Corrosion resistance of steel treated with different silane / paint systems

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Abstract

This work reports a comparative study on the corrosion resistance of low carbon steel substrates pre-treated with different pure silane solutions and painted. The silanes used to pre-treat the steel panels were 3-aminopropyltriethoxysilane (γ -APS), 3-glycidoxypropyltrimethoxysilane (γ -GPS) and bis(3-triethoxysilylpropyl)amine. The study also considered other commercial silane solutions with ureido, amino and epoxy organofunctional groups, and two bis-functional silanes: bis-(gamma-trimethoxysilylpropyl)amine (BAS) and 1,2-bis(triethoxysilyl)ethane (BTSE). A conventional phosphate type pre-treatment was also applied for comparative purposes. The pre-treated panels were then finished with an alkyd / polyester aminoplast base paint. Likewise, another set of panels were coated with an acrylic / urethane type paint. Different tests were conducted to evaluate the anti-corrosive ability of the different silane / paint systems: outdoor exposure in an atmosphere of moderate aggressivity; accelerated corrosion test (salt-fog test); and electrochemical impedance spectroscopy (EIS). The results show that the steel pre-treated with certain silanes, especially γ -APS, yields similar results to conventional phosphate pre-treatment.

Keywords: silane, paint, atmospheric exposure, salt fog test, EIS

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1. Introduction

Organic coatings afford corrosion protection by forming a physical barrier between the metallic substrate and the environment. In practice, a conversion coating treatment consisting of a chromate or phosphate compound is incorporated into the coating system to ensure adequate protection of the metallic substrate and to improve coating adhesion. The high efficiency / cost ratio of Cr(VI) compounds, especially chromates, has led these substances to be widely used as corrosion inhibitors to prevent the corrosion of different metals and alloys. However, chromate and similar hexavalent chromium compounds have been reported to be toxic and carcinogenic and constitute a health risk in the working environments where they are normally handled.¹

The search for more ecological alternatives to chromating for the protection of metallic structures has led to the development of different types of non-toxic and environmentally friendly coatings. In this respect, mention may be made of low temperature cationic plasma deposition;² sol-gel coatings;³ silane solutions;^{4,5} and even silanes modified with rare earth salts,⁶⁻⁸ SiO_2 ⁹ and inhibitors¹⁰.

Silane-based pre-treatments have emerged as a potentially valuable alternative to the use of phosphates and chromates.^{4,5} Silane technology is based on a group of environmentally safe organic-inorganic silicon-based chemicals (“trialkoxysilanes” or “silanes”) which offer corrosion protection of metals and stable adhesion to a broad range of paints. These pre-treatments are moreover easy to apply, inexpensive, and comply with current environmental concerns.

1.1 Silane chemistry

Organofunctional silanes have the structure $\text{X}_3\text{Si}(\text{CH}_2)_n\text{Y}$, where X represents a hydrolysable group such as methoxy or ethoxy and Y usually represents a specific functional end group. These groups are typically $-\text{SH}$, $-\text{OH}$, $-\text{NH}_2$, etc. and are selected according to the chemistry of the organic molecule, e.g. a paint, to be bonded to the substrate. When the silane is

symmetrical around the Y functional group, i.e. if there are two trialkoxy (X_3) groups in the molecule, the molecules are called bis-functional silanes and have the structure $X_3Si(CH_2)_nY(CH_2)_nSiX_3$. The ethoxy or methoxy groups are hydrolysed when water is added to the system, and the resulting $-Si-OH$ silanol groups can react with metal hydroxide groups on the substrate surface to form a $Si-O-M$ covalent bonded metal/film interface. The final result of the silane pre-treatment is a dense silicon and oxygen rich coating which constitutes a protective physical barrier and reduces the access of aggressive species.

Silanes are considered for use on various metals: aluminium and aluminium alloys,¹¹⁻¹⁹ copper,²⁰ steel,^{21,22} zinc,^{23,24} galvanised and electrogalvanised steel,^{22,25-31} and more recently on magnesium alloys.³²⁻³⁶

The behaviour of a wide variety of silanes such as γ -UPS (γ -ureidopropyltriethoxysilane), VS (vinyltriethoxysilane), BTSE (bis-1,2-[triethoxysilyl]ethane), γ -APS (γ -aminopropyltriethoxysilane), etc., has been studied and has shown them to be effective anticorrosive agents if applied in appropriate process conditions.³⁷ This means controlling a series of parameters in the application process, such as the concentration (the main factor influencing the coating thickness),^{25,38-41} hydrolysis time,^{42,43} methanol / water ratio,⁴⁴ silane solution pH,^{45,46} and the silane layer curing process (considered an essential factor for corrosion protection purposes).^{11,40-42,47,48}

On the other hand, the preferential orientation of a silane molecule on an inorganic surface is with the silanol function joined to the surface and the organofunctional group facing outwards, i.e. in order to optimise the performance of the silane, the organofunctional group must not interact with the metallic substrate. For instance, γ -APS silane absorption on the metallic surface may be achieved through the NH_2 group. The protonation of amino groups at the interface is related with the interaction of the silane functional group with the metallic substrate, creating regions of weakness at the interface where bonds are originated by instable hydrogen bridges (Metal-OH with NH_2), or also in the silane layer ($Si-OH$ groups reacting with NH_2).⁴⁹

Data reported in the literature confirms adhesion failures at the metal/silane interface associated in most cases with the protonation of amino groups.⁵⁰

1.2. Aim

The purpose of this work was to investigate the applicability of different silane base treatments on steel substrates from the point of view of corrosion resistance and adhesion of the subsequently applied organic coating, in comparison with a conventional phosphate type pre-treatment.

Three types of organofunctional silanes have been used: 3-aminopropyltriethoxysilane (γ -APS), 3-glycidoxypropyltrimethoxysilane (γ -GPS) and bis(3-triethoxysilylpropyl)amine. Some tests have also been carried out using other commercial silane solutions with ureido, amino and epoxy organofunctional groups and the bis-functional silanes: bis-(gamma-trimethoxysilylpropyl)amine (BAS) and 1,2-bis(triethoxysilyl)ethane (BTSE).

The panels were then finished with a low thickness paint film and the anti-corrosive ability of the different silane / paint systems was assessed by means of outdoor corrosion testing (Madrid atmosphere), accelerated corrosion testing (salt spray) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1 Specimen preparation

Silanes have been applied on EN10025 cold rolled steel specimens with dimensions of 50 mm x 100 mm. The steel specimens were previously cleaned with a commercial alkaline degreaser (PRODEX 8120®), a stage considered to be fundamental to obtain an active surface.

The tested pure silanes, supplied by Degussa®, are shown in Table I (a).

The different silane solutions were prepared in the following way: (a) γ -APS silane solution was prepared by mixing 0.5% water, 1% or 2% silane and isopropanol (balance), achieving a solution of pH 11; (b) γ -GPS silane solution was prepared by mixing 4% water, 1% or 2% silane and

isopropanol (balance). The pH was adjusted to 4.5 using acetic acid before the γ -GPS was added; and (c) bis-amine solution was prepared by mixing 0.3% water, 1% or 2% silane, and isopropanol (balance), adding acetic acid to lower the pH to 6.

The solutions were hydrolysed for 1 h, for the γ -APS and γ -GPS silanes, and for 5 h for the bis-amine silane, under constant stirring.

The steel specimens were submerged in the different solutions for 60 seconds, decanted to eliminate the excess solution, and cured in an oven at 75°C for 15 minutes.

A conventional phosphate type pre-treatment (PRODEFOS 1113®) was also used for comparative purposes.

Bearing in mind that the choice of a silane is determined by the capacity of its organofunctional group to react with the organic polymer, two types of topcoat paints have been selected: an alkyd/polyester aminoplast base paint (BRUSINT SE GRIS 03650), supplied by ProCoat Tecnologías, S.L.®, of an average thickness of 40 μm , and an acrylic / urethane type paint of the same film thickness (RESISTEX C137), supplied by Leigh's Paints®, only for the specimens pre-treated with a 1% silane concentration. The paints were applied, according to the manufacturers' recommendation, by air-spraying. The alkyd/polyester paint was subsequently cured in an oven during 20 min at 150°C, while the acrylic /urethane panels were dried for seven days prior to testing.

Commercial silane solutions were applied to one series of specimens, as shown in Table I (b). The application process of these solutions was as follows: dilution to 10% and 25% in distilled water and constant stirring of the solution for 1 hour. The pH of the silane solutions was 6.5 (UPS), 3.8 (GLYCH), 10.5 (APS), 4 (BTSE) and 5 (BAS). The specimens were submerged in the different solutions for 60 seconds, decanted to eliminate the excess solution, and then dried in an oven at 90°C for 20 minutes. An alkyd/polyester aminoplast base paint with an average thickness of 60 μm was subsequently applied.

Duplicates of each set of panels were studied in the different tests described in subsequent sections.

2.2 Adhesion test

Adhesion tests have been carried out on unexposed specimens and on specimens exposed to the atmosphere for two years. The tests have been performed with an AT-1000 electronic adhesion meter in accordance with standard ASTM D 4541.⁵¹ The instrument uses the pull-off method, measuring in kgf the force required to detach a dolly with a small surface area glued to the organic coating. The force necessary to detach this area is the measure of adhesion strength. The dollies, of 20 mm in diameter, were firmly glued to the surface of the coated panels using a 2-component epoxy adhesive. The adhesive was allowed to cure for 24 hours at room temperature. After curing, a slot was drilled around the dolly through the film until the substrate was reached to avoid the effect of peripheral coatings.

As well as the adhesion strength, this test also provides information on the type of failure. The split may be an adhesive break (between the coating and the substrate), a cohesive break (break within a coating layer), a combination of both, or a failure of the glue. This information is very important since it determines the weakest area in the coating system.

2.2 Atmospheric exposure test

The testing station was located on the roof terrace of the National Centre for Metallurgical Research in Madrid. The atmosphere is classified with a moderate corrosivity index, C2 for low-carbon steel, according to ISO 9223.⁵² The specimens have been evaluated after 1 and 3 years of exposure.

2.3 Salt spray test

The procedure is based on ASTM B117⁵³ and consists of constant spraying with a 5% NaCl solution in a testing cabinet in which the temperature is maintained at 35°C. The total duration of the test was 1000 hours, and specimens were withdrawn for assessment after different testing times. As in the atmospheric exposure test, a series of painted panels with a defect, made using a

scribing tool with a metal tip, have also been included in this test. The defect was about 3 cm in length and penetrated all the way through to the base metal. These test panels were evaluated by measuring the total delamination of the paint film from the substrate, in millimetres, on both sides of the scribed line (loss of adhesion between paint film and steel).

2.4 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were performed using a potentiostat/galvanostat (AutoLab EcoChemie PGSTAT30) equipped with a FRA2 frequency response analyser module in a classic three-electrode cell with a working area of 9.62 cm². Ag/AgCl and stainless steel were used as reference electrode and counter electrode, respectively. Frequency scans were carried out by applying a ± 5 mV amplitude sinusoidal wave perturbation, close to the corrosion potential. Five impedance sampling points were registered per decade of frequency in the range from 100 kHz to 1 mHz. The impedance data was analysed using the electrochemical impedance software ZView® (Version 2.9c, Scribner Associates, Inc., USA).

The painted panels were subjected to EIS testing in 0.6M NaCl for about 16 weeks. Measurements were made after 1 day, 2 days, 1 week, 2 weeks, 3 weeks, 4 weeks, 8 weeks and 16 weeks in order to determine the change in pore resistance of the paint.

3. Results and Discussion

3.1 Outdoor test

Adhesion measurements (Figure 1) were carried out prior to exposing the specimens to the atmosphere. The best adhesion was presented by the specimens pre-treated with the γ -GPS silane at both concentrations (1 and 2%), while the poorest corresponded to the conventional phosphate pre-treatment (Figure 1(a)). After two years of exposure the adhesion of the γ -GPS silane worsened significantly and the best value was obtained for the specimen pre-treated with 1% γ -APS silane. It is interesting to note the greater adhesion of the specimens treated with the different silanes, before and after ageing, compared to the conventional pre-treatment.

Attention is also drawn to the poor adhesion obtained with the acrylic / urethane paint (Fig. 1(b)), without and with 1% silane pre-treatment, prior to its exposure to the atmosphere, compared to the alkyd / polyester paint. After two years of atmospheric ageing the adhesion of this paint improved, considerably in some cases. It should be noted that in these three systems (Fig. 1(b)) the failure mode was adhesive, i.e. at the metal/paint interface, whereas in the case of the specimens not exposed to the atmosphere failure occurred at the paint/glue interface.

During atmospheric exposure, and given that the painted area away from the scribe remained without any significant change, only the specimen area around the scribe was considered. The specimens were assessed by measuring the maximum distance of the paint film affected by total delamination on either side of the scribe.

The results obtained are displayed in Figure 2(a). After one year of exposure there is no great difference between the different pre-treatments, but after three years the differences are clearer. The specimens pre-treated with 1% γ -APS silane are those that present the least delamination, corroborating the results obtained on the adhesion specimens (Fig. 1(a)), with even better behaviour than the conventional phosphate pre-treatment.

Comparing the two tested paints (see Figure 2(b)), attention is again drawn to the deficient behaviour obtained with the acrylic/urethane paint, as in the adhesion tests. The results are in all cases worse than those obtained for the alkyd/polyester paint for the same silane and concentration. This underlines the importance of the right choice of silane for the paint that is subsequently to be applied; both elements of the system must be compatible.

As has been mentioned in the experimental procedure, besides the tests performed with 3 pure silanes, some tests were also carried out using five other commercial silane solutions (see Table I (b)). Three of these were monosilanes with ureido (UPS), amino (APS) and epoxy (GLYCH) organofunctional groups and the other two were bisfunctional silanes BAS and BTSE.

The results of pull-off measurements are shown in Figure 3. After two years of exposure the best adhesion was found with the specimens pre-treated with APS and UPS monosilanes at a 25% concentration. The adhesion was poorer for the 10% concentration and, as can be seen in Figure 4, which shows the results for 3 years of atmospheric exposure, the specimens pre-treated with these two silanes at that concentration presented the greatest delamination.

A good adhesion value, similar to that of the monosilanes, is also obtained for the specimen pre-treated with 25% BTSE bis-silane, which does not have an organofunctional group to bond with the paint. There are cases in which the paint adhesion cannot always be explained with specific reactions between the silane functional groups and the paint. Sometimes, this bonding may consist of the formation in the interfacial region of an interpenetrating network,⁵⁴⁻⁵⁶ in which the silane disperses in the polymer matrix with a greater silane concentration closer to the inorganic substrate and a gradually decreasing silane concentration away from the inorganic substrate. This explains how specimens pre-treated with non-functional silanes like BTSE can yield good adhesion values.

However, the type of failure obtained in this case with 25% BTSE, and with the other tested bis-silane, 25% BAS, was cohesive but with different points of adhesive failure, as can be seen in Figure 5. This would indicate areas of weakness at the metal/paint interface with the consequent loss of adhesion in these zones.

3.2 Exposure test in salt fog cabinet

Delamination of the paint film is evaluated around the scribe, as in the atmospheric exposure tests, and the results obtained are shown in Figure 6(a).

Information can only be obtained for short exposure times (~ 100 hours), where the best behaviour is shown by the specimen with the conventional phosphate pre-treatment, which presents delamination of less than 1 cm in the first 400 hours of exposure. The remaining pre-treatments present delaminations of more than 1 cm after only 100 hours of testing.

The results obtained with the acrylic/urethane paint (Figure 6(b)) again show similar delaminations (between 2 to 3 cm) but after 800 hours of testing.

In the case of the commercial silanes (Table I (b)), the salt fog exposure results (see Figure 7) show that the least paint delamination at the scribe is presented by the steel pre-treated with the 25% UPS silane solution, which maintains excellent adhesion after the first 250 hours of salt fog exposure. The good behaviour of this silane has previously been reported in other studies on electrogalvanised steel.⁵⁷

The greatest paint delamination is obtained for the steel pre-treated with 25% GLYCH and 10% BAS silanes. In the latter case it is known that the secondary amine -NH- protonates in the presence of water according to the following equation:

forming -NH_2^+ groups that in turn release hydroxide ions. This explains the basic pH of this solution. As a result of such a high pH the solution tends to form a gel, and so acetic acid must be added in order to lower the pH and stabilise the solution.⁵⁸ The protonation of these secondary amines causes the pre-treated surface of the metal to become positively charged, electrostatically attracting chloride ions from the medium. The need to add HAc in order to stabilise the solution also causes the OH^- ions to neutralise and shifts the balance of the reaction to the right. As a result, more NH groups protonate and the silane layer would become positively charged and increasingly hydrophilic.

3.3 Electrochemical study (EIS)

The model in Figure 8 represents an equivalent circuit frequently used to account for the behaviour of painted metals.⁵⁹ R_e is the electrolyte resistance, C_p and R_p denote the electric capacitance and ionic resistance of the coating, respectively; C_{dl} and R_t are the double layer capacitance and charge transfer resistance at the substrate / coating interface, respectively, and Z_d is the diffusion impedance.

Paint coating degradation arises from the joint simultaneous effects of several factors including permeation of the coating by water, oxygen and various ions, changes in the coating adhesion, etc. The degradation process usually influences the shape and size of the impedance diagrams.⁶⁰ Painted metals typically give Nyquist diagrams consisting of two semicircles (or arcs) and a low frequency tail, which can overlap each other to a greater or lesser extent. The high frequency semicircle is usually related to the paint coating, while the medium / low frequency semicircle is related to substrate corrosion; a low frequency tail is related to diffusion.⁵⁹⁻⁶¹

The diameter of the high frequency semicircle in the Nyquist diagram coincides with R_p and the diameter of the low or medium frequency semicircle with R_t . This model has been used to interpret impedance measurements and obtain information on the evolution of the metal / pre-treatment / paint system with testing time.

As has been noted above in the experimental procedure, the EIS study was only performed with the silane specimens listed in Table I (a) and coated with the alkyd / polyester paint. Table II shows the C_p and R_p values calculated from the impedance diagrams obtained for different immersion times, and Figure 9, as can be seen, is a representation of some of these values. C_p has remained practically constant throughout the test, which R_p has tended to decrease, reflecting a certain deterioration of the coating in contact with the saline solution. The small variation of C_p suggests that the measured values mainly reflect the original characteristics of the paint film (thickness, permittivity and surface area), and to a much lesser extent its state of degradation. The solution has probably penetrated the coating via discrete pathways, whose tiny cross-sectional area scarcely alters the overall surface area of the paint coating [59,61]; the duration of the test has been insufficient to reach a strong state deterioration of the coating.

In contrast, the absolute value of the cross-sectional area of the high conductivity pathways must have considerably increased during the test, which is translated into a notable reduction in the R_p value.

In the event of any important deterioration in the paint film, the impedance diagram would have clearly shown the effects of the faradaic corrosion reaction in the uncovered areas of the metallic substrate. However, no such trend has clearly been seen in the impedance diagrams obtained in this work. For variable and transitory nature, forms, which have occasionally appeared in the drawing of diagrams, to low or medium frequency cannot be considered representative of the system and give information about typical behaviors. These forms may relate to changing states of a dynamic process of opening and tamponage by corrosion products of microscopic pores in the paint film. The R_p values obtained for long immersion times are of an order of magnitude close to 10^7 ohms, and these values indicate an intermediate coating quality following the criteria of Lee and Mansfeld for classification of the (barrier) protective properties of polymer coatings.⁶²

The results obtained correspond to an intermediate stage in the paint film degradation process. The metal/paint system's response to the applied electrical signal can be described almost exclusively in terms of the values of R_p and C_p in the equivalent circuit of Figure 8.

Considering that the C_p values have remained practically constant throughout the test, all the information on the behaviour of the painted specimens has been deduced from the variations observed in the R_p values.

The electrochemical behaviour of the coated systems shows that pre-treatment with silanes is compatible with the alkyd paint system. Of all the silanes used to pre-treat the steel, 2% γ -APS and 1% and 2% γ -GPS are those that have yielded the best results, with similar R_p values to those of the steel with conventional phosphate pre-treatment (Fig. 10). The 1% bis-amine is that which have offered the most deficient behaviour.

4 Conclusions

From the results obtained the following conclusions may be drawn:

- 1% γ -APS (amino functional group) pre-treated specimens offer good adhesion to the alkyd / polyester base paint after two years (adhesion test) and three years (total delamination around the scribe) of outdoor exposure in an atmosphere of moderate aggressivity, even outperforming the reference phosphate type treatment.
- In the most aggressive environment (salt fog test) attention is drawn to the good behaviour of the 25% UPS silane (ureido functional group), which also shows good adhesion (adhesion test) after atmospheric ageing, similar to that of the phosphate (reference conventional treatment).
- The ac impedance results in 0.6M NaCl show that the γ -APS (2%) and γ -GPS (1 and 2%) silanes offer similar behaviour to the conventional phosphate pre-treatment.
- Importance of the existence of good compatibility between the components of the silane / paint system. The acrylic / urethane system was seen to be incompatible with the tested silanes, leading to highly deficient results. This was not the case with the alkyd / polyester paint.

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5 References

1. Toxicological Profile for Chromium, Agency for Toxic Substances, US Public Health Service, Report no. ATSDR/TP-88/10, July 1989.
2. Twite, RL, Bierwagen, GP, "Review of Alternatives to Chromate for Corrosion Protection of Aluminum Aerospace Alloys." *Prog. Org. Coat.*, 33 (2) 91-100 (1998).
3. Gugliemi, M, "Sol-gel Coatings on Metals." *J. Sol-Gel Sci. Tech.*, 8 (1-3) 443-449 (1997).
4. van Ooij, WJ, Zhu, D, Palanivel, V, Lamar, JA, Stacy, M, "Overview: The Potential of Silanes for Chromate Replacement in Metal Finishing Industries." *Silicon Chemistry* 3 (1) 11-30 (2006).
5. van Ooij, WJ, Zhu, D, Stacy, M, Seth, A, Mugada, T, Gandhi, J, Puomi, P, "Corrosion Protection Properties of Organofunctional Silanes—An Overview." *Tsinghua Sci. Technol.* 10 (6) 639-664 (2005).
6. Cabral, AM, Trabelsi, W, Serra, R, Montemor, MF, Zheludkevich, ML, Ferreira, MGS, "The Corrosion Resistance of Hot Dip Galvanised Steel and AA2024-T3 Pre-treated with Bis-[triethoxysilylpropyl]tetrasulfide Solutions Doped with $\text{Ce}(\text{NO}_3)_3$." *Corros. Sci.* 48 (11) 3740-3758 (2006).
7. Trabelsi, W, Cecílio, P, Ferreira, MGS, Yasakau, K, Zheludkevich, ML, Montemor, MF, "Surface Evaluation and Electrochemical Behavior of Doped Silane Pre-treatments on Galvanized Steel Substrates." *Prog. Org. Coat.* 59 (3) 214-223 (2007).
8. Suegama, PH, de Melo, HG, Benedetti, AV, Aoki, IV, "Influence of Cerium (IV) Ions on the Mechanism of Organosilane Polymerization and on the Improvement of its Barrier Properties." *Electrochim. Acta*, 54 (9) 2655-2662 (2009).

9. Montemor, MF, Cabral, AM, Zheludkevich, ML, Ferreira, MGS, "The Corrosion Resistance of Hot Dip Galvanised Steel Pretreated with Bis-functional Silanes Modified with Microsilica". *Surf. Coat. Tech.* 200 (9) 2875-2885 (2006).
10. Palanivel, V, Huang, Y, van Ooij, WJ, "Effects of Addition of Corrosion Inhibitors to Silane Films on the Performance of AA2024-T3 in a 0.5 M NaCl Solution." *Prog. Org. Coat.* 53 (2) 153-168 (2005).
11. De Graeve, I, Vereecken, J, Franquet, A, Van Schaftingen, T, Terryn, H, "Silane Coating of Metal Substrates: Complementary Use of Electrochemical, Optical and Thermal Analysis for the Evaluation of Film Properties." *Prog. Org. Coat.* 59 (3) 224-229 (2007).
12. Hu, JM, Liu, L, Zhang, JQ, Cao, CN, "Electrodeposition of Silane Films on Aluminium Alloys for Corrosion Protection." *Prog. Org. Coat.* 58 (4) 265-271 (2007).
13. Cabral, AM, Duarte, RG, Montemor, MF, Ferreira, MGS, "A Comparative Study on the Corrosion Resistance of AA2024-T3 Substrates Pre-treated with Different Silane Solutions: Composition of the Films Formed." *Prog. Org. Coat.* 54 (4) 322-331 (2005).
14. Zhu, D, van Ooij, WJ, "Corrosion Protection of Metals by Water-based Silane Mixtures of Bis-[trimethoxysilylpropyl]amine and Vinyltriacetoxysilane." *Prog. Org. Coat.* 49 (1) 42-53 (2004).
15. Franquet, A, Biesemans, M, Terryn, H, Willem, R, Vereecken, J, "Study of the Interaction of Hydrolysed Silane Solutions with Pre-treated Aluminium Substrates." *Surf. Interface Anal.* 38 (4) 172-175 (2006).
16. Chico, B, Pérez, ML, de la Fuente, D, Morcillo, M, "Study of the Behaviour of Silane-base Pretreatments Applied on Aluminium Substrates." *Proc. of the 16th International Corrosion Congress, Peking, China, September 2005.*

17. Susac, D, Sun, X, Mitchell, KAR, "Adsorption of BTSE and γ -APS Organosilanes on Different Microstructural Regions of 2024-T3 Aluminum Alloy." *Appl. Surf. Sci.* 207 (1-4) 40-50 (2003).
18. Song, J, van Ooij, WJ, "Bonding and Corrosion Protection Mechanisms of γ -APS and BTSE Silane Films on Aluminum Substrates." *J. Adhes. Sci. Technol.* 17 (16) 2191-2221 (2003).
19. van Ooij, WJ, Zhu, D, "Electrochemical Impedance Spectroscopy of Bis-[triethoxysilylpropyl]tetrasulfide on Al 2024-T3 Substrates." *Corrosion* 57 (5) 413-427 (2001).
20. Deflorian, F, Rossi, S, Fedrizzi, L, "Silane Pre-treatments on Copper and Aluminium." *Electrochim. Acta* 51 (27) 6097-6103 (2006).
21. Van Schaftingen, T, Le Pen, C, Terryn, H, Hörzenberger, F, "Investigation of the Barrier Properties of Silanes on Cold Rolled Steel." *Electrochim. Acta* 49 (17-18) 2997-3004 (2004).
22. Sundararajan, GP, van Ooij, WJ, "Silane Based Pretreatments for Automotive Steels." *Surf. Eng.* 16 (4) 315-320 (2000).
23. Yuan, W, van Ooij, WJ, "Characterization of Organofunctional Silane Films on Zinc Substrates", *J. Colloid Interf. Sci.* 185 (1) 197-209 (1997).
24. Sinapi, F, Forget, L, Delhalle, J, Mekhalif, Z, "Self-assembly of (3-mercaptopropyl)trimethoxysilane on Polycrystalline Zinc Substrates towards Corrosion Protection." *Appl. Surf. Sci.* 212-213 (15 May) 464-471 (2003).
25. Bexell, U, Mikael Grehk, T, "A Corrosion Study of Hot-dip Galvanized Steel Sheet Pre-treated with γ -mercaptopropyltrimethoxysilane." *Surf. Coat. Tech.* 201 (8) 4734-4742 (2007).

26. Montemor, MF, Rosqvist, A, Fagerholm, H, Ferreira, MGS, "The Early Corrosion Behaviour of Hot Dip Galvanised Steel Pre-treated with Bis-1,2-(triethoxysilyl)ethane." *Prog. Org. Coat.* 51 (3) 188-194 (2004).
27. Puomi, P, Fagerholm, H, "Characterization of Hot-dip Galvanized (HDG) Steel Treated with γ -UPS, VS, and Tetrasulfide." *J. Adhes. Sci. Technol.* 15 (5) 509-533 (2001).
28. Puomi, P, Fagerholm, H, "Characterization of Hot-dip Galvanized (HDG) Steel Treated with Bis-1,2-(triethoxysilyl)ethane and γ -aminopropyltriethoxysilane." *J. Adhes. Sci. Technol.* 15 (8) 869-888 (2001).
29. Kim, HJ, Zhang, J, Yoon, RH, Gandour, R, "Development of Environmentally Friendly Nonchrome Conversion Coating for Electrogalvanized Steel." *Surf. Coat. Tech.* 188-189 (November-December) 762-767 (2004).
30. Fedel, M, Olivier, M, Poelman, M, Deflorian F, Rossi, S, Druart, ME, "Corrosion Protection Properties of Silane Pre-treated Powder Coated Galvanized Steel." *Prog. Org. Coat.*, 66 (2) 118-128 (2009).
31. Komh, G, Lu, J, Wu, H, "Post Treatment of Silane and Cerium Salt as Chromate Replacers on Galvanized Steel." *Rare Earths*, 27 (1) 164-168 (2009).
32. Cecchetto, L, Denoyelle, A, Delabougliise, D, Petit, JP, "A Silane Pre-treatment for Improving Corrosion Resistance Performances of Emeraldine Base-coated Aluminium Samples in Neutral Environment." *Appl. Surf. Sci.*, 254 (6) 1736-1743 (2008).
33. Montemor, MF, Ferreira, MGS, "Electrochemical Study of Modified Bis-[triethoxysilylpropyl]tetrasulfide Silane Films Applied on the AZ31 Mg Alloy." *Electrochim. Acta.*, 52 (27) 7486-7495 (2007).

34. Montemor, MF, Ferreira, MGS, "Analytical and Microscopic Characterisation of Modified Bis-[triethoxysilylpropyl]tetrasulphide Silane Films on Magnesium AZ31 Substrates." *Prog. Org. Coat.*, 60 (3) 228-237 (2007).
35. Zucchi, F, Grassi, V, Frignani, A, Monticelli, C, Trabanelli, G, "Influence of a Silane Treatment on the Corrosion Resistance of a WE43 Magnesium Alloy." *Surf. Coat. Tech.*, 200 (12-13) 4136-4143 (2006).
36. Zhang, J, Wu, C, "Corrosion Protection Behaviour of AZ31 Magnesium Alloy with Cathodic Electrophoretic Coating Pretreated by Silane." *Prog. Org. Coat.*, 66 (4) 387-392 (2009).
37. Child, TF, van Ooij, WJ, "Application of Silane Technology to Prevent Corrosion of Metals and Improve Paint Adhesion." *Trans IMF* 77 (2) 64-70 (1999).
38. Franquet, A, Terryn, H, Vereecken, J, "Composition and Thickness of Non-functional Organosilane Films Coated on Aluminium Studied by Means of Infra-red Spectroscopic Ellipsometry." *Thin Solid Films* 441 (1-2) 76-84 (2003).
39. Chico, B, Pérez, ML, de la Fuente, D, Morcillo, M, "Effect of Silane Solution Concentration on the Anticorrosive Protection of Pretreatments Applied on Steel." in: Fedrizzi, L, Terryn, H, Simões, A (eds.), *Innovative Pre-treatment Techniques to Prevent Corrosion of Metallic Surfaces*, pp. 148-157. Woodhead Publishing Ltd., Cambridge (2007).
40. Franquet, A, De Laet, J, Schram, T, Terryn, H, Subramanian, V, van Ooij, WJ, Vereecken, J, "Determination of the Thickness of Thin Silane Films on Aluminium Surfaces by Means of Spectroscopic Ellipsometry." *Thin Solid Films*, 384 (1) 37-45 (2001).
41. Franquet, A, Le Pen, C, Terryn, H, Vereecken, J, "Effect of Bath Concentration and Curing Time on the Structure of Non-functional Thin Organosilane Layers on Aluminium." *Electrochim. Acta* 48 (9) 1245-1255 (2003).

42. Zhu, D, van Ooij, WJ, "Structural Characterization of Bis-[triethoxysilylpropyl] tetrasulfide and Bis-[trimethoxysilylpropyl]amine Silanes by Fourier-transform Infrared Spectroscopy and Electrochemical Impedance Spectroscopy". *J. Adhes. Sci. Technol.* 16 (9) 1235-1260 (2002).
43. Pantoja, M, Díaz-Benito, B, Velasco, F, Abenojar, J, del Real, JC, "Analysis of Hydrolysis Process of γ -methacryloxypropyltrimethoxysilane and its Influence on the Formation of Silane Coatings on 6063 Aluminium Alloy." *Appl. Surf. Sci.*, 255 (12) 6386-6390 (2009).
44. Abel, ML, Joannic, R, Fayos, M, Lafontaine, E, Shaw, SJ, Watts, JF, "Effect of Solvent Nature on the Interaction of γ -glycidoxypyltrimethoxy silane on Oxidised Aluminium Surface: a Study by Solution Chemistry and Surface Analysis." *Int. J. Adhes. Adhes.* 26 (1-2) 16-27 (2006).
45. Gener, M, Chico, B, Simancas, J, de la Fuente, D, Morcillo, M, "Caracterización Superficial de Nuevos Pre-tratamientos a Base de Silanos Aplicados Sobre Aluminio." *Rev. Metal. Madrid*, Vol. Extr. 428-432 (2005).
46. Chico, B, Gener, M, de la Fuente, D, Simancas, J, Morcillo, M, "Análisis Superficial de Pre-tratamientos Base Silano Aplicados sobre Substratos de Acero." *Proc. of Latincorr 2003*, Santiago de Chile, Chile, October 2003.
47. Chico, B, Galván, JC, de la Fuente, D, Morcillo, M, "Electrochemical Impedance Spectroscopy Study of the Effect of Curing Time on the Early Barrier Properties of Silane Systems Applied on Steel Substrates", *Prog. Org. Coat.* 60 (1) 45-53 (2007).
48. Franquet, A, Terryn, H, Vereecken, J, "IRSE Study on Effect of Thermal Curing on the Chemistry and Thickness of Organosilane Films Coated on Aluminium." *Appl. Surf. Sci.* 211 (1-4) 259-269 (2003).

49. Subramanian, V, van Ooij, WJ, "Silane Based Metal Pretreatments as Alternatives to Chromating." *Surface Engineering*, 15 (2) 168-172 (1999).
50. Horner, MR, Boerio, FJ, Clearfield, HM, "An XPS Investigation of the Adsorption of Aminosilanes onto Metal Substrates." *J. Adhesion Sci. Technol*, 6 (1) 1-22 (1992).
51. ASTM D4541 "Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers", ASTM, Philadelphia (2002).
52. ISO 9223, "Corrosion of Metals and Alloys. Corrosivity of Atmospheres", ISO (1992).
53. ASTM B 117-97, Test Method for Salt Spray (fog) Testing", ASTM, Philadelphia, (1997).
54. van Ooij, WJ, Zhu, DQ, Prasad, G, Jayaseelan, S, Fu, Y, Teredesai, N, "Silane Based Chromate Replacements for Corrosion Control, Paint Adhesion, and Rubber Bonding." *Surf. Eng.*, 16 (5) 386-396 (2000).
55. Williams, B, "A Systematic Study of the Effect of Deposition Conditions for Organosilane Coverage on Zinc-coated Steel." *Proc. of the 47th Chemists' Conference*, Scarborough, UK, June 1995.
56. Plueddemann, EP, "Silane Primers for Epoxy Adhesives." *J. Adhesion Sci. Technol.*, 2 (3) 179-188 (1988).
57. van Ooij, WJ, Child, T, "Protecting Metals with Silane Coupling Agents." *Chemtec*, February 26-35 (1998).
58. Zhu, D, van Ooij, WJ, "Enhanced Corrosion Resistance of AA 2024-T3 and Hot-dip Galvanized Steel Using a Mixture of Bis-[triethoxysilylpropyl]tetrasulfide and Bis-[trimethoxysilylpropyl]amine" *Electrochimica Acta* 49 (7) 1113-1125 (2004).
59. Feliu, S, Galván, JC, Morcillo, M, "The Charge Transfer Reaction in Nyquist Diagrams of Painted Steel." *Corros. Sci.*, 30 (10) 989-998 (1990).

60. Galván, JC, Feliu, S, Morcillo, M, "Reproducibility of Electrical Impedance Data for a Metal / Paint System." *Prog. Org. Coat.*, 17 (2) 135-142 (1989).
61. Feliu, S, Galván, JC, Morcillo, M, "An Interpretation of Electrical Impedance Diagrams for Painted Galvanized Steel." *Prog. Org. Coat.*, 17 (2) 143-153 (1989).
62. Lee, CC, Mansfeld, F, "Automatic Classification of Polymer Coating Quality Using Artificial Neural Networks." *Corros. Sci.*, 41 (3) 439-461 (1999).

Figure Captions

- Figure 1. Adhesion strength of pre-treated steel surfaces with the silanes (Table I(a))
- Figure 2. Creepback (paint delamination) in scribe area of pre-treated steel specimens after 3 years of atmospheric exposure. (a) with the alkyd / polyester paint, and (b) comparison between the alkyd / polyester and acrylic / urethane paints.
- Figure 3. Adhesion strength of alkyd / polyester paint on steel surfaces pre-treated with commercial silane solutions (Table I (b)).
- Figure 4. Creepback in scribe area of pre-treated steel specimens (Table I (b)) after 3 years of atmospheric exposure. Finishing paint: alkyd / polyester.
- Figure 5. Failure mode obtained when subjecting to the pull-off test the steel specimens pre-treated with 25% BAS and BTSE silanes after 2 years of exposure to the atmosphere.
- Figure 6. Creepback in scribe area of pre-treated steel specimens after different salt fog exposure times. (a) alkyd / polyester paint, and (b) acrylic / urethane paint.
- Figure 7. Creepback of pre-treated steel specimens (Table I (b)) after different salt fog exposure times. Finishing paint: alkyd / polyester.
- Figure 8. Equivalent circuit for interpreting impedance data of a metal/paint system.
- Figure 9. Nyquist diagrams obtained for different silane/paint systems.
- Figure 10. R_p resistance values obtained from impedance diagrams after 16 weeks of exposure to the salt-fog test.

Figure 1.

Atmospheric Exposure

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Salt-Fog Test

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Table I. Silane compositions

(a) Pure:		
Silane	Designation	Chemical formula
3-aminopropyltriethoxysilane)	γ -APS	$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_2\text{CH}_3)_3$
3-glycidoxypentyltrimethoxysilane	γ -GPS	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2\text{O}(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
Bis(3-triethoxysilylpropyl)amine	Bis-amine	$(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_2\text{CH}_3)_3$
(b) Commercial:		
15% APS in water	APS	$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_2\text{CH}_3)_3$
2.0% Glycidoxysilane in water	GLYCH	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2\text{O}(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
4.2% UPS en agua	UPS	$\text{H}_2\text{N}-\text{CO}-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OR})_3$
2.93% BTSE in water	BTSE	$(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_2\text{CH}_3)_3$
9.5% BAS in water	BAS	$(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$

Table II. Capacitance (Cp) and ionic resistance (Rp) values obtained from impedance diagrams. (Working area: 9.62 cm²).

		Immersion time in NaCl 0.6 M, days							
Pre-treatment	Cp (F) Rp (ohm)	1	2	7	14	21	28	56	112
Phosphate (conventional)	Cp	2.4 e-9	---	2.6 e-9	2.0 e-9	2.0 e-9	2.0 e-9	1.9 e-9	2.2 e-9
	Rp	3.7 e9	---	3.1 e9	7.5 e7	5.4 e7	5.6 e7	6.8 e7	4.7 e7
γ -APS 1%	Cp	---	---	2.7 e-9	2.6 e-9	2.4 e-9	2.4 e-9	2.5 e-9	2.5 e-9
	Rp	---	---	5.2 e7	4.0 e7	3.3 e7	2.3 e7	2.2 e7	1.2 e7
γ -APS 2%	Cp	3.5 e-9	---	---	3.5 e-9	3.5 e-9	3.6 e-9	3.6 e-9	3.1 e-9
	Rp	6.4 e8	---	---	4.1 e8	2.9 e8	2.9 e8	2.6 e8	9.7 e7
γ -GPS 1%	Cp	2.1 e-9	---	2.1 e-9	1.1 e-9	1.1 e-9	1.1 e-9	1.2 e-9	1.2 e-9
	Rp	3.5 e9	---	3.4 e8	8.8 e7	6.9 e7	5.0 e7	5.3 e7	5.5 e7
γ -GPS 2%	Cp	1.2 e-9	1.2 e-9	1.3 e-9	1.3 e-9	1.3 e-9	1.3 e-9	1.3 e-9	1.4 e-9
	Rp	1.8 e8	1.1 e8	5.6 e7	2.7 e7	2.4 e7	2.5 e7	5.5 e7	6.5 e7
Bis-amine 1%	Cp	---	2.3 e-9	2.0 e-9	---	4.1 e-9	1.3 e-9	1.6 e-9	1.6 e-9
	Rp	---	2.5 e7	3.6 e6	---	7.7 e4	1.9 e5	6.1 e5	1.8 e5
Bis-amine 2%	Cp	1.9 e-9	2.0 e-9	1.8 e-9	---	---	1.9 e-9	1.8 e-9	1.8 e-9
	Rp	6.1 e7	7.9 e7	7.3 e7	---	---	3.1 e7	2.2 e7	1.9 e7