Alkyd coatings containing polyanilines for corrosion protection of mild steel

G.S. Gonçalves a, A.F. Baldissera a, L.F. Rodrigues Jr. a, E.M.A. Martinib, C.A. Ferreiraa,∗

a LAPOL/PPGEM, Universidade Federal do Rio Grande do Sul, BP 15010, 91501-970, Porto Alegre, RS, Brazil
b Laboratório de Eletroquímica, Instituto de Química, Universidade Federal do Rio Grande do Sul, PB 15003, CEP 91501-970, Porto Alegre, RS, Brazil

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ABSTRACT

A study was carried out to investigate the performance of anti-corrosion coatings obtained from alkyd paints containing polyaniline and polyaniline derivatives applied on carbon steel. The polyaniline, the polyaniline derivatives and the paints were characterized through FTIR and Raman spectroscopies and thermogravimetric analysis. Cyclic voltammetry studies showed that polyaniline and its derivatives gave electroactive properties to the paints. Accelerated corrosion experiments (salt spray and humidity chamber) revealed a significant improvement in the performance of the coatings which contained the electroactive polymer compared to conventional coatings. These results were verified by evaluation of the electrical resistance and capacitance measurements of the films using electrochemical impedance spectroscopy. For some of the samples, the Raman spectra demonstrated the presence of an oxide layer at the coating/substrate interface composed basically of Fe₂O₃ and Fe₃O₄. The results of this study reinforce the possibility of protecting carbon steel against corrosion through the formation of a protective layer of oxides using coatings which contain electroactive polymers.

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1. Introduction

Conducting polymers (CP) have been extensively studied in recent years due to a great variety of possible applications in several fields, such as in energy storage systems, electrocatalysis [1–3], electrodialysis membranes [4–7], sensors [8–10] and anticorrosion coatings [11–16]. They exhibit different oxidation states and behave as electronic or mixed conductors [17]. The role of a CP coating is to prevent contact of the substrate with a corrosive environment and reduce the corrosion rate. In some cases, the redox behavior of the coating provides the substrate with anodic protection [18]. The level of protection against corrosion afforded by a CP coating is dependent on both its structural and electronic properties [13,18,19]. Among the well known conducting polymers polyaniline (PAni) and polypyrrole (PPy) have gained particular interest from researchers over the past two decades owing to their electronic applications and their potential use as anti-corrosion coatings [13,20,21]. Polyaniline is one of the most readily prepared conducting polymers [22], it has controllable electrical conductivity, excellent environmental stability and easy processability [23,24]. It has several oxidation forms, namely emeraldine salt, emeraldine base, pernigraniline and leucoemeraldine, but only the emeraldine salt form is conductive.

The mechanisms proposed to explain the anti-corrosion action of polyaniline on ferrous surfaces are many, however, most authors agree that the passivation of iron and its alloys is promoted by the formation of adjacent layers of iron oxides [18,25–28] or nitride [29]. Wessling and Lu et al. [25,26] observed that the emeraldine salt is immediately reduced on contact with iron in the presence of water, with consequent oxidation of the metal and formation of a double layer of oxides. In the presence of oxygen, PAni oxidize and enables the reconstitution of the oxide layer if the coating is damaged.

Spinks et al. [30] demonstrated the ability of either PAni or PPy coatings to provide corrosion protection of steel. The experimental evidence shows that the PC galvanically coupled to the metal causes an anodic shift in the corrosion potential and some authors argue that this shift causes passivation and anodic protection. This mechanism is supported by studies showing stable oxide formation on the metal surface after contact with the conducting polymer. Rohwerder et al. [31] postulated that continuous coatings of a conducting polymer will fail to provide corrosion protection in the presence of larger defects, which they cannot passivate, and will show a fast break-down of the whole coating by fast reduction. This phenomenon is caused by high cathodic mobility in the reduced polymer, which is due to the gradual transformation of the polymer into a “freeway” for fast cation transport with increasing progress of the reduction front.

Andrew et al. [32] state in their patent that the emeraldine base (EB) form of PAni can perform better than the emeraldine salt (ES). Wei et al. [33] reported a similar behavior for PANi-EB and acid-doped forms of PANi as protective coatings for cold rolled steel in an aqueous NaCl medium. The PANi-EB was found to offer good corrosion protection as evidenced by the increase in the corrosion...
The (NH₄)₂S₂O₈ solution was added dropwise and the reaction was hydrochloric acid (HCl) for acidification of the medium. The ratio of ammonium persulfate ((NH₄)₂S₂O₈) as the oxidant agent and the merization of the monomers o-methoxyaniline (CH₃OC₆H₄NH₂) and aniline (C₆H₅NH₂), using ammonium persulfate ((NH₄)₂S₂O₈) as the oxidant agent and hydrochloric acid (HCl) for acidification of the medium. The ratio between monomer and oxidant was the same for all syntheses. The (NH₄)₂S₂O₈ solution was added dropwise and the reaction was maintained for 6 h at −5 ± 3°C. The polymer obtained was filtered, undoped by stirring in an ammonium hydroxide (NH₄OH) solution and then doped again with different acids.

Undoped polyaniline (PAni EB) and polyanilines doped with HCl (PAni HCl), p-toluenesulfonic acid (PAni pTSA), dodecylbenzenesulfonic acid (PAni DBSA), or camphorsulfonic acid (PAni CSA) were obtained. Poly(o-methoxyaniline) (PM pTSA) and poly(o-ethoxyaniline) (PE pTSA) were doped with p-TSA.

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyd resin</td>
<td>35.1</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3.0</td>
</tr>
<tr>
<td>Green halogen</td>
<td>0.6</td>
</tr>
<tr>
<td>Solvents</td>
<td>35.0</td>
</tr>
<tr>
<td>Other</td>
<td>22.8</td>
</tr>
<tr>
<td>Active component</td>
<td>3.0</td>
</tr>
</tbody>
</table>

2.2. Paint preparation

The paints were prepared using pigment dispersion equipment. The components were weighed according to a defined formulation (Table 1) and dispersed in a high rotation mechanical shaker and later mixed in a ball mill. Common alkyd resins are polyesters synthesized by reacting carboxylic acids such as phthalic anhydride, glycerin and fatty acids from different vegetal oils [36]. The size of particles dispersion, evaluated with a Fineness of Grind Gage (BVK Gardner), was between 5 and 6 Hegman (40 and 30 μm). One of the paints contained zinc chromate (Zn₂CrO₄) as a pigment.

2.3. Preparation of the test specimens

The paints were applied on cold laminated SAE 1020 steel sheets (160 mm × 75 mm × 0.8 mm) using an airless gun. The test specimens were then left in a dust-free location until the total drying of the coatings.

2.4. Characterization of the samples

2.4.1. Infrared spectroscopy

Infrared spectroscopy was carried out using a Perkin Elmer FTIR spectrometer model Spectrum 1000. The samples of different polymers were mixed with KBr, pressed and then analyzed.

2.4.2. Raman spectroscopy

Raman spectroscopy was performed with a Dilor-Jobin Yvon Labram spectrometer equipped with a 1024-diode multichannel detector using a He/Ne laser (17 mW) at an excitation wavelength of 633 nm. The data were treated with the Labspec software and the spectral interval ranged from 1200 to 2000 cm⁻¹.

2.4.3. Thermogravimetric analysis

The thermogravimetric analysis was carried out with a TA Instruments model TGA 2050 analyzer using Thermal Advantage software for the data treatment. All samples were analyzed under N₂ atmosphere using a heating rate of 20 °C/min.

2.4.4. Electrical conductivity

The conductivity measurements were obtained using the four-point method. The polymeric material to be analyzed was compressed into cylindrical forms with 25 mm diameter. The measurement system consists basically of a Signatone four-fixed tip holder (S-301-6 model) and a Keithley 2400 source.

2.4.5. Cyclic voltammetry

The cyclic voltammetry tests were conducted with an EG&G potentiostat model PAR 373 controlled by the EG&G PAR M 270 program. A three-electrode cell was used. An Ag/AgCl electrode was used as the reference and a platinum grid as the counter electrode. The working electrode consisted of a platinum sheet onto which the paints were applied, coating an area of 1 cm². Platinum was used because steel is much more active than the polymeric layers within the range of potential used in this test. The cyclic voltammetry was carried out between −0.2 and 1.2 V (Ag/AgCl) with a scan rate of 50 mV/s. The samples were submitted to 50 consecutive cycles in two different media: 1.0 M HCl and 3.5 wt% NaCl.

2.4.6. Film thickness measurement

The magnetic induction method was applied to measure the film thickness with a Fischer Instrumentation Ltd model Dualscope MP20 gage. The measurements were repeated 6 times and the average and standard deviation were calculated. The film thickness was measured and the average thickness obtained was 50.6 (±1.1) μm, which was controlled to allow a comparative analysis of the different coatings.

2.4.7. Humidity chamber experiments

The humidity chamber experiments were carried out using a closed chamber with a relative humidity of 100% at 38 °C, in accordance with the ABNT standard, and also fulfilled the following criteria: bubble size (NBR 5841/81), bubble density (NBR 5841/81), rusting degree (NBR 5770/84) and underlayer migration (NBR 787/76).
Table 2
Identification of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active component</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-PAni HCl</td>
<td>PAni HCl</td>
</tr>
<tr>
<td>T-PAni DBSA</td>
<td>PAni DBSA</td>
</tr>
<tr>
<td>T-PAni pTSA</td>
<td>PAni pTSA</td>
</tr>
<tr>
<td>T-PAni CSA</td>
<td>PAni CSA</td>
</tr>
<tr>
<td>T-PAni EB</td>
<td>Undoped PAni</td>
</tr>
<tr>
<td>T-PE pTSA</td>
<td>Poly(o-methoxyaniline) TSA</td>
</tr>
<tr>
<td>T-STD</td>
<td>Zinc chromate</td>
</tr>
<tr>
<td>T-BCO</td>
<td>Without active component</td>
</tr>
</tbody>
</table>

2.4.8. Electrochemical impedance spectroscopy

The impedance measurements were carried out with an EG&G model PAR 273 A/96 potentiostat, coupled to a Schlumberger frequency response analyzer model Solartron SI 1255 FRA.

For this experiment a three-electrode cell was employed, however, the electrolyte was a 1.0 M HCl solution and the working electrode consisted of an SAE 1020 steel sheet on which the paint was applied. The exposed area of the coating was limited to 10 cm² [37]. The amplitude of sinusoidal perturbation was 10 mV at the open circuit potential. The frequency range was 100 kHz to 10 mHz. Experiments were performed in duplicate and the results are presented through Nyquist and Bode diagrams.

3. Results and discussion

3.1. Paint processing

Nine samples, with the same basic formula, were obtained, differing only in the active component of protection against corrosion. The percentage of active component was 3 wt% related to the resin. Other means the sum of filler and active component, if present. Table 2 provides a description of the samples and the active anti-corrosion component.

3.2. Paint characterization

3.2.1. Infrared spectroscopy

Infrared analysis was carried out on all paint samples to verify whether degradation of the electroactive polymer chain occurred after the processing, and also to monitor for possible spectral effects of interactions between the components of the basic formula and the conductive polymer. Fig. 1 shows the spectra of samples T-BCO, T-STD and T-PAni HCl.

It was verified that the only changes in the spectra were the bands at 1494 cm⁻¹ and 1465 cm⁻¹ which appeared in the case of the paint containing PAni HCl. These bands are attributed to the presence of the conductive polymer and are related to the stretching of the C=C link of the quinoid and benzenoid ring, present in the spectrum of the pure polymer at 1558 cm⁻¹ and 1474 cm⁻¹. The displacement of the bands to lower regions may be due to interaction between the conductive polymer and the resin of the paint. The other bands detected are attributable to the polymer (alkyd) used to produce the paints [38].

3.2.2. Raman spectroscopy

The Raman spectroscopy analysis highlighted the presence of the active polymers in the paints. Fig. 2 shows the Raman spectra for the PAni DBSA, T-PAni DBSA and T-BCO samples. The spectrum for the paint sample T-PAni DBSA is, as a whole, the sum of the spectra of the polymer PAni DSBA and basic paint formula represented by the T-BCO sample, confirming that the presence of the conductive polymer in the paint after the processing did not generated any significant modification in its chemical structure.

3.2.3. Thermal stability

The thermal stability characteristics of the coatings evaluated through thermogravimetric analysis are very similar. As an example, Fig 3 shows the thermograms obtained for the samples T-PE p-TSA and T-BCO, respectively, which are almost identical, the only difference being the presence of around 3% conductive polymer in the T-PE p-TSA sample.

According to Fig. 3, two small mass losses occur at between around 130 °C, probably due to loss of humidity and residual solvents from the paint production process. From this temperature to 600 °C it is possible to observe a considerable mass loss related to degradation of the base-resin of the paint. The peaks for the loss of the resin and the conductive polymer coincide (Fig. 4).

The results show that the coating can be used under conditions that do not surpass 170 °C, which is the onset temperature of the resin base degradation. The high residual percentage (49%) is due to the amount of inorganic charges and additives used in the paint formula.

3.2.4. Cyclic voltammetry experiments

The electrochemical stability of the paints was evaluated by cyclic voltammetry experiments. The voltammograms display a similar shape, as shown in Fig. 5. The paints containing PAni
retained electrochemical activity and stability even after 50 cycles, a condition necessary to protect against corrosion according to data reported in the literature [25,26].

For the paint samples, the voltammograms show current peaks related to redox pairs in the same potential region as those presented by the conducting polymer samples (voltammograms of the PC alone are not displayed), showing that the electroactive component is the conducting polymer. The current densities of the coatings are lower than those observed for the polymers alone. This behavior is to be expected, since the matrix in which the conductive polymers are dispersed is not electroactive, and the polyaniline concentration added to the paint is low. The electrolyte (HCl or NaCl) did not influence the cyclic voltammetry results.

3.2.5. Humidity chamber experiments
Humidity chamber experiments were carried out for all coatings. The T-PAni HCl and T-PAni EB samples showed the best performances, since there was no blister formation, even for time periods longer than 668 h. The T-PE pTSA sample showed blister formation with low density after 72 h of the experiment; however, the result remained unaltered until the end of the experiment. The T-PM pTSA sample showed blister formation with low density after 48 h, while the T-BCO and T-STD samples showed blister formation with high density in less than 48 h. The T-PAni DBSA, T-PAni CSA and T-PAni pTSA samples showed bubble formation with high density in less than 24 h. All samples showed minimal rusting at the end of the experiment with the exception of the T-PM pTSA sample which showed a small degree of rusting.

The aspect of the T-PAni EB sample at the beginning and at the end of the experiment (668 h), and of the T-STD samples at the beginning and after 48 h of the experiment, can be seen in Fig. 6.

3.2.6. Raman spectroscopy
Regardless of the mechanisms proposed to describe the protection against corrosion using conductive polymers, most authors agree that it is promoted by the formation of a double layer of Fe2O3 and Fe3O4 [26,39].

In order to identify the oxides present at the coating/substrate interface, Raman analysis was carried out after the samples underwent the humidity chamber experiment. Figs. 7 and 8 show the Raman spectra obtained on analyzing different points of the coating/substrate interface for the T-PAni EB, T-STD and T-BCO samples, respectively.

The spectrum of Fig. 7 shows an oxide layer composed of Fe2O3 and Fe3O4 that is typical of the samples T-PE pTSA, T-PM pTSA, T-PAni HCl and T-PAni EB. A spectrum of a Fe3O4 sample was added to

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**Fig. 2.** Raman spectra: (a) PAni DBSA, (b) T-PAni DBSA and (c) T-BCO.

**Fig. 3.** TGA thermogram of T-BCO.

**Fig. 4.** TGA thermogram of T-PE pTSA.
this figure to help to interpret the peak at 653 cm$^{-1}$, characteristic of this oxide and absent in the spectrum of Fe$_2$O$_3$ as can be seen in Fig. 8. The formation of a layer mainly composed of Fe$_2$O$_3$ was observed for the samples T-PAni CSA, T-PAni DBSA, T-PAni pTSA and T-STD. On the other hand, no oxide formation was observed in the case of the T-BCO sample (Fig. 9).

The formation of the Fe$_2$O$_3$ oxide in the T-STD sample can be attributed to the zinc chromate present in this coating. The Cr$^{6+}$ ions reduce to Cr$^{3+}$, oxidizing the Fe$^0$ to Fe$^{3+}$, which reacts with water or oxygen to form ferric oxide.

Same samples containing conductive polymers induced the formation of a layer composed of Fe$_2$O$_3$ and Fe$_3$O$_4$. The formation of different types of oxide is a function of the redox potential and the species with lower potential will be preferentially formed.

It is proposed that the formation of Fe$_3$O$_4$ occurs when the oxygen concentration at the oxide–metal interface is deficient (Eqs. (1)–(5)). Thus, the presence of Fe$_3$O$_4$ in only some of the samples containing conductive polymers may be related to the quantity and distribution of the polymer in the matrix of the base paint. It is possible that the larger the quantity and the better the spread of the
Conductive polymer the more compact the first layer of Fe₂O₃ will be, inhibiting the passage of oxygen through the oxide, leading to the formation of the Fe₃O₄ layer.

$$\text{Fe}^0 + \text{H}_2\text{O} = (\text{FeOH})_{ads} + \text{H}^+ + e^- \quad (1)$$

$$\text{(FeOH)}_{ads} + \text{H}_2\text{O} = [\text{Fe(OH)}_2]_{ads} + \text{H}^+ + e^- \quad (2)$$

$$[\text{Fe(OH)}_2]_{ads} + \text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{H}^+ + e^- \quad (3)$$

$$2\text{Fe(OH)}_3 = \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (4)$$

$$[\text{Fe(OH)}_2]_{ads} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \quad (5)$$

The presence of Fe₂O₃ and Fe₃O₄ oxides in the samples which provided a greater degree of protection may indicate that the protection is, indeed, promoted by metal oxidation and active polymer reduction, creating a protective layer, in agreement with the mechanisms proposed by other authors.

It was also verified that the coatings with better performance in the humidity chamber were those containing greater amounts of pure polymer.

### 3.2.7 Electrochemical impedance spectroscopy experiments

The following coatings were selected as representatives of the electrochemical impedance results: T-STD and T-BCO which are classical formulations and were used to compare the performance of coatings containing conductive polymers; T-PAni EB and T-PE.
pTSA, which showed the best performance in the accelerated corrosion experiments; and T-PAni pTSA, to observe the influence of the dopant acid. The results were compared to uncoated steel.

The Nyquist diagram for the uncoated sample showed capacitive arcs at the open circuit potential, soon after its immersion in HCl (Fig. 10a). The polarization resistance ($R_p$) fluctuated between 10 and 20 $\Omega$ cm$^2$. On the other hand, the solution resistance ($R_s$) increased from 5 to 45 $\Omega$ cm$^2$ after the first 24 h of the experiment. This $R_s$ increase (shift of the arc on the real impedance axis) can be attributed to the intense formation of insoluble corrosion products that diminish the conductivity of the medium next to the working electrode. After 144 h of the experiment a thick layer of corrosion products could be observed over the exposed surface and Warburg impedance appears on the Nyquist diagram represented by an axis with a 45° inclination from the horizontal, which characterizes a mass transport process by diffusion.

All samples coated with paints containing PAni showed similar behavior in the initial hours of the experiment (Figs. 11 and 12). A line almost parallel to the imaginary impedance axis shows a capacitive behavior in the first moments of immersion. At this point the circuit of the electrochemical cell is open, with no contact between the electrolyte and the working electrode due to the high electrical resistance of the film.

One hour after immersion all samples showed a capacitive arch, characteristic of an RC representation in parallel. The larger diameters of the arcs for the coated samples (Figs. 11a and 12a) compared to the non-coated steel (Fig. 10a) show that $R$ is related to the resistance of the film coating ($R_f$) and $C$ to the film capacitance ($C_f$). The diameter of these capacitive arcs fluctuates with immersion time, indicating a variation in the film resistance, $R_f$. In the first 3 h $R_f$ decreases and thereafter it shows an oscillatory behavior.

This decrease in the film resistance ($R_f$) during the initial moments of immersion is attributed to the contact established between the working electrode and the electrolyte by the diffusion of the latter through the pores of the coating up to the substrate/coating interface. Some samples, such as T-PE pTSA and
T-STD, unlike the others, still show high resistance values in the first hour of the experiment, probably due to the samples having different porosity characteristics.

After 3 h of the experiment, all samples showed a minimum film resistance value, except for the T-PAni EB sample which showed a minimum value in the first hour. The Nyquist diagram shows an inductive arch at low frequencies for some immersion times, which may be related to oxidative dissolution of the substrate after permeation of the coating by the electrolyte.

With the corrosive attack, the resistance values, both of the film and the electrolyte, increase again, the most likely cause being the formation of corrosion products which block the pores, making mass transport more difficult. The increase in electrolyte resistance can be observed in the Nyquist diagram through the shift in the resistance rates at a frequency of 100 kHz to higher values and this may be associated with the formation of insoluble corrosion products.

For all samples, the film resistance increases until a maximum value is reached at around 5 and 7 h of the experiment. The maximum resistance values for the film coatings vary with sample type. The coatings containing electroactive polymers show values in the range of 4.5–6.0 kΩ cm², while the standard sample showed a value of 2.5 kΩ cm². At this point of the experiment, the Nyquist diagrams no longer show inductive components at low frequencies, probably due to interruption of the corrosion process with permanent oxide formation under the metallic surface.

This difference in the $R_f$ values reveals the possibility that the coating acts as a physical barrier, which separates away from the metallic substrate and moves to the medium and also forms a redox pair, in which the conductive polymer reduces, oxidizing and passivating the base metal.

After reaching the maximum resistance ($R_f$) values, the samples showed different behaviors. In the case of the T-BCO sample, the resistance values continuously decreases until values close to those of non-coated steel, which may be related to the subcutaneous delamination of the coating, and subsequent detachment of the film.

The T-STD sample showed a significant decrease in the resistance values after they peaked. However, the values remained stable at around 1.0 kΩ cm² until the end of the experiment.

The T-PAni pTSA sample (Fig. 12) showed a similar behavior to the T-BCO sample, with a continuous drop in the resistance until...
Electrolyte resistance ($R_e$), film resistance ($R_f$) and film capacitance ($C_f$) values were obtained from the log $|Z|$ versus log($f$) Bode diagrams of the different systems (Figs. 11b and 12b). The $R_e$ values were obtained through extrapolation from the high frequency region level and $R_f$ from the low frequency region level ($R_e + R_f$).

The slope of the curve in the intermediate frequency region allows an evaluation regarding whether the system is predominantly resistive, capacitive, or inductive, or even a combination of these properties. All extrapolated lines displayed slope values close to $-1$, showing that the capacitive behavior predominates in the total impedance, in this frequency range. The linear correlation coefficient was also calculated and all curves had values close to 1, showing a negligible dispersion of the points around the line.

The capacitance $C$ value was determined from the Bode diagram, using the following equation:

$$C = \frac{1}{2\pi f |Z|}$$

where $f$ is the frequency, in Hz.

Fig. 13 shows the variation in the capacitance $C$ with sample immersion time.

The T-PAni pTSA, T-PAni EB and T-BCO samples showed an increase in $C$ followed by a decrease in the first 5 h of the experiment. The T-PE pTSA and T-STD samples showed no capacitance peaks in the first few hours. This may be related to the differences in the porosity of the coatings. The non-coated steel sample showed high $C$ values compared to the coated samples.

The T-BCO and T-PAni pTSA samples showed a continuous increase in $C$ for the duration of the experiment, which may indicate that the electrolyte is continuously entering the film pores, or that the metal surface under the film is increasing in area because of a corrosion process.

The T-STD, T-PE pTSA and T-PAni EB samples showed stable $C$ values after the first 50 h of the experiment, evidencing that all film pores were filled with electrolyte. The maximum $C$ value for the T-STD sample was approximately $2.5 \times 10^{-5}$ F/cm², while for the T-PE pTSA and T-PAni EB samples the maximum capacitance rates were around $8.0 \times 10^{-6}$ F/cm² after almost 400 h of the experiment.

The capacitance values observed at the end of the experiment for the T-PAni pTSA and T-PAni EB samples are of the same order of magnitude as the $C$ values of compact oxides, which upholds the possibility that a protective oxide is formed due to the presence of the conductive polymers, in agreement with the results obtained in the previous experiments described.

Regardless of the protection mechanism, the low capacitance values of the T-PAni pTSA and T-PAni EB samples show a significant improvement in the performance of these coatings compared to the values for the T-BCO sample, which is the reference and contains the classical anticorrosion pigment zinc chromate.

The $R_i$ values of the film coatings were plotted as a function of time after the first hour of immersion and are presented in Fig. 14. As previously observed, the resistance of the coated samples initially increases and then decreases, reaching stable values within the experimental period for some samples. The high $R_i$ at the beginning of the test shows the dielectric character of the film that separates the metallic substrate from the solution. The $R_i$ value drops over time, due to the absorption of electrolyte by the film through the pores until it reaches the metal and leads to corrosion under the film. For some samples, $R_i$ reaches a constant value after 50 h of immersion indicating that the development of paths in which the electrolyte moves through in the film pores [37], or the transport of corrosion products from the metallic substrate out of the film, reaches a stationary state.
4. Conclusions

Infrared and Raman spectroscopy demonstrated that there was no degradation of the polymers during incorporation into the base paint.

All paint samples presented electroactivity in 1 M HCl and some samples presented electroactivity in 3.5% NaCl.

Incorporation of undoped PANi and PANi doped with HCl into conventional coatings leads to an improvement in the performance of the coatings in the humidity chamber.

Raman spectroscopy analysis of the coating samples that underwent the humidity chamber experiment revealed the presence of an oxide layer at the coating/substrate interface, mainly composed of Fe$_2$O$_3$ and Fe$_3$O$_4$ in the samples containing PANi EB, PANi HCl and PE pTSA. The fact that the oxide layer is present in the samples that showed the best results constitutes strong evidence that the protection in this experiment was promoted by the presence of the oxide. Samples for which only Fe$_2$O$_3$ was detected displayed a lower performance in the corrosion experiments.

Electrochemical impedance spectroscopy experiments carried out in 1.0 M HCl aqueous solutions showed that, after the first 24 h of experiment, some coatings had capacitance values of the same order of magnitude as those of protective oxides. In these same samples, both the resistance and capacitance remained stable after 15 days of immersion.

Overall, the results presented herein reinforce proposals that protection of carbon steel against corrosion occurs through the for-
formation of a protective layer of oxides when using coatings obtained from paints containing electroactive polymers.

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