



Effect of zinc-free phosphate-based anticorrosion pigment on the cathodic disbondment of epoxy-polyamide coating



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ABSTRACT

In the field of protective coatings, zinc-free pigments are proposed as promising anticorrosion compounds due to their excellent environmentally-friendly profile. In this paper, cathodic disbonding performance of a solvent-borne epoxy primer incorporating strontium aluminum polyphosphate (SAPP) as a zinc-free phosphate-based anticorrosion pigment was investigated. Regardless of the applied potential, the presence of SAPP in the coating formulation caused slower growth of the delamination area in comparison to ZP. According to the data obtained from EIS and SEM/EDX, this behavior was attributed to locally controlled pH and the precipitated film restricting active zones available for electrochemical reactions.

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1. Introduction

From the technical and economical points of view, one of the most effective approaches to control corrosion in metallic structures embedded in an electrolyte is to combine protective coating and cathodic protection. An organic coating can reduce the current requirement for cathodic protection [1]. Under the influence of cathodic polarization, a loss of coating adhesion may, however, occur. Therefore, cathodic disbonding can be considered to be the main degradation mechanism for cathodically protected coated steel structures. In fact, the loss of adhesion arises from the cathodic reaction which causes the generation of a strong alkalinity at the coating/metal interface in the presence of alkali metal cations [1–5]. The degree of disbondment is a function of several factors such as service temperature, coating formulation, dry film thickness, chemical nature of polymer/binder, applied potential, electrolyte composition and surface treatment. In this sense, the roles of environmental conditions as well as factors related to the coating film in cathodic disbonding have been investigated by several researchers [6–12]. The influence of anticorrosion pigment type on the cathodic delamination is subject of interest in this work. In the coating formulation, anticorrosion pigments that limit the kinetic of cathodic reactions are effective in prolonging

coating life [13–16]. Comparing to zinc phosphate (ZP), the previous publications could provide evidence for the superiority of new generations of phosphate-based anticorrosion pigments including zinc cation [14,15]. The adhesion retention of epoxy-polyamide coating was shown to be enhanced by the use of zinc aluminum polyphosphate (ZAPP), which represents the third generation of phosphate-based anticorrosion pigments. The ability of ZAPP incorporated organic coating to resist disbondment was linked to the precipitation of a layer on the surface [15]. The deposition formed on the surface in the ZAPP extract was composed of zinc hydroxide/phosphate and iron phosphate, as detected by XPS [17]. According to Ogle et al. [18], the phosphate layer is able to absorb hydroxyl ions, leading to a decrease in disbondment. Also, the introduction of zinc aluminum phosphate (ZPA), which is a second generation phosphate-based anticorrosion pigment, within an epoxy coating was reported to control growth of disbonded area [14]. Despite superior performance of the two anticorrosion pigments in comparison with ZP as one of the most extensively used alternatives for the carcinogenic chromates, current trends point to zinc-free pigments as future products because of their excellent environmentally-friendly profile [19–21]. Since the European Community restricted the employment of zinc (directive 76/464 EEC, codified as 2006/11/EEC), modification of the conventional ZP pigment through the replacement of zinc cation with calcium, strontium and aluminum has gained much attention. [22]

This study intends to assess the role of strontium aluminum polyphosphate (SAPP) as zinc-free phosphate-based anticorrosion

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Table 1
ICP-OES analysis results of extracts of pigments at different pH values.

		Solubility (mg/l)		
		[Zn]	[P]	[Sr]
ZP	Unadjusted pH	7.89	1.46	–
	pH 10	6.93	3.13	–
SAPP	Unadjusted pH	–	11.63	182.06
	pH 10	–	26.2	204.8

pigment in resistance of a solvent-borne epoxy primer to cathodic disbonding. It is noteworthy that the epoxy-polyamide paint has been extensively used in a wide variety of industries [23]. Characterization of the pigment extracts promoted a better understanding of cathodic delamination performance. Moreover, the effect of SAPP on cathodic disbondment of the epoxy coating was further assessed using the EIS technique and SEM/EDX surface analysis.

2. Experimental

2.1. Materials

Mild steel plates were polished followed by solvent degreasing with acetone. For electrochemical tests in the solution phase, an area of 1 cm² of each plate was exposed to the solutions while the rest were sealed.

The anticorrosion pigments used in this study were zinc phosphate and strontium aluminum polyphosphate known under the 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 and then filtered. Pigment extracts were prepared at different pH conditions. In addition to the extract with no external pH modification, two pigment extracts were obtained at pH values of 10 and 12.8 through the addition of NaOH. An inductively coupled plasma-optical emission spectrometer [Varian Vista Pro ICP-OES] was used to determine concentrations of dissolved species in the pigment extracts without pH modification and with pH value of 10. Table 1 presents the results of ICP-OES at different pH conditions. In case of the pigment extract provided at pH value of 12.8, the solubility for ZP and SAPP was 0.203 and 0.581 g/l, respectively. The pH variation determined using a WTW pH meter model 315i after the extract preparation is shown in Table 2.

Pigments were incorporated into the coatings with characteristics shown in Table 3 at a lambda (PVC/CPVC) of 0.6. The critical pigment volume concentration (CPVC) was calculated based on the oil absorption method [24]. A dispersion of pigments was prepared in the epoxy resin using a high speed disk disperser. The dispersion was milled to obtain 15 μm fineness. The prepared liquid paints were applied on mild steel substrates using a quadrangular film applicator (Neurtek instruments). Prior to coating application, the panels were polished to achieve a surface with roughness of 3–5 μm (peak to valley) and then degreased by acetone. After a 7-day curing

Table 2
Variation of pH values after extraction in different conditions.

pH value after 24-h extract preparation	pH value before introduction of pigment	
	3.5% NaCl solution containing	
	SAPP	ZP
5.72	6.48	Unadjusted pH
6.85	8.21	pH 10
12.19	12.38	pH 12.8

period under ambient condition, the coated samples were sealed with a mixture of beeswax and colophony resin, leaving a central area of 4 cm² unmasked.

2.2. Methods

All electrochemical measurements were carried out employing Autolab instrument model PGstat12. To perform EIS measurements, a conventional three-electrode cell including the prepared specimen as working electrode, a platinum counter electrode and a Ag/AgCl (3 N KCl) reference electrode was used. EIS measurements were executed at open circuit potential (OCP) within the frequency domain 10 kHz to 0.01 Hz using a sine wave of 10 mV amplitude peak to peak. Data analysis was made using ZSimpWin software.

Electrochemical potential and current noise were simultaneously measured in a freely corroding system employing two nominally identical working electrodes of the same area and a Ag/AgCl (3 N KCl) reference electrode. The area of each electrode exposed to the solution was about 1 cm². The three electrodes were immersed in the NaCl solutions containing pigment extracts at 25 °C without de-aeration. The reference electrode was placed in the middle of 1-cm distance between the two working electrodes. During the electrochemical measurements, the cell was placed in a Faradic cage to minimize possible external electromagnetic interference. The noise data were recorded for 1024 s at a sampling rate of 1 s. The potential and current noise data collected in the time domain were transformed in the frequency domain through the fast Fourier transform (FFT) method. After removing the DC trend through moving average removal (MAR) method, EN data was analyzed using GPES software.

In order to perform cathodic disbonding test, an artificial hole was provided on each coating. The circular hole was mechanically milled in the coating down to the substrate using a flat milling tool with a diameter of 1 mm. The coating systems were polarized at two cathodic protection potentials –1 and –1.5 V vs. Ag/AgCl in a 3.5% (w/w) NaCl solution. After the test, radial cuts were made through the coating intersecting at the center of the perforation by a sharp knife. To determine the disbonded area, the loosened coating was lifted with the point of knife. It is important to note that EIS measurements were performed before the coating was cut in order to record the disbonded area.

Table 3
Characteristics of pigmented coating.

Resin	Curing agent	Additives	Solvent	Dry film thickness (μm)	Pigment			
					Oil absorption (g/100 g)		Density (g/cm ³)	
					ZP	SAPP	ZP	SAPP
Epoxy bisphenol A	Polyamide	Dispersing and wetting agent, thickener	Mixture of xylene, MEK, butyl glycol and normal butanol	45 ± 5	20	40	3.7	2.9

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