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Investigation on zinc phosphate effectiveness at different pigment volume concentrations via electrochemical impedance spectroscopy

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Abstract

This research is based on studying corrosion inhibitive effect of zinc phosphate at different pigment volume concentration (PVCs) in epoxy–polyamide system. EIS has been examined at open circuit potential (OCP) after 7 days of immersion in 3.5% NaCl solution to indicate electrochemical properties of epoxy coated mild steel at different levels of pigmentation. Coating capacitance, coating resistance, double layer capacitance and charge transfer resistance have been extracted from fitting of EIS results with an electrical circuit, while impedance magnitude at 100 mHz and phase angle (θ) at 10 kHz have been extracted directly from bode plots. Also OCP behavior was examined. Results showed best performance at PVC = 36.5%.

Keywords: Zinc phosphate; Epoxy coating; EIS; PVC; CPVC

1. Introduction

Organic coatings, because of high ionic resistance could be useful materials to protect metals from corrosion. During service life defects form in the coating, this results in corrosion underneath the organic coatings. Corrosion inhibitive pigments are introduced in organic coatings to control the corrosion and its consequences, e.g. cathodic delamination and anodic undermining.

One of suggested anticorrosive pigments is zinc phosphate. Zinc phosphate is known as green pigment against toxic pigments like chromate pigments. Inhibitive action of zinc phosphate pigment is not well understood. Many researches have been done in aqueous extract of zinc phosphate and its dispersions in polymeric films but very different results are reported [1–12]. Some authors believe that because of low solubility of zinc phosphate it can not act as an inhibitor and it is only an expensive extender. Some authors pointed out that zinc phosphate increases barrier properties of organic coatings, while others reported no barrier effect of this pigment. It is stated that zinc phosphate hydrolyzes to form zinc hydroxide and secondary phosphate ions. Phosphate ions form basic iron(III) phosphate as a complex on the iron surface. Although useful information are obtained from previous researches but pigment blends were used that makes the system so complicated and in many cases interaction between pigments were omitted. More researches are needed to understand inhibitive mechanism of zinc phosphate pigment clearer. In this research in order to eliminate the synergistic or antagonistic effect of other pigments, only zinc phosphate is used to make single component pigmented system.

PVC of organic coatings has great effect on corrosion protection performance of organic coatings, so it was tried to evaluate the effect of zinc phosphate volume concentration on the electrochemical properties of epoxy coated mild steel via electrochemical impedance spectroscopy (EIS). EIS is a well known electrochemical test that makes it easy to simulate

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the electrochemical behavior of coated steel with an electrical model.

2. Experimental

Critical pigment volume concentration (CPVC) was calculated with oil absorption (OA) method [13]; it was 52.2%. Then seven level of pigmentation were selected, these PVCs were 31.3, 36.5, 41.7, 46.9, 52.2, 57.4 and 62.6%. Zinc phosphate (Nubiola) dispersions with the grind of 10 μm in epoxy resin (Epikote 1001 Shell) were prepared while used additives, like dispersing agent (EFKA 5244) and thickening agent (Aerosil) were added in the same proportion (1%, v/v) to all PVCs. Also in the unpigmented sample (blank sample) the same proportion of additives were used. Samples were mixed with calculated amount of polyamide (Crayamid 115) and applied on degreased mild steel (Q-Panel). Coatings where cured at room temperature for 7 days then an area of 4 cm^2 of coated mild steel with dry film thickness of 30 ± 2 μm was selected for EIS test. The rest area of plates sealed with beeswax-colophony mixture. Three replications were prepared for each coating to ensure repeatability. Specimens were immersed in 3.5% NaCl solution and EIS tests were examined after 7 days of immersion. EIS tests were carried out with AUTOLAB G12 at OCP with 10 mV perturbation, in the frequency range of 10 mHz–10 kHz. Reference electrode and counter electrode were Ag/AgCl and platinum, respectively.

3. Results and discussions

EIS measurements were fitted with AUTOLAB FRA software by the electrical model shown in Fig. 1 [14–17]

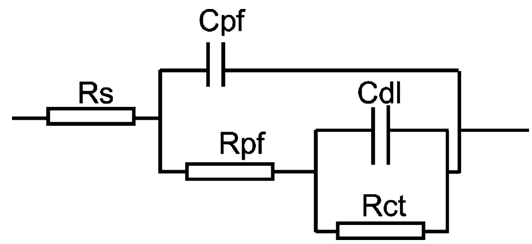

Fig. 1. Electrical model of EIS results.

that has the best fitting results. Then electrical elements of coated mild steel were extracted. A typical fitting is given in Fig. 2.

Average values of calculated (coating capacitance, coating resistance, double layer capacitance and charge transfer resistance) and measured (impedance magnitude at 100 mHz and phase angle at 10 kHz) electrical elements for pigmented systems are plotted vs. PVC in Figs. 3 and 4 respectively. Also average values of OCP for pigmented systems are provided in Fig. 4.

Electrical elements of unpigmented epoxy coated mild steel after 7 days of immersion are given in Table 1.

3.1. Coating capacitance (C_{pf})

C_{pf} of blank sample (Table 1) after 7 days of immersion is lower than the capacitance of pigmented coatings (Fig. 3). Also it is evident that the slops of increase in C_{pf} with PVC (Fig. 3) in the range of PVC = 31.3–52.2% is lower than the slop of increase in the range of PVC = 52.2–62.6%. Increase of C_{pf} with PVC is also reported by Guenbour et al. [8]. Increase of C_{pf} with PVC could be related to two phenomena; (1) higher relative permittivity (ε_r) of pigment to binder that results in higher dry coating capacitance [18] and (2) higher ε_r of water that increases wet coating capacitance [19]. It

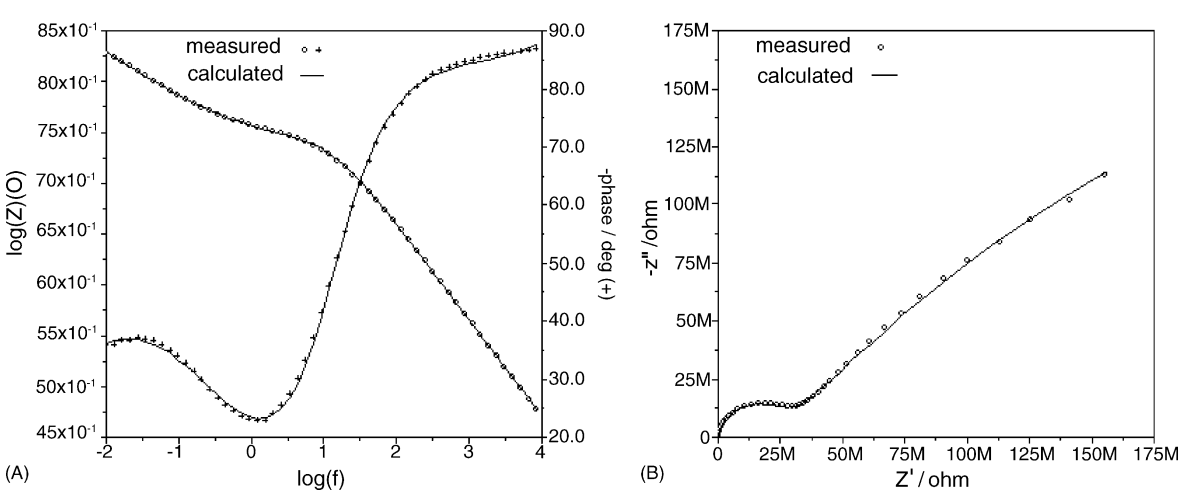

Fig. 2. A typical fitting of EIS results for epoxy coated mild steel at PVC = 36.5% after 7 days of immersion in 3.5% NaCl solution, $C_{pf} = 1.583E - 10$ F/cm^2, $R_{pf} = 2.776E + 7$ ohm cm^2, $C_{dl} = 3.767E - 14$ F/cm^2, $R_{ct} = 7.84E + 8$ ohm cm^2, $\theta = 86.93^\circ$, $Z = 7.345E + 7$ ohm cm^2.