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Anticorrosion performances of epoxy coatings modified with polyaniline: A comparison between the emeraldine base and salt forms

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ABSTRACT

The protection against corrosion imparted by epoxy paints modified by the addition of polyaniline emeraldine base (0.3% w/w) and $Zn_3(PO_4)_2$ (10% w/w) has been investigated and compared. For this purpose, accelerated assays through corrosion cycles, which simulate the marine conditions, have been performed using a home-made robotized equipment. Results were compared with those recently obtained for a formulation constituted by the same epoxy paint modified with polyaniline emeraldine salt (0.3% w/w) [E. Armelin, R. Pla, F. Liesa, X. Ramis, J.I. Iribarren, C. Alemán, Corr. Sci. 50 (2008) 721.]. A detailed analysis of the results using the ASTM standard method D-1654-79 allows to conclude that the coating modified with polyaniline emeraldine base performs better than both the unmodified coating and the coatings modified with the inorganic corrosion inhibitors. This behaviour should be attributed to a mechanism based on the ability of polyaniline emeraldine base to store charge. On the other hand, as the epoxy paint modified with the latter polymer provides better results than the formulation containing $Zn_3(PO_4)_2$, we conclude that inorganic corrosion inhibitors, which may have detrimental effects on both the environment and the human health, can be replaced by a small concentration of environmentally friendly organic polymers.

1. Introduction

Organic coatings are widely used to protect metallic substrates from marine environment. For reliable performance, inorganic pigments that release corrosion inhibiting substances are usually added to the formulation of these organic coatings. Indeed, the coatings need to be highly pigmented to ensure long-term protection, corrosion inhibitors being constantly released into the environment. Unfortunately, nearly all powerful corrosion inhibitors may have detrimental effects on both environment and human health due to their toxic and carcinogenic nature. Thus, novel approaches are sought to replace conventional anticorrosive inorganic pigments.

In recent years, we reported that conducting polymers (CPs) can be successfully used as anticorrosive additive to modify the formulation of conventional organic coatings (paints) [2], the most important benefit of our technology being that a very low concentration of CP is needed. Interestingly, we found that the chemical nature of the anticorrosive additive can extend from polythiophene [3–7] or polypyrrole [1,4,7] derivatives to polyaniline [1,8,9], typically abbreviated PAni.

PAni is the CP most extensively studied, which should be attributed to its chemical stability, relatively high electrical conductivity and, specially, the simplicity of its synthetic production [10]. Many studies have provided strong indications that coatings based on PAni improve the resistance of steel against corrosion. DeBerry [11] and Wessling [12,13] stressed the passivation of the metal surface responsible of the protective activity of PAni when the CP is directly used as a primer. In the case of steel substrate, the passive layer was formed by $Fe_3O_4/\gamma\text{-}Fe_2O_3$. A similar mechanism with oxides forming a barrier coat was also reported by Schauer et al. [14]. On the other hand, studies on doped CPs showed that corrosion is prevented by the generated electric field, which restricts the flow of electrons from the metal to the outside oxidizing species [15]. In contrast, a barrier mechanism based on a high diffusion resistance against corrosive ions has been used to explain the corrosion protection imparted by the emeraldine base of PAni (PAni-EB) [16], which is the non-conductive form of this polymer.

In a recent study we investigated the efficacy of the conducting emeraldine salt form of PAni (PAni-ES), among other CPs, as anticorrosive additive for an epoxy paint based on diglycidyl ether of bisphenol A and polyamide [1]. The concentration of the CP in the paint formulation was varied from 0.3 to 1.5% w/w. Interestingly, accelerated corrosion assays showed that the addition of PAni-ES improves the resistance of the paint, the highest inhibition of corrosion being obtained for the lowest CP concentration, i.e. 0.3%

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w/w. Furthermore, this CP polymer was found to act as an adhesion promoter. This protecting activity was fully consistent with results reported in early studies about the performance of PAni coatings [11–14].

In this work we extend our previous study to PAni-EB. For this purpose, a small concentration of this polymer (0.3% w/w) was added to the same epoxy paint previously used for PAni-ES [1]. This will allow a reliable comparison between the anticorrosive properties of PAni-EB and PAni-ES. Furthermore, accelerated corrosion assays has been also performed using a modified coating that was obtained by adding 10% w/w of $Zn_3(PO_4)_2$, which is a conventional corrosion inhibitor typically used in the epoxy paint studied here. The aim of these assays is to check if CPs, in this case PAni, are so or even more effective against corrosion than conventional inorganic pigments in order to replace them. Thus, this work reports a rigorous comparison of the strength as corrosion inhibitors of PAni-EB, PAni-ES and $Zn_3(PO_4)_2$. Following our previous studies on CPs [2–9], the corrosion assays performed in this work consisted on cyclic short term exposures of coated steel panels to accelerated ageing conditions in 3.5% NaCl solution at room temperature.

2. Methods

The unmodified epoxy paint and the formulations with PAni-EB, PAni-ES and $Zn_3(PO_4)_2$ have been denoted as epoxy, epoxy + PAni-EB, epoxy + PAni-ES and epoxy + $Zn_3(PO_4)_2$, respectively. Pinturas Hempel S.A., manufacturers of paints for marine and protective use, kindly supplied the epoxy primer used in this work. This paint was prepared by mixing a stoichiometric amount of Epikote 828 (Hexion) and Crayamid 140 (Cray Valley), a mixture of inert pigments (PVC = 27%) and a mixture of alcoholic solvents and aromatic hydrocarbons (15% w/w). This composition was free of anticorrosive pigments and additives. A complete characterization of this epoxy paint was provided in our previous work [7]. PAni-EB and $Zn_3(PO_4)_2 \cdot 4H_2O$ were purchased from Aldrich (CAS n°: 476706, $M_w \sim$ 10,000) and Nubiola Inoganic Pigments (CAS n° 7779-90-0), respectively. A naval steel (St F111) has been employed as metallic substratum for corrosion experiments. The elemental composition of this steel is: C = 0.20%, Mn = 1.40%, S = 0.045%, and N = 0.009%, the density being 7.90×10^3 kg/m^3. Rectangular test pieces of 40 mm × 50 mm × 1 mm with a diameter hole of 6.5 mm were previously degreased with acetone and stored in dried atmosphere until the coating application, using calcium chloride as dryer in a recipient connected to the vacuum.

Structural characterization of epoxy, epoxy + PAni-EB and epoxy + $Zn_3(PO_4)_2$ films was performed using a Jasco 4100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. Samples were placed in an attenuated total reflection accessory with thermal control and a diamond crystal (MkII Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma). Thermogravimetric analyses were carried out with a PerkinElmer TGA-6 thermobalance at a heating rate of 10 °C/min under nitrogen atmosphere and a temperature range from 30 to 850 °C. The mechanical characteristics of the three formulations were evaluated using stress–strain assays with a Zwick Z2.5/TN1S testing machine. Finally, the electrical conductivity (σ) of the formulations was measured on films using the sheet-resistance method following a previously described procedure [17].

Regular films for structural, thermal, mechanical and electrical measurements were prepared by evaporation at room temperature of the volatile organic solvent of the paint formulation. Plate samples with a length of 30 mm, a width of 3 mm and a thickness of 100–250 μm were cut out from the films for stress-strain experiments. The deformation rate was 10 mm/min. All the mechanical and electrical parameters reported in this work, i.e. Young's modulus, tensile strength, elongation at break and electrical conductivity, correspond to the average of 10 independent measurements.

Table 1
Composition (in g) of the formulations used in this work.

Paint	Base	AD[a]	Xylene	Hardener	DFT[b]
Epoxy	41.4	–	12.5	8.6	138 ± 10
Epoxy + PAni-EB	82.5	0.3	10.6	17.2	125 ± 11
Epoxy + $Zn_3(PO_4)_2$	74.8	10	16.1	15.3	113 ± 21

[a] AD = anticorrosive additive.

[b] Dry film thickness (in μm), which corresponds to one coat and the average of 10 independent measurements.

Paints were applied by immersion of the metallic substrate in a base/solvent/hardener composition with the mixing ratio recommended by the manufacturer. These compositions, which include the mass of the anticorrosive additive, are detailed in Table 1. In the case of $Zn_3(PO_4)_2$, small quantities of BYK 500 (0.0809 g) and BYK 525 (0.0457 g), from BYK Chemie, were required to aid the pigment dispersion. Initially, PAni-EB was dissolved in xylene, after this being added to the mixture. It should be remarked that a good homogenization of the mixture is necessary to allow a suitable application on the metallic substrate and to obtain a covering power able to guarantee the desired protective characteristics. This procedure yielded samples with a film thickness of around 110–140 μm after one coat (Table 1). Thickness measurements were performed using a machine model Uno-Check Fe from Neurtek S.A. company.

Accelerated corrosion tests were performed using a home-made equipment developed at our laboratory (Fig. 1). It consists of a support to put steel pieces, which is controlled by a programmable device, and a bath containing an aggressive solution medium. The device allows program-controlled cycles that simulate marine conditions, each operating cycle being formed by the following steps: (i) immersion of the painted steel pieces (15 min) into a corrosive aqueous solution medium containing NaCl (3.5 wt.%, pH 6.6); (ii) wringing of the steel pieces (30 min); (iii) drying (10 min) forced with bulbs (230 V, 100 W); and (iv) cooling at room temperature

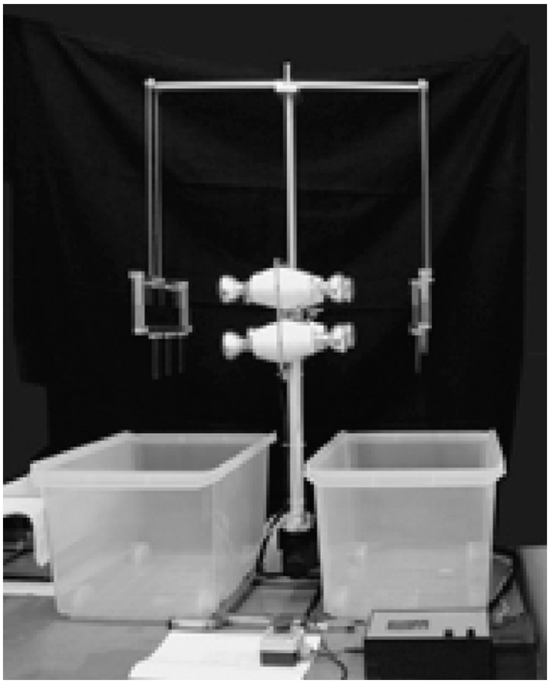

Fig. 1. Automatic home-made equipment used to perform accelerated corrosion tests.