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Lifetime prediction of waterborne acrylic paints with the AC–DC–AC method

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Abstract

In this study an accelerated method for the evaluation of painted metals is proposed. Specifically, the proposed method has been applied in a study of the process of degradation of two water-based paints applied to a carbon steel surface. The technique is based on the application of cycles combining measurement of electrochemical impedance spectra, cathodic polarisation steps, and recording of the evolution of the corrosion potential of the system in function of time. The results obtained from this method are compared with those obtained from studying the evolution of the impedance spectra of both systems in function of the time of immersion, for periods of immersion of the order of 200 days.

The results obtained indicate that the method proposed does not introduce alternations in the degradation mechanism of the paints studied. Moreover, it gives a considerable reduction of the time required for tests, since it is possible simulate, in hours, degradation processes that normally take place over hundreds of days. Lastly, the method has been demonstrated to have sufficient sensitivity to detect changes in the protective properties of the systems studied.

Keywords: Water-based paints; Steel; EIS; AC–DC–AC method; Cathodic delamination

1. Introduction

The substitution of traditional coatings that utilise organic compounds as solvents by others of new formulation, based on the use of water as solvent, is a strategy that has been under development over the past 20 years. The main impulse driving the market towards the use of water-based products is the pressure of the regulations aimed at reducing adverse environmental impacts by encouraging the use of products with low content in volatile organic compounds (VOCs) [1].

In the face of the growing number of new products coming onto the paint market, it is becoming necessary to find methods for the rapid evaluation of the anticorrosive protective capacity of these coatings, in function of their specific conditions of application. The key factor for a test method to be considered practical is that there should be a good correlation between the laboratory and the real field tests in predicting the length of the useful life of the paint in service [2].

Electrochemical methods, principally electrochemical impedance spectroscopy (EIS), have come to be employed successfully in monitoring the changes that take place in the physical properties of a paint during its exposure in a particular corrosive medium [3–5]. However, from reliable measurements of EIS, it is difficult to make predictions of the evolution over time of the behaviour of a paint, or to make comparisons between different metal–paint systems as to how they will evolve.

In this study, a method of evaluation has been devised based on performing cycles in which measurements of EIS over the course of time are combined with tests of corrosive stress by means of cathodic polarisation. This method (AC–DC–AC) has been applied to predicting the useful life of acrylic water-based paints. The results obtained have been compared with classic tests for the evaluation of paints. This comparison demonstrates that this method could prove to be a very useful tool for the rapid evaluation and classification of paints with respect to their anticorrosive behaviour [6].

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2. Experimental

2.1. Material and preparation of test pieces

The behaviour of two acrylic water-based paints has been studied. The first is a commercial paint, Intercryl 506, produced by International Coatings (Paint 1). The second is a new formulation paint, composed of an acrylic resin with a zinc phosphate content of 17% by volume in dry paint (Paint 2). Both contain zinc phosphate as inhibitor pigment. The material tested was a carbon steel of low alloy, type AISI 1010, in the form of rectangular test pieces of 100 mm × 150 mm × 2 mm. As a prior step to the process of painting, the samples were subjected to a surface preparation treatment of St2 type brushing according to the standard UNE 48302. Next the samples were degreased with acetone and the paint was applied. For this a short-pile roller was employed, applying sufficient layers of paint to give a thickness of 75 μm in one case and of 100 μm in another, these being the two paint thicknesses selected for this study.

The test pieces thus prepared were subjected to the tests described in the following sections of the paper. Additionally, an incision using a grater pencil was made in some of these test pieces, in the form of a scratch of 1 cm length, for later evaluation of the behaviour in solution.

2.2. Electrochemical measurements

The protective capacity of the coatings was evaluated by monitoring the behaviour of the samples in immersion tests, using electrochemical techniques. For this, electrochemical cells were constructed in which an area of 13 cm^2 of one of the painted surfaces of the test pieces was exposed; the test piece thus served as the working electrode (Fig. 1). A solution of 3.5% NaCl was utilised as the aggressive medium. A saturated calomel electrode was used as the reference electrode, and a graphite bar as the counter-electrode. A 1287 potentiostat coupled to a 1255 frequency response analyser (FRA), both from Solartron, was used to make the electrochemical measurements.

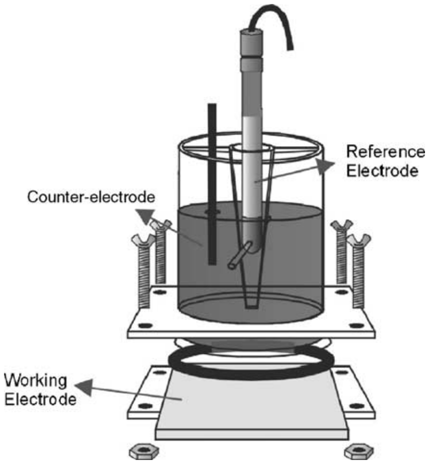

Fig. 1. Experimental device: electrochemical cell.

2.2.1. Electrochemical impedance spectroscopy

Electrochemical impedance spectra were recorded over the course of time for the painted test pieces, observing the degradation of the system over a maximum period of 230 days. The range of frequencies employed for recording the impedance spectra was from 10^5 to 10^{-2} Hz, and the amplitude of the signal was 10 mV with respect to the corrosion potential.

2.2.2. Accelerated AC–DC–AC technique

The procedure consisted of the following phases:

(I) Recording of EIS at the rest potential (OCP). This indicates the current state of the metal–paint system.
(II) Application of cathodic polarisation at -2 V for 20 min.
(III) Recording of the potential for 180 min, until a new stationary state is reached.

Steps I–III are repeated by means of programmed cycles, until the loss of the protective capacity of the coating is observed in the EIS record of Step I of the following cycle. The approximate length of time required for a cycle is 3.5 h.

The potential applied in Step II and the duration of Steps II and III may vary in function of the characteristics of the system studied. The values proposed correspond to those that have led to the best results for the systems studied here.

3. Results and discussion

3.1. Accelerated AC–DC–AC technique, compared with EIS

Fig. 2 presents the impedance spectra obtained by applying the AC–DC–AC method to samples painted with the Paint 1, to a thickness of 75 μm. In this figure it can be observed that after four cycles of cathodic stress, the sample loses its protective properties. This finding can be deduced clearly from the corresponding Bode diagrams, in which a considerable decrease of the modulus of impedance is observed. The moment when the modulus of impedance falls below $10^6\ \Omega\,\text{cm}^2$ was set as the criterion that degradation of the paint has been produced. In this particular case, the initial value of $2 \times 10^6\ \Omega\,\text{cm}^2$ decreases to $4 \times 10^4\ \Omega\,\text{cm}^2$ after four cycles.

In the diagrams included in Fig. 2, it is observed that, after applying the first cycle, there is an increase in the impedance of the system. In [7] a detailed study is made of the behaviour of this paint, and it is proposed that this initial increase in the impedance of the system is due to the inhibitory effect of the zinc phosphate pigments.

Fig. 3 gives the results obtained in the study of the evolution, with time of immersion, of the EIS diagrams

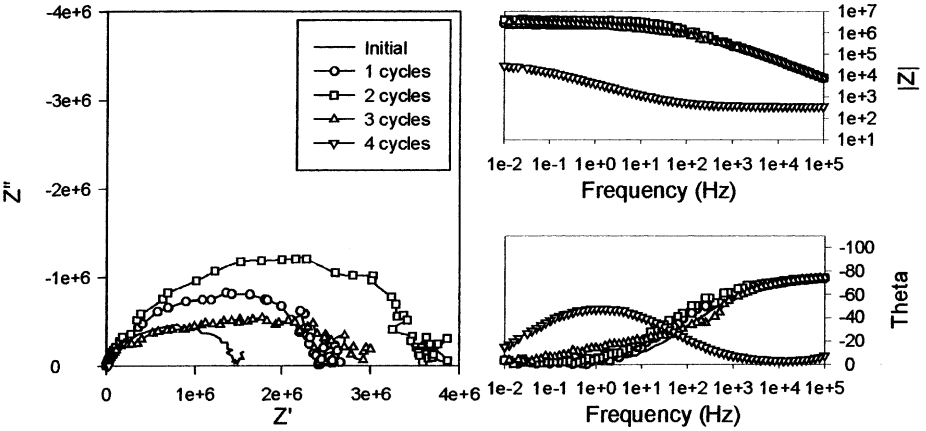

Fig. 2. EIS spectra after applying cycles of AC–DC–AC method to Paint 1 (75 μm).

corresponding to this same system. The duration of this study was 230 days, a period in which the degradation of the paint took place. From observation of these diagrams, it can be deduced, firstly, that as a consequence simply of the exposure, there is also an increase of the impedance during the first days of exposure. It is after 200 days when a decrease of the impedance of the system begins to be observed, with degradation occurring by 230 days.

If the diagrams included in Figs. 2 and 3 are compared, it can be deduced that, by applying the AC–DC–AC method, the system follows an evolution similar to that produced naturally. Further, as can be confirmed in Fig. 4, the spectra obtained after four AC–DC–AC cycles and after 230 days of exposure present considerable similarity.

Fig. 5 shows the spectra obtained by the applying the AC–DC–DC method to samples with Paint 2. If these spectra are compared with those included in Fig. 2, it can be observed that the two systems follow a different evolution. In Paint 2, unlike the findings with Paint 1, a decrease of the impedance is observed from the first cycle. This same evolution can be observed in the spectra recorded in the experiments of free immersion, Fig. 6. Degradation with time evolution is more usual in paints, when ion and water penetrates into the coating and electrochemical reactions (corrosion) take place at the polymer–metal interface.

In Fig. 5, it can be observed that, after the second cycle, impedance values of less than $10^6\ \Omega\ \mathrm{cm}^2$ are obtained; hence it could be considered that, at this point, the coating is not protecting the painted surface adequately [8,9]. However, the change is not too significant in comparison with the values obtained after the first cycle. It is after the third cycle when a dramatic variation of the EIS spectrum takes place. The loss of the protective effect of the paint can be observed clearly in the Bode diagrams, by the variation that is produced in the impedance values in the high frequency range.

Fig. 6 presents the EIS diagrams corresponding to the immersion tests. In this figure, it can be observed that the degradation of this paint takes place gradually from the first weeks of immersion, with the definitive degradation of the system occurring by 185 days. This trend coincides with that observed by applying cycles of cathodic stress. Additionally, the time and the number of cycles necessary for the paint to be degraded are less than those observed for Paint 1.

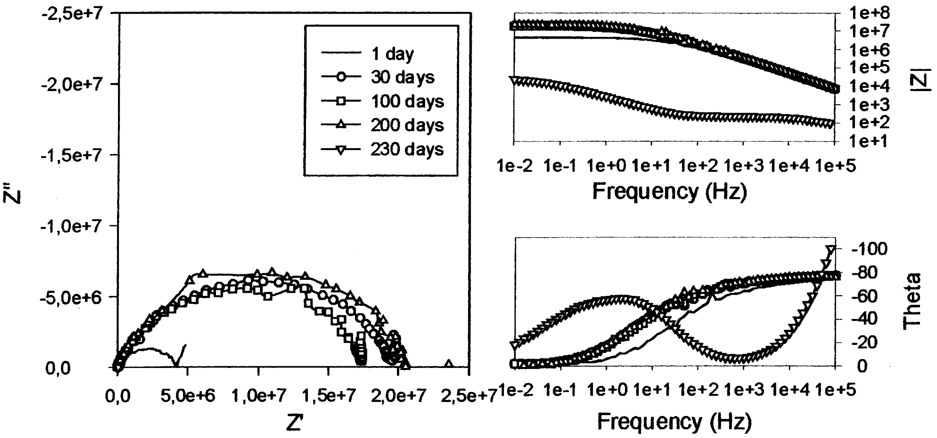

Fig. 3. EIS evolution of samples coated with Paint 1 and immersed in a 3.5% NaCl solution.

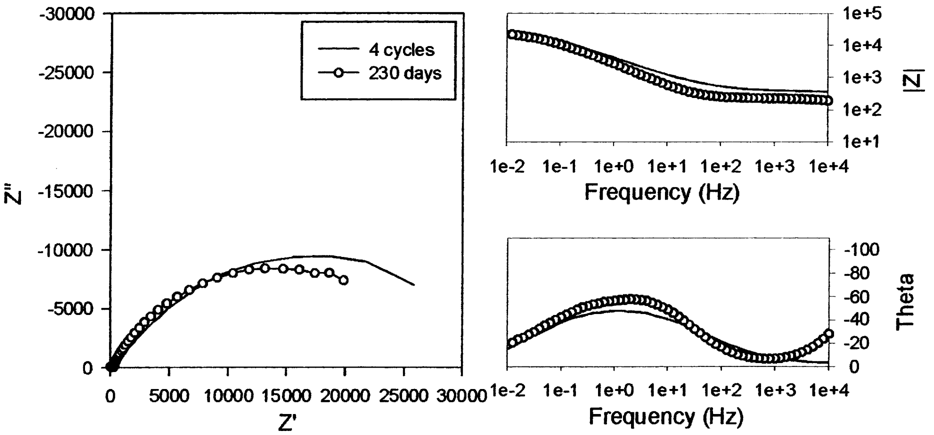

Fig. 4. EIS spectra after four cycles with AC–DC–AC and 230 days of immersion for Paint 1 (75 μm).

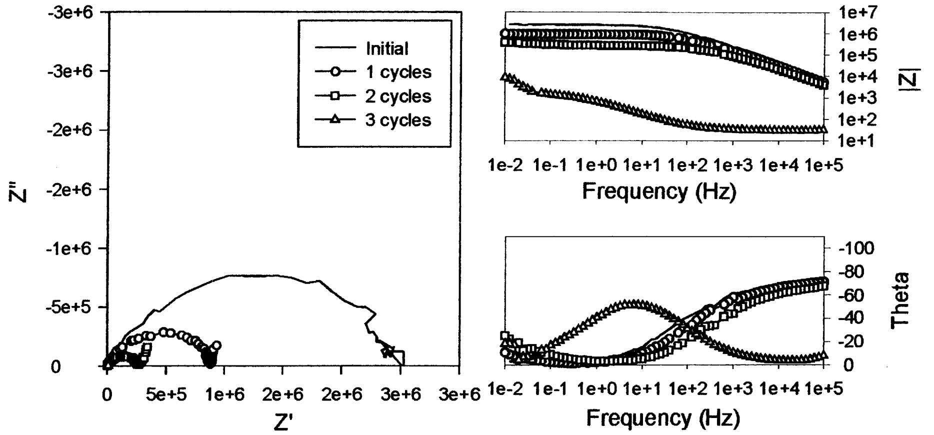

Fig. 5. EIS spectra after applying cycles of AC–DC–AC method to Paint 2 (75 μm).

In summary, the results obtained indicate that a good correlation exists between the studies made by means of immersion and by means of AC–DC–AC cycles. This would be a first test of the validity of the procedure proposed as an accelerated method of evaluation of painted metals.

The test method proposed is based on accelerating the delamination of the coating by means of cathodic polarisation. It can be deduced, therefore, that this method would find application in coatings that are degraded in service by cathodic delamination. Therefore, in systems that may be more susceptible to oxidative degradation, the accelerated

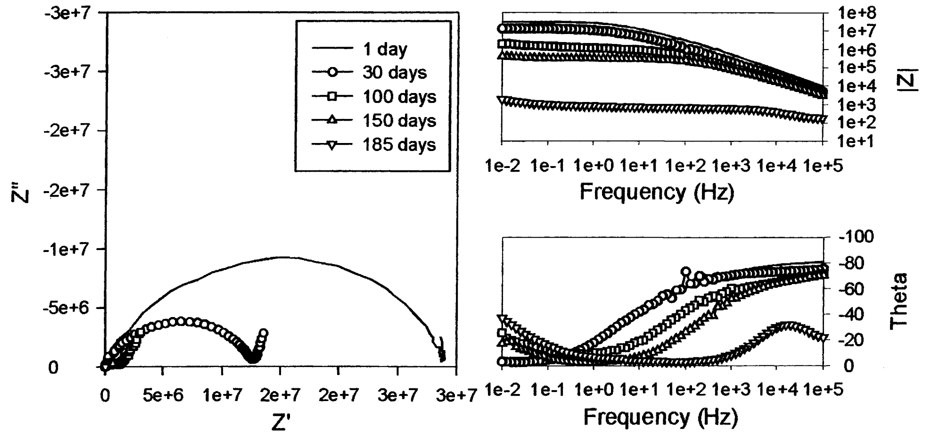

Fig. 6. EIS evolution of samples coated with Paint 2 and immersed in a 3.5% NaCl solution.

method could be applied with anodic stress. In the case of the paints studied here, both methods were tested and it was confirmed that the system could only be degraded by the application of cathodic stress.

In the bibliography, it is proposed that the degradation of painted steels takes place when water and oxygen penetrate the coating film, this phenomenon causing the separation of the paint from the metal [10]. This process is termed cathodic delamination and is initiated in defects such as scratches or scoring, pores or zones of the paint with reduced density of crosslinking. The anodic reaction or oxidation of the metal is physically separated (takes place in adjacent zones) from the cathodic reaction of oxygen reduction. In the cathodic zones, a high concentration of OH^- ions is generated, which raises the pH of the medium, causing the loss of adherence between the metal and the paint [11]. While the steel under the blistering customarily presents a bright appearance, with no signs of corrosion, once the coating has separated from the substrate, the metal is left exposed to the medium and the polymeric coating no longer provides it with protection. Hence, a determining factor in preventing the system from suffering cathodic delamination will be that the electrical layer at the interface should not develop between the substrate and the paint. This is achieved by improving the barrier properties of the coating and increasing the adherence between the metal and the paint, although these two qualities are generally associated one with the other. Thus, to achieve a good adherence in dry and wet conditions, a solution is to improve the impermeability of the film, preventing water from easily reaching the substrate and breaking polar bonds [12].

3.2. Study of the effect of paint thickness, by means of AC–DC–AC

In accordance with the discussion in the preceding part, one of the possible ways to avoid or delay the appearance of cathodic delamination processes is to improve the barrier properties of the polymeric films. This objective can be met by the addition of anticorrosive pigments or by increasing the thickness of the layer of paint. Given that the paints studied here contain inhibitive pigments, it was decided to study the effect of the coating thickness on the protection conferred on the steel.

Hence, the AC–DC–AC technique has been used to study the behaviour of the two paints applied at a thickness of 100 μm. Fig. 7 includes the data corresponding to the study made with Paint 1. In this figure, it can be observed, firstly, that by increasing the thickness, an improvement is obtained in the initial properties, compared with when the same paint is applied at 75 μm. Moreover, on increasing the thickness, the evolution observed in the impedance diagrams with the number of cycles is similar to that observed for 75 μm thickness. In other words, there is an increase in the impedance in the first cycles, but this then diminishes.

Additionally, in Fig. 7 it can be seen that the increase of thickness produces a better behaviour over time. When Paint 1 was applied at a thickness of 75 μm, its degradation took place after four cycles of cathodic stress. In Fig. 7 it can be seen that the number of cycles before degradation increases to 10 when a thickness of 100 μm is utilised. A similar behaviour is observed for Paint 2: when working with a thickness of 100 μm, the degradation is not produced until after six cycles of stress, against the three cycles measured for 75 μm. Again, evolution of EIS with cycles is similar to that observed for 75 μm thickness (Fig. 8).

In short, in the two systems studied, increasing the thickness of the paint provides an improvement in the corrosion behaviour. The AC–DC–AC technique proposed has been demonstrated to be sensitive to these improvements. This result demonstrates the potential usefulness of the method proposed for evaluating this type of system.

3.3. Study of paints with defects, by means of EIS

In the bibliography there are descriptions of accelerated methods, based on the study of systems in which artificial

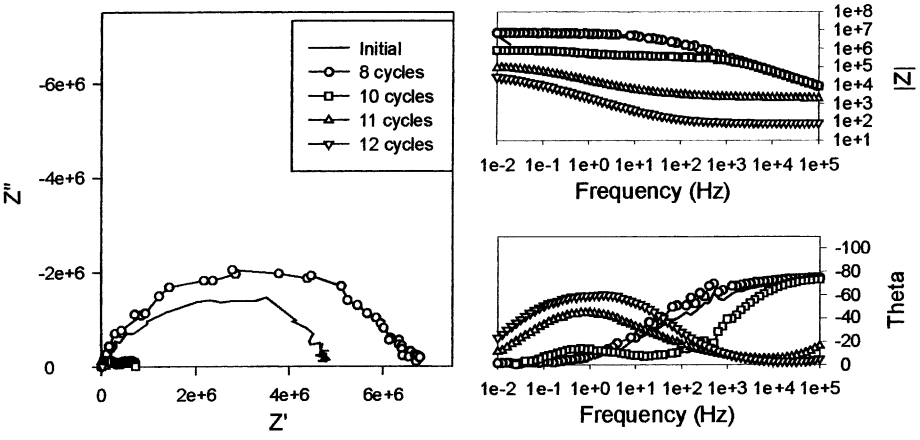

Fig. 7. EIS spectra after applying cycles of AC–DC–AC method to Paint 1 (100 μm).

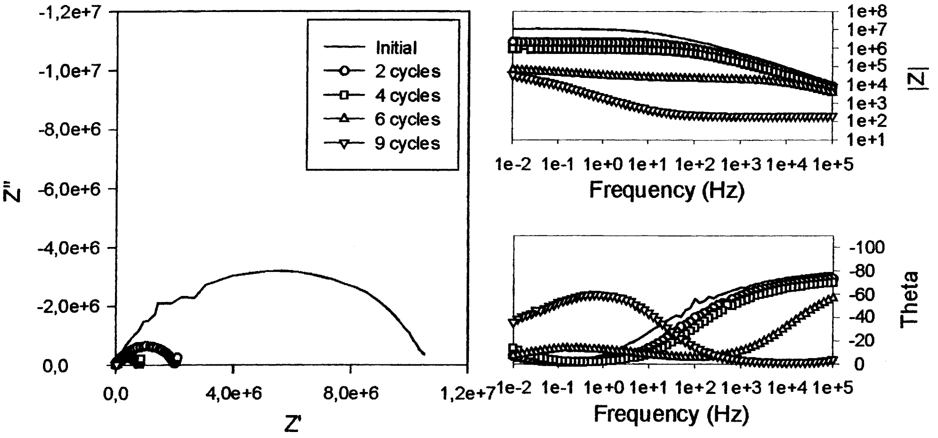

Fig. 8. EIS spectra after applying cycles of AC–DC–AC method to Paint 2 (100 μm).

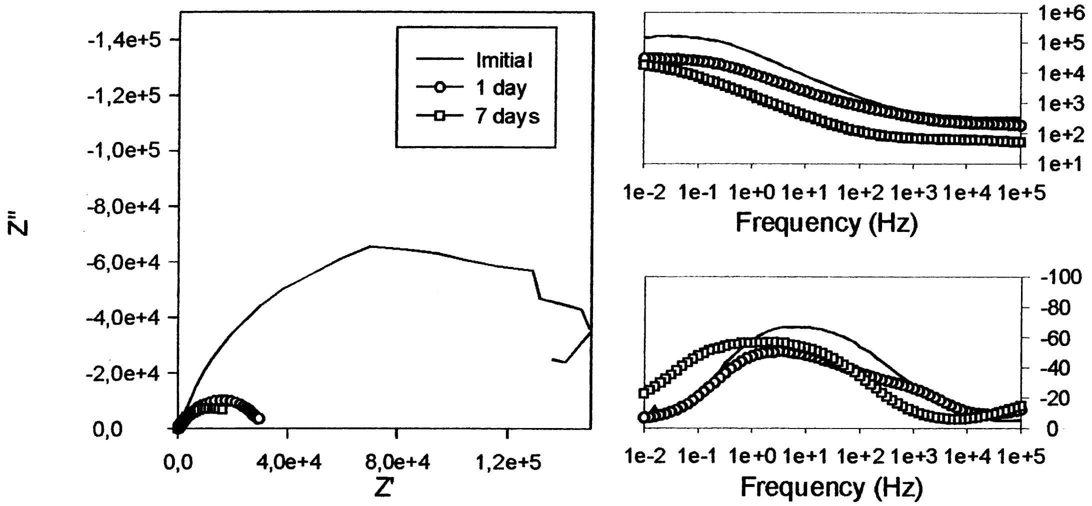

Fig. 9. EIS evolution of samples coated with Paint 1 and with an induced artificial defect immersed in a 3.5% NaCl solution.

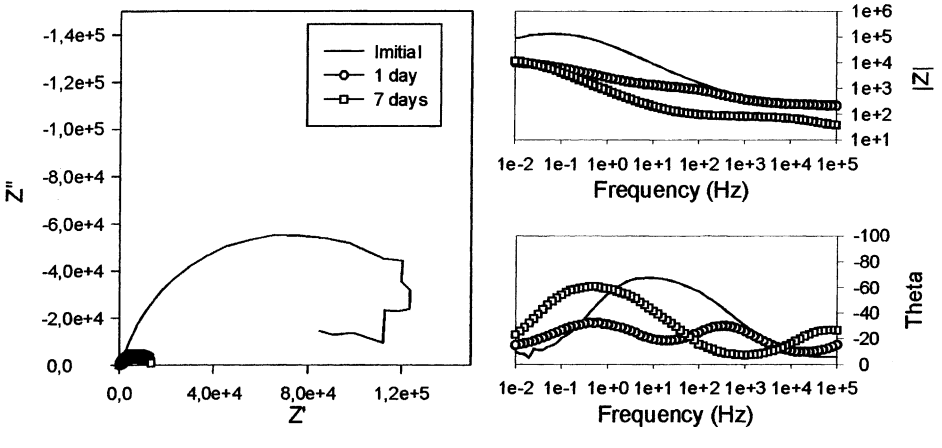

Fig. 10. EIS evolution of samples coated with Paint 2 and with an induced artificial defect immersed in a 3.5% NaCl solution.

defects in the protective film have been induced. The method is based on the assumption that similar defects may exist in real systems and that these could be the means by which the process of degradation of the paint commences. However, it is suggested in some publications that, under these conditions, the mechanisms of degradation may differ with respect to those affecting intact films [13].

Figs. 9 and 10 present the EIS spectra for a week recorded on test pieces with the two paints studied, applied at 75 μm, but on which an artificial defect has been induced.

The first factor to be noted from these results is that, in the case of Paint 1, a variation in the temporal evolution of the impedance spectra is produced, with respect to that recorded for the film without defects. This suggests that, in agreement with [13], the evolution of mechanism of degradation of the paint varies when the defect is induced in the film. Further, both paints present very low impedance values from the first spectrum, less than $10^6\,\Omega\,\text{cm}^2$, which causes the method to lose sensitivity in detection when the process of degradation is initiated.

In short, in accordance with the results obtained, applying the method to samples with artificial defects causes changes in the evolution of mechanism of degradation of the paint and has a low sensitivity.

4. Conclusions

A new electrochemical method for the evaluation of painted metals is proposed. The AC–DC–AC method allows the process of evaluation of paints to be considerably accelerated.

This method also reliably reproduces the process of degradation observed in conditions of free exposure to the action of the corrosive medium and has sufficient sensitivity to detect changes in the protective properties of the systems studied.

Lastly, this technique may be a promising strategy for rapid evaluation and classification of the lifetime prediction of coating systems with respect to its anticorrosive behaviour.

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References

[1] E. Spengler, F.L. Fragata, I.C.P. Margarit, O.R. Mattos, Prog. Org. Coat. 30 (1997) 51.
[2] D.A. Claydon, International Protective Coatings, Akzo Nobel. England (2002).
[3] F. Mansfeld, J. Appl. Electrochem. 25 (1995) 187.
[4] P.L. Bonora, F. Deflorian, L. Fedrizzi, Electrochem. Acta 41 (1996) 1073.
[5] F. Galiano, D. Landolt, Prog. Org. Coat. 44 (2002) 217.
[6] J. Hollaender, Food Addit. Contam. 14 (6–7) (1997) 617.
[7] M. Bethencourt, F.J. Botana, M.J. Cano, M. Marcos, R.M. Osuna, Prog. Org. Coat. 47 (2003) 164.
[8] J.M. Mc Intyre, Prog. Org. Coat. 27 (1996) 201.
[9] D. Greenfield, D. Scantlebury, J. Corros. Sci. Eng. 3 (5) (2000) 1.
[10] S. González, R.M. Souto, Materiales y Procesos Electródicos 1 (2002) 83.
[11] H. Leidheiser Jr., Corrosion, Source Book, ASM, NACE, Ohio, 1984, p. 215.
[12] M.C. Perez Perez, Doctoral Thesis, Universidad de Vigo, 1998, p. 42.
[13] C.G. Oliveira, M.G.S. Ferreira, Corros. Sci. 45 (2003) 139.