Evaluation of Environmentally Friendly Paints Over Bare Steel Using Electrochemical Techniques

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ABSTRACT

The protective characteristics and properties of various applications, be it single or multi-coating, of bare steel with ecological paint have been studied using electrochemical techniques. Tests have been carried out with epoxy polyamine, epoxy amine and epoxy acrylic as undercoat and acrylic polyurethane and acrylic paint as second coat. It was found that the best system was a single coat of epoxy amine. A single coat of acrylic polyurethane (50 µ m) is not sufficient to protect the substrate efficiently and signs of corrosion are to be observed under the substrate from the initial moments of immersion onwards. The Nyquist profiles obtained from the EIS measurements are an excellent fit to a parallel equivalent circuit R(R(C(RC))).

Keywords: ecological paint, bare steel, corrosion, EIS

INTRODUCTION

When steel, a metal widely used as the main structural material in different applications, is in contact with an aggressive environment it can corrode. Therefore, in order to delay and/or to reduce the deteriorating action of corrosive media, a number of metallic and organic coatings have been developed. Organic coatings, particularly paints, constitute one of the most widely employed methods of protection to prevent the corrosion of steel. The most frequently used paints are those that utilise volatile organic compounds (VOCs) as solvents. Nowadays, so-called ecological paints have been the subject of analysis for some time. They were developed for various reasons, amongst the main reasons of which were the drastic reduction in the Volatile Organic Compounds (VOCs) in the present legislation, together with the economic importance of finding cheaper and more profitable types of paint [1-3]. The main group of ecological finishes studied include water-based types,

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systems with a high solids (i.e. low solvent) content and the paints 100% free of organic solvents [4].

The present legislation has inclined towards the drastic reduction of the use of VOCs in order to protect against and reduce environmental degradation. The use and emission of VOCs into the environment has increased dramatically over the last twenty years and has produced 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 [5-7] has led many paint manufacturers to look into systems of anti-corrosive paints such as those based on zinc phosphates [8].

The new generation of paints that employ non-contaminating inhibitors and water as solvent usually suffer from the problem that they don't achieve as good anticorrosive performance as the paints that they are intended to replace [9]. The aim of this work is to study the behaviour of five types of differing ecological paints on bare steel using impedance measurements.

EXPERIMENTAL

Paint Systems

The samples studied were bare steel rectangular test pieces of 100 mm x 150 mm x 2 mm with a minimum surface preparation of Sa2½. Five systems of differing paint types were tested: epoxy polyamine + acrylic polyurethane (average thickness of 150 µm) (E-1-C) and epoxy amine + acrylics (average thickness of 160 µm) (E-2-C) respectively. The systems called E-3-C, E-4-C and E-5-C are single coat systems used with epoxy amine, epoxy polyamine and acrylic polyurethane with an average thickness of 100, 100 and 50 µm respectively. In table 1, the main characteristics of the paint systems are shown.

Table 1: Main features of the priming coats employed.

Type of resin	% solids content	Pigment
Polyamine epoxy	85 ± 1	Aluminium flake
Acrylic polyurethane	52 ± 1	–
Polyamide epoxy	56 ± 1	Micaceous iron oxide (MIO)
Acrylic	44 ± 1	–

Electrochemical Impedance Spectroscopy

Each paint system was submitted to EIS measurements. We worked with a flat cell which guarantees that the solution is stagnant and which allowed a working area of 5.56 cm^2. Figure 1 is a schematic representation of the cell used in the study. All the measurements were taken inside a Faraday cage for electrical isolation. Capacitance measurements were taken at 48 hours, 144 hours, 216 hours, 312 hours, 384 hours, 480 hours, 552 hours, 648 hours, 720 hours and 816 hours. The conditions of measurement were as follows: frequency scan of 10 – 50 kHz, an AC amplitude of 10 mV rms with 14 measurement points per decade. At the same time, impedance measurements were carried out at a range of frequencies which spanned between 10 kHz and 100 mHz. A solution of 5% NaCl was utilised as the aggressive medium. A saturated calomel electrode was used as the reference electrode and a platinum mesh as counter-electrode.
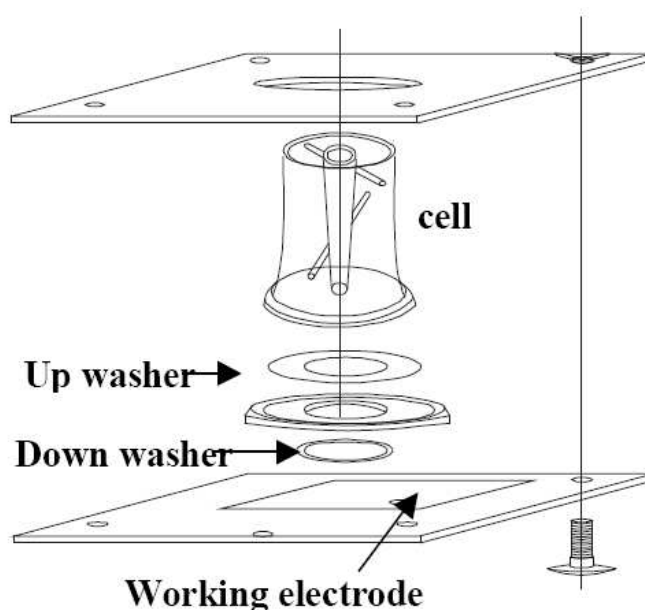

Figure 1: The electrochemical plane cell used in the study, with 5.56 cm^2 of working area is appreciated with glass cell and compound inferior support by three washers, two rubber and a rigid of teflon that guarantee the water tightness of the system

ZSimpWin [10] software was used to model the data obtained in order to analyse which equivalent circuit best fitted the data. An EG&G Princeton Applied potentiostat, model 263, and a Lock-in EG&G Princeton Applied Research 5210 automatic operation amplifier were used.

EXPERIMENTAL RESULTS

Electrochemical Impedance Spectroscopy

Figure 2 (a to c) gives a figurative representation of the variations in the EIS profile according to the time of immersion and the different type of format tested.

In general terms, over short periods of immersion, the capacity behaviour was exactly the same as can be observed in Figure 2. As the time of immersion increased, more time constants appear in the system. The fit of the impedance values obtained was carried out using the equivalent circuit showed in Figure 3. Results of the circuit fitting for different immersion times for the different paint systems are shown in table 2. The evolution of the two time constants are the same in the five cases in study, that is to say, a regular increase of the C_{dl} and the corresponding R_{ct} decrease.

Table 2: Parameter values for the different paint systems (0, 48 and 216 hours) (R in $\Omega \cdot cm^2$ and C in F).

| Hours of immersion	C_p	n1	R_p	C_{dl}	n2	R_{ct}
E-1-C 0	$5,24 \cdot 10^{-10}$	0,916	$1,29 \cdot 10^6$	$1,17 \cdot 10^{-09}$	0,508	$4,37 \cdot 10^9$
E-1-C 48	$1,19 \cdot 10^{-09}$	0,863	$4,53 \cdot 10^7$	$1,20 \cdot 10^{-08}$	0,361	$5,04 \cdot 10^8$
E-1-C 216	$1,48 \cdot 10^{-09}$	0,899	–	$5,60 \cdot 10^{-08}$	0,132	$4,68 \cdot 10^7$
E-2-C 0	$1,31 \cdot 10^{-09}$	0,877	$5,55 \cdot 10^8$	$2,25 \cdot 10^{-09}$	0,601	$4,34 \cdot 10^{10}$
E-2-C 48	$2,14 \cdot 10^{-09}$	0,847	$1,63 \cdot 10^8$	$5,94 \cdot 10^{-09}$	0,779	$3,26 \cdot 10^8$
E-2-C 216	$3,12 \cdot 10^{-09}$	0,835	$6,09 \cdot 10^7$	$1,02 \cdot 10^{-08}$	0,694	$1,40 \cdot 10^8$
E-3-C 0	$3,16 \cdot 10^{-09}$	0,861	$5,38 \cdot 10^5$	$1,36 \cdot 10^{-06}$	0,439	$1,85 \cdot 10^{12}$
E-3-C 48	$1,28 \cdot 10^{-09}$	0,869	$4,08 \cdot 10^7$	$6,12 \cdot 10^{-08}$	0,545	$1,14 \cdot 10^8$
E-3-C 216	$1,58 \cdot 10^{-09}$	0,884	$2,57 \cdot 10^7$	$1,68 \cdot 10^{-08}$	0,318	$2,24 \cdot 10^8$
E-4-C 0	$3,41 \cdot 10^{-09}$	0,871	$3,12$	$3,32 \cdot 10^{-07}$	0,953	$6,44 \cdot 10^5$
E-4-C 48	$3,48 \cdot 10^{-09}$	0,142	$1,197$	$5,14 \cdot 10^{-09}$	0,852	$6,96 \cdot 10^5$
E-4-C 312	$1,41 \cdot 10^{-09}$	0,307	$9,99 \cdot 10^{-3}$	$7,54 \cdot 10^{-10}$	1	$1,44 \cdot 10^5$
E-5-C 0	$2,66 \cdot 10^{-09}$	0,875	$9,10 \cdot 10^2$	$2,16 \cdot 10^{-09}$	0,861	$1,52 \cdot 10^7$
E-5-C 120	$9,70 \cdot 10^{-10}$	1	$1,869 \cdot 10^3$	$1,53 \cdot 10^{-05}$	0,445	$1,02 \cdot 10^4$
E-5-C 216	$8,70 \cdot 10^{-10}$	1	$3,199 \cdot 10^3$	$6,74 \cdot 10^{-06}$	0,648	$1,00 \cdot 10^4$
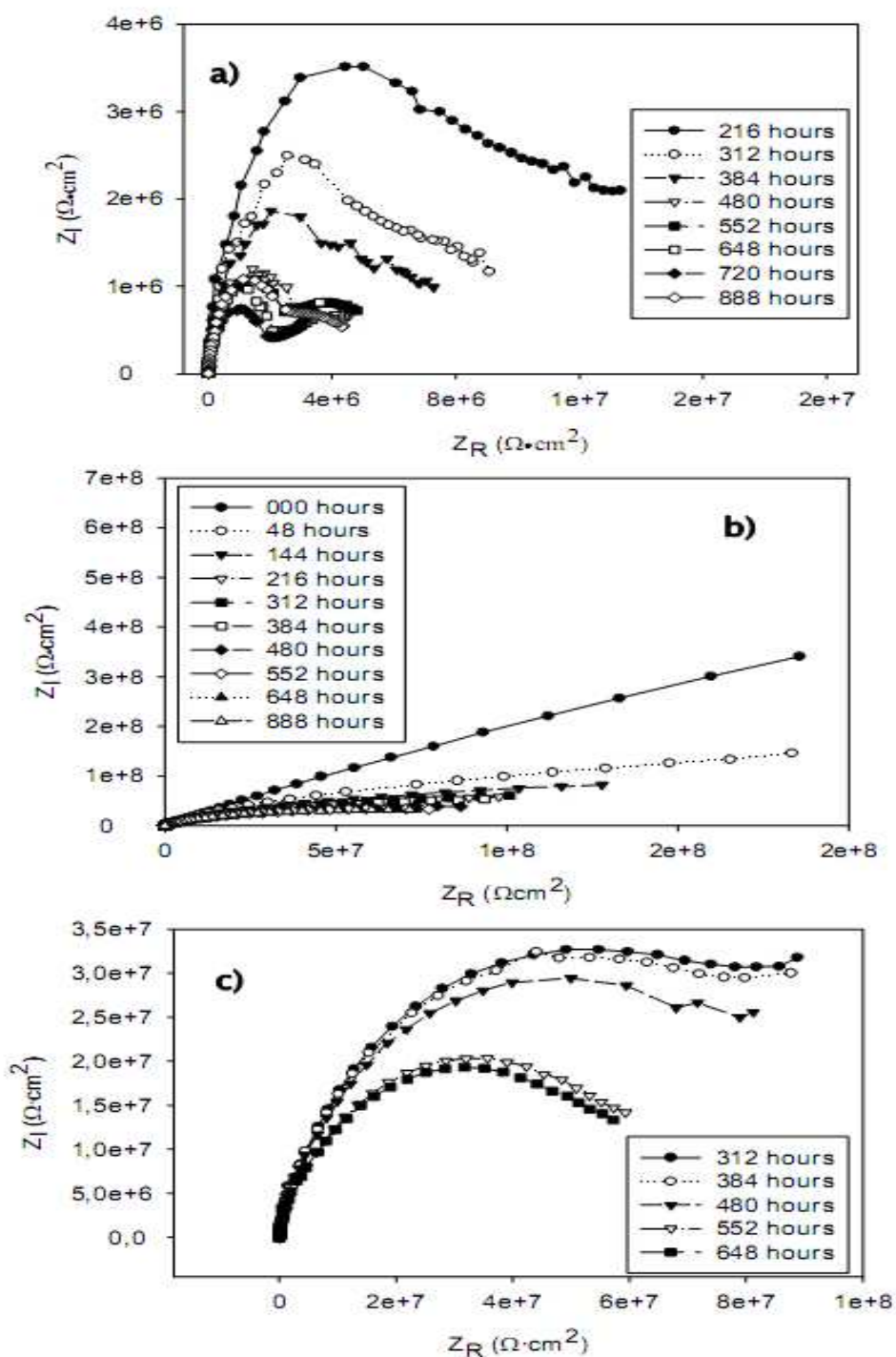
Figure 2: The variation in the Nyquist diagrams for the paint system: (a) E–1–C (epoxy polyamine (100 μm) + acrylic polyurethane (50 μm)); (b) E–2–C (epoxy amine (100 μm) + acrylics (60 μm)) over 888 hours of immersion; (c) E–3–C (epoxy amine (100 μm)) over 648 hours of immersion.
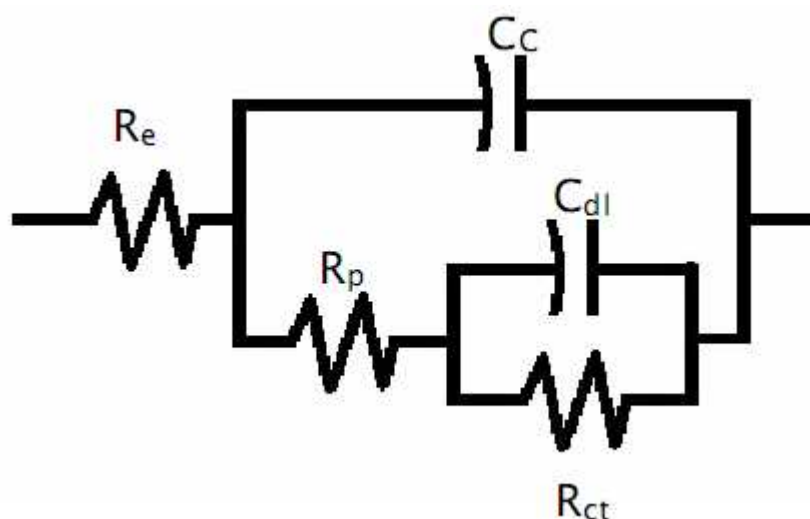
Figure 3: Equivalent circuit, used for modeling the impedance data where R_e is the solution resistance, R_p and C_c the paint film resistance and paint film capacitance, respectively; C_{dl} the double layer capacitance and R_{ct} the charge transfer resistance of an electrochemical (corrosion) process.

The capacity behaviour observed for the epoxy polyamine + acrylic polyurethane system (E-1-C) is over short periods of time (<2 days). Over that time, a semi-circle is to be observed at high frequencies, which indicates a degradation of the coating system. From the data modelling of the results obtained with various equivalent circuits, we can extract the R_p values for this type of system. The value of R_e is small in comparison with R_p and, therefore, can be ignored. The circuit used in each case was the one 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 phase constants.

The epoxy amine + acrylic systems (E-2-C) and the epoxy amine (E-3-C) showed capacitive behaviour over the whole interval of exposure, with this behaviour even more evidenced in the case of the format E-2-C. In the other three coating systems, the capacitive behaviour was to be observed in the first few moments of immersion (< 2 days). For long periods of immersion, in the case of the systems E-1-C and E-5-C, the size of the high frequency semi-circle is modified whereas the low frequency data present a depressive semi-circle. Both semi-circles vary according to the increase in the time of exposure and become progressively smaller.

It can be seen, then, from the impedance diagrams that the coating systems E-1-C, E-4-C and E-5-C present the same Nyquist profile made up of two phase constants, much the

same as occurs in the case of the formats E-2-C and E-3-C, which present the same profile made up of one phase constant.

System E-5-C offers a less defined behaviour than the rest of the systems under study, above all, in the initial stages of immersion. The E-5-C format could not be modelled consistently due to the fact that from initial immersion, corrosion was observed under the layer of paint. The data modelling which corresponds to the E-4-C system reveals a low resistance of the layer of paint (some 100 times inferior to the others) and a high percentage of penetration of water, with indication of corrosion observed some 888 hours of immersion. The resistance of the layer of the products of corrosion diminished drastically 216 hours after immersion.

Using the impedance measurements for each system, we analyzed the variation in the variables R_p and C_c 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 fluctuate according to the coating system. Systems E-2-C and E-3-C present higher R_p values and have greatest variation in the same. System E-2-C presents initial values of R_p at 1.4×10^8 ($\Omega \cdot cm^2$) in the first hours of immersion, later to fall to values of 5.6×10^4 ($\Omega \cdot cm^2$) after 888 hours of immersion. In contrast for system E-3-C, the variation in is from 3.7×10^7 ($\Omega \cdot cm^2$) to 7.4×10^5 ($\Omega \cdot cm^2$) over the same time interval. 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-2-C and E-3-C, the values of R_p are initially over 10^7 $\Omega \cdot cm^2$, reaching values of up to 10^8 $\Omega \cdot cm^2$ in the case of the system E-2-C in the initial moments of exposure. Systems E-4-C and E-5-C present much lower initial values (10^4 ($\Omega \cdot cm^2$)), with the values registered for the E-4-C standing at 10^5 $\Omega \cdot cm^2$ in the initial moments of immersion.

In the case of system E-5-C, very evident processes of corrosion are to be observed under the substrates as of the initial moments of immersion since there are two clearly differentiated time constants. The values measured initially for R_p (of the order 10^4 $\Omega \cdot cm2$) indicate that the system is not effectively separated from the aggressive medium in this case. The initial measurements of the EIS of this system could not be carried out with reproducibility due to the instability of the system.
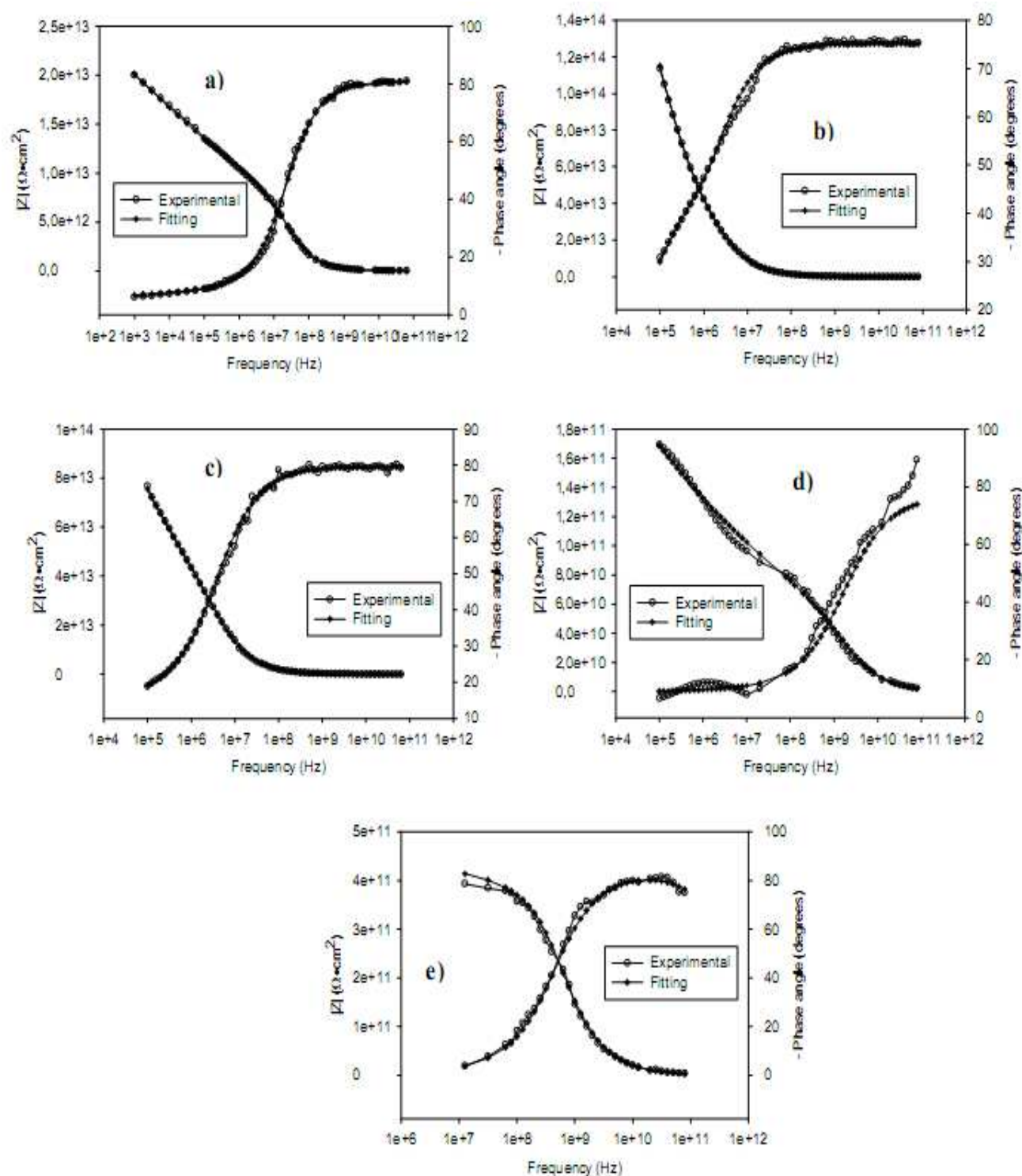
Figure 3: Measured (O) and fitted (+) Bode plots for the five paint systems after 216 hours of immersion: (a) (E–1–C; (b) E–2–C; (c) E–3–C; (d) E–4–C and (e) E–5–C.

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A decrease in the R_p and C values was noted in the systems studied as the time of immersion increased. The rest of the paint systems showed no evident indication of corrosion after 888 hours of exposure. The variation observed in the gradient of R_p over t can be explained on the basis of two phenomena: the increase in the density of the pore and the partial sealing of the pores due to the 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 different paint systems [11,12].
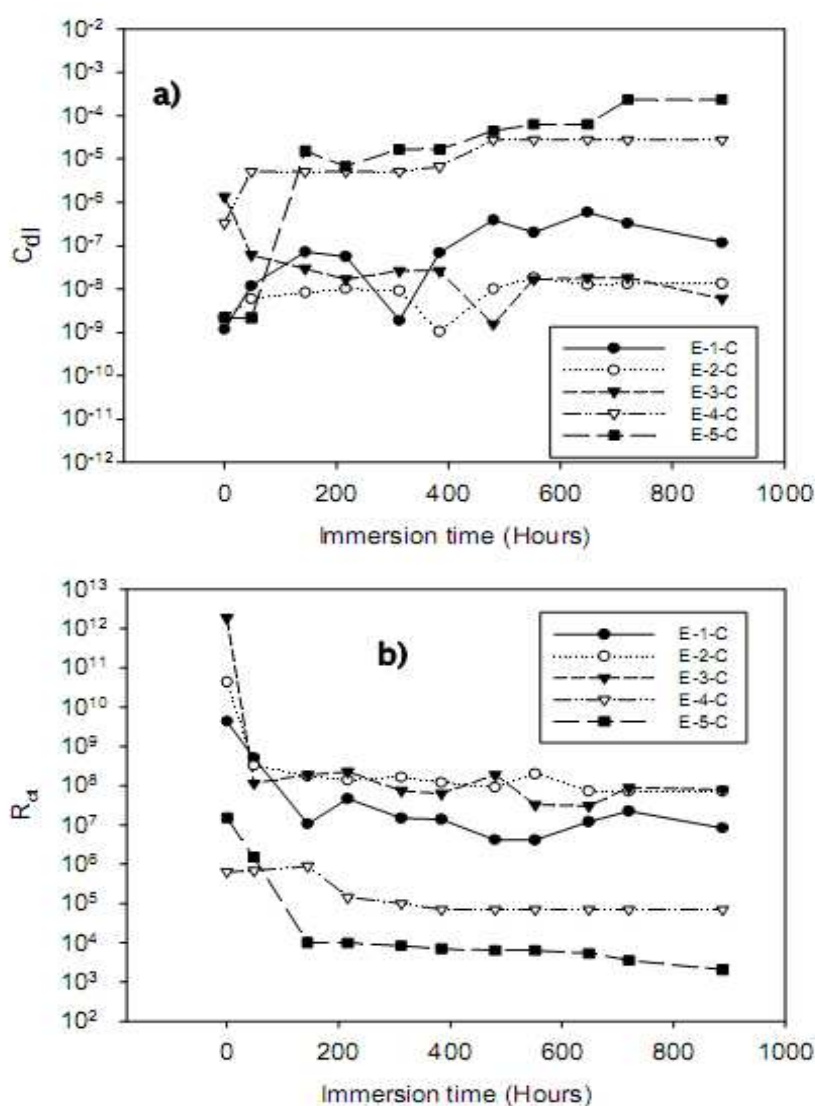

Figure 4: Evolution of the double layer capacitance (a) and the charge transfer resistance (b) for the five paint systems

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WATER UPTAKE

The capacity of the paint system was determined using equation 1 [13].

$$C = \varepsilon\varepsilon_0 \cdot \frac{S}{d} \quad \text{.... (1)}$$

Given the fact that the dielectric constant of the paint covering is small compared with that of water [14], water uptake produces an relatively large increase in the capacitance of the coat of paint. The capacitance behaviour in all of the systems in our study is the same. In the initial moments of immersion, this is small and diminishes drastically in the first moments of immersion to stabilize later. In figure 4 we can see some of the Nyquist diagrams obtained over the varying times of immersion.

The capacitance shown in the circuit used in the modelling of the data obtained uses a constant phase element (CPE) expressed as follows:

$$Z = (j\omega)^n / Y^0 \quad \text{.... (2)}$$

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

The n coefficient of the CPE varies considerably over the first few moments of immersion to then decrease over the first few hours of immersion then stabilizing after long times of exposure.

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 [15] which is as follows:

$$\Phi = \frac{\log(C_t / C_0}{\log 80} \quad \text{.... (3)}$$

Where Φ is the fraction of the volume of water in the coating, C_t is the capacitance of the layer of paint over 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 20°C, which is the average temperature for the experiment.

As the period of immersion increases, so does the value of Φ, eventually stabilizing, as does the coating capacitance. The system, which presents the lowest levels of change (water penetration), is for E-3-C, with a percentage of 0.5% after 10 hours and 19.8% after 888 hours. Systems E-1-C and E-2-C present very similar intervals (4.5% and 3.4% after 10 hours and 40.4% and 36.8% after 888 hours respectively). Systems E-4-C E-5-C present short intervals at 10 hours (5.4% and 35% respectively) which become extremely high after 888 hours (>38%). In comparison with other studies, the values of water uptake found here are lower [13].

It can be observed quite clearly that coating systems E-1-C, E-2-C and E-3-C, and above all the last of these, work extremely well on non-oxidised bare steel with minimum surface preparation Sa2½. The E-C-4 paint system presents water uptake values much higher than the rest whereas the E-5-C system presents clear signs of corrosion of the metallic substrate as of the initial moments of immersion.

We should point out that the coating system with one sole coat of epoxy amine of 100 μm presents water uptake levels comparable to the multi-layer system of the same undercoat together with a second acrylic layer.

The other two single coat systems present worse behaviour. Thus, the system which consists in a single layer of epoxy polyamine presents water uptake values of 5.4% in the initial stages of exposure whereas the two layer system presents values of 3.4%. However, as the time of immersion increases, the behaviour differs considerably between the two systems and deterioration under the substrate in the single layer system can be observed whereas the water uptake in the two layer system does not go beyond 37% after 888 hours of immersion.

From the analysis of the impedance data, we can see that the resistance associated with the coat of paint presents very similar values over the first few moments of immersion (6.9 x 10^6 $\Omega \cdot cm^2$ for the two layer system and 2.7 x10^5 $\Omega \cdot cm^2$ for the single layer system), values which differ notably after 888 hours with differences of up to ten units between said values. The values of capacity do differ considerably as of the first few moments of immersion and throughout the whole experiment, with values of 0.19 μF for the two layer system and values of 40 μF for the single layer system.

When analyzing the difference between the behaviour of the system consisting in epoxy amine + acrylics and the single coat of epoxy amine, the results for capacity and impedance showed high levels of similitude. Thus, we can see that both present resistance values for

the layer of paints around $5 \cdot 10^5$ $\Omega \cdot cm^2$ on initial exposure, which decreases progressively over the rest of the experiment. The capacity measurements differ in order of magnitude due, logically, to the difference in the thickness of the layers of paint applied, with values of 0.03 μF for the two layer system and 0.2 μF for the single layer.

The epoxy amine undercoat is shown to be an effective single coat system to check the corrosive process although the same cannot be said for the single layer systems of epoxy polyamine and acrylic polyurethane.

Conclusions

From the analysis of the different formulae for systems of ecological paints, we can see that the best results are obtained with a single coat of epoxy amine, 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 format of painting with a single layer of acrylic polyurethane (50 μm) does not protect the substrate efficiently either, with signs of corrosion evident under the substrate as of the initial moments of immersion.

From the results obtained using EIS, we can observe that the Nyquist profiles obtained are an excellent fit to the equivalent circuit R(R(Q(RQ))), offering minimum margins of error as compared with other circuits experimented with. In the initial moments of immersion, these diagrams present capacitive profiles, increasing the number of time constants as the time of immersion increases.

The values obtained for water uptake are much inferior to those found for other systems of non – ecological, with higher values of resistance offered by the layers of paint in general.

Acknowledgements

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