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Evaluation of Ecological Organic Paint Coatings via Electrochemical Impedance Spectroscopy

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The behaviour of five different water-based anticorrosive paint systems for the corrosion protection of carbon steel surfaces was evaluated by electrochemical impedance spectroscopy (EIS). Epoxy-polyamine, epoxy-amine and epoxy-acrylic resins as primer coats, and acrylic-polyurethane and acrylic paints as top coats, were investigated both in single layer and double-layer applications. The best protection was provided by the epoxy-amine resin, whereas acrylic-polyurethane exhibited the poorest characteristics and signs of corrosion could be observed since the initial moments of immersion onwards. The impedance spectra could be satisfactorily fitted by employing an equivalent circuit which corresponds to a porous barrier film.

Keywords: Organic coating, Carbon steel, Corrosion protection, Ecological organic paint, Electrochemical impedance spectroscopy

1. INTRODUCTION

Environmental regulations directed to reduce environmental degradation and public health hazards have raised a major interest in the development of ecological paints which comply the legal requirements for paint formulations with low volatile organic compounds (VOC) contents, whereas they should not be too costly to prevent them from wide use [1-4]. In particular, the emission of VOC into the environment has experienced a huge increase over the last twenty years and has let to the onset of serious problems of air pollution and, thus, health risks. This, together with the fact that many of the anti-corrosive pigments used present high levels of toxicity, such as lead oxide and chromate paints [5-

8], has led many paint manufacturers to develop water-based anti-corrosive paint systems which combine a high solid content and are zero VOC [4,9,10]. The performance of paint systems is often established on the basis of atmospheric exposure and accelerated salt spray laboratory tests, but electrochemical techniques such as Electrochemical Impedance Spectroscopy (EIS), or surface-sensitive techniques such as Scanning Electronic Microscopy (SEM) or Fourier Transformed Infra-Red Spectroscopy (FTIR), have come to be employed successfully in monitoring the physicochemical changes occurring during the exposure of a metal-coating system to a given corrosive environment. From such combined investigations, though difficulties are often met during attempts to correlate accelerated laboratory tests with the results of conventional atmospheric exposures [11,12], the EIS technique have probed to be very useful for the detection of pores or defects in the coating [13,14] at significantly earlier times. Indeed, relevant information regarding both the electrochemical behaviour of the metal/coating system and the extent of the unprotected metallic areas can be extracted from the analysis of the impedance spectra [15-26].

Herein we report on the effectiveness of five commercial water-based paint systems for the corrosion protection of carbon steel panels as derived from electrochemical impedance spectroscopy measurements. 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.

Five different paint systems directly applied on carbon steel were tested. The steel plates had a chemical composition (%wt/wt): Cr (0.001), S (0.001), C (0.001), and Fe (balance). The metal samples were subjected to a surface preparation of *Sa2½* prior to the application of the coatings. Both single-coat and two-coat paint systems were applied to the substrates to produce the paint systems under investigation. Characteristics of the paint systems are listed in Table 1. Once cured, samples were introduced in the electrochemical cell.

Table 1. Main characteristics of the five waterborne paint systems.

Coating system number	Coating system component	Coating thickness
E-1-C	Epoxy-amine (single-coat)	100 μm
E-2-C	Epoxy-polyamine (single-coat)	100 μm
E-3-C	Acrylic-polyurethane (single-coat)	50 μm
E-4-C	Epoxy-polyamine + acrylic-polyurethane (double-coat)	100 μm (primer) + 50 μm (top coat)
E-5-C	Epoxy-amine + acrylics (double-coat)	100 μm (primer) + 60 μm (top coat)

Figure 1 depicts the flat electrochemical cell employed, in which the painted coupons were placed at its bottom with the coated side facing upwards to the test solution. The working electrode surface was 5.56 cm^2. The three-electrode cell arrangement was used in the experiments, completed with a saturated calomel electrode (SCE) as reference electrode, and a platinum mesh as counter electrode. The electrochemical cell was placed inside a Faraday cage. The test solution was a 3 wt.% NaCl aqueous solution, open to air, held at room temperature.

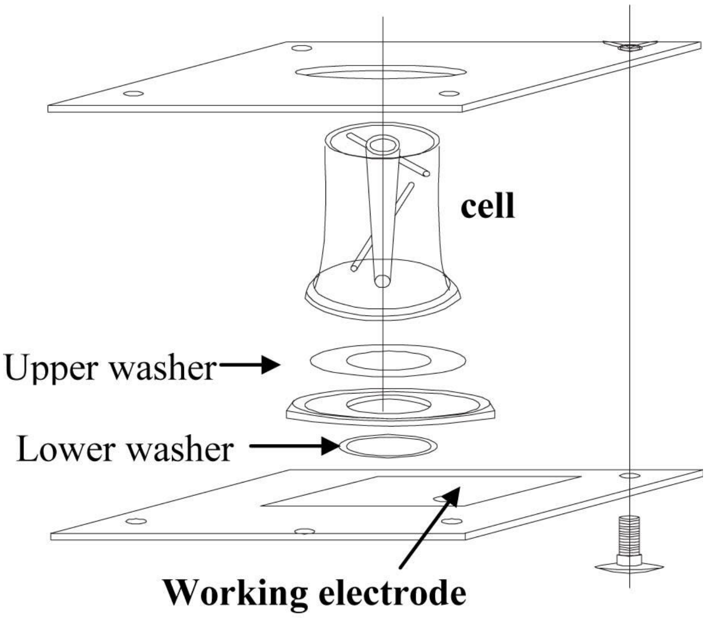

Figure 1. Electrochemical flat cell used for impedance measurements (schematic). The area of the sample exposed to the test electrolyte was established at the bottom of the cell by using two rubber o-rings and a rigid Teflon holder to guarantee the water-tightness of the system

Electrochemical impedance data were obtained using a computer-controlled EG&G Model 5210 lock-in amplifier connected with an EG&G Model 263A potentiostat. All the paint systems under consideration were alternately submitted to two different EIS programmes, which differed in the frequency range covered. Firstly, coating capacitance measurements were conducted in 40-data sets taken at selected exposure times of the coated systems in the test environment, namely after 48, 144, 216, 312, 384, 480, 552, 648, 720, and 816 hours. In this case, 8 logarithmically-spaced frequency values were taken in the range 10 – 50 kHz, using a 10 mV amplitude for the sinusoidal voltage. On the other hand, impedance spectra were collected over the 10 kHz – 100 mHz frequency range, with 14 values per decade, and the amplitude of the sinusoidal voltage signal was the same. *ZsimpWin* [27] software was used 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% NaCl solution, at room temperature. The behaviour of the five studied systems is summarized in Figures 2 (single-coat paints) and 3 (double-coat paints), in which typical examples of the Nyquist and Bode impedance plots obtained for the coated samples are shown. As it was expected, the impedance decreased with exposure time. Initially, an almost capacitive behaviour was observed for the systems in the high frequency range of the spectra, which extended to quite low frequencies in the case of the *E-5-C* paint system, whereas sample *E-3-C* exhibited the smallest capacitive range and a rather extended resistive region could be clearly observed in the low-frequency range even at the beginning of the exposure.

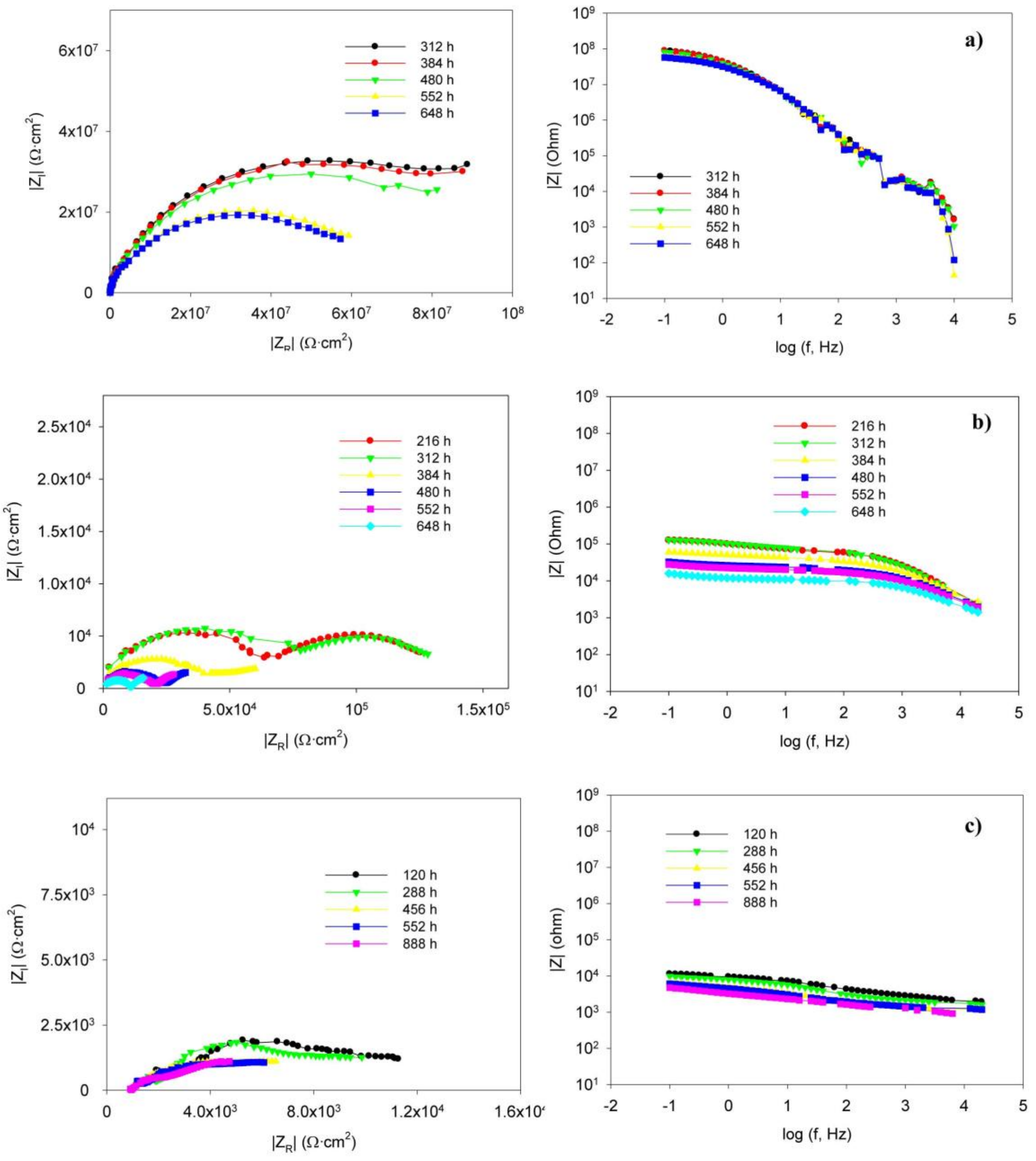

Figure 2. Experimental impedance spectra of carbon steel samples coated with different ecological paint systems measured during their exposure to 3 wt.% NaCl solution. EIS corresponded to: (a) epoxy-amine (*E-1-C*), (b) epoxy-polyamine (*E-2-C*), and (c) acrylic-polyurethane (*E-3-C*) paints at different exposure times as indicated in the graphs. Complex plane plots are given on the left-hand side and Bode plots are given on the right-hand side.

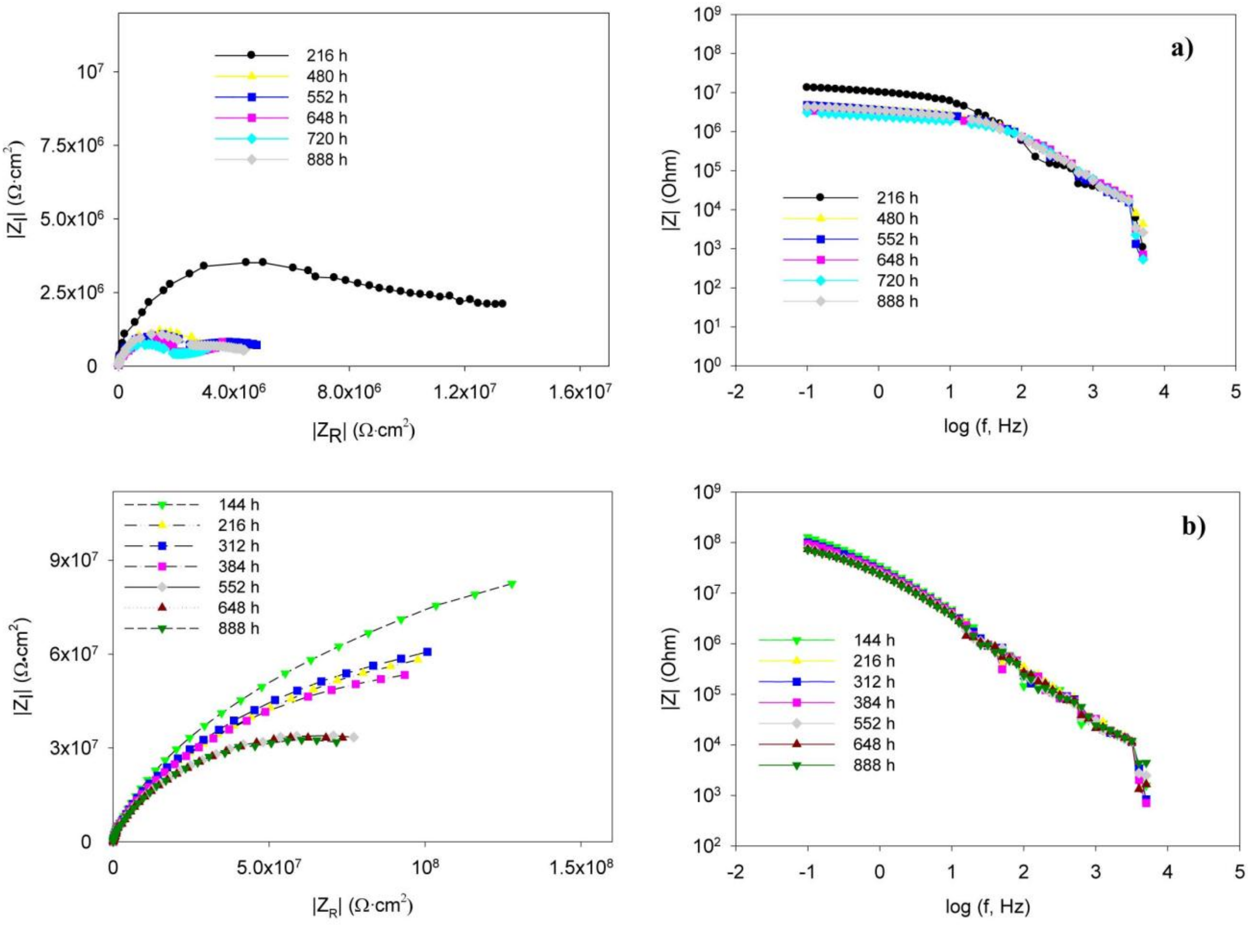

Figure 3. Experimental impedance spectra of carbon steel samples coated with different ecological paint systems measured during their exposure to 3 wt.% NaCl solution. EIS corresponded to: (a) epoxy-polyamine + acrylic-polyurethane (*E-4-C*), and (b) epoxy-amine + acrylics (*E-5-C*) paints at different exposure times as indicated in the graphs. Complex plane plots are given on the left-hand side and Bode plots are given on the right-hand side.

3.1. Variations of the coating capacitance at earlier exposures: the uptake of water by the paint systems.

The capacitance of the paint systems was determined using the following equation [28]:

$$C = \varepsilon \varepsilon_0 \frac{S}{d} \qquad (1)$$

Given the fact that the dielectric constant of a paint layer is small compared with that of water [29], water uptake produces an enormous change in the capacitance of the coatings. In Figures 4 (single-coat paints) and 5 (double-coat paints) some typical Nyquist diagrams measured in the high frequency range between 10 and 50 kHz for various immersion times are given. A general trend for the capacitance was observed for all of the systems under study, namely, the capacitance values were small at immersion, they diminished abruptly during early exposures and would only stabilise at later times.

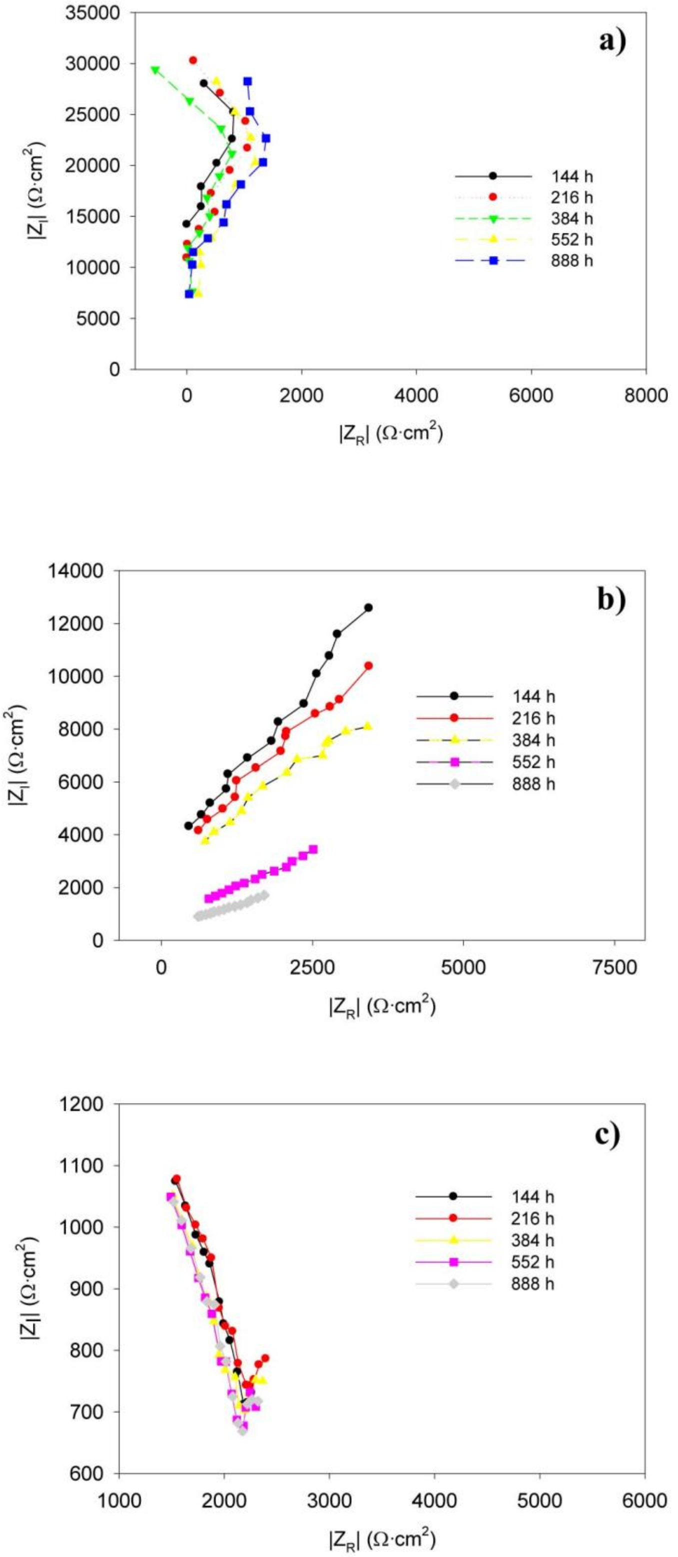

Figure 4. High-frequency impedance spectra (complex plane plots) of carbon steel samples coated with different ecological paint systems measured during their initial exposure to 3 wt.% NaCl solution. EIS corresponded to: (a) epoxy-amine (*E-1-C*), (b) epoxy-polyamine (*E-2-C*), and (c) acrylic-polyurethane (*E-3-C*) paints at different exposure times as indicated in the graphs.

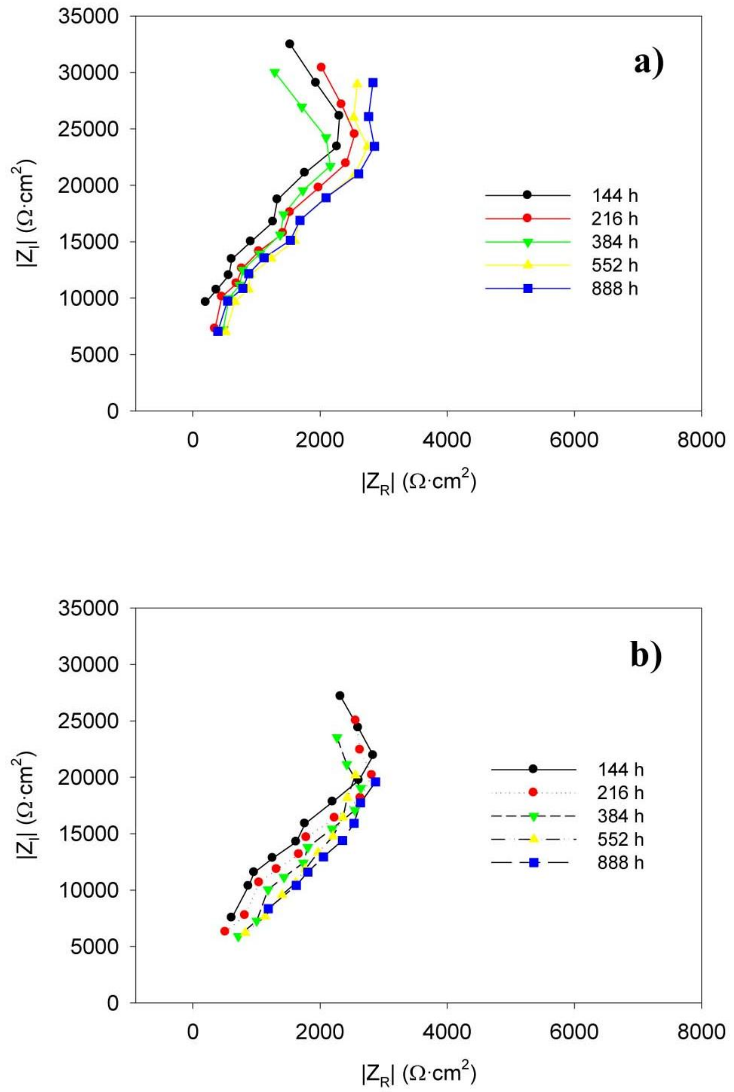

Figure 5. High-frequency impedance spectra (complex plane plots) of carbon steel samples coated with different ecological paint systems measured during their initial exposure to 3 wt.% NaCl solution. EIS corresponded to: (a) epoxy-polyamine + acrylic-polyurethane (*E-4-C*), and (b) epoxy-amine + acrylics (*E-5-C*) paints at different exposure times as indicated in the graphs.

To adequately fit the capacitance component with the electric equivalent circuit used in the modelling of the data (see Fig. 6a), a constant phase element (CPE) had to be employed, which can be expressed as follows:

$$Z = \frac{(j\omega)^n}{Y^0} \qquad (2)$$

where Z is the CPE impedance, j is the imaginary number ($j^2 = -1$), ω is the angular frequency (rad s^{-1}), n is the constant phase angle of the CPE (rad), and Y^0 is a constant of the CPE (mho).

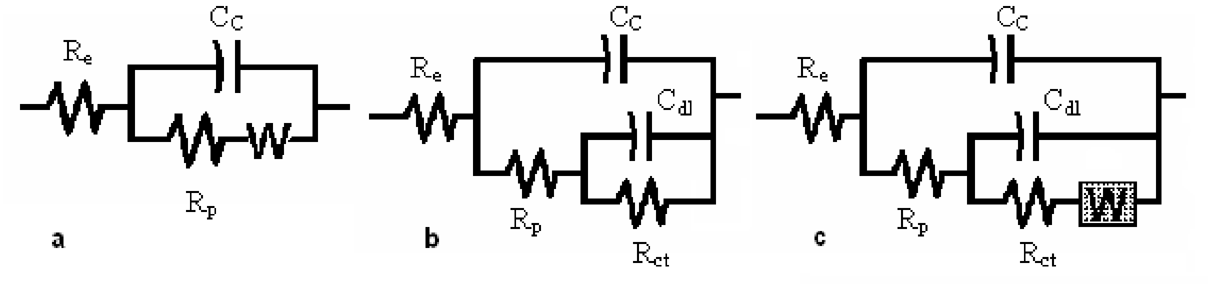

Figure 6. Electrical equivalent circuits used to model the behaviour of the paint systems under investigation. R_e is the solution resistance; R_p and C_C are the resistance and the capacitance of the paint film, respectively; C_{dl} is the double layer capacitance at the metal-electrolyte interface; R_{ct} is the charge transfer resistance of an electrochemical (corrosion) process; and *W* is a Warburg element.

The *n* coefficient of the CPE was observed to vary greatly over the first few moments of immersion, then decreased over the first few hours of immersion, and finally stabilised after relatively long exposures.

On the other hand, the relationship between the fraction in volume of water in the coating and the capacitance (considering that water is distributed uniformly throughout the coating) is established via the equation given by Brasher and Kingsbury [30] which is the following:

$$\Phi = \frac{\log\left(C_t / C_0\right)}{\log 80} \tag{3}$$

where Φ is the fraction of the volume of water in the coating, C_t is the capacitance of the paint layer for time *t*, C_0 is the capacitance of the layer of paint when $t = 0$, and 80 is the relative permeability of the water at 20ºC which is the average temperature for the experiment.

As time elapsed, the values of Φ increased steadily and levelled off in parallel to the stabilization of the capacitance values for each paint system. The system which presents the smallest uptake is *E-1-C*, with ratios of 0.46% after 10 hours and 20% at 888 hours. The other two single-coat systems, *E-2-C* and *E-3-C*, delivered intermediate uptakes after 10 hours (5.4% and 35 % respectively), but became extremely high at 888 hours (ca. 100%). Analogously, the two-coat systems, *E-4-C* and *E-5-C*, were found to exhibit very similar ratios at all times, namely 4.5% and 3.4% after 10 hours, and 40% and 37% at 888 hours, respectively. In comparison with a previous study from our laboratory in which non-ecological paint systems were considered [24], the values of water uptake found here are smaller.

3.2. Evolution of impedance spectra of system coatings with immersion time.

The measured spectra could be analysed in terms of the two equivalent circuits depicted in Figures 6b and 6c. They are characteristic of a defective organic coating, though the number of time constants required to adequately describe the experimental spectra had to be increased in order to account for the different processes developing in the metal-coating systems exposed to the test environment as time elapsed. Initially, satisfactory fits could be obtained in all cases by using an equivalent circuit which contained two *R(CPE)* elements in series with the cell resistance, whose symbol is *R(Q(R(QR)))*, and it is shown in Figure 6b. At longer exposures, occurring at different immersion times for each paint system, the circuit which best fitted the data was that shown in Figure 6c, and the corresponding symbol is *R(Q(R(Q(RW))))*.

The epoxy-amine + acrylics (*E-5-C*) and the epoxy-amine (*E-1-C*) paint systems showed an extended capacitive behaviour over the duration of the experiments, with this behaviour even more evidenced in the case of the coating formulation *E-5-C*. In the other three paint systems, the capacitive behaviour was to only be observed in the first few moments of immersion. Indeed, the initial capacitive behaviour greatly decreases in extent over the frequency range for the paint system consisting of epoxy polyamine + acrylic polyurethane (*E-3-C*) for very short immersions (< 2 days). As of that time, a semi-circle developed in the high frequency range which is an indication of the degradation of the coating system. From the modelling of the results data obtained from the application of the equivalent circuits, the R_p values for this system were extracted. The value of R_e is small in comparison with R_p and, therefore, can be ignored. The circuit used in each case was that which gave the minimum error with the minimum number of elements and which, basically, the one which gave the best behaviour was made up of two time constants.

For longer immersion periods and coating systems *E-2-C* and *E-3-C*, the size of the high frequency semi-circle greatly changed whereas the low frequency data followed a depressed semi-circle. Both semi-circles varied with the elapse of time becoming progressively smaller. Furthermore, the Nyquist plots for the sample *E-1-C* also exhibited two time constants, whereas formulations *E-4-C* and *E-5-C* presented only one time constant. Among these, the system *E-5-C* delivered less defined spectra than the rest of the systems under study, particularly at the initial stages of immersion. Indeed, the spectra could not be fitted coherently due to the fact that as of the initial moments of the study, corrosion was already observed under the coating film, thus originating enormous discrepancies within the impedance data.

From the analysis of the impedance spectra in terms of the equivalent circuits of Figure 6, the impedance parameters R_p and C_C could be determined. Changes in the magnitudes of these parameters, as a function of their exposure time to the test solution, were next employed in order to evaluate the variation of the properties of the coating applied over the time of immersion and the different configurations of the paint format. The R_p values fluctuated depending on the system under consideration. The systems exhibiting the highest R_p values were *E-1-C* and *E-5-C*, both containing epoxy-amine as primer, and they also showed the greatest variations in this parameter. Thus, *E-5-C* presented R_p values *ca.* $1.4 \cdot 10^8$ $\Omega \cdot cm^2$ initially, later to fall to values around $5.6 \cdot 10^4$ $\Omega \cdot cm^2$ after 888 hours of immersion, whereas the variation of R_p for the system *E-1-C* over the same period of time was between $3.7 \cdot 10^7$ $\Omega \cdot cm^2$ and $7.4 \cdot 10^5$ $\Omega \cdot cm^2$. In both cases, the most significant decrease in R_p was produced after 480 hours of exposure. In general terms, we can say that in the systems *E-1-C, E-4-C* and *E-5-C*, the values of R_p are in excess of 10^7 $\Omega \cdot cm^2$, reaching values of up to 10^8 $\Omega \cdot cm^2$ in the case of the system *E-5-C* at the beginning of the experiment.

Conversely, the coating systems *E-2-C* and *E-3-C* present much lower values for the coating resistance (in the order of 10^4 $\Omega\cdot cm^2$), and the higher values only amounted to 10^5 $\Omega\cdot cm^2$ and were exhibited by *E-2-C* shortly after immersion. In the case of *E-3-C*, very evident processes of corrosion were observed under the coating as of the initial moments of immersion, which are evidenced in the EIS spectra through the observation of two clearly differentiated time constants. The values measured initially for R_p, of the order of 10^4 $\Omega\cdot cm^2$, are an indication that the underlying metal is not effectively separated from the aggressive test environment. Indeed, EIS measurements could not be carried out with acceptable reproducibility due to the enormous instability of the electrochemical system.

Though a decrease in both R_p and C_C values occurred for all the coating systems considered as time elapsed in the electrolyte, the rest of the painted systems showed no evident indications of corrosion up to 888 hours of exposure. The reported variation of R_p with time can therefore be explained on the basis of two concurrent phenomena: an increase in the density of the pores, and the partial sealing of the pores due to the precipitation of corrosion products, with the former effect proving more evident in the initial stages of immersion. The same behaviour has been observed by other authors for other paint systems [31,32].

3.3. Comparative remarks.

From the foregoing, it can be concluded that the paint systems *E-3-C*, *E-4-C* and *E-5-C*, and specially the last two, work extremely well on non-oxidized carbon steel with minimum surface preparation *Sa2½*. Conversely, the *E-2-C* formulation presents water uptake values much higher than the rest, whereas *E-3-C* presents clear signs of corrosion of the metallic substrate as of the initial moments of immersion. It must also be noticed that the single-coat system *E-1-C* (i.e., 100 μm thick epoxy-amine) exhibits water uptake values close to those found for the double-coat system containing the same primer and an acrylic top coat (*E-5-C*).

The other two single-coat systems exhibit worse behaviour. Thus, the system which consists in a single layer of epoxy-polyamine, *E-2-C*, exhibited significantly lower coating resistance values (two orders of magnitude lower than those exhibited by the sample *E-1-C*), a high uptake of water, and evidences of corrosion could be observed at the end of the experiment (after 888 hours). The resistance of the layer of corrosion products diminished drastically 216 hours after immersion. The poor protection characteristics provided by this resin to carbon steel are also evidenced from its comparison with the corresponding two-coat system. In this way, though similar water uptakes were observed in the initial stages of exposure for the two paint systems (i.e., 5.4% for *E-2-C* and 3.4% for *E-4-C*), as the time of immersion increased, their electrochemical behaviours differed considerably between the two that the water uptake by the double-coat system did not go beyond 37% after 888 hours of immersion, whereas degradation below the coating was observed in the single-coat paint.

From the analysis of the impedance data, it can be observed that the resistance associated with the paint coating presents very similar values over the first few moments of immersion ($6.87\cdot 10^6$ $\Omega\cdot cm^2$ for the two-coat system and $2.73\cdot 10^5$ $\Omega\cdot cm^2$ for the single-coat system), values which differ notably after 888 hours with differences of more than one order of magnitude. The values of the coating capacitance differ considerably as of the first few moments of immersion and throughout the whole experiment, with values of 34 $nF \cdot cm^{-2}$ for the two-coat system, and of 7.2 $\mu F \cdot cm^{-2}$ for the single-coat system.

When analysing the difference between the behaviour of the systems consisting of epoxy-amine + acrylics (*E-5-C*) and the single coat of epoxy amine (*E-1-C*), the results from the capacitance and the impedance showed a major similitude. Thus, both present coating resistance values around $5 \cdot 10^5$ $\Omega \cdot cm^2$ on initial exposure which decrease progressively over the remaining experiment. The capacitance data differ in one order of magnitude due to the difference in the thickness of the layers of paint applied, with values of 5.4 $nF \cdot cm^{-2}$ for the two-coat and 36 $nF \cdot cm^{-2}$ for the single-coat system.

Finally, the epoxy-amine primer has shown to be an effective single-coat system to protect carbon steel from the corrosive attack, although the same cannot be said for the other two single-coat systems based on epoxy-polyamine and acrylic-polyurethane.

4. CONCLUSIONS

From the analysis of the impedance spectra measured for different waterborne paint systems, the excellent characteristics towards the anticorrosion protection of carbon steel provided by a single-coat application of epoxy-amine was demonstrated. And this happened in detriment of the epoxy-amine + acrylic-polyurethane system, in that the former presents lower values of water uptake and higher values of resistance for the layer of paint.

The application of a single-coat of acrylic polyurethane (50 μm) did not protect the substrate efficiently either, and clear signs of metal corrosion under the coating could be observed almost from the initial moments of immersion.

Most of the EIS spectra could be fitted with an equivalent circuit containing two R(CPE) components of symbol *R(R(Q(RQ)))*, delivering very small error distributions compared to other equivalent circuits. In the initial moments of immersion, the Nyquist diagrams present capacitive profiles, and the number of time constants present in the spectra increased with the duration of immersion in the test electrolyte.

The water uptake values determined for these waterborne coating systems were found to be systematically smaller than those previously determined from non–ecological paint formulations, as well as higher values of the coating resistance supplied by the polymer layers in general.

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