

Comparison Between Electrochemical Impedance and Salt Spray Tests in Evaluating the Barrier Effect of Epoxy Paints

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O objetivo deste trabalho é o estabelecimento da confiabilidade de um teste eletroquímico baseado em medidas de impedância eletroquímica de sistemas substrato metálico/filme orgânico/eletrolito aquoso em função do tempo de imersão. Assim, sistemas aço naval/filmes de epóxi betuminosa ou esmalte epoxídico/solução de NaCl 3% foram escolhidos para provar o teste. Foram comparados os resultados eletroquímicos e aqueles obtidos por avaliação visual usando o padrão ASTM D-610. A concordância total entre os resultados dos testes eletroquímico e visual permitem confirmar que a técnica descrita é altamente encorajadora, pois ela provou que um teste bastante simples (como a impedância eletroquímica) pode, sob certas condições, indicar se um filme de tinta anticorrosiva é capaz de proteger satisfatoriamente, bem como detectar diferenças entre as propriedades anticorrosivas de produtos disponíveis comercialmente.

The aim of this work is to establish the reliability of an electrochemical test based on the electrochemical impedance measurements of metallic substrate/organic coating/aqueous electrolytes as a function of immersion time. Thus, naval steel/epoxy-bituminous or epoxy-enamel coats/3% NaCl solution systems were chosen in order to try out the test. The electrochemical results and those obtained from visual assessment using the ASTM standard D-610 were compared. The total agreement between the results of the electrochemical and visual tests allow to confirm that the described technique is highly encouraging, as it has proven that a fairly straightforward test (like electrochemical impedance) can, under certain circumstances, indicate whether an anticorrosive paint coating is able to satisfactorily protect, as well as to detect differences between the anticorrosive properties of commercially available products.

Keywords: corrosion, impedance measurements, salt spray test, epoxy paints

Introduction

Though there exists a great variety of commercial equipments for carrying out electrochemical tests based on "in-situ" impedance measurements in the systems metal/organic coating/electrolyte, their higher development was made in laboratories where the possibility to have available a greater quantity of more sophisticated instruments led to a better implementation of simpler, quicker and more reproducible methods to determine the protection degree afforded by the organic coatings on the metallic substrate.

The tests must allow: a) the evaluation of anticorrosive, intermediate and topcoat paint properties; b) the quality control of painted instruments, structures or parts, and c) the prediction of their service behavior.

Transitory or stationary DC techniques were commonly used because they allow the assessment of some kinetic parameters used in the corrosion rate calculation for acti-

vation controlled processes; however they have important limitations which, in many cases, may nullify their employment¹⁻⁴. With painted metals, such limitations are related to both the high ohmic resistance (on the order of several M Ω) due to the barrier effect of some organic coatings, and to the diffusion controlled corrosion processes. Likewise, the DC flux produces other interfacial processes, that may mask the accurate determination of the most adequate electrochemical parameter (charge transfer resistance) used in the corrosion rate calculation⁵. In such a case, the practical conditions are far from the theoretical ones used for the statement of the Stern-Geary equation⁶; therefore, the calculated corrosion rate may not be correct⁷.

Nevertheless, at the present time the industry applies a method based on high DC voltage (50-100 V) to detect defects, air bubbles, etc. This method is only effective to identify very low resistance values (0-1000 Ω); but intact

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organic coatings have a resistance range on the order of $10^4 - 10^{12} \Omega \text{ cm}^2$.

The AC measurements do not present these objections because they bring into play only those processes whose time constants are less than the alternancy period of the electric field. Therefore, the use of small electrical signals in a large frequency range may provide the necessary information to deduce both the qualitative and the quantitative contribution of each element to the equivalent circuit reproducing the analyzed electrochemical interface. During the last decade, considerable success has been achieved through the use of wide frequency scan electrochemical impedance analysis. Many examples in the literature illustrate the utility of this method with regard to various types of coatings and oxide films on iron and steel⁸⁻¹⁷. However, relatively few reports have been published describing the results obtained from commercially available protective organic paints.

The aim of this work is to compare the experimental results related to the protective performance of two epoxy paints (epoxybituminous and epoxy-enamel) applied in different thicknesses on naval steel plates and exposed to either a 3% NaCl solution (electrochemical test) or a stand-

ardized aggressive environment (salt spray test, ASTM Standard D-117).

Experimental Details

SAE 1020 naval steel plates (15x8x0.2 cm) were employed as metallic substrate. The surface was sandblasted to AS 2^{1/2} (SIS Standard 05 59 00/67). The plates were degreased with toluene and coated with the paints whose formulations are shown in Table 1. The organic coatings were applied by means of a Bird applicator. During the drying period (7 days) the coated plates were placed in a desiccator at a constant temperature ($20 \pm 2^\circ \text{C}$). The dry-film thickness was measured by Foucault currents using a bare sanded plate and known thickness standards as reference.

On each coated plate were placed two cylindrical acrylic tubes. An epoxy adhesive was used in order to achieve good adhesion to the metallic substrate. The geometrical area of each cell was 14 cm^2 . A large area graphite cylinder was used as counter-electrode while a saturated calomel electrode (SCE) was employed as reference. The electrolytic solution was 3% NaCl, and all the measurements were carried out at room temperature ($20 \pm 2^\circ \text{C}$).

Samples similar to those used for the electrochemical testes but with their edges and back side isolated by a $600 \mu\text{m}$ film of an epoxybituminous paint were exposed, in duplicate, for 500 h in a salt spray cabinet. Its operating characteristics were in accordance with ASTM Standard D-117.

At different immersion times, electrochemical impedance measurements in the frequency range $10^{-3} \text{ Hz} \leq f \leq 5 \times 10^5 \text{ Hz}$ were performed in the potentiostatic mode at the corrosion potential using a Frequency Response Analyzer (Solartron FRA 1255) and an Electrochemical Interface (EI 1186). The

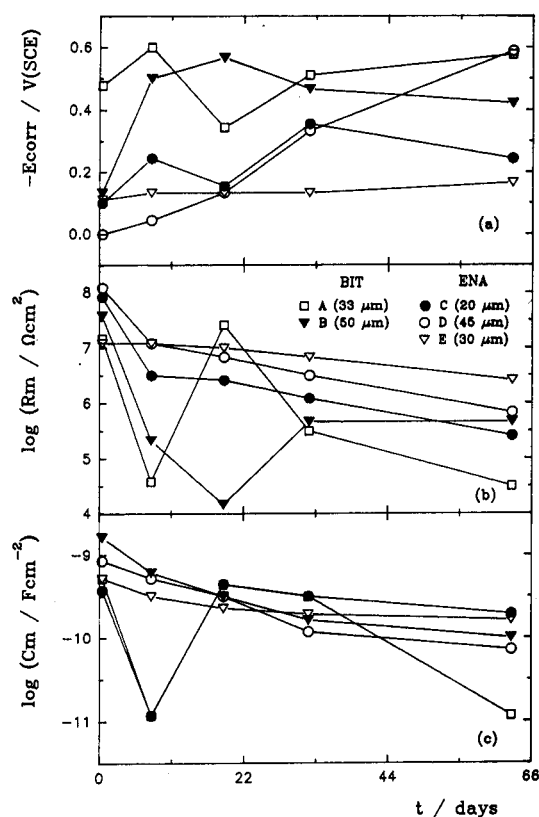


Figure 1. a) Corrosion potential (E_{corr}); b) ionic resistance (R_m), and; c) dielectric capacitance (C_m) vs. immersion time (t) for epoxybituminous paints (BIT, samples A and B) and epoxy-enamel (ENA, samples C, D and E).

Table 1. Chemical composition (g/100 g) of the paints used.

Paint	Components	
Epoxybituminous	Epoxy resin (70% solids)	44.00
	Bituminous material	20.50
	Talc	20.50
	Polyamide	9.00
	Hardener	2.50
Epoxy-enamel	Isopropyl alcohol	3.50
	Epoxy resin (70% solids)	35.20
	Titanium dioxide (TiO_2)	17.50
	Moistening	0.30
	Polyamide	14.50
	Hardener	0.50
	Xylene	25.00
	MIK	3.50
	Butyl Alcohol	3.50

amplitude of the applied AC voltage was 10 mV peak to peak. All data were processed with an AT Olivetti PCS 286 and a set of programs developed at the CIDEPINT. The visual evaluation of the samples submitted to those different tests was done using the 1-10 scale of the ASTM Standard D-610.

Results and Discussion

Figure 1a shows the corrosion potential (E_{corr}) vs. immersion time (t) curves for epoxybituminous and epoxy enamel coated naval steel, samples A and B and samples C, D and E, respectively, with low thicknesses (20-50 μm). For sample E the corrosion potential remained constant during the 60-day immersion, while those corresponding to samples A, B, C and D tended rapidly to more active values at short immersion times; this displacement was continuous for sample D and oscillatory for samples A, B and C.

Impedance spectra contain valuable information about the electrical coating parameters and kinetics of the corrosion processes taking place on the metallic substrate. Due to the dynamic character of rust formation, the impedance spectra of coated steel/3% NaCl solution systems change throughout the exposure time. A fairly good description of the experimental impedance diagrams was obtained in terms of a transfer function analysis using non-linear fit routines like those developed by Boukamp¹⁸; the complex nature of the processes at a coated steel interface makes it necessary to derive models that account for the impedance data measured at such interfaces.

Figures 1b and 1c show, respectively, the ionic resistance (R_m) and the dielectric capacitance (C_m) of the membrane vs. t . The fluctuations of R_m and C_m with t are according to those of E_{corr} . The stability of E_{corr} for sample E (Fig. 1a) is similar to that of R_m and C_m . Otherwise, the fast changes of E_{corr} for samples A, B, C and D to more active values are accompanied by R_m and C_m ones, indicating that at this time the protective capacity of the paint begins to decrease while the corrosion of Fe as Fe^{++} increases rapidly. Sometimes, samples A and C did not respond to the general equivalent circuit¹² used for fitting the experimental data, due to the fast deterioration of their thin coatings. Therefore, R_m and C_m changes were not those predicted by the theory, making it difficult, if not impossible, to determine their physical meaning. Nucleation, growth, and accumulation of the corrosion products in the coating defects lead to an increase in the barrier effect accompanied by changes of E_{corr} and R_m to values indicating a greater protection (more positive E_{corr} and higher R_m) and, in general, a quasi-stability of C_m . New changes of these parameters, in the opposite direction, suggest that the corrosion-protection cycle is starting in other less resistant areas of the organic film. This process feeds back on itself until the organic coating is totally degraded.

Figures 2a-c show the experimental values of E_{corr} , R_m and C_m for samples with thicker coatings. The E_{corr} vs. t

curves (Fig. 2a) illustrate that, except for sample N, the potential remains steady for 65 days of immersion. At longer exposure times, samples F, I, L, and M have a low tendency to reach more active values but always below -0,1 V (SCE). The evolution of R_m denotes that: 1) sample N is the most unstable; 2) the ionic resistance of sample F starts to decrease from the 19th day of immersion, and; 3) for samples G, H, I, J, K, L and M, R_m does not change for 100 days. The initial R_m decrease and C_m increase (Fig. 2c), are attributed to water absorption accompanied by elution of the soluble components of the paint¹⁹. From the behaviour of samples F, G, H, I, J, K, L, M and N after 100 days of immersion: $-E_{\text{corr}} > 0.1$ V (SCE); $R_m > 10^7 \Omega \text{cm}^2$ and $C_m < 10^{-9} \text{F cm}^{-2}$, it can be inferred that epoxy paints thicker than 80 μm show an excellent protective behavior and absence of damage. These results are in good agreement with those obtained from water permeability measurements²⁰. Thus, by comparing the transport properties of the epoxybituminous paint (diffusion coefficient $D = 7.58 \times 10^{-9} \text{cm}^2 \text{s}^{-1}$; solubility $S = 9.68 \times 10^{-3}$ and permeability $P = 7.33 \times 10^{-11} \text{cm}^2 \text{s}^{-1}$) and the epoxy enamel coating ($D = 4.60 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$, $S = 7.90 \times 10^{-3}$ and $P = 3.64 \times 10^{-10} \text{cm}^2 \text{s}^{-1}$) it can be concluded that the epoxybituminous paint is less

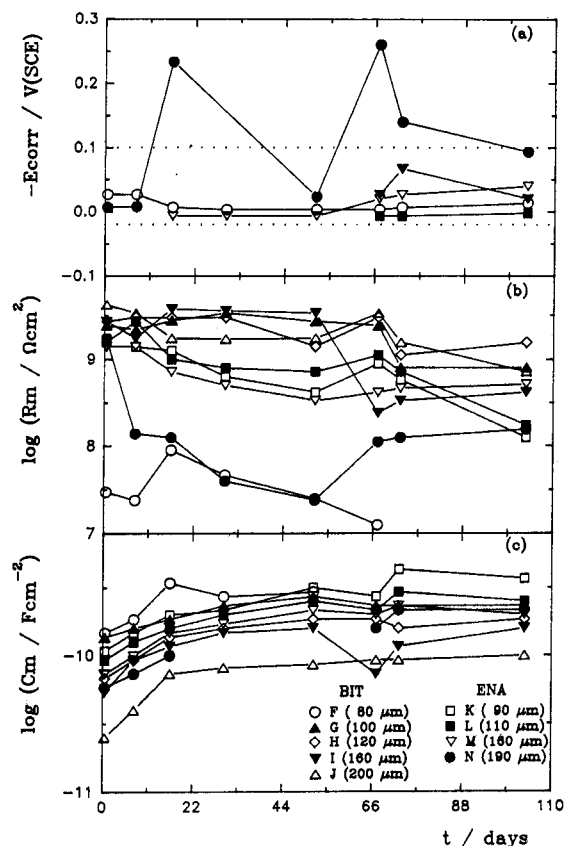


Figure 2. a) Corrosion potential (E_{corr}); b) ionic resistance (R_m), and; c) dielectric capacitance (C_m) vs. immersion time (t) for epoxybituminous paints (BIT, samples F, G, H, I and J) and epoxy-enamel (ENA, samples K, L, M and N).

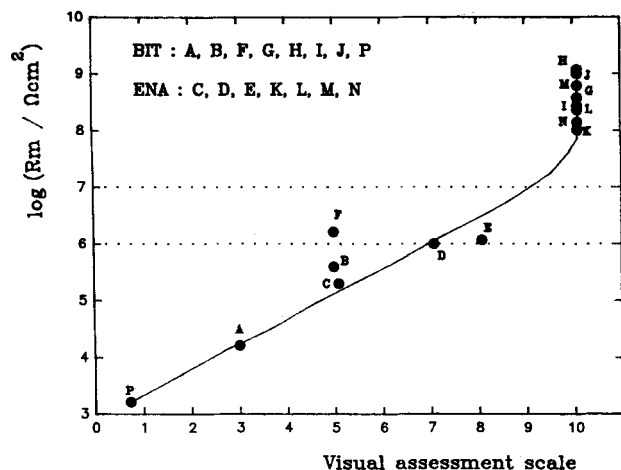


Figure 3. Correlation between $\log R_m$ and the results obtained by visual inspection (visual assessment scale), for every sample.

permeable due not only to its greater chemical inactivity but also to its solids content.

Figure 3 summarizes the experimental results obtained from the salt spray tests and electrochemical impedance measurements. A good agreement between the visual assessment of the corrosion degree (ASTM Standard D-610) and the ionic resistance R_m measured at the end of the test can be observed. The corrosion scale averages between 1 and 10 and the $\log R_m$ between 3 (for the reference bar steel sample) and 10. The thicker organic films are correlated with higher R_m values and greater protection degree. Therefore, it can be expected that if the coatings are applied with a thickness adequate for each specific service condition, a successful anticorrosive protection will be maintained for longer periods.

Conclusions

The current experimental results demonstrate that a non-destructive laboratory technique will indicate if, under certain environmental conditions, the anticorrosive protection afforded by a paint or a painting scheme is satisfactory ($R_m > 10^7 \Omega \text{ cm}^2$, $C_m < 10^{-9} \text{ F cm}^{-2}$ and a value of 8-10 in the scale of visual assessment). The test also seems to be useful for predicting the behavior of organic coatings exposed to aqueous environments, which could be profitable in quality control. Nevertheless, it is assumed that the study must be extended to other paints, substrates and environments, all of which are now in progress.

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