Electrochemical Impedance Spectroscopy Investigation of the Corrosion Resistance of a Waterborne Acrylic Coating Containing Active Electrochemical Pigments for the Protection of Carbon Steel

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The aim of this work was to investigate the corrosion resistance of a water-based commercial paint system applied on carbon steel. Electrochemical impedance spectroscopy (EIS) in the conventional three-electrode configuration was employed to test the various components of the paint system during their exposure to 3 wt.% NaCl aqueous solution. An efficient protection against corrosion was provided by the acrylic polymer containing zinc phosphate pigments when it was applied as a multilayer system. In this way, the high density of pores produced in the polymer matrix during the curing process could be avoided to become direct ionic pathways for the transport of aggressive species from the environment towards the surface of the underlying metal substrate.

1. INTRODUCTION

Organic coatings are widely employed in the corrosion protection of most metal surfaces, particularly steel. They provide a barrier against corrosive species present in the environment, due to their high resistance to oxygen, water and ions transport. The effectiveness of the corrosion protection provided by the coating requires good adhesion properties between the metallic substrates and the coating, coating stability for long periods, and low permeability towards corrosive species. In most technological cases involving harsh environments, these polymeric layers are not sufficient, and longer and more effective corrosion protection is achieved by adding corrosion inhibitors and pigments. The corrosion inhibition depends on the nature of the pigment and its distribution in the polymeric coating,

dosage and compatibility with the polymer binder. Protection is provided through any of the following mechanisms: (1) reduction of the transport of aggressive species into the polymer matrix by producing longer diffusion pathways due to tortuosity produced by inert components [1-5], (2) metal passivation by oxidizing pigments that promote either the onset of passivation or the formation of conversion layers on the metal to be protected, as well as inhibitive pigments [3,6-11], and (3) sacrificial galvanic coupling with the metal by more active electrochemical metal systems [1,3,5,12-16].

The use of volatile components (VOC) in organic coating formulations for corrosion protection is a major environmental concern. Currently there is intensive research activity directed towards the development of paint systems which combine a high solid content and are very low or even zero VOC [17]. Unfortunately, organic coating systems using water as solvent and non toxic pigments often do not achieve as good an anticorrosive performance as the paints they are intended to replace [18-20], thus requiring the design and testing of new paint systems for long-term protection of steel.

In this paper we report the electrochemical characterization of a commercial waterborne acrylic paint system containing zinc pigments that offers a high potential for the protection of carbon steel. The anticorrosive properties of the organic coating were evaluated by accelerated electrochemical tests using electrochemical impedance spectroscopy (EIS), a technique that is used widely to characterize the behaviour of coated metals immersed in aqueous electrolyte environments [20-33]. This study is a part of a research project aimed at evaluating the anticorrosive behaviour of different ecological paints for the protection of metallic structures.

2. EXPERIMENTAL

2.1. Materials and chemicals

Table 1. Coating characteristics of the painted specimens investigated.

Sample characteristics	Coating thickness
Primer (single-coat)	28.5 ± 0.4 μm
Primer (single-coat)	94.8 ± 1.4 μm
Primer (double-coat)	(96.0 ± 4.1) μm (first layer) + (80.0 ± 4.4) μm (second layer)
Primer + topcoat	(91.4 ± 1.6) μm (primer) + (89.0 ± 3.9) μm (top coat)

Carbon steel plates were employed as metallic substrates. Metal surfaces were abraded to a final 2000 grit finish, subsequently washed in acetone, ethanol and doubly distilled water, and then dried prior to the coating process. A commercial paint system from Sigma Coatings B.V. (Amsterdam, The Netherlands) was considered, consisting of an acrylic primer containing zinc phosphate as pigment (*Sigma Aquacover 20*), and an acrylic topcoat (*Sigma Aquacover 40*). In order to investigate the performance of the various components of the paint coating, selected samples were coated only

with the primer applied either as one or two coat layers, and other samples were coated with the two components of the paint system. The different combinations considered in this work are given in Table 1. The paint was prepared in the laboratory in order to control the quality of the coatings. The samples were painted with a withdrawing technique using an accurate speed motor and a system of gears, and then allowed to cure at room temperature and humidity for five days prior to testing. The thickness of the dry coatings was measured with a Mega-Check FN Coating-Thickness-meter (List-Magnetik GmbH, Germany).

Solutions were prepared from analytical grade reagents and twice-distilled water. The testing media was 3 wt.% NaCl. Experiments were carried out at ambient temperature (ca. 20ºC) in naturally aerated solutions.

2.2. Electrochemical evaluation

The electrochemical measurements made use of a conventional three-electrode arrangement and an automated EG&G Princeton Applied Research model 2263 *Parstat* controlled from a PC computer. The painted coupons were placed at the bottom of the flat electrochemical cell with the coated side facing upwards to the test solution. The working electrode surface was 6.5 cm^2. A large area cylindrical stainless steel plate situated around the specimen was used as the counter electrode. The potential of the working electrode was determined against a saturated sodium-chloride calomel electrode (*sce*). The electrochemical cell was placed inside a Faraday cage.

The electrochemical impedance tests were carried out for the samples left at their open circuit potential in the test electrolyte. AC impedance data were obtained by applying a sine wave perturbation at frequencies between 10 kHz and 1 mHz. The amplitude of the AC voltage signal was ±30 mV. The data quality acquisition was established in 15 cycles at each frequency, thus providing good signal-to-noise ratios at all frequencies. The software used to acquire and analyze the data allowed representation of the data in terms of both Bode (logarithm of the impedance modulus |Z| and phase angle *Φ* as a function of the logarithm of the frequency *f*) and Nyquist (imaginary component of the impedance as a function of the real component) plots. The impedance spectra were modelled using Yeum's "Z*SimpWin 2.00*" software [34] to derive the equivalent circuit that best fitted the experimental data.

3. RESULTS AND DISCUSSION

Measurements of electrochemical impedance have been carried out at the open circuit potential (E_{corr}) after immersion for different times in 3 wt.% NaCl solution, at room temperature. The measured impedance spectra can be displayed in the form of a complex plane plot, also called Nyquist diagrams, and/or as Bode diagrams. The Nyquist plot displays the impedance data by the complex variables and separated into the real, Z_R, and the imaginary, Z_I, parts, expressed in Ω cm^2. In the Bode diagram the frequency dependence of the absolute magnitudes of the impedance modulus, $|Z|$, and the phase

angle, Φ, are plotted instead. The advantages of this procedure are that the data for all measured frequencies are shown and a wide range of impedance values can be displayed simultaneously. The frequency dependence of $\log|Z|$ and Φ indicate whether one or more time constants are present in the system.

Selected examples of the Nyquist and Bode impedance plots obtained for the coated samples at different exposures in the test electrolyte are shown in figures 1-4. They were obtained for the carbon steel substrates painted with different combination of the two components of the paint system as described in Table 1. Changes in the impedance characteristics as a result of the exposure of the specimens to the corrosive environments could be deduced from the comparison of the spectra. From a cursory observation of these plots it can be deduced that major differences in the corrosion resistance conferred by the coating layers to the underlying metallic substrate as well as in the time evolution of their electrochemical behaviour upon exposure to the test electrolyte occur for the various coated specimens. These variations are related to the number, nature and thickness of the coating layers applied on the metal. In some cases, the polymeric film did not provide effective protection to carbon steel against corrosion in 3 wt.% NaCl aqueous solution, whereas in others an effective protection was provided by the waterborne coating system instead. In the following, the various systems will be considered separately as to establish the optimum paint conditions for effective anticorrosion protection of carbon steel using the waterborne paint system under consideration.

Application of the primer coating in one single layer is considered first. The EIS data contained in Figures 1 and 2 correspond to the same polymer matrix applied directly on carbon steel differing exclusively in the thickness of this organic layer. When the thin film is considered (namely 29 μm thick), the formation of a poorly protective film on steel is clearly evidenced from the observation of both Bode-modulus and Bode-phase diagrams at all times. Low impedance modulus values in the order of 10^4 Ω cm^2 were measured even at the earliest exposures, whereas the response of the system must be described as resistive over all the frequency range (as characterized by phase angles smaller than 45 degrees). In fact, breakdown frequencies (i.e., characteristic breakdown frequency, f_b, is the frequency at which the phase angle $-\Phi = 45°$ in the capacitive-resistive transition region) could only be determined from the spectra measured during the first week, and they phase angles are far from 90 degrees at all frequencies. That is, the polymeric film applied on the carbon steel substrate did not provide an effective barrier towards the transport of aggressive species from the electrolyte, and could not effectively protect this system against corrosion.

A better situation was observed with the thicker coating applied on carbon steel, shortly after immersion in the test electrolyte. Initial modulus values in the low frequency range of the impedance spectra amounting ca. 10^7 Ω cm^2 were observed this time (cf. Figure 2), and even a small frequency range with phase angles in excess of 45 degrees could be observed in the Bode-phase diagrams at the high frequency limit). Despite these observations, phase angles were always smaller than 80 degrees, which would be an indication of a dielectric behaviour. That is, the polymeric film when applied at dry thickness in excess of 95 μm form a barrier layer, though this film is very porous and cannot effectively protect the carbon steel substrate.
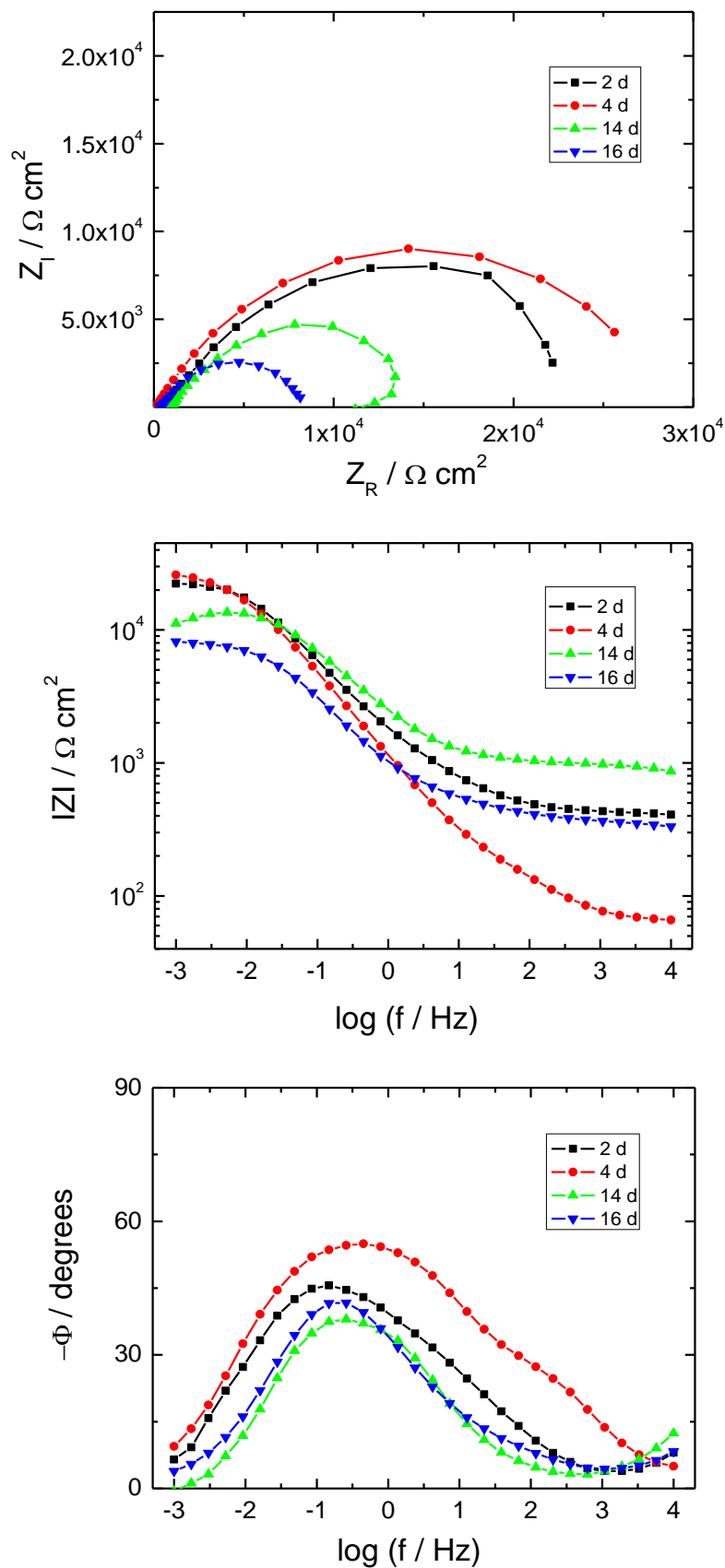
Figure 1. Experimental impedance spectra of a carbon steel coated with an acrylic primer film containing zinc phosphate pigment (*Sigma Aquacover 20*) in 3 wt.% NaCl aqueous solution at different exposure times as indicated in the graphs. Coating thickness: 29 μm.
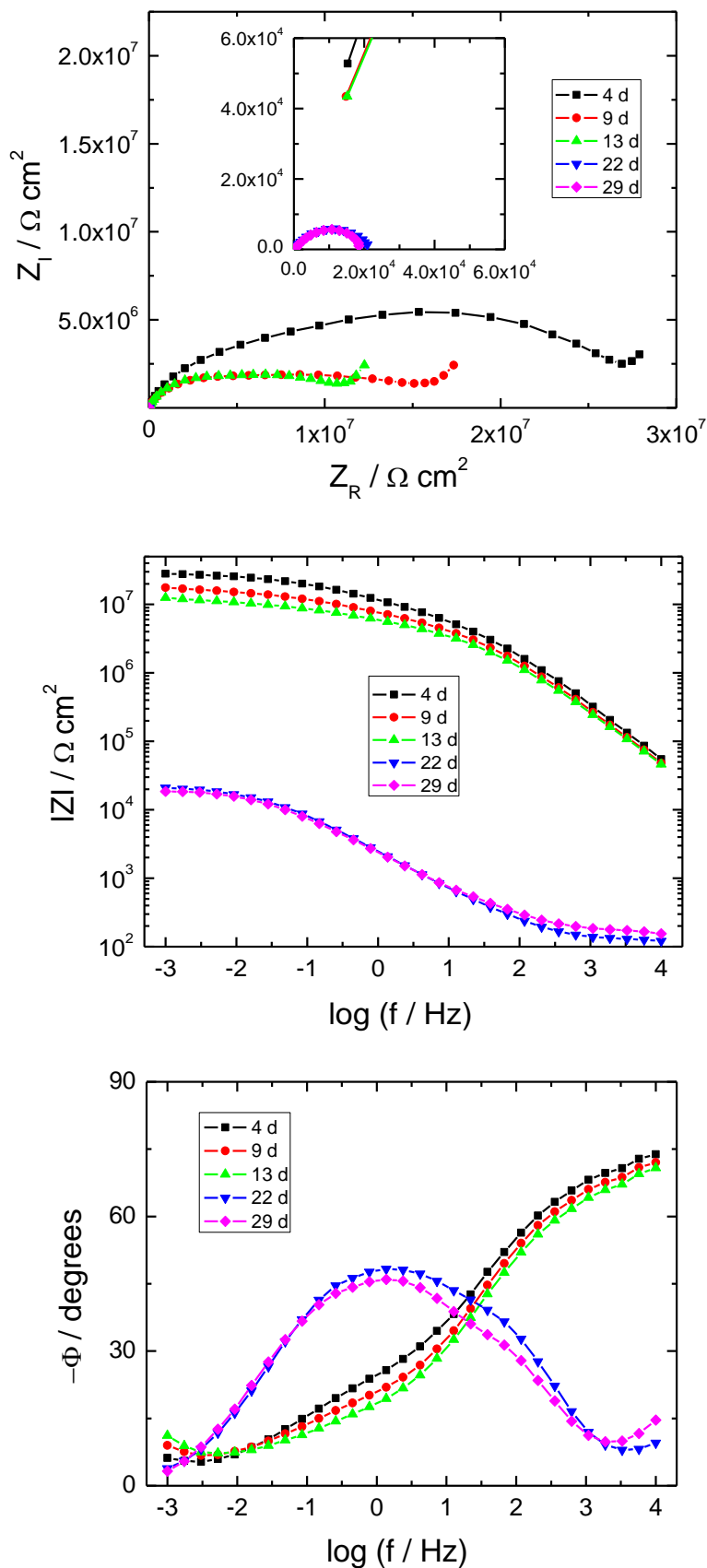
Figure 2. Experimental impedance spectra of a carbon steel coated with an acrylic primer film containing zinc phosphate pigment (*Sigma Aquacover 20*) in 3 wt.% NaCl aqueous solution at different exposure times as indicated in the graphs. Coating thickness: 95 μm.
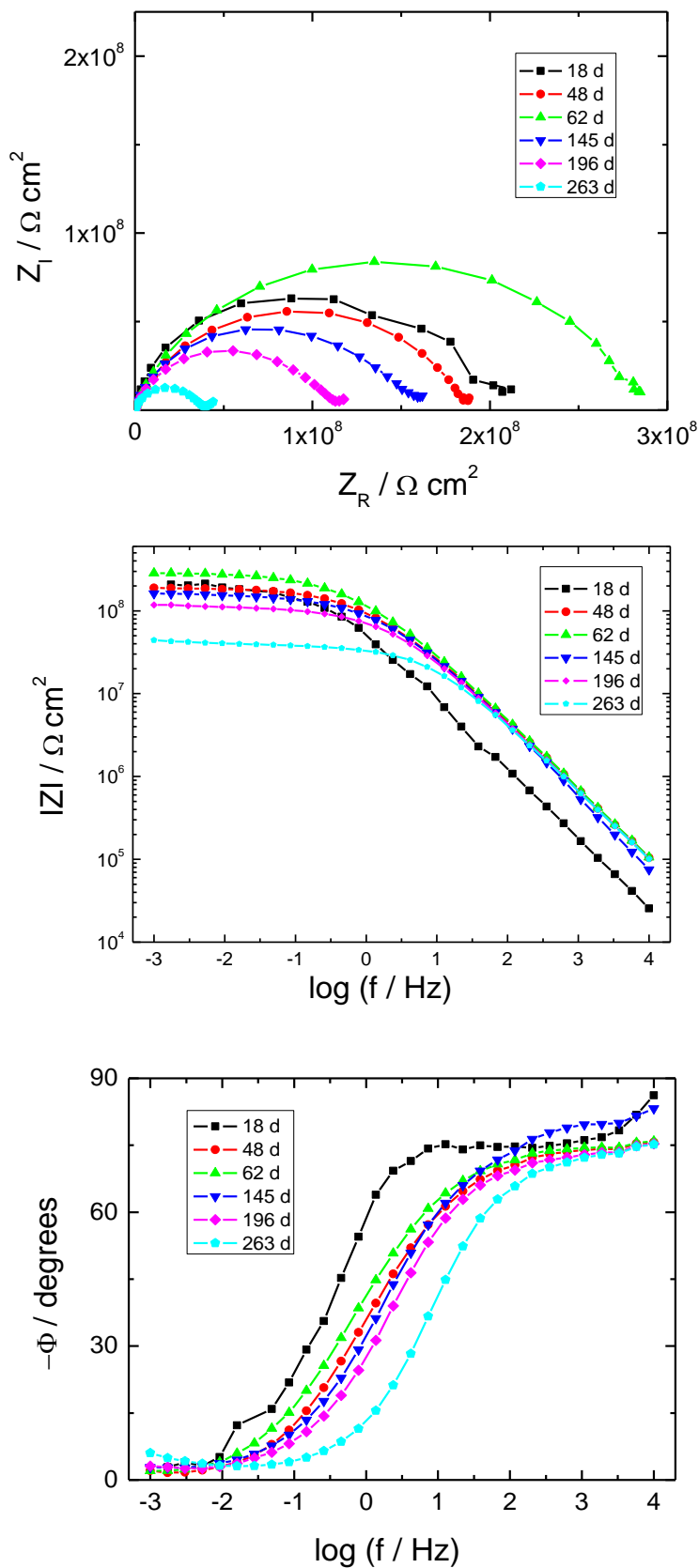
Figure 3. Experimental impedance spectra of a carbon steel coated with an acrylic primer film containing zinc phosphate pigment (*Sigma Aquacover 20*) in 3 wt.% NaCl aqueous solution at different exposure times as indicated in the graphs. The coating was applied as two consecutive layers of coating thickness: 96 μm + 80 μm.
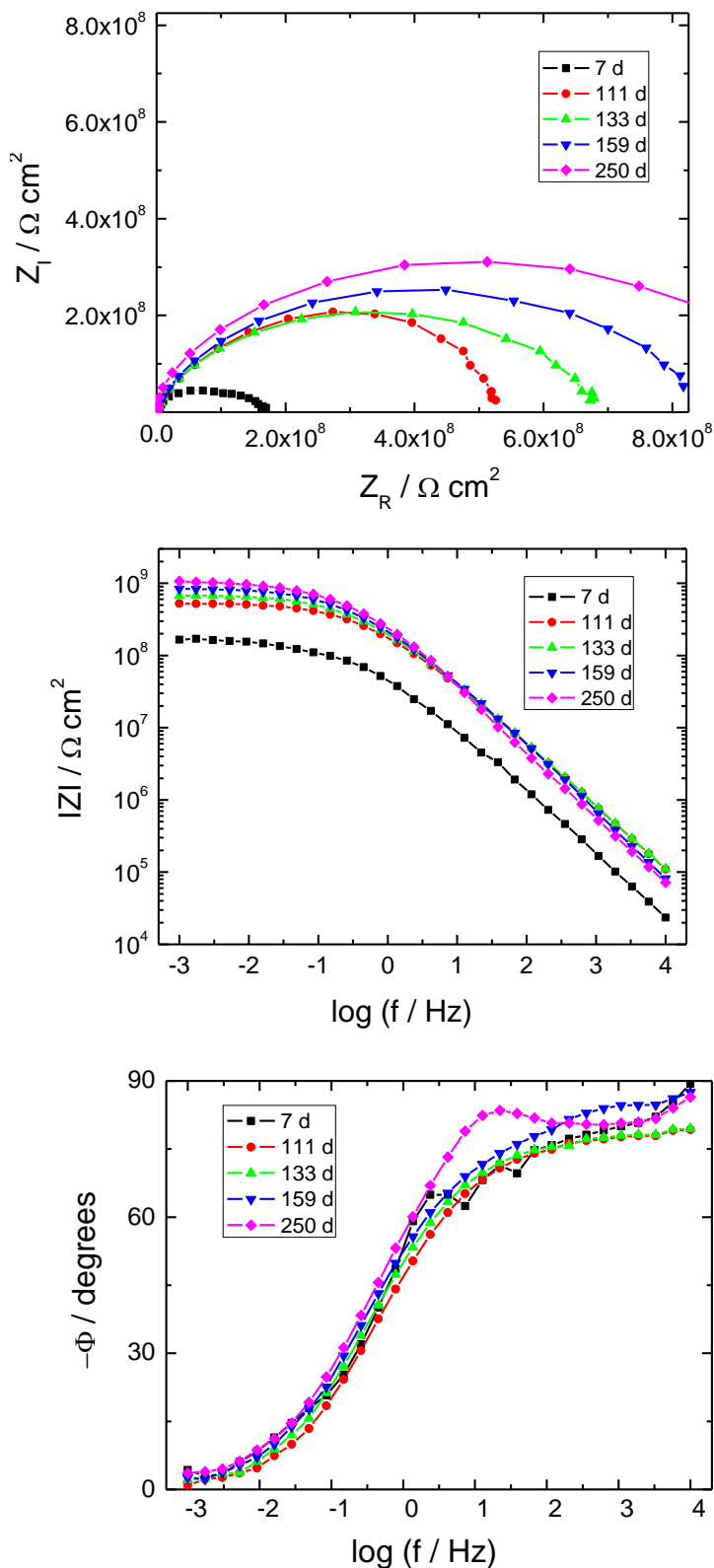
Figure 4. Experimental impedance spectra of a carbon steel coated with an acrylic primer film containing zinc phosphate pigment (*Sigma Aquacover 20*) and an acrylic topcoat film (*Sigma Aquacover 40*) in 3 wt.% NaCl aqueous solution at different exposure times as indicated in the graphs. The coating was applied as two consecutive layers of coating thickness: 91 μm + 89 μm, respectively.

To get a confirmation that porosity of the polymeric layer is a major concern with this waterborne coating system, the carbon steel samples coated with the thick film primer were coated with a new layer of a similar thickness. That is, the steel substrate coated by two film primer layers was considered next. The rationale for this procedure was that in the event of a significant distribution of pores formed in the coating during the curing process, the application of two layers will make highly improbable that the pores developed in each layer would be located exactly in the same position. Thus, no pores directly communicating the electrolyte with the underlying substrate would be formed that will operate as ionic pathways for the transport of species from the electrolyte through the coating (see sketches depicted in Figure 5).
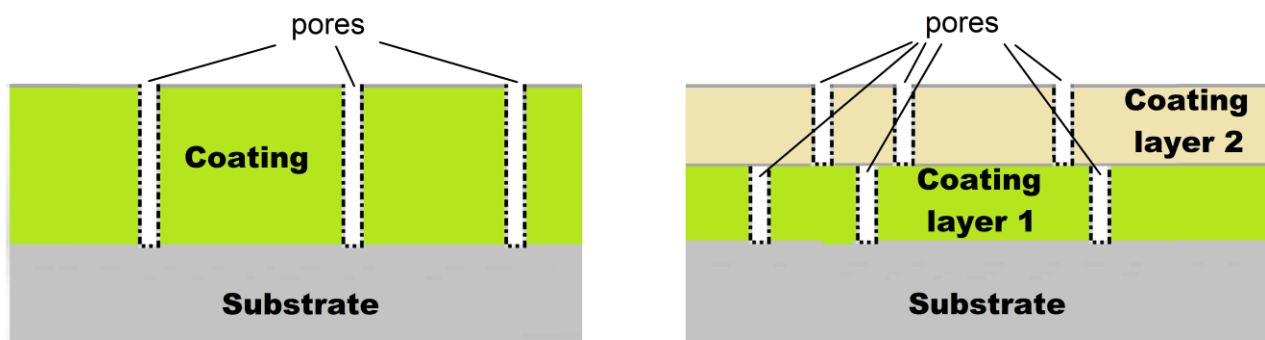

Figure 5. Sketches depicting pore distribution for a polymeric coating applied in either (left) one, or (right) two layers.

The validity of our consideration is immediately demonstrated from the inspection of the impedance spectra depicted in Figure 3. Impedance values in excess of 10^8 Ω cm^2 are now obtained during almost half a year, which can be regarded to correspond to a coating system that effectively protects the underlying metal substrate. Though some improvement could be expected because of the added thicker coating resulting on the metal, the improvement is far greater than that obtained between the previous two cases with only one layer application. More interestingly, the impedance modulus seems to increase with the elapse of time for 3 months, clearly indicating that zinc phosphate particles are effectively conferring an additional protection through the passivating/inhibitive mechanism first proposed by Meyer [35]. In a neutral solution, the oxidation of a corroding metal M releases electrons that are consumed by the oxygen molecules dissolved in the electrolyte, leading to the release of OH$^-$ ions in the environment,

$$M \rightarrow M^{z+} + z \text{ e-} \tag{1}$$
$$O_2 + 2\,H_2O + 4\,\text{e-} \rightarrow 4\,OH^- \tag{2}$$

In the progressively alkalinized solution, zinc phosphate undergoes hydrolysis according to reaction:

$$Zn_3(PO_4)_2 + 2\,H_2O + 4\,OH^- \rightarrow 3\,Zn(OH)_2 + 2\,HPO_4^{2-} \tag{3}$$
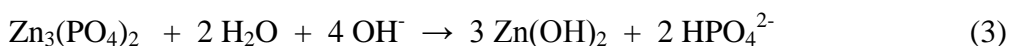
As result, protection is provided to the corroding metal from the combined effect of the formation of a conversion layer between hydrogenphosphate ions and steel, and the blockage of the exposed surface due to the precipitation of a protective layer of zinc oxy-hydroxides.

Despite the protecting effect of pigments in the coating for the protection of the metal for a significantly more extended period of time, the rather poor sealing capacity of the coating is responsible for the later deterioration of the electrochemical behaviour of the system. In fact, new ionic pathways are developed through the coating, that eventually lead to the exposure of the underlying metal to the electrolyte. At sufficiently long exposures, a significant amount of pigments are consumed and they are not longer available in the concentrations necessary to effectively block all the pores, and a decrease with time of the coating resistance results. Then, the magnitude of the impedance modulus decreases in a slow pace with the elapse of time, and less wide capacitive frequency ranges are found in the spectra.

Improved sealing of the coating system is achieved by using a topcoat free from the inhibitive zinc phosphate pigments. As it can be observed from the inspection of the EIS diagrams given in Figure 4, the impedance modulus are observed to increase with the elapse of time for as long exposures as 390 days, which is an indication that the active pigments in the coating continue providing their additional protection to the coating by forming corrosion precipitates in the pores of the inner layer and a conversion layer on the metal. Furthermore, the occurrence of a rather wide capacitive region in the Bode-phase diagrams is also observed for frequencies greater than 10 Hz, which is characteristic of a barrier film with good corrosion protection characteristics.

Thus, both two-layer systems show the same features towards protection of carbon steel for a rather extended initial period of exposure to the environment, that confirms that the zinc phosphate pigments are an effective component to assist the corrosion protection of this paint system for steel, especially as long protection is envisaged. Yet, the coating containing these pigments seem to cure less efficiently regarding the development of pores through the polymeric matrix, and a more effective sealing of the polymeric film would be required. This goal is effectively achieved by applying a final pigment-free layer to the system.

Time evolution of the protection characteristics of the films was better established by deriving the parameters related to the coating performance from the impedance spectra. The EIS spectra were analysed in terms of the equivalent circuit for a defective organic coating [36-38] that is depicted in figure 6. It assumes that the corrosion of the coated metal is controlled by the same mechanism that occurs on the bare metal but with a greatly reduced active surface area.
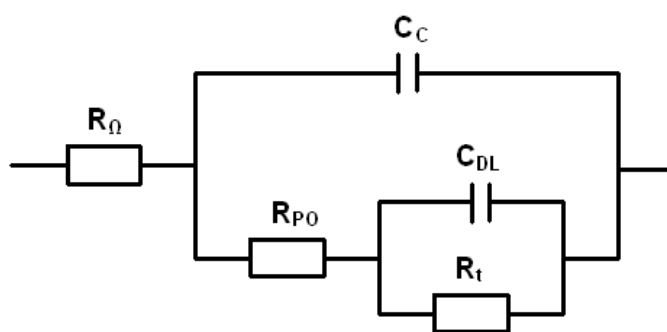

Figure 6. Equivalent electrical circuit for a defective organic coating [33-35].

The equivalent circuit consists of the resistance R_Ω of the test electrolyte and electrical connectors, the capacitance C_C of the intact coating layer, the pore resistance R_{PO} due to penetration of electrolyte, the polarization resistance of the substrate R_t, and the double-layer capacitance at the substrate/electrolyte interface C_{DL}. Analysis of the impedance spectra in terms of this equivalent circuit allowed for the parameters C_C and R_{PO} to be determined. Changes in the magnitudes of these parameters as a function of the immersion time in the test solution for the two-layer coated specimens are plotted in figure 7.
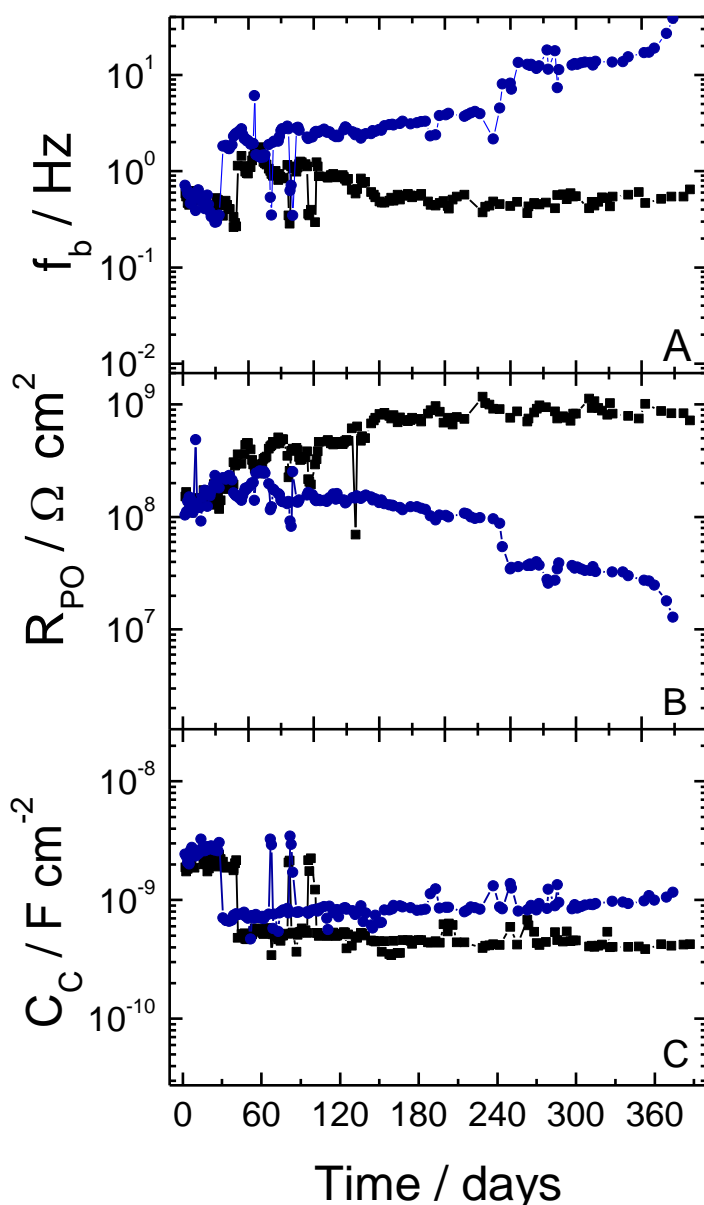

Figure 7. The time dependence of (A) the breakdown frequency f_b, (B) the coating capacitance C_C, and (C) the coating resistance R_{PO} values determined for the two-layer coated steels during immersion in 3 wt.% NaCl aqueous solution. Symbols correspond to specimens in which the coating is: (●) two layers of *Sigma Aquacover 20* primer; and (■) one layer of *Sigma Aquacover 20* primer and another layer of *Sigma Aquacover 40* topcoat.

Though no significant differences can be established from the time evolution of the coating capacitance of the two painted specimens, which is consistent with both behaving as a barrier film for the duration of the experiments, differences can be observed for both the breakdown frequency and the coating resistance. For the latter, two different trends are found with time. The coating resistance steadily decreases with time when both layers contain active pigments, whereas the opposite occurs when the topcoat was used instead. The onset of pigment action is detected by inspecting the corresponding breakdown frequencies. Though both systems behave quite similarly for about one month, the opening of ionic pathways is then finally produced from the existing pores of the coating. Though the effective corrosion protection operated by the zinc phosphate particles in the coating leads to the progressive blockage of the pores by the precipitation of corrosion products in the pores, they may become progressively exhausted in the case of the two-layer primer application. The new decrease in the breakdown frequencies with time shows that the total delaminated area decreases again progressively. On the contrary, breakdown frequencies do not decrease with time in the case that both layers contain the active pigment (cf. Figure 7).

Therefore, the waterborne acrylic system described in this work has shown to be an effective corrosion protection system for carbon steel provided that it is applied in two layers, due to the extensive pore formation that occurs during curing. This procedure is shown to be more effective than the typical resource of producing even thicker coating films. More effective sealing of the polymeric layer is achieved when the topcoat is pigment-free.

4. CONCLUSIONS

From the analysis of the impedance spectra of coated carbon steel specimens immersed in 3 wt.% NaCl aqueous solution at ambient temperature, the excellent anticorrosion protection characteristics of a waterborne acrylic paint system have been demonstrated when applied in at least two layers. A high density of pores in the coating is formed during the curing process, and the establishment of ionic pathways through the coating that eventually lead to the direct contact of the underlying metal with the aggressive environment can only be slightly delayed through the application of thicker coatings. But long lasting protection was obtained when the coating was applied in two layers, due to the low probability that pores in the two layers might interconnect. Furthermore, the presence of active redox pigments that can act through a combined passivating and inhibitive mechanism with respect to steel, would eventually lead to the precipitation of corrosion products in the pores that become progressively sealed in this way.

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