

Triplex systems: Accelerated and outdoor tests

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The protective paint/galvanized steel system is called duplex and it is claimed that protects steel from corrosion synergistically. The triplex system adds a pretreatment between the paint and the substrate in order to enhance the corrosion protection or paint adhesion. In this work, the behavior against the corrosion of electrogalvanized steel pretreated with a commercial silane, mercaptopropyltrimethoxysilane (MTMO) or a chromium(III)-based solution (Cr) was studied. Pretreated samples were painted with an alkyd system and exposed in humidity, prohesion chambers or xenon lamp artificial weathering. Besides, some of them were exposed in outdoor experimental station (Posadas, Misiones Province, Argentina, 27° 22'S and 55° 53'W) for 5 years. The evolution of the different triplex systems was evaluated by visual observation, loss of gloss, color variation, loss of adhesion, and electrochemical impedance spectroscopy. A painted sample without pretreatment was used as control. Subjected to accelerated tests, the highest protective efficiency was obtained in samples pretreated with MTMO or Cr. However, in the outdoor tests the best behavior corresponds to the control samples because the pretreated ones failed due to adhesion problems.

KEYWORDS

accelerated tests, electrochemical impedance spectroscopy, electrogalvanized steel, service conditions, silane

1 | INTRODUCTION

Temporary protection is design to protect metals from corrosion for a short period.^[1,2] Among the most widely pretreatments used for temporary protection onto zinc or its alloys, are those based on chromate and phosphate. These pretreatments are highly effective and easy to apply, but as they are harmful for human health and the environment,^[3,4] new pretreatments have been lately developed. Among these new developments, silanes are one of the most investigated.^[5,6] The general formula of these compounds is R-Si-(OR')₃, where R is a carbon chain, functionalized or not and OR' is an ethoxy or methoxy group, which is easily hydrolysable. Silanes form a protective film onto the substrate, which adheres by a covalent Si—O—metal bond formed by the products of OR' groups' hydrolysis and the

oxide-hydroxides film present on the metal, Figure 1.^[7] Besides, the remaining hydrolyzed groups can condense into —Si—O—Si chains forming a dense layer with a three dimensional network that acts as an effective barrier against corrosion.

However, before placing the metal in service conditions, a long-term anticorrosive protection, generally a coating, must be applied. This latter can be applied directly on the pretreatment if they are compatible, the pretreatment is in good condition and the metallic substrate is not corroded. Otherwise, the pretreatment must be removed before painting because premature failure of the protective system might occur.

The objective of this work was to evaluate the protection afforded by different triplex (metal/pretreatment/paint) systems subjected to standardized and outdoor service tests. Thus, the corrosion behavior of

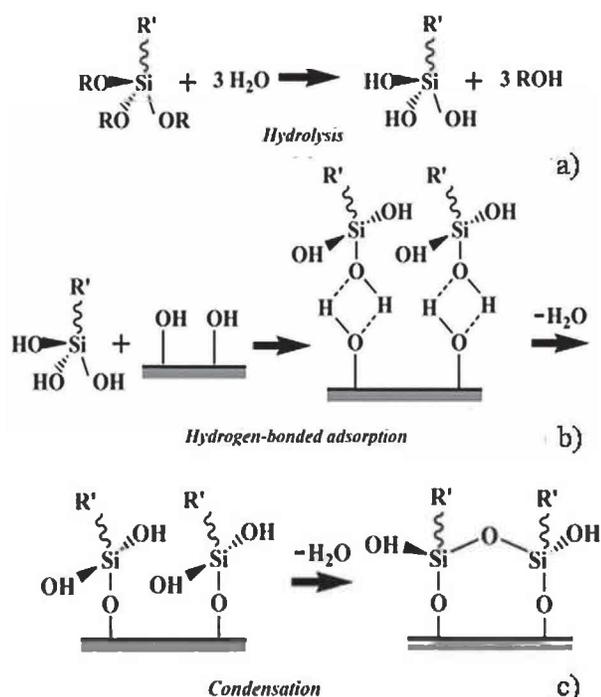


FIGURE 1 Silanes reactions scheme

electrogalvanized steel pretreated and painted with an alkyd system (anticorrosive + top coat) was studied. The pretreatments were a commercial silane (SIVO®), mercaptopropyltrimethoxysilane (MTMO), and a chromium(III)-based solution (SurTec 609 Zeta Coat Concentrate®). As control, electrogalvanized steel sheets (EG) without pretreatment were used. Samples were exposed to the humidity and prohesion chambers and xenon lamp artificial weathering. During the exposure, and according to the test, color and gloss changes, corrosion, blistering, and chalking degrees were evaluated. The metal/coating adhesion and the impedance modulus $|Z|$ of each sample were evaluated before and after its exposure to the xenon lamp or outdoor.

TABLE 2 Zinc film physical characteristics (μm)

Mean roughness (Ra)	0.49
Maximum depth (Rt)	5.8
Mean depth (Rzd)	3.72
Mean thickness	7.92

Replicates of these samples were exposed in the Posadas's experimental station for 5 years. Along this time, the corrosion, blistering, and chalking degrees as well as changes in gloss, color, adhesion, and electrochemical impedance were evaluated. The station main climatological characteristics can be seen in Table 1.

2 | EXPERIMENTAL PART

2.1 | Samples preparation

Samples of $15 \times 7.5 \times 0.070$ cm of electrogalvanized steel were used. The zinc films physical characteristics are shown in Table 2. The roughness was measured by a Hommel® tester T1000, while zinc thickness was determined by gravimetry. The samples were electrochemically cleaned immersing them for 20 s in a 10% weight/volume (w/v) sodium hydroxide and applying a cathodic current of 9 A.

Afterwards, and according to the supplier recommendations, the samples were pretreated as follows:

ES samples: a set of panels were immersed for 0.5 min in a 50% volume/volume (v/v) solution of commercial silane (SIVO 160®) employing distilled water as solvent. Samples were cured for 20 h at 20°C .^[8]

EM samples: another set of panels were immersed for 1 min in MTMO 4% v/v solution previously hydrolyzed for 1 h in water/methanol (1.0/1.5 v/v, pH = 4) solution. Samples were cured in oven for 10 min at 80°C .^[9,10]

EZ samples: a third set of replicates was immersed for 0.5 min in chromium(III)-based solution diluted 1:1 with

TABLE 1 Average weather data of the Posadas station during the testing period

Month	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Maximum temperature ($^\circ\text{C}$)	37.5	38.6	37.2	30.3	28.4	30.9	29.5	31.3	35.6	35.1	37.1	37.65
Minimum temperature ($^\circ\text{C}$)	16.1	13.5	12.5	9.3	6.9	-0.6	5.9	6.1	4.6	13.3	14.7	17.95
Maximum temperature ($^\circ\text{C}$)	29.9	33.3	27.8	26.1	23.5	16.9	18.3	21.9	26.4	26.9	29.2	33.8
Minimum temperature ($^\circ\text{C}$)	20.01	21.9	17.95	16.2	14.5	16.7	10.0	10.2	15.1	18.5	18.2	22.1
Average temperature ($^\circ\text{C}$)	26.8	26.9	23	21.6	18.4	16.8	15.3	20.0	21.0	22.4	24.9	27.9
Relative humidity (%)	71	70.7	78.75	80.45	87.7	80.6	77.9	73.9	66.6	76.7	67.1	73.8
Dew point ($^\circ\text{C}$)	20.6	20.4	18.45	17.65	16.1	13.1	11.2	14.8	13.9	17.7	17.7	21.9
Number of rainy days	7.5	4.5	1.5	0	0	9.0	6.0	7.0	6.0	11.0	7.0	9.5
Total precipitation (mm)	39.0	5.4	0.4	0	0	141.7	63.6	152.4	87.1	342.0	395.0	203.9
Time of wetness (h)	139.5	189.1	282.9	295.0	672.0	344.3	272.8	288.8	184.3	336.0	189.0	433.5

TABLE 3 Paints composition

Composition (% by volume)	Anticorrosive paint	Top coat
Zinc molybdophosphate	9.4	–
TiO ₂	3.8	10.8
Barium sulphate	9.1	–
Talc	9.1	–
Alkyd resin (1:1)	43.6	66.2
White spirit	25.0	23.0

distilled water at pH = 4. The samples were cured for 20 h at 20 °C.^[11,12]

As control, EG samples without pretreatment (*E samples*) were used.

2.2 | EIS measurements of the pretreated samples

After the pretreatments' curing, EIS measurements were performed at the corrosion potential and in potentiostatic mode using a sinusoidal signal of 15 mV peak-to-peak amplitude over the frequency range from 1.10^{-2} to 1.10^5 Hz. The value of the impedance modulus at low frequencies was selected as the assessment parameter of the total resistance to the system corrosion.^[13,14] Each electrochemical cell was built using an acrylic tube tightly bound to the painted sample by means of an O-ring and four clamps; the exposed area was 15.9 cm², and distilled water was used as electrolyte. The counter and reference electrodes were a large platinum mesh and a saturated calomel electrode (SCE), respectively.

2.3 | Applying of the painting system on the pretreated samples

Replicates of all the pretreated panels were coated with alkyd-resin based paints up to a dried film thickness of 170 μm the anticorrosive and 30 μm the top coat paint. In both paints formulations the Alkipol 434/50 A from Diransa San Luis, Argentina^[15] was the resin, and white spirit the solvent; zinc molybdophosphate, titanium dioxide, barium sulphate, and talc complete the pigment formula for the anticorrosive paint, while only TiO₂ was the pigment in the top coat formula,

TABLE 4 Codes for the painted panels

Painted sample name	Pretreatment
E	No pretreatment
ES	Commercial silane (SIVO®)
EM	MTMO
EZ	SurTec 609 Zeta Coat Concentrate

**FIGURE 2** Protection system scheme. [Color figure can be viewed at wileyonlinelibrary.com]

Table 3. The paints were prepared in a ball-mill, dispersing the pigments with the resin and the solvent for 24 h.

Panels were kept under laboratory conditions (20 ± 3 °C and $45 \pm 5\%$ of relative humidity) for 7 days before testing.

Table 4 shows the codes employed for the painted panels and Figure 2 a scheme of the triplex protection system.

2.4 | Tests before exposure

2.4.1 | Color

The color of the painted panels was determined using the CIELab color space. The CIELab color space proposed by the Commission Internationale de l'Eclairage (CIE) is one of the most used systems to evaluate color. Represented in a cylindrical system, this space is defined by three variables: lightness (*L*), and two coordinates (*a* and *b*). This system includes the vertical axis (*L*), that indicates clarity or darkness, and a horizontal plane defined by the *a* and *b* axis. The *a* axis represents the variation red–green, being positive (+*a*) for red and negative (–*a*) for green, while the *b* axis represents the variation yellow–blue, being positive (+*b*) for yellow and negative (–*b*) for blue.^[16,17]

The total color-difference parameter (ΔE) was calculated using measurements performed at different times as:

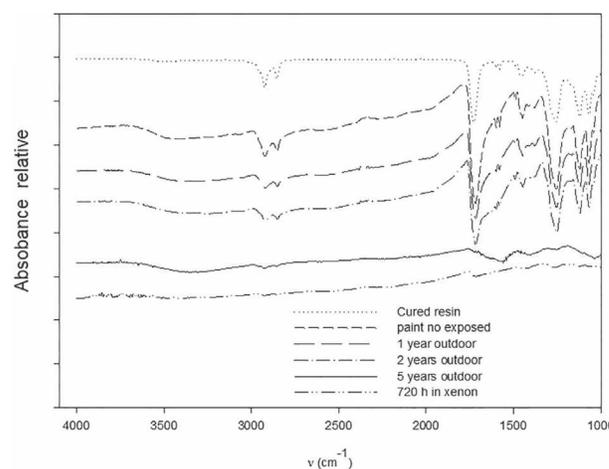
**FIGURE 3** FTIR spectra of the top coat before and after outdoor environment or xenon lamp exposure

TABLE 5 Adhesion test (ASTM D 3359^a)

Sample	Before exposure	Xenon lamp		Outdoor	
		After 720 h	After 1 year	After 2 years	After 5 years
E	0B	0B	0B	0B	0B
ES	0B	0B	0B	0B	No paint left on the panels
EM	0B	0B	0B	0B	No paint left on the panels
EZ	1B	0B	0B	0B	No paint left on the panels

^a%, of the painted area removed; 1B, 35–65; 0B, greater than 65.

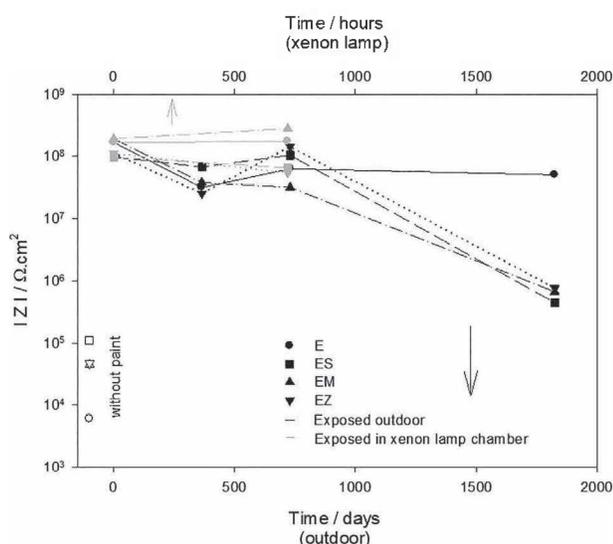


FIGURE 4 Evolution of the low frequency impedance modulus during the xenon lamp or outdoor environment exposure of the tested samples

$$\Delta E = \sqrt{(L - L_p)^2 + (a - a_p)^2 + (b - b_p)^2} \quad (1)$$

where L , a , and b are the panels CIELab parameters at the beginning of the test, and L_p , a_p , and b_p , the corresponding ones for the same panels along the test.

2.4.2 | Gloss

Changes of the paint gloss were measured at 60°, and evaluated as follows:

$$\Delta G = \frac{G - G_p}{G} \quad (2)$$

where G represents the panels gloss value at the beginning, and G_p at the end of the exposure.

The color and gloss measurements were done by a BYK GARDNER gloss-meter.

2.4.3 | FTIR

FTIR spectra were taken before the exposure by a Perkin Elmer® Spectrum One Spectro-photometer. The spectra were recorded as an average of 10 scans with a resolution of 1 cm⁻¹ in the range 650–4000 cm⁻¹.

As the gloss loss, both the color change and the FTIR spectra only depend on the characteristics of the top coat and are not related with the pretreatment; only some samples were evaluated. However, these tests orient about the protective system degradation and were used to follow the resin degradation.

2.4.4 | Adhesion

After the curing, the paint system/pretreated substrate dried adhesion was evaluated by the tape test standard method ASTM D 3359.^[19]

TABLE 6 Blistering and corrosion degrees of painted panels exposed in the humidity chamber^a

Time (h)	E		ES		EM		EZ	
	A	C	A	C	A	C	A	C
360	4F	10	8F	10	8F	10	2M	10
720	2F	10	8F	10	6F	10	2MD	10
1440	2F	10	8F	10	6F	10	2MD	10

^aA, blistering degree; C, rusting degree.
The creepage from the scribe of all the samples was evaluated with 10.

Rusting degree		10		9		8		6
Rusted area %		0		0.03		0.1		1
	Frequency	Dense (D)	Medium dense (MD)		Medium (M)		Few (F)	
Blistering degree	Size	10	8		6, 4		2	
	Comments	No blistering	Smaller size blister easily seen by unaided eye		Progressively larger sizes			

2.4.5 | EIS

The electrochemical impedance spectroscopy (EIS), at the corrosion potential, was performed as before employing the painted panels as working electrode. The measurements were done at different exposure times depending on the test.

2.5 | Accelerated tests

In order to expose the metal directly to the aggressive environments, a scribe mark was done on the painted surfaces

before placing the panels in the accelerated tests chambers. The creepage from the scribe was evaluated by the standard ASTM D 1654.^[20]

Sets of three panels were exposed to the humidity (ASTM D 2247^[21]) or the prohesion (ASTM G 85)^[20] chambers. Rusting (ASTM D 610^[22]) and blistering (ASTM D 714^[23]) degrees as well as the creepage from the scribe (ASTM D 1654^[20]) were evaluated after 360, 720, and 1440 h.

While in the humidity chamber the panels were exposed to 100% of relative humidity and 40 °C, in the prohesion cabinet

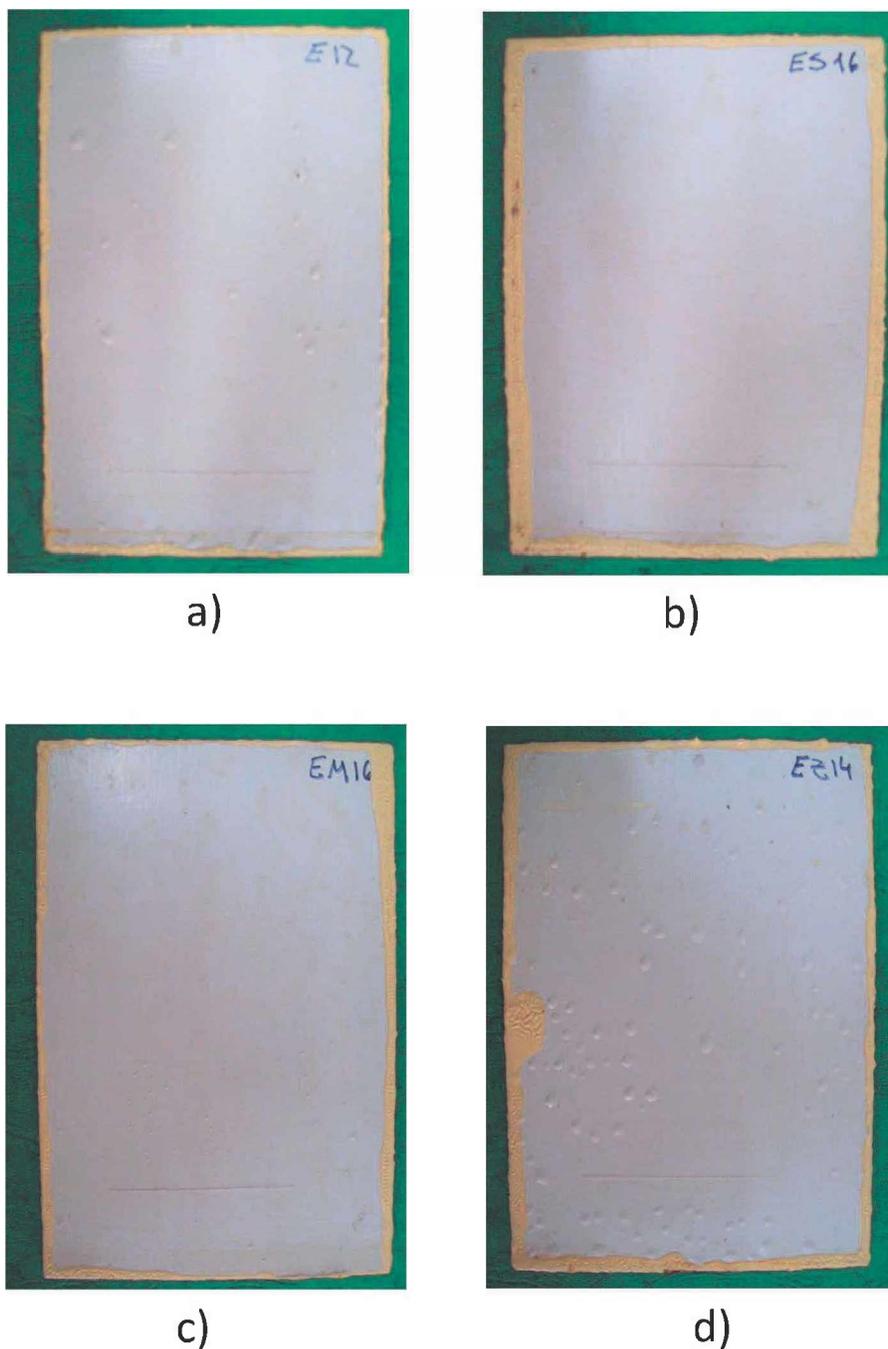


FIGURE 5 Photographs of the panels exposed in the humidity chamber for 360 h: (a) E; (b) ES; (c) EM; (d) EZ. [Color figure can be viewed at wileyonlinelibrary.com]

the cycle was 1 h of spray at 25 °C followed by 1 h of dried at 35 °C. The spray solution was 0.05 w/w% of sodium chloride and 0.35 w/w% of sodium sulphate.

Another set of panels were exposed to xenon lamp artificial weathering (Q-sun®) test (ASTM G 155^[24]), under cycle number 1 in ASTM G-155 (irradiance 0.35 W/m²·nm at 340 nm, 18 min of distilled water spray, followed by 102 min of light at 63 ± 3 °C). CIELab color space parameters and gloss were evaluated after 360, 528, 623, and 720 h of exposure. FTIR spectra, adhesion tape-test, creepage from the scribe, and impedance modulus (|Z|) were evaluated after 720 h.

Rusting and blistering degrees were evaluated after 360 and 720 h of exposure. Besides, as the resins can be degraded by the radiation action, the chalking degree was evaluated by adhering and removing 5 cm adhesive tape from the surface. The tape was placed against a dark surface and evaluated by the ASTM D 3274 standard.^[25]

2.6 | Outdoor exposure in the Posadas station

For each applied pretreatment, five pretreated galvanized steel sheets were painted and exposed outdoor for 5 years. Dirt accumulation was evaluated first by the ASTM D 3274^[25] standard; then, the panels were cleaned up using tap water and the color parameters, gloss as well as adhesion and |Z| were assessed. As well, the rusting, blistering degrees were evaluated by the ASTM D 610 and 714 standards, respectively.^[22,23]

FTIR spectra of the topcoat of some samples were done along outdoors exposure in order to study the resin degradation evolution.

3 | RESULTS

3.1 | Before exposure

The FTIR spectra of the cured alkyd resin, as reference, and of the unexposed alkyd paint can be seen in Figure 3. The main

peaks are due to glycerol (≈2900 cm⁻¹), and C=O stretching in linseed oil (1720 and 1250 cm⁻¹).^[26]

The results obtained after the dried adhesion test indicated that the pretreatments do not enhance paint adhesion to electrogalvanized steel and it was qualified as 0B in every case. It must be noted that the paint was almost completely removed when the cross cuts were made (Table 5), indicating not only the lack of adhesion but also the brittleness of the paint. Despite these results, the different tests were carried with the aim of studying the effect of the pretreatments on extending the useful life referred to the anticorrosive properties of the protective system.^[10,11,27]

After the coating curing, the impedance modulus (|Z|) value was ≈10⁸ Ω cm⁻² in every case, Figure 4.

3.2 | Accelerated tests

3.2.1 | Humidity chamber

In the humidity chamber no corrosion signs appeared on the panels along the test. However, all the samples presented some blistering degree after 360 h of exposure and, in some cases that increased as the time elapsed. E samples presented bigger blisters than the silanes pretreated samples (Table 6).

The qualification of the creepage from the scribe was 10 for all the samples during the whole assay.

Figure 5 shows photographs of the panels exposed for 360 h, time to which the blistering began.

3.2.2 | Prohesion chamber

No corrosion signs appeared on the panels even after 1440 h of exposure, however, the blistering degree was important in the case of EM samples (few but big blisters, qualification: 2F) after 1440 h. In the damage area, the paint was completely delaminated in the E samples after 720 h of exposure (Table 7 and Figure 6a), while in the pretreated samples no delamination occurred. Figure 6b–d show ES, EZ, and EM panels after 720 h of exposure.

TABLE 7 Blistering degree and creepage from the damage area of the painted panels exposed in the prohesion chamber^a

Time (h)	E		ES		EM		EZ	
	A	X	A	X	A	X	A	X
360	10	10	10	10	10	10	10	10
720	10	0	10	10	10	10	10	10
1440	10	0	10	10	2F	10	10	10

^aA, blistering degree; X, evaluation at the scribe area.
The corrosion degree of all the samples was evaluated with 10.

	Frequency	Dense (D)	Medium dense (MD)	Medium (M)	Few (F)
Blistering degree	Size	10	8	6, 4	2
	Comments	No blistering	Smaller size blister easily seen by unaided eye	Progressively larger sizes	

Evaluation at the scribe area: 10: 0 mm; 9: <0.5 mm; 8, between 1 and 0.5 mm.

3.2.3 | Exposure to the xenon lamp artificial weathering

Figure 3 shows the FTIR spectrum of the alkyd topcoat paint exposed for 720 h to the xenon lamp. It can be seen that the resin' peaks are not defined due to its important degradation.

Gloss and color parameters are shown in Figure 7. The gloss diminishing was very important up to about the first

400 h of exposure, but then that parameter remained almost constant. The change in total color-difference parameter along the test could be due to the wash away of the chalking products. These products are washed away during the spray period exposing non-degraded resin and restoring the color of the paint.

The loss of adhesion was qualified as 0B (complete delamination) for all the samples after 720 h of exposure, Table 5.

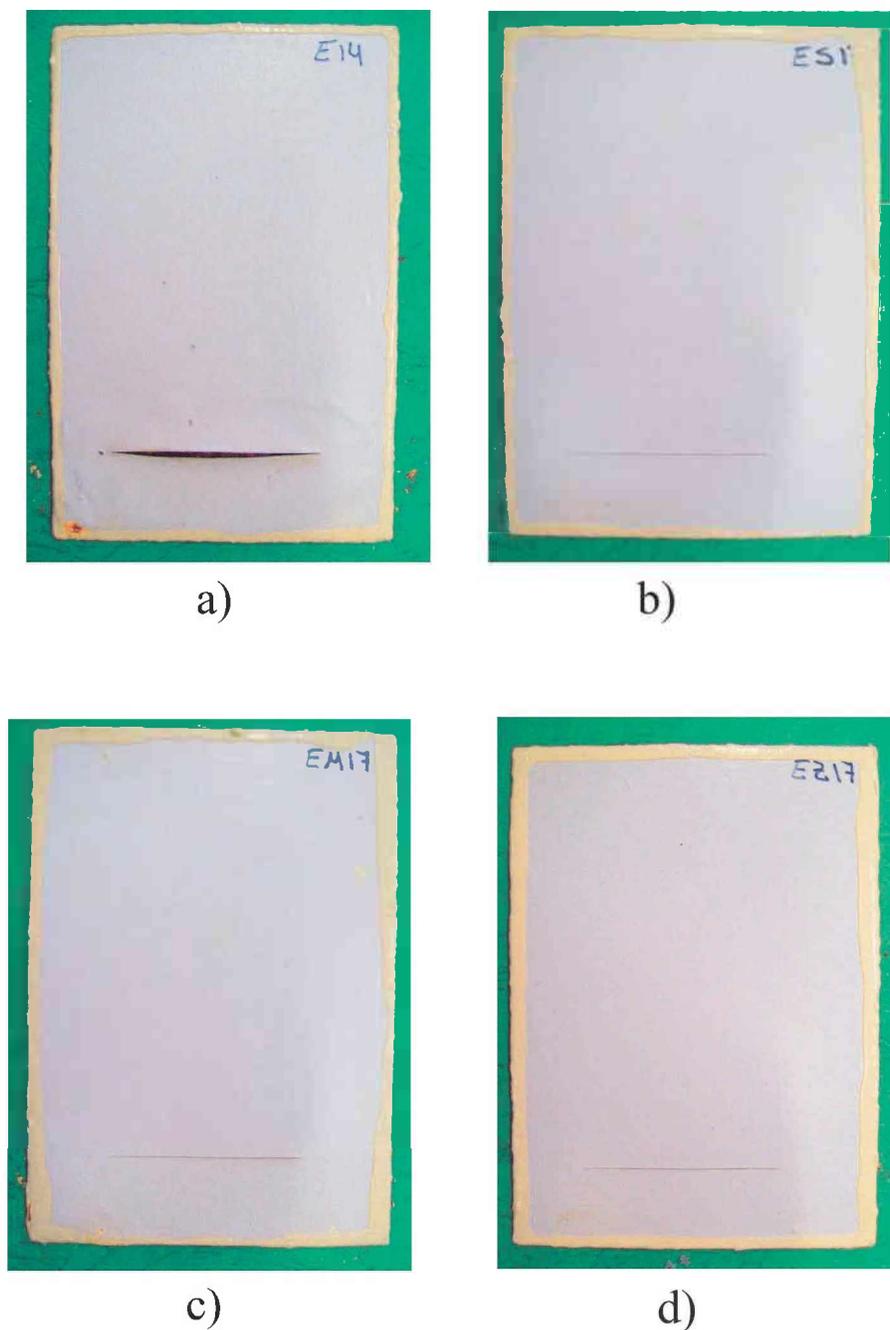


FIGURE 6 Photographs of the panels exposed in the prohesion chamber for 720 h: (a) E; (b) ES; (c) EM; (d) EZ. [Color figure can be viewed at wileyonlinelibrary.com]

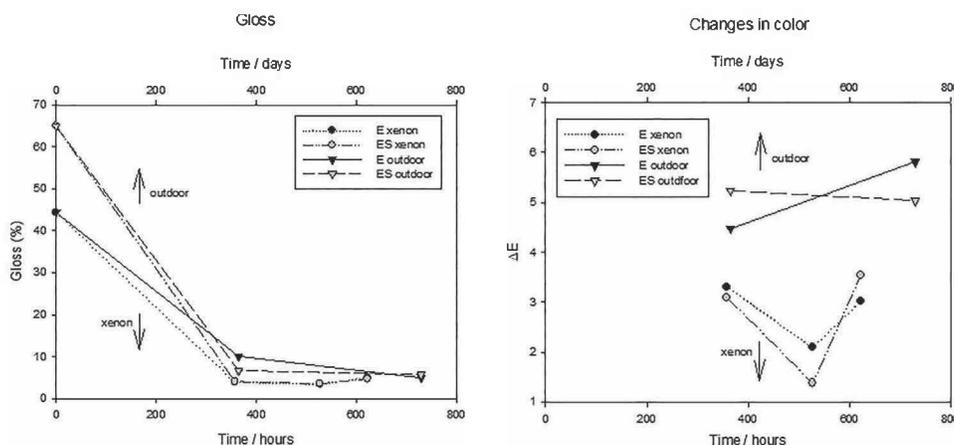


FIGURE 7 Gloss and color changes in panels exposed to xenon lamp or outdoor environment

EIS measurements carried out on the intact area of the same samples, after 720 h of exposure to xenon lamp, show that the behavior of all of them was quite similar, that is, the $|Z|$ did not significantly change, Figure 4. They also had no corrosion or blistering.

For all the samples the chalking degree was 4–5S after 360 h, but it increased up to 4S on reaching the 720 h of exposure.

After 720 h of exposure none of the panels presented blisters or corrosion dots. The failure at the scribe was important in the case of samples ES (qualification: 4). In the case of samples EM and EZ the creepage from the scribe was not tested (Table 8).

3.3 | Outdoor exposure

Gloss and color changes after 365 and 730 days of outdoor exposure are shown in Figure 7. It can be seen than the main changes in gloss, comparing with the panel before exposition,

occurred during the first 365 days of exposure and that the differences among the samples were not important. On the contrary, the total color difference between the exposed and the non exposed samples were important ($\Delta E \approx 5$) and can be seen by naked eye.^[18] In these cases, the chalking is not important as the samples were clean with water before the measurements.

Figure 3 shows the FTIR spectra of one sample after 1, 2, and 5 years of outdoor exposure. As seen, the resin degradation progress is evidenced by the decrease in the relative intensity of its peaks, and also because some of them lose definition as the exposure time elapses. The vibration band at 3400 cm^{-1} , due to OH stretching is broadening and a band at 1630 cm^{-1} , due to conjugated double bonds along the oil chain, appeared.^[26]

The EIS measurements, done after 365 and 730 days of outdoor exposure, showed that all the samples presented high impedance values ($|Z| \approx 10^8\ \Omega\text{ cm}^{-2}$) at low frequencies. This value was maintained during the first 2 years of exposure

TABLE 8 Blistering and corrosion degrees and creepage from the damage area of the painted panels exposed in the xenon lamp artificial weathering^a

Time (h)	E			ES			EM			EZ		
	A	C	X	A	C	X	A	C	X	A	C	X
720	10	10	9	10	10	4	10	10	–	10	10	–
^a A, blistering degree; C, corrosion degree; X, evaluation at the scribe area. The corrosion degree of all the samples was evaluated with 10. –, not evaluated.												
Rusting degree	10			9			8			6		
Rusted area %	0			0.03			0.1			1		
	Frequency	Dense (D)	Medium dense (MD)				Medium (M)			Few (F)		
Blistering degree	Size	10	8				6, 4			2		
	Comments	No blistering	Smaller size blister easily seen by unaided eye				Progressively larger sizes					

Evaluation at the scribe area: 10: 0 mm; 9: <0.5 mm; 8, between 1 and 0.5 mm.

showing that the anticorrosive protection afforded by the coating system was very effective in avoiding the water or electrolyte permeation up to the metallic substrate. After 5 years, the $|Z|$ value of E samples (painted but not pretreated) was still high, and the coat of paint was intact. In the triplex systems the $|Z|$ value was reduced to about $6.10^5 \Omega \text{ cm}^{-2}$, being slightly higher than that of the samples only pretreated. Such a result is indicating that even in this latter condition the coating offered some protection degree. In no case the $|Z|$ value of the coated samples reached the estimated ($6.10^3 \Omega \text{ cm}^{-2}$) for the bare electrogalvanized steel, Figure 4.

During the first 2 years of assay, all the samples showed an important layer of dirt (6S), however, once this layer was removed no corrosion or blisters appeared. After the first year of exposure the chalking degree was 2S, but elapsed 2 years it was 5S; the adhesion was always 0B, and subjected to the cross cut test, the paint layer was easily broken. After 5 years of exposure, no paint layer remained adhered in the pretreated + painted ES, EM, and EZ samples; only on the no-pretreated panels (samples E) a delaminated but intact paint layer was found, Figure 8.

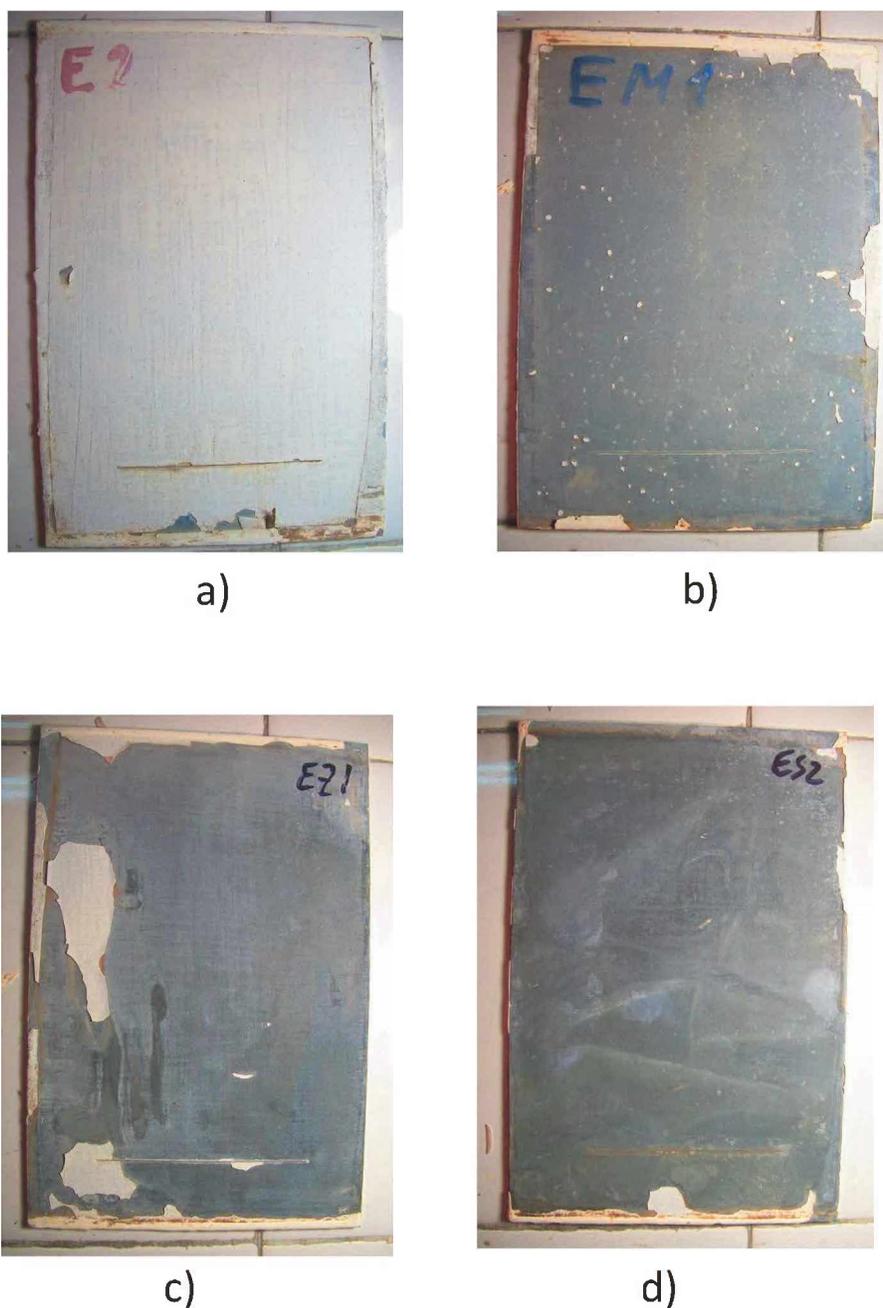


FIGURE 8 Photographs of the panels after 5 years exposure to outdoor environment: (a) E; (b) EM; (c) EZ; (d) ES

TABLE 9 Protective efficiency^[28]

Protection efficiency (%)	Blistering degree	Creepage from the scribe	Corrosion degree
100		10	9
95			8
90		9	7
85			
80		8	6
75	8F		
70	6F	7	5
65	4F		
60	2F	6	4
55	8M		
50	6M	5	
45	4M		
40	2M	4	3
35	8MD		
30	6MD	3	
25	4MD		

4 | DISCUSSION

In order to evaluate the protective performance of the triplex systems exposed in different environments, the protective efficiency was evaluated as:^[28]

$$\text{Protective efficiency (PE)} = 0.25 (\text{blistering degree} + \text{creepage degree} + 2 \times \text{corrosion degree})$$

And the relationship among blistering degree, creepage from the scribe and corrosion degree is shown in Table 9.

Table 10 shows that, exposed in the humidity or prohesion chambers, the electrogalvanized steel sheets samples pretreated with MTMO (EM) or SIVO® (ES), and then coated with an alkyd paint system, were the best protected against the corrosion since in both cases the coating PE was greater than

92%. In EZ samples, the high blistering degree in the humidity chamber made that the coating PE was less than 80. In E samples, the coating PE was 90 in the humidity chamber (big but few blisters), and 75 in the prohesion one due to the premature adhesion failure in the scribe zone. This difference could be due to the fact that the pretreatment offered better corrosion protection in the area where the paint layer had been scribed, as well that in the prohesion test the scribe exposed the metallic substrate of E samples in direct contact with the saline solution.

In the xenon artificial weathering, the evaluation of the corrosion, blistering and chalking degrees was 10 in all the samples.

Related to the FTIR spectra (Figure 3), in the outdoor test a progressive degradation of the resin due to the action of the sun radiation can be seen. However, the spectra obtained after 720 h exposure to the xenon lamp indicate a higher degradation degree as the resin peaks are less define than in the spectra corresponding to the sample exposed outdoor for 5 years. This may be due to that the UV radiation was more intense in the xenon lamp than in the outdoor. These changes are related to those of the gloss and the high chalking degree. The gloss values diminished in the xenon lamp and in outdoor tests after 400 h and 1 year, respectively, but then they remained almost unchanged up to ending the test. By its part, the color changes were more important during the outdoor test probably due to the adhesion of microparticles such as soil, dirt, and microorganisms, which were not completely removed during the cleaning step.

The $|Z|$ value, around $10^8 \Omega \text{ cm}^{-2}$, remained almost unchanged from the beginning up to 720 h in xenon lamp or 2 years of outdoors exposure. After 5 years outdoor, the paint system applied on the pretreated samples was completely delaminated and removed from the substrate surface. However, the $|Z|$ was higher than in the case of the electrogalvanized steel pretreated, indicating that a certain protection level was still present. The $|Z|$ value for the untreated but painted panels (E) was the highest one.

TABLE 10 Protective efficiency percentage offered by each pretreatment^[28]

Paint	After 720 h of accelerated tests			Mean protective efficiency	Outdoor		
	Humidity chamber	Prohesion chamber	Xenon lamp		1 year	2 years	5 years
E	90.0	75.0	97.5	87.5	95	92.5	92.5
ES	93.8	100.0	85.0	92.9	95	95	^a
EM	92.5	90.0	The creepage was not evaluated	91.2	95	95	^a
EZ	78.8	100.0	The creepage was not evaluated	89.0	95	95	^a

^aNo paint left.

5 | CONCLUSION

The pretreatments under study did not enhance electro-galvanized steel/paint adhesion but the integration of pretreatments based on MTMO or SIVO® enhance the anticorrosion performance of the triplex coating system in humidity and prohesion chambers. Samples pretreated with chromium(III)-based solution enhance the protection in the prohesion chamber but failed in the humidity one because a significant blistering degree takes place.

In the xenon lamp test, there was no difference among the triplex systems performance, however, an important resin degradation occurred after 720 h of exposure, so important that the resin seemed more degraded than after 5 years of outdoor exposure.

In order to study the anticorrosive performance of the triplex system, different types of tests must be done, as the results differ depending on the conditions of the tests.

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