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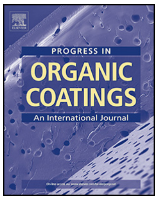

Sodium zinc phosphate as a corrosion inhibitive pigment

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ABSTRACT

A sodium zinc phosphate pigment synthesized using a co-precipitation method and characterized by X-ray diffraction was investigated for its corrosion inhibition activity in comparison with the commercial zinc phosphate using EIS in a 3.5% NaCl solution. A mild steel surface analysis after exposure to the test solutions was conducted using scanning electron microscope-energy dispersive X-ray and infrared spectroscopies. The results indicate that the corrosion inhibitive performance of the synthesized pigment is higher than that of the commercial zinc phosphate. This can be the result of the synthesized pigment's relatively high solubility, which affects the precipitation of a phosphate layer onto the mild steel surface and the modification of the crystalline structure of the corrosion products in the presence of the inhibitive pigment. The salt spray and wet pull-off tensile strength results revealed an improved corrosion protection of the coatings formulated with SZP.

1. Introduction

Chromates have been widely used as corrosion inhibitive pigments. Considering the discipline, regulations, and notifications for protecting the environment against chromate toxicity, the use and application of chromates has been restricted. This has led to efforts toward finding non-toxic high-performance inhibitors as alternatives of toxic anticorrosion pigments. Since long, zinc phosphate (ZP) has been used as the most common non-toxic pigment [1–3]. This pigment is introduced and examined in most of the resins like alkyds, chlorinated rubber, epoxy, and oil-based resins for corrosion inhibition [4–6]. There is no consensus on the mechanism of ZP pigment inhibition [7]. Some researchers believe that the addition of ZP to a coating leads to an improvement in the corrosion protection because of the increase in the barrier properties of the coating [8,9]. However, Zubielewicz and Bastos et al. reported that ZP cannot provide protective behavior through electrochemical activity or through a barrier effect [10,11]. Various methods have been presented to improve the anticorrosion behavior of ZP [12,13]. The second and third generations of phosphate pigments are the results of the cationic and/or anionic modification of the chemical structure of ZP [14,15].

Among the families of ZP pigments produced by the cationic modification of the chemical structure of ZP, aluminum zinc phosphate [16,17], iron zinc phosphate [3], and potassium zinc phosphate [18–20] are synthesized and examined for their corrosion inhibition activity. Wei et al. [21] compared the corrosion inhibition of different pigments of this generation (aluminum zinc phosphate and potassium zinc phosphate) with ZP in the extract solution and coating. In the pigment extract solution, the corrosion inhibition efficiency of potassium zinc phosphate was found to be higher than that of aluminum zinc phosphate and ZP. The relatively low inhibition of ZP in comparison to the modified pigments was connected to its relatively low solubility, which led to less dissociation of PO_4^{3-}. It was shown that aluminum zinc phosphate, like potassium zinc phosphate, can release more Zn^{2+} and PO_4^{3-} than the ZP pigment.

Although the inhibitive activity of potassium zinc phosphate was previously reported [19], the relatively small ionic radius of sodium as compared to potassium can result in differences in the crystalline structure and solubility of the synthesized pigment and consequently, its corrosion inhibition performance.

In this study, we have focused on the synthesis, characterization, and corrosion inhibition of sodium zinc phosphate (SZP). For this purpose, we have synthesized SZP using the co-precipitation method and compared its inhibitive performance to that of commercial ZP using electrochemical impedance spectroscopy (EIS). In order to gain an insight into the mechanism of corrosion

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inhibition, the surface composition of mild steel specimens after exposure to the test solutions was examined using scanning electron microscope-energy dispersive X-ray (SEM-EDX) and infrared (IR) spectroscopies.

2. Experimental

2.1. Materials

Zinc chloride, phosphoric acid (85%), sodium hydroxide, and triethanolamine were obtained from Merck and the ZP pigment from Nubiola; all the materials were used as received without further purification. Epoxy resin (Epikote 828) and polyamine (Epikure F205) were purchased from Shell Company.

2.2. Synthesis of SZP pigment

Zinc chloride (8.1 g) was added to a phosphoric acid solution (which was prepared by dissolving 6.2 ml of H_3PO_4 (85%) in 100 ml of deionized water), and the mixture was stirred with a magnetic stirrer to achieve complete dissolution. Then, 3.5 ml of triethanolamine was added to this mixture, and the solution was further stirred for 15 min. A caustic soda solution (which was prepared by dissolving of 3.6 g of caustic soda in 80 ml of deionized water) was added to the above-mentioned solution and stirred for 3 h. The mixture was then heated to 100 °C for 24 h. The precipitate was recovered by filtration, washed to neutral pH, and dried at 100 °C.

2.3. Characterization of SZP pigment

2.3.1. Powder X-ray diffraction

Powder X-ray diffraction (XRD) was performed using a PW 1800 Philips X-ray spectrometer with Cu Kα radiation ($\lambda = 1.54060$ Å) on the synthesized pigment in the 2θ range from 10° to 90° at rate of 2.5°/min.

2.4. Morphology of SZP pigment

The morphology and the structure of the SZP were investigated using a Philips scanning electron microscope (model LEO 1455VP).

2.5. Evaluation of inhibitive properties of pigments

Mild steel samples with the composition mentioned in Table 1 were cut down into pieces having a surface area of 1 cm^2. A braided wire was attached to one side of the samples by brazing, and then, the steel samples were mounted using unsaturated polyester. The mounted samples were abraded using Emery paper 600 and 800. Finally, the samples were washed using methanol to remove any remaining contamination.

One gram of each pigment was stirred separately in 1 l of 3.5% NaCl solution for 24 h and filtered to obtain the extract solutions. A blank solution of 3.5% NaCl containing no pigment was also prepared for use as the reference solution. Then, the mild steel samples were immersed in the test solutions for 1, 4, and 24 h at 25 °C.

The EIS measurements were conducted using Ivium Compactstat (Netherlands) in a three-electrode cell containing Ag/AgCl (3 M KCl), graphite, and the mild steel as the reference, counter, and working electrodes, respectively. The EIS measurements were implemented at an open-circuit potential using 10-mV perturbation in a frequency range of 10 kHz to 10 mHz. The measured spectra were analyzed using the Iviumsoft software.

2.6. Surface analysis of mild steel specimens after exposure to test solutions

2.6.1. SEM-EDX

The mild steel panels with dimensions of 1 cm × 1 cm and thickness of 2 mm were immersed in 100 ml of test solutions for 24 h; then, the samples were washed with distilled water and dried. The surface morphology and the composition of the specimens were evaluated using SEM-EDX.

2.6.2. IR spectroscopy

The corrosion products formed on the mild steel specimens after exposure to the test solutions were characterized by IR spectroscopy. An IR analysis was conducted on KBr disks in the region of 400–4000 cm^{-1} by Perkin Elmer-Spectrum One.

2.7. pH measurement

The pH of the test solutions before and after the 24-h contact with the mild steel surface was measured using a Metrohm 744 pH meter.

2.8. Inductively coupled plasma-optical emission spectrophotometer (ICP-OES) measurements

The prepared extracts were analyzed in order to determine the concentration of the dissolved species. The analysis was conducted using the ICP-OES of Varian Company (Australia), model Vista-PRO.

2.9. Evaluation of protection performance of pigments in epoxy coating

The pigment dispersion in resin was prepared by addition of SZP pigment (5%, v/v) to 4 g epoxy resin and ultrasonicated to obtain 16 μm fineness of the dispersion. The pigment dispersion was mixed with polyamine at the stoichiometric ratio of polyamine to epoxy. The blank coating with no SZP pigment was considered as a reference coating. The specimens were abraded by emery paper 800, and then cleaned by acetone. The coatings were applied using 90 μm bar coater on mild steel panels. All coatings were cured at 80 °C for 40 min. The samples with a dry film thickness of 42 ± 1 μm were X-scribed.

The corrosion performance of the coated specimens was evaluated in a neutral salt spray test, following the procedure of ASTM B 117 and employing 5% (50 g l^{-1}) sodium chloride solution at 25 ± 2 °C. Prior to exposure, the backs and the edges of the specimens were covered with hot melt mixture of beeswax and colophony resin. The specimens were removed from the salt spray chamber after 270 h and representative areas were imaged with a digital camera. The images were then used to evaluate the corrosion performance of the coated specimens. The delaminated coating was removed along the scribed area; then, wet pull-off tensile strength was examined using Defelsko Positest on undisbonded area.

3. Results and discussions

3.1. Characterization of pigments

Fig. 1 shows the XRD result for the synthesized pigment (SZP). Two forms of SZP, namely $NaZnPO_4$ and $NaZn_2PO_4(HPO_4)$,were detected as the major phases and ZnO as the minor phase. According to the relative intensity of the diffraction peaks, it could be deduced that $NaZnPO_4$ was the dominant phase in the synthesized pigment.