

Evaluation of Zinc-Rich Paint Coating Performance by Electrochemical Impedance Spectroscopy

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A influência da concentração em volume de pigmento e o conteúdo do veículo alquídico empregado na formulação de revestimentos de tinta rica em zinco (TRZ) foram investigados para avaliar a proteção à corrosão de substratos de aço em água do mar. Tanto as técnicas eletroquímicas *dc* quanto as *ac* foram usadas para se obter uma visão mais profunda no que diz respeito ao efeito da composição do revestimento sobre a resistência à corrosão de TRZ alquídico como uma função do tempo de imersão em água do mar artificial. Testes acelerados padrões foram realizados com as superfícies de aço pintadas para avaliar o grau de enferrujamento e de formação de empolas.

The influence of pigment volume concentration ($C_{v,p}$) and alkyd vehicle content employed in the formulation of zinc-rich paint (ZRP) coatings has been investigated to evaluate the corrosion protection of steel substrates in sea water. Both *dc* and *ac* electrochemical techniques have been used to gain a deeper insight concerning the effect of coating composition on corrosion resistance of alkydic ZRP as a function of immersion time in artificial sea water. Standard accelerated tests were carried out with the painted steel surfaces in order to assess the degree of rusting and blistering.

Keywords: *zin-rich paints, impedance, corrosion*

Introduction

The ability of coatings to protect metallic structures against corrosion generally depends on coating characteristics, as well as on properties of the metal/coating interface. For iron-type metallic substrates exposed to either industrial or marine atmospheres, zinc-rich coatings are commonly used for corrosion to protection^{1,2}. Thus, zinc-rich primers (ZRP) with organic or inorganic binders are extensively employed to protect steel structures from corrosion when they are in contact with aggressive media such as sea water. Both pigment volume concentration and binder content can markedly affect the performance of a ZRP. Commonly, two fundamental protection mechanisms operating in the ZRP can be recognized, namely the galvanic protection stage and the barrier effect stage^{3,4}.

The aim of the present paper is to investigate the corrosion protection behavior of zinc-rich alkyd paints for different pigment volume concentration ($C_{v,p}$) and vehicle levels, using electrochemical impedance spectroscopy (EIS) and open circuit corrosion potential measurements at different exposure times in artificial sea water. ASTM standard test procedures were carried out to assess the rusting and degree of blistering suffered by the coated steel surfaces, as well as to evaluate typical physicochemical properties.

Experimental

SAE 1020 (UNS G10200) steel plates 20 x 8 x 0.2 mm were used as the metallic substrate. Metal surfaces were sandblasted to AS 2_{1/2} degree (SIS Standard 05 59 00/1967), degreased with toluene and coated with paints whose $C_{v,p}$ varied in the 76-88% range. For the sake of comparison, in

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samples with relatively low Zn content (76-77%), chlorinated rubber was added to the coating composition. The ZRP thickness (about 60 μm) was measured with an electromagnetic gauge employing bare sanded plates and standards of known thickness as reference. The experimental set-up and the electronic equipment used for the *dc* and *ac* electrochemical measurements have been described elsewhere³⁻⁵. Potentials were measured and are referred to in the text against a saturated calomel electrode (SCE). Electrochemical impedance spectroscopy (EIS) measurements in the frequency range of $1 \text{ mHz} \leq f \leq 65 \text{ kHz}$ were performed in the potentiostatic mode at the corrosion potential after different exposure times in artificial sea water prepared according to the ASTM Standard D-1141/90. For impedance measurements, an activated Pt probe was coupled to the SCE through a 10 μF capacitor to reduce phase shift errors at high frequencies.

The following standard accelerated tests were carried out on painted steel samples: (i) salt spray cabinet for 500 h (ASTM B 117/85); (ii) immersion in top water (500 h), in white spirit (24 h), in 1% HCl (24 h), and in 1% NaCl (24 h), according to BS 3900 G5/76; (iii) aging in weatherometer (300 h); and (iv) pull-off adhesion (ASTM D-4541/85).

Results and Discussion

The dependence of the corrosion potential E_{corr} on immersion time in artificial sea water illustrates the galvanic protection supplied to the steel substrate by alkyd ZRP coatings loaded with different $c_{v,p}$. The observed gradual shift of E_{corr} towards more positive values suggests a progressive deterioration of the coating. Initially, E_{corr} is about -1.10 V, a value which lies in the range of the corrosion potential of pure zinc electrodes in sea water⁶, whereas after prolonged exposure time in the electrolyte it reaches the typical value corresponding to the corrosion potential of steel in sea water (-0.65 V). The more negative E_{corr} measured in the case of samples containing chlorinated rubber indicates a greater availability of the protective Zn pigment, even for $c_{v,p}$ values lower than those used in the other samples.

For the naval steel/ZRP/artificial sea water system, both Bode and Nyquist plots at different immersion times showed that the Zn content and the binder concentrations employed in the paint formulation strongly affect the corrosion behavior of ZRP coatings tested in this work. Impedance spectra were analyzed by using non-linear fitting routines according to the following total transfer function:

$$Z_T(j\omega) = R_\Omega + Z \quad (1)$$

where $\omega = 2\pi f$, R_Ω corresponds to the electrolyte resistance, and Z denotes the frequency response of the corrosion system, which can be expressed by:

$$Z^{-1} = \text{CPE}^{-1} + \frac{R_C + R_{DO} (jS)^{-1/2} \tanh(jS)^{1/2} + R_A}{[R_C + R_{DO} (jS)^{-1/2} \tanh(jS)^{1/2}] R_A} \quad (2)$$

In Eq. 2, the constant phase element CPE involves a capacitance C and a parameter α that was close to 0.5, which is a typical value of active porous electrodes. The resistance R_C can be associated with the series combination of the electrolyte resistance inside the pores and the charge transfer resistance of the oxygen reduction reaction (ORR). Therefore, a finite diffusion impedance was considered to account for the transport process involved in the cathodic partial reaction through the coating, being $S = l^2 \omega/D$ where l and D denote the diffusion length and the diffusion coefficient, respectively, and R_{DO} represents the diffusion resistance when $\omega \rightarrow 0$. On the other hand, R_A is related to the charge transfer resistance of the Zn dissolution process occurring in parallel with the ORR.

Figures 1 and 2 show the good agreement between the experimental results and calculated data. Accordingly, it is possible to evaluate the relative impedance contributions of the anodic and cathodic processes. Thus, the dependences of R_A , R_C , and C on the immersion time are depicted in Figs. 3-5, respectively.

Measurements carried out with samples whose compositions include 87-88% of pigment concentration were interrupted after about 25 days of immersion, since blistering of the coatings were visually detected. This fact can be attributed to a loss of the coating adhesion properties caused by insufficient binder content. Accordingly, the higher the binder content the lower the $c_{v,p}$ levels, and consequently the longer the useful lifetime.

The changes of the capacitance values, the increase of the resistances R_A and R_C , and the appearance of a diffu-

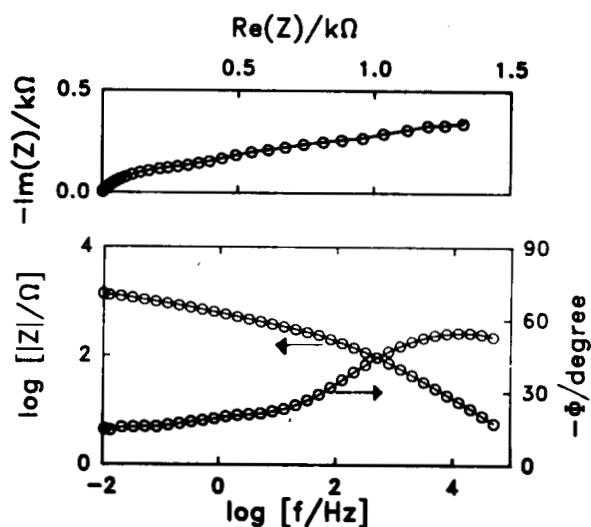


Figure 1. Experimental (o) and simulated (-) Nyquist and Bode plots obtained for a sample containing $c_{v,p} = 86\%$ after 15 days immersion in artificial sea water.

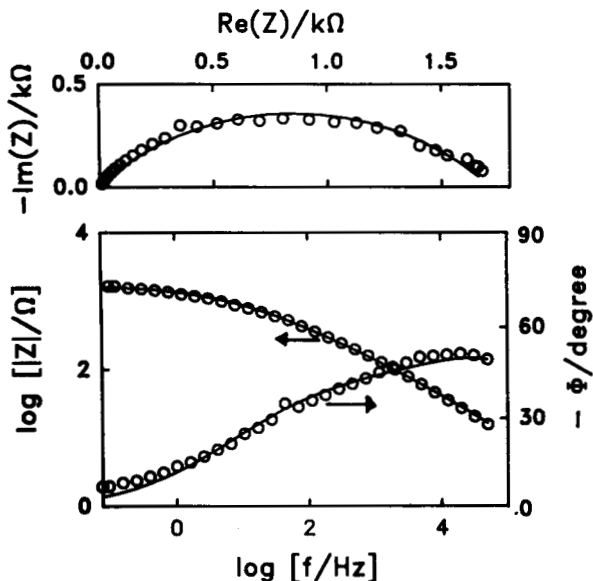


Figure 2. Experimental (o) and simulated (-) Nyquist and Bode plots obtained for a sample containing $c_{v,p} = 77\%$ and chlorinated rubber, after 34 days immersion in artificial sea water.

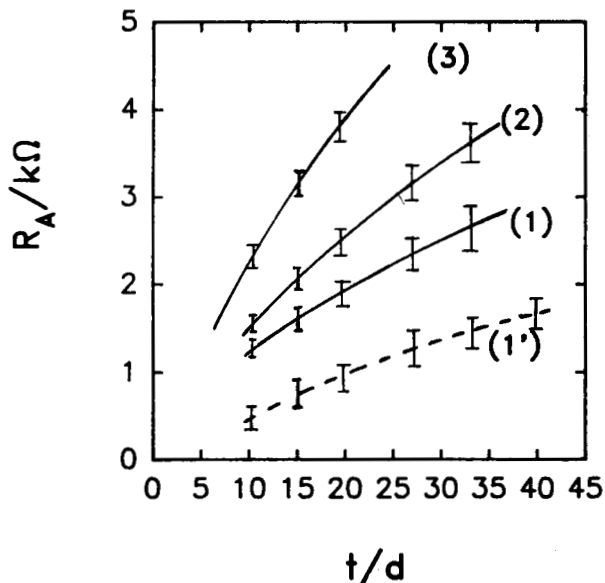


Figure 3. Dependence of R_A on immersion time for samples whose Zn contents are: 77% (curves 1 and 1', without and with chlorinated rubber, respectively), 85% (curve 2), and 88% (curve 3).

sional process with increasing immersion time can be explained by the accumulation of zinc corrosion products within the pores of the coating. This decreases the effective pore radius in the ZRP, diminishes the area of the Zn/solution interface, and provokes a progressive loss of electrical connection between the Zn particles.

The cathodic protection effect was practically similar for samples with $c_{v,p}$ values in the range of 76-85%, although a relatively faster deterioration was found for samples whose zinc content was about 76-77%. These results

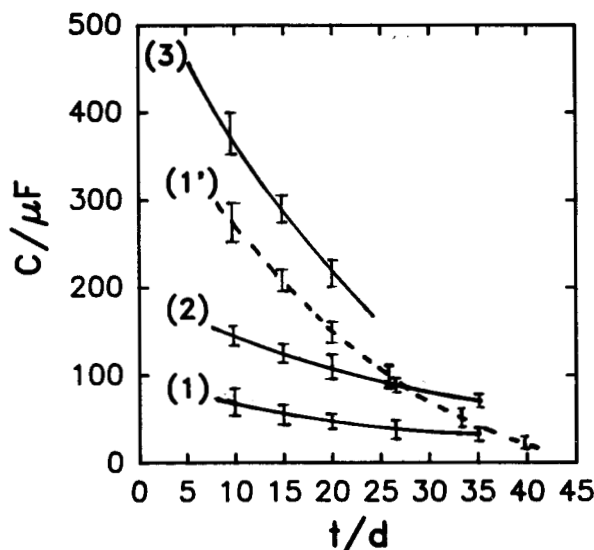


Figure 4. Dependence of C on exposure time for samples indicated in Figure 3.

exhibit satisfactory agreement with the conclusions derived from standard accelerated physicochemical tests.

Before immersion in the electrolyte, the pull-off adhesion test carried out on painted steel panels revealed the characteristic good interfacial bonding forces (28-30 kg cm^2) between the zinc rich alkyd paints and the metallic substrate. However, after exposure to either artificial sea water or electrolytes used in the different standardized tests, the adhesive forces were weakened (up to 80% in some cases). This produces blistering and/or delamination of the coating, effects that can be attributed to the pressure exerted by the aqueous solution accumulated at the metal/coating interface. Likewise, the adhesion loss process could be accelerated because of an increase of alkalinity in the cathodic areas. Therefore, in the present case, the experimental results can be explained, assuming that the ORR is enhanced by the large electrochemical activity of the Zn pigment particles and also favored by the increase of the local pH. Under these circumstances, the modified (with an unsaturated oil) alkyd resin-based ZRP coatings used in this work are able to react with either an alkaline medium or the Zn particles to generate complex soaps. This improves the barrier effect but reduces the adhesion forces, as was observed.

Taking into account that the highly reactive anti-corrosive ZRP coatings are not directly exposed to the aggressive medium, since they are usually covered with an almost impermeable topcoat paint which modifies (generally delaying) the kinetics of the interfacial processes, zinc-rich alkyd paints can be used to protect naval steels. Standard physicochemical tests and visual assessment also indicate that this type of primer afford satisfactory corrosion protection performance.

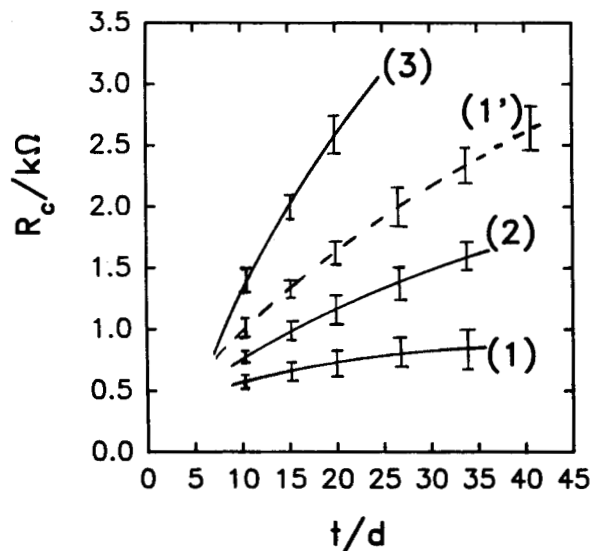


Figure 5. Dependence of R_c on exposure time for samples indicated in Figure 3.

Conclusions

EIS was found to be a useful tool for assessing the protective behavior of ZRP organic coatings. The whole set of impedance spectra was interpreted using a non-linear fitting routine according to transfer function analysis employing a suitable physical model. Results clearly demonstrate that the galvanic protection stage requires good

electrical contact among the zinc particles. In samples with a Zn content higher than 80%, the cathodic protection effect was still in action after about 45 days of immersion in sea water.

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