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Monitoring the degradation of a high solids epoxy coating by means of EIS and EN

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Abstract

This paper reports a study of the degradation processes suffered by steel samples painted with a high solid content epoxy coating. Because this coating shows a high resistance when exposed to NaCl solutions, HCl solutions were employed to accelerate the corrosion processes. Macroscopic images were used to observe the coating degradation. Then electrochemical techniques, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) were employed to monitor the corrosion behaviour of the system studied. A close correlation was found between EIS and EN data. Several parameters were estimated using these techniques: R_{po}, R_{ct}, C_{c}, C_{dl} and $Z_{0.1\,\mathrm{Hz}}$ using EIS, and R_{n} using EN. In addition, a new parameter estimated by means of EN was employed, $Z_{0.1\,\mathrm{Hz}}$(EN). The evolution of all these parameters with time enabled the effective monitoring of the degradation stage of the coating.

Keywords: Monitoring; EIS; EN; High solid coating; Degradation

1. Introduction

Increasing the percentage of solids in conventional solvent-borne paints represents one of the earliest attempts to decrease the content in volatile organic compounds (VOCs) of a coating formulation and to comply with increasingly stringent environmental requirements [1]. Coatings with a high solids content use less paint to achieve the same thickness obtained with other conventional formulations. The result of this is that less volatile solvent is released into the environment.

By definition, a high solids coating typically contains more than 60% solids by weight or more than 80% solids by volume [2]. This technological solution is currently adopted by the automotive, aerospace, and marine industries for use in a variety of formulations. The major advantage associated with the use of this kind of coating is that the same equipment can be used to apply both the novel high solids and conventional solvent-borne paints. Against this, the major disadvantage of high solids paint lies in the higher viscosities exhibited by the coating formulations. In addition, these coatings still contain a significant, albeit reduced, amount of traditional solvents and diluents [2].

Recently epoxy solvent-free coatings have been increasingly adopted by the marine industry [3]. The system studied in this paper is a two-component solvent-free coating, based on epoxy resin and cured with amines. This coating has excellent resistance to corrosion, chemical products and oil, and is usually employed as a monolayer intended to protect steel structures and storage tanks.

Because the coating studied presents excellent behaviour in NaCl solution, an acid media has been used as corrosive environment, in order to accelerate the degradation of the metal-coating system. After the tests, corroded samples were characterised by visual examination. The degradation degree of this system was measured by means of two different electrochemical techniques: electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN). In the literature, the behaviour of different coatings in corrosive media has been monitored by means of EIS [4–9] and EN [10–16]. The main objective of the present work is to validate these techniques as tools for monitoring the degradation of this novel organic coating. In addition, in this paper a new parameter, the impedance at 0.1 Hz estimated with electrochemical noise, $Z_{0.1\,\mathrm{Hz}}$(EN), is proposed to follow the degradation of the system. Finally, the correlation between

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Table 1
Main characteristics of the Sigmaguard CSF paint

Description	Two-component solvent-free amine cured epoxy coating
Colours and gloss	Green-gloss
Mass density	Approximately 1.3 g/cm^3
Solids content	100% by volume
VOC (supplied)	Maximum 17 g/l
Recommended dry film thickness	300 μm
Theoretical spreading rate	3.3 m^2/l for 300 μm
Flash point	Base and hardener: above 65 °C

parameters derived from both electrochemical techniques was established.

2. Experimental

The behaviour of "Sigmaguard CSF", a commercial high solids-content and solvent-free epoxy paint produced by Sigma Coatings, has been studied. Table 1 gives the most important technical characteristics of this paint. Naval steel, AISI1006, has been employed as metallic substratum. The samples studied were rectangular test pieces of 100 mm × 150 mm × 2 mm, dry pressure-blasted until a finish of type ISO-Sa 2 1/2 was obtained. The paint was then applied by airless spray to a thickness of approximately 300 μm, the optimum thickness recommended in the technical data sheet of the paint.

The protective capacity of the coating was evaluated by monitoring the behaviour of the painted samples in immersion tests, using cells in which an area of 13 cm^2 of the painted surface was exposed to a solution of HCl 3 M. This aggressive medium was employed to accelerate the degradation of the immersed samples.

A 1287 potentiostat coupled to a 1255 frequency response analyser (FRA), both from Solartron, was used for the impedance measurements. The frequency measurement range employed for recording the impedance spectra was 10^5 to 10^{-2} Hz, and the signal amplitude was 20 mV versus the corrosion potential. A saturated calomel electrode was used as reference electrode and a graphite bar, as counter-electrode. Electrical circuits were fitted with Zview software, using the non-linear method of least squares.

Table 2
Physical parameters measured after immersion test

Physical parameters	Standard	Measured value
Blistering	ASTM D 714	MD 4
Oxide	ASTM D 610	9 (0.03%)
Adherence	ISO 2409	1

The electrochemical noise potential and current signals were measured simultaneously using two electrochemical cells coupled and joined by a saline bridge. This is a classic configuration employed for this technique [15–21]. A Solartron 1287 potentiostat controlled by the Corrware program was employed to carry out the experiments. In order to average the values of the parameters analysed, four consecutive electrochemical noise records were measured in each exposure time. 2048 points were taken in each record, at a sampling velocity of 2.15 points/s; therefore the time of each record was approximately 15 min.

In parallel, samples tested in the double EN cell were also characterized by means of EIS, recording separately the signal of each sample and that of the coupled system. These measurements allow us to compare results obtained when using both electrochemical techniques.

3. Results and discussion

3.1. Macroscopic characterisation

Samples were immersed in HCl solution until evidence of degradation was obtained by electrochemical techniques. All the samples studied present an equivalent aspect after the immersion tests (Figs. 1 and 2). As can be observed in these figures, the coated metal system underwent blistering, oxidation and loss of adherence. In order to evaluate the extent of the degradation process several physical parameters were measured at the end of the immersion test, according to the standards specified in Table 2.

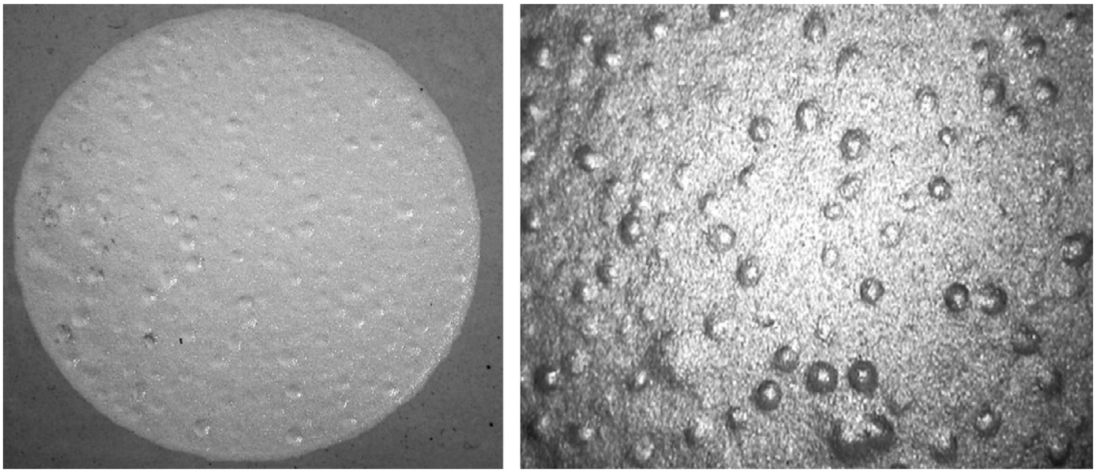

Fig. 1. Optical microscope image of an immersed coated metal sample (left) and the magnification of the blistering observed (right).

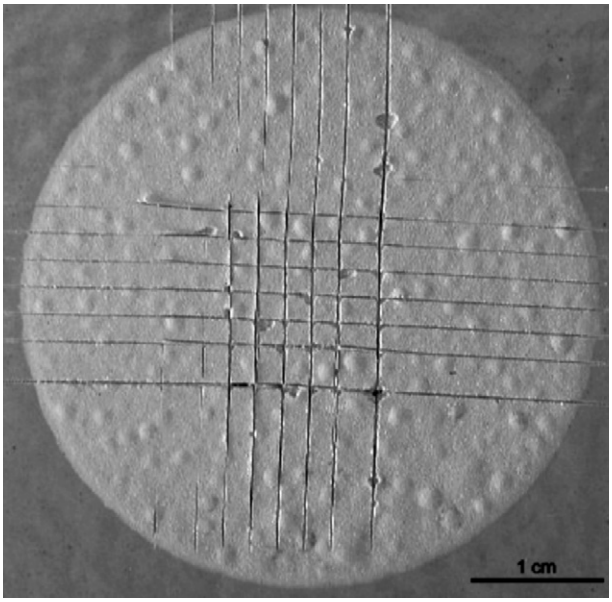

Fig. 2. Optical microscope image of an immersed coated metal sample after an adherence test.

From the results included in Table 2, it can be deduced that blistering is the main mechanism that degrades the studied coating. In Figs. 1 and 2, it can be observed that, as a consequence of their chemical degradation, the coating studied develops anodic blistering. This kind of failure is usually presented in acid media [22]. These blisters are originated by the migration of ions through the coating film. Then an anodic reaction takes place in the centre of the blisters and a cathodic reaction at their periphery.

In order to examine the evolution of the coating systems, transversal sections of the exposed samples were obtained at different stages of degradation. Fig. 3 shows pictures of a sample: (a) without degradation, (b) with some evidence of degradation, and (c) with failures in the coating corresponding to degradation.

In accordance with these figures, two main processes can occur in parallel: the chemical degradation and the loss of adherence of the coating. As a consequence various channels develop in the coating. These channels are employed by the corrosive media to reach the metal surface provoking the loss of the protection provided by the paint.

3.2. Electrochemical impedance spectroscopy

Fig. 4 includes the impedance spectra corresponding to painted samples immersed in acid media after different periods of time. The dataset included in Fig. 4 reveals two main features. Firstly, as can be observed in Fig. 4(b), the impedance modulus of the recorded spectra decreases with the immersion time. This indicates that EIS is sensitive to the changes that occur in the samples during the degradation process.

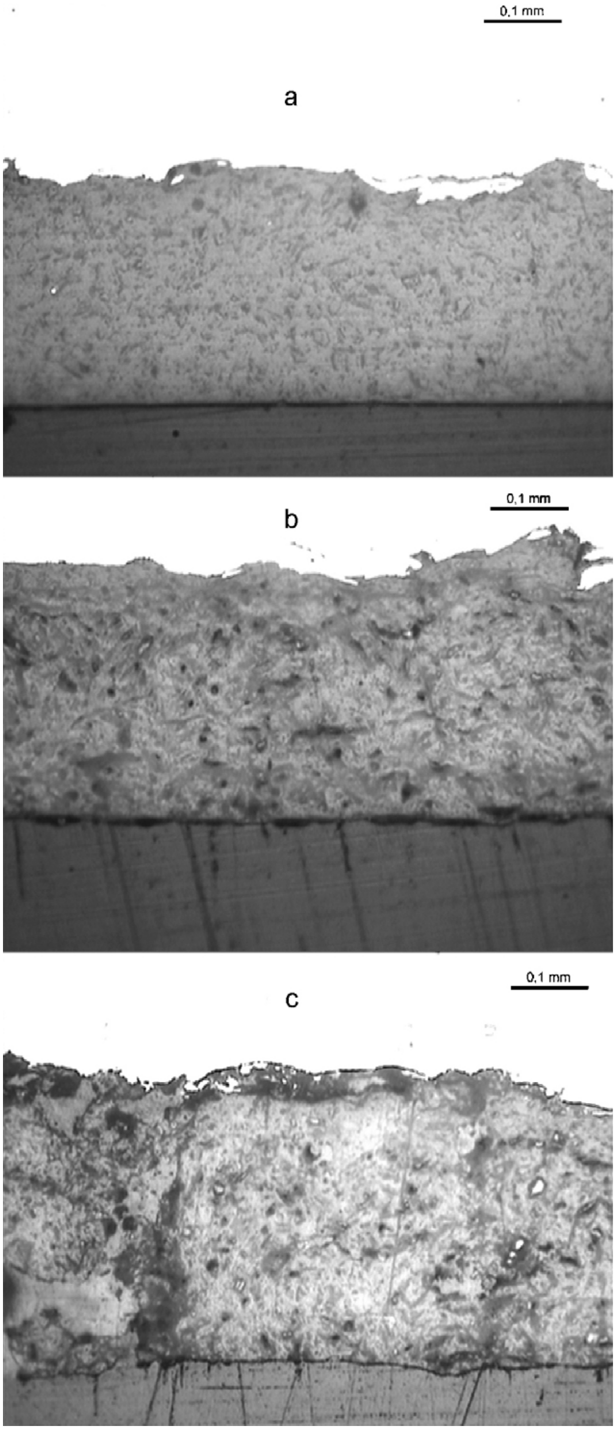

Fig. 3. Transversal section images of coated steel samples after: (a) initial days of immersion; (b) 7 days of immersion in acid media (evidence of chemical degradation can be observed); (c) 14 days of immersion (showing the existence of channels that permit the access of the electrolyte to the metal).

In order to perform a detailed interpretation of the EIS data, an equivalent circuit can be proposed. To select the appropriate equivalent circuit, several considerations must be taken into account. The first finding to be considered is that, in the Nyquist diagrams of Fig. 4(a), two semicircles appear after the 9th day of immersion. Further, in coated metal samples, the high frequency interval is usually related to dielectric properties of organic coatings, while the low frequency range corresponds to the metal response during the corrosion process [4]. Based on these considerations, the equivalent circuit shown in Fig. 5 has been selected for simulating the response of the studied system.

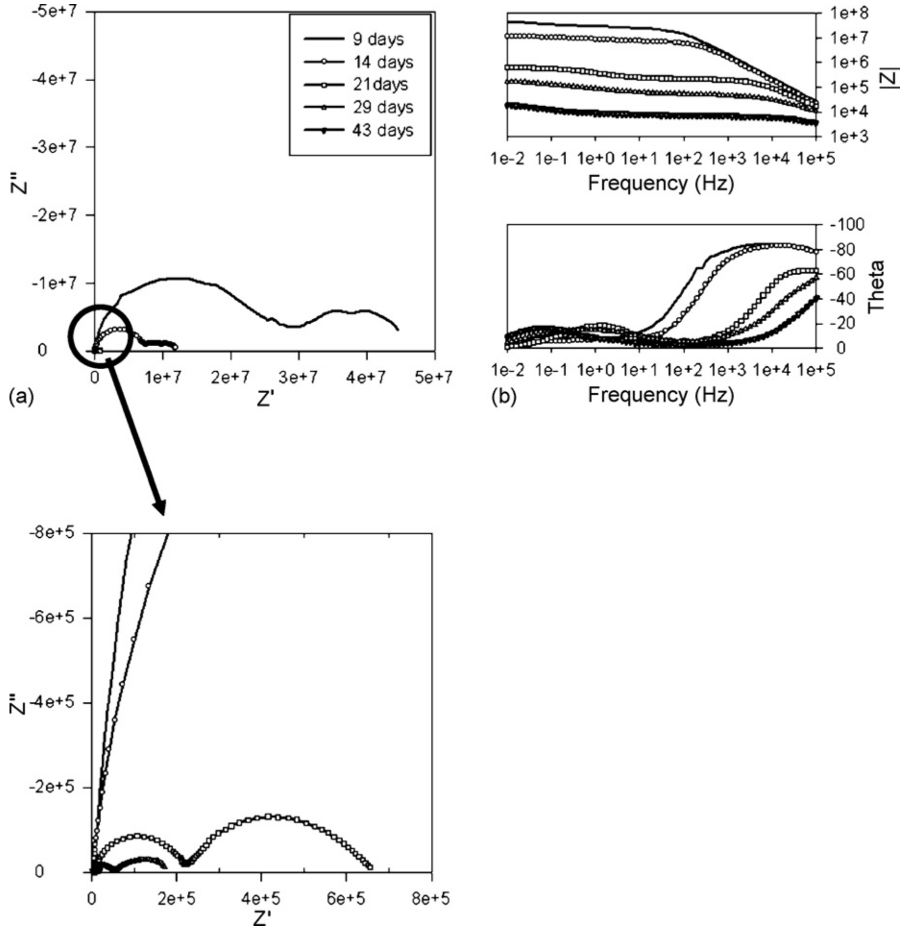

Fig. 4. EIS of coated samples immersed in acid media after the indicated periods of time: (a) Nyquist diagrams and (b) Bode diagrams.

According to Ref. [5], in the equivalent circuit of Fig. 5, R_e represents electrolyte resistance, that is, the resistance between the working electrode and the reference electrode; C_c is the capacity of the coating film and R_{po} is the pore resistance. In this paper, the increase of C_c is used as a measure of the degree of degradation of the paint, whilst R_{po} is related to the absorption of water or to the permeability of the paint. The second time constant of the spectra represents the electrochemical process, taking place at the metal-coating interface. Thus, C_{dl} is the double-layer capacity and can be used as a measure of the paint's loss of adhesion. R_{ct} symbolizes the charge transfer resistance, associated with the kinetic of the corrosion process. This parameter is proportionally inversed to the corrosion rate and to the area where oxidation occurs. Its natural tendency is to decrease with the exposure time.

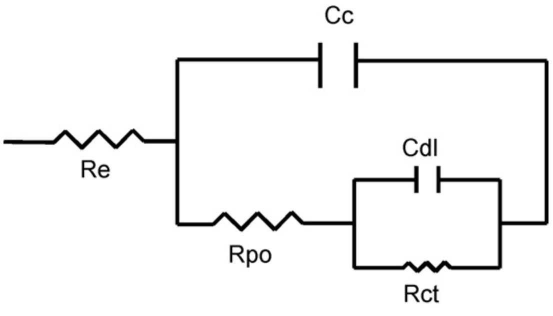

Fig. 5. Equivalent circuit for painted metals.

Several criteria for the evaluation of coatings performance have been reported in the literature based on the element values of the equivalent circuit. As a general rule, in Ref. [6] it is proposed that a metal-coating system that has a good performance against corrosion show high values of R_{po} and R_{ct} and low values of C_c and C_{dl}. There is no general agreement, but according to some authors [5,7,8], values of pore resistance lower than 10^7 or $10^6\ \Omega\,cm^2$ reveal that coatings present poor behaviour as metal protection. Since the appearance of the second semicircle reveals that the metal corrosion has started, other authors [9] consider that the time when the second semicircle appears is more important than the values taken by the elements of the circuit.

By fitting the spectra in Fig. 4 to the proposed equivalent circuit in Fig. 5, values of the above-cited parameters have been obtained (Table 3).

Note that, during the initial days of first immersion, only one semicircle is defined in the spectra. So only the values corresponding to C_c and R_{po} can be calculated. In accordance with the criteria reported above, the coating shows an excellent performance at the beginning of the exposure.

Once the second semicircle is defined, the evolution of all the elements in the circuit can be followed. Thus, in Table 3 it can be

Table 3
Evolution of electrical elements from equivalent circuit

Time (days)	C_c (F/cm^2)	R_{po} (Ω cm^2)	C_{dl} (F/cm^2)	R_{ct} (Ω cm^2)
1 h	4.17×10^{-11}	3.35×10^{9}		
2	6.86×10^{-11}	7.12×10^{8}		
7	1.01×10^{-10}	4.11×10^{7}		
9	1.13×10^{-10}	2.19×10^{7}	5.02×10^{-8}	3.42×10^{7}
14	1.65×10^{-10}	6.62×10^{6}	1.20×10^{-7}	5.95×10^{6}
16	5.01×10^{-10}	4.01×10^{5}	5.15×10^{-7}	5.01×10^{5}
21	1.10×10^{-9}	2.22×10^{5}	1.01×10^{-6}	4.26×10^{5}
24	2.14×10^{-9}	1.33×10^{5}	2.03×10^{-6}	3.16×10^{5}
27	3.59×10^{-9}	8.88×10^{4}	3.66×10^{-6}	2.29×10^{5}
29	5.79×10^{-9}	5.02×10^{4}	7.81×10^{-6}	1.55×10^{5}
33	5.62×10^{-9}	2.27×10^{4}	2.32×10^{-5}	9.41×10^{4}
36	2.22×10^{-9}	2.55×10^{4}	3.76×10^{-5}	7.76×10^{4}
43	1.53×10^{-8}	6.93×10^{3}	1.60×10^{-4}	2.10×10^{4}

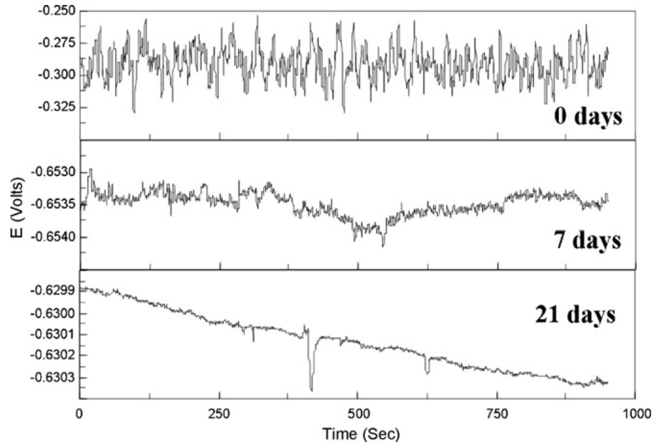

Fig. 7. Potential noise records for the exposure times indicated.

observed that, while the values of C_c and C_{dl} increase with exposure time, those corresponding to R_{po} and R_{ct} decrease. From the values calculated for the latter two parameters, it can be stated that coating studied provides a good anticorrosive behaviour for the first 2 days of exposure to 3 M HCl solution. It provides a doubtful degree of protection against corrosion in the period of 9–14 days. However, after 14 days of immersion, the coating has clearly lost its protective properties.

In Ref. [23], an alternative parameter, $Z_{0.1\,Hz}$, is used to evaluate the protective properties of organic coatings. This parameter is defined as the impedance modulus of the metal-coating system at frequency 0.1 Hz. Thus, high values of $Z_{0.1\,Hz}$ are associated to a high protection capacity of the coating. In general, coatings with values of $Z_{0.1\,Hz} > 10^8\ \Omega\,cm^2$ are considered as providers of an excellent anticorrosive protection; while values of $Z_{0.1\,Hz} < 10^6\ \Omega\,cm^2$ are presented by coatings with poor anticorrosive protection [23].

Fig. 6 includes the evolution of parameter $Z_{0.1\,Hz}$, calculated from EIS measurements, for the indicated periods of exposure to the corrosive environment. As can be observed, $Z_{0.1\,Hz}$ values decrease rapidly over the exposure time. According to the values in Fig. 6 and taking into consideration the criteria previously mentioned, after 14 days of immersion, the coating loses its protective properties. These results agree with those obtained from R_{po} values and indicate that $Z_{0.1\,Hz}$ can be used as a parameter for the characterisation of metal-coating systems. From a full analysis of the proposed equivalent circuit, it can be concluded that when the coating maintains its protective properties, $Z_{0.1\,Hz}$ represents the behaviour of R_{po}. However, when the coating is degraded, $Z_{0.1\,Hz}$ values are dominated by R_{ct}. $Z_{0.1\,Hz}$ values can be obtained directly from only one experimental measurement. In addition no simulation procedure is needed for its estimation. This is an advantage versus R_{po}, which must be obtained by fitting the full EIS spectra.

3.3. Electrochemical noise

In Fig. 7 three potential noise records in function of the exposure time are shown. Similarly, Fig. 8 shows the current noise records for the same exposure times. According to the metallographic and EIS analysis already described, each of these records corresponds to one of the three degradation stages presented by the system studied.

In Fig. 7, it can be seen that the potential noise values are more noble at the beginning of the exposure (−0.25 to −0.35 V versus SCE). For higher times of exposure, the corrosion potential decreases to more active values (between −0.60 and 0.70 V). Note that in this figure, the longer the exposure time, (and con-

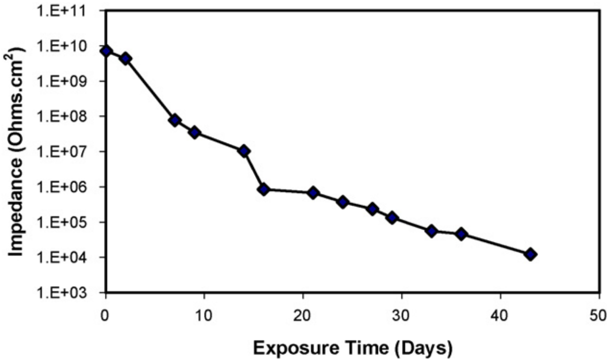

Fig. 6. Evolution of $Z_{0.1\,Hz}$ parameter vs. immersion time.

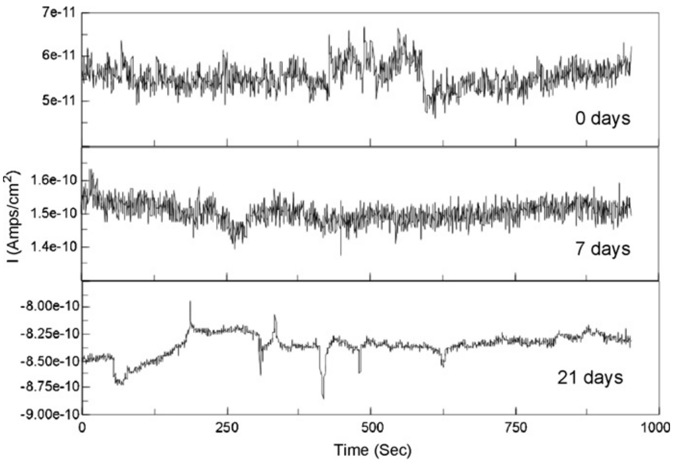

Fig. 8. Potential noise records for the exposure times indicated.

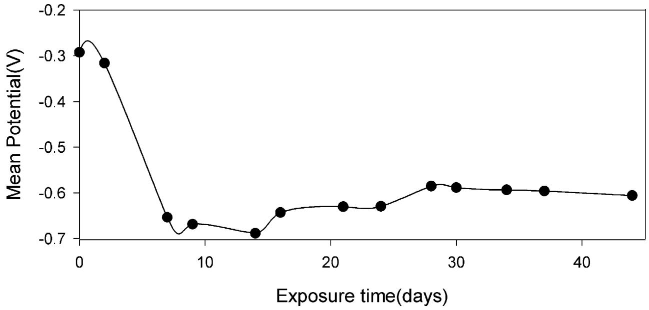

Fig. 9. Mean Potential values at different days of exposure.

sequently, the more degraded the coating), the lower are the amplitudes of the potential noise.

Similarly, Fig. 8 shows the current noise values for the three degradation stages of the painted metal studied. It can be seen in this figure that the signals fluctuate more when the exposure time is longer. In addition, current noise values between 4 and $7 \times 10^{-11}\,\mathrm{A\,cm^{-2}}$ were found during the stage of excellent protection (0 days); between 1.3 and $1.7 \times 10^{-10}\,\mathrm{A\,cm^{-2}}$, for doubtful protection (7 days); and values close to $1 \times 10^{-9}\,\mathrm{A\,cm^{-2}}$, for degraded samples (21 days).

To obtain a more accurate analysis of EN data, several statistical parameters were estimated. In Fig. 9 the mean potential values of the records have been plotted in function of the immersion time. It can be seen that during the first 2 days of immersion the system has noble potential values (about −0.3 V), while after 7 days the potential suddenly falls to more active values (below −0.6 V). These values are closer to the free potential of bare steel. This displacement toward active values can be related to a loss in the coating's protective properties. It is usually accepted that, the more active the corrosion potential, the more susceptible to oxidation is the metal surface under the coating [24].

With the aim of verifying that the activity of the system studied increases with the exposure time, noise resistance (R_n) values of the time records were estimated. This parameter is one of the most commonly used for the interpretation of electrochemical noise [21,25]. In several cases, R_n is equivalent to the polarisation resistance (R_p) measured with linear polarisation [15,21,25], therefore it is proportionally inverse to the corrosion rate. R_n can be estimated by dividing the standard deviation of the potential by the standard deviation of the current [15,26–28]:

$$R_n = \frac{\sigma_E}{\sigma_I} \tag{1}$$

Transforming EN time records to the frequency domain, the values of the impedance at 0.1 Hz, $Z_{0.1\,\mathrm{Hz}}$(EN), can also be estimated. The values of this new parameter were calculated using the estimation of the PSDs of the potential and current signals (Eq. (2)). PSDs were estimated by means of FFT. By averaging the PSDs of four consecutive records, one smoothed PSD was obtained for each exposure time:

$$Z_{0.1\,\mathrm{Hz}}(\mathrm{EN}) = \frac{\sqrt{\mathrm{PSD_E}}}{\sqrt{\mathrm{PSD_I}}}(0.1\,\mathrm{Hz}) \tag{2}$$

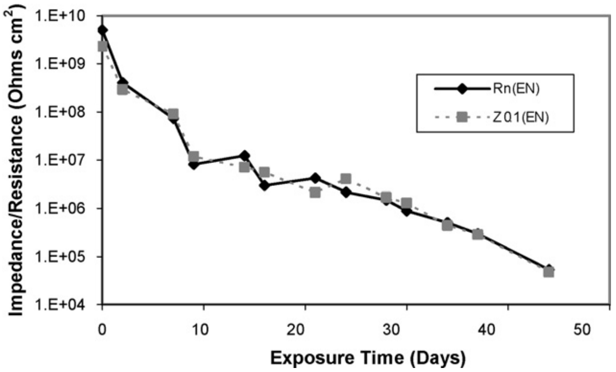

Fig. 10. Comparison of R_n and $Z_{0.1\,\mathrm{Hz}}$ values measured with EN.

In Fig. 10, the calculated values of both R_n and $Z_{0.1\,\mathrm{Hz}}$(EN) have been included. As can be observed, R_n and $Z_{0.1\,\mathrm{Hz}}$(EN) values were found to be very similar. Thus, the longer the exposure time, the lower the values of R_n and $Z_{0.1\,\mathrm{Hz}}$(EN). Therefore, the evolution of these parameters with the immersion time shows the same trend as those derived from EIS measurements. From these results, the applicability of EN as a tool for monitoring paint behaviour can be confirmed.

Some attempts have been reported in the literature to establish a relationship between R_n values and paint behaviour. Thus, values of R_n equal to or higher than $10^9\,\Omega\,\mathrm{cm}^2$ are typically measured for excellent coatings [10–12]. However, the line that divides good and poor behaviour is not clear. Some authors claim that a coating presenting an R_n value below $10^6\,\Omega\,\mathrm{cm}^2$ is not protective [12], while others think that the line should be drawn at $10^7\,\Omega\,\mathrm{cm}^2$ [13]. According to these considerations, it can be stated that the coating studied showed excellent anticorrosive behaviour before the 2nd day of immersion, doubtful protective behaviour in a period of 2–7 days and poor behaviour after 14 days of exposure in HCl.

3.4. Correlation between EIS and EN

Values of the parameter $Z_{0.1\,\mathrm{Hz}}$, calculated using both EIS and EN have been included in Fig. 11 for comparison. As can

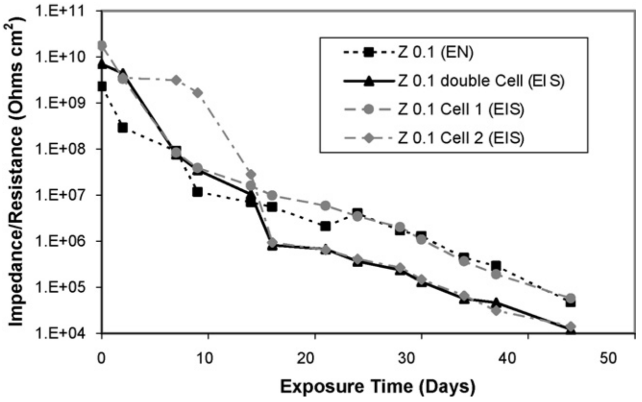

Fig. 11. Comparison of R_n and $Z_{0.1\,\mathrm{Hz}}$ values measured with EIS and EN.

be observed in this figure, all these parameters show a similar behaviour. Therefore, the higher the exposure time, the lower the values of all these parameters. This evolution is related to the higher activity in the system and the lower protection provided by the coating mentioned before. In addition, it can be observed that a good agreement exists between the parameters calculated using EIS and EN.

4. Conclusions

In this paper, two electrochemical techniques, EIS and EN, have been employed to monitor the behaviour against corrosion of a steel painted with a high solid content epoxy coating. In order to accelerate the corrosion processes, an HCl solution was employed as corrosive medium.

In general terms, a good correlation between data obtained with both techniques was found. Thus, EIS data were fitted to an equivalent circuit, so that the evolution of various characteristic parameters of the system, such as R_{po}, R_{ct}, C_{c} and C_{dl}, could be followed. In addition, the impedance at frequency 0.1 Hz, $Z_{0.1\,\mathrm{Hz}}$, was estimated. This latter parameter, relatively easy to measure, also allows us to monitor the corrosion stage of the system.

Additionally, the behaviour of the system was followed by EN, using two parameters: R_{n} and a new parameter, $Z_{0.1\,\mathrm{Hz}}(\mathrm{EN})$. From these two parameters it was possible to distinguish between the different stages of degradation that the system suffered.

Finally, a good correlation degree was found between EIS and EN data. In conclusion, parameters derived from these two electrochemical techniques can be effectively employed as tools to monitor degradation processes in these kinds of coating. The results obtained show that the parameters proposed can be used to detect changes in the degradation stage of the metal-coating system.

Acknowledgments

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References

[1] D. Stoye, W. Freitag, Paints, Coatings and Solvents, Wiley–VCH, Weinheim, Germany, 1998, pp. 105–109.
[2] K.D. Weiss, Progress in Polymer Science 22 (1997) 203–245.
[3] R.M. Osuna, PhD, Puerto Real, Cádiz, April, 2005.
[4] L. Beaunier, I. Epelboin, J.C. Lestrade, H. Takenouti, Surf. Technol. 4 (1976) 237.
[5] A. Amirudin, D. Thierry, Prog. Org. Coat. 26 (1995) 1–28.
[6] N. Tang, W.J. van Ooij, G. Górecki, Prog. Org. Coat. 30 (1997) 255–263.
[7] J.M. McIntyre, Prog. Org. Coat. 30 (1997) 255–263.
[8] F. Deflorian, S. Rossi, P. Kamarchik, L. Fedrizzi, P.L. Bonora, Prog. Org. Coat. 27 (1996) 201–207.
[9] B. del Amo, R. Romagnoli, C. Deyá, J.A. González, Prog. Org. Coat. 45 (2002) 389–397.
[10] Q. Le Thu, G.P. Bierwagen, S. Touzain, Prog. Org. Coat. 42 (2001) 179–187.
[11] C.T. Chen, B.S. Skerry, Corrosion 47 (1991) 598–611.
[12] G.P. Bierwagen, L. He, J. Li, L. Ellingson, D.E. Tallman, Prog. Org. Coat. 39 (2000) 67–78.
[13] D.J. Mills, S. Mabbutt, Prog. Org. Coat. 39 (2000) 41–48.
[14] C.P. Woodcock, D.J. Mills, H.T. Singh, Prog. Org. Coat. 52 (2005) 257–262.
[15] S. Turgoose, R.A. Cottis, in: B.C. Syrett (Ed.), Corrosion Testing Made Easy: “Electrochemical Impedance and Noise”, NACE International, Houston, USA, 1999, pp. 1–149.
[16] J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, D.L. Dawson (Eds.), Electrochemical Noise Measurement for Corrosion Applications (ASTM STP 1277), ASTM, West Conshohocken, PA, USA, 1996, pp. 1–476.
[17] D.A. Eden, Corrosion’98, Paper 386, NACE, Houston, TX, USA, 1998, pp. 1–31.
[18] A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, Electrochim. Acta 44 (1999) 4805–4816.
[19] A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, J.M. Sanchez-Amaya, Electrochim. Acta 46 (2001) 2353–2361.
[20] J.M. Sanchez-Amaya, R.A. Cottis, F.J. Botana, Corros. Sci. 47 (2005) 3280–3299.
[21] J.M. Sanchez-Amaya, F.J. Botana, M. Bethencourt, Corrosion 61 (2005) 1050–1060.
[22] H. Leidheiser Jr., Corrosion of painted metals—a review, in: Corrosion Source Book, ASM, NACE, Ohio, 1984.
[23] M. O’Donaghue, R. Garret, D. Vijay, P. Roberts, T. Aben, Mater. Perform. (2003) 36–40.
[24] D. Santagata, P.R. Seré, C. Elsner, A. Di Sarli, Prog. Org. Coat. 33 (1998) 44–54.
[25] R.A. Cottis, Corrosion 57 (2001) 265–285.
[26] D.A. Eden, D.G. Hladky, J.L. Dawson, Corrosion’86, Paper No. 274, NACE, Houston, TX, 1986.
[27] A.N. Rotwell, D.A. Eden, Corrosion’92, Paper 223, NACE, Houston, TX, USA, 1992.
[28] C. Gabrielli, F. Huet, M. Keddam, Electrochim. Acta 31 (1986) 1025–1039.