

Development of a electrophoretic sol-gel coating for stainless steel

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Abstract

A sol-gel coating was developed for a stainless steel substrate. The coating consists of a single layer consisting of PhTMS and TEOS, applied by electrophoretic deposition with the following -1V, -1.2V, -1.4V and -1.6V potentials. Coatings produced by sol-gel processes have been extensively studied in recent years mainly in the field of hybrid and inorganic coatings. particularly for medical purposes, in the production of coatings more environmentally friendly and also as anticorrosive coatings.

The various coatings were characterized by optical microscopy, scanning electron microscopy, electrochemical impedance spectroscopy (Electrochemical Impedance Spectroscopy) and contact angle. The most homogeneous coatings were obtained at the most negative potentials. The best properties were obtained with electrophoretic deposition at -1.6V. The developed coating, which caused an overall impedance increase of about one order of magnitude, was characterized by a very rough, very thin morphology which had a contact angle of 88°.

Keywords: Stainless steel, sol-gel, organosilanes, electrophoretic deposition, hydrophobicity.

I. Introduction

The interest of novel coatings with well tailored properties has been increasing. The key idea is to adjust the surface characteristics of the materials while keeping the bulk properties. The resulting system combines good mechanical properties of the metallic substrate with good surface resistance of ceramic materials. The sol-gel process is a chemical method that enables the production of ceramics, glasses and composite materials under mild conditions. The synthesis starts with a colloidal suspension named "sols" that usually consists of inorganic metal salts or organic components dispersed in water, or in an organic solvent or in a water-organic mixture. Then, through acid or basic catalysis the sol will react, giving way to hydrolysis, condensation and gelation of the precursors. The last step is a thermal treatment to promote drying and sintering which give consistency to the final material [1].

Organosilanes are sol-gel precursors which general formula is $R'_n\text{-Si-(OR)}_{(4-n)}$. This kind of precursor has the silicon atom (Si) as the main element, -OR is a hydrolysable group typically methoxy, ethoxy or isopropoxy, and R' is a non-hydrolysable group, for example, amino, vinyl or alkyl [2].

Dip-coating and electrophoretic deposition (EPD) are different methods to apply sol-gel coatings on substrates, and there are many studies that compare the quality of final coatings obtained for each case [3, 4]. Dip-coating allows the application on any type of substrate, conductive or not, also it can deposit any type of material, ceramic, glasses and polymer. The film formation is easily controlled by the withdrawal rate, the solution viscosity, surface tension and evaporation [5]. However, the final results of the coatings are not always adequate, mainly due incomplete substrate covering, bad adhesion of the film or appearance of defects during the drying step. EPD is an alternative method that has the limitation of requiring conductive substrates because it is necessary to apply a potential differential between two electrodes. The final properties depend upon the applied potential, surface charge

of particles, deposition time and particle mass percentage in solution. Through this method it is possible to produce homogeneous and adherent coatings by a combined electrochemical and aggregation mechanism [6].

Coatings produced by this method can show a porous structure when observed along all the cross section [7], which can be a limitation for some applications. Among the possible applications for sol-gel based coatings, it is interesting to mention the recent developments related with superhydrophobic behavior [8], anti-corrosive treatments to replace environmental harmful compositions [8] and coatings with enhanced properties such as hardness. The properties aimed are hydrophobic behavior and improved corrosion resistance [9,10]. The coated system was characterized morphologically, electrochemically and concerning its hydrophobicity. This coating may be of interest for a number of applications, namely medical instruments, aeronautic, construction and housewares.

II. Experimental methods

Material

Three types of solvents were used in the preparation of the solutions

- High purity water (H₂O milipore)
- Absolute ethanol (EtOH, 99.9%, Merck)
- NaNO₃ solution, 0.5 M

Precursors of the sol-gel process:

- Tetraethyl orthosilicate (TEOS, 99%, Sigma-Aldrich)
- Phenyl trimethoxysilane (PhTMS, 97%, Sigma-Aldrich)

Hydrochloric acid (HCl, 37%, 1M) was used to adjust the pH of the solutions and to act as a catalyst.

Sol preparation and deposition

The solution for EDP was prepared by adding 2 mL of PhTMS to a mixture of 60 mL of EtOH and 10 mL of H₂O with stirring (400 rpm) then 4 mL of a solution of NaNO₃ (0.5 M). The pH of the solution is then adjusted with 1 mL HCl to the range 2-3. The solution is allowed to hydrolyze for 12 hours at room temperature at 35° C. After hydrolysis of PhTMS the solution was colorless. The TEOS is then added and allowed to hydrolyze between 2 to 3 hours. After the two hydrolyses the solution was colorless and it was not possible to visually distinguish suspended particles. The stainless steel AISI 304 was subjected to a cleaning scheme to uniform the surfaces of the substrate to be coated. Thus eliminating some contaminants that could impair the adhesion of the film. The cleaning scheme of the substrate consists of a polishing with 1000 grit SiC sandpaper, then washed with milipore deionized water, taken to ultrasound bath in ethanol for 5 minutes and finally washed again with milipore water and dried with compressed air. A three-electrode system was used, with the stainless steel plate as working electrode, a saturated calomel electrode (SCE) as the reference and a platinum plate with a large exposed area as the counter electrode. The working and counter electrodes were kept at a fixed distance of 1,5 cm. Potential differences applied during electrodeposition process were selected based upon results of cyclic voltammetry. The potential applied was in 1-1.6V range vs. SCE and deposition time was 5 minutes. After electrophoretic deposition, the samples were rinsed with distilled water to remove the excess of solvent, and then oven-cured at 120°C for 1 hour.

Kinetics, morphological and electrochemical characterization of the films

The electrochemical measurements were all carried out using a conventional three-electrode cell, including a stainless steel working electrode, a SCE reference and a platinum counter electrode. All measurements were made at room temperature, using a *GAMRY PC4* potentiostat.

Cyclic voltammetry of the bare steel was used for the choice of the potential in the electrophoretic deposition. Four cycles were performed in the cathodic range, down to -3V versus open circuit potential (OCP).

The microstructural characterization and thickness measurement of the films were performed by emission scanning electron microscopy (FEG-SEM, JEOL JSM-7001F) at an accelerating voltage of 5kV and 15 kV. The samples were sputter coated with gold for surface conductivity. The energy dispersive X-ray spectroscopy, EDS (INCA 250, Oxford Instruments, UK), was used for elemental chemical analysis.

The stability of the films on the surfaces was evaluated by electrochemical impedance spectroscopy (EIS) performed in 0.1 M NaCl using a potential source *GAMRY PC4* potentiostat. A using a glued glass the samples with an exposed area of 7 cm². The electrodes were left under open circuit potential for 1 hour before each spectrum. Spectrum were recorded in the frequency range of 100 kHz to 10 mHz, using a 10 mV.rms perturbation. For durability evolution, EIS spectrum were recorded during 24 hours to 72 hours.

Contact angles were measured in each sample, the values were measured in three different parts of the sample, and in each of the samples the values were measured for 5 minutes with an immersion velocity of $U_0 = 3$ mm/min and a depth of 6mm for each sample. For these tests, a goniometer (*Krüß GmbH*) equipped with a tensiometer (*Krüß GmbH, K12*) was used. The data were analyzed through the K12/14 Contact Angle program (*Krüß Laboratory Desktop, Krüss GmbH, Hamburg, Germany*). The contact angle value was estimated from the mean of each measurement for three measurements for the same sample through a linear regression.

III. Results

a. Selection of a range of potentials to prepare films by EPD in TEOS+PhTMS

The first step in this work was to select the potentials to be applied to the electrophoresis cell. We intend to promote the reduction of oxygen in the working electrode, a study was carried out through a cyclic voltammetry, within the cathodic potential, from the open circuit potential - Figure 1. We can then check, from the values of current, that the reduction of oxygen occurs and becomes significant from -1V during the first cycle, since it is the potential from which the beginning of the linear variation of the current with the potential, typically of the reduction / oxidation process of the oxygen. For higher potentials, very low currents are present, with mass transfer processes influencing the deposition, since the generated ions are dispersed into the solution, not allowing the formation of a layer of near the electrode surface.

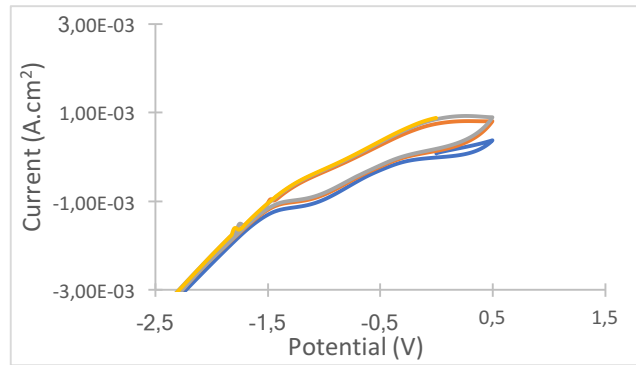


Figure 1 - Cyclic voltammetry of bare stainless steel in the TEOS+PhTMS solution.

b. Production and characterization of the electrophoretic TEOS+PhTMS

Regarding the visual aspect, it is observed in all the samples that have deposited the presence of the risks of the polish in comparison with that of bare steel (a), there is still the presence of a structure of dry mud common in all the samples with which deposition of film this effect is caused by curing in the oven at 120°C. Another important aspect is the pink colour present in the samples, this colour is more noticeable in the samples prepared to the highest powers as -1,4V and -1,6V.

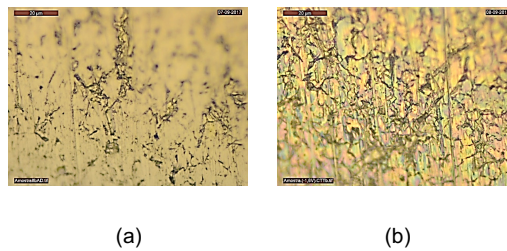


Figure 2 – Visual aspect of deposition material for different potential.

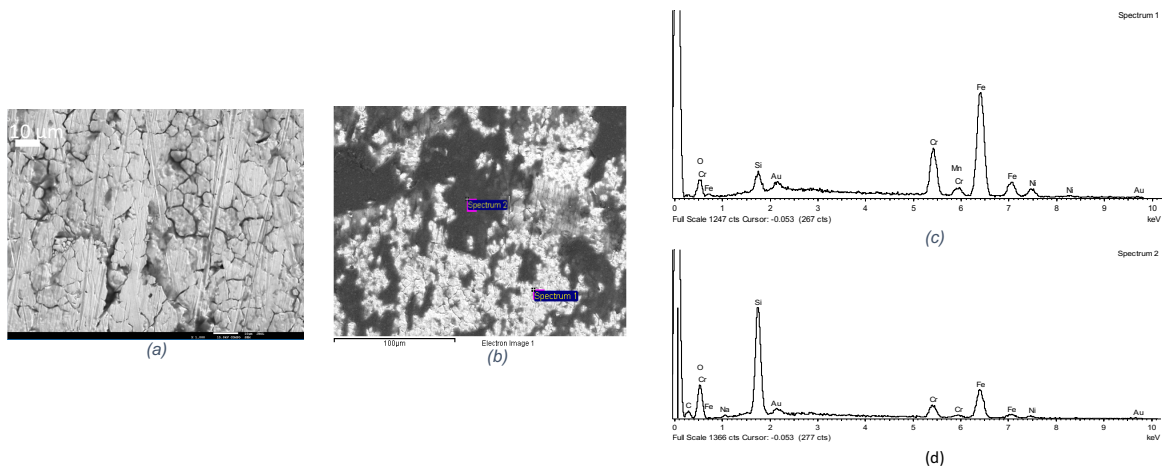


Figure 3 - Micrograph of the -1.2V film with backdrops (a), micrograph of the -1.2V film (b) and its analysis EDS and spectrum 1 (c) and spectrum 2 (d)

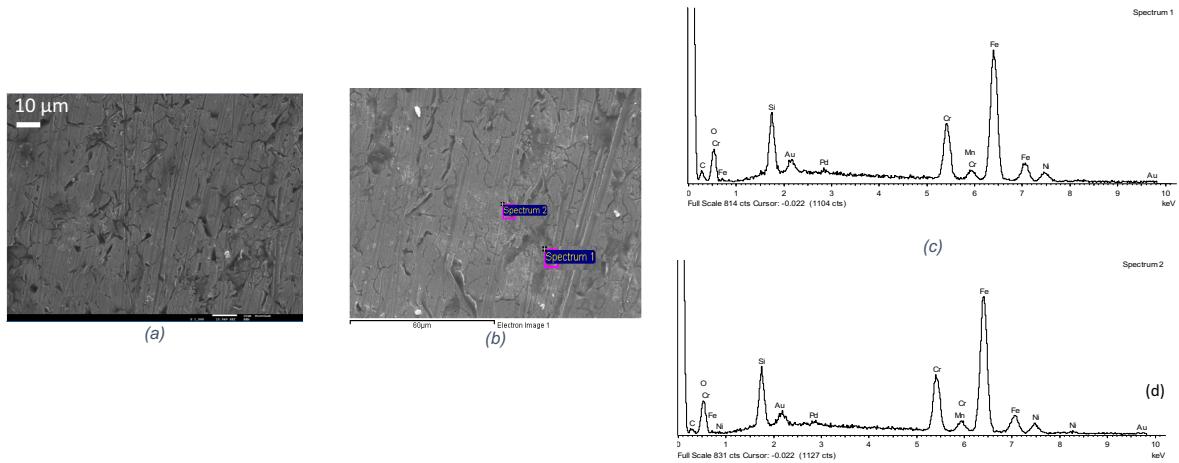


Figure 4 - Micrograph of the -1.6V film with backdrops (a), micrograph of the -1.2V film (b) and its analysis EDS and spectrum 1 (c) and spectrum 2 (d)

SEM inspection was of great use mainly in the observation of the coatings obtained at -1.2V and -1.6V because they presented regions where the appearance of the obtained film could not be observed visually.

The film formed at -1.2V in figure 3 shows that the steel is covered by a coatings since the different morphology of the steel 304 presented a dry mud structure, EDS analysis (figure 3) (backdrops) revealed that there were areas of the sample that seemed to demonstrate that there had been no deposition of the coating, these dark areas shows that the silicon on the surface (figure 3) in the others that have a light almost white tone have silicon but not in such large quantities we have a high iron spike. The samples of -1.2V Figure 3 had still beads, were then observed by EDS revealing these beads with high intensity of silica. Samples were also observed where impedance tests were performed can be observed cracks in the film.

The film obtained at -1.6V was slightly more homogeneous, although appearance of dry mud is visible, when we use lower energies (15kV), it is verified that there is a thin film above the cracks that makes the (figure 4) show a more homogeneous film. A spheres and cracks were observed, it can be concluded that there was corrosion in this area due to exposure to the chloride ion.

Coatings obtained at -1.2V by placing the samples at 70° in the SEM, although these samples were subjected to impedance tests, it was possible to have the thickness perception. SEM bars were placed to facilitate measurements, thicknesses ranging from 1 μm to 3 μm.

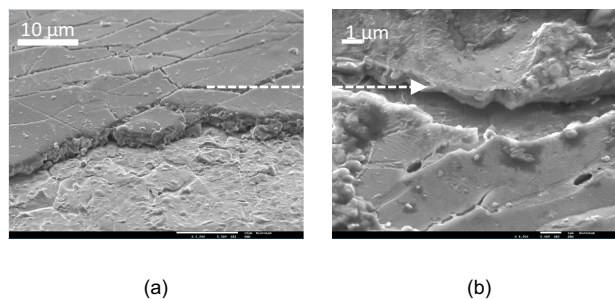


Figure 5 - Film micrograph of -1.2V at 70°.

c. Electrochemical analysis

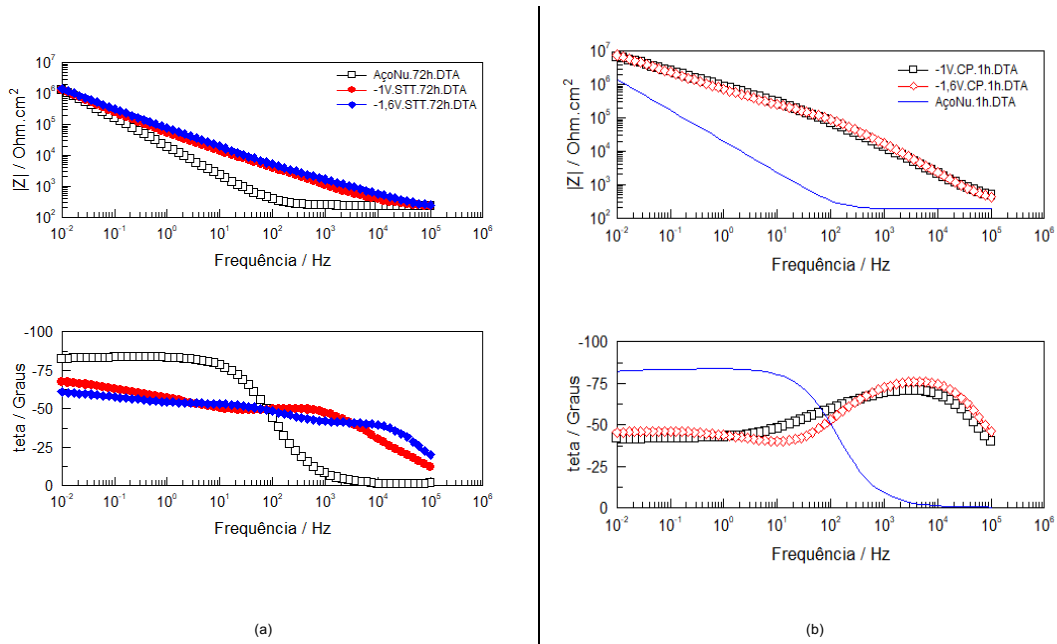


Figure 6 - Impedance spectra after 2 hours of immersion in NaCl 0,1M, for the films obtained at stainless steel, -1V, -1,2V, -1,4V and -1,6V, without polishing and without heat treatment (a) and with polishing and heat treatment (b)

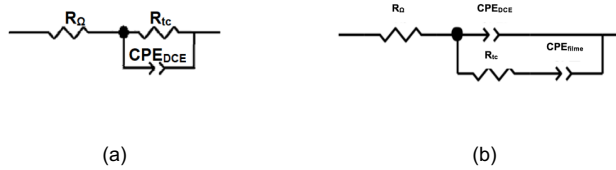


Figure 7 - EE's for the blank (a) and the films obtained at -1V, -1,2V, -1,4 and -1,6V (b).

Table 1 - Low frequency impedance and ECC components values for the electrophoretic films.

Sample	$ Z _{(0,01\text{Hz})}$ ($\Omega \cdot \text{cm}^2$)	CPE_{film} ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n_{film}	CPE_{DCE} ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n_{DCE}	R_{tc} ($\Omega \cdot \text{cm}^2$)
2 hours						
Blank	$1,43 \times 10^6$	-	-	$9,44 \times 10^{-6}$	0,93	$2,85 \times 10^7$
-1V	$7,10 \times 10^6$	$4,61 \times 10^{-7}$	0,43	$2,47 \times 10^{-8}$	0,88	337
-1,2V	$6,53 \times 10^6$	$2,03 \times 10^{-8}$	0,92	$4,66 \times 10^{-7}$	0,41	$1,16 \times 10^5$
-1,4V	$2,58 \times 10^6$	$2,06 \times 10^{-8}$	0,91	$1,24 \times 10^{-6}$	0,39	$1,24 \times 10^5$
-1,6V	$7,68 \times 10^6$	$2,38 \times 10^{-8}$	0,89	$5,46 \times 10^{-7}$	0,52	$1,25 \times 10^5$
72 hours						
Blank	$1,37 \times 10^6$	-	-	$9,16 \times 10^{-6}$	0,93	$2,62 \times 10^7$
-1V	$3,89 \times 10^6$	$1,21 \times 10^{-6}$	0,58	$7,49 \times 10^{-7}$	0,77	292
-1,2V	$3,17 \times 10^6$	$1,48 \times 10^{-8}$	0,95	$8,28 \times 10^{-7}$	0,36	$1,35 \times 10^4$
-1,4V	$2,00 \times 10^6$	$1,13 \times 10^{-8}$	0,96	$3,17 \times 10^{-7}$	0,26	$1,47 \times 10^5$
-1,6V	$6,70 \times 10^6$	$2,53 \times 10^{-8}$	0,89	$5,31 \times 10^{-7}$	0,54	$1,68 \times 10^5$

To evaluate the protective properties of the films, impedance measurements were performed on open circuit potential after two hours and 72 hours of immersion in 0.1M NaCl. The tests were performed for samples prepared in two conditions one group without polishing and without heat treatment, another group with polishing and heat treatment. The results show that samples prepared without polishing and without heat treatment have an electrochemical behaviour comparable to that of bare stainless steel.

The reference sample for bare stainless steel has a single time constant in the impedance spectrum, which is composed of the electric double layer (C_{DCE}) at the stainless steel interface and the load transfer resistance (R_{tc}).

For the remainder of the samples, two time constants were observed, one referring to the processes together the stainless steel surface, composed by the resistance to the transfer of charge (R_{tc}) and by the C_{DCE} , and another time constant relative to the film, which is composed by the capacity of the film (C_{film}).

We can then observe several effects, firstly the fact that the polishing and the heat treatment affect the capacity of the coatings produced to the various potentials and secondly to differences with the potentials and finally the behaviour without the 72 hours. It is clearly observed an increase of the overall impedance in relation to the samples without polishing and without heat treatment, we can thus conclude that there is a better adhesion to the substrate. On the other hand, the increased potential also leads to an increase in impedance which has already been confirmed previously. Over time a decrease in impedance is observed, but the load transfer resistance (R_{tc}) does not decrease as drastically as in coatings produced without polishing and without heat treatment. Still according to the tables, it is verified that the film capacity remains more stable during the 72 hours of the tests.

In summary, the impedance results allow us to distinguish three different behaviours: bare stainless steel shows a single time constant in the impedance spectrum, which is composed of the capacity of the double electric layer at the stainless steel interface and the load transfer resistance.

Another fact to be mentioned is that the time constants are not well defined in both cases. This fact may be caused by these films being obtained by electrodeposition there may be the formation of clusters of coatings in certain areas. The heterogeneity of the film may have been responsible for a higher impedance signal in the low frequency zone, since the mean value of the contribution of the different zones becomes higher due to the agglomerates thicker than the film itself, thus form a and thus increases corrosion resistance.

Therefore, these factors are reflected in the morphology of the system, showing a decrease in the contact area of the electrolyte with the steel surface, which causes an increase in the substrate protection.

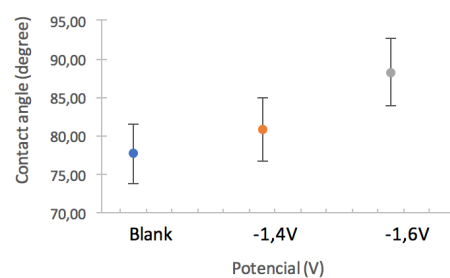
d. Wettability analysis

The wettability of surface increase for higher cathodic applied potentials – figure 8

Table 2 - Contact angles and their mean and standard deviation for bare steel, -1.4V and -1.6V

Sample	Angle (θ)	Average (θ)	Standard deviation
Blank	76,74	77,70	0,89
	77,47		
	78,89		
-1,4V	77,06	80,84	2,90
	81,36		
	84,1		
-1,6V	86	88,27	1,71
	88,68		
	90,13		

Figure 8 - Contact angles for bare steel, -1.4V and -1.6V.



As in all samples the deposited material was the same except for the bare steel, they must then have the same surface tension value. The increase of the contact angle with the increase of the applied potential can be explained by the decrease of the roughness and porosity of the obtained films. These characteristics are typical of the films produced by this technique.

IV. Discussion

The use of the sol-gel process for the manufacture of coatings on stainless steel, using the electrophoretic deposition technique to apply the coating, allowed to develop a coating with low porosity and roughness, with a slightly hydrophobic behavior and good durability under the conditions tested.

The use of TEOS (2mL) and PhTMS (2mL), which contains both silica particles, but have different functions, TEOS has as its main function the connection to the substrate and with PhTMS binder to the substrate, PhTMS aims to modify the behavior and thereby render the coating hydrophobic.

The hydrolysis step is critical for the conversion of TEOS + PhTMS to the formation of the network on the substrate. This process is controlled by the pH normally located between 3-4, some difficulties have been encountered in this field of pH control, for above pH we are witnessing a condensation effect, a white color is exhibited and consequently the turbidity of the solution. On the other hand, the mass transfer processes (convection and diffusion) lead to the dispersion of these ions in solution, which leads to an attenuation of the effect of the increase of the pH. Let us assume that in a non-stirred medium the mass transfer processes occur in a similar way, and that they are independent of the applied potential, only the production rate of OH^- ions will be dependent on the potential. The more negative the potential the faster we will reach the basic pH required for the growth of the coatings to begin.

With electrophoretic deposition, it is expected that the basic local environment where the formation of a dense and more rigid gel will occur, thus increasing the critical thickness at which the coating begins to break. This may be due to the increase in time, the initially acidic sun becomes more and more basic at increasing distances from the surface of the working electrode (due to the diffusion of hydroxyl ions), and the hydrolysis and condensation begin to be promoted only on the surface, but also in the sun, producing complex species that are added to the surface layer in a homogeneous way.

By simple test it was possible to check the adhesion of the coating to the substrate, it was observed to pull out with tape, they were not removed from the surface, which indicated empirically that there is a good adhesion to the stainless steel.

In this work, cathode potentials were applied to the working electrode to cause OH^- ions to form on the surface of the substrate due to the reduction of the oxygen, and to raise the pH locally in the solution near the surface, promoting the condensation of the precursors and consequently, the formation of the silica gel. The selection of the potentials to be applied in the electrophoretic deposition was done by means of the stainless steel polarization in the solution of TEOS + PhTMS, it is observed that to potentials below -1,6V the coatings exhibit good adhesion qualities.

The morphology of the surface, in particular with regard to the contact angle, deposited coatings consist of silica, methyl group and phenyl groups that theoretically make the surfaces hydrophobic. If the material is smooth and the plane of the contact angle is less than 90° , the roughness will cause the contact angle to decrease. In case the static contact angle is greater than 90° , the existence of roughness will cause an increase of the contact angle. Thus, if the smooth substrate is hydrophobic, the roughness insert will make it more hydrophobic. The hydrophobicity of a material is modulated by the roughness insertion. The hydrophobicity of the coating results from two factors, the high real area of the coating the chemical properties of the phenyl group.

The coatings deposited on the substrates without polishing and without heat treatment present a slight increase in the coating/stainless steel system impedance compared to the bare steel. This slight increase is related to the possible lack of homogeneity of the coating and its poor adhesion due to low surface roughness. The decrease in the impedance at the time of the unpolished and non-heat treated coatings may be related to some electrochemical reactivity of the coating in the study electrode, on the other hand, the low porosity and low minor area results in a reduction of coating capacity.

In the case of coatings deposited on substrates with polishing and heat treatment, we have an increase in impedance as the potential decreases. Therefore, in this case we have a solution system (NaCl) / coating / metal (steel), although the increment is only in relation to the bare steel, this coating is compact and thin because it presents a barrier effect. These films also show high electrochemical stability after 24 hours but also after 72 hours decreasing their overall impedance.

In short, coatings obtained at more negative potencies show better results, both in relation to the hydrophobicity with respect to the increase in impedance. The hydrophobic behavior can be explained by the morphology and a greater homogeneity as the nature of the chemical compounds that constitute the solution. Increased surface hydrophobicity also leads to increased impedance, which results in less interaction between the solution and the stainless steel surface.

V. Conclusions

This work led to the elaboration of a coating for stainless steel, using the sol-gel process, obtained by electrophoretic deposition in TEOS + PhTMS. These coatings were characterized by scanning electron microscopy, electrochemical impedance spectroscopy and contact angle measurement. The best properties were achieved with the coatings prepared at the most negative potentials. The coatings have a homogeneous visual appearance, increased corrosion resistance, good durability and a moderately hydrophobic behaviour, with contact angles around 90°.

The visual inspection of the samples revealed some differences, this fact is important as they change the aesthetics for possible applications. This gave opaque and whitish coatings, which alters the surface of the metal.

Scanning electron microscopy inspection revealed slightly homogeneous coatings, with a fissured and slightly rough appearance. These films present some particles with a thickness of 1-3 μm .

Electrochemical impedance spectroscopy revealed differences between samples with different treatments. For the unpolished samples and without heat treatment, the poor adhesion to the substrate and also the low resistance to corrosion are very evident, since they had values very similar to those of bare steel. For the polished and thermally treated samples there are significant differences, we have an increase of impedance in relation to the bare steel, these samples revealed that after 72 hours we have the decrease of the global impedance in relation to the beginning of the tests.

The measurement of the contact angles was also effective in distinguishing the presence and behaviour of the coating on the surface. The samples -1.4V and -1.6V show hydrophobic behavior as they approach contact angles in the order of 90°, another fact is to mention that the samples were only coated on one side, which influences the measurements because the Wilhmely method that takes into account the two sides of the samples. Important fact, therefore, leads to a significant decrease of the contact angles measured by this technique. It was still possible to demonstrate that the surface was altered by the coating of TEOS + PhTMS and that as the potential decreases (evolves in the negative direction) the contact angle will tend to increase.

The study added useful information to the work reported in the literature. In the case of electrophoretic deposition of TEOS + PhTMS, its deposition in glass and aluminium and in a single deposition step had previously been studied, but had not been studied with respect to stainless steel and its adhesion there to, respect to their protection capabilities. In the present work, a relatively little studied process was used with regard to deposition in one step and in the production of superhydrophobic and hydrophobic coatings resistant to corrosion.

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