# Silanes and tannin coatings: comparison between single and double layers

Pedro H. P. de Moraes[a], Álvaro Meneguzzi[b], Henrique Ribeiro Piaggio Cardoso[c]

## *Abstract*

Every year lots of machines, which have an important role in the society, must be replaced because of the corrosion. In order to reduce these losses, better coatings have been developed. The goal of this work is to compare two coatings which were developed in this laboratory in a previous research, and to evaluate the influence of the double layer confronted with the single one. The first protective coating was developed using tetraethoxysilane (TEOS); the second one was made with a combination of vinyltriethoxysilane (VTES) and Weibull tannin. Aluminium 1100 was chosen as a substrate. Six groups of samples were prepared in triplicate. Each group received a different coating or a different number of layers. An electrochemical impedance spectroscopy analysis (EIS) was conducted to evaluate the efficiency of the corrosion protection. A contact angle analysis was used to evaluate the surface hydrophobicity. Finally, X ray fluorescence (XRF) was used for the morphological characterisation. After all the results were analysed, the samples with double layer of VTES combined with tannin showed the best anticorrosive properties in the EIS analysis. The coating revealed great protective characteristics and it is also environmentally acceptable. Therefore, we concluded the coating is a good option to replace some of the current coatings.

**Keywords**: aluminium, corrosion, tannin, tetraethoxysilane, vinyltriethoxysilane.

## Introduction

The extensive development of organosilicon chemistries in the last decades produced commercial advances in the automotive, aerospace, and electronics markets. (1) One important branch of research is the use of silanes as coatings for corrosion protection of metals. However, these coatings are typically too thin and non-uniform, what reduces the protection against corrosion. (2) In order to improve the silane layer proprieties, there are some alternatives that have been taken into account, such as: applying electrochemical deposition, loading the film with corrosion inhibitors, adding nanoparticles such as silica, alumina, and cerium oxide into the thin films, and using different layers of silane. (3)
The alternatives chosen to be tested in this work were the use of tannin, which it is expected to act as a corrosion inhibitor, and the double layer of silane. In this experiment aluminium samples were covered, using the sol-gel process with different silanes coatings. Two precursor solutions were prepared, the first one containing the non-functionalized silane TEOS, and the second one using the functionalized silane VTES combined with Weibull

[a] Master student, Materials Engineering - UFRGS
[b] PhD, Professor - UFRGS
[c] PhD student, Materials Engineering - UFRGS

tannin. In order to analyse the influence of the number of layers and the order it was applied, six groups of samples were prepared with different coating or different number of layers.
This research aims to determine what combination of layers results in the best corrosion protection for the aluminium substrate. The minor objectives are to understand the double layered coating performance and the influence of the tannin in the silane coating.

## Methodology

Samples made by commercially pure aluminium sheets of 100 mm x 50 mm x 1 mm were used as substrate. All sheets were cleaned using running water and neutral soap, then a towel moistened in acetone (Acetone P. A. – Neon Comercial Ltda.) was rubbed on the surface to ensure that all the organic dirties were removed. Finally, the samples were immersed for 300 s in an alkaline degreasing solution (Saloclean 667N – Klintex Insumos Industriais Ltda.) which were preheated to 70 °C. The cleaning and degreasing efficiency were verified by the breaking water test. After this, all samples were dried with compressed air jet and stored in a desiccator.
The sol-gel process was used for the silane coating deposition. Two silanes solutions were prepared with the following compositions in volumetric percentage: the first solution containing 4% of TEOS (Aldrich Chemistry 97%), 48% of deionized water, 48% of ethyl-alcohol (Synth® 95 % P.A.), and the second solution containing the same percentage of deionized water and ethyl-alcohol, 4% of VTES (Aldrich Chemistry 97%), and 2 g/L of Weibull tannin (Tanac). In both solutions the original pHs were kept (equal 5). After mixed all components, they were lived in constant stirring for 24 h for the hydrolysis reaction occur.
A disc elevator MA 765 (Marconi Equipamentos para Laboratórios Ltda.) was used to control the immersion and withdrawal speed (420 mm/min), and also the dwell time (2 min) of the samples in the solution. After the immersion, the samples were open air dried for 15 min and placed inside oven with the temperature of 100 °C for 1 h (4) in order to promote the condensation reaction. This process was repeated once in the samples that received the double layer coating. The “Table 1” shows the name of the sample and its coating. Each sample was prepared in triplicate.

**Table 1 -** Silane coating over each aluminium sample

| Name | First layer | Second layer |
|---|---|---|
| Sample A | TEOS | VTES + tannin |
| Sample B | VTES + tannin | VTES + tannin |
| Sample C | TEOS | TEOS |
| Sample D | TEOS | - |
| Sample E | VTES + tannin | - |
| Sample F | - | - |

A EIS was executed to analyse the protective performance of the coatings. The equipment applied was a potentiostat (Autolab PGSTAT 302, software Nova 1.11), a reference electrode of Ag | AgCl, a contra-electrode made of a platinum wire, and the working electrode was the sample. An area of 0,64 cm² of the sample was exposed to the NaCl 0,1 mol/L electrolyte for 48h before the test started. The highest frequency set was 105 Hz and the lowest was $10^{-2}$ Hz, with a range of 10 mV which resulted in a total of 71 dots. The results were shown on Nyquist charts.
The contact angle analysis was conducted using the equipment drop-shape analyser (DSA30 – Kruss). Water drops with the size of 3 μL were placed upon the sample surface. The drops

were analysed with the software (Surftens47). The results are the average of 3 drops angles measured upon each triplicate sample. For the morphological characterization of the coating a XRF test was conducted using que equipment (SI TITAN – Bruker).

## Results and discussion

The "Figure 1" illustrates the corrosion resistance of each sample obtained in the EIS test. In order to make it easier to understand, only one polarization curve of each triplicate was placed in the Nyquist chart.

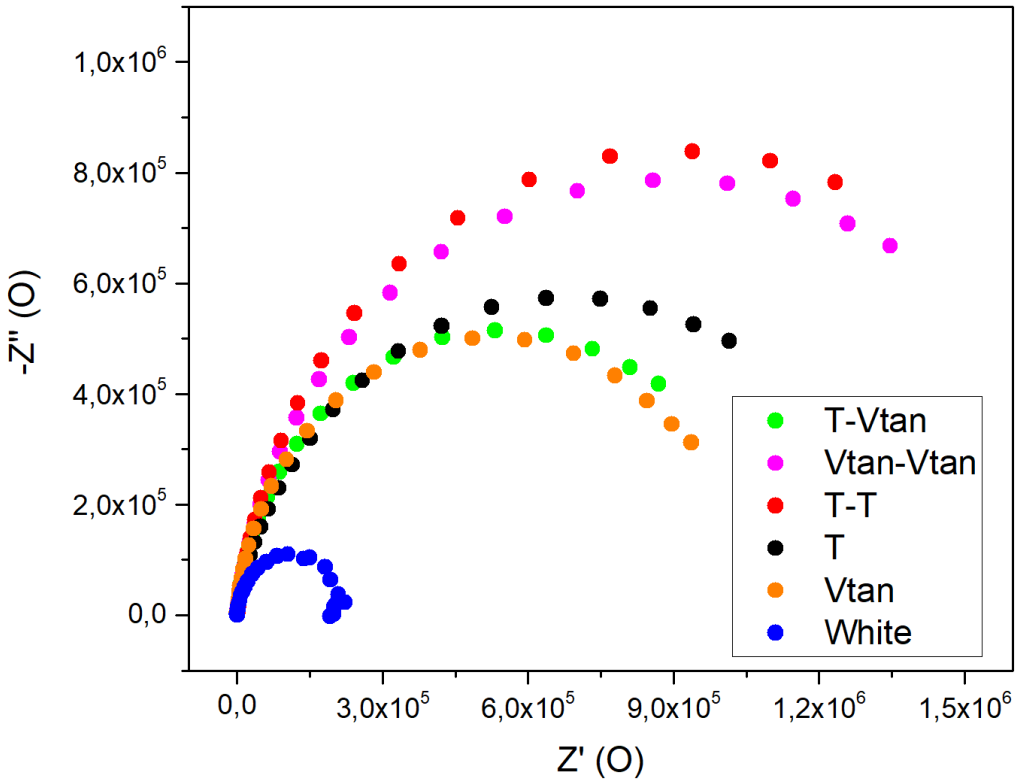


**Figure 1** - Nyquist chart on 48 h immersion of samples in aqueous solution of NaCl 0,1 mol/L

The sample that was covered by double layer of TEOS and the sample covered by double layer of VTES combined with tannin presented the best corrosion resistance in the EIS test. As expected, the sample without any coating showed the lowest resistance. The two samples which received a simple layer revealed intermediate anticorrosive proprieties. The "sample A" which had the first coating of TEOS and the second of VTES combined with tannin presented results very close to the single layer samples.
In the contact angle test "Figure 2", it is possible to compare the hydrophobicity of each surface.

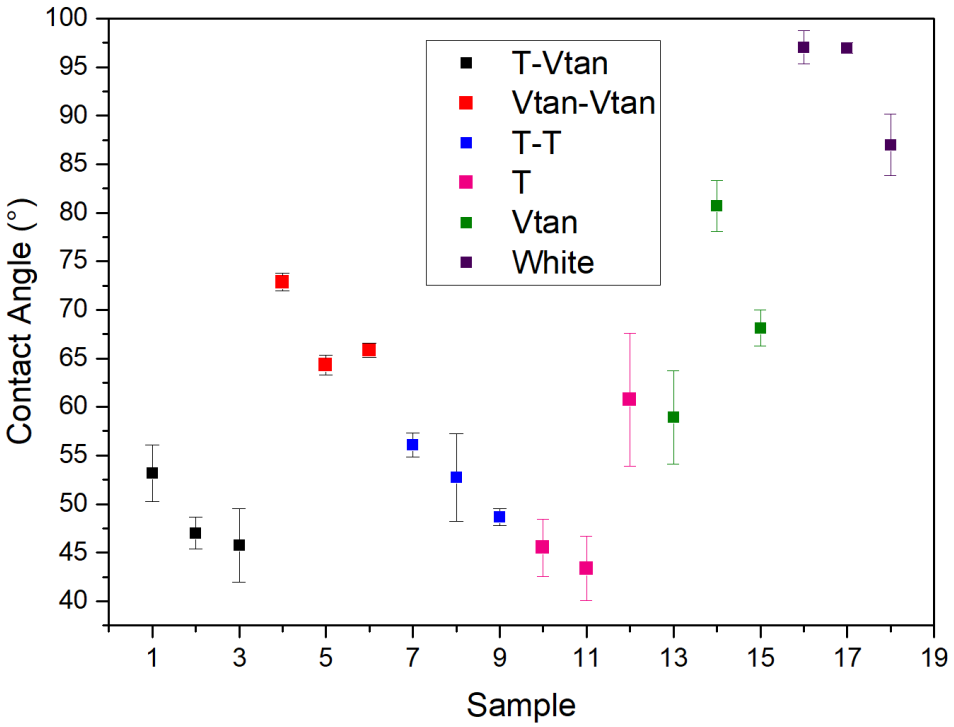


**Figure 2 -** Contact angle of a 3 µL drop on the samples surface

The chart shows that among the coated samples, the ones covered with Vtan (single and double layer) presented higher contact angles than the ones covered by TEOS. The contact angle of the "sample A" was very close to the samples coated with TEOS (single and double layer). The white sample (without coating) showed the highest contact angle, an average of 93°. (5) The "Figure 3" compares a high (Sample F) and a low (Sample D) contact angle obtained in this analysis.

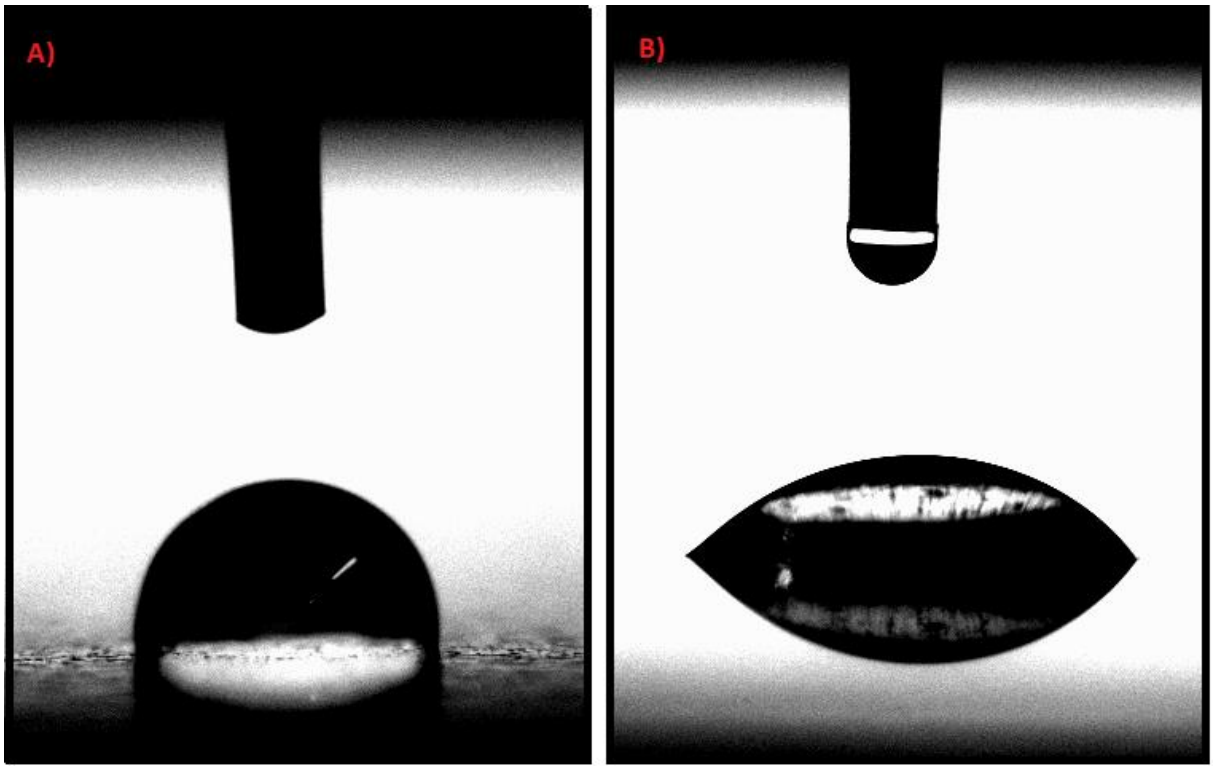


**Figure 3 - Comparison between the contact angle of the sample F and sample D, respectively**

Many studies about hydrophobic surfaces connect the high contact angle with lower corrosion rates. It happens because the higher contact angle the least contact between the electrolyte and the metallic surface. (6) However, comparing the results of “Samples D and F” in the EIS test it is possible to conclude that other variables affect the corrosion resistance more than the contact angle does.

The silane coating forms a very thin layer, which can not be measured using the general technics. (7) However, some researches link the percentage of silicon on the surface to the silane layer thickness. (8) The percentage of silicon was obtained with the XRF analysis in order to compare the thickness of the coatings, as it is shown on “Figure 4”.

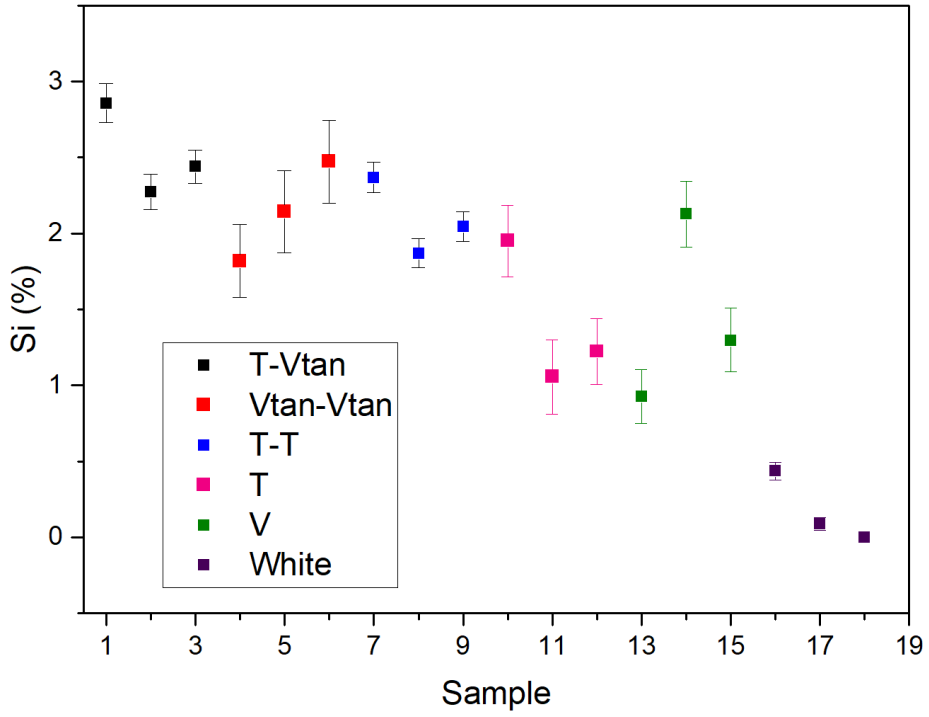


**Figure 4 -** Percentage of silicon obtained by XRF analysis

As expected, the XRF analyses showed that the double layer coatings have a higher percentage of silicon compared to the single ones. Consequently, it can be inferred that the double immersion coatings are thicker. These results agreed with the ones found on the EIS test. The "Sample A" presented a slightly higher percentage when compared to the other two double layer samples.

## Conclusions

- The Samples B and C (double layer of VTES combined with tannin and double layer of TEOS, respectively) reported the highest corrosion resistance in the EIS test.
- All silane coatings improved the corrosion resistance in the EIS test compared to the sample without coating.
- The silane coatings tested reduced the hydrophobicity of the aluminium surface.
- The three double layer samples presented higher percentage of silicon compared to the others. However, the "Sample A" showed a slightly higher percentage.
- The double layer of TEOS (Sample C) was the best option among the coatings tested because of its good corrosion resistance and the lower price when compared to the others.

## References

(1) VAN OOIJ, W. J.; ZHU, D.; STACY, M.; SETH, A.; MUGADA, T.; GANDHI, J.; PUOMI, P. Corrosion protection properties of organofunctional silanes—an overview. **Tsinghua Science & Technology**, v. 10, n. 6, p. 639–664, 2005.

(2) MOREIRA, V. B.; FERREIRA, J. Z.; MENEGUZZI, Á. PRÉ-TRATAMENTO POR DEPOSIÇÃO ELETROASSISTIDA DE VINILTRIETOXISSILANO (VTES) PARA A PINTURA DE ALUMÍNIO. **Tecnologia em Metalurgia Materiais e Mineração**, 2018.

(3) NADERI, R.; FEDEL, M.; DEFLORIAN, F.; POELMAN, M.; OLIVIER, M. Synergistic effect of clay nanoparticles and cerium component on the corrosion behavior of eco-friendly silane sol–gel layer applied on pure aluminum. **Surface and Coatings Technology**, v. 224, p. 93–100, jun. 2013.

(4) LI, Y.-S.; WRIGHT, P. B.; PURITT, R.; TRAN, T. Vibrational spectroscopic studies of vinyltriethoxysilane sol–gel and its coating. **Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy**, v. 60, n. 12, p. 2759–2766, out. 2004.

(5) BERNARDIN, J. D.; MUDAWAR, I.; WALSH, C. B.; FRANSES, E. I. Contact angle temperature dependence for water droplets on practical aluminum surfaces. **International journal of heat and mass transfer**, v. 40, n. 5, p. 1017–1033, 1997.

(6) HE, T.; WANG, Y.; ZHANG, Y.; LV, Q.; XU, T.; LIU, T. Super-hydrophobic surface treatment as corrosion protection for aluminum in seawater. **Corrosion Science**, v. 51, n. 8, p. 1757–1761, ago. 2009.

(7) GARCIA, B. P. **ASSOCIAÇÃO DE TANINOS E SILANO NA PASSIVAÇÃO DE AÇO GALVANIZADO**. 2017. Universidade Federal do Rio Grande do Sul., Escola de Engenharia. Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais., 2017.

(8) MOREIRA, V. B. Deposição eletroassistida de organossilanos como pré-tratamento para a pintura de substratos metálicos. 2016.