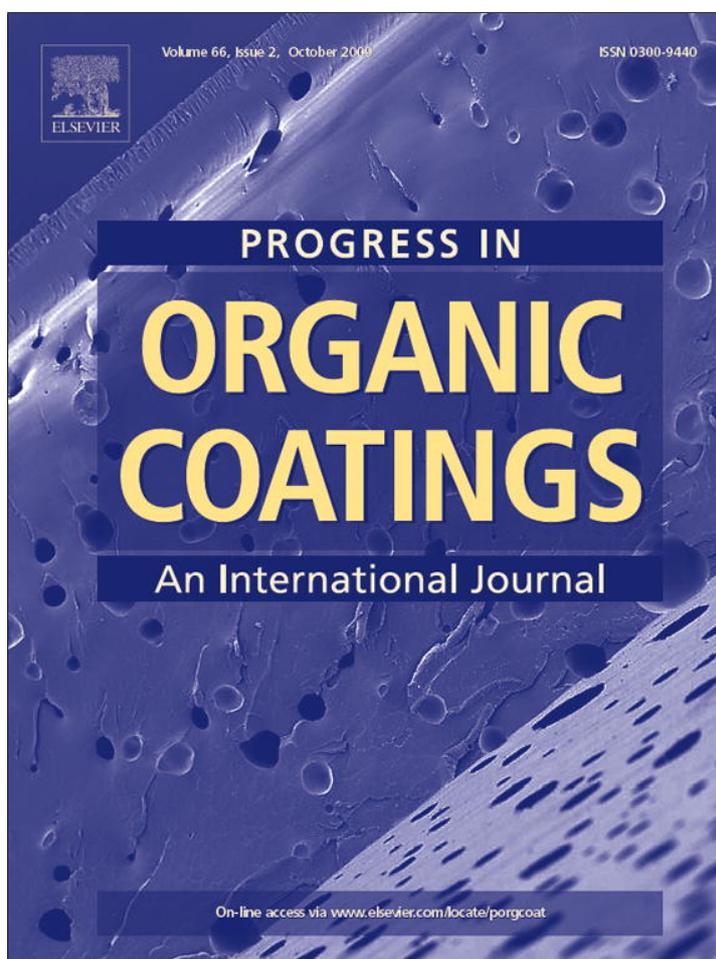


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Corrosion protection properties of silane pre-treated powder coated galvanized steel

M. Fedel^a, M. Olivier^b, M. Poelman^c, F. Deflorian^{a,*}, S. Rossi^a, M.-E. Druart^b^a Department of Materials Engineering and Industrial Technology, University of Trento, Via Mesiano 77, 38100 Trento, Italy^b Service de Science des Matériaux, Faculté Polytechnique de Mons, 9, rue de Houdain, B-7000 Mons, Belgium^c Materia Nova, Parc Initialis, Av. N. Copernic, 1, B-7000 Mons, Belgium

ARTICLE INFO

Article history:

Received 11 December 2008

Received in revised form 12 June 2009

Accepted 18 June 2009

Keywords:

Galvanized steel

Silane pre-treatments

Adhesion

Powder coating

Corrosion

Cathodic delamination

EIS

ABSTRACT

Silane based products are becoming an interesting material for pre-treatment deposition, because, for the environmental compatibility, they can be used as substitutes of traditional pre-treatments like chromates. Silanes have been studied as new pre-treatments before organic coating deposition for many different metals, including aluminium, copper and zinc.

In this work, some results concerning the properties of water-based silane pre-treatments on galvanized steel will be presented.

Galvanized sheets obtained by continuous hot dip process were considered. A silane based bath containing a mixture of three different silanes were used for the pre-treatment deposition (Glycidoxypropyltrimethoxysilane, Tetraethoxysilane and Methyltriethoxysilane).

The obtained pre-treatments were characterized by SEM observations, FT-IR and ToF-Sims analysis. The corrosion protection properties of the pre-treated galvanized samples were studied using industrial accelerated tests (like salt spray exposure) and electrochemical measurements (polarization curves and electrochemical impedance spectroscopy (EIS) measurements), as a function of the different curing conditions. The pre-treated galvanized sheets were further coated with an epoxy-polyester powder coating, in order to verify the adhesion promotion properties and the corrosion protection performances of the complete protective system.

The coated samples were characterized by EIS measurements with artificial defect in order to study the interfacial stability (adhesion) in wet conditions and monitor the coating delamination.

The electrochemical data were compared with adhesion measurements obtained by cathodic delamination tests. The electrochemical tests showed that the silane layer acts not only as a coupling agent between the inorganic substrate and the organic coating, but it also ensures a good barrier effect against water and oxygen.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In the last two decades, the potential of organofunctional silane molecules for the replacement of chrome conversion treatments has been the topic of a huge number of studies [1–7]. Silanes have been widely studied as coupling agents between inorganic and organic materials since the first works of Pluddemann [8]. Concerning corrosion science, a lot of efforts have been made to apply these materials as adhesion promoters between metallic substrates and organic coatings used for protection against corrosion phenomena [9–11]. The chemistry of silanes and the mechanism of interaction of these molecules with a metallic substrate and an

organic coating have been widely explained and are reported in Refs. [12–14]. Silanes films not only ensure the adhesion between metal substrates and organic coatings but they also provide a thin, but efficient, barrier against oxygen diffusion to the metal interface [15]. Compared to the traditional chromate conversion treatments the only drawback of silanes is that they do not provide an active protection to the metallic substrate. In fact, when water and aggressive ions reach the surface of the metal, silane layers are not able to ensure an active inhibition of the corrosion process as well as chromates compounds.

For this reason, and in general to improve the protection properties of the silane layers, several attempts have been made adding cerium and lanthanum salts [16] or CeO₂ and LaO₂ nanopowders [17] to the silane films. In addition, the performances of silane layers filled with silica particles were also evaluated [18].

* Corresponding author. Tel.: +390461882437; fax: +390461881977.
E-mail address: defloria@ing.unitn.it (F. Deflorian).

The effectiveness of silanes as pre-treatment on several metals (aluminium, magnesium, steel) and their environmental friendly characteristics have been widely demonstrated [19].

Though literature is full of studies regarding the properties of the silane surface conversion film itself [1–4,20], the investigations of the complete protection system (metal–silane pre-treatment–organic coating) are not so abundant [21].

In this study a complete protection system containing silane based pre-treatments was evaluated. In particular the corrosion performances of a hot dip galvanized steel treated with silane molecules and covered with an organic coating were analyzed. The aim is to develop a corrosion resistant protection system consisting of only “environmentally friendly” elements. For this purpose, besides using silane pre-treatments instead of chromates, the galvanization bath contains no lead [22] and the powder coating deposition prevents problems due to the volatile organic compounds (VOCs). Moreover, in order to realize a complete ecologic protection system, the silane solution is completely water-based.

The galvanization consists of a zinc layer obtained by a continuous process. The silane solution consist of an experimental mix of three different silanes molecules: γ Glycidoxypropyltrimethoxysilane (γ GPS), Tetraethoxysilane (TEOS) and Methyltriethoxysilane (MTES). γ GPS is an organofunctionalized silane composed of a short carbon backbone with an epoxy functionalized tail and a Si atom substituted with 3 (–O–CH₃) groups. Due to the presence of the epoxy group this molecule ensures an active interaction with the organic coating. TEOS and MTES, after hydrolysis, form an inorganic network on metallic surfaces and give rise to the inorganic phase responsible of the barrier properties of the silane film.

The organic coating is an epoxy-polyester resin. The chemical affinity of the epoxy groups between the silane layer and the organic coating has been properly designed to enhance the adhesion.

Because of the experimental nature of the silane mixture, a commercial water-based silane pre-treatment was used for comparison. In addition, a common industrial pre-treatment such as fluozirconate conversion treatment has been applied for a further comparison, in order to have a complete overview of the different performances of the different pre-treatments.

The characterization of the corrosion protection performances of the complete protection system and the analysis of the silane pre-treatment as neat have been performed by means of chemical and electrochemical techniques (FT-IR, ToF-Sims, EIS, potentiodynamic polarization), accelerated laboratory tests (salt spray chamber, cathodic polarization) and observations with either optical and electron microscope (ESEM). The properties of the different silane layers were underlined and the corrosion protection properties of the complete system were analyzed and discussed.

2. Experimental procedure

2.1. Samples preparation

γ GPS (99% pure), TEOS (99% pure) and MTES (99% pure) were purchased from Degussa and used as received without further purification. The silane solution was prepared dissolving 10 wt.% of the silane mixture in deionized water. The mixture consists of an equal weight percentage of each one of the three silane molecules. The pH was adjusted to 4 adding hydrochloric acid. The solution was vigorously stirred for 1 h before dipping the samples in the silane solution. This lapse of time provides a good degree of hydrolysis of the silane molecules.

The Commercial silane used for comparison is a SIVO[®] water-based silane (supplied by Degussa), whose composition is patented. The dilution is 10 wt.% in water. No modification of the pH of the solution was performed (product specification). Also this solution

Table 1
Name and features of the studied samples.

Name of the sample	Silane treatment	Heat treatment (15 min)	Organic coating
Galvanized steel	–	–	Epoxy-polyester
Silane HT120	Silane mix	120 °C	Epoxy-polyester
Silane HT180	Silane mix	180 °C	Epoxy-polyester
Commercial silane	SIVO	120 °C	Epoxy-polyester
FluoZirc	Fluozirconate conversion treatment	–	Epoxy-polyester

was stirred for 1 h before the dipping of the galvanized samples.

Before the immersion in the silane solution the hot dip galvanized steel sheets (Zn alloy: 0.25 wt.% Al supplied by Arcelor Mittal, Belgium) were degreased with acetone and ultrasounds for 15 min. Afterwards they were cleaned in an alkaline solution containing KOH (Gardoclean[®], supplied by Chemetall) for 10 min at 50 °C. This treatment provides an alkaline etch and a chemical activation of the surface. After rinsing in tap water and then in deionized water, the galvanized panels were dipped for 5 min in the silane solutions. A heat treatment in oven followed the layer deposition. SIVO[®] coated samples were cured at 120 °C for 15 min (as specified by the supplier) while the samples treated with the mixture of silane were cured at two different temperatures, in order to investigate the effect of the curing temperature on the film itself and on the complete protection system. Thus, the samples coated with the experimental mixture were cured at 120 °C and 180 °C for 15 min. Table 1 summarizes the features and characteristics of the different pre-treated samples.

The fluozirconate treatment is an industrial pre-treatment consisting of the dip of the galvanized sample into a solution containing HF and ZrO₂. This treatment provides the formation of a protective film of hydrated compounds of fluorine, zinc, zirconium and oxygen.

The organic coating consists of an epoxy-polyester resin supplied, applied as powder and cured at 210 °C for 15 min by Pintarelli s.r.l. (Italy). The average thickness of these coatings is 70 μ m.

For comparison the organic coating was applied on the silane pre-treated samples and also on the bare galvanized steel and on fluozirconated samples (Table 1).

2.2. Experimental techniques

All electrochemical tests were performed using a Princeton Applied Research Potentiostat 273A and Schlumberger HF Frequency Response Analyser SI 1255. A classical three electrodes arrangement was used. An Ag/AgCl (+0.205 V vs SHE) electrode and a platinum ring were used as reference and counter electrode, respectively. Electrochemical impedance measurements were performed on the pre-treated samples. The frequency range used for these measurements was from 100 kHz to 10 mHz while the signal amplitude was 5 mV. The immersed area was 7.1 cm². The impedance measurements were taken regularly for a convenient lapse of time. The electrolyte used was 5.8% NaCl. Electrochemical impedance measurements were also performed on scratched coated samples. The signal amplitude was 10 mV and the immersed area 9.9 cm². The electrolyte used was 0.3 wt.% Na₂SO₄.

Cathodic and anodic polarization tests were performed on the pre-treated samples. The conductive solution was 3.5% NaCl and the immersed area was 9.9 cm², the curves were obtained after 1 h of immersion with a scan rate of 0.2 mV/s.

Cathodic disbonding test was performed on the organic coated scratched samples. This test was performed in a 0.3 wt.% Na₂SO₄ solution. Concerning the organic coated samples, a 2 cm long scratch was mechanically produced on the paint film in order to

Table 2
Cycles used for the cathodic disbonding test.

Cycle 1 (5×)	OCP: 1 h	DC: −1.6 V vs Ag/AgCl during 30 min
Cycle 2 (10×)	OCP: 1 h	DC: −1.3 V vs Ag/AgCl during 5 h

monitor the evolution of the disbonding process. The cathodic delamination tests were performed at constant potential: −1.2 V vs Ag/AgCl. Moreover, in order to reduce the testing time, two different cathodic delamination cycles were performed. The first cycle consists of 30 min at −1.6 V (vs Ag/AgCl) and 1 h at the OCP. This cycle was repeated five times. The second cycle consists of 5 h at −1.3 V vs Ag/AgCl followed by 1 h at the OCP (open circuit potential). This cycle was repeated 10 times. Table 2 summarizes the different cycles.

The thickness of the thin silane layer was determined using a ToF-Sims. These measurements were carried out on an IOF TOF IV spectrometer equipped with an argon analysis ion gun. The etching conditions were 3 keV, 20 nA rastered over a 300 μm × 300 μm for 30 s.

The FT-IR measurements were carried out by using a Varian 4100 FT-IR Excalibur Series and analyzed by considering the evolution of the transmittance as a function of the wave number.

In addition, qualitative tests such as exposure in the salt spray chamber and immersion in swelling solvent such as n-methylpyrrolidone were performed [23]. The salt spray exposure was

carried out in compliance with the ASTM B117 standard (samples inclination 45°). The immersion in n-methylpyrrolidone was at 50 °C, a few degrees below the glass transition temperature. The ESEM images were collected using a Philips XL30 equipment. Contact angle measurements were also performed, aiming at investigating the hydrophobic/hydrophilic properties of the pre-treated surfaces. These measurements were performed using a Digidrop Contact Angle Meter, GBX Scientific Instruments. The contact angle was measured with three different liquids to determine the dispersive and polar components of the surface energy of the layers. The liquids used are water, formamide and diiodomethane.

3. Results and discussion

3.1. Samples without organic coating

3.1.1. Surface analysis

Fig. 1 shows the ESEM images obtained by using the GSE detector for the bare galvanized sample and the silane coated samples. In particular, Fig. 1a shows the GSE ESEM image of the bare galvanized steel surface, Fig. 1b the Silane HT120 coated surface, Fig. 1c the silane HT180 coated surface and Fig. 1d the Commercial silane coated surface. Because their very low thickness the silane films (1b–d) do not modify the roughness of the surface, they follow the morphology of the galvanized surface (1a).

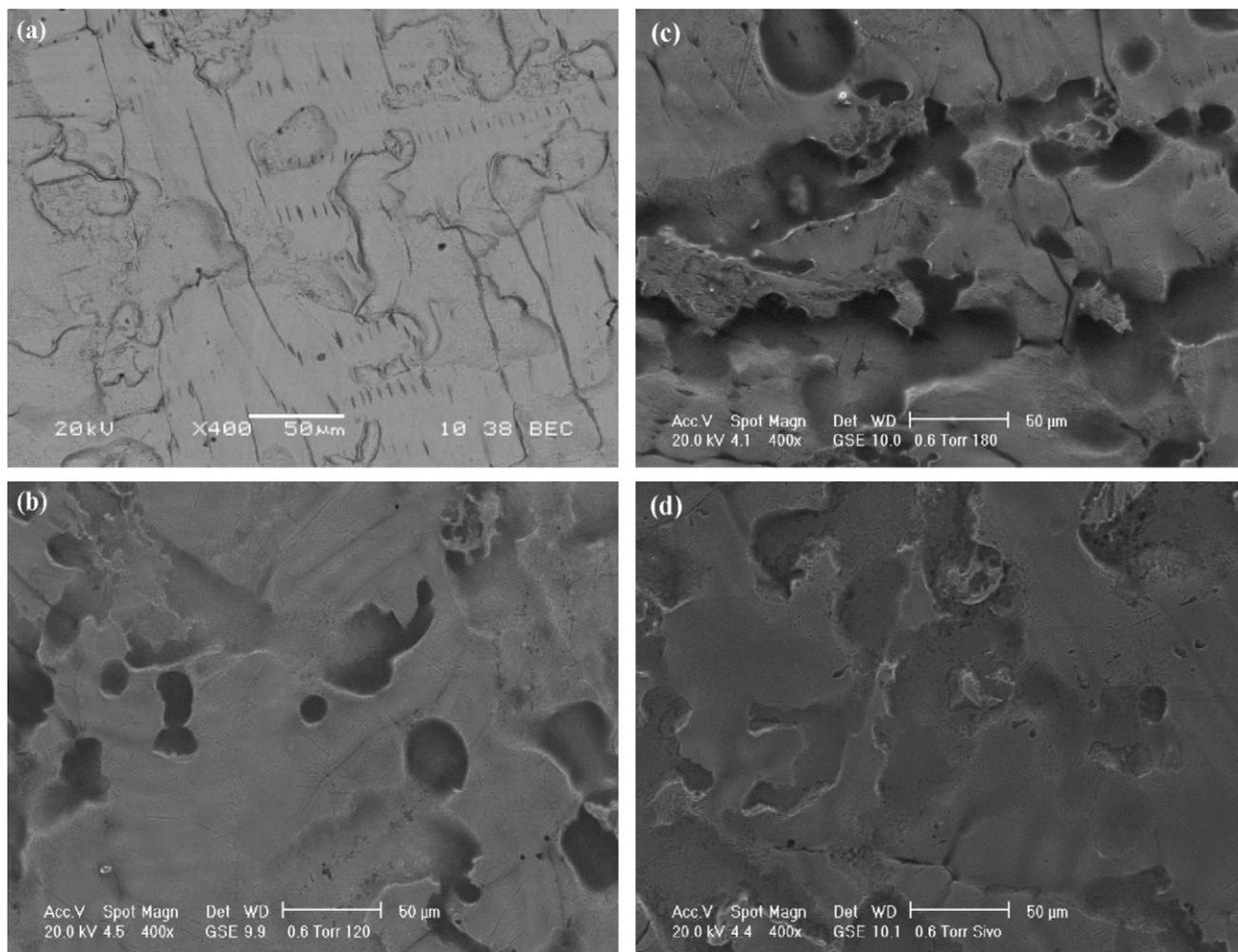


Fig. 1. GSE ESEM images of the bare galvanized steel surface (a), the Silane HT120 coated surface (b), Silane HT180 coated surface (c) and the Commercial silane coated surface (d).

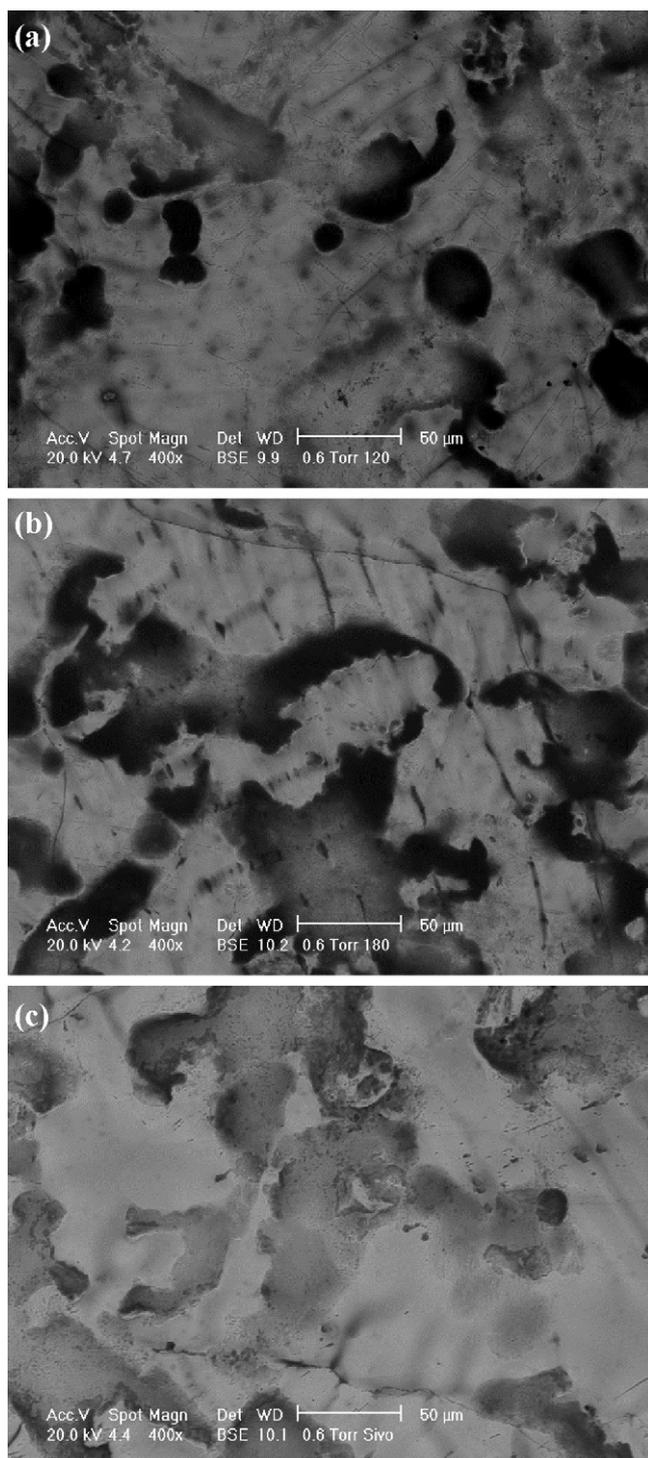


Fig. 2. BSE images of the Silane HT120 coated surface (a), Silane HT180 coated surface (b) and the Commercial silane coated surface (c).

The three different layers seem to be quite homogeneous and there are no clearly visible differences among them. Fig. 2a–c depicts the same samples analyzed by using the BSE detector of the ESEM. Considering the pictures showed in Fig. 2, different areas are observable. In fact there are white “islands” with a sort of black contour. A localized EDXS analysis demonstrates that the dark portions of the pictures are richer in silane (highlighted by the higher intensity of the peak corresponding to the silicon) than the bright areas.

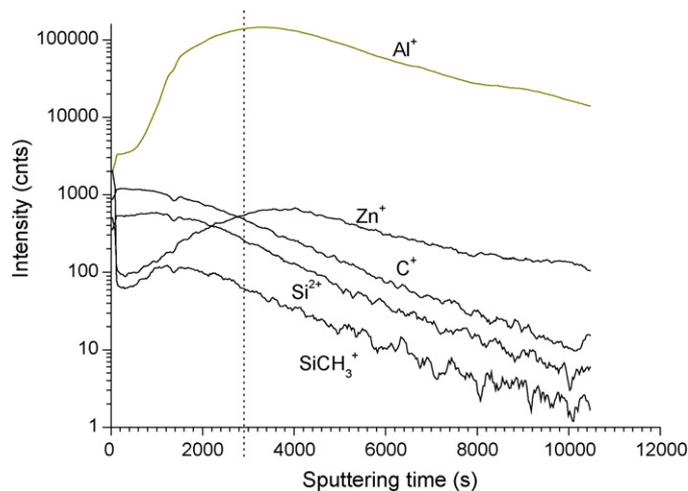


Fig. 3. ToF-Sims profile of Silane HT120 sample.

Table 3

Thickness of the hybrid films measured using ToF-Sims.

Sample	Thickness (Å)	Additional information
Silane HT120	3000	
Silane HT180	1000	High reticulation
Commercial silane	2200	

Despite the film is present over the whole surface, probably there are several accumulations of silane molecules in particular areas of the surface of the sample, where several hollows are observable.

The thickness of the hybrid coupling films was measured by means of the ToF-Sims (Time of Flight–Secondary ions mass spectroscopy). Fig. 3 shows an example of ToF-Sims profile showing the increase of the Al and Zn signal and the decrease of carbon and silicon compounds, due to the silane layer, for Silane HT120 sample. The layer thickness was estimated from the sputtering time shown in the dotted line. Table 3 summarizes the obtained numerical values and some additional information provided by the experimental analysis.

The film obtained curing the silane mixture at 180 °C is thinner and denser compared to the film cured at 120 °C; this results can be explained by the fact that condensation reactions are promoted by heat. Thus, the film cured at 180 °C is characterized by a highly reticulated Si–O–Si network. This denser reticulation, confirmed by ToF-Sims measurements, was observed on the FT-IR spectra. It is indeed possible to note for the Silane HT180 an intense Si–O–Si peak (1080 cm⁻¹) and smaller Si–OH peak (3373 cm⁻¹) if compared with the same peaks measured on Silane HT120 samples or the Commercial silane, also cured at 120 °C (Fig. 4). The thickness of the Commercial silane film is comparable to the thickness of the experimental silane mixture films.

3.1.2. Contact angle measurements

The chemical properties of the films were analyzed measuring the contact angle of the treated samples with water (θ_{water}). In addition, from the measurements of contact angles θ of three different liquids with the silane layers, the dispersive α_s^d and polar α_s^p components of the surface energy of the layers were determined by using the Owens–Wendt model. The surface energy is the sum of dispersive and polar components. These components are connected by the equation of the liquid adhesion work W_a on the solid, given by

$$W_a = \sigma_L(1 + \cos \theta) = 2(\sigma_s^d \sigma_L^d)^{0.5} + 2(\sigma_s^p \sigma_L^p)^{0.5} \quad (1)$$

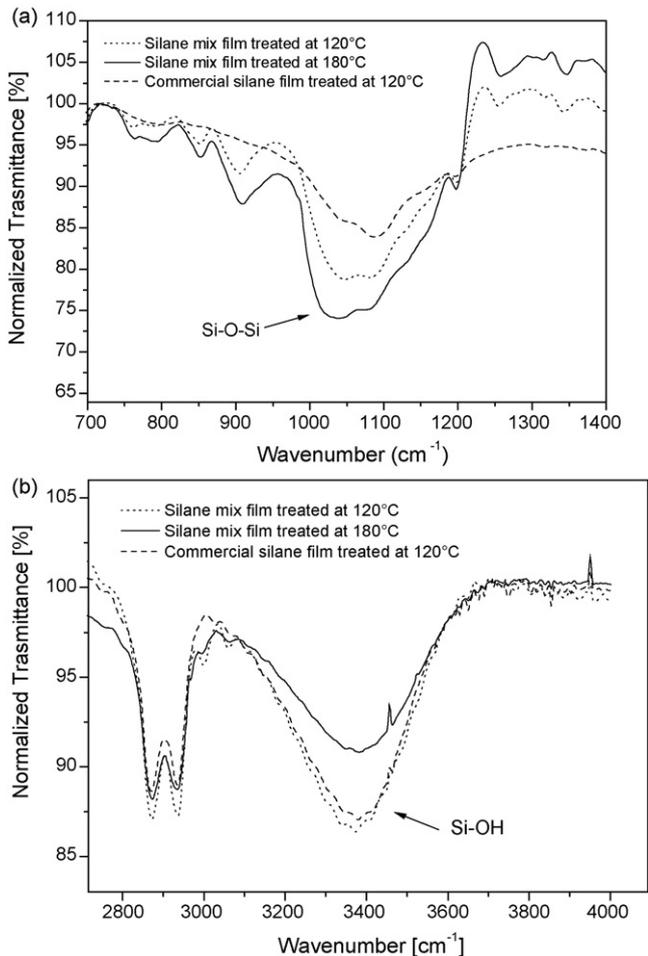


Fig. 4. FT-IR spectra of the silane samples cured at different temperatures: (a) Si–O–Si peaks and (b) Si–OH peaks.

Table 4
 σ_s , σ_s^p , σ_s^D and θ_{water} for each hybrid coupling film.

Sample	σ_s (mJ/m ²)	σ_s^p (mJ/m ²)	σ_s^D (mJ/m ²)	θ_{water} (°)
Silane HT120	44.9	13.8	31.1	61
Silane HT180	43.4	10.3	33.1	67
Commercial silane	57.6	24.6	33.0	17

Table 4 shows the values of σ_s , α_s^p , α_s^D and the contact angle of each film with water (θ_{water}).

The experimental data highlight that the Commercial silane film is very hydrophilic, with a contact angle of 17°, while both the silane mixture treated at different temperatures have a higher value. Between them, the silane mix treated at lower temperature is slightly more hydrophilic compared to the film treated at higher temperature. The differences are mainly due to the polar component of the surface (α_s^p) that changes markedly between the samples. It seems that increasing the reticulation causes a decrease of the amount of SiOH groups as observed by FT-IR and consequently leads to an increasing surface hydrophobicity.

3.1.3. Electrochemical measurements

Electrochemical impedance measurements were carried out to characterize electrochemically the hybrid films. Figs. 5 and 6 show the Bode diagrams after 1 and 7 days of immersion in NaCl solution, respectively.

The sample Silane HT180 maintains a value of the total impedance, which is high for a pre-treatments, also after 7 days

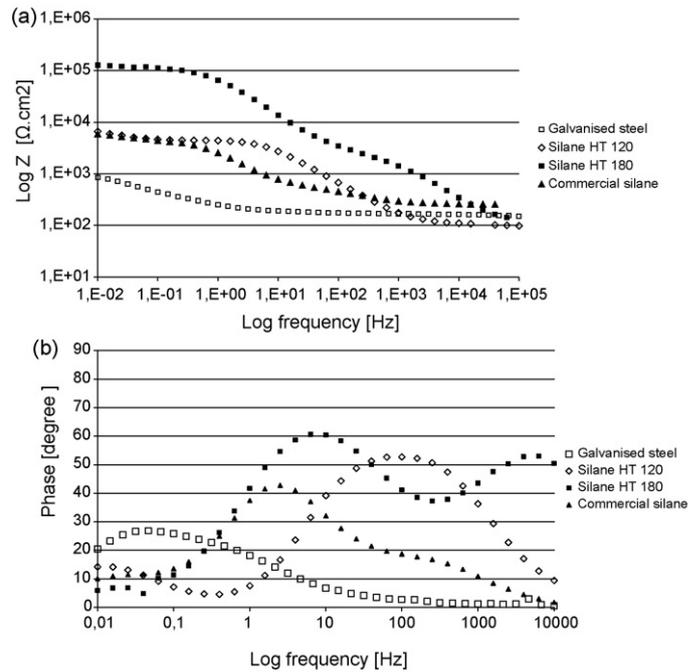


Fig. 5. Bode modulus (a) and phase (b) after 1 day of immersion in 5.8 wt.% NaCl.

of continuous immersion in the conductive solution. The barrier properties of this film seem to be good and probably correlated with the dense and stable network of Si–O–Si bonds. Instead of this, the sample treated with the same silane solution, but cured at lower temperature, shows a decrease of the low frequency impedance modulus. However, the value of the total impedance after 1 day of immersion and the value of the phase angle at intermediate frequencies indicates that the film ensures a slight protection of the substrate. Fig. 7 shows the absolute values of the low frequency impedance modulus for the different treated samples and for the untreated galvanized steel as a function of the immersion time in the electrolyte. The impedance data of the uncoated samples only

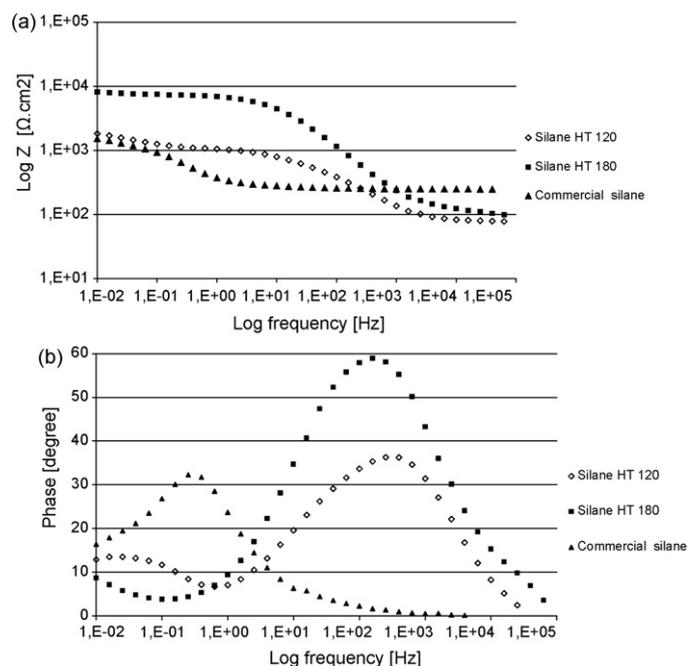


Fig. 6. Bode modulus (a) and phase (b) after 7 days of immersion in 5.8 wt.% NaCl.

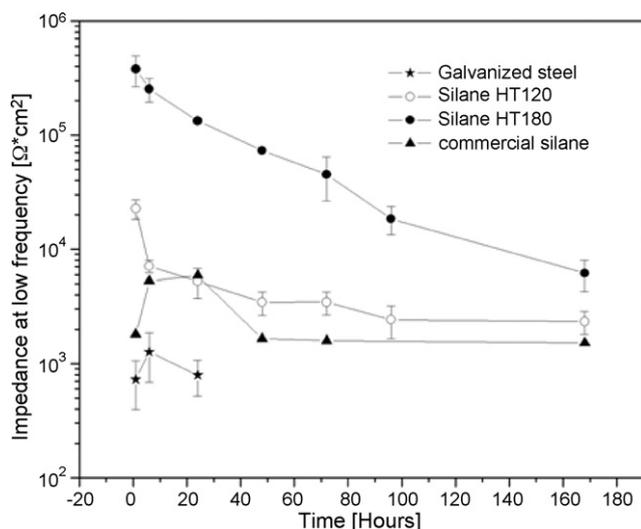


Fig. 7. Absolute values of the impedance modulus at low frequency with time in 5.8 wt.% NaCl solution.

refer to the first hours of immersion because of the formation of corrosion products that affects the measurements.

It is important to underline that silane hybrid films are not designed to interact directly with a corrosive solution, but to be actually a coupling agent. Thus even if a good initial barrier effect is observed, this barrier will be more or less rapidly degraded by the electrolyte resulting in the initiation of metallic corrosion.

The Commercial silane shows the lowest performances. It was demonstrated by means of contact angle measurements that the film is very hydrophilic. Thus the electrolytic solution probably swells easily the commercial film and the barrier properties decrease immediately after the first hours of immersion. Considering the Bode phase in Fig. 5, it is interesting to note that in comparison with the other films, Silane HT180 have two clearly visible time constants. The second loop was observed with measurements performed on similar samples and it has been the object of several studies [24]. However, the correct physical meaning is still unknown but we may expect that the two time constants are associated to two different silane structures, one related to bulk silane layer and the second one related to the interface.

The electrochemical properties of the film were also investigated by means of anodic and cathodic polarization measurements. Fig. 8 shows the polarization curves collected after 1 h of immersion in the conductive solution (3.5 wt.% NaCl). Great differences are observable between the cathodic polarization measurements performed on different samples. In fact there are about three orders of magnitude between the cathodic currents of the sample HT180 and the bare galvanized surface. Observe that all the silane coated

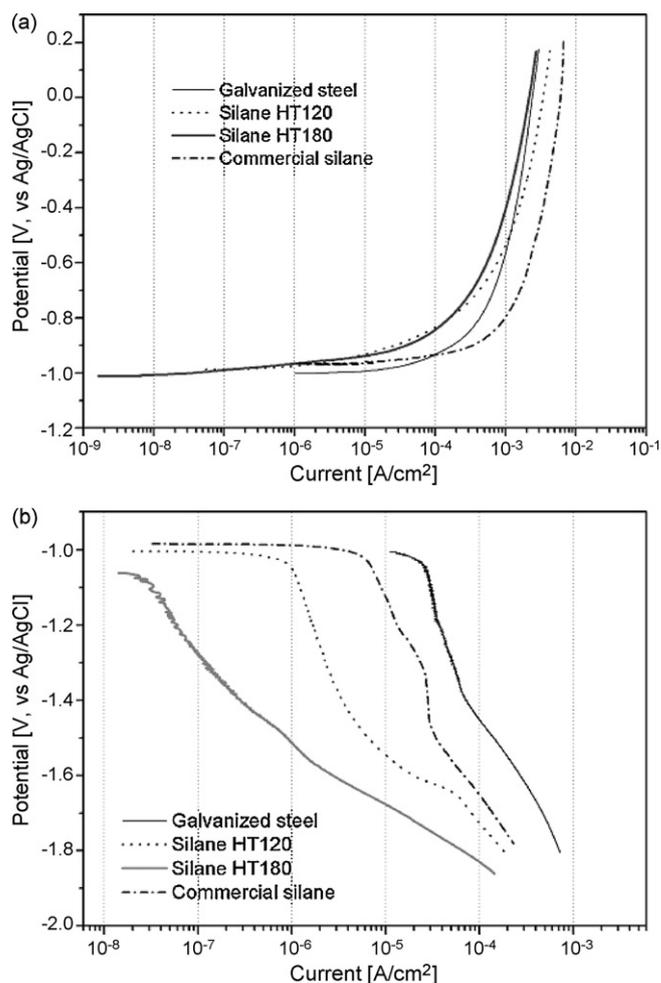


Fig. 8. Anodic (a) and cathodic (b) polarization curves obtained after 1 h of immersion in 3.5 wt.% NaCl solution.

samples have a lower cathodic current than the sample without conversion film. The high degree of reticulation of sample Silane HT180 leads to very good barrier properties, underlined by the very low current density. Sample Silane HT120 shows a good inhibition of the oxygen reduction, even if not as effective as the sample cured at higher temperature. The Commercial silane seems again to present the lowest properties. Despite the great differences in cathodic polarization, the anodic curves look very similar. No evident differences are noticeable between the different samples. The commercial film has a slightly higher current density, but the absolute value is not very far from that obtained with the other samples.

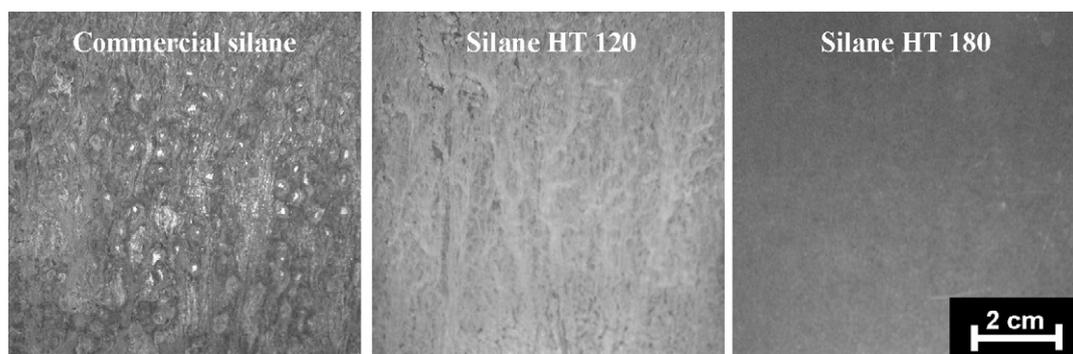


Fig. 9. Commercial silane (left), Silane HT 120 (middle) and Silane HT180 (right) after 24 h of exposure in the salt spray chamber.

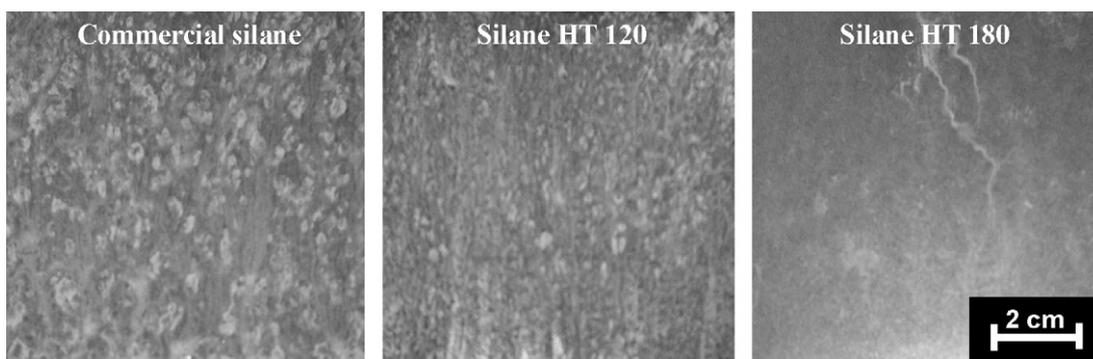


Fig. 10. Commercial silane (left), Silane HT 120 (middle) and Silane HT180 (right) after 72 h of exposure in the salt spray chamber.

Probably the protection ensured by the silane film against corrosion is due to the reduction of the active areas in contact with the electrolytic solution and to the barrier properties against the diffusion of water, oxygen and ions.

3.1.4. Salt fog exposure

The properties of the coupling films were also checked using an industrial and qualitative test such as the exposure to the salt spray chamber. Figs. 9 and 10 depict the experimental results after 24 and 72 h of exposure, respectively.

This test confirms the electrochemical results. Considering Fig. 9, it is evident that after 24 h of exposure the Commercial silane treatment is completely deteriorated and huge amount of white rust (zinc corrosion products) is present on the sample surface. On sample Silane HT120 little quantity of white rust is present, while the coating of Silane HT180 looks undamaged and no white rust is observable. After 72 h of exposure the sample coated with the Commercial silane is completely covered by corrosion products. On the Silane HT120 covered sample white rust is easily visible. The sample covered with Silane HT180 film begins to show a small amount of corrosion products.

The sample treated with the experimental mix ensures very good barrier protection against the environment despite it is a coupling agent. The network formed by the TEOS and MTES molecules probably lead to the formation of a reticulated film on the surface of the metal. The high degree of intermolecular bonds (Si–O–Si) lead to the formation of a film with considerable barrier properties, in particular for a pre-treatment.

3.2. Samples with the organic coating

The application of a powder coating allows us to check the effect of a silane coupling film on the properties of the complete protection system. It is also possible to investigate if the heat treatment at high temperature affects the coupling potential of the silane molecules.

An epoxy-polyester powder coating has been applied on the pre-treated samples. For comparison the organic coating has been also applied on the untreated galvanized steel and on a fluozirconated galvanized steel sample.

In order to characterize the interfacial stability, and so the ability of the pre-treatment to assure coating adhesion even in the presence of defects, two different experimental approaches were used.

The samples with an artificial scratch were characterized using EIS measurements in order to monitor the loss of adhesion. Moreover, two different cathodic delamination tests were performed in order to measure the coating disbonding: the first cathodic disbonding test was done at constant potential -1.2 V vs Ag/AgCl. In order to verify if it is possible to reduce the testing time, a second

set of cathodic delamination tests was done using cyclic procedures, described in Table 2.

The scratches for EIS measurements have a standard length of 20 mm and the thickness of the cutter (about 0.1 mm). The samples were immersed in a 0.3 wt.% Na_2SO_4 solution for 1 week. The progress of the corrosion phenomena was regularly monitored. Figs. 11 and 12 show the Bode modulus and phase after 2 and 48 h of immersion, respectively. The samples with the Commercial silane and fluozirconated pre-treatments show low impedance values indicating a degradation of the protective system and are not

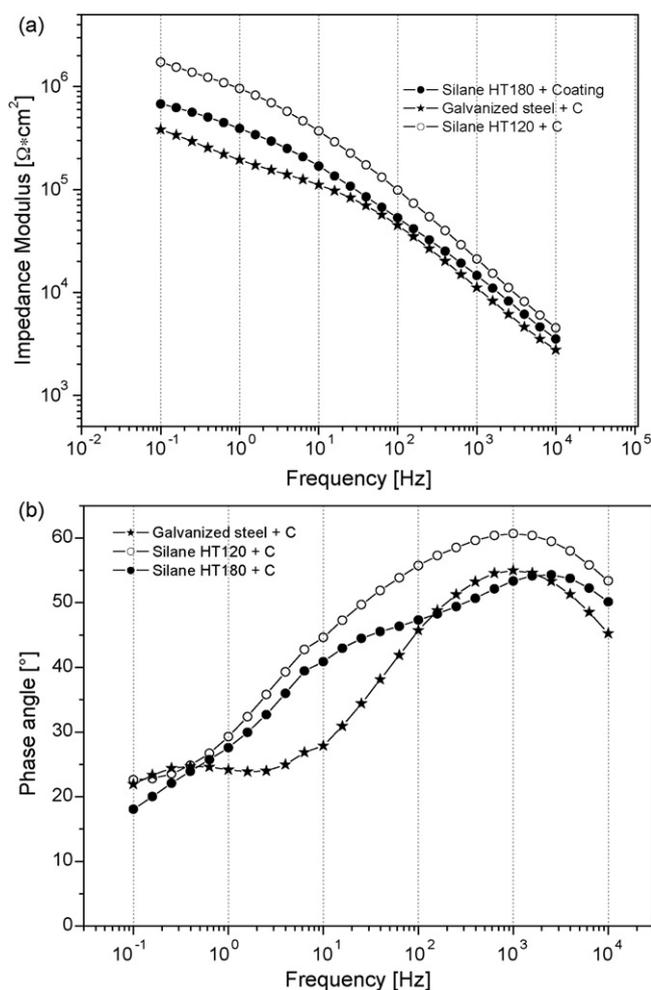


Fig. 11. Bode modulus (a) and phase (b) plots of coated samples after 2 h of immersion in 0.3 wt.% Na_2SO_4 solution.

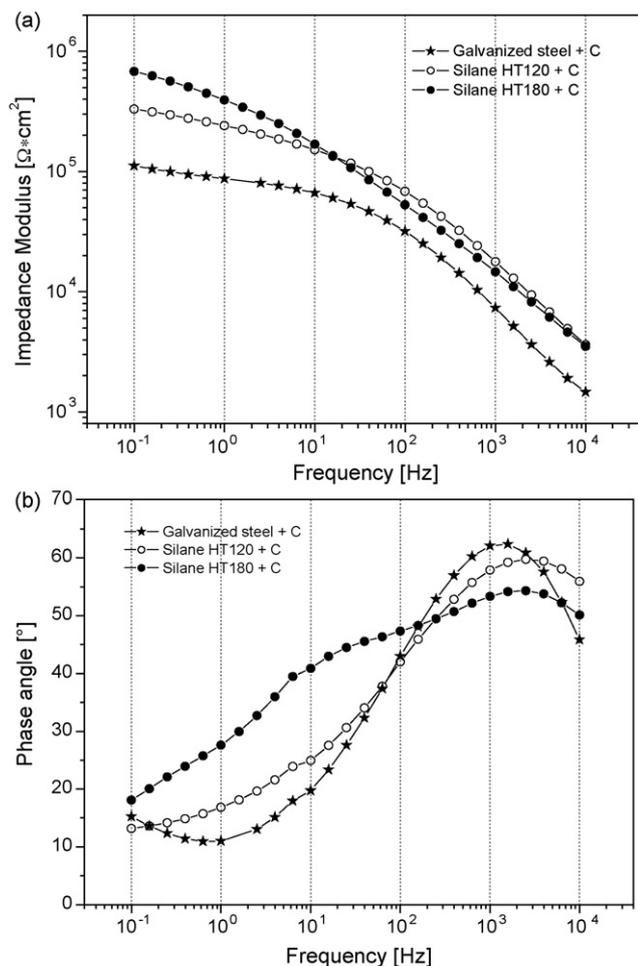


Fig. 12. Bode modulus (a) and phase (b) plots of coated samples after 48 h of immersion in 0.3 wt.% Na_2SO_4 solution.

reported in Figs. 11 and 12. The samples treated with the silane mix seem to ensure a better resistance against the penetration of the electrolyte between the metal and the coating. This fact is proved by the limited decrease of the values of impedance of these samples from 2 to 48 h of immersion.

In order to analyze in deep the behaviour of the silane mix treated samples, several parameters were extracted from the experimental impedance data using a suitable equivalent circuit model. In addition to the electrical parameters describing the contribution to the impedance of the organic coatings (R_p and C_c) (generally not observed experimentally because of the macroscopic defect), two time constants are generally visible: one related to the presence of oxides and one related to the bare metal/electrolyte interface. For monitoring the delamination process we analyzed the evolution of the high frequency time constant [25]. The capacitance value obtained is proportional to the exposed metal surface area. As a consequence, higher the capacitance value, higher the extent of the detachment between the coating and the substrate. Fig. 13 shows, as an example, the tendency of the capacitances (C_{hf}) for the sample without pre-treatments (galvanized steel). It is clear that there is a continuous trend showing an increase of the capacitance related to the delamination process, which is common for all the materials. At the end of the test (120 h of immersion), in order to compare the different silane pre-treatments, we calculated the ratio between the final C_{hf} value (after 120 h) and the initial value (Fig. 14). This ratio is an indication of the enlargement of delamination, and smaller is the value, more stable is the interface. From the data in Fig. 14 it is

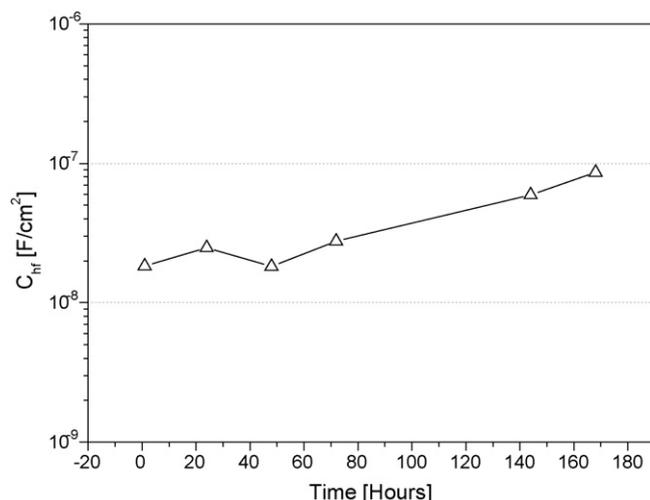


Fig. 13. Double layer capacitance with time of immersion in 0.3 wt.% Na_2SO_4 solution for coated galvanized steel.

clear that stability of the silane mix cured at 180°C (Silane HT 180) is higher.

In order to highlight the different resistances against the disbonding of the coating, cathodic disbonding tests have been performed. The samples were scratched and immersed in the electrolytic solution.

The first delamination test was performed at constant potential ($-1.2\text{V Ag}/\text{AgCl}$). The results, obtained after 5 days are shown in Fig. 15. The sample's ranking is evident: the silane mix samples (Silane HT120 and HT 180) show a limited delaminated area, while the samples fluozirconated and pre-treated with the Commercial silanes show a delaminated area very similar to the delaminated area of the samples without pre-treatment.

In order to try to reduce the testing time, some cyclic cathodic delamination tests were performed following the parameters described in Table 2.

After the end of every complete cycle of the accelerated test the detachment of the coating has been evaluated. Table 5 shows the linear extent of the detachment of the coating at the end of each complete cycle. The extent is expressed as linear dimension of the detached area along the artificial scratch. The data of Table 5 indicate the interval between the higher and the lower extent of the detachment among the three measurements performed. If only one number is present, it means that the three measurements overlap.

Sample Silane HT180 + C shows the best performance in every experimental condition. The linear detachment for this sample is

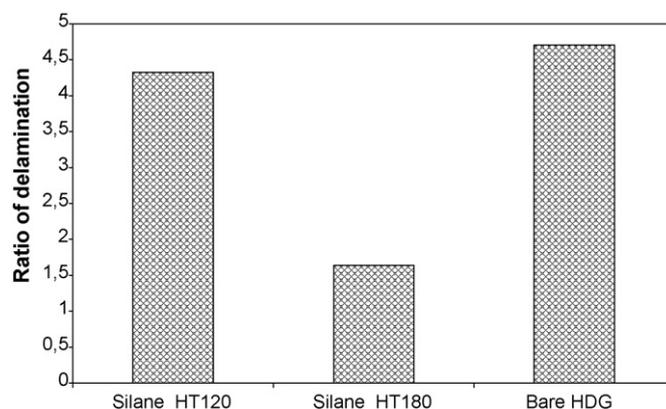


Fig. 14. Ratio of delamination (final C_{dl} divided by initial C_{dl}) after 120 h of immersion in 0.3 wt.% Na_2SO_4 solution.

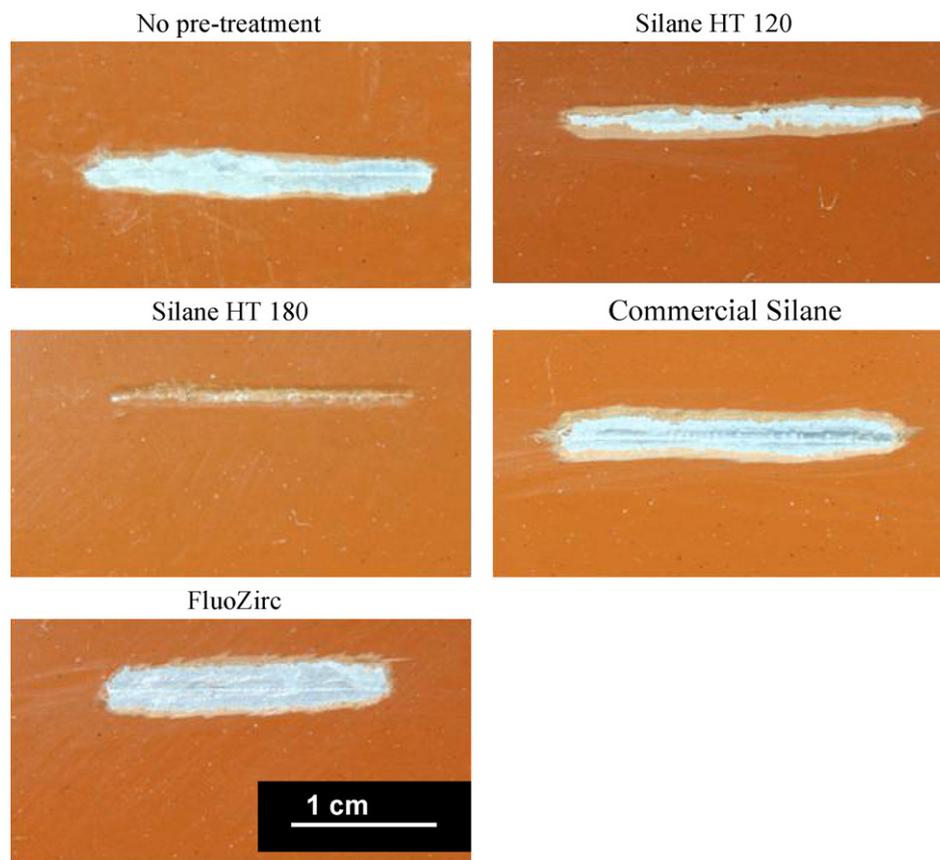


Fig. 15. Coating delamination of the different samples after 5 days of cathodic delamination test at constant potential.

the lowest regardless of the cycle. The treatment with the experimental mix cured at 180 °C ensures good adhesion between the metallic substrate and the coating. The clearest results are obtained with Cycle 2 (60 h total testing time) where the different behaviour of the samples can be easily measured, proving the unsatisfactory behaviour of the Commercial silane and the galvanized steel samples. Remark that these results are consistent with the electrochemical measurements and the constant potential delamination test, but the testing time is reduced by a factor at least two.

The adhesion between the top coat and the substrate was measured using a swelling solvent such as *n*-methyl-pyrrolidone. This molecule is able to swell the paint and to induce stresses between the polymer and the metallic substrate. The lower the adhesion between the powder coating and the substrate, the earlier the detachment occurs. Fig. 16a–e shows the experimental results after 6 h of immersion in the swelling solution at 50 °C.

The untreated sample and the sample with the fluozirconate conversion treatment (Fig. 16a and b, respectively) show a clearly visible detachment of the coating. Concerning other samples, the detachment of the organic coating is not complete but a huge

number of blisters are observable. Since this test is purely qualitative, sample Silane HT180 + C seems to ensure the highest adhesion between the substrate and the coating. This fact is highlighted by the lower density of blisters. Sample Silane HT120 + C and Commercial silane + C are quite similar, even if the blisters of the sample treated with the experimental mix look bigger than the blisters on the Commercial silane treated sample. The good results obtained with a curing temperature of 180 °C must consider the fact that this temperature has not to be exceeded, because it is very close to the temperature at which the epoxy ring opens. This event has to be avoided because the premature opening of the epoxy ring can affect negatively the adhesion between the polymer and the hybrid film.

This technological test corroborates partially the results of the other experiments. In particular it confirms the low adhesion between the samples treated with no silane coupling films. In addition it confirms the very good performance of sample Silane HT180 + C. Note that, in this case, the sample treated with the Commercial silane does not behave as bad as demonstrated with other experimental tests (i.e., cathodic disbonding).

This fact can be explained by the assumption that the Commercial silane treatment ensures a rather good dry adhesion between the polymer and the substrate. Despite of this, when a scratch is realized on the surface, the silane film is directly in contact with the environment (or aggressive solution, as in the experimental test) and it can be easily attacked. The test performed on the uncoated pre-treated samples proved the low resistance of this coupling film against a corrosive environment. In the cathodic disbonding test the electrolyte is directly in contact with the cut edge of the coupling film. The conductive solution probably hydrolyzes it and moves forward between the polymer and the metal accelerating the detachment of the powder coating.

Table 5

Linear extent of the detachment for each sample after the different cycles of cathodic delamination test.

	Linear extent of the detachment (mm)	
	Cycle 1	Cycle 2
Galvanized steel + C	1.5–2.0	5.0–8.0
FluoZirc + C	2.0	3.0
Silane HT120 + C	0.0–1.0	4.0–5.0
Silane HT180 + C	0.0	1.0–3.0
Commercial silane + C	1.5–2.0	8.0–10.0

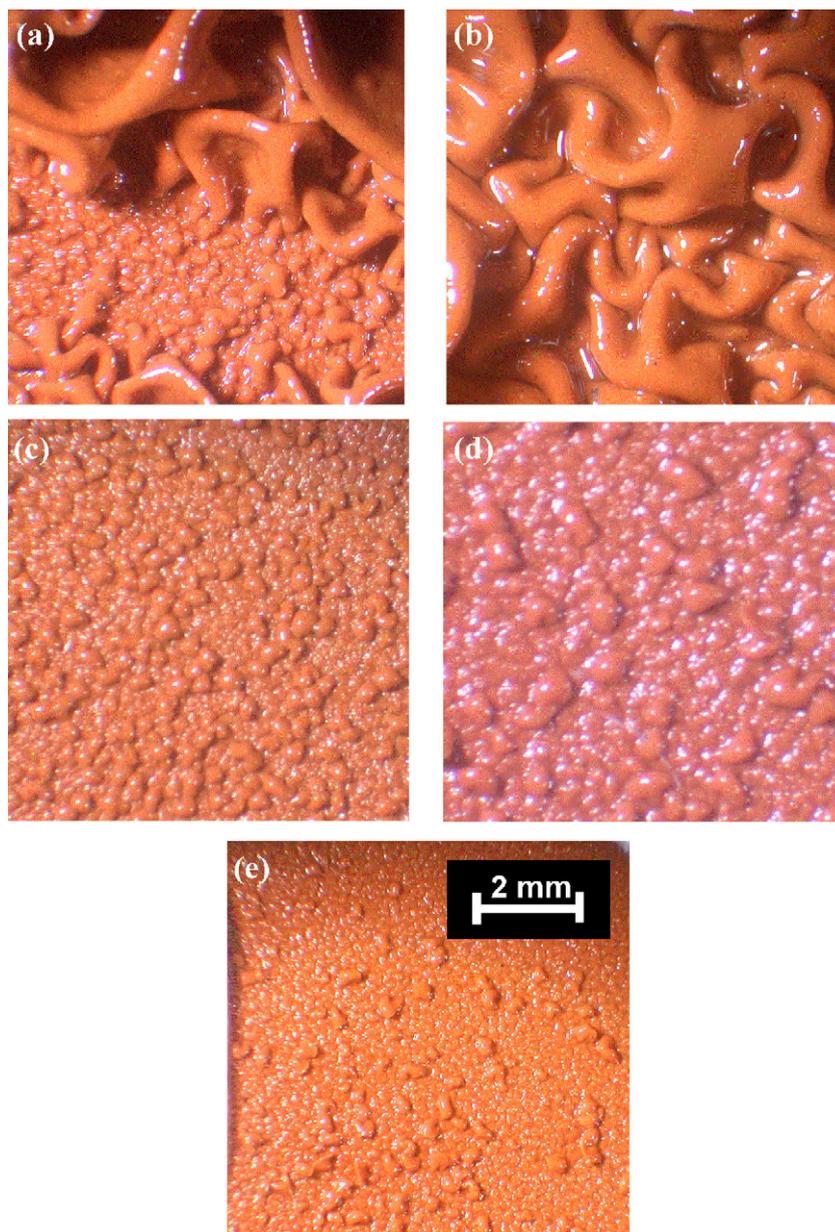


Fig. 16. Galvanized steel + C (a), FluoZirc + C (b), Commercial silane + C (c), Silane HT120 + C (d) and Silane HT180 + C (e) after 6 h of immersion in n-methylpyrrolidone at 50 °C.

4. Conclusions

In the present work the corrosion protection performances of a complete environmentally friendly protection system were evaluated. In particular the properties of an experimental hybrid silane layer were investigated. The results of the electrochemical analysis highlighted the good barrier properties of the innovative silane film, especially when cured at 180 °C. The high temperature of the curing leads to the formation of a dense and highly interconnected silane film. The experimental tests performed on the whole protection system confirmed the key role of the experimental silane pre-treatment. In fact, it ensures not only a barrier effect against water and oxygen, but it acts as an adhesion promoter between the galvanized substrate and the polymer. The treatment Silane HT180 ensures the best corrosion protection properties as compared to the other pre-treatments.

Acknowledgements

The Authors would like to gratefully acknowledge Evonik-Degussa GmbH (Germany) for the provision of chemicals, Pintarelli s.r.l. (Italy) for the support in applying the powder coating, Arcelor Mittal (Belgium) for the supply of the galvanized steel samples and the C.G.R.I.-D.R.I. for their financial support. The Authors would also like to thank Arnaud Pipers for assisting with the salt spray test and the polarization measurements.

References

- [1] K.L. Mittal (Ed.), *Silanes and Other Coupling Agents*, VSP, Utrecht, 1992.
- [2] K.L. Mittal (Ed.), *Silanes and Other Coupling Agents*, vol. 2, VSP, Utrecht, 2000.
- [3] K.L. Mittal (Ed.), *Silanes and Other Coupling Agents*, vol. 3, VSP, Brill, 2004.
- [4] K.L. Mittal (Ed.), *Silanes and Other Coupling Agents*, vol. 4, VSP, Brill/Leiden, 2007.

- [5] W.J. van Ooij, Proceedings ICEPAM 2004, Oslo, Norway, 16–18, 2004, 2004, <http://www.sintef.no>.
- [6] F. Deflorian, S. Rossi, L. Fedrizzi, *Electrochim. Acta* 51 (2006) 6097.
- [7] M.G.S. Ferreira, R.G. Duarte, M.F. Montemor, A.M.P. Simoes, *Electrochim. Acta* 49 (2004) 2927.
- [8] E.P. Plueddemann, *Composites 1* (1970) 321.
- [9] D. Zhu, W.J. van Ooij, *Corros. Sci.* 45 (2003) 2177.
- [10] W.J. van Ooij, D. Zhu, M. Stacy, A. Seth, T. Mugada, J. Gandhi, P. Puomi, *Tsinghua Sci. Technol.* 10 (2005) 639.
- [11] D. Zhu, W.J. van Ooij, *Prog. Org. Coat.* 49 (2004) 42.
- [12] E.P. Plueddemann, *Silane Coupling Agents*, 2nd ed., Plenum Press, New York, 1990.
- [13] Z. Pu, W.J. van Ooij, J.E. Mark, *J. Adhes. Sci. Technol.* 11 (1997) 29.
- [14] M.L. Abel, R. Joannic, M. Fayos, E. Lafontaine, S.J. Shaw, J.F. Watts, *Int. J. Adhes.* 26 (2006) 16.
- [15] P.H. Suegama, H.G. de Melo, A.A.C. Recco, A.P. Tschiptschin, I.V. Aoki, *Surf. Coat. Technol.* 202 (2008) 2850.
- [16] M.F. Montemor, M.G.S. Ferreira, *Prog. Org. Coat.* 63 (2008) 330.
- [17] M.F. Montemor, W. Trabelsi, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, A.C. Bastos, M.G.S. Ferreira, *Electrochim. Acta* (2008), doi:10.1016/j.electacta.2008.03.069.
- [18] M.F. Montemor, A.M. Cabral, M.L. Zheludkevich, M.G.S. Ferreira, *Surf. Coat. Technol.* 200 (2006) 2875.
- [19] W. Trabelsi, L. Dhouibi, E. Triki, M.G.S. Ferreira, M.F. Montemor, *Surf. Coat. Technol.* 192 (2005) 284.
- [20] K.H. Wu, C.M. Chao, T.F. Yeh, T.C. Chang, *Surf. Coat. Technol.* 201 (2007) 5782.
- [21] F. Deflorian, S. Rossi, L. Fedrizzi, M. Fedel, *Prog. Org. Coat.* 63 (2008) 338.
- [22] H. Asgari, M.R. Toroghinejad, M.A. Golozar, *Appl. Surf. Sci.* 253 (2007) 6769.
- [23] W.J. van Ooij, R.A. Edwards, A. Sabata, J. Zappia, *J. Adhes. Sci. Technol.* 7 (1993), 897.
- [24] L.M. Palomino, P.H. Suegama, I.V. Aoki, M.F. Montemor, H.G. De Melo, *Corros. Sci.* 50 (2008) 1258.
- [25] F. Deflorian, L. Fedrizzi, *J. Adhes. Sci. Technol.* 13 (1999) 629.