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Evaluation of paint systems on A36 steel through electro-chemical techniques: Corrosion resistance of container tanks

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Abstract

In this research work, the corrosion resistance of plate steel used in the construction of cylindrical container tanks of seawater was evaluated. These container tanks are usually used for fighting fires on the coast of the Arequipa-Peru region, where the shortage of drinking water is significant. The study was based on immersion tests of 2 × 2 cm square test plates in 3.5 wt.% NaCl solution. Five paint systems were studied, varying only in the primers: P1-860 (inorganic zinc silicate); P1-ZC (epoxy-zinchromate); P1-850 (organic rich in zinc); P1-600 (reinforced inorganic zinc) and P1-SP1000 (high solids epoxy-amine). All systems consisted of a primer coat, an epoxy middle coat and a polyurethane topcoat. To characterize the behaviour of each system, the electrochemical impedance spectroscopy (EIS) was mostly used. In addition, the scanning Kelvin probe (SKP) and scanning electrochemical microscopy (SECM) were used as local techniques. The first three paint systems (P1-860, P1-ZC and P1-850) showed an invariable value of impedance modulus up to 3360 h of immersion in NaCl. The last two paint systems (P1-600 and P1-SP1000) showed a decrease in impedance modulus by more than one order of magnitude. This research provides a clear contribution of results obtained by global electrochemical techniques such as EIS, establishing excellent tools for monitoring the performance of organic anticorrosive coatings.

Keywords

Plate steel; seawater storage tank; corrosion resistance; epoxy coating; electrochemical impedance spectroscopy

Introduction

Nowadays, an economic, competitive and current alternative to protect steel from the aggressive environment, such as seawater, is constituted by organic and inorganic anticorrosive coatings. Among the most important organic coatings applied for improving the corrosion resistance of steels

are paints that contain an epoxy-type resin. Paints are made up of two components that react to form a hard and inert coating. These two components (component A and component B) consist of an epoxy resin with pigments and extenders, in addition to a curing agent called a hardener. These paints are widely used as primary coatings on pipes, ships and any structure that is immersed in seawater due to their strong chemical and wear resistance, excellent adhesion, as well as impermeability and resistance to alkalis [1,2].

Another system that is still used in this field is zinc chromate pigments. It has been shown that these pigments are good anodic inhibitors, as well as good cathodic inhibitors that hinder the reaction of oxygen reduction [3,4]. The important protective ability of zinc chromate pigments shows that they are very effective against metallic corrosion. However, the great disadvantage of Cr^{6+} ions containing compounds is their toxic effects on human health, due to their carcinogenic effects, as well as contamination of the environment, which resulted in significant restrictions on their use [5].

Recent research has shown that the modifying formula of paints by adding conductive polymers in low concentrations significantly increases the protective properties of the coating. In addition, they are an efficient option and are capable of replacing inorganic anticorrosive pigments that are generally used but can be detrimental to both health and the environment [6]. Armelin *et al.* [6] studied the ability of conductive polymers to operate as an anticorrosive additive in marine paints, finding that a low concentration of conductive polymers allows better protection against corrosion to metallic substrates compared to unmodified paints. Additionally, they indicated that excellent results are obtained when polythiophene (PTh) derivatives are used as epoxy paint additives. In another study, Armelin *et al.* [7] concluded that the negative and damaging effects generated by inorganic corrosion inhibitors on human health and the environment could be minimized by replacing them with a small concentration of ecological organic polymers.

Various studies on hybrid coatings have shown positive results on the effects of corrosion on steel surfaces. Among these, we find the study by Chen *et al.* [8], who prepared a hybrid silicone-epoxy and pre-hydrolyzed tetraethoxysilane (HTEOS) coating through the sol-gel process, with high solids content, showing good flexibility and better impact resistance. On the other hand, Sanaei *et al.* [9] studied the corrosion inhibiting effect of a hybrid pigment composed of Zn^{2+} cations and organic compounds. The incorporation of this hybrid pigment in the epoxy ester coating markedly improved its inhibition properties. It was also shown [10] that effective inhibition of corrosion for steel is achieved by the hybrid pigmentation based on zinc acetylacetonate/urtica dioica, which shows protection effectiveness against corrosion of 99.995 % after two months.

Inorganic coatings, such as inorganic zinc silicates and epoxy-amine coatings with a high content of solids, represent a step forward in the field of paint coatings for protection against atmospheric corrosion. These new isocyanate-free coatings exhibit low levels of volatile organic compounds (VOC) due to the high solids content associated with their low viscosity, good heat and stability to UV radiation, and excellent chemical resistance [5].

Based on all these facts, the objective of this study was to evaluate the effects of different paint systems on the corrosion resistance of plate steel used in the construction of cylindrical container tanks of seawater for fighting fires on the coast of the Arequipa-Peru region.

Experimental

Coatings, surface preparation and properties of coated steel

The paint systems, which are used for commercial purposes in Peru were supplied by CHROMA. Prior to the application of paint coatings, the specimens were shot-blasted with shot steel abrasive

to Sa2 grade according to SSPC SP10, reaching an average roughness of 70 µm. The coatings were subsequently cured for 15 days under normal environmental conditions before being subjected to electrochemical impedance tests. The steel specimens were supplied by ACEROS AREQUIPA S.A. with chemical and mechanical characteristics given in Tables 1 and 2.

Table 1. *Chemical composition of A36 steel tested (Source: Aceros Arequipa)*

Quality ASTM*	Maximum content, %				
	C	Mn	P	S	Si
A36	0.25	0.8-1.20**	0.040	0.050	0.40

*quality calculated according to the procedure of the American Society for Testing and Materials; **thickness less than ¾ inch.

***Table 2.*** *Mechanical properties of A36 steel (Source: Aceros Arequipa)*

Quality	ASTM standard	Yield limit, kg cm^{-2}	Tensile strength, kg cm^{-3}	Elongation, %
Structural	A36	2.550	4.080-5.610	20

The basic characteristics of paint coatings used to study corrosion of A36 steel are shown in Tables 3 and 4. Likewise, photographs of A36 steel specimens with different coatings are shown in Figure 1.

Table 3. *Proposed paints systems*

| Paint system	Primer DFT, µm	Intermediate DFT (epoxy), µm	Top coat DFT (polyurethane), µm	Total DFT, µm
P1-A36	Bare steel			
P1-860	57 (organic silicate Zn)	170.60	29.12	257.30±5.08
P1-ZC	55.29 (epoxy zynchromate)	166.96	43.94	266.19±9.91
P1-850	58.17 (organic zinc-rich)	168.15	30.74	257.05±10.41
P1-600	71.46 (reinforced inorganic Zn)	173.91	24.39	269.75±6.60
P1-SP1000	Epoxy amine	-	-	269.49±6.89
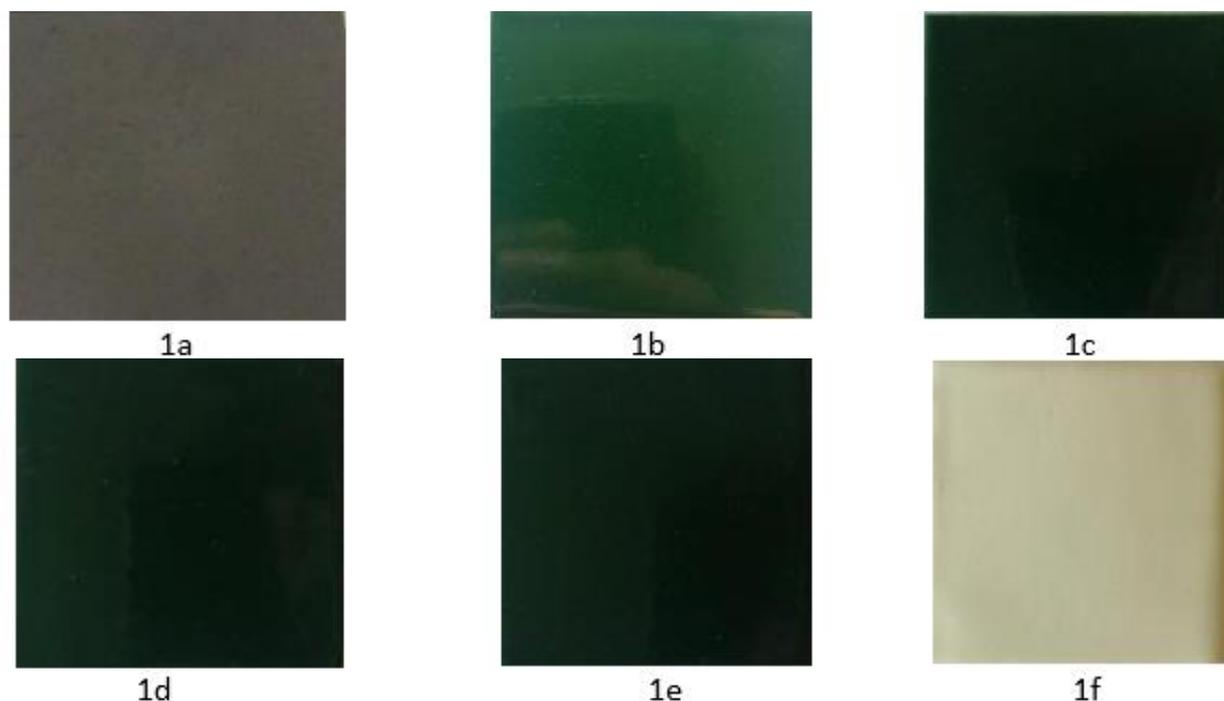
Figure 1. *Photographs of A36 steel specimens with different coatings: (1a) P1-A36; (1b) P1-860; (1c) P1-ZC; (1d) P1-850; (1e) P1-600; (1f) P1-SP1000*

Table 4. Composition of coatings

| Coating	Characteristics
P1-A36	Hot rolled with oxide coating
P1-860	Zinc primer based on inorganic ethyl silicate. Contains metallic zinc powder (62 %), providing cathodic protection
P1-ZC	Epoxy with zinc chromate as an inhibitor pigment
P1-600	Coating of two components of zinc ethyl silicate inorganic, reinforced with glass flakes (80% solids).
Epoxy	Epoxy coating formulated with lamellar pigments (micaceous iron oxide) and magnesium silicate. Based on a mixture of two epoxy resins. One is a solid in a low molecular weight solution and the other a liquid that reacts with a polyamidoamine with dimethylaminomethylphenol.
Polyurethane	Polyurethane coating based on the combination of a hydroxylated acrylic resin with an aliphatic polyisocyanate. The second coat of all systems is epoxy paint and the third coat is polyurethane. All systems that will be performed in marine environment consist of 3 coats. The study considers only different primers (the first coat).
P1-SP1000	Multipurpose epoxy-amine compound of 100% solids by volume

Adhesion tests

The method used to evaluate the adhesion of all paint systems was the adhesion test, according to the standard D4541 type III [11]. The test was carried out with a Hydraulic Push Off Adhesion Tester (HATE brand). Cyanoacrylate glue was applied to bond two dollies per painted sample, allowing a curing time of 24 h before pulling. The dollies used were 20 mm in diameter, which gave a contact area of 3.14 cm^2. In this type of test, the rupture can be adhesive, cohesive, a combination of both, or glue failure [12]. The ready-to-test specimens are shown in Figure 2.
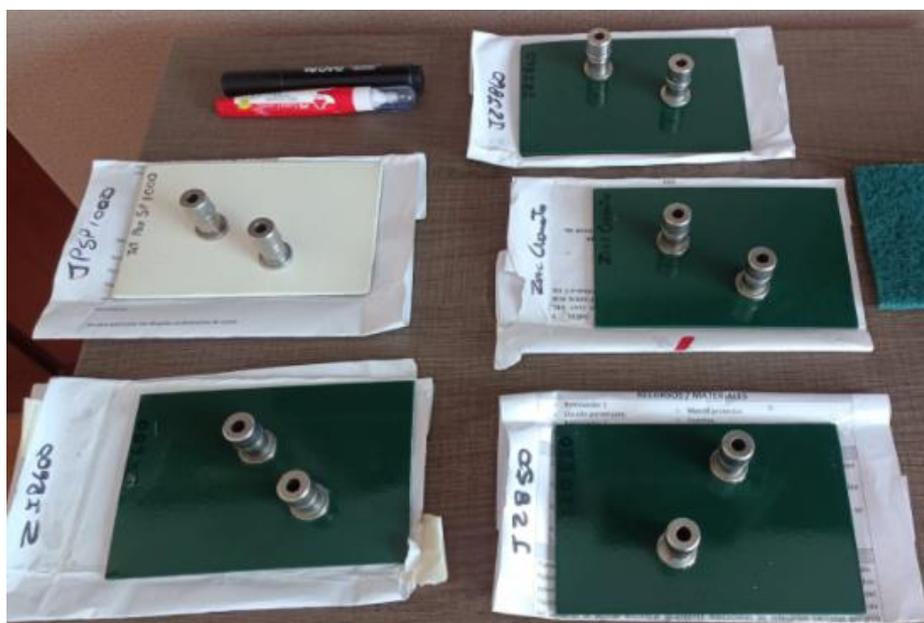
Figure 2. Test panels with dollies glued in duplicate on each paint system

Measurement of corrosion potential with scanning Kelvin probe (SKP)

The scanning Kelvin probe (SKP) is a variation of the atomic force microscope (AFM) that makes it possible to map not only the surface morphology of solid samples but also their electrical potential, which is directly related to the corrosion potential [13]. To determine the surface activity (Volta potential) of the specimens at time zero, SKP shown in Figure 3 was used through a 50 μm diameter tip of Ni-Cr alloy, scanning area of 500 × 500 μm at a velocity of 0.4 μm s^{-1} in an environment free of aggressive agents, maintaining a humidity of 85% and a temperature of 25 °C. The results will be presented in the form of a potential map, using that of A36 steel as a reference.
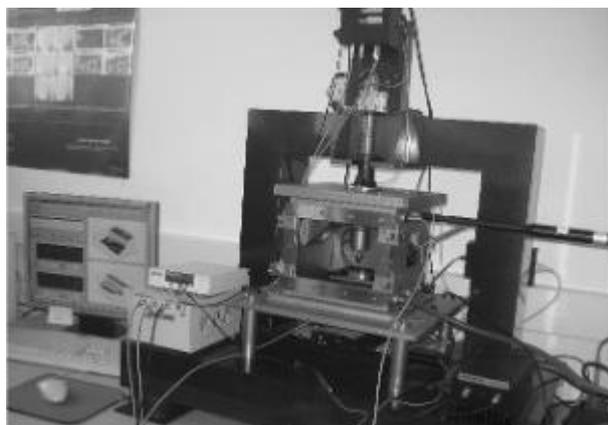
Figure 3. Scanning Kelvin probe (CENIM-Spain)

Measurement of coating integrity with scanning electrochemical microscope (SECM)

Among the methods used to map local microscopic processes, scanning electrochemical microscopy (SECM) has the unique ability to recognize active/passive regions and enables the characterization of surfaces with resolution in the micrometer range or lower [14].

To determine the integrity of five paint systems studied, the samples were analyzed by scanning electrochemical microscopy (Figure 4), using 1.1 mM of ferricyanide solution in 0.1 M KCl as the mediating electrolyte. A platinum microelectrode with a diameter of 25 µm, measuring an area of 500×500 µm and reducing the current limit value to 80 % was also used. The results will be presented on maps of the intensity of the current.
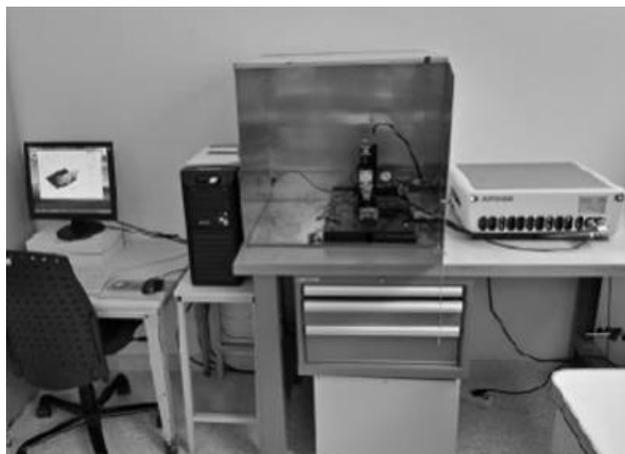
Figure 4. Scanning electrochemical microscope (CENIM-Spain)

Electrochemical impedance spectroscopy (EIS) tests

The impedance measurements were carried out gradually until reaching 3696 h of exposure, using Gamry Potentiostat/Galvanostat/ZRA Reference 3000 equipment. It was carried out at a frequency scanning between 100,000 and 1 Hz, with a disturbance amplitude of 10 mV. In the experimental set-up, a cell with three electrodes shown in Figure 5 was used. Graphite counter-electrode, a working electrode (the applied test tubes) and a saturated calomel electrode as a reference electrode were used in the working solution of 3.5 wt.% NaCl. The samples were immersed for 30 min in the working solution before EIS measurements, which was needed for stabilization of the open circuit potential.

The data obtained by impedance measurements were simulated by means of an equivalent electrical circuit. The free software used for the simulations was Gamry Echem Analyst Version 6.04

and the circuit components were consequently related to the physicochemical phenomena that occurred in the system.

Figure 5. Arrangement of the electrochemical cell connected to Gamry 3000 equipment

Results and discussion

Results of adherence test

According to the results of adhesion tests reported in Table 5, it can be observed that all paint systems failed 100 % in the glue, with the exception of dolly 2 of the P1-SP1000 system, which failed 1 % by adhesion and 99 % glue. On the other hand, it is evident that the pressure at which the glue fails is above 8 MPa (1000 psi).

Table 5. Summary of adhesion test results for five paint systems

| Paint system	N° of dolly	Thickness, μm	Pressure, MPa	Failure
P1-860	1	254	10.34	100 % glue
	2	254	8.27	100 % glue
P1-ZC	1	259.08	11.03	100 % glue
	2	261.62	10.34	100 % glue
P1-850	1	266.7	11.72	100 % glue
	2	256.54	9.65	100 % glue
P1-600	1	261.62	12.41	100 % glue
	2	266.7	11.03	100 % glue
P1-SP1000	1	261.62	15.17	100 % glue
	2	261.62	17.24	1 % cohesion, 99 % glue

Characterization of surface activity

Scanning Kelvin probe (SKP)

Figure 6 is the comparative representation of potential maps of five paint systems obtained by means of the SKP at zero time.

It can be observed in Figure 6 that P1-860 and P1-SP1000 systems are thermodynamically more stable since they present positive potentials throughout the studied area. This means that these paint systems are resistant to corrosion to a greater degree than A36 steel. At the other side, P1-ZC,

P1-850 and P1-600 systems present zones of positive potential and zones of negative potential, indicating microscopic faults and possible zones of corrosion.
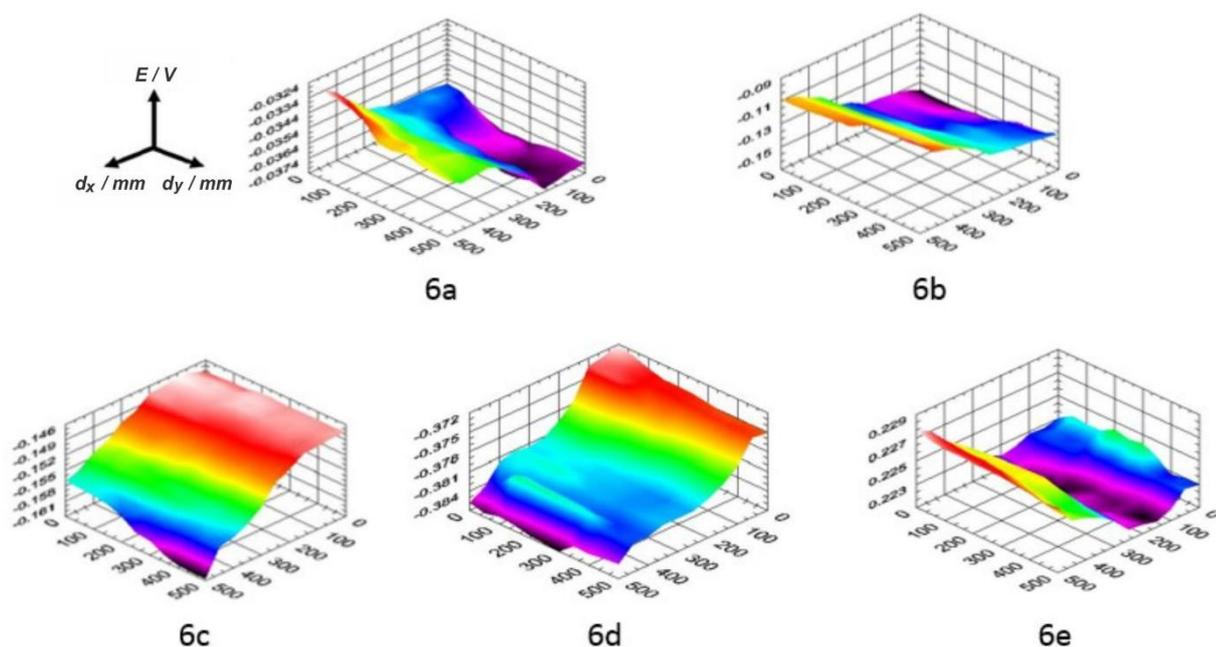
Figure 6. *Potential maps obtained by SKP at zero time of five paint systems studied: (6a) P1-860; (6b) P1-ZC; (6c) P1-850; (6d) P1-600; (6e) P1-SP1000*

Scanning electrochemical microscopy (SECM)

The maps of the intensity of current obtained by means of a scanning electrochemical microscope are presented in Figures 7 and 8, where the electrochemical activity of the surface of paint systems can be observed in greater detail since here, a quantitative variable of corrosion is registered.
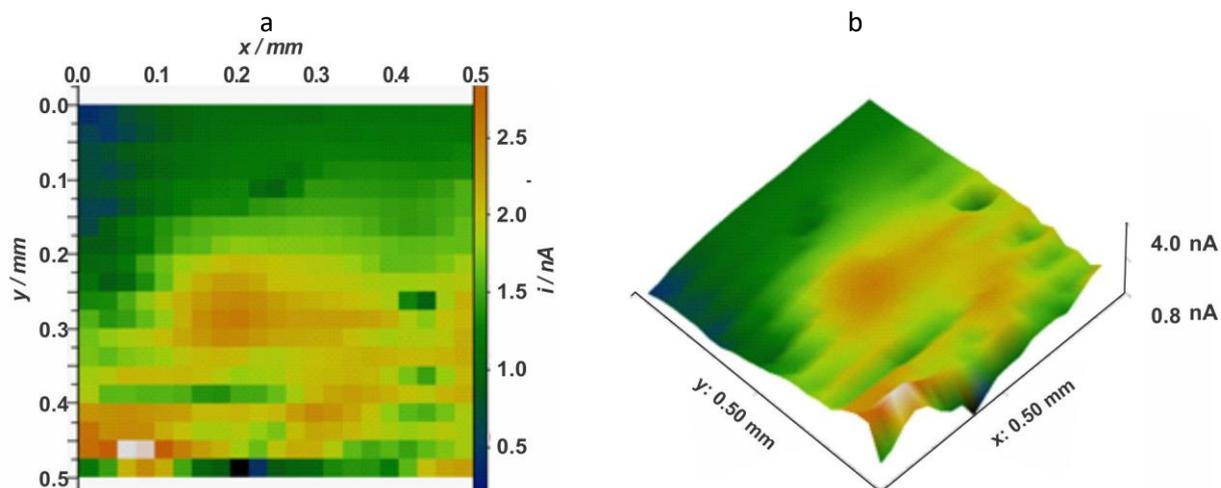
Figure 7. *Maps of current intensity obtained by SECM of five paint systems studied: (a) P1-600a; (b) P1-600b*

The current intensity measured for P1-860 ranges between 0.8 and 4 nA, showing on the map a greater homogeneity and protective character of the coating compared to the other samples. However, there are some small imperfections present, which over time may cause pores in the paint. In samples P1-ZC, P1-850, P1-600, and P1-SP1000, the variation of the intensity of the current is similar (from 0 to 20 nA). However, large areas of the studied section can be observed where the current is close to zero, indicating a high degree of metal protection. Nevertheless, in some areas (about 10 %), an increase in the current intensity is observed, evidencing faults in the coating.
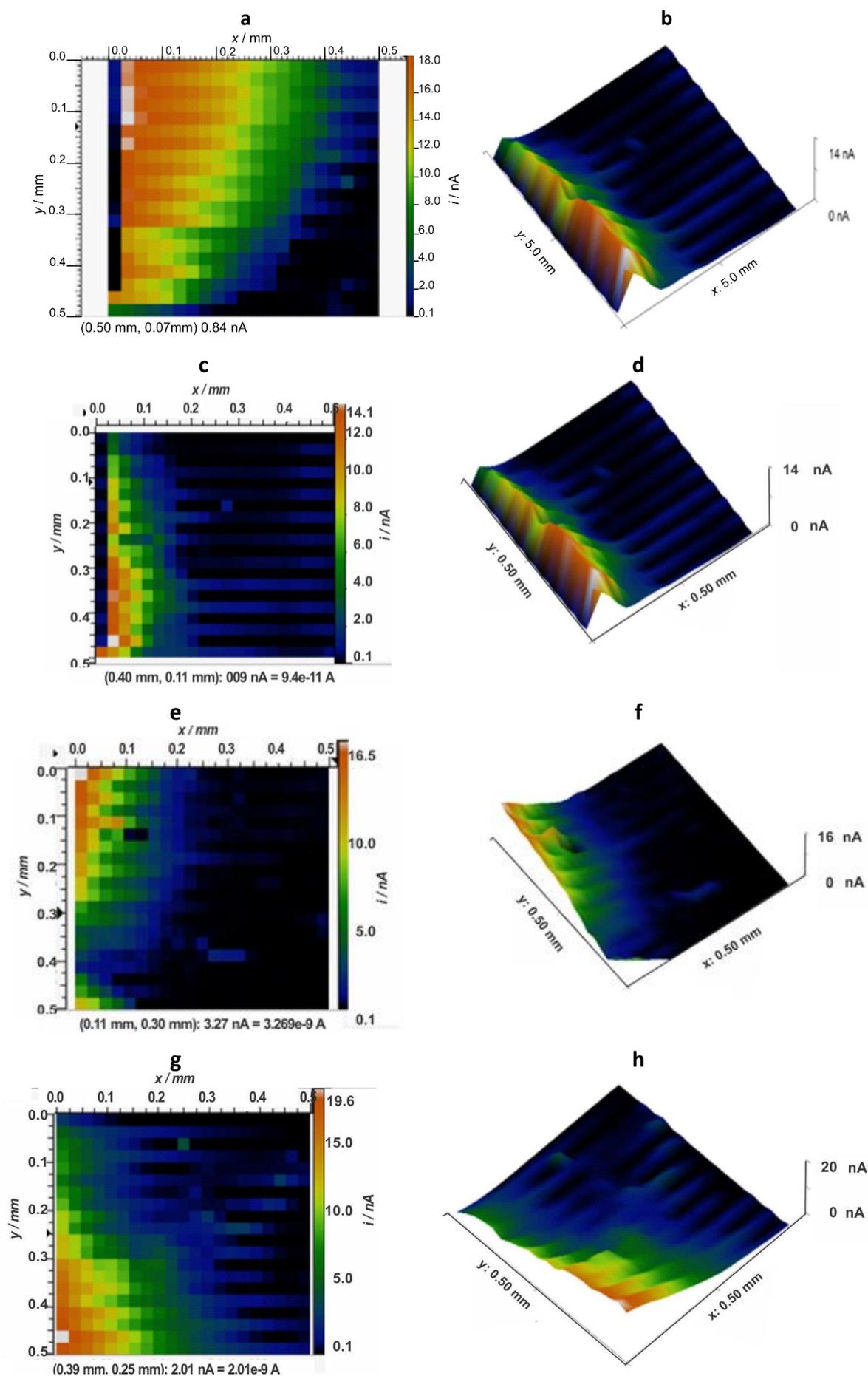
Figure 8. Maps of current intensity obtained by SECM of five paint systems studied: (a) P1-850a; (b) P1-850b; (c) P1-860a; (d) P1-860b; (e) P1-SP1000a; (f) P1-SP1000b (g) P1-ZCa; (h) P1-ZCb

Electrochemical impedance spectroscopy characterization

P1-860 paint system

The components of the system were provided by the company CHROMA-Peru. The primer has a dry film zinc content of 86 % and is called cold galvanizing, as it protects the steel from corrosion through galvanic protection. The VOC content is 367.3 g L^{-1}. Its formulation meets the requirements specified in the UNE 48293-2007 standard. The evolution of the impedance modulus $|Z|$ of this system over 3360 h of immersion in NaCl solution is shown in Figure 10 in the form of Bode modulus plots (log $|Z|$ *vs.* log frequency).
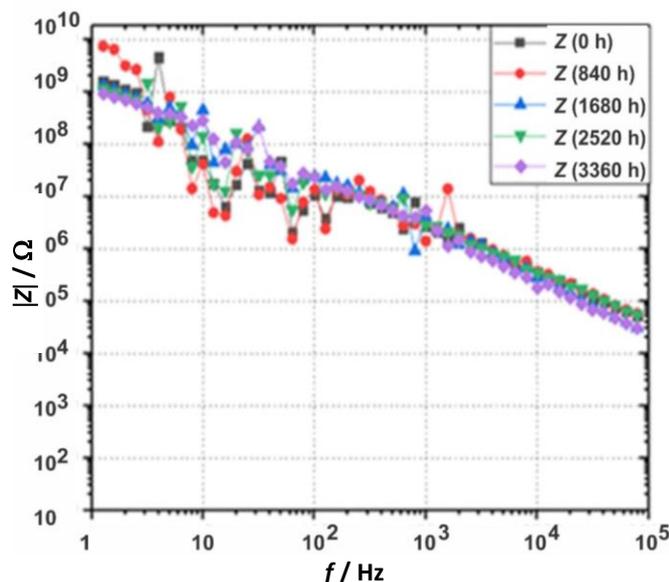
From Figure 9 it can be concluded that the impedance modulus remained almost invariable over time. This is probably due to the fact that the fluid has not come into contact with the substrate. Therefore, it can be concluded that P1-860 system presents an excellent barrier property, acting as an almost perfect condenser with capacitive behavior, and $|Z|$ of the order of 10^9 Ω at the frequency of 1 Hz [15]. In order to understand the behavior of this system, Nyquist diagrams (Z_{im} *vs.* Z_{real}) measured at zero time and 3360 h of contact with the fluid are presented in Figure 10.
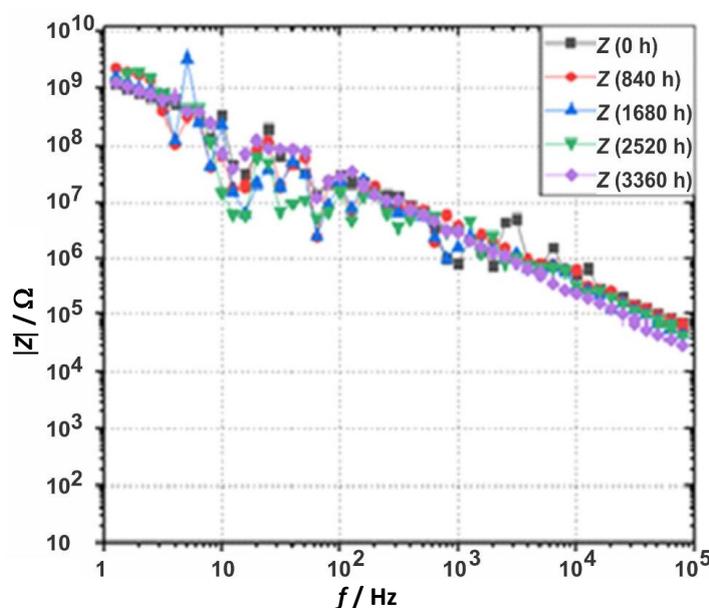
Figure 9. *Evolution of impedance modulus Bode plots of P1-860 paint system with immersion time in 3.5 wt.% NaCl*
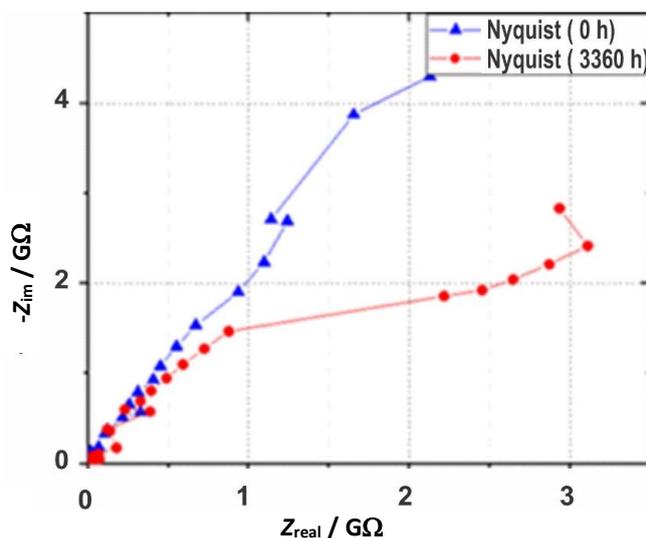
Figure 10. *Nyquist diagrams for P1-860 paint system at 0 h and 3360 h of exposure in 3.5 wt.% NaCl*

Despite somewhat scattered data, Figure 11 shows some differences in the capacitive behavior of the studied system. At 3360 h of contact with the fluid, a higher deviation from capacitive behavior can be observed, with the impedance values that decreased slightly, *i.e.* by less than an order of magnitude (GΩ).

P1-ZC paint system

The primer studied in this system is an epoxy-based paint with zinc chromate inhibitor provided by CHROMA PERÚ, recommended to protect the steel as a base or first coat. The evolution of the impedance modulus of this system up to 3360 h of immersion in NaCl solution is shown in Figure 11.

Figure 11. *Evolution of the impedance modulus Bode plot of P1-ZC paint system with immersion time in 3.5 wt.% NaCl*

From Figure 12, it can be concluded that the impedance modulus remained almost invariable over time, suggesting, as for the previous sample (Figure 12), that the fluid did not come into contact with the substrate. Therefore, it can be concluded that the P1-ZC system also presents an excellent barrier property, acting as an almost perfect condenser with capacitive behavior and $|Z|$ of the order of GΩ, at the frequency of 1 Hz [16]. The Nyquist diagrams are presented in Figure 12 at zero time and at 3360 h of contact with the fluid.
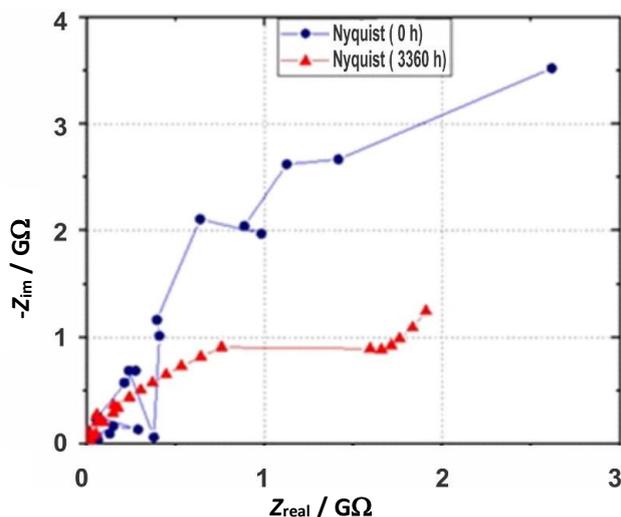

Figure 12. *Nyquist diagrams for P1-ZC paint system at 0 h and 3360 h of exposure to 3.5 wt.% NaCl*

Figure 12 shows differences in the impedance behavior of the studied system. At 3360 h of contact with the fluid, impedance became less capacitive and decreased slightly, although by less than an order of magnitude (GΩ).
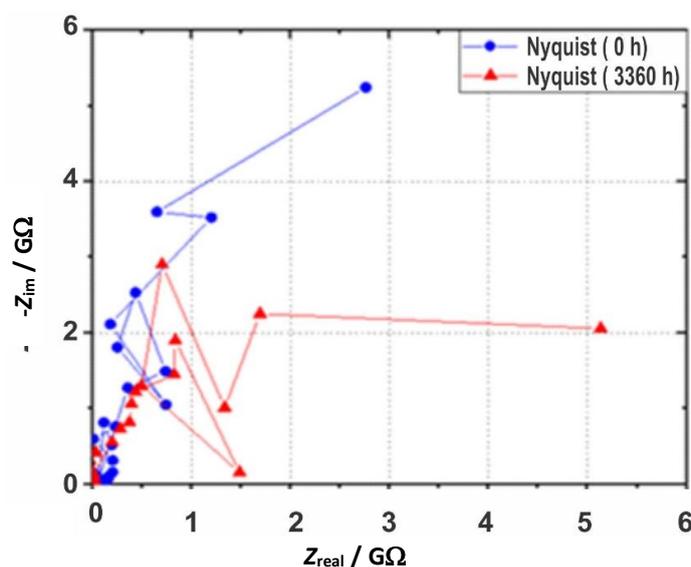
P1-850 paint system

The P1-850 system is constituted of an organic primer rich in zinc with a high content of powder of zinc (85 % zinc in the dried film) and a VOC content of 270 g L^{-1} in the epoxy base. The evolution of the impedance modulus of this system over 3360 h of immersion in NaCl solution is shown in Figure 13.
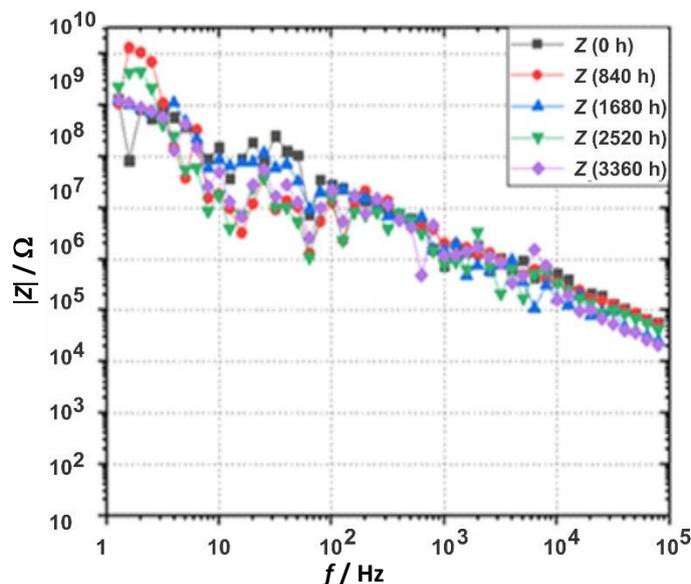
Figure 13. *Evolution of impedance modulus Bode plots of P1-850 paint system with immersion time in 3.5 wt.% NaCl*

From Figure 13, it can be concluded that the impedance modulus remained almost invariable over time as for previous samples shown in Figures 10 and 12. Again, this happens probably because the fluid did not come into contact with the substrate. Therefore, it can be concluded that the organic system rich in zinc/epoxy/polyurethane also has an excellent barrier property, acting as an almost perfect condenser with capacitive behavior and $\left|Z\right|$ of the order of GΩ at the frequency of 1 Hz [16].

The Nyquist diagrams are presented at zero time and at 3360 h of contact with the fluid in Figure 14.

Figure 14. Nyquist diagrams for P1-850 paint system at 0 h and 3360 h of exposure to 3.5 wt.% NaCl

Figure 15 shows highly dissipated data but also some differences in the impedance behavior of the system studied. At 3360 h of contact with the fluid, the response deviates from capacitive behavior and impedance decreases, although less than one order of magnitude (GΩ).

P1-600 paint system

This system has a primer that was created in Peru four years ago. It constitutes a new generation of coatings called modified inorganic zinc, hybrid, or reinforced, equivalent to zinc ethyl silicate (in terms of performance), but with characteristics of application which are more environmentally friendly since its VOC content is almost 20 % lower in emissions.

In terms of performance, this has been increased due to the higher content of solids by volume (80 % approx.) in its formulation, which improved its performance per m^2 of the coated surface compared to the inorganic zinc of the conventional formulation. The evolution of the impedance modulus of this system during 3360 h of immersion in NaCl solution is shown in Figure 15.

From Figure 15 it is concluded that the impedance modulus is gradually decreased with time, which is particularly evident at the lowest frequencies. After 3660 h, $|Z|$ decreased by almost two orders of magnitude at low frequencies, evidencing the gradual deterioration of the inorganic zinc coating.

With the purpose of understanding the behavior of this system, the Nyquist diagram is presented in Figure 16 at zero time and at 3360 h of contact with the fluid.
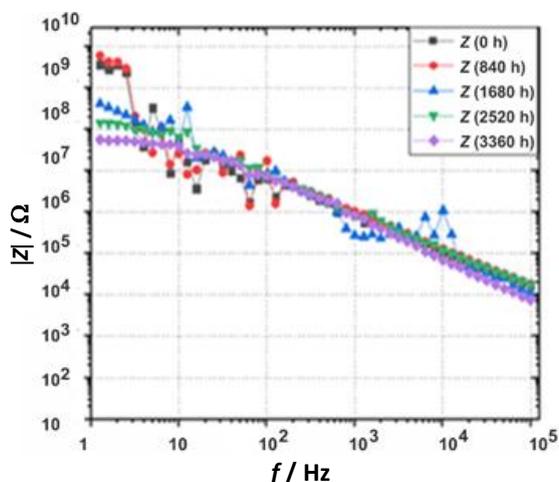

Figure 15. *Evolution of impedance modulus Bode plots of P1-600 paint system with immersion time in 3.5 wt.% NaCl*
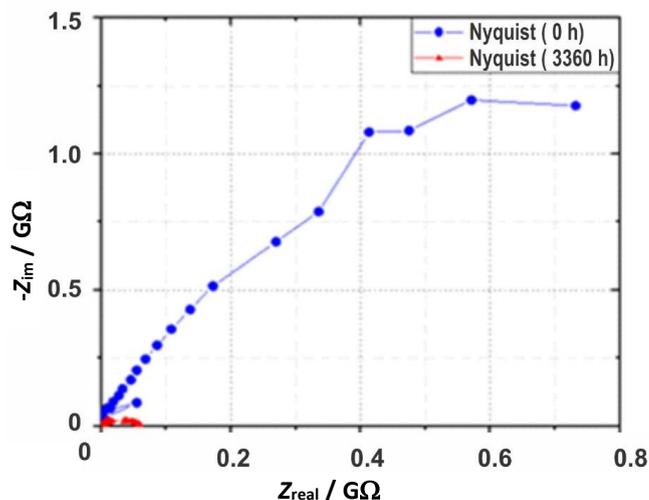
Figure 16. *Nyquist diagrams for P1-600 paint system at 0 h and 3360 h of exposure to 3.5 wt.% NaCl*

In Figure 16, significant differences are observed in the impedance behavior of the studied system. At 3360 h of contact with the fluid, the capacitive curve is strongly bent and impedance values are significantly decreased from GΩ to MΩ.

After 3660 h the coating did not act as a barrier and showed some resistive contribution due to corrosion.

In the equivalent circuit shown in Figure 17, R_e denotes the uncompensated part of electrolyte resistance, while R_{po}, R_{ct}, C_c and C_{dl} represent the resistance of the coating to electrolyte penetration, the resistance of charge transfer at the substrate/electrolyte interface, coating capacitance and interfacial double-layer capacitance, respectively. Figure 18 shows the degree of adjustment of measured and simulated data obtained with the proposed equivalent circuit in the form of a Bode plot (log |Z| and phase angle *vs.* log frequency).
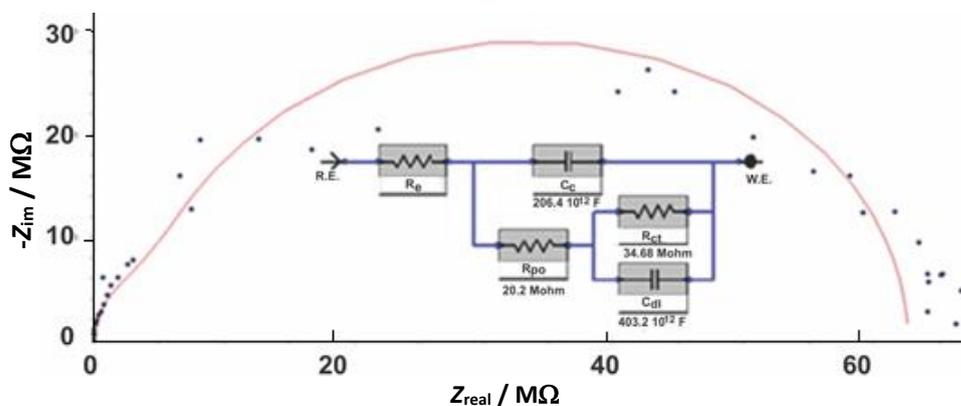
Figure 17. *Nyquist diagram of the P1-600 paint system after 3360 h of exposure to 3.5 wt.% NaCl and simulation results calculated using the associated equivalent circuit*
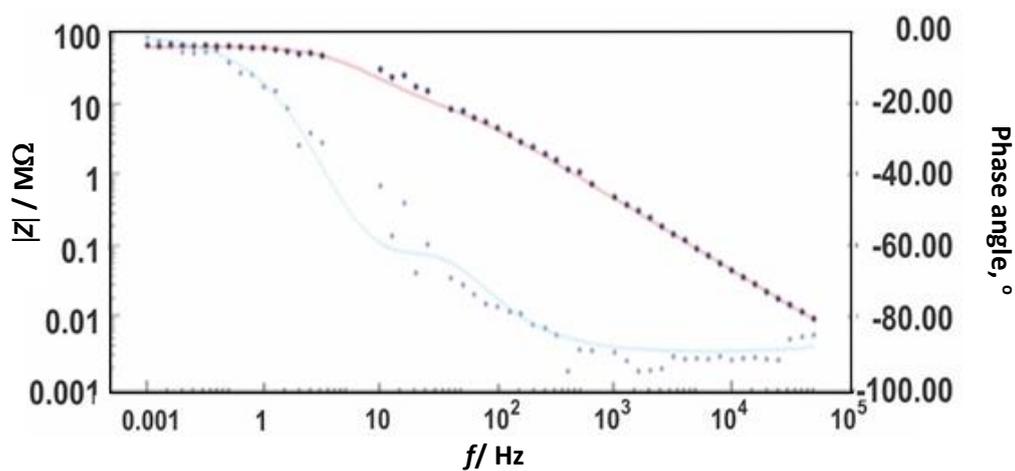

Figure 18. *Bode diagram of the P1-600 paint system after 3360 h of exposure to 3.5 wt.% NaCl and simulation results calculated using equivalent circuit in Fig. 16*

P1-SP1000 paint system

Jet Pox SP 1000 is a multipurpose epoxy-amine with excellent anticorrosive protection. It is a barrier-type coating with high solids content (98 %) and a minimum VOC content of 5 to 12 g L^{-1}. The evolution of the impedance modulus of this system over 3360 h of immersion in NaCl solution is shown in Figure 19.
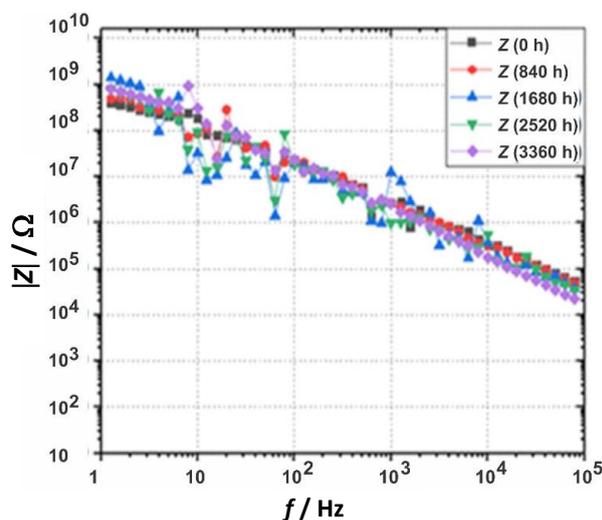

Figure 19. *Evolution of impedance modulus Bode plots of P1-SP1000 system with the immersion time in 3.5 wt.% NaCl*

In Figure 20 it can be observed that at low frequencies (1 Hz), where the capacitive behavior of the coating is usually characterized, a decrease in impedance capacitive slope is observed over time, indicating an influence of some resistive contribution. For the purpose of a better understanding of the behavior of this system, the Nyquist diagram is presented in Figure 21 at zero time and 3360 h of contact with the fluid, which is more sensitive in highlighting the capacitive behavior of the system.
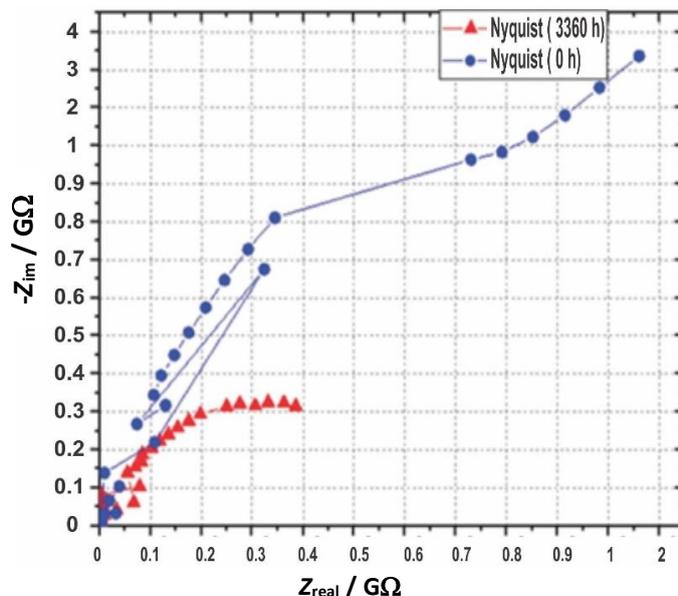

Figure 20. *Nyquist diagrams for P1-SP1000 paint system at 0 h and 3360 h of exposure to 3.5 wt.% NaCl*

For P1-SP1000 system after 3660 h of exposure, Figure 20 shows a significant decrease of lower frequency impedance values at least by order of magnitude. Also, the prominent deviation from pure capacitive behavior of the painting system studied suggests certain fails in corrosion protection.

Comparative results

Finally, the impedance modulus of all five tested systems at the end of tests (3360 h) are presented in Figure 21, in order to select the system that would best protect A36 steel immersed in seawater.
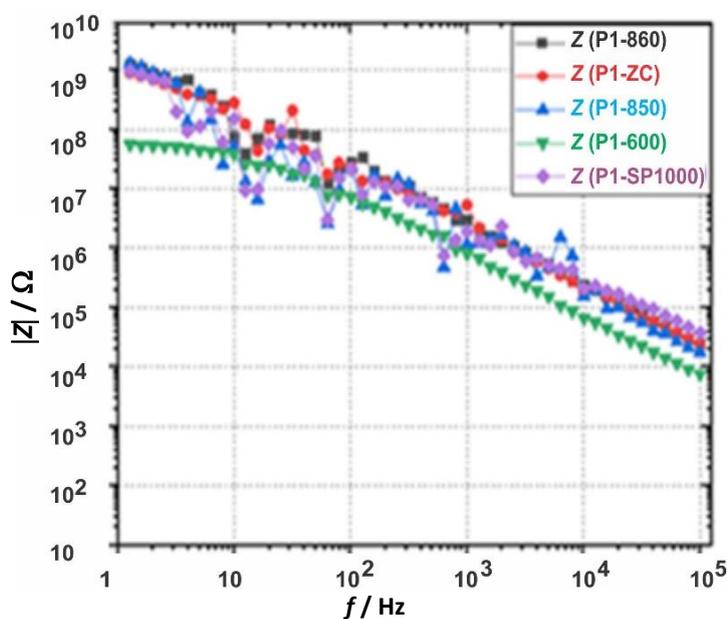

Figure 21. *Impedance modulus Bode plots of five paint systems studied after 3360 h of immersion in 3.5 wt.% NaCl*

The lower performance of P1-600 system is probably due to the higher permeability of the coating and not its adhesion to the substrate since all the systems reported good adhesion to the metal. According to forms and impedance magnitudes at low frequencies shown in Figure 21, it is observed that the paint systems P1-860, P1-ZC and P1-850 retain their stability throughout 3360 h of immersion. Paint systems P1-600 and P1-SP1000 systems, however, show certain deterioration of capacitive behavior and impedance more than one order of magnitude less than other paint systems.

Conclusions

- Regarding the adherence of organic coatings to metal, it is concluded that there is strong adhesion between paint systems and metal since in the majority of cases, the failure has occurred with the paint interface/glue at a pressure greater than 8 MPa.
- From the potential maps obtained by means of the scanning Kelvin probe at zero time, it can be concluded that P1-860 and P1-SP100 systems better protect the metallic substrate, while the other systems present possible micro corrosion defects.
- From the current intensity maps obtained by scanning electrochemical microscopy, it can be concluded that P1-860 system presents greater homogeneity and protective character to the substrate, while the other systems present greater variability in the intensity of the current.
- For P1-860, P1-ZC and P1-850 paint systems, the modulus of impedance was high and invariable with respect to time up to 3360 h of immersion in 3.5 wt.% NaCl, showing excellent protection of A36 steel.
- The SP-1000 system reports a decrease in the impedance modulus by order of magnitude up to 3360 h of immersion in NaCl. However, this paint system turns out to be the most environmentally friendly due to its lower VOC.
- The Jet Zinc P1-600 system exhibited a lower impedance modulus by three orders of magnitude compared to other systems, evidencing its lower ability to protect A36 steel in seawater.
- The global electrochemical techniques used in this research work, such as EIS, constitute excellent tools for monitoring the performance of organic anticorrosive coatings, which allows a description of the physical-chemical phenomena that may be occurring on the coating, as well as estimation of its performance or degradation throughout time.

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