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Contribution to a better understanding of different behaviour patterns observed with organic coatings evaluated by electrochemical impedance spectroscopy

M.C.S.S. Macedo^a, I.C.P. Margarit-Mattos^{a,b}, F.L. Fragata^c, J.-B. Jorcin^d, N. Pébère^d, O.R. Mattos^{a,b,*}

^a LNDC – Laboratório de Ensaaios Não-Destrutivos e Corrosão “Prof. Manoel de Castro” – PEMM-DEMM-COPPE-EE-UFRJ, Caixa Postal 68505, CEP 21945970 Rio de Janeiro, Brazil

^b Univ. Federal do Rio de Janeiro, DPI/EQ, Rio de Janeiro, Brazil

^c Centro de Pesquisa de Energia Elétrica – CEPEL/ELETRORBRAS, Brazil

^d Université de Toulouse, CIRIMAT, UPS/INPT/CNRS, ENSIACET-118, route de Narbonne 31077 Toulouse Cedex 04, France

Corresponding author. Address: LNDC – Laboratório de Ensaaios Não-Destrutivos e Corrosão “Prof. Manoel de Castro” – PEMM-DEMM-COPPE-EE-UFRJ, Caixa Postal 68505, CEP 21945970 Rio de Janeiro, Brazil. Tel.: +55 21 2562 8550; fax: +55 21 2290 1554.

E-mail address: omattos@metalmat.ufrj.br (O.R. Mattos).

A B S T R A C T

In the present paper, three different coatings (epoxy, alkyd, polyurethane paints) were characterized by electrochemical impedance measurements, permeability tests, free-standing film impedance and local impedance measurements. The increase in resistance with immersion time of alkyd paint was linked to the nature of the polymeric network and not to phenomena occurring at the metal/paint interface. For polyurethane paint, local impedance was not able to detect defects in the paint, which was attributed to the fact that the defects are smaller than those observed in alkyd paint and also that they are less active and homogeneously distributed through the coating. Although electrochemical impedance methods (global and local) are excellent tools to monitor the behaviour of organic coatings, these techniques alone are not sufficient to screen different paints.

Keywords:

A. Organic coatings

B. EIS

B. LEIS

C. Anomalous behaviour

1. Introduction

Bacon et al. [1], Wormwell and Brasher [2] and Mayne [3] were the pioneers of the use of dc and ac techniques to screen paints. Mayne [3] was the first to perform impedance measurements at a constant frequency (1 kHz) to evaluate paint performance. In 1976, Epelboin et al. [4] measured, over a large frequency range, the impedance of painted iron. They proposed a general equivalent electrical circuit (Fig. 1), in which R_e was the electrolyte resistance, C_c and R_c were paint related and Z_F was associated with faradic processes occurring at the metal/paint interface. Based on this circuit, a general behaviour is considered: for the early stage of paint exposure to an aggressive medium, the impedance spectrum only characterizes the insulating properties of the coating. Indeed, R_c is almost infinite and C_c is very low; consequently a straight line parallel to the imaginary part in the Nyquist diagram is observed. Later, due to electrolyte penetration through the coating (mainly water), C_c increases and R_c decreases with immersion time and a capacitive loop is obtained. Finally, once the electrolyte reaches the metal/paint interface, faradic processes occur and new loops

are detected in the impedance spectra. This classical behaviour has often been described in the literature. A simplified circuit, derived from that proposed by Epelboin et al. [4], is habitually reported to evaluate the corrosion performance of organic coatings. In this circuit, the faradic impedance, Z_F is replaced by a charge transfer resistance, R_t [5]. Thus, from the plots of the impedance diagrams versus exposure time in an aggressive solution, the corrosion protection afforded by organic coatings can be determined: the quality of the paint being mainly related to the time necessary to detect faradic processes. Indeed, the longer the time, the better the paint is. This typical behaviour seems to be well verified for epoxy paints with organic solvent. However, for a water-based epoxy coating, Le Pen et al. [6] have shown that impedance increased during the first days of immersion. Spengler et al. [7] also verified the same behaviour for a water-based acrylic paint. Different works in the literature have mentioned the same discrepancies between this pragmatic approach to screen paints and the actual behaviour of the samples [8–12]. Thus, although the global impedance of paints usually decreases with the time of immersion in an aggressive solution, the opposite behaviour can occur for particular systems. In some cases, for example with polyurethane paints, the appearance of the sample and the electrochemical impedance results do not appear to be correlated [7]. Starting from these considerations, the present study was performed on three different paint systems: an epoxy coating, an alkyd coating and a polyurethane coating). Our intention was to contribute to a better understanding

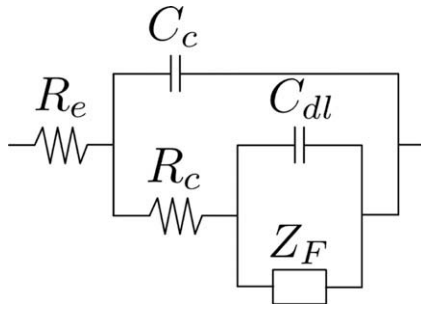


Fig. 1. Equivalent circuit usually proposed to describe the behaviour of the metal/coating interface. (R_e : electrolyte resistance/ R_c : resistance of the solution in the pores of the coating/ C_c : capacitance of the coating/ C_{dl} : double layer capacitance/ Z_F : faradic impedance.)

of these anomalous impedance variations as function of exposure time in a sodium chloride solution. The samples were first characterized by conventional electrochemical impedance spectroscopy (EIS) for both free-standing films and attached films deposited on carbon steel. From the impedance diagrams, the values of the paint film resistance and capacitance, C_c and R_c , respectively, were considered in order to follow the modification of the coating properties with immersion time. The parameters were obtained graphically without a fitting procedure. Permeability tests were also carried out to determine the rate at which water vapour penetrates through the organic coatings. Finally, local electrochemical impedance spectroscopy (LEIS) was performed to detect any defects in the organic coatings on a microscopic scale. From the experimental results, the screening of paints based only on classical monitoring using impedance measurements with the immersion time is discussed.

2. Experimental

1010 carbon steel plates (15 cm × 10 cm), were jetted with glass micron spheres and cleaned with toluene before application of the coatings. All the samples were prepared at the same temperature and humidity. Three paints were tested: epoxy, alkyd and polyurethane. Information on coating formulation is provided in Table 1. The liquid paints are applied by air spraying and cured at room temperature. The coating thicknesses are given in the figures for the different paint systems.

For the painted samples, a classic three-electrode cell was used: the working electrode with an exposed area of 20 cm², a saturated calomel reference electrode and a platinum counter electrode. The cell was placed inside a Faraday cage. For the free-standing films, a four-electrode arrangement was used. Conventional electrochemical impedance measurements were performed using Gamry ZRA equipment over a frequency range of 40 kHz to 2.5 mHz with 7 points per decade.

Table 1
Composition of the organic coatings.

Organic coatings	Polyamide epoxy	Brilliant alkyd	Aliphatic polyurethane
Pigments	TiO ₂ and inert filler (24.30%)	TiO ₂ and inert filler (31.63%)	TiO ₂ (rutile) (22%)
Resin	Epoxy 1001/1004 + versamid115 polyamide (37.59%)	Long alkyd in soy oil (32.32%)	38%
Solvent	Aromatic and oxygenated (38.11%)	Aliphatic 36.05%	Glycol ethyl acetate (80%), aromatic (10%) and ethyl acetate (10%)
PVC	17.07%	23.26%	13.2%

The samples were submitted to total immersion in a 1% NaCl solution. The impedance diagrams were obtained at different exposure times up to 50 days.

Permeability tests were also carried out according to ASTM D1653 (water vapour method) and moreover, impedance measurements were performed for free-standing alkyd and polyurethane films in de-aerated and aerated solutions.

Local electrochemical impedance spectroscopy (LEIS) was carried out with a Solartron 1275. This method uses a five-electrode configuration. A dual probe (or bi-electrode) was placed in the solution for local impedance measurements. The measurements were made from the ratio of the applied AC voltage to the local AC current density. The applied voltage ($\Delta V_{\text{applied}}$) was the potential difference between the working electrode and the reference. The local AC current density (i_{local}) was calculated using Ohm's law:

$$i_{\text{local}} = \frac{\Delta V_{\text{local}}}{d} \times \kappa \quad (1)$$

where κ is the conductivity of the electrolyte and d the distance between the two probes. The local impedance Z_{local} is calculated by the relationship:

$$Z_{\text{local}} = \frac{\Delta V_{\text{applied}}}{i_{\text{local}}} \quad (2)$$

The corrosive medium was a 0.001 mol/L NaCl solution in contact with air. Local impedance measurement requires a low conductivity medium ($9.4 \times 10^{-5} \text{ S cm}^{-1}$) to optimize resolution. With the experimental set-up used, only the normal component of the current was measured.

For local electrochemical impedance mapping (LEIM) the probe was stepped across an area of 32,000 × 24,000 μm. The step size was 1000 μm in the X and Y directions. The excitation frequency chosen was 2 kHz. For clarity, admittance was plotted rather than impedance.

All the measurements were obtained from at least three experiments to ensure reproducibility.

3. Results and discussion

3.1. Classical behaviour of organic coating degradation: epoxy coating

The epoxy paint system presents the exact behaviour well described by Mayne [3]: at flaws in the paint, the electrolyte penetrated through the coating, subsequently causing faradic processes at the metal/paint interface. Fig. 2 shows an example of this behaviour, very often reported in the literature [1–14]: for short immersion times, only one capacitive loop is detected and the size of the loop decreases with increasing immersion time. The

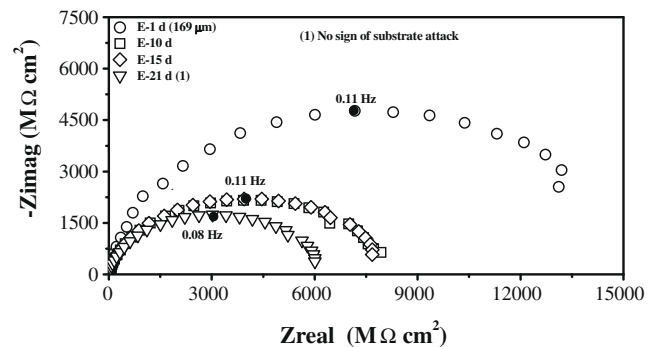


Fig. 2. Impedance diagrams in Nyquist coordinates for the epoxy coating as a function of immersion time in 1% NaCl solution.

variation of the values of C_c and R_c , extracted from the impedance diagrams, versus exposure time are given in Fig. 3 for two different samples. As can be seen, C_c increases with the immersion time due to water uptake (Fig. 3a) whereas R_c decreases with time (Fig. 3b). After 20 days of immersion, no sign of substrate attack (corrosion) was observed and the values of capacitance and resistance remained constant. For longer immersion times, new processes appeared (not reported here) corresponding to faradic processes and corrosion attack was observed underneath the paint. The impedance diagrams for the free-standing film are given in Fig. 4 for different immersion times. They are characterized by a single capacitive loop. The size of the loop decreases during the first 7 days of immersion (C_c increases during the same period) and then R_c and C_c remain constant. This result will be used as a reference for comparison with the other coatings.

3.2. First anomalous behaviour type of organic coating degradation: alkyd coating

Fig. 5 shows the increase of the size of the impedance diagrams for the alkyd coating when the immersion time increases. Independently of the immersion time, the diagrams are characterized by a depressed capacitive loop but it is noteworthy that after 15 days of

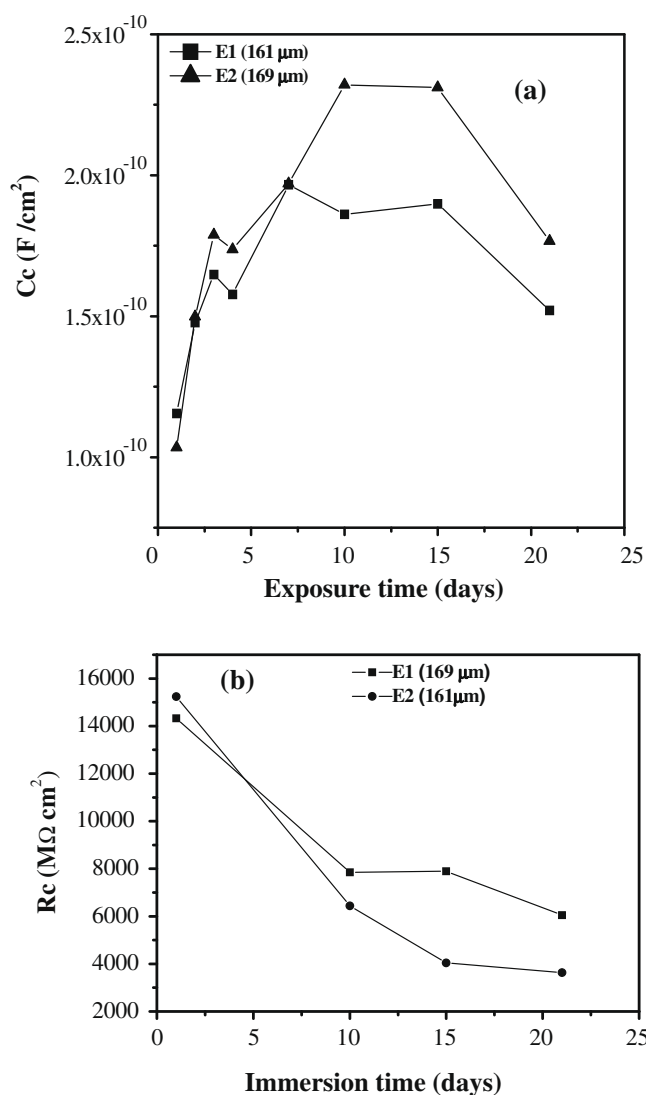


Fig. 3. C_c (a) and R_c (b) versus immersion time in 1% NaCl solution for the epoxy coating (results of two independent trials).

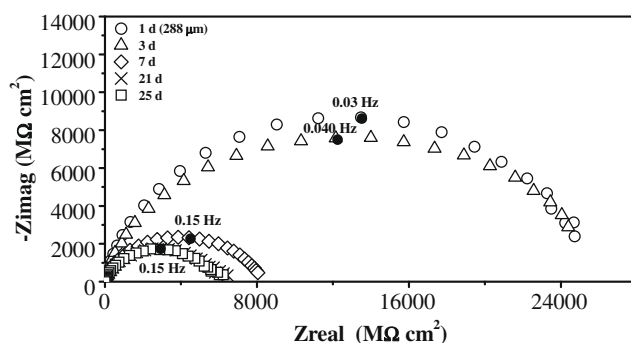


Fig. 4. Impedance diagrams in Nyquist coordinates in 1% NaCl solution for free-standing epoxy film.

immersion, delamination and under-film corrosion appeared. This behaviour is the opposite of that observed for the epoxy paint, where the capacitive loop on the impedance diagram decreased with time. For the alkyd coating, the R_c values increased significantly during the first 30 days of immersion (from about 2000 MΩ cm² after 3 days of immersion to 10,000 MΩ cm² after 30 days of immersion).

In Fig. 6a, the impedance diagrams were obtained for the alkyd free-standing films in a de-aerated solution. For comparison, the results obtained for the same exposure times for an as-prepared 1% NaCl solution are reported in Fig. 6b. When the experiments were performed in de-aerated medium, the impedance diagrams were almost identical for 3 days (180–220 MΩ cm²). Conversely, in aerated conditions, impedance increased from 280 to 685 MΩ cm² from 4 h to 3 days. This seems to indicate that oxygen plays a specific role in the coating behaviour which allows the resistance increase for the alkyd coating to be explained. The oxygen can react with the double bonds and some complementary links can be formed. This could explain the increase of the film resistance, although this additional cross-linking process is not sufficient to avoid corrosion attack. Moreover, permeability tests discussed later in the paper will show that the oxygen effect, although important, is not sufficient to explain the observed anomalous behaviour of alkyd paint.

Several authors have attributed the increase of the resistance with time to a film-forming process [15–17]. This means that the cross-linking is not entirely complete and the coating has not reached its final structure when the impedance measurements were obtained. To verify this assumption, the alkyd coating was cured at room temperature for 6 months. The impedance diagrams obtained for different immersion times (1, 10, 21 and 50 days) for the cured specimens (not shown) revealed similar behaviour to that obtained for specimens without curing (Fig. 5): the impedance increased as the exposure time to the aggressive solution

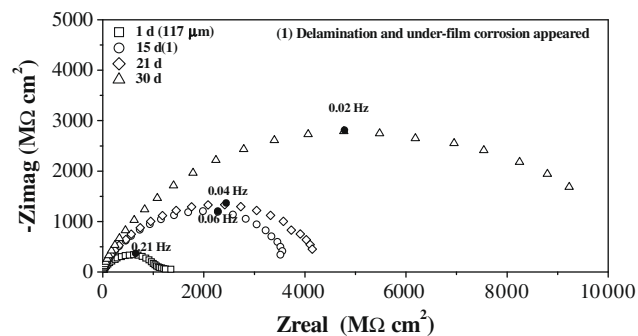


Fig. 5. Impedance diagrams in Nyquist coordinates for the alkyd coating as a function of immersion time in 1% NaCl solution.

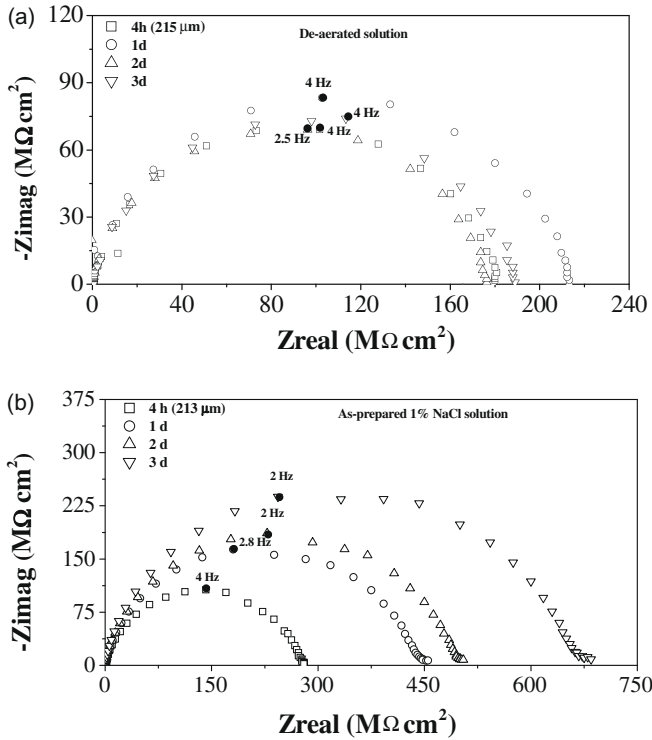


Fig. 6. Impedance diagrams obtained for free-standing alkyd films in a de-aerated solution (a). Impedance diagrams obtained for free-standing alkyd films for an as-prepared 1% NaCl solution (b).

increased. The impedance results indicate that the anomalous behaviour observed for the alkyd coating when it is in contact with an electrolyte, is linked to the nature of the polymer itself and it is not a phenomenon occurring at the metal/coating interface, such as, for example, the accumulation of corrosion products.

3.3. Second anomalous behaviour type of organic coating degradation: polyurethane coating

Another non-classic behaviour of paints is the lack of correlation between defects and the impedance data. Fig. 7 presents impedance diagrams characterized by a capacitive loop with the same order of magnitude as those measured for the epoxy coating (Fig. 2). After about 20 days of immersion, some corrosion attacks became clearly visible but the impedance did not change significantly. On the contrary, after 30 and 50 days of immersion the impedance increased.

The variations of R_c for the polyurethane coating are reported in Fig. 8. R_c oscillations are observed but the values remain high,

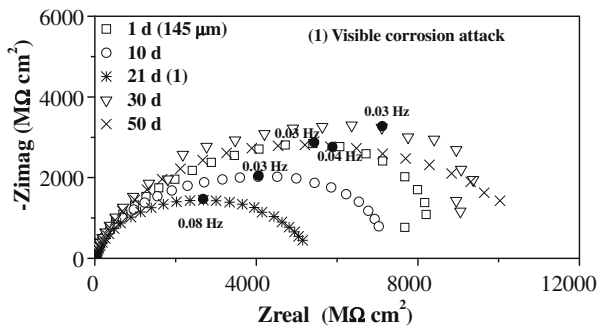


Fig. 7. Impedance diagrams in Nyquist coordinates for the polyurethane coating as a function of immersion time in 1% NaCl solution.

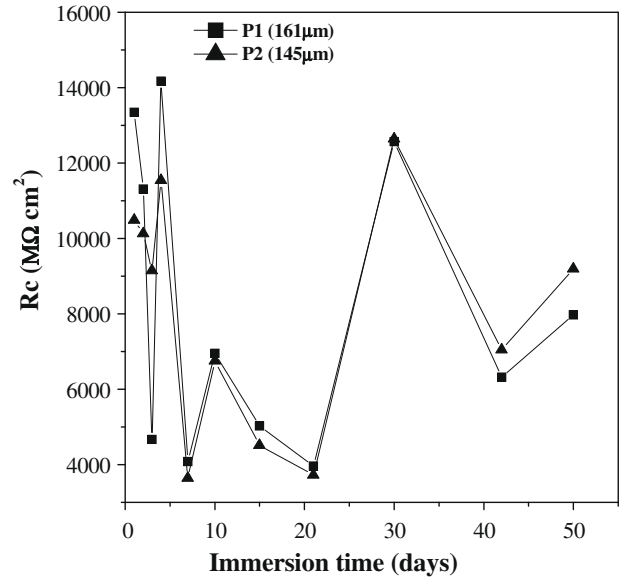


Fig. 8. R_c versus immersion time in 1% NaCl solution for the polyurethane coating (results of two independent trials).

although corrosion occurs after 20 days of immersion. Spengler et al. [7] reported the presence of blisters in polyurethane paints with substrate corrosion underneath which had not been detected by impedance. Indeed, the authors measured very high impedance for samples presenting blisters. They explained that the blisters were independent cells not connected to the bulk system and they demonstrated that impedance did not take the occluded processes into account. The open question is why some blisters are detected by impedance and others not.

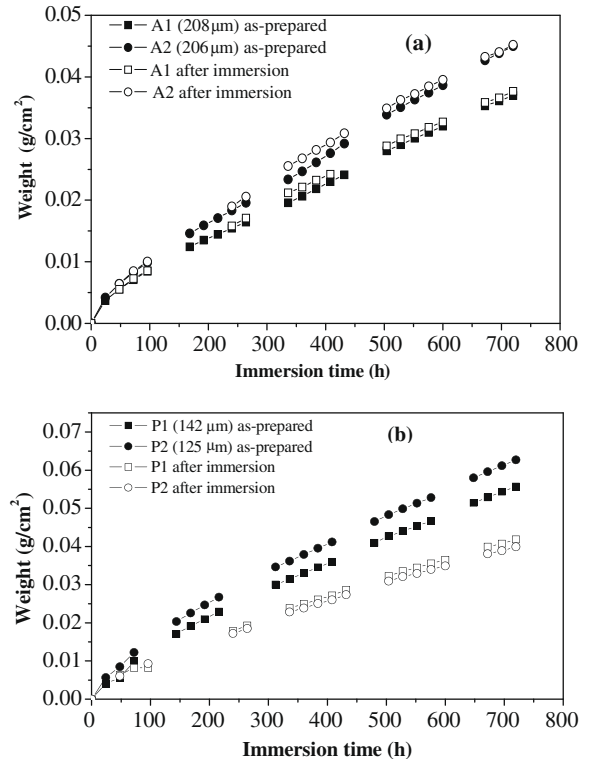


Fig. 9. Permeability tests as a function of exposure time for the alkyd (a) and the polyurethane (b) coatings (results of two independent trials).

Permeability tests for the alkyd and polyurethane coatings as a function of exposure time were performed. The following protocol was used: the permeability was first measured periodically over 750 h. Then, the samples were left for 6 months in a silica-gel dryer, immersed in distilled water for 15 days and finally dried again for 24 h. The permeability tests were repeated in the same conditions as previously. The results are reported in Fig. 9a and b for the alkyd and polyurethane coatings, respectively.

For the alkyd coating, the permeability values are the same for the two experiments. This shows the reversibility of the process linked to water uptake. This is surprising since, as we have previously mentioned, the oxygen introduced by water uptake should modify the microstructure of the coating. These results show that the influence of oxygen exists but is not sufficient to account for the anomalous behaviour of the alkyd paint. On the contrary, for the polyurethane coating it can be seen that the permeability decreased for the second run of experiments. This indicates that the water uptake by the coating provoked a change in its microstructure; the results clearly underline the non-reversibility of the process. The modification of the coating microstructure (both alkyd and polyurethane coatings) during water uptake was analyzed by local electrochemical impedance measurements.

3.4. Local impedance

Fig. 10 presents local impedance maps obtained for the alkyd coating after different immersion times in the NaCl solution:

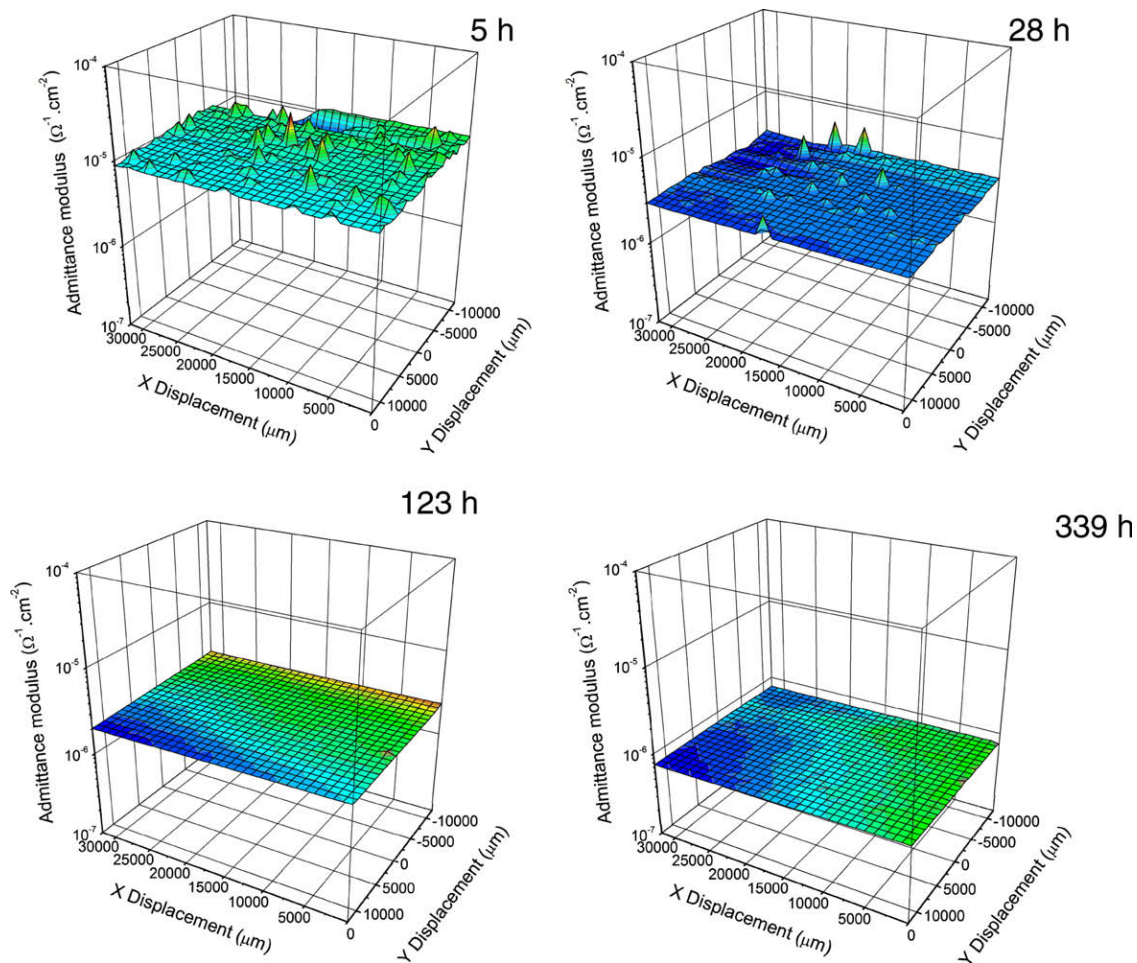


Fig. 10. Local impedance maps plotted at 2 kHz for the alkyd coating.

numerous peaks are present. This indicates that the coating was heterogeneous. Locally, admittance is higher (the impedance is lower) and as a consequence, the properties of the film in these regions are not the same. The “defects” present in the coating have a diameter of about a hundred micrometers and locally induced high currents. The defects are scattered all over the surface. Maps plotted for different exposure times, not reported here, revealed that some peaks decreased as the exposure time increased. In addition, the admittance decreased (the impedance increased) progressively between 5 and 28 h. These results match very well the previous global impedance measurements. For longer immersion times, it can be seen that the number of peaks decreased, and after 123 h of immersion no peaks were observed on the maps. However, the admittance still continued to decrease (the impedance increased) and a stationary state was observed after about 339 h of immersion. This behaviour is totally coherent with the global impedance seen in the previous figures.

For the polyurethane paint (Fig. 11), the local admittance is almost constant over the whole surface and no peaks are apparent. The local measurements were different from those obtained for the alkyd paint and were probably related to the size of and activity in the defects existing in the paint. Indeed, for the polyurethane coating, when the defects were small, the local impedance measurements were unable to detect them. Moreover, if the defects are small coupled with the irreversible changes observed in the polymer due to water uptake, this area can be easily blocked and the blisters are no longer in contact with the bulk system and hence, not detected by either global or local impedances.

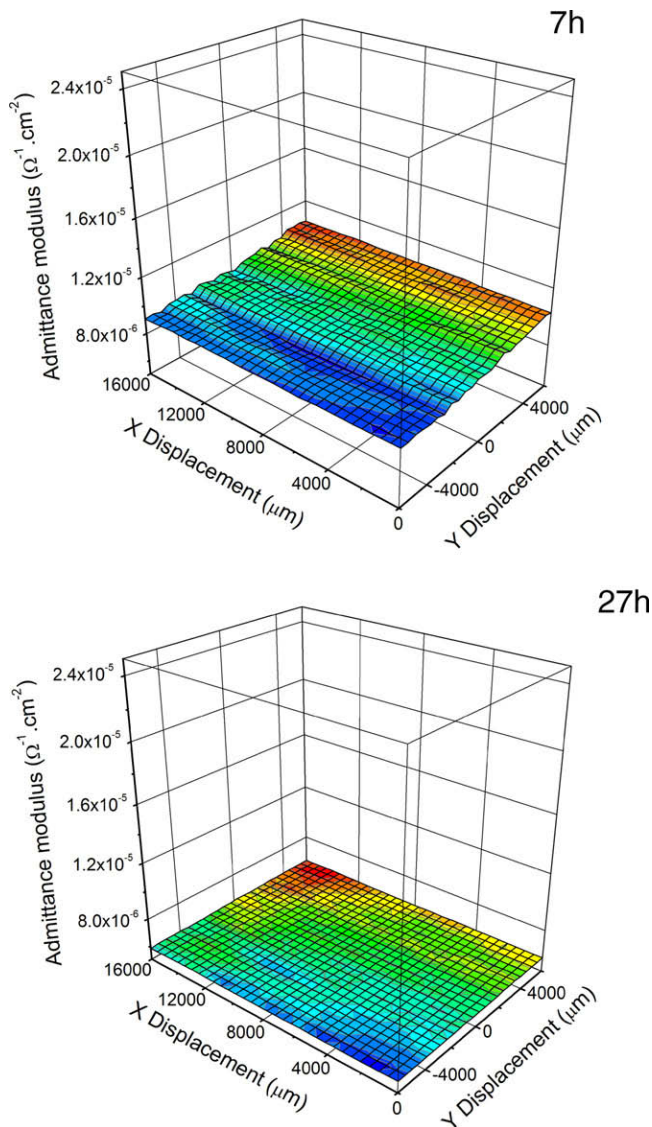


Fig. 11. Short immersion local impedance maps plotted at 2 kHz for the polyurethane coating.

The above results show that impedance data are strongly influenced by the nature of the polymer used in the paints. Each system presents peculiarities and it is not possible to correlate the presence of corrosion with the impedance behaviour. It is clear that deeper studies are necessary to better understand the properties of various paints and particularly, the relationship between solution permeation and the corrosion processes occurring.

4. Conclusion

Conventional electrochemical impedance spectroscopy was coupled with permeability tests, free-standing film impedance and local impedance measurements. It was shown that the increase of the resistance of alkyd paint can be attributed to the nature of the polymeric network and not to phenomena occurring at the metal/paint interface. Oxygen introduces structural changes in the polymer but this effect seems to be reversible. For alkyd paint local impedance corroborates the results obtained by the global impedance measurements. For polyurethane paint, local maps were not able to detect defects in the paint. This can be due to the fact that the defects were smaller than those observed in the alkyd paint and also that the activity in them was lower. These areas, once permeated by the electrolyte, are the regions where non-reversible structural changes occur in the film. Finally, it can be concluded that electrochemical impedance (both global and local) is an excellent tool to monitor the behaviour of organic coatings. However, a deeper understanding of the electrolyte/paint film interactions is absolutely essential to correctly analyze the impedance data. Thus, it is not possible to classify the performance of the different paints by only monitoring the global impedance with time. No general pattern of behaviour for paint systems emerges and any correlation between R_c and C_c versus time and the paint performance is doubtful. The use of complementary techniques is essential to better understand such complex systems.

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References

- [1] R.C. Bacon, J.J. Smith, F.M. Rugg, *Ind. Eng. Chem.* 40 (1948) 16.
- [2] F. Wormwell, D.M. Brasher, *J. Iron Steel Inst.* 164 (1950) 141.
- [3] J.E.O. Mayne, *J. Soc. Chem. Ind.* 66 (1947) 93.
- [4] L. Beaunier, I. Epelboin, J.C. Lestrade, H. Takenouti, *Surf. Technol.* 4 (1976) 237.
- [5] K. Bonnel, C. Le Pen, N. Pébère, *Electrochim. Acta* 44 (1999) 4259.
- [6] C. Le Pen, C. Lacabanne, N. Pébère, *Prog. Org. Coat.* 46 (2003) 77.
- [7] E. Spengler, F.L. Fragata, I.C.P. Margarit, O.R. Mattos, *Prog. Org. Coat.* 30 (1997) 51.
- [8] I.C.P. Margarit, O.R. Mattos, *Electrochim. Acta* 44 (1998) 363.
- [9] J. Kittel, N. Celati, M. Keddad, H. Takenouti, *Prog. Org. Coat.* 41 (2001) 93.
- [10] J. Kittel, N. Celati, M. Keddad, H. Takenouti, *Prog. Org. Coat.* 46 (2003) 135.
- [11] S.R. Taylor, *Prog. Org. Coat.* 43 (2001) 141.
- [12] M.D.G. Destreri, J. Vogelsang, L. Fedrizzi, F. Deflorian, *Prog. Org. Coat.* 37 (1999) 81.
- [13] C. Le Pen, C. Lacabanne, N. Pébère, *Prog. Org. Coat.* 39 (2000) 167.
- [14] P.R. Sperry, B.S. Snyder, M.L. O'Dowd, P.M. Lesko, *Langmuir* 10 (1994) 2619.
- [15] F. Lin, D.J. Meier, *Langmuir* 10 (1995) 2726.
- [16] K.L. Hoy, *J. Coat. Technol.* 68 (1996) 33.
- [17] S.J.F. Erich, J. Laven, L. Pel, H.P. Huinink, K. Kopinga, *Prog. Org. Coat.* 52 (2005) 210.