



The corrosion inhibitive properties of various kinds of potassium zinc phosphate pigments: Solution phase and coating phase studies



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ABSTRACT

Potassium zinc phosphate (PZP) pigments were synthesized using different mole ratios of KOH/ZnCl₂, i.e. 1.5, 2, 2.5, 3, 3.5 and 4. The inhibition effects of the pigments were studied in the extract solution by polarization test and electrochemical impedance spectroscopy (EIS). The surface morphology was studied by scanning electron microscope (SEM). Surface analysis was performed by X-ray photoelectron spectroscopy. Pigments were also incorporated into the epoxy coating and salt spray and pull-off tests were implemented to investigate its corrosion protection properties.

It was found that the mole ratio of KOH/ZnCl₂ could significantly affect the corrosion inhibition properties of the PZP. Increasing the KOH/ZnCl₂ mole ratio up to 2.5 caused significant improvement of the corrosion inhibition properties of the PZP both in the solution and coating phases. It was shown that PZP 2.5 could release Zn and P ions more than PZP 3.5 indicating its higher solubility in the 3.5 wt.% NaCl solution. PZP could significantly retard both anodic and cathodic reactions rates through releasing high amounts of Zn and P ions. PZP 2.5 enhanced the corrosion protection properties of the epoxy coating more than PZP 3.5 and decreased the adhesion loss significantly.

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1. Introduction

Organic coatings have been widely used to protect metals against corrosion. Anticorrosive pigments are added to the organic coatings in order to obtain long term corrosion protection properties [1–4]. The anticorrosive pigments are able to enhance the corrosion protection properties of the coatings through three main protection mechanisms including barrier, inhibitive and sacrificial [3–8]. Among these mechanisms, anticorrosive pigments with inhibitive action have been used to obtain coatings with longer corrosion protection service life. Zinc chromate is a well-known type of active corrosion inhibitive pigment which had been used in the organic coatings formulations. The mechanism of corrosion protection of this pigment is based on releasing solubilized inhibitive species which could form a protective layer on the metal surface. This pigment had been used for many years as an effective inhibitive pigment in the organic coatings. However, it has toxic and carcinogenic nature which contaminates the environment and represents a risk to human health [9–13]. Zinc phosphate and related substances are suggested as possible replacements for the

chromates. However, the results reported in the literature showed less inhibitive performance of the zinc phosphate compared to chromate type pigments. This is attributed to its low solubility in water [12–15]. Therefore, attempts have been carried out to improve the corrosion inhibitive performances of the zinc phosphates through several physical and/or chemical modifications. In this way, the pigment solubility in water can be improved resulting in the increase of its inhibition properties. The second and third generations of the zinc phosphates have been developed in this way [16–20]. Naderi et al. investigated the inhibition effects of the zinc aluminum polyphosphate (ZAPP) and zinc aluminum phosphate (ZPA) pigments in the 3.5 wt.% NaCl solution on the mild steel specimens [19,20]. They found that polyphosphates showed better inhibitive action than orthophosphate. Compared to the conventional zinc phosphate (ZP) pigment, ZAPP and ZPA showed water solubility much greater than ZP. This resulted in more inhibitive properties of these two pigments than ZP. The corrosion inhibition mechanism of these two pigments has been referred to a protective layer precipitation on the metal surface. Polyphosphates include higher phosphate content than orthophosphate. As a result, it can produce stronger chelates with multivalent metal cations. These show that modification or replacement of the cationic and/or anionic parts of the pigment can lead to the pigment inhibition performance improvement. Iron, aluminum, potassium, sodium and lithium have been used for this purpose

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[21–29]. To the best of our knowledge there is no systematic study on investigation the effects of KOH/ZnCl₂ mole ratio on the phase composition and its correlation with corrosion inhibition properties of the PZP both in solution and coating phases.

In the present work, a series of PZPs, having different chemical compositions and phase structures, were synthesized by changing KOH/ZnCl₂ mole ratio. The inhibition properties of the pigments were studied preparing pigments extracts in the 3.5 wt.% NaCl solution and introducing them in the epoxy coating matrix. Electrochemical techniques including potentiodynamic polarization and EIS were used to investigate the inhibition properties of the pigments on the mild steel surface. SEM/EDS and XPS analyses were utilized to investigate the morphology and chemical composition of the films precipitated on the steel surface. Salt spray and pull-off tests were conducted in order to investigate the corrosion resistance and adhesion properties of the epoxy coatings containing PZPs on the steel substrate.

2. Experimental

2.1. Materials and sample preparation

A series of potassium zinc phosphate pigments (PZP) were synthesized using different mole ratios of KOH/ZnCl₂ i.e. 1.5, 2, 2.5, 3, 3.5 and 4. Zinc chloride (Merck, 0.06 mol) was added to 85 wt.% phosphoric acid solution (Merck, 0.06 mol) and distilled water (100 ml). This mixture was stirred until complete dissolution was achieved. In the next step, a solution of KOH (Merck) in distilled water (80 ml) was added to the above solution. The mixture was stirred for 3 h and heated up to 100 °C for 12 h. The resulted residue was recovered by filtration, washed by distilled water and dried at 100 °C. Samples obtained were denoted according to Table 1.

The inhibition effects of the pigments prepared were studied on the surface of mild steel specimens (St-37). The mild steel panels have the following chemical composition: Al: 0.04, S:0.05, P:0.05, Mn:0.32, Si:0.34, C:0.19 and Fe:99.01 (wt.%). Samples were abraded by emery papers of 600, 800, 1200 and 2400 grades followed by acetone degreasing. Finally, the samples were rinsed with distilled water and dried in an oven at 40 °C.

2.1.1. PZP extracts preparation

To prepare the extracts, 1 g of the PZP was stirred in 1 L of 3.5 wt.% NaCl solution for 24 h. The solutions were then filtered for further analysis. The concentration of dissolved species in the pigment extracts was measured by an inductively coupled plasma-optical emission spectrometer [Varian Vista Pro ICP-OES]. The pH values of the solutions containing PZPs extracts were assessed by a Metrohm model 827 pH lab.

2.1.2. Epoxy coating preparation

Epoxy coatings containing 15 wt.% of PZP and ZP were prepared. For this purpose, the epoxy resin of Araldite GZ7 7071X75 (based on bisphenol-A in a xylene solution) was prepared from Saba Shimi Co. The epoxy value, density and solid content of the resin were 0.1492–0.1666 eq/100 g, 1.08 g cm⁻³ and 74–76%, respectively. Pigments were then added to the epoxy resin and dispersed by a pearl-mill for 8 h in order to obtain an average particle size up to 10 μm. EFKA-2025, a silicone based defoamer in cyclohexanone

solvent, was used at maximum consumption of 0.1 wt.%. BYK-306, a polyether modified polydimethylsiloxane in xylene and 2-phenoxyethanol solvents, was locally provided and used as surface modifier at maximum consumption of 0.5 wt.%. In the next step, the mill base was mixed with a stoichiometric amount of a polyamide curing agent (epoxy/hardener (w/w)=2.3/1). The hardener used in this study was based on an amido polyamide, CRAYAMID 115, from Arkema Co. The solid content, density and viscosity at 40 °C of the hardener are 50%, 0.97 g/cm³ and 50,000 cps, respectively. At the end, the coatings prepared were applied on the cleaned and abraded steel samples using a film applicator. All of the coatings were cured at 120 °C for 30 min. The dry film thickness of 52 ± 3 μm was measured for the samples by Defelsko Posi Tector 6000.

2.2. Techniques

2.2.1. Electrochemical measurements

The corrosion performance of the steel specimens was studied in 100 cc of test solutions. Polarization curves were obtained employing AUTOLAB G1. The test was carried out in a conventional three electrode cell including steel specimen (1 cm² area) as working electrode, platinum as counter electrode and saturated Ag/AgCl as reference electrode. The polarization curves were obtained at sweep rate of 1 mV/s in the range of ±100 mV from open circuit potential (OCP). The electrochemical impedance spectroscopy (EIS) measurements were conducted in a three electrode cells (like the one used in the polarization test) at the frequency range and peak to zero amplitude of 10 kHz–100 mHz and ±10 mV, respectively. The impedance data was analyzed by NOVA 1.8 software.

The EIS and polarization measurements were carried out 3 times to ensure the repeatability of the measurements. All experiments were conducted at different immersion times of 2, 4, 24 and 48 h on 1 cm² of the samples.

2.2.2. Surface analysis

The surface morphology and composition of the steel specimens exposed to the solutions with and without pigment extract were studied by a scanning electron microscope (SEM) model Philips XL30 (equipped with energy dispersive spectroscopy: EDS). The SEM analysis was done after 70 h immersion at 25 °C. Also, the composition of the film deposited on the metal surface was studied by a Specs EA 10 Plus energy dispersive X-ray photoelectron spectroscopy (XPS) equipped with a concentric hemispherical analyzer (CHA). In this experiment, the radiation source (at pressure of 10⁻⁹ mbar) was Al K_α. The shift of binding energies (BE) was calibrated with respect to reference peak of carbon at binding energy of 285 eV.

2.2.3. Corrosion protection studies of epoxy coatings

The epoxy coated samples were exposed to salt spray for evaluation of the corrosion protection performances of the samples. For this purpose, the x-scribed coatings were exposed to salt spray test cabin according to ASTM B117 (NaCl 5 wt.% solution) for 100 h.

The adhesion strength values of the coatings applied on the steel substrates were also measured after 100 h exposure to salt spray by a Posi Test pull-off adhesion tester (DeFelsko). For this purpose, the aluminum dollies were glued on the surface of the epoxy coating using a two-part Araldite 2015 (Huntsman advanced materials, Germany) adhesive. Samples were then kept at ambient temperature for 24 h to insure that the glue fully cured. Finally, a slot was made around dollies and they were pulled at a speed of 10 mm/min normal to the coating surface until the epoxy coating was detached from the steel substrate. Measurements were performed on three replicates to ensure the repeatability of data.

Table 1
Sample coding for the pigments synthesized by changing KOH/ZnCl₂ mole ratio.

Name of pigments	PZP 1.5	PZP 2	PZP 2.5	PZP 3	PZP 3.5	PZP 4
KOH/ZnCl ₂ mole ratio	1.5	2	2.5	3	3.5	4

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