

## Silanes as adhesion promoters in waterborne epoxy paints

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### ABSTRACT

The aim of this work was to study mercaptopropyltrimethoxysilane (MTMO), aminopropyltrimethoxy silane (AMEO) glycidoxypropyltrimethoxysilane (GLYMO) and glycidoxypropyltriethoxysilane (GLYEO) as adhesion promoters between an epoxy waterborne paint and electrogalvanized steel.

The metallic substrate was brushed with hot water and detergent, electrochemically cleaned, immersed in the hydrolysed silanes solutions and dried at 110 °C for 1 h. Finally, the pretreated substrates were painted by brush. The paint used was an epoxy-poli-amidoamine whose dried film thickness was  $85 \pm 15$   $\mu$ m. As control a replicate of the substrate without silane pretreatment was used (Z).

After curing, the painted samples were exposed in the salt spray or in the humidity chambers. Rusting and blistering degrees, adhesion and failure at the scribe were evaluated along the exposure. The experimental results showed differences among the pretreatments performance, especially in the loss of adhesion and failures at the scribe. The paint on both the GLYEO pretreated and the Z samples lost most of its adhesion after 30 days of exposure in the chambers. For the MTMO pretreated and the Z samples the failure at the scribe started to be important after 30 days in the salt spray chamber, while for the GLYEO pretreated samples it occurred after 60 days in the humidity chamber.

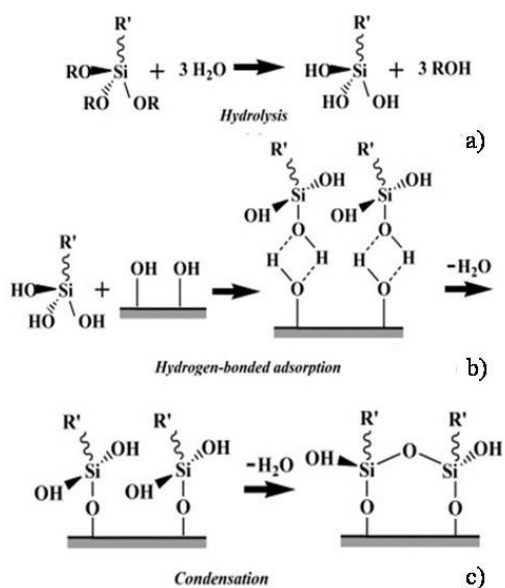
Key words: silanes, electrogalvanized steel, adhesion, paint

### INTRODUCTION

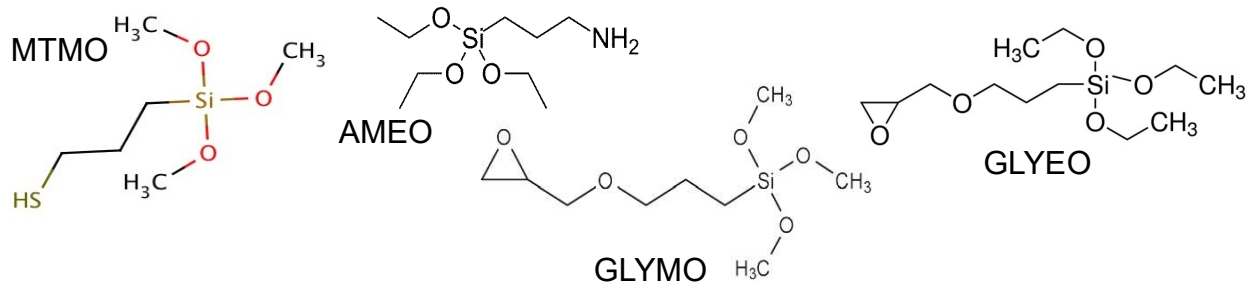
Temporary protection is design to protect metals from corrosion for a short period [1]. Among the most widely pretreatments used for temporary protection onto zinc or its alloys, are those based on chromate and phosphate. However, new develops such as silanes are being investigated [2-5]. The general formula of these compounds is R-Si-(OR')<sub>3</sub>, where R is a carbon chain, functionalized or not and OR' is an ethoxy o 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 [6]. Besides, the remaining hydrolysed groups can condense forming a dense layer with a three dimensional network that acts as an effective barrier against corrosion (Figure 1). On these pretreatments, before placing the metal in service conditions, a long term anticorrosive protection, generally a coating must be applied. This coating is selected according to the R functionalized group present in the silane, in order to form a covalent bond between this group and the resin of the coating [7, 8].

The objective of this work was to evaluate the protection afforded by electro-galvanized steel pretreated with mercaptopropyltrimethoxysilane (MTMO), aminopropyltrimethoxysilane (AMEO), glycidoxypropyltrimethoxysilane (GLYMO) or glycidoxypropyltriethoxysilane (GLYEO) and painted with an epoxy-poli-amido-amine waterborne paint. Samples without silane were used as controls (Z). Figure 2 shows the chemical structure of the silanes studied. The corrosion behaviour of pretreated painted samples was studied by exposure to salt spray and humidity chambers where rusting and blistering degrees, adhesion and failure at the scribe were evaluated along time.

Results showed differences among the pretreatments performance, especially in the loss of adhesion and failures at the scribe. The paint on both the GLYEO pretreated and Z samples lost most of its adhesion after 30 days of exposure in the chambers. For the MTMO pretreated and Z samples the failure at the scribe started to be important after 30 days in the salt spray chamber, while for the GLYEO pretreated samples it occurred after 60 days in the humidity chamber. These results cannot be explained only by the interaction between the silanes and the oxide-hydroxides film on the electro-galvanized steel and of those with the epoxy groups of the paint's resin.



**Figure 1: Silanes reactions scheme.**



**Figure 2. Chemical structure of the silanes.**

## EXPERIMENTAL PROCEDURE

### Samples preparation

Electro-galvanized steel samples (15 x 7.5 x 0.070 cm) were brushed with hot water and detergent, and electrochemically cleaned by immersion for 25 s in a 10% (w/v) NaOH, and applying a cathodic current of 3 A.

The silane solutions were prepared by adding 1% of silane to a 9/1 isopropyl alcohol/distilled water at natural pH (pH = 5). The solutions were stirred for 40 min. Finally, the cleaned samples were immersed in the silane solutions for 1 min, dried by hot air, and cured in stove for 1 h at 110 °C.

The paint was prepared as two components, being the component A: anticorrosive pigment (7.2 g), talc (3.9 g), barite (8.9 g), titanium dioxide (8.3 g), mica (2.4 g), distilled water (32.8 g), curing agent (32.2 g), antifoaming (0.2 g), pH-stabilizer (0.9 g); and the component B: resin (81.0 g), distilled water (18.3 g), antifoaming (0.7 g). Before painting, the components A and B were mixed as 2.1/1 w/w. The cured samples were painted by brush up to a dried film thickness of  $85 \pm 15 \mu\text{m}$  and kept under laboratory conditions for 15 days.

Table 1 shows the codes for the samples.

Painted sample name	Pretreatment
Z	No pretreatment
M	MTMO
A	AMEO
G	GLYMO
Y	GLYEO

**Table 1. Codes for the painted samples**

### Accelerated tests

After curing, the dried adhesion of the pretreated substrate/paint samples was evaluated by the tape test method (ASTM D 3359 standard) [9] and, in order to expose the metal directly to the aggressive environments, a scribe mark was done on the painted surfaces before placing the samples in the accelerated tests chambers.

For each pretreatment a set of three samples was exposed to the humidity (HC, ASTM D 2247 [10]) or the salt spray (SSC, ASTM B 117 [11]) chambers. Blistering (ASTM D 714 [12]) and rusting

(ASTM D 610 [13]) degrees as well as the creepage from the scribe (ASTM D 1654 [14]) and adhesion were evaluated after 336, 720, 1080 and 1440 h.

## RESULTS

The dried adhesion of the paint to the pretreated substrates is shown in Table 2. As seen, in the Z (sample without silane) and M (with MTMO) painted samples the organic coating was not removed by the tape but in the A, Y and G samples it was between 5 and 15 %. However, after 720 h in the chambers, the adhesion in the Z and Y (with GLYEO) samples diminished and more than the 15% of the paint was removed. On the contrary, the M, A and G samples exposed in the SSC or in the HC showed adhesion values similar to the dried ones.

Sample	Before exposure	After 720 h of exposure	
		Humidity chamber	Salt spray chamber
Z	5B	2B	1B
M	5B	5B	4B
A	4B	4B	4B
G	3B	3B	3B
Y	4B	2B	1B

\* % of the painted area removed: 5B: none; 4B: less than 5%; 3B: 5-15%; 2B: 15-35%; 1B: 35-65%; 0B: greater than 65%

**Table 2. Adhesion test.**

None sample presented rusting points along the exposure in the chambers. The blistering (size and frequency of blisters) degree increased along the exposure time and in a different degree according to the pretreatment. After 336 h in the HC, the M and A (with AMEO) samples presented a high frequency of blisters but the size, as in the other cases, were the smaller the unaided eye can see. After 1440 h, the size of these blisters increased, but the frequency was the same. In the other cases, the blisters size and frequency increased, being 6M for the Z, G, and Y samples after 1440 h.

Time (h)	Z		M		A		G		Y	
	B*	R <sup>#</sup>	B*	R <sup>#</sup>	B*	R <sup>#</sup>	B*	R <sup>#</sup>	B*	R <sup>#</sup>
336	8F	10	8D	10	8MD	10	8F	10	8F	10
720	8M	10	8D	10	8MD	10	8M	10	8D	10
1440	6M	10	6D	10	6MD	10	6M	10	6M	10

\* B: Blistering degree: frequency: dense (D), medium dense (MD), medium (M), few (F); size: 10 (no blistering), 8 (Smaller size blister easily seen by unaided, 6, 4 and 2 are progressively larger sizes

<sup>#</sup> R: Rusting degree: 10 (rusted area 0 %), 9 (rusted area between 0.03 and 0.1 %), 8 (rusted area between 0.1 and 0.3 %)

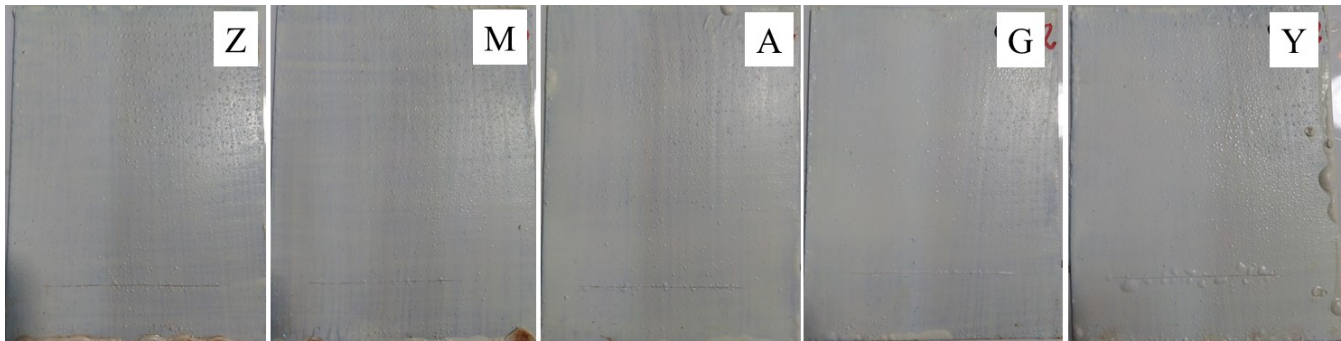
**Table 3. Blistering and rusting degrees of painted samples exposed in the HC.**

In SSC, the blisters size also increased along the time, but only in the Z and M samples the frequency changed from F to MD, Figure 1.

Time (h)	Z		M		A		G		Y	
	B	R	B	R	B	R	B	R	B	R
336	8F	10	8F	10	8F	10	8F	10	6F	10
720	2F	10	2F	10	8F	10	8F	10	4F	10
1080	2MD	10	2MD	10	6F	10	4F	10	2F	10

**Table 4. Blistering and rusting degrees of painted samples exposed in the SSC**

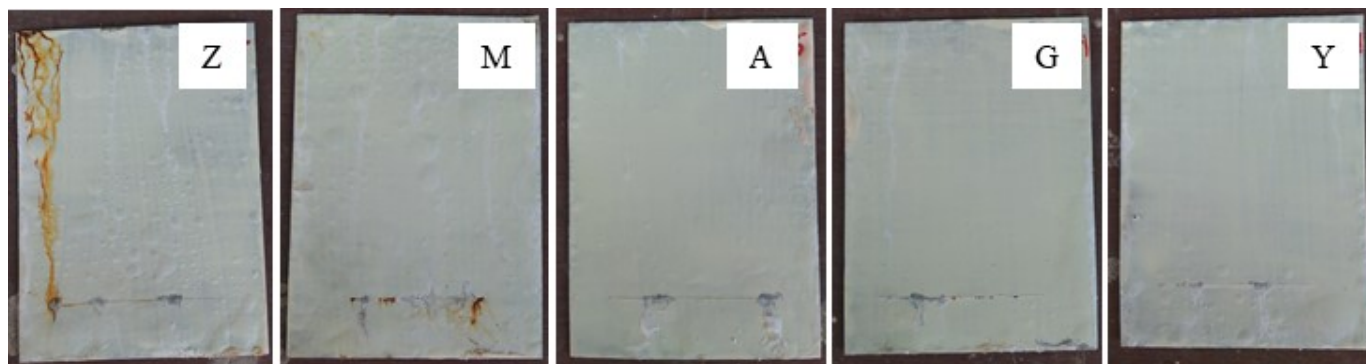
In the Z (without silane) samples the failure at the scribe started after 168 h in the HC, when blisters could be seen around the scribe. Blisters appeared after 336 h on A and Y pretreated samples while the G and M samples were evaluated with 10 after 720 h. After 1440 h, the A, G, and M samples presented blisters with an 8 qualification while on the scribe of the Z and Y samples the blisters were qualified with 6 and 4, respectively (Figure 3).



**Figure 3. Photographs of the exposed samples after 1440 h in the HC.**

In the case of samples exposed in the SSC, only the sample with GLYMO displayed a delaminated area around the scribe after 168 h, this area developed white corrosion after 336 h. The Z and M samples presented grey corrosion after 336 h while the Y and A samples showed white corrosion products. Blisters appeared after 720 h in the M and A samples, being bigger in M than on AMEO. At the end of the tests, all the samples presented blisters of different size, Figure 4.

Red corrosion products due to the oxidation of the underlying steel appeared after 1080 h in the Z, M, and G samples.



**Figure 4. Photographs of the exposed samples after 1080 h in the SSC.**

## CONCLUSIONS

Except the GLYEO, the other tested silanes enhanced the paint adhesion after some exposure time in the humidity or in the salt spray chambers. Pretreated with AMEO, the coated samples presented the better overall adhesion, as the tape test adhesion was constant and quite high along the tests, while the blisters size was medium and the frequency few in the salt spray chamber. Besides, no steel corrosion product appeared on the scribe after the exposure in the chambers.

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