

ANALYSIS OF CORROSION INHIBITORS ADDITION TO SILANE FILMS ON PROTECTIVE ACTION OF CARBON STEEL

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Abstract. *The contribution of this work is to study the influence of corrosion inhibitors addition in double layers of monosilane on the AISI 1010 steel substrate. The results obtained were compared with those found in double layers of monosilane on the same steel without corrosion inhibitors. The silanes used in this work were: VS (Vinyltriethoxysilane) and GPTMS (Glycidoxypopyltrimethoxysilane). The corrosion inhibitors used were: CeCl₃ and CrO₃. The CeCl₃ was added to VS and CrO₃ was added to GPTMS. The silane layers were obtained by dip-coating method. The EIS and polarization results showed that the CeCl₃ addition was effective in significant increased of the substrate corrosion resistance. Tests were also made by MEV to detect elements of the inhibitors and Si on the substrate surface and uniformity of the film obtained. Humidity measurements were carried out into a humid chamber. The humidity was not significant due to the thinness of the films and their affinity with water. Silane coatings reveal to be promising in order to replacement of conventional treatments such as phosphate and chromate. The corrosion inhibitors addition improves the corrosion protection conferred on the substrate under those coatings.*

Keywords: *Silanes, Corrosion Inhibitors, CeCl₃, CrO₃, Corrosion protection.*

1. INTRODUCTION

Nowadays silanes are largely known due its wide use as coupling agents in composite materials through their organic – inorganic interface.

The pre-treatments of silanes have shown promising results, attracting the attention of industry in recent years, because silanes improve temporary protection against corrosion on substrate and contribute to the adhesion of organic coatings applied subsequently. Besides it causes lower environmental impacts, if it is compared with chromate and phosphate (Bossardi, 2009).

From the 90's, it is remarkable a growing number of published works that use protective coatings against corrosion based on silane. Many researches are mentioning that they have obtained good results using organosilanes for corrosion protection of different substrates. Palanivel (2005) has obtained satisfactory results using organosilanes doped with corrosion inhibitors on an aluminum alloy and Montemor (2007) using bis-silanes films doped with cerium salts and SiO₂ nanoparticles on galvanized steel. Also, the coating of copper (Zucchi, 2004), common steel (Ramos, 2009), zinc (Yuan, 1997) and magnesium alloys (Grassi, 2006) for silanes are notably efficient.

The mechanism of corrosion protection is simple, because it does not involve electrochemical protection; it happens through a physical barrier. The silane curing promotes a dense and adherent film that interfere the corrosion, difficult the ions passage from the environment to the metallic substrate. That film becomes a hydrophobic barrier (Zhu, 2003).

Cabral et al. (2006) has obtained, with cerium nitrate addition, a bis-silane film more efficient in protection against corrosion of galvanized steel and aluminum alloys and for more time. That effect is justified for the porosity of film decreasing and the Ce³⁺ ions action as corrosion inhibitors. According Palanivel (2005), the cerium salt promotes a self-healing capacity on silane films, since those films concentrate inhibitor elements as reservation, releasing them when it is necessary.

Suegama et al. (2009) has obtained a bis-silane film doped with Ce^{4+} ions which presented a better corrosion resistance, appearance and larger thickness, compared with silanized substrates. The protection mechanism involves the releasing of Ce^{3+} ions.

The objective of this work is to study the addition effect of corrosion inhibitors, $CeCl_3$ and CrO_3 , in monosilane films on carbon steel AISI 1010. It was obtained a monosilane film composed by double layer; the first layer is formed by VS and the second is formed by GPTMS.

2. EXPERIMENTAL

The used samples were AISI 1010 steel plates. The steel plates were cut in rectangles of dimension 60 x 25 x 1.5 mm. The plates were immersed in acid solution for pickling and in alkaline degreasing solution. They were kept immersed there until the use in order to remove the dirt from the handling and guarantee the presence of OH radicals on the substrate. The used monosilanes were VS - Vinyltriethoxysilane (Z-6518) – functional, cross-linker (Dow Corning, 2006) and GPTMS - Glicidoxipropiltrimetoxisilane (Z-6040) – functional (Dow Corning, 2006).

VS has vinyl group and GPTMS has epoxy group. According the manufacturer, VS is a good crosslinker, therefore, it was used to form the base layer.

For silane solution elaboration, it is used deionized water, acetic acid p.a. (Synth) and ethanol p.a. (Synth). First, it was prepared the mixture of 50% in volume of water and 50% in volume of ethanol. The pH was adjusted for range from 4.0 to 4.5 with acid acetic, after it was add 2% in volume of silane. The VS solution was hydrolyzed for 20 minutes and the GPTMS solution was hydrolyzed for 30 minutes. The solution was hydrolyzed using magnetic stirring at room temperature.

Cerium chloride and chromic acid were used as corrosion inhibitors. The cerium chloride ($CeCl_3$) was added in VS silane solution before hydrolysis in 13g/l proportion of solution. The chromic acid (CrO_3) was added in GPTMS silane solution before hydrolysis in 0.5g/l proportion. The chloride cerium was added in the base layer, ensuring that it has contact with the metal, acting as corrosion inhibitor.

The steel plates were immersed in silane solution under stirring for 2 minutes, accord to the figure 1.

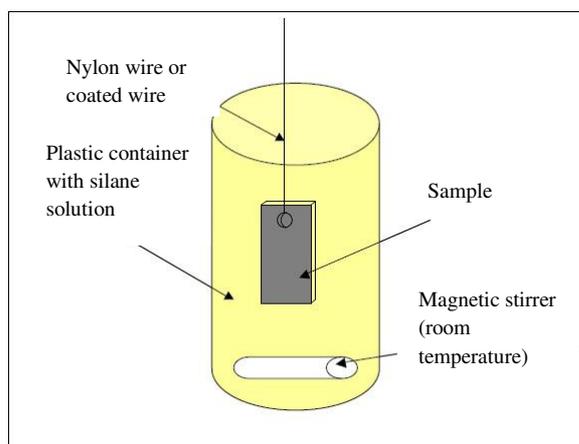


Figure 1. Schematic representation of immersion method of samples in silane solution (Adapted from Oliveira, 2006)

The silane layers were cured in resistive furnace at 150 °C. The VS layer remained into the furnace for 10 minutes and the GPTMS layer remained for 30 minutes.

The polarization curves were collected using a 0.1 M NaCl solution at room temperature. Measurements were obtained in potentiostat PGSTAT302[®] of AUTOLAB[®], with a scan rate of 0.001V/s. The electrochemical cell was consisted of three electrodes: counter electrode, as counter electrode was used a platinum wire, reference electrode, as reference electrode was used saturated calomel electrode with KCl (ECS); work electrode, the sample with a defined area in 1 cm² was used as work electrode.

The electrochemical impedance spectroscopy measurements were obtained in open circuit potentiostat in the frequency range from 40 MHz to 10 mHz with ten points per logarithmic decade using an PGSTAT302[®] of AUTOLAB[®]. The used disturbance potential has amplitude of 10 mV_{rms}. The electrochemical cell was constituted for three electrodes, it was the same used for polarization test. The spectra were obtained in 0.1 M NaCl solution at room temperature, after 5 minutes, 1 hour, 24 hours, 48 hours, 72 hours and 144 hours of immersion of sample in this solution. The dates were collected through Frequency Response Analyser (FRA) software also of AUTOLAB[®]. The graphs were plotted in Nyquist diagram.

The saturated humid chamber test simulated an atmosphere with high humidity and high temperature. The test was conducted in accordance with NBR 10443 and ASTM 2247 standards. The samples were exposed for 24 and 48 hours.

The silanized samples were metalized with platinum in order to be analyzed by Scanning Electronic Microscopy (SEM) and also elemental analysis by Energy Dispersive Spectroscopy (EDS) using scanning electronic microscopy JEOL - JSM 5800.

For the description of the results, it has been utilized the following nomenclature: VS + GPTMS for VS as first layer and GPTMS as the second; VS + CeCl₃ + GPTMS for the VS doped with CeCl₃ as first layer and GPTMS as the second; and VS + GPTMS + CrO₃ for VS as first layer and GPTMS doped with CrO₃ as second.

3. RESULTS AND DISCUSSION

3.1. Polarization Curves

The figure 2 presents the anodic and cathodic polarization plots of the studied silane combinations. Among the presented plots, it is highlighted the steel coated with VS + CeCl₃ + GPTMS.

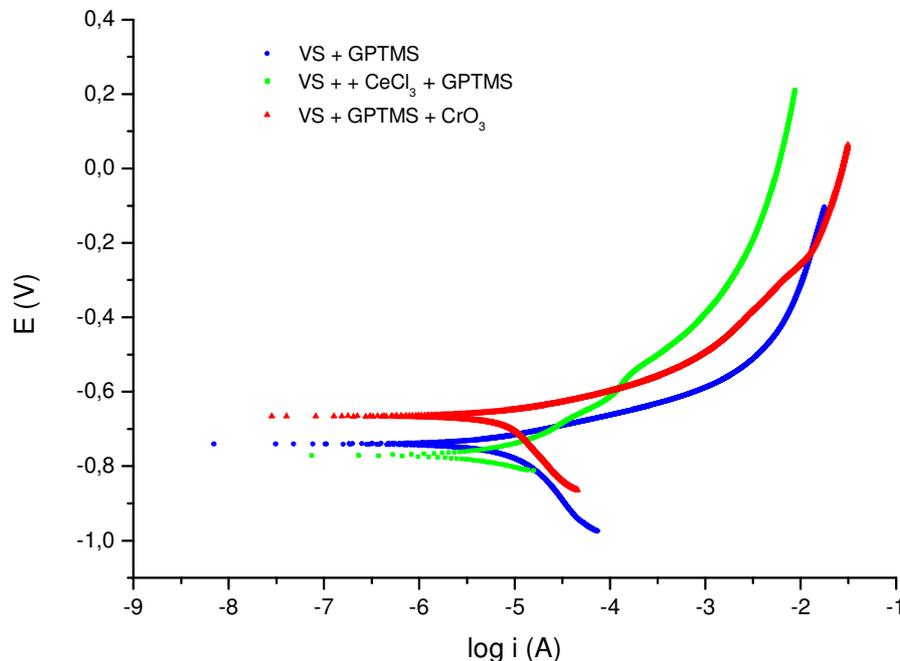


Figure 2. Anodic and cathodic polarization plots in 0.1 M NaCl for different combinations of silane and corrosion inhibitors layers: 0.001 V/s

The steel coated with layer VS + CeCl₃ + GPTMS had a higher active corrosion potential. There is a shift in the potential in cathodic direction and reduction in the cathodic current density. The same compartment could be seen by Palanivel (2005). According to him, that electrochemical effect is due to the blocking in cathode areas of material by cerium salts and consequently the reduction of the corrosion general rate.

Comparing VS + GPTMS with VS + CeCl₃ + GPTMS plots, it is observed that although the potential has shifted toward to the cathodic area in Ce presence, the anodic area is much more polarized, indicating higher corrosion resistance. This indicates which coating silane doped with cerium chloride improves corrosion protection by reducing corrosion potential.

The VS + GPTMS and VS + GPTMS + CrO₃ samples presented similar electrochemical behaviors.

3.2. Electrochemical Impedance Spectroscopy (EIS)

The EIS results are presented in Nyquist diagram in figures 3, 4, 5, 6 and 7 for different silane layers at different analysis time.

The VS + GPTMS double layer shown in figure 3 has followed the expected tendency. It can be seen which the double layer has a high corrosion resistance with less time into the solution for 24 and 48 hours. After that time the electrical current is decreased due to oxidation on the metal surface.

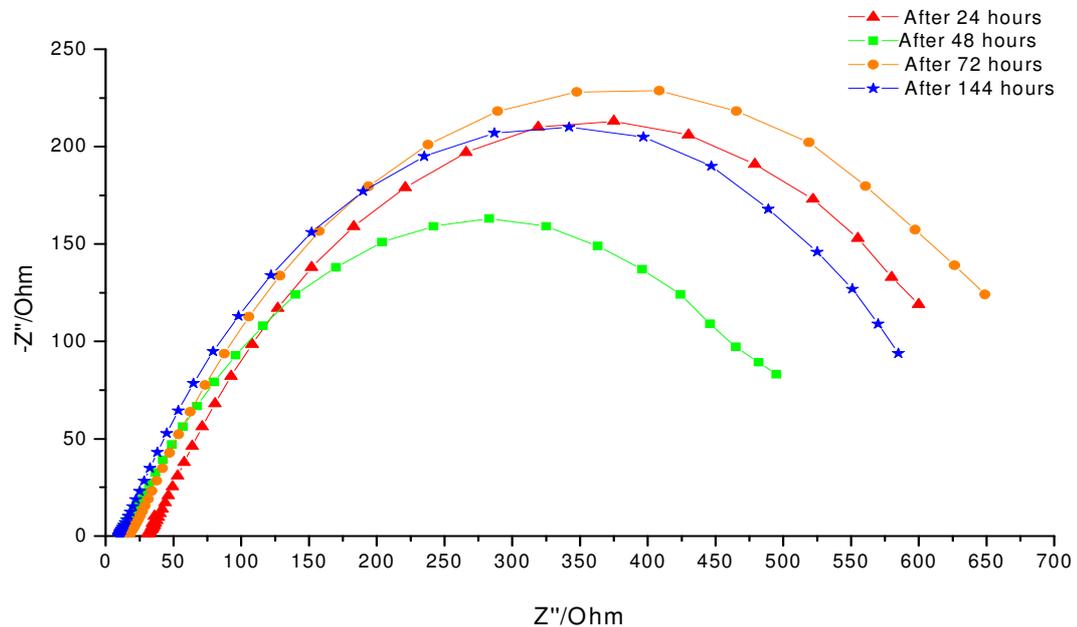


Figure 3. VS + GPTMS Nyquist diagram for different immersion times in 0.1 M NaCl solution

The VS + GPTMS + CrO₃ double layer shown in figure 4 presented similar results if compared with the case shown in the figure 3. The chromate was add on the second silane layer, therefore, it is improbable that the chromate has contact with the substrate and passive it, explaining the low EIS values.

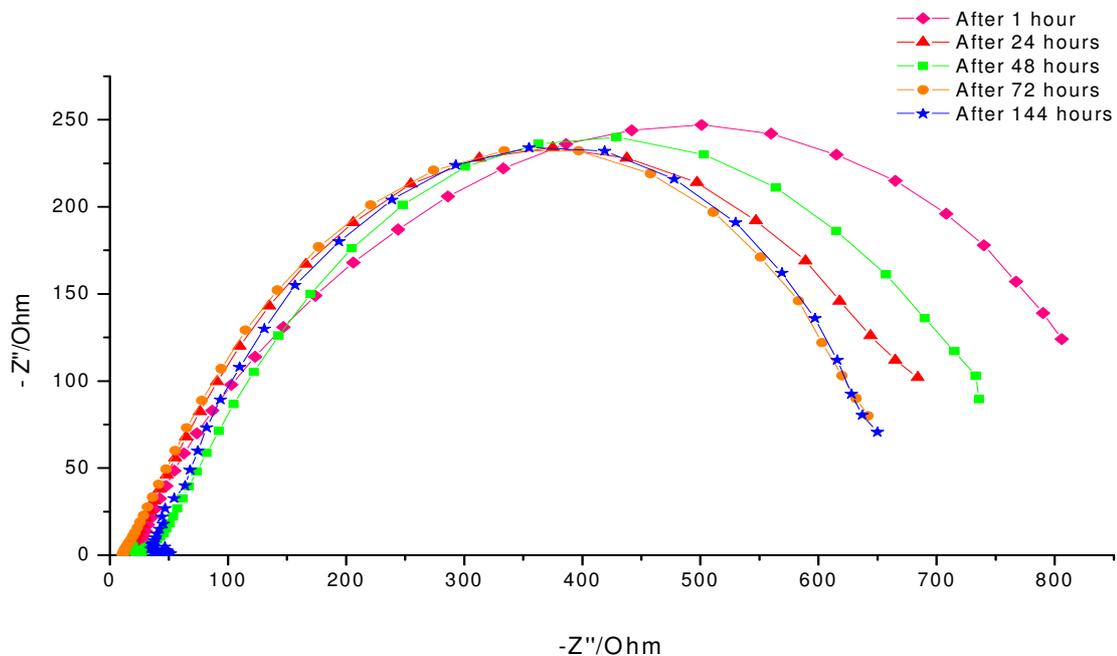


Figure 4. VS + GPTMS + CrO₃ Nyquist diagram for different immersion times in 0.1 M NaCl solution

The figure 5 shows the EIS results for VS + CeCl₃ + GPTMS double layer. The best EIS results were obtained in this coating. It proved which the cerium chloride addition on silane film increased the electrical resistance; it provides a better protection against corrosion on the substrate. Even in long times, this coating showed a better

result than those firsts. It confirms which cerium chloride act as a corrosion inhibitor. Probably it acts similarly as cerium nitrate described by Palanivel (2005).

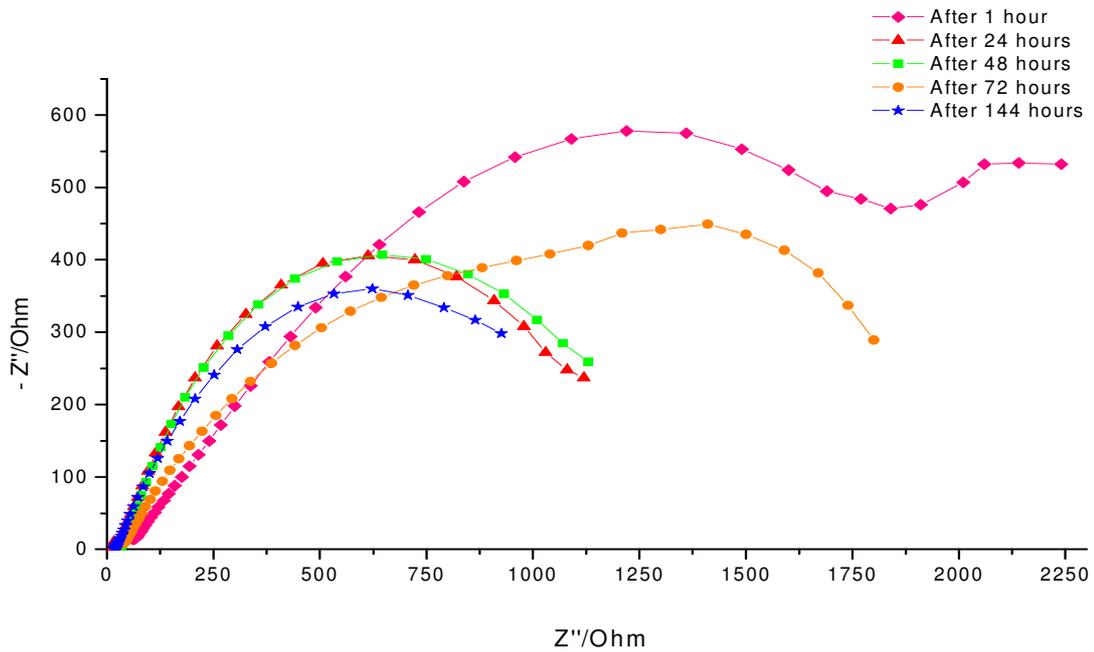


Figure 5. VS + CeCl₃ + GPTMS Nyquist diagram for different immersion times in 0.1 M NaCl solution

The figure 6 presents a comparing among the different coatings obtained in 1 hour of immersion in 0.1 M NaCl solution. It is evident a better corrosion protection associated to the electrical resistance increasing on the steel coated by VS + CeCl₃ + GPTMS, in agreement with polarization results.

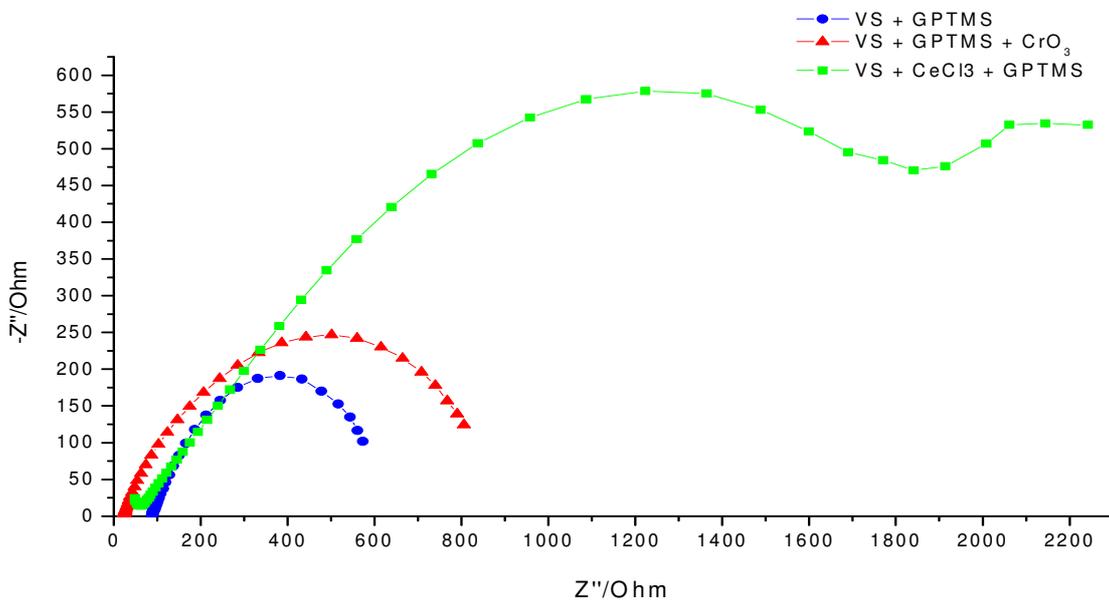


Figure 6. Nyquist diagram of silanized steel with different layers after 1 hour in immersion in 0.1 M NaCl solution

The figure 7 shows a comparing among the impedance results for different silane coatings obtained at 144 hours in immersion in 0.1 M NaCl solution. It shows a reduction in electrical resistance compared with the figure 6. The best results are still obtained on steel coated by VS + CeCl₃ + GPTMS.

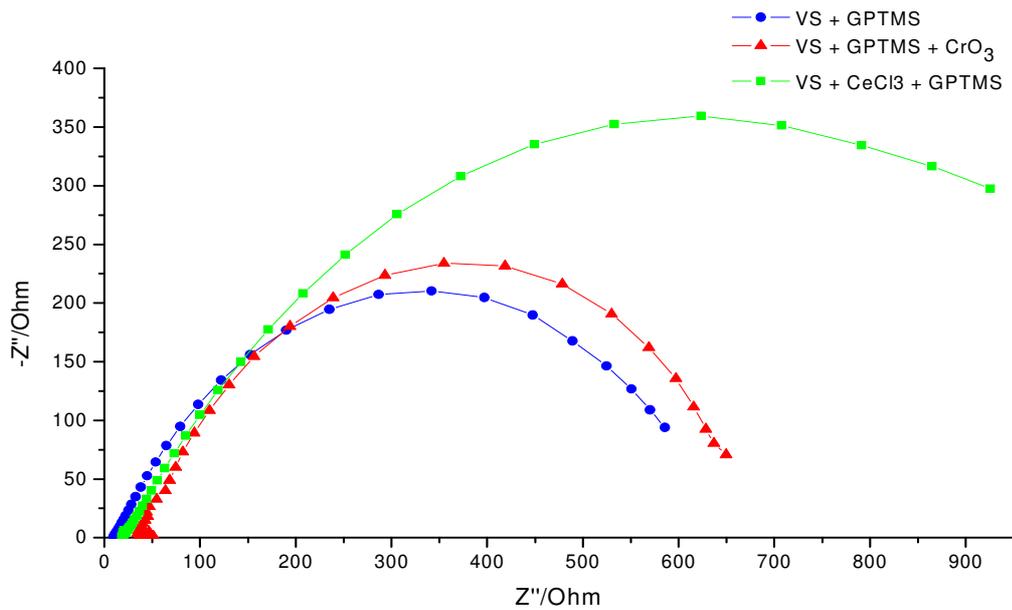


Figure 7. Nyquist diagram of silanized steel with different layers after 144 hours in immersion in 0.1 M NaCl solution

3.3. Humid Chamber

The humid chamber results are listed in table 1.

Table 1. Humid chamber results.

Samples	24h	48h
VS + GPTMS	V3	V4
VS + GPTMS + CrO ₃	V4	V4
VS + CeCl ₃ + GPTMS	V5	V5
Steel	V3	V4

The results obtained in humid chamber test are not significant, because the silane layer is very thin and very susceptible to the water presence. It is estimated that the silane layers were hydrolyzed by saturated steam presence.

3.4. Scanning Electronic Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

The figure 8 shows the SEM images for VS + GPTMS and the table 2 presents the EDS results. It shows that the VS + GPTMS layer has light and dark regions, indicating that the film is not homogenous. Moreover, it was possible to detect through the EDS analysis the silicon, carbon and oxygen presence. They are the silane main components.

It is reported by Ramos (2009) a similar fact. The silicon peaks are the highest in dark regions. The formation of those dark zones may have occurred during the drying step, in which drops of silane solution becomes smaller accord to the time, creating distinct regions with a higher silicon presence. Another possible explanation is the occurrence of silane condensation reaction. It can lead to the polymerization and Si cluster precipitation.

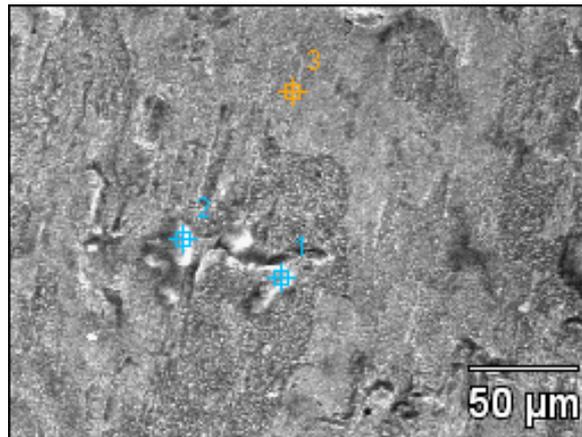


Figure 8. SEM images for silanization with VS + GPTMS. Blue point: pt_1; Blue point: pt_2. Orange point: pt_3

Table 2. EDS results for silanization with VS + GPTMS.

	<i>C (%)</i>	<i>O (%)</i>	<i>Si (%)</i>	<i>Fe (%)</i>
<i>VS + GPTMS_pt1</i>	74.29	6.94	8.47	10.30
<i>VS + GPTMS_pt2</i>	78.23	7.22	8.44	6.10
<i>VS + GPTMS_pt3</i>	63.06		2.01	34.93

The figure 9 shows the SEM images for VS + CeCl₃ + GPTMS. It is visible which the Ce influences the silane film formation. It improves the film crosslink, forming a more homogenous film. Therefore, it is possible to explain the anticorrosion properties improvement in that material. It was not possible to confirm the Ce presence by EDS results showed in table 3, because that analysis is punctual.

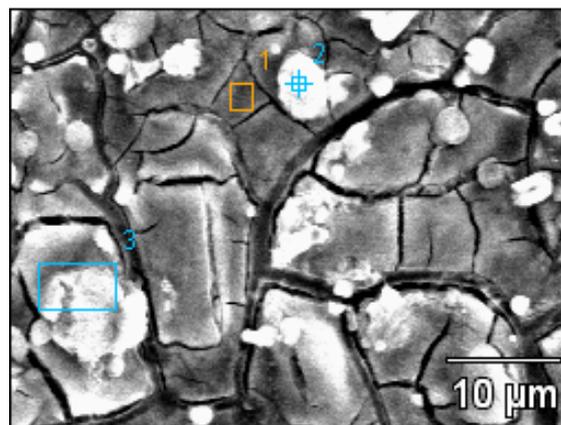


Figure 9. SEM images for silanization with VS + CeCl₃ + GPTMS. Orange point: pt_1; Blue point: pt_2. Blue rectangle: pt_3

Table 3. EDS results for silanization with VS + CeCl₃ + GPTMS.

	<i>C (%)</i>	<i>O (%)</i>	<i>Si (%)</i>	<i>Fe (%)</i>
<i>VS + CeCl₃ + GPTMS_pt1</i>	37.18			57.78
<i>VS + CeCl₃ + GPTMS_pt2</i>	50.08	21.03		17.13
<i>VS + CeCl₃ + GPTMS_pt3</i>	49.21	24.55	0.83	13.45

The figure 10 shows the SEM images for VS + GPTMS + CrO₃ and the table 3 shows the EDS results. The image obtained by SEM is similar to the image of figure 8. There are light and dark regions that indicate which the film is not homogeneous.

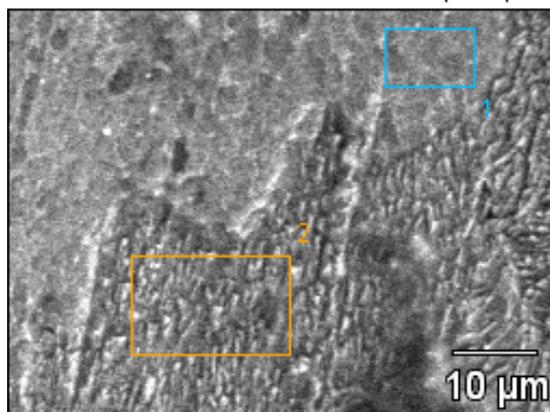


Figure 10. MEV images for silanization with VS + GPTMS + CrO₃. Blue rectangle: pt_1; Orange rectangle: pt_2

Table 3. EDS results for silanization with VS + GPTMS + CrO₃.

	C (%)	Al (%)	Si (%)	Fe (%)
VS + GPTMS + CrO ₃ _pt1	45.24		1.74	53.02
VS + GPTMS + CrO ₃ _pt2	54.17	3.08	3.01	39.74

4. CONCLUSIONS

The corrosion inhibitors addition such as CeCl₃ improves the corrosion protection of the substrate coated by double layer of monosilanes.

The silane layer that presented the highest corrosion resistance was the VS + CeCl₃ + GPTMS. Therefore, that layer is the most indicated in order to coat carbon steel pieces. Moreover, it is more environmentally appropriated than treatments which use chrome.

The thickness of silane layer formed is too thin and susceptible to the water presence. Therefore, it is necessary to use a coating on the silane layer for protection.

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6. RESPONSIBILITY NOTICE

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