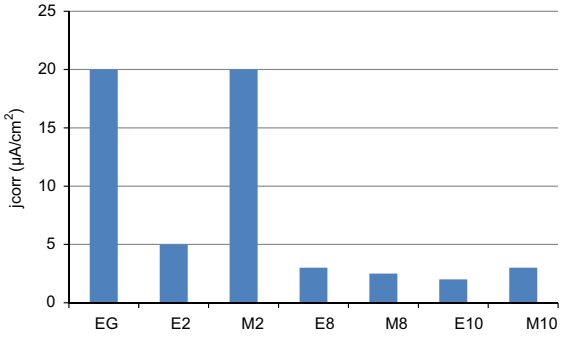

Fig. 2. Corrosion current density (J_{corr}) of bare and pretreated samples.

2.2.2. Ethanol/water solvent mixture

The MTMO hydrolysis was also done in ethanol/water (15/1 v/v) solution [27]. In this case, 4% (v/v) MTMO was hydrolyzed in the solvent mixture at 22 ± 1 °C for 1 h. The pH of the ethanol/water solution was adjusted to 4 with acetic acid. The electro-galvanized steel sheets were immersed in the MTMO solution for 1 min and then cured in an oven considering the same conditions indicated in the previous paragraph.

The used solvents mixtures, curing conditions, samples code and painted samples code are presented in Table 1.

2.3. Pretreated samples

2.3.1. Cyclic voltammetry and polarization curves

As recommended by Titz et al. [28], CV was performed in aerated borate solution (35 g/L of H_3BO_3 and 40 g/L of $Na_2B_4O_7.10H_2O$) from −1500 to 0 mV versus saturated calomel electrode (SCE) with a scan rate of 100 mV/s. In this electrolyte, the

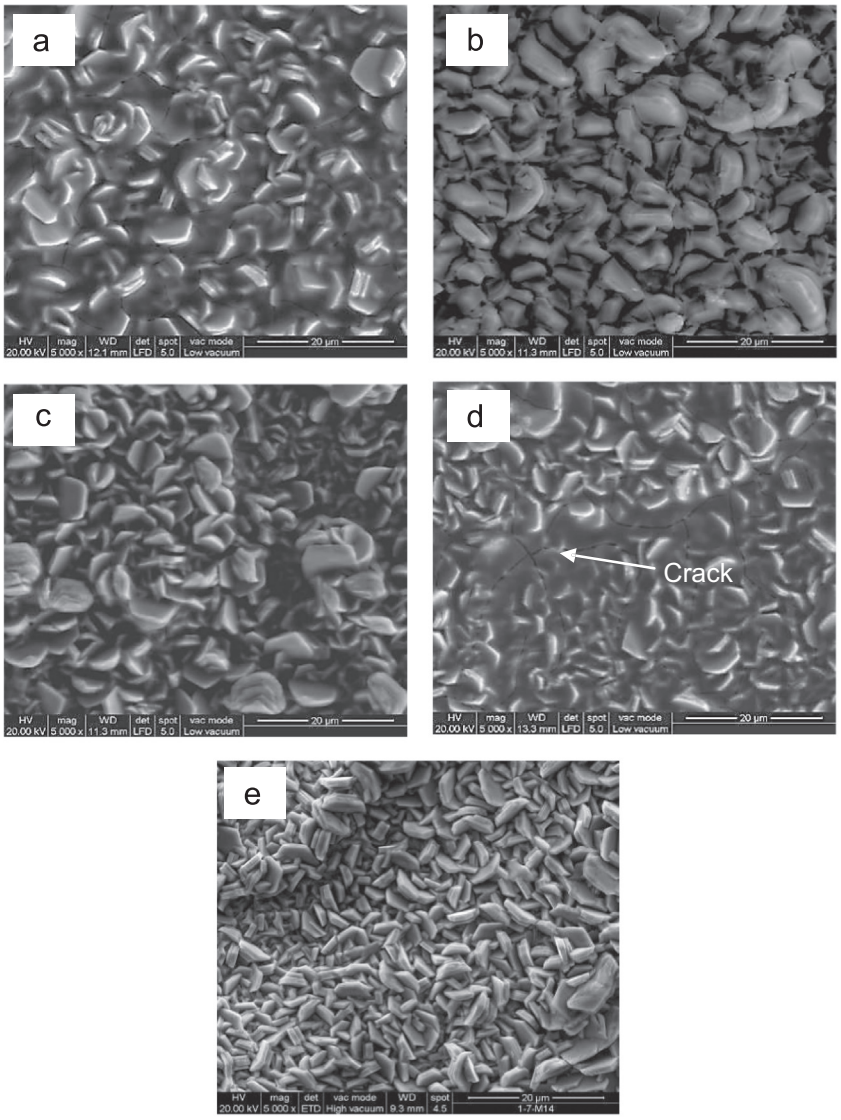

Fig. 3. Microphotographs of the pretreated samples (5000 ×). a) M8; b) E8; c) M10; d) E10; e) EG.

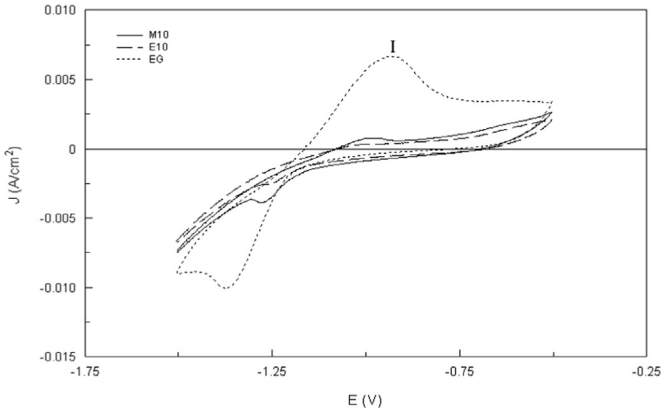

Fig. 4. Cyclic voltammetry of the M10, E10 and EG samples.

current density curves for zinc electrodes showed a dissolution anodic peak followed by a passive region. Integration of this peak gave an anodic charge proportional to the active Zn surface area. Therefore, as the silane-based coating protects the substrate only as a physical barrier, the coating porosity may be evaluated by this technique [29].

Polarization curves in 0.05 M NaCl solution at 22 ± 1 °C, with a potential sweep rate of 0.166 mV/s in the range ± 50 mV from the open circuit potential (OCP) were obtained by a Potentiostat/Galvanostat PAR 273 A controlled by the CorrWear® software. The working electrode (pretreated electro-galvanized steel sheets) area was 1 cm^2. A Pt ring of great area and a SCE were used as counter and reference electrodes, respectively. The corrosion current density (J_{corr}) was determined by linear extrapolation of the anodic E vs. J curves at the corrosion potential (OCP) [22,30–32]. Before each polarization run, the immersed working electrode was kept at rest until a stable OCP reading was obtained.

Three replicates were tested.

2.3.2. Film examination and characterization

The pretreated samples were observed by SEM, while the protective film composition was characterized by EDS using a FEI Quanta 200® microscope with electron detector Apollo 40® and EDAX® detector.

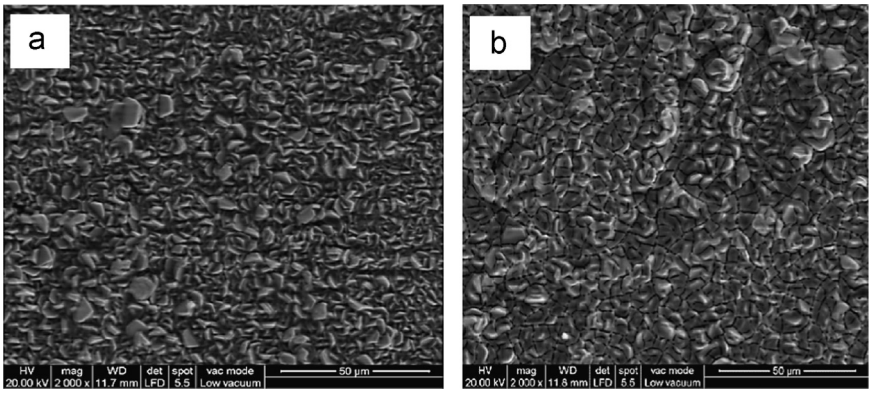

Fig. 5. Microphotographs of the pretreated samples (2000 ×). a) M2; b) E2.

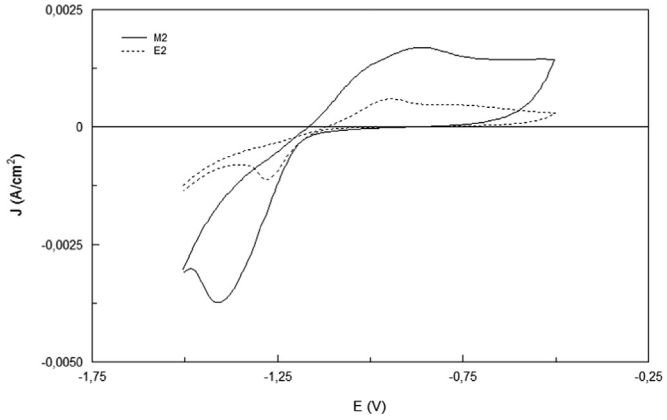

Fig. 6. Cyclic voltammetry of the M2 and E2 samples.

Table 2
Summary of some results.

Sample code	Film morphology		Painted sample code	Adhesion failure
M2	Thin	No cracks but pores	PM2	Chemical interaction; failure for cohesion
M8		Cracks	PM8	
M10		Few cracks	PM10	
E2	Thick	Cracks	PE2	Physical interaction; silane-paint failure
E8		Completelly cracked	PE8	
E10		Few cracks	PE10	

2.3.3. Exposure to environmental chambers

To simulate storage conditions the samples were placed in the laboratory at controlled conditions of 20 °C and 80% relative humidity for 85 days. Three replicates of the different sample types were then placed in the HC (ASTM D2247 standard) or in the PC (ASTM G85-A5 standard) for 264 h. The prohesion test included the exposure to alternating cycles with NaCl 0.05% (w/v) and $(NH_4)_2SO_4$ 0.35% (w/v) spray at 25 °C followed by heating up to 35 °C. This chamber simulates an urban-industrial environment.

In both chambers the corrosion degree (ASTM D610 standard) was evaluated. Bare electro-galvanized steels panels were also exposed as controls.

2.4. Painted samples

A set of the pretreated samples was coated with an alkyd paint to evaluate the duplex system corrosion behavior. The paint composition was: 9.4% of zinc molybdophosphate as anticorrosive pigment, 3.8% of TiO_2, 9.1% of talc, 9.1% of barium sulfate, 43.6% of alkyd resin (1:1) and 25% of mineral spirit, by volume. The dried paint thickness (80 ± 5 µm) was measured by a coating thickness gauge from Schwyz.

2.4.1. Assays on painted panels

Dried adhesion tests were conducted by tape test (ASTM D 3359 standard) and impact (ASTM D 2794 standard) methods.

The samples were placed in the SSC (ASTM B117 standard) for 49 days. The corrosion and/or blistering degrees (ASTM D610 or ASTM D714 standards, respectively) were evaluated over time.

3. Results and discussion

3.1. Pretreated samples

The polarization curves performed on bare and pretreated samples cured at 80 °C or 100 °C show that the corrosion current density of the treated samples is around one order of magnitude less than the corresponding to the bare electro-galvanized samples (Fig. 2); no significant effect of the solvent hydrolysis or curing conditions was observed. However, SEM images of those samples display that the film morphology was highly dependent on both, the co-solvent hydrolysis and the curing temperature (Fig. 3). When cured at 80 °C, the films obtained using methanol as co-solvent exhibit very thin cracks (≈ 0.2 µm) while those built-up in ethanol seemed to be not only thicker but also completely cracked, Fig. 3a and b, respectively.

The increase of 20 °C in the curing temperature produced morphological changes. The films observed on M10 and E10 samples show less cracks than those on M8 and E8 samples, Fig. 3c and d, respectively. For comparison purposes, Fig. 3e shows the SEM image of the bare metal substrate. Cracks occur during the polymerization process due to internal stresses generated within the coating, especially in hard films. Hydrolyzed with ethanol, the coatings are thicker but have higher level of cracks that do not reach the zinc substrate. This is evidenced by the results obtained in the cyclic voltammetry, where in samples cured at 100 °C, the area under the curve of the anodic peak (I) for both alcohols is similar and negligible compared to that of the EG sample, Fig. 4. This indicates that the porosity of the two coatings is similar and, therefore J_{corr} values are also similar since these coatings protect the substrate only by physical barrier effect. The film composition obtained by EDS was similar for both coatings hydrolyzed with methanol or ethanol as co-solvent (C/Si/S = 1.0-2.9/1.0/0.6-0.7).

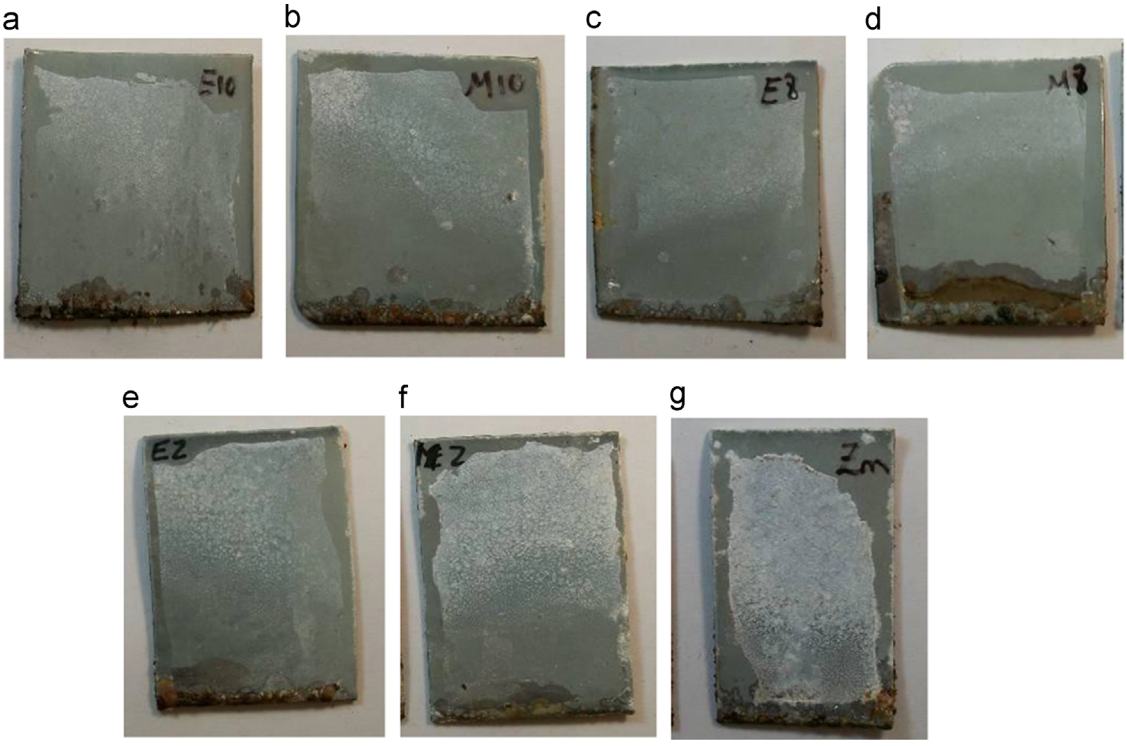

Fig. 7. Photographs of the pretreated samples after 264 h of exposure in the HC. a) E10;, b) M10; c) E8; d) M8; e) E2; f) M2; g) EG.

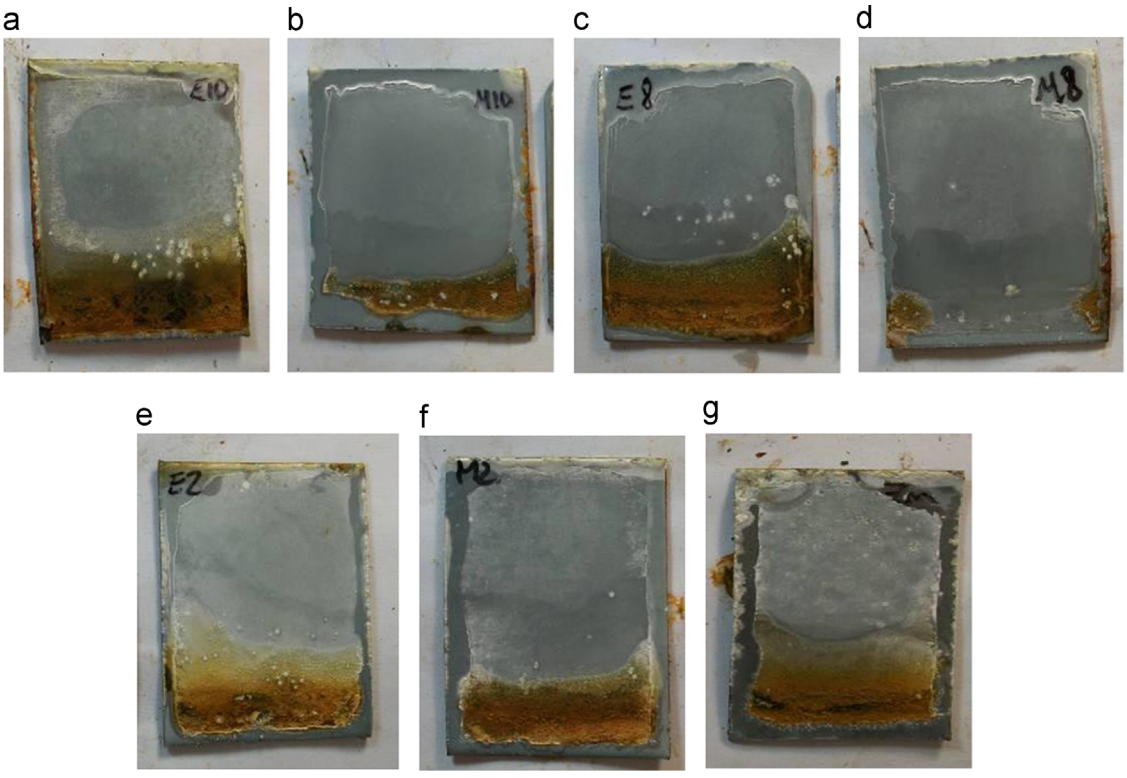

Fig. 8. Photographs of the pretreated samples after 264 h exposure in the PC. a) E10; b) M10; c) E8; d) M8; e) E2; f) M2; g) EG.

Fig. 2 shows that the corrosion behavior of M2 and E2 samples was quite different as a function of the used co-solvent. M2 seemed to be unprotected, $J_{corr}(M2) \cong J_{corr}(EG)$, whereas E2 samples showed a substantial protection level, $J_{corr}(E2) \cong 0.25 \times J_{corr}(EG)$. On the surface of M2 samples, the zinc structure is clearly observed (Fig. 5a), indicating that the coating formed was very thin. No cracks were observed at higher magnification, but the film may have a high density of nanopores, which is evidenced by the J_{corr} values as well as by the presence of the anodic peak in the cyclic voltammetry, Fig. 6. However, E2 samples showed thicker coatings and micro-cracks, Fig. 5b.

Some of these results are presented in Table 2. The differences between replicates were less than 1%.

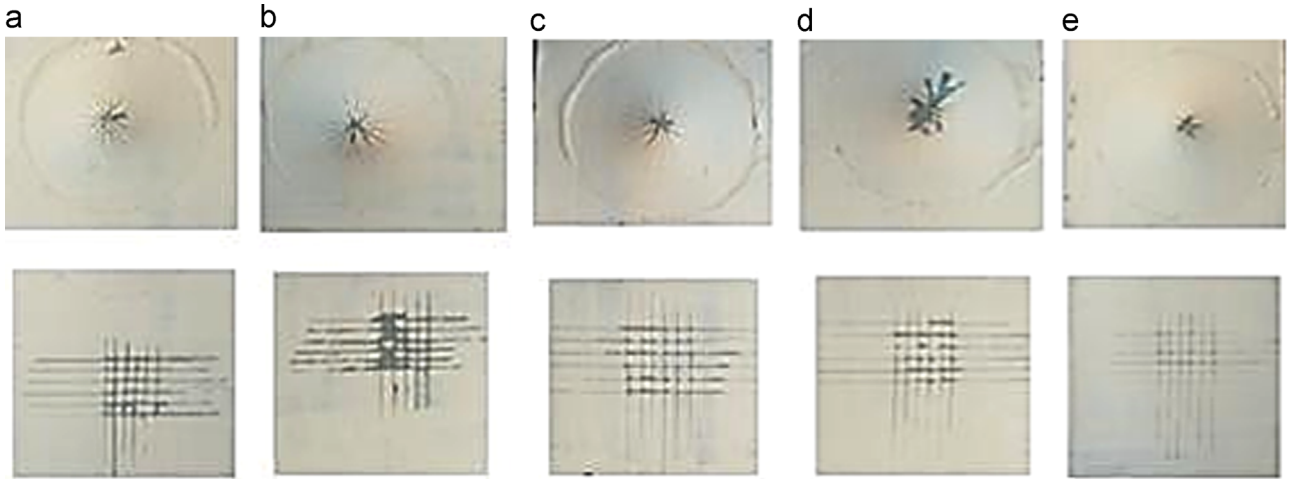

Fig. 9. Results of the dry adhesion tests (above: impact test; below: tape test). a) PM10; b) PE10; c) PE2; d) PM2; e) PEG.

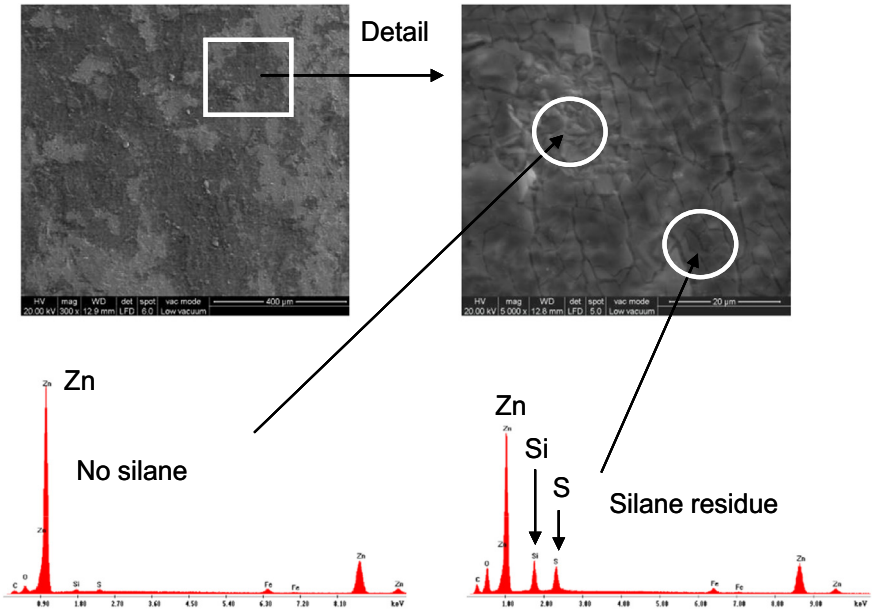

Fig. 10. SEM and EDS of the paint underneath area after adhesion test in PE8 sample.

After 264 h of exposure in HC the samples cured at 80 °C or 100 °C (hydrolyzed with methanol or ethanol) presented the best performance. Of the samples cured at 20 °C, E2 had a slightly better performance than M2. Finally, the sample without pre-treatment showed the worst performance, Fig. 7. In EG samples some iron corrosion products could be observed, which would be indicative of a certain loss of galvanic protection.

Under prohesion exposure conditions, especially the M8 and M10 samples cured at high temperatures, exhibited better corrosion performance than the rest of the tested ones while the E8 and E10 samples behaved quite similar to EG ones, Fig. 8.

3.2. Painted samples

Paint-silane adhesion would be the result of two effects: the first is related to the covalent bonds between the silane and the alkyd resin, and the second to the paint capability of penetrating the silane film between the cracks and thus to get better physical adhesion.

The adhesion tests showed that MTMO does not enhance the alkyd paint/electro- galvanized steel adhesion. Conversely, after the adhesion tests, a slightly more deteriorated coating was seen by naked eye in the pretreated samples, Fig. 9. With methanol as co-solvent, PM2 samples adhesion was similar to that of PM10

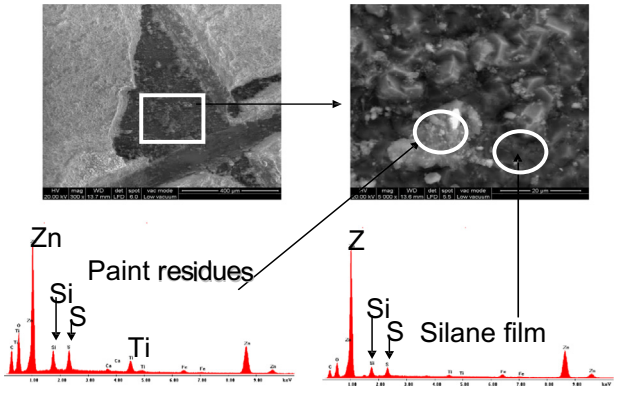

Fig. 11. SEM and EDS of the paint underneath area after adhesion test in PM8 sample.

Table 3
Evaluation of corrosion and blistering degrees of painted samples as a function of the exposure time in the SSC.

Sample	Exposure time (h)					
	576		816		936	
	Corrosion [a]	Blistering [b]	Corrosion [a]	Blistering [b]	Corrosion [a]	Blistering [b]
PE2	10	2F	10	2F	9	2F
PE8	9	10	9	6F	9	2F
PE10	10	10	10	8F	10	4F
PM2	9	6M	9	2M	9	2M
PM8	9	4F	9	2F	9	2F
PM10	10	10	10	2F	10	2F
PEG	10	4M	10	4M	9	4MD

Blisters's size: 10, no blisters; 8 smallest sizes seen by unaided eye, 6, 4, 2, sizes progressively larger.
[a] Corrosion degree: 10, no rusting; 9, less than 0.03% of surface rusted.
[b] Blisters's frequency: MD, medium dense; M, medium; F, few.

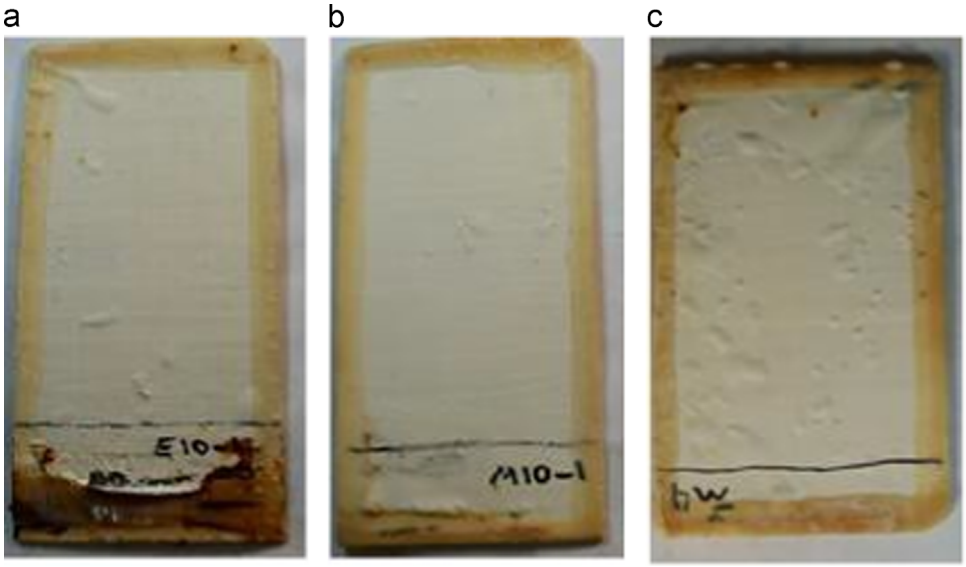

Fig. 12. Photograph of the painted samples after 936 h exposure in the SSC. a) PE10; b) PM10; c) PEG.

samples while with ethanol, PE2 samples had better adhesion than those cured at higher temperatures.

In PE8 samples, the areas under the removed paint did not display any sign of this film since no Ti (from TiO_2) was detected by EDS, Fig. 10. MTMO was present only in some parts of the surface, while in the others neither S nor Si was detected, indicating that the adhesion at the silane film/metal interface was the main failure. In PM8 samples studied by EDS the presence of Ti was detected, therefore, the failure was of cohesion, i.e. between layers of the paint film, Fig. 11.

The most important peaks of the EDS were marked.

When the ethanol/water mixture was used as hydrolysis co-solvent, the presence of cracks seemed to be more important than the chemical interactions since the higher adhesion was found in PE2 samples, i.e. where the crack number was also higher. In PE8 or PE10 samples there were fewer cracks, the paint could not interact adequately with the silane film and the silane/paint adhesion failed, Fig. 9.

If the methanol/water mixture was the hydrolysis solvent, the chemical interactions between the resin of the paint and the silane seemed to be more important independently of the film cracking degree. These chemical interactions allowed part of the paint to remain adhered to the substrate after the adhesion test; in other words, the fail was of cohesion between paint layers.

After the adhesion tests carried out by impact, SEM and EDS studies showed that on PM8 samples some traces of paint remained present while on PE8 samples only some silane traces were detected, in agreement with the tape test results.

Table 2 shows some of these results.

The evaluation of painted samples pretreated with MTMO and exposed to the SSC showed that the best protective behavior was obtained when the silane films were cured at 100 °C. In these cases, after 936 h of exposure no corrosion signs appeared on the painted surface, Table 3. Under the other curing conditions, the corrosion performance was similar to PEG (control). When the blistering degree was evaluated, the pretreated samples showed blisters whose size was similar to that of those formed on the blank, however, its frequency was much lower, Fig. 12. These results indicate that the pretreatment with MTMO did not improve the dry adhesion between electro-galvanized steel and alkyd-based paint, but increased the organic coating delamination resistance when it is exposed in an aggressive environment. As seen in Table 3, the co-solvent influence on the corrosion performance and blistering degree of samples cured under the same conditions was low.

4. Conclusions

In high humidity environments, MTMO films provide temporary protection to electro-galvanized steel. Nevertheless, in media with Cl^- and SO_4^{-2} ions, the results were not satisfactory.

The temporary protective capacity provided by the MTMO improved when the effect supplied by the coating cured at 20 °C for 2 days was compared with that obtained after curing at 80 °C or 100 °C for 10 min. The major difference was found when the hydrolysis was carried out with methanol. Increases ranging from 80 to 100 °C did not produce significant changes in the corrosion behavior of the system.

Taking into account that the results employing the different co-solvent were unimportant and being ethanol less toxic than methanol, its used is recommended. The MTMO incorporation to the metal/paint interface does not enhance the dry adhesion of the studied system. However, after the system was exposed to an aggressive environment, the delamination resistance of the organic coating increased.

The curing of the silane coating on electro-galvanized steel sheets at 100 °C improved the corrosion protection provided by the alkyd paint.

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