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Evaluation of the influence of experimental parameters in the formation of a vinyltrimethoxysilane film on 1010 carbon steel through electrochemical impedance spectroscopy and contact angle techniques

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ABSTRACT

The influence of experimental parameters on the formation of vinyltrimethoxysilane (VTMOS) film to protect 1010 carbon steel against corrosion by electrochemical impedance spectroscopy (EIS) and contact angle measurements was evaluated. Specimens were developed from three 2^3 factorial designs and an uncoated sample, where the EIS and contact angle were regarded as response variables. The results of coated samples were satisfactory as compared to those of uncoated carbon steel, as the former were better protected against corrosion, besides being more hydrophobic. The optimized specimens showed considerably increased EIS and contact angle values. It is concluded that the design of experiments developed favors to obtain a best finish of VTMOS silane on 1010 carbon steel, according to the EIS and contact angle techniques.

1. Introduction

Phosphating and chromating pretreatments are applied to steels before they pass through the painting process used in industry as methods to improve corrosion prevention and enhance coating adhesion characteristics. These processes are still widely used because of their efficiency. However, due to high operational costs, coupled with environmental issues and the costs associated with the treatment of the residues produced that are toxic and carcinogenic, efficient 'green' pretreatments are being sought to replace them. One of the potential alternatives involves the use of silanes (functional or organofunctional), which generate residues of low toxicity, requiring minimal treatment for appropriate discharge, and which offer protection against corrosion and adhesion [1–5].

The use of silanes has been proposed as a protection method against corrosion for different metallic substrates, providing protection even without the application of a paint layer after treatment with a silane film [6–9].

Electrochemical impedance spectroscopy (EIS) has shown to be quite useful in evaluating the pre-treatment performance of silane-coated carbon steel [10,11]. The purpose of characterizing organic protective coating by EIS is to obtain information about the properties of the system, such as the presence of defects, interface reactivity, adhesion, water barrier properties, etc. The knowledge of these properties is very useful in predicting the anti-corrosive behavior of the formed film [12]. The contact angle measurements, in turn, pose an important tool to characterize the wettability of solids, i.e., the hydrophobicity degree [13].

The aim of this study was to assess the influence of experimental parameters on the formation of vinyltrimethoxysilane monolayer (VTMOS) to protect 1010 carbon steel against corrosion through EIS and contact angle measurements.

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Table 1
Matrix of experiments and specimens codes developed for the first factorial design.

Variables	P1N1	P1N2	P1N3	P1N4	P1N5	P1N6	P1N7	P1N8
Ratio of DI water/ethanol	1:2	2:1	1:2	2:1	1:2	2:1	1:2	2:1
Concentration of silane (%)	6	6	2	2	6	6	2	2
Hydrolysis time (h)	48	48	48	48	2	2	2	2

2. Experimental

2.1. Silane and steel used

In this study, VTMOS has been used; as this is a monosilane, it only has one silicon atom, three hydrolysable groups, and a vinyl-type organic-functional group, and acts as a crosslinking agent, besides being a good network maker. The choice for 1010 carbon steel as a substrate was motivated by the fact that this metal has low anti-corrosion properties, since the presence of alloying elements with these properties is little significant, not to mention its importance and applicability in many industrial sectors.

2.2. Process layer formation

Substrates of 1010 carbon steel were obtained in the dimensions of 25 mm × 50 mm × 0.9 mm. The specimens were treated with grit of emery paper, pickled in a solution of deionized water (DI) and HCl 7% (v/v) for 5 min, and degreased in a solution of deionized water and 5% Saloclean 619 (v/v) in which they remained until silanization. The Saloclean 619 is formulated with sodium salts, emulsifiers, nonionic surfactants and humectants, supplied by Klintex Insumos Industriais Ltd. This treatment was also performed for the steel samples that were not coated with silane.

Solutions of VTMOS silane using ethanol and water as solvent, adjusted to pH 4 with acetic acid, were hydrolyzed under magnetic stirring. After that, silanization was carried out using a speed-controlled manual process for a single immersion of carbon steel samples in the hydrolyzed solution, characterizing the formation of a monolayer. Finally, the specimens were subjected to curing in an oven at different times and temperatures.

2.3. Planning of experiments designed to study

Nine quantitative factors were evaluated from three 2^3 factorial designs, as shown in Tables 1–3. The factors were chosen from the key variables that may influence the formation of a good film, whereas the levels were chosen based on a review of those currently far more used for coating metals with silane [10,11,14–17], which were considered at level (0); thereafter, a minus level (−) and a plus level (+) relatively distant from each other have been established. During the first study of design 1, for example, the factors of other designs were maintained at level (0), i.e., without any variation. The same was seen when the experiments corresponding to designs 2 and 3 have been conducted. The samples were prepared in duplicate, totaling 16 specimens for each factorial design; as for each condition, one specimen has been used for EIS and the other for measuring contact angles.

Based on the factorial design results, two new specimens have been developed from the best results of each factorial design, as a function of EIS tests and the contact angle, i.e., respecting the highest levels of the factors. These specimens were tested in the same way as the others.

2.4. Characterization by impedance and contact angle

EIS was conducted in a non-stirred reaction medium, at room temperature, in a three-electrode cell for flat samples. The used electrochemical cell consisted of a reference electrode of Ag/AgCl/3 M KCl, a one-electrode platinum foil, steel samples (coated or not) as an working electrode with an exposed area of 1 cm^2, and a 0.1 mol L^{-1} NaCl solution as the electrolyte. The used potentiostat/galvanostat was EG&G/PAR, model 273A, connected to a Solartron1255B frequency analyzer.

Prior to EIS, the measurement of open circuit potential (EOC) was carried out as a function of time. That has been done because the knowledge of the open circuit potential as a function of time is essential as the disturbance applied to the electrode occurs around the potential for corrosion. This means that the EIS only should be performed after the metal-stabilization potential is complete (Ecorr constant), as the steady-state conditions may avoid result problems in low frequencies [18–20]. Immersion- and EOC stabilization-period was 1 h for all specimens. This monitoring was carried out using the software PowerSuite.

EIS was obtained after the immersion period of EOC. The impedance diagrams were obtained in the frequency range of 50 kHz at 5 MHz, with 10 readings per logarithmic decade and a perturbation potential of 10 mV. Data control was carried out using the ZPlot2 software. For plotting results in the form of Nyquist diagrams, the software products ZView2 and Microcal® Origin® 7.0 have been used.

The real impedance of the low frequency of 0.04 Hz was regarded as a quantitative response to EIS tests, because it represented the resistance of the silane film to corrosion and the metal–medium interaction in a 0.1 mol L^{-1} NaCl solution [8].

Table 2
Matrix of experiments and specimens codes developed for the second factorial design.

Variables	P2N1	P2N2	P2N3	P2N4	P2N5	P2N6	P2N7	P2N8
Grit of emery paper	2500	400	2500	400	2500	400	2500	400
Hydrolysis temperature (°C)	90	90	30	30	90	90	30	30
Cure temperature (°C)	200	200	200	200	100	100	100	100

Table 3
Matrix of experiments and specimens codes developed for the third factorial design.

Variables	P3N1	P3N2	P3N3	P3N4	P3N5	P3N6	P3N7	P3N8
Immersion time (min)	30	2	30	2	30	2	30	2
Immersion velocity (mm s^{-1})	1.6	1.6	25	25	1.6	1.6	25	25
Cure time (min)	60	60	60	60	20	20	20	20