

VINYLTRIETHOXYSILANE ELECTRO-ASSISTED DEPOSITION AS A PRETREATMENT FOR PAINTING ALUMINUM

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ABSTRACT

Silane coatings are a promising alternative to chromate conversion coatings for aluminum, as their efficacy as a pretreatment for painting has already been observed. The standard method for obtaining these coatings is the dip-coating in sol-gel technique. This may lead to non homogeneous films, impairing their barrier protection against corrosion. Such difficulty may be overcome by the use of silane electro-assisted deposition, which favors the silane condensation as a consequence of water electrolysis. In this study, vinyltriethoxysilane films were produced by both dip-coating and electro-assisted deposition techniques and compared to a chromate conversion coating as a pretreatment for a polyurethane organic coating. Comparisons were made using potentiodynamic polarization, electrochemical impedance spectroscopy, salt spray test, paint adherence test and energy dispersive spectroscopy. Whilst the silane coating did not increase corrosion protection, promising observations that electro-assisted deposition may lead to more homogeneous films, when compared to the conventional technique, were made.

Keywords: Silane, Electro-assisted deposition, Aluminum, VTES, Organic coating

INTRODUCTION

In order to improve corrosion protection or for aesthetic reasons, surface treatments, such as conversion coatings or organic coatings, are used in aluminum and its alloys. For organic coatings, the chemical inertness of the natural aluminum oxide layer is an obstacle to be overcome, once it impairs the paint adhesion to the surface, demanding for painting pretreatments.⁽¹⁾

Pretreatments for painting must provide barrier protection against corrosion, as well as promote paint adhesion to the substrate, either by chemical or mechanical means. Among these pretreatments, chromate conversion coatings are the most efficient ones, but its use is restricted due to the risk that Cr⁺⁶ ions represent to the environment, which stimulates the search for equally efficient and more environmentally friendly alternatives.^(2; 3)

In this context, silane coatings are an emerging alternative for replacing chromate conversion coatings as a pretreatment for painting, once its efficiency on promoting paint adherence and improving corrosion protection has already been observed^(4; 5; 6; 7). This success is mainly resultant from two factors: the barrier protection provided by the crosslinked structure containing Si-O-Si and Si-O-Metal covalent bonds⁽⁸⁾ and the possibility of selecting silanes with convenient functionalities, which may result in properties like hydrophobicity⁽⁹⁾ and chemical affinity to organic coatings^(6; 10; 11; 12).

As the corrosion protection provided by such films is exclusively dependent, in the absence of corrosion inhibitors, of its barrier properties, it is crucial that the silane coating is homogeneous and crosslinked⁽⁴⁾, however the most usual technique for obtaining such coatings by dip-coating in sol-gel may lead to non-homogeneous films⁽¹³⁾.

The electro-assisted deposition, proposed in 1999 by Shacham et al.⁽¹⁴⁾ aiming to overcome this inconvenience, is based on promoting water electrolysis by electrochemical method, increasing the OH⁻ concentration (and increasing the pH, consequently) in the cathodic surface, favoring silane condensation reactions, which may result in more homogeneous, crosslinked and corrosion resistant films^(8; 13; 15; 16; 17; 18; 19).

In the present work, AA 1100 aluminum sheets were pretreated by electro-assisted deposition in vinyltriethoxysilane (VTES) sol-gel. This pretreatment was compared to conventional dip-coating, as well as chromate conversion coatings and non-treated samples, all of them painted with polyurethane varnish.

Corrosion properties of the pretreatments were compared by potentiodynamic polarization, electrochemical impedance spectroscopy and salt spray tests, paint adherence was measured by pull-off test, and Si mapping by energy dispersive spectroscopy (EDS) provided information about the silane films' distribution and coverage.

EXPERIMENTAL

Sample preparation

The sample preparation followed the steps shown in Figure 1, which are described below.

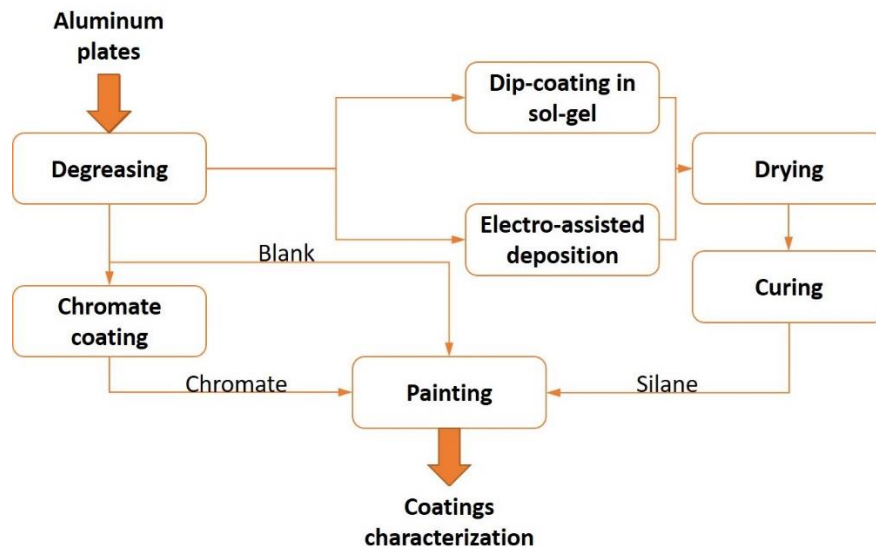


Figure 1. Flowchart of sample preparation.

Degreasing: the AA 1100 aluminum plates (100 mm x 50 mm x 0,5 mm) were immersed in commercial alkaline degreasing bath (Saloclean 667N – Klintex Insumos Industriais Ltda.) for 5 minutes at $70\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$, then rinsed with deionized water and dried with hot air stream. Blank samples were painted after this procedure.

Chromate coating: the degreased plates were immersed for 5 minutes at room temperature in hexavalent chromate solution (674B – SurTec do Brasil Ltda.), then rinsed with deionized water and dried with hot air stream. The chromate samples proceeded to painting process afterwards.

Dip-coating in sol-gel: the sol-gel was prepared by stirring 6% VTES/47% Water/47% ethanol, with pH set to 4 with acetic acid, for 24 hours at room temperature. The samples were then immersed in the sol-gel for 5 minutes with a Marconi MA 765 and lifted at a constant rate of 210 mm/min. This procedure was followed by drying.

Electro-assisted deposition: the electro-assisted deposition was carried out in an Autolab PGSTAT302 connected to a three-electrode cell, with AISI 304 stainless steel plates as counter electrodes, a Ag|AgCl reference electrode and the aluminum degreased plate as the work electrode. The cell was filled with the sol-gel, as described above, and the open circuit potential (OCP) was measured between the reference and work electrodes for 10 seconds. The deposition potentials were applied for 5 minutes, and then the samples proceeded to drying. The used

deposition potentials were -0,4 V, -0,8 V and -1,2 V, all relative to the OCP measured for each cell.

Drying: the coated samples were dried in an oven for 10 minutes at 60 °C in order to remove excess liquid from the coatings.

Curing: the curing was executed in an oven for 1 hour at 125 °C for all samples.

Painting: the samples were painted with polyurethane varnish (Verniz Majestic PU Brilhante) by dip-coating and lifted at a constant rate of 420 mm/min with a Marconi MA 765.

Characterization methods

The potentiodynamic polarization was performed with an Autolab PGSTAT302 from -0,5 V to +0,5 V relative to OCP at a 0,004 V/s scan rate. A three-electrode cell was used, with Ag|AgCl reference electrode, platinum counter electrode and the coated samples as work electrode. The electrolyte was a 0,1 M NaCl solution and the area of the sample exposed to the electrolyte was 0,63 cm². From the experimental curves, corrosion current densities were estimated using Tafel plots.

Using the same equipment and cells from the potentiodynamic polarization, the EIS analysis was carried out with 10 mV excitation amplitude at OCP, from 10⁶ to 10⁻¹ Hz. The measures were performed 3 and 24 hours after assembling the cells, i. e. after 3 and 24 hour of exposure of the coated samples to the electrolyte.

Salt spray tests were executed according to ABNT NBR 8094 standard.

Paint adherence tests were made with a portable adhesion tester DeFelsko PosiTest AT-A as described in ASTM D4541-09 standard, with 20 mm dollies and a pull-off rate of 0,2 MPa/s.

EDS was the only analysis performed in non-painted samples. It was made with a Zeiss EVO MA10 electronic microscope. Areas of the samples had the Si presence mapped, resulting in images where the black color indicates the absence of Si and white and gray dots indicate the presence of Si, which is an indicative of the silane film distribution, once it is mainly formed by Si atoms. Using the image analysis software ImageJ, the proportion area covered by Si was calculated, giving, for the sake of comparison, an evidence of the coverage provided by each pretreatment.

RESULTS AND DISCUSSION

Potentiodynamic polarization

The corrosion current densities observed for all the pretreatments are shown in Figure 2.

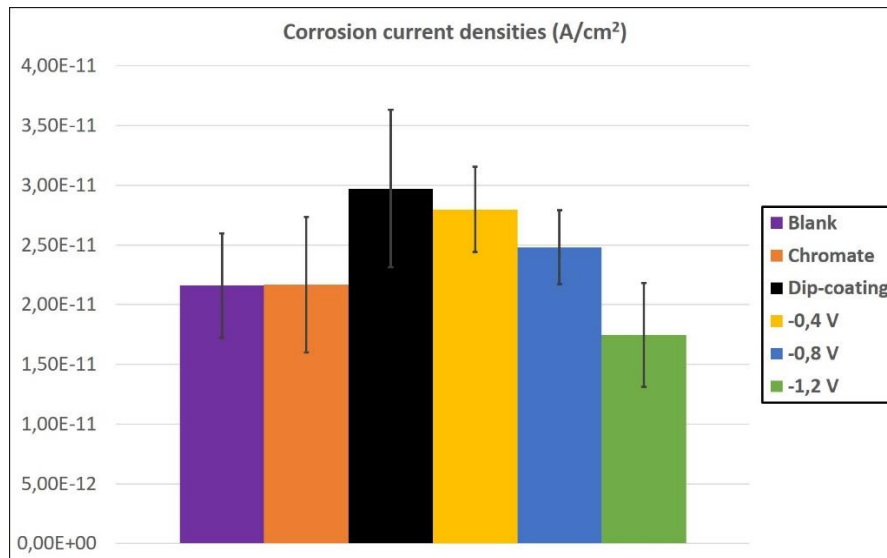


Figure 2. Corrosion current densities estimated from potentiodynamic polarization curves in 0,1 M NaCl.

As seen in Figure 2, all the observed corrosion current densities are similar, taking into account the standard deviation for each pretreatment, and are close to 20 pA/cm². These current densities would result in corrosion rates, in case of general uniform corrosion, from 1×10^{-7} to 4×10^{-7} mm/year, which is an evidence of the efficient protection of the coating system.

It is possible that the protection provided by the varnish is good enough to mask any difference resulting from the use of the pretreatments, explaining the relative similarity between the measured values.

Electrochemical impedance spectroscopy

The Nyquist diagram for the measurements carried out 3 hours after cell assembling is shown in Figure 3.

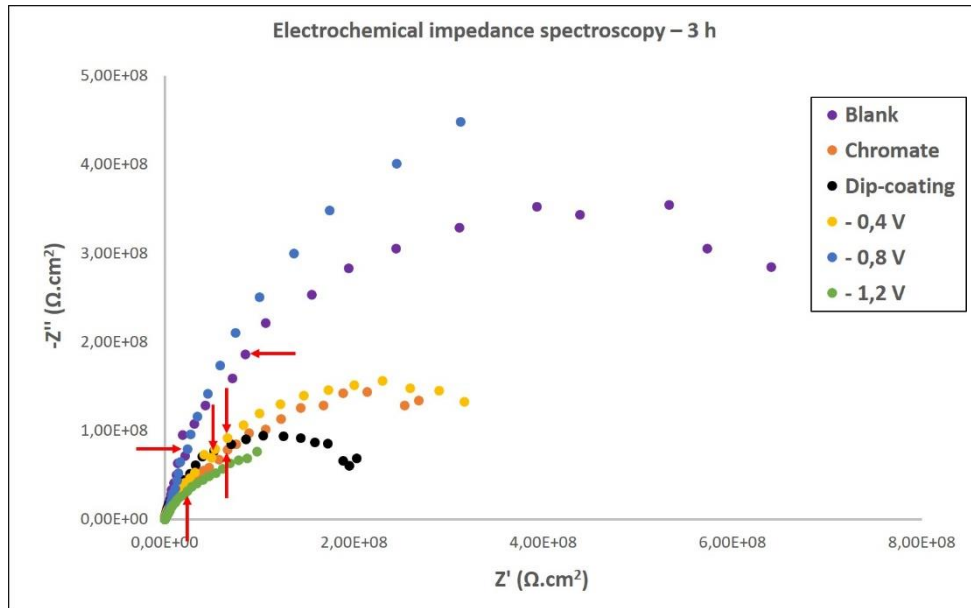


Figure 3. Nyquist diagram for the EIS measurements carried out after 3 hours of exposure to the 0,1 M NaCl electrolyte. The red arrows indicate the measures at 1 Hz excitation frequency.

The comparison between the indicated points at 1 Hz shows that, after 3 hours of exposure to the electrolyte, the Blank (non-treated) sample has higher impedance than all of the silane coated and Chromate samples. This behavior is also noticed after 24 hours of exposure, as shown in Figure 4.

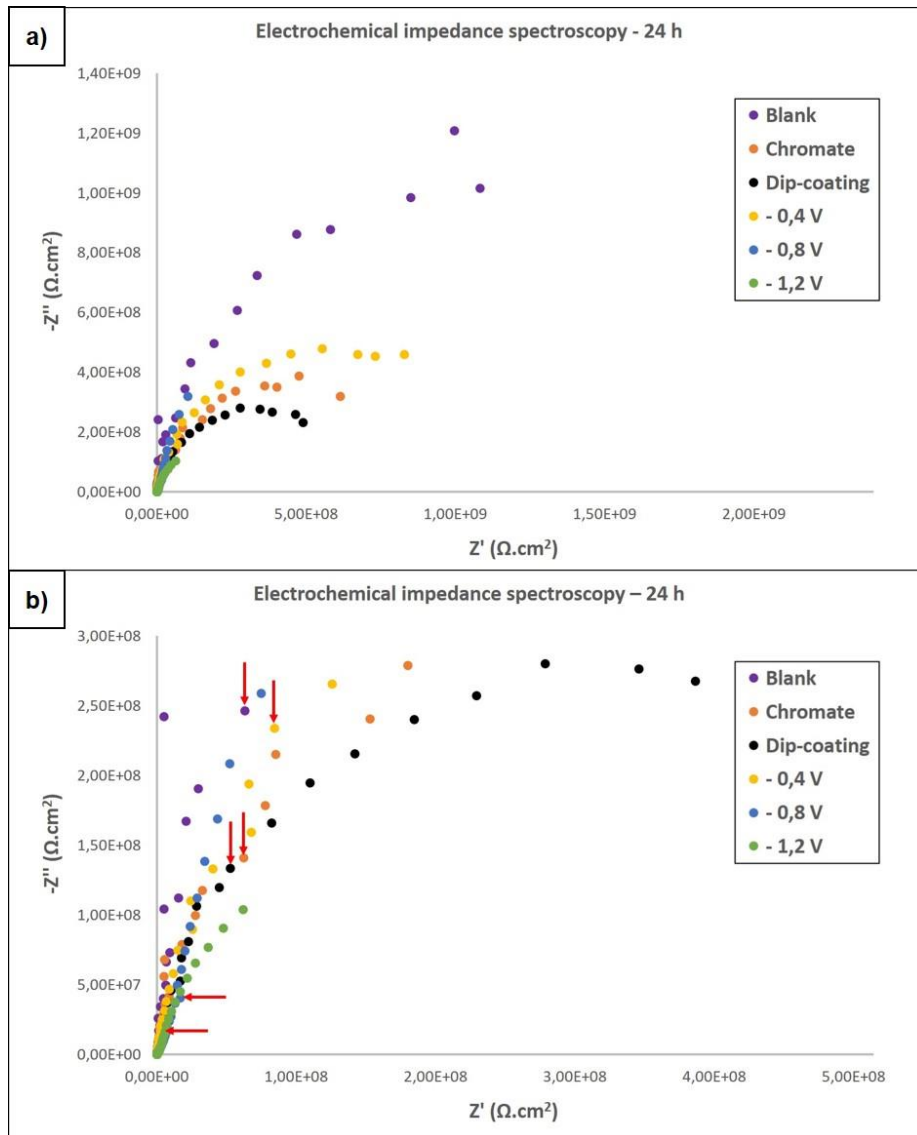


Figure 4. a) Nyquist diagram for the EIS measurements carried out after 24 hours of exposure to the 0,1 M NaCl electrolyte. b) Zoom in the lower Z' and -Z'' region of the same diagram. The red arrows indicate the measures at 1 Hz excitation frequency.

After 24 hours of exposure the samples coated by electro-assisted deposition at -0,8 V and -1,2 V show the lowest impedance values, while the pretreatment at -0,4 V resulted in higher impedance values than chromate conversion coating.

An increase in the impedance values from 3 to 24 hours of exposure is noticed for all samples, which is unusual, once the degradation of the coating is expected to occur during the exposure, leading to a decrease in the measured values.

Organic coatings are usually significantly more permeable to water than to chloride ions⁽²⁰⁾, therefore it is possible that the organic coating permeates water beneath the coating, allowing the aluminum oxide layer to grow with no pitting, which

would occur in case the chloride ions were permeated⁽²¹⁾. To test this hypothesis, non-coated aluminum samples were analyzed in 0,1 M NaCl and in deionized water, and the Nyquist diagrams for these analysis are displayed in Figure 5a and Figure 5b, respectively.

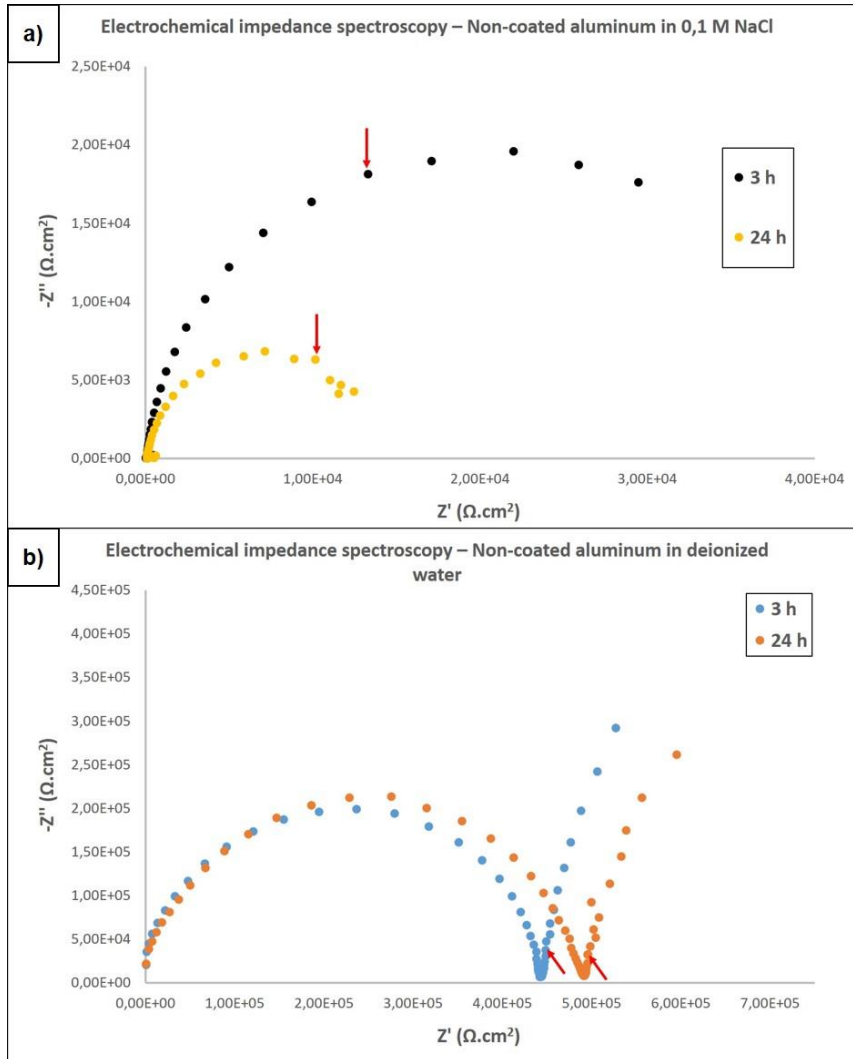


Figure 5. Nyquist diagram for the EIS measurements carried out after 3 and 24 hours of exposure to the a) 0,1 M NaCl solution and b) deionized water. The red arrows indicate the measures at 1 Hz excitation frequency.

While the 0,1 M NaCl electrolyte caused a decrease in the impedance values as a consequence of pitting in the natural oxide layer, the samples exposed to deionized water showed an increase in the measured impedance values, which may be caused by the growth of the aluminum oxide layer.

These analyses show that the considered hypothesis, i. e. the permeation of water allows the growth of the oxide layer beneath the organic coating, is plausible.

Salt spray test

After 1440 hours of exposure to salt spray, none of the samples has shown corrosion damage, confirming the efficient corrosion protection provided by the coating system in Cl⁻ rich environment.

Paint adhesion

The paint adhesion measures are shown in Figure 6.

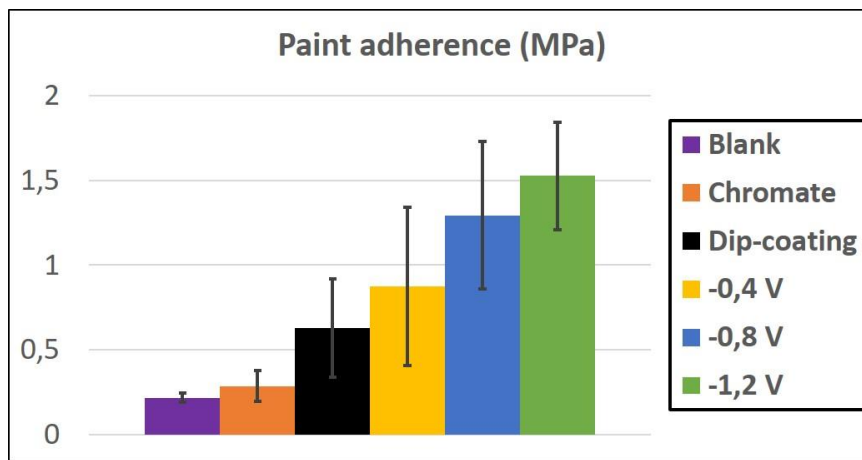


Figure 6. Paint adherence measures by pull-off with portable adherence tester.

The use of the electro-assisted deposition technique resulted in higher adherence measures for the polyurethane varnish in aluminum compared to both conventional chromate coating and dip-coating method, which is an important feature for a pretreatment for painting.

Energy dispersive spectroscopy

The Si maps obtained at 52x magnification are displayed in Figure 7.

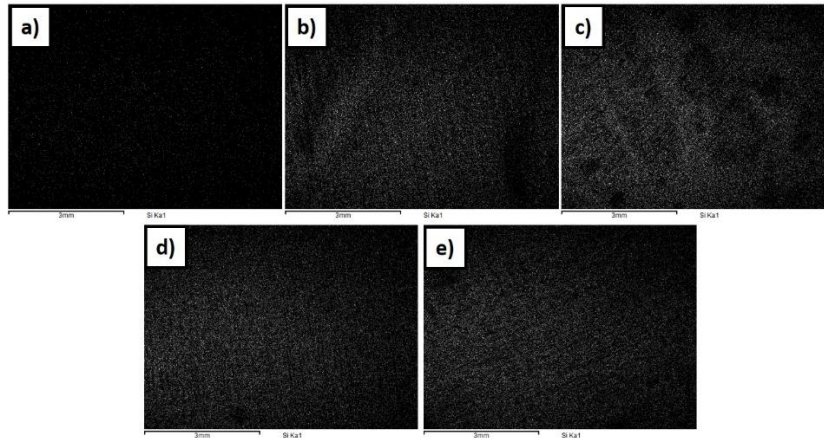


Figure 7. Si maps obtained by EDS at 52x magnification. The white and grey dots indicate the presence of silicon. a) Blank, b) Dip-coating, c) -0,4 V, d) -0,8 V and e) -1,2 V.

Dip-coating (Figure 7b) and -0,4 V (Figure 7c) resulted in less homogeneous distributions of silicon, indicating a the formation of less homogeneous films when compared to the samples coated at -0,8 V (Figure 7d) and -1,2 V (Figure 7e).

The proportional area containing Si calculated for all samples using the image analysis software ImageJ are shown in Table 1.

Table 1. Proportional areas containing silicone for each pretreatment calculated from EDS Si mapping.

Pretreatment	Area containing Si (%)
<i>Blank</i>	2,36
<i>Dip-coating</i>	21,58
<i>-0,4 V</i>	23,86
<i>-0,8 V</i>	28,18
<i>-1,2 V</i>	25,45

The pretreatments at -0,8 V and -1,2 V provided greater coverage of the substrate when compared to the conventional dip-coating technique, which may be the reason for the higher paint adherence measured for these pretreatments.

The visual analysis of the Si maps in Figure 7, alongside with the higher presence of Si on the surface and improved paint adherence resulting from the use

of the electro-assisted deposition technique, confirm the success of this technique in forming more homogeneous silane films.

CONCLUSION

The electro-assisted deposition of VTES resulted in more homogeneous silane films, which provided higher paint adherence to aluminum when compared to the conventional dip-coating technique.

The corrosion protection provided by the organic coating is efficient, and it has not been increased by the use of any silane pretreatment.

EIS results indicate that there is an oxide layer growth under the organic coating after 24 hours of exposure to the 0,1 M NaCl solution as a possible consequence of the water permeability of the varnish. It is possible that this behavior is restricted to a limited time of exposure, after which the varnish degradation would result in loss of corrosion protection.

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