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Mechanistic approach for evaluation of the corrosion inhibition of potassium zinc phosphate pigment on the steel surface: Application of surface analysis and electrochemical techniques

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ABSTRACT

Potassium zinc phosphate pigment was synthesized through a co-precipitation method. Then, the steel panels were immersed in 3.5% NaCl solution containing potassium zinc phosphate pigment extract and in the blank 3.5% NaCl solution (containing no pigment) at different immersion times. X-ray diffraction and scanning electron microscope were employed in order to characterize the composition and morphology of the pigment. Corrosion inhibition of the pigment in the extract solution was studied by linear polarization test. The morphology and composition of the film precipitated on the surface of steel panels were investigated by energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy techniques. Solubility of pigment in the extract solution and the rate of ions consumption were studied by employing an inductively coupled plasma-optical emission spectrometer.

Results showed that potassium zinc phosphate has sufficient water solubility to provide corrosion inhibition on the steel surface. The inhibitive spices like Zn^{2+} and PO_4^{3-} ions could form protective layer over the anodic and cathodic regions of the metal surface, restricting the aggressive species access to the metal surface. It was found that the inhibition mechanism of potassium zinc phosphate pigment changed during the immersion. Zn^{2+} ions precipitated on the anodic sites of metal surface at short immersion times affecting the anodic reaction rate but PO_4^{3-} ions formed protective layer over the cathodic regions at longer immersion times affecting the cathodic reaction rate.

1. Introduction

Different kinds of organic/inorganic pigments are added to the organic coatings formulations in order to obtain long term corrosion protection properties on the steel substrates. The anticorrosion properties of the pigments depend on the size, shape and chemical nature of the pigments. There are three main categories of anticorrosive pigments (barrier, sacrificial and inhibitive pigments) which have been developed in recent years [1–7]. Among these pigments, using inhibitive pigment is the most promising way of approaching reliable anticorrosion performance. The inhibitive pigments due to water solubility could release the inhibitive species. The released ions can form protective film on the metal surface restricting the aggressive species access to the active sites of the metal surface. One of the most popular types of the inhibitive pigment is zinc chromate which exhibits excellent inhibitive performance and it has been used in large extent in the protective paints formulations [8,9]. However, the use of this pigment has been limited in recent years due to its toxicity and environmental problems. It has been attempted to find proper replacements for the chromate based pigments. In this regard, zinc phosphate (ZP) has been introduced as less toxic pigment. However, the corrosion inhibitive action of this pigment is too low due to its slight water solubility. In fact, the solubility and also the type of inhibitive species released by the pigment are the most important parameters affecting its inhibitive behavior. The water solubility of zinc phosphate is too low and because of that it could not provide efficient corrosion inhibitive properties. Several physical/chemical modifications, both on the anions and cations of the ZP, have been proposed in order to enhance the pigment water solubility when exposed to corrosive electrolyte [10–12]. Taking the advantages of the modification of ZP, second and third generations of the phosphate-based anticorrosive pigments have been developed. Iron zinc phosphate, potassium zinc phosphate (PZP), aluminum

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zinc phosphate and lithium zinc phosphate [12–17] are some examples of the cationically modified ZP pigment. It is shown that the modified pigments could show greater inhibitive properties compared to the conventional ZP pigment. The optimization of synthesis condition and evaluation of anticorrosion properties of the ZP pigment modified with potassium have already been studied [14]. It was found that PZP pigment could produce better corrosion protection properties on steel than ZP due to its higher water solubility. However, the inhibition mechanism of PZP has not been systematically investigated in any works.

The aim of this work is studying the inhibition mechanisms of PZP in the extract solution on the steel substrate. PZP was synthesized through a co-precipitation method and its inhibitive properties were studied in the extract solution. Polarization test and open circuit potential (OCP) measurements were done in order to evaluate the performance of steel sample in the 3.5 wt% NaCl solution containing PZP extract. Pigment solubility in 3.5 wt % NaCl solution and ions consumption during the steel sample immersion in the extract solution were evaluated by an inductively coupled plasma-optical emission spectrometer (ICP-OES). The film formation mechanism and the composition of the layer precipitated on the steel surface were investigated by X-ray photoelectronic spectroscopy (XPS) and scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS).

2. Experimental

2.1. Materials and the procedure of pigment synthesis

PZP was synthesized by a co-precipitation method. For this purpose, 0.06 mol of zinc chloride was added to the phosphoric acid solution (0.06 mol phosphoric acid in 100 ml distilled water). Then, the mixture was stirred until complete dissolution was obtained. In the next step, 3.5 ml triethanolamine was added to this mixture and the solution was stirred for 15 min. After that, KOH solution, prepared in distilled water (80 ml), was added to the solution. The ratio of $ZnCl_2$/KOH was 2.5. Finally, the mixture was stirred for 3 h and heated at 100 °C for 12 h. The residue was recovered by filtration, washed to neutral pH and dried at 100 °C.

All chemicals used were of synthesis grade and were used as received without any further purification and were obtained from Merck.

2.2. Pigment extract preparation

The PZP extract in 3.5 wt% NaCl solution was obtained. For this purpose, 1 g of the pigment was stirred in 1 L of 3.5 wt% NaCl solution for 24 h. Finally, the mixture was filtered and the solution containing pigment extract was used for further studies. The concentration of the ions presented in the solution containing pigment extract was measured by an inductively coupled plasma-optical emission spectrometer [Varian Vista Pro ICP-OES]. A 3.5 wt% NaCl solution without pigment extract was also prepared as blank solution in this study. Also, the pH values of the solutions without and with PZP extract were measured by a Metrohm model 827 pH lab. The measurements were carried out before and after 70 h immersion of steel sample in the solutions.

2.3. Characterization

2.3.1. PZP characterization

X-ray diffraction (XRD) analysis was performed in order to evaluate the phase composition of PZP. The XRD pattern was measured in reflection geometry using a Bruker D8 advanced instrument with a curved Ge (111) monochromator ($CuK\alpha_1$ radiation, $\lambda = 1.54060$ A). SEM (Philips XL30)) was also used in order to investigate the morphology of the pigment.

2.3.2. Anticorrosion properties measurements

The corrosion behavior of steel samples immersed in the solutions containing pigment extract was studied. The composition (wt %) of the steel panel used in this study was Fe:99.01, Al:0.04, S:0.05, P:0.05, Mn:0.32, Si:0.35 and C:0.18. The samples were grinded by emery papers of 600, 800, 1200 and 2400 grades and then washed by acetone. The open circuit potential (OCP) values of steel samples were measured in the solution containing pigment extract at different immersion times. This potential was measured by a HIOKI model voltmeter with respect to the Ag/AgCl reference electrode (saturated KCl solution). Polarization test was done by employing AUTOLAB G1 at the sweep rate of 1 mV/s from −100 mV to +100 mV of OCP. The polarization test was performed in a conventional cell containing mild steel (working electrode), platinum (as counter electrode) and saturated Ag/AgCl (as reference electrode).

2.3.3. Surface characterization

SEM model Philips XL30 (equipped with EDS (SAMx)) was used to investigate the morphology of the film precipitated on the surface of steel panels immersed in the solutions without and with PZP extract. The film composition was also studied by a Specs EA 10 Plus XPS equipped with a concentric hemispherical analyzer (CHA). In this experiment, the radiation source was Al K_α (at pressure of 10^{-9} mbar). Moreover, the shift of binding energies (BE) was calibrated with respect to the reference peak of carbon at binding energy of 285 eV.

3. Results and discussion

3.1. Pigment characterization

The XRD pattern and SEM micrograph of the pigment powder are shown in Fig. 1. It can be seen that PZP is composed of $KZn_2H(PO_4)_2$ phase in accordance with JCPDC card numbers of 00-020-1445 and 01-070-2189 which is the main detected phase. According to SEM photo there is agglomeration of rods appeared as plates with defined edges.

3.2. Open circuit potential (OCP) measurements

The steel panels were dipped in the solutions without and with PZP extract. The OCP values were recorded at different immersion times and the results obtained are given in Fig. 2. The digital photographs showing the visual performances of samples are also presented in Fig. 2.

Fig. 2 shows more positive OCP values of the samples immersed in the solution with pigment extract than those dipped in the blank solution. The most positive OCP values are observed at the beginning of immersion (immersion times shorter than 2 h). The corrosion product appeared as brown rust on the surface of the steel samples immersed in the blank solution after 0.5 h immersion. However, no corrosion product can be seen on the surface of the sample immersed in the solution containing PZP extract. This indicates that PZP containing extract could exhibit proper inhibition action on the steel surface. The OCP diagram of the sample immersed in the solution with PZP extract can be divided into three main parts. The first region is at immersion times between 0 and 2 h where the OCP reached the most positive values. The OCP decreased at region 2 (immersion times between 2 and 8 h) and finally reached a constant value at region 3