Influence of different surface cleaning processes to obtaining coatings with silane and tannin for corrosion protection of galvanized steel.

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Abstract

In light of increasing pollution levels, commonly used substances that are harmful to the environment are being reconsidered. An alternative to the use of chromuim, which is toxic and carcinogenic, is the use of silanes as protective coatings. Since silanes only provide barrier type corrosion protection, the natural inhibitor tannin is used in this study in order to evaluate its synergy and inhibitory capacity. The study was divided into two parts, always using the galvanized steel substrate. The first part consisted of a degreasing step, followed by immersion in a solution of 2% TEOS silane, 49% alcohol, and 49% water. In the second part of the study, the substrate was cleaned by a sequence of degreasing, pickling and degreasing to work with surfaces consisiting of only silane and silane/tannins combinations. The tannin was added at a concentration of 2g / L. After immersion, all samples were subjected to a curing period of 1 hour in an oven at 100 ° C. The potentiostatic polarization analysis showed a corrosion rate in the tenths of millimeters per year in the specimens tha underwent only degreasing and silane coating, and in the mm units for specimens that also went through pickling. SEM and EDS analyses confirmed the presence of silane in the substrate. Cleaning only by degreasing provides the best results when the goal is silanization protection in galvanized steel. Further study is necessary to prove the efectiveness of the use of tannin, along with TEOS silane considering the parameters used.

Keywords: Silane, Tanine, Galvanized Steel, Organic coating, Pretreatment

Introduction

A major challenge faced by today's society is the need to combine the anti-corrosion ability of protective coatings to procedures that are less polluting and that do not use toxic substances in order to have less impact on the environment. The cost of prevention is normally less than the replacement of parts, as well as possible long replacement time of damaged components that may further increase the cost.

Because of anticorrosive characteristics, mechanical resistence and ductility, galvanized steel is widely used, along with one or more protective coatings against corrosion, in the automotive, construction, tubing, and sheet metal industries. Usually, the first treatment

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consists of a chromate-based conversion coating to improve the galvanized steel's resistance to corrosion, and to increase adhesion of the substrate with the subsequent organic layer. This is to date the most effective treatment method (1). Through research, scientific societies seek alternatives to the carcinogenic cromium based pretreatments.

Silane-based and phosphate-based coatings are two known alternatives that are already used in the industrial sector, for obtaining surfaces able to withstand and contain the damage caused by corrosion. Despite having less environmental impact, these methods also generate waste, however, this waste is much smaller compared to the products generated by the use of chromium as corrosion protection.

Silanes are good coupling agents that produce a satisfactory bond between the organic and inorganic interfaces, and create good adhesion between ink and substrate, thus, resulting in the generation of less toxic waste and requiring a simpler disposal process than the chromium based agents.

In addition to these two alternatives, organic substances that can contribute to the containment of corrosion in various materials are being studied more and more. One of such substances is the natural corrosion inhibitor tannin, which is extracted from plants, as well as being nontoxic and biodegradable (2) .

In this research the tannin has the purpose of improving some factors that are undesirable in the use of silanes, such as uneveness in the coating. Since the silanes work as a barrier type protection to the metal, the coating must be dense and preferentially hydrophobic, however the layer formed is usually not of good quality, exposing cracks, gaps and pores in its structure (3).

For these reasons, the addition of a corrosion inhibitor to the silane is a possible alternative for improving both the performance of the coating, and the corrosive properties of the treated substrate.

Experimental

This study was divided into two parts, the first being carried out with only one surface cleaning process, an alkaline degreasing step, which was done in order to remove fats and oils present on the substrate. In the second part of the study, it was stipulated that the samples would undergo a more rigorous impurity elimination process of consisting of degreasing, pickling and degreasing steps. After the removal of surface oils and fats surface achived by the first alkaline degreasing step, pickling was performed in order to remove any oxides remaining from the confection of the galvanized steel. The third degreasing step was done with the intent of attaining the largest possible amount of hydroxyls on the surface, which essential for the bonds of silanol groups with the substrate to occur, thus promoting a more homogenous and effective coating. To ensure the effectiveness of the cleaning process, all samples underwent and passed the water break test.

Galvanized steel was the substrate used in all of the procedures. The degreasing was done with the alkaline degreaser, Saloclean 667N supplied by Klintex®. Each specimen was immersed for 10 minutes in the degreasing solution at a temperature of 70 °C. The pickling step was performed with 65% nitric acid, and an immersion time of 1 minute.

The silane solutions were made using 98% TEOS type silane, supplied by Sigma-Aldrich. The silane was dissolved in deionized and distilled water and ethanol in the ratio 2% silane, 49% water, and 49% ethanol. For samples with tannin, the natural inhibitor was dissolved in the same solution at a concentration of 2g / l. Different TEOS silane hydrolysis times were chosen, ranging from 2 hours to 48 hours. A pH of 2.5 was chosen for the study

and was achieved with Synth® 99.7% glacial acetic acid. The chromate-based conversion coating was carried out using the same parameters with a solution of Na2S, CrO3 and NaCl and an immersion time of 1 minute. All analyses and samples were repeated three times.

The immersion step was carried out with a MA 765 Marconi disk elevator set at a descent and ascent speed of 420mm/min and a 2 minute immersion time since the film thickness does not change much with immersion times ranging from 30 seconds to 30 minutes (4).

After being coated with the silane film, all samples were placed an oven for 1 hour at 100 ° C for a curing step which is necessary to adequately finalize the protective film.

Three electrode cells with 0.1M NaCl solution, an Ag/AgCl reference electrode and a platinum counter electrode were used for potentiostatic polarization tests. The working electrode was the substrate being analyzed. All SEM images and EDS graphs were done at a 500x magnification.

Results and discussion

Polarization Potentiodynamic 1

The figure (1) below shows the polarization graph obtained with different hydrolysis times and TEOS silane coating compared with the chromatized and blank samples that were only degreased.

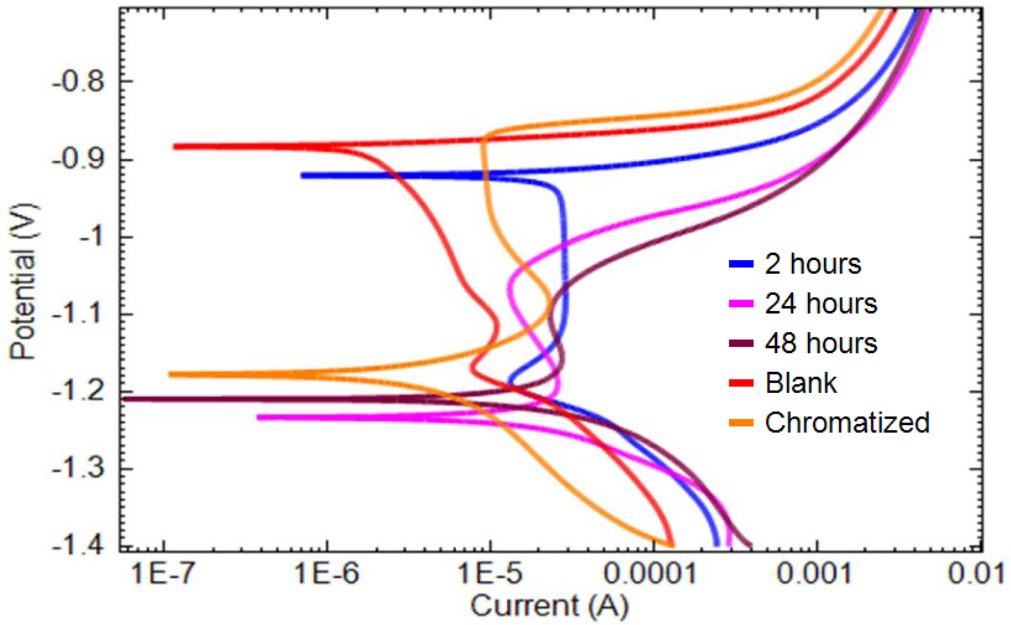

Figure 1 Potentiodynamic polarization for different hydrolysis times compared with cromatized and blank samples that were only degreased.

Corrosion rate

Corrosion rates calculated by potentiodynamic polarization are shown in Table 1.

Table1. Corrosion rates for samples coated with silane compared with blank and chromatised that have a single degreasing.

Sample pretreatment	Average corrosion rate (mm/year)
2 hours	0.068574
24 hours	0.21403
48 hours	0.25445
Blank	0.17602
Chromatized	0.14934

The results obtained with the coated samples of silane suffered only degreasing were reasonable presenting very close corrosion rates to shaded samples and corrosion potentials obtained by different hydrolysis times had values below the corrosion potential of the blank sample which means also better oxidative protection giving a good result with the set parameters.

Polarization Potentiodynamic 2

The figure (2) shows a polarization graph obtained with different hydrolysis times compared with samples of blank and chromatised for the samples which have undergone a greater cleaning process of surface following degreasing, pickling and degreasing more subsequent coating with silane TEOS.

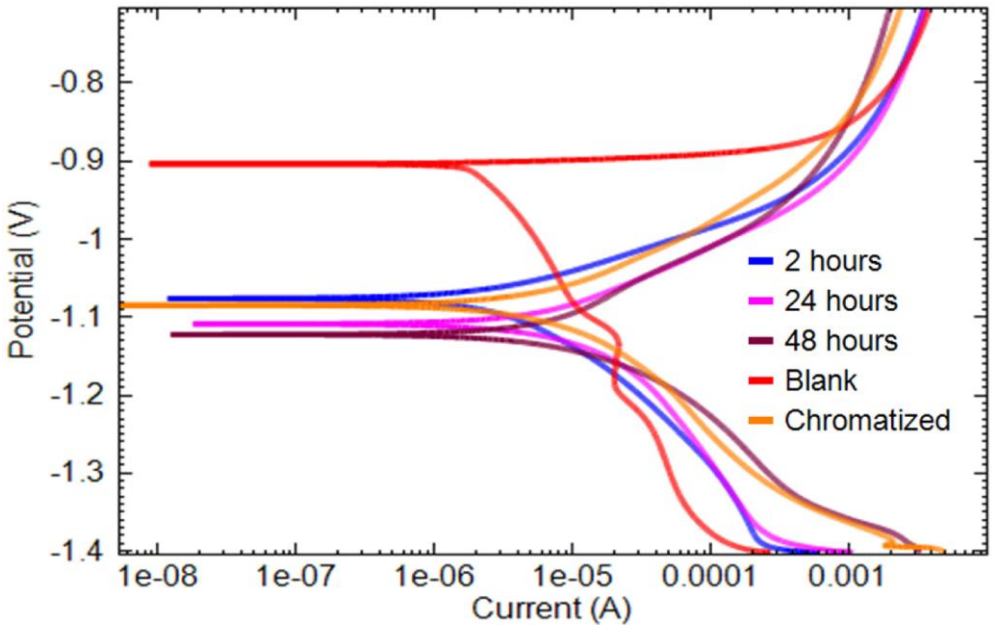

Figure 2. Potentiodynamic polarization for different hydrolysis times compared with shaded and blank samples that have undergone a process of degreasing, pickling and degreasing.

Corrosion rate

Corrosion rates calculated by potentiodynamic polarization are shown in Table 2.

Table 2. Corrosion rates for samples followed a degreasing process, pickling and degreasing coated with silanizing compared with blank and chromatised.

Sample pretreatment	Average corrosion rate (mm/year)
2 hours	5.6832
24 hours	2.0612
48 hours	3.0669
Blank	5.6277
Chromatized	0.3428

The results obtained with the samples with silane coating process experienced a degreasing, pickling and degreasing were not as significant as those which suffered only a degreasing step. Corrosion rates were considerably higher compared to the previous ones, resulting in more active surfaces when exposed to corrosion despite all the corrosion potential present values obtained below the blank patch corrosion potential.

Polarization Potentiodynamic 3

The Figure (3) shows the polarization graph obtained with different hydrolysis times compared with samples of blank and chromatised for the samples which have undergone a greater cleaning process of surface following degreasing, pickling and degreasing more subsequent coating with TEOS silane with the incorporation of the natural tannin inhibitor in the composition.

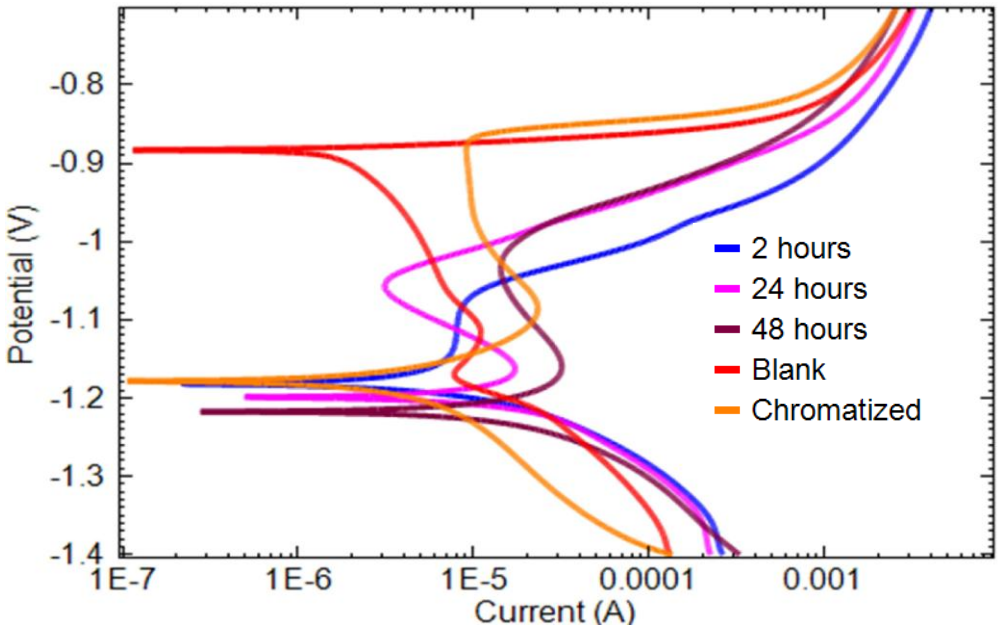

Figure 3. Potentiodynamic polarization for different hydrolysis times compared with shaded and blank samples that have undergone a process of degreasing, pickling and degreasing with tannin incorporation into the solution.

Corrosion rate

Corrosion rates calculated by potentiodynamic polarization are shown in Table 3.

Table 3. Corrosion rates for samples followed a degreasing process, pickling and degreasing coated with silanization with tannin, compared with blank and chromatised.

Sample pretreatment	Average corrosion rate (mm/year)
2 hours	1.3775
24 hours	4.2154
48 hours	3.1305
Blank	5.6277
Chromatized	0.3428

The results obtained with samples coated with silane tannin who have suffered a degreasing process, pickling and degreasing were not as significant as those which suffered only a degreasing step. The corrosion rates shown were high compared with only degreased, resulting in more active surfaces when exposed to corrosion despite all the corrosion potential present values obtained below the blank patch corrosion potential.

Scanning electron microscope and Energy-dispersive X-ray spectroscopy

To better understand how the tannin inhibitor reacts on the surface with the silane TEOS type verified through SEM and EDS compositions with all different hydrolysis times achieved with the sample of blank and chromatized like after being cleaned and cured. The figure 4 shows the result of the interaction.

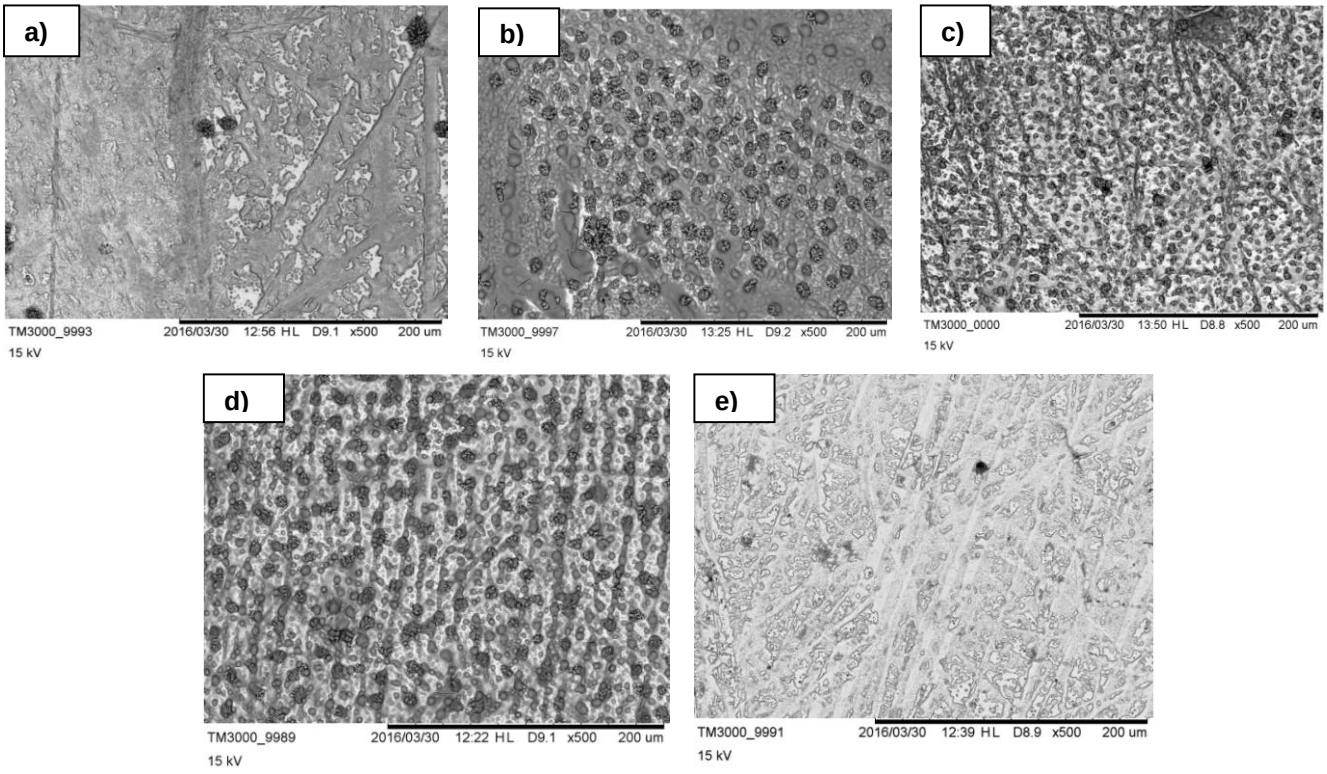

Figure 4 Images obtained by SEM showing the different surfaces with all employees hydrolysis times. The figures show a) 2 hours hydrolysis, b) 24 hours hydrolysis, c) 48 hours hydrolysis, d) Blank, e) chromatised.

Samples made by MEC and by EDX analysis showed a small percentage amount of silicon on the substrate compared to the percentage amount by weight of zinc, but also show that both compounds are present in the galvanized layer.

Conclusions

From the results obtained using the two types of surface pre-treatment, the corrosion rates and potentiodynamic polarization corrosion potential graphs showed that samples cleaned only with the degreasing procedure have been more protected than those that underwent the more rigorous degreasing, pickling and degreasing process. Corrosion rates brought data that differ in the order of ten times which suggests very different corrosion protection between the two processes. This result also suggests that the degreasing-only process of surface cleaning is the most suitable to attain better results.

The use of tannin in conjunction with the silane coating did not prove to be effective when tested on the pieces that went through the rigorous, three-step cleaning process. The use use should be studied in samples that are only degreased for a concrete result about its effectiveness with the parameters used.

References

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