



The impact of pigment volume concentration on the protective performance of polyurethane coating with second generation of phosphate based anticorrosion pigment



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ABSTRACT

In this study the effect of conventional zinc phosphate and zinc aluminum phosphate, which represents second generation of phosphate based anticorrosion pigments, on the performance of a polyurethane coating was studied. While zinc phosphate modification was proved to be effective on the corrosion resistance, EIS data facilitated the determination of the optimum pigment volume concentration in which the coating offered the most efficient protection. The superiority of zinc aluminum polyphosphate was attributed to the release of more inhibiting species, leading to the formation of a protective layer at the coating/substrate interface. In addition to the assessment of the impact of pigment content on the resistance of polyurethane primer to cathodic disbonding, the dependency of adhesion strength on the pigment type was also studied using pull-off test.

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1. Introduction

Polyurethane (PU) coatings have gained an increasing attention in the paint and coating industry due to their good abrasion resistance, low temperature flexibility, excellent weathering resistance and desirable mechanical and chemical properties [1,2]. PU coatings have the potential to be used on a wide range of structures under different circumstances, in particular on cathodically protected surfaces. It is well known that the combination of cathodic protection and organic coatings can ensure a long-term protection. Therefore, resistance to cathodic disbonding is a key requirement for protective coatings. According to the literature, a variety of factors can affect the adhesion of coatings to the cathodically polarized steel substrates [3–5]. Inclusion of anticorrosion pigments in protective coatings is evident to enhance the resistance to disbondment [6–8] as well as improving the protective performance [9,10]. Among several types of anticorrosion pigments, those belonging to the electrochemical active class can increase the resistance of charge transfer across the metal surface by forming a passive film [11–13]. As a replacement for toxic chromium compounds, zinc phosphate (ZP) has been of great interest and is widely used in

the formulation of protective coatings. The inhibitive action of zinc phosphate is attributed to the hydrolysis process arising from permeation of electrolyte into the polymeric matrix [14–18]. However, low solubility of the anticorrosion pigment, which causes undesirable inhibition performance, has made some modifications necessary [16,19,20]. Due to the modified solubility, second generation of phosphate-based anticorrosion pigments, which usually have higher phosphate content, seem to reveal superior performance in comparison with conventional zinc phosphate [21–24].

In addition to pigment type, the pigment volume concentration (PVC) is a valuable guide parameter for paint formulators. Basically, PVC is considered a highly influential factor in various coating characteristics. Transport, mechanical, and corrosion properties of the coating film may undergo changes as PVC varies. In other words, majority of coating properties might encounter an abrupt change at the critical pigment volume concentration (CPVC) [13,25–27]. When the lambda ($\lambda = \text{PVC}/\text{CPVC}$) is equal to one, all pigment particles can be wet with a monomolecular layer of binder. In addition, sufficient amount of binder is remaining to fill all of the void spaces, which exist among the pigment particles.

The objective of this research is to study the role of ZPA, as a second generation of phosphate based anticorrosion pigment, on the protective performance and adhesion properties of a solvent-borne polyurethane coating. The pigment content in which the most efficient protection and bonding strength are provided was

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Table 1
The elemental composition of the steel panel.

Elements	Fe	C	Si	Mn	P	S	Al
%wt	99.01	0.19	0.34	0.32	0.05	0.05	0.04

Table 2
Technical data for the anticorrosion pigments.

	Oil absorption	Density (g/cm ³)	Average particle size (μm)	CPVC (%)
ZP	20	3.7	2–3.5	55.82
ZPA	40	3.1	2–3.5	42.98

determined by electrochemical impedance spectroscopy and pull-off test. Moreover, the effect of pigment type and concentration on cathodic disbonding performance of the PU coating was examined.

2. Experimental

2.1. Materials

Table 1 shows the composition of steel specimens (10 cm × 7 cm × 0.15 cm) used in this research.

Technical data for zinc orthophosphate hydrate and zinc aluminum orthophosphate hydrate that are known under the trademarks ZP and ZPA, respectively, according to the supplier (Heubach Ltd.) is presented in Table 2. Acrylic based resin (Desmophen A 160) and Isocyanate based hardener (Desmodur N 75) at 3:1 ratio, both supplied by Bayer, were used to produced solvent-borne polyurethane coating.

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 to achieve saturation conditions.

Pigments were incorporated into the coatings at different lambdas ($\lambda = \text{PVC}/\text{CPVC}$) ranging from 0.5 to 0.7. The coatings characterization is presented in Table 3. To obtain PVC, CPVC was calculated using Eq. (1) [28]:

$$\text{CPVC} = \left(\frac{1}{1 + (\text{OA} \times \rho / 93.5)} \right) \quad (1)$$

where OA and ρ represent the oil absorption and pigment density, respectively.

A dispersion of pigments was prepared in the acrylic resin using a high speed disk disperser. The dispersion was milled to obtain 15 μm fineness. The prepared liquid paints were applied on the acetone degreased plates using a quadrangular film applicator (Neurtek instruments). After a curing period of seven days under ambient condition, the coated samples were sealed with a mixture of beeswax and colophony resin, leaving a central area of 9 cm² unmasked. In addition, a pigment-excluded coating (Blank) was prepared to employ as a reference.

Table 3
Coatings characterization.

Resin	Hardener	Additives	Solvent	Pigment	Dry film thickness (μm)
Acrylic based (Desmophen A160)	Isocyanate based (Desmodur N 75)	Dispersing/wetting agent, thickener, defoamer	Mixture of butyl acetate, xylene, butyl glycol and normal butanol	ZP, ZPA	35 ± 3

2.2. Methods

To study the corrosion behavior of the coated samples during a 90-day immersion period in 3.5 wt% NaCl solution, EIS measurements were carried out with the use of an AUTOLAB PGSTAT12 instrument at open circuit potential. The frequency domain ranged from 10 kHz to 0.01 Hz and the perturbation amplitude was set at 10 mV. A three-electrode cell including an Ag/AgCl (3 N KCl) reference electrode, the studied sample as working electrode and the platinum counter electrode was used to run the EIS tests. Data analysis was carried out by utilizing FRA software.

A Positest digital pull-off adhesion tester (DeFelsko Corp.) was used to determine the adhesion strength of the PU coatings at dry state and after 90 days of immersion in 3.5 wt% NaCl solution.

In order to perform cathodic disbonding test, an artificial hole of 4 mm in diameter was made on each coating. A magnesium sacrificial anode was used to apply approximately −1500 mV_{Cu/CuSO₄} to the samples immersed in the test solution including 1 wt% NaCl, 1 wt% Na₂SO₄, and 1 wt% Na₂CO₃. The disbonded area was determined after 15 and 30 h of immersion.

Scanning electron microscopy (SEM) model Philips XL30 was employed to study the morphology of the film formed on the surface after 24 h exposure to the pigment extracts.

3. Results and discussion

Pull-off test was employed to study the effect of pigmentation on adhesion strength of the coatings before and after exposure to the saline solution (Fig. 1).

Some notable features are derived from the bar diagrams. Fig. 1 shows that the most effective adhesion strength occurred at lambda 0.6 for both anticorrosion pigments. The bar plots in Fig. 1 also show that increasing pigment concentration adversely affected the adhesion performance. The bonding strength of the samples pigmented at lambdas 0.65 and 0.7 is even less than the bonding strength of the sample without any ZPA and ZP. Furthermore, superior adhesion to the steel substrate was obtained in the presence of ZPA. Thus, the pigment content and the pigment chemical structure both could be considered as influential factors in the coating bond strength.

As the electrolyte reaches the coating/metal interface, hydrolysis of the interfacial adhesion bonds may occur, which could result in coating detachment and eventually spreading of corrosion products beneath the coating [1,2,6]. The hydroxyl ions produced at the cathodic regions may increase the rate of interfacial disbondment. Moreover, the ferrous ions generated at anodic zones can be oxidized to ferric ions and form corrosion products [1,3]. According to the literature, the ZP and ZPA anticorrosion pigments have been reported to improve the adhesion strength by two main ways. First, the pigments are capable of retarding the diffusion of corrosive electrolyte to the coating metal interface through enhancing barrier properties [15,29]. Second, precipitation of a protective layer on the substrate surface is probable in the presence of the electrochemically active pigments [6,15]. The deposited film may restrict

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