Progress in Organic Coatings 76 (2013) 302–306

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Electrochemical examining behavior of epoxy coating incorporating zinc-free phosphate-based anticorrosion pigment

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ARTICLE INFO

Article history:
Received 17 August 2012
Received in revised form
26 September 2012
Accepted 28 September 2012
Available online 22 October 2012

Keywords:
Mild steel
EIS
Electrochemical noise
Protective coatings
Anticorrosion pigments

ABSTRACT

Protective performance of the epoxy primer containing strontium aluminum polyphosphate (SAPP) as a zinc-free phosphate-based anticorrosion pigment is aimed to assess in this work through taking advantage of electrochemical impedance spectroscopy (EIS) and electrochemical noise method (ENM). The absence of zinc offers an excellent environmentally friendly profile to the class of inhibiting compound. In the pigment extracts, the electrochemical techniques revealed superiority of SAPP compared to the conventional zinc phosphate (ZP). The behavior was connected to precipitation of a protective layer on the surface exposed to SAPP. In comparison with ZP, the most effective SAPP content in the protective primer was then determined using EIS.

1. Introduction

Anticorrosion pigments make an important contribution to the performance of protective coatings. In other words, they are capable of enhancing the protection through chemical/electrochemical or physical mechanisms [1–3]. As a distinguished representative for electrochemically active class, chromate-based pigments have been reported to exhibit excellent inhibitive behavior; however, due to increasing concerns for environmental protection and potential health hazard associated with chromates, their use has been heavily restricted [4–7]. Of the proposed alternatives for the toxic chromium VI containing substances, zinc phosphate (ZP) plays a significant role in the protective primer formulation, although it has been is reportedly shown not to provide the same level of inhibition revealed by chromates [8–11]. An efficient approach to overcome the drawback might be the coating films incorporated with new generations of phosphate-based anticorrosion pigments [12–18]. Revealing the inhibitive mechanisms, the previous publications could provide obvious evidence for superiority of zinc aluminum phosphate (ZPA) and zinc aluminum polyphosphate (ZAPP) representing second and third generations of phosphate-based pigments, respectively [19–22]. The present work intends to evaluate the role of strontium aluminum polyphosphate (SAPP) as zinc-free phosphate-based anticorrosion pigment in protective performance of a solvent-borne epoxy primer through electrochemical impedance spectroscopy (EIS). In comparison with conventional ZP, the effective SAPP pigment content in the protective primer has been examined. Providing an excellent environmentally friendly profile could be considered as an important advantage of zinc elimination.

To obtain insight into the corrosion inhibition, the behavior of mild steel panels exposed to the pigment extracts in 3.5% (w/w) NaCl solution was investigated by taking advantage of EIS, electrochemical noise method (ENM), spontaneous fluctuations of the potential and the current of a freely corroding system at low frequencies which provide useful kinetic and mechanistic information [23–25], as well as inductively coupled plasma-optical emission spectrometer (ICP-OES) analysis of the pigment extracts.

2. Experimental

2.1. Materials

The mild steel plates were polished and then solvent degreased by acetone. For electrochemical tests, an area of 1 cm^2 of each plate was exposed to the solutions while the rest were sealed. In this research work, the anticorrosion pigments were zinc phosphate and strontium aluminum polyphosphate known under the

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http://dx.doi.org/10.1016/j.porgcoat.2012.09.026

Table 1
Technical data of the pigmented coatings.

Resin	Curing agent	Additive	Solvent	Pigment/Filler	Anticorrosion pigment (% w/w)				Dry film thickness (μm)
					ZP	SAPP			
						1	2	3	
Epoxy bisphenol A	Polyamide	Dispersing/wetting agent, thickener, defoamer	Mixture of xylene, MEK, butyl glycol and normal butanol	TiO_2, talc, barite	10.94	10.94	8.205	5.47	33 ± 3

trademarks ZP and SAPP (Heubach Ltd.), respectively. In order to prepare extracts, 2 g of each pigment was stirred in 1 l 3.5% (w/w) NaCl aqueous solution for 24 h then filtered. Solubility of the anticorrosion pigments was analyzed using an ICP-OES [Varian Vista Pro ICP-OES]. The compositions of the coatings used in this study are given in Table 1. The primers were formulated with different contents of SAPP anticorrosion pigment while the pigment volume concentration (PVC) value is approximately kept constant in all formulations. A dispersion of pigments and fillers was prepared in the epoxy resin employing a high speed disk disperser; afterwards the dispersion was milled to obtain 15 μm fineness. Then, the prepared liquid paints were applied on the acetone degreased plates using a quadrangular film applicator (Neurtek instruments). After a seven-day curing period, the coated samples were sealed, leaving a central area of 4 cm^2 unmasked.

2.2. Methods

A three-electrode cell including the Ag/AgCl (3 N KCl) reference electrode, the studied sample as working electrode and the platinum counter electrode was used to run EIS tests. The impedance measurements were made on the plates using a sine wave of 10 mV amplitude peak to peak at the open circuit potential, OCP. The frequency range was usually from10 kHz down to 10 mHz. The working, counter and reference electrodes were connected to the terminals of an Autolab instrument. Data analysis was made using ZSimpWin software. The noise data were recorded during 1024 s at sampling rate of 1 s. Data analysis for ENM after removing DC trend using moving average removal (MAR) method was made with GPES software.

3. Results and discussion

As can be seen from Fig. 1 depicting typical Bode diagram of the steel specimens after 24 h immersion in sodium chloride solutions containing pigment extracts, the spectra revealed two quit different behaviors. This means that the plot of the bare metal exposed to ZP extract is characterized by only one time constant while two relaxation times could be observed in the presence of SAPP. Hence,

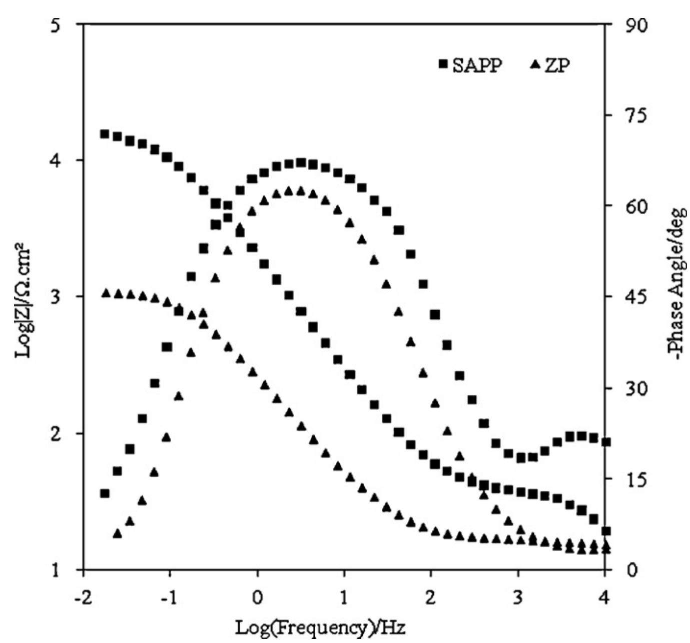

Fig. 1. Typical Bode diagrams of the bare metal specimens exposed to 3.5% NaCl solutions containing pigment extracts for 24 h.