Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–15

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Improvement in the protective performance of epoxy ester coating through inclusion of an effective hybrid green corrosion inhibitive pigment

Elham Salehi [a], Reza Naderi [a,*], Bahram Ramezanzadeh [b]

[a] School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, PO Box 11155-4563, Tehran, Iran
[b] Department of Surface Coatings and Corrosion, Institute for Color Science and Technology (ICST), PO 16765-654, Tehran, Iran

ARTICLE INFO

Article history:
Received 12 August 2017
Revised 27 September 2017
Accepted 28 September 2017
Available online xxx

Keywords:
Mild steel
Hybrid inhibitive zinc acetate/urtica dioica pigment
Synergistic inhibitive effect
Epoxy ester coating
Electrochemical method
Surface analysis

ABSTRACT

The protection function of a new hybrid green corrosion inhibitive pigment based on zinc acetate (ZnA) and Urtica Dioica (U.D.) in solution and coating (epoxy ester) phases was studied by electrochemical techniques and surface analysis. The increased corrosion resistance of bare mild steel in NaCl solution with the hybrid pigment extract was associated with precipitation of a protective film whose composition was analyzed using SEM/EDX and XPS. EIS assessment of metallic samples covered by coatings with and without an artificial defect indicated the impact of the inhibiting species released from the organic/inorganic pigment particles on the active protection performance.

1. Introduction

The use of organic coating as one of the conventional methods to protect steel substrates against corrosive environments has been prevailed in the last decades [1–6]. To improve the barrier properties and corrosion protection performance of organic coatings, various inorganic and organic pigments have been already proposed [7,8]. Among various classes of pigments, the inhibitive ones have been reported to provide coatings with reasonable protective properties during a long service life even when there is a slight mechanical damage in the film structure [9–14]. Chromates and red lead are two conventional electrochemically active pigments which have been widely used for many years; however, the usage of these pigments are strongly restricted because of their toxicity [15–18]. The common alternative for the toxic pigments is zinc phosphate (ZP), providing no desirable protection due to low solubility in water [19]. Different ways have been proposed in the literature to modify the pigment structure, leading to introduction of second and third generations of phosphate based corrosion inhibitive pigments [20–23]. Naderi et al. have showed effectiveness of modification of zinc phosphate through examining the corrosion inhibition performance of different phosphate based pigments including zinc aluminum phosphate (ZAP), zinc aluminum polyphosphate (ZAPP), strontium aluminum polyphosphate (SAPP), zinc aluminum molybdenum orthophosphate (ZAM) and zinc calcium strontium aluminum orthophosphate silicate (ZCP) in solution phase as well as coating systems [6,16,20,24]. It was evident in the all studies that precipitation of a protective insoluble layer on the active sites is responsible for superiority of the modified corrosion inhibitive pigments [25,26].

Another approach reported in the literature is to replace zinc phosphate with organic inhibitors. The inhibitive power of the organic compounds, mostly showing good performance in acidic environments, is suggested to be related to the formation of a thin layer on the active sites of the metal surface [27–31]. Some studies could confirm the effective corrosion inhibition performance of azole compounds as organic inhibitors in acidic media [32–34]. The results revealed that the high inhibition efficiency was related to the molecular structure of organic inhibitors and the inhibition mechanism was arisen from surface adsorption of inhibitor molecules blocking the active areas. However, the addition of azole-based organic inhibitors to the formulation of organic coatings was found to have no significant impact on the corrosion protection or cathodic disbonding [35,36]. The organic inhibitors usually offer no effective corrosion protection as used alone in neutral and alkaline environment. The problem is

* Corresponding author.
E-mail address: rezanaderi@ut.ac.ir (R. Naderi).

https://doi.org/10.1016/j.jtice.2017.09.049
1876-1070/

overcome through taking advantage of an inhibition synergism between organic and inorganic inhibitors [37,38]. For instance, the synergistic inhibition effect of zinc acetylacetonate and benzothiazole on the corrosion of mild steel in sodium chloride solution was shown by amoozadeh and mahdavian [39]. Further, addition of the mixture of these inhibitors to the epoxy coating resulted in an improvement in the corrosion protection properties. As another problem, direct addition of organic inhibitors might have negative effect on the protective performance of organic coatings. High solubility of organic inhibitors leads to an increase in the coating water uptake and uncontrollable release of the inhibiting species causing fast exhaustion of the self-healing potential. Moreover, the reaction of active groups of organic inhibitors with the functional groups of coating has an adverse effect on the cross-linking density [40]. The simultaneous use of organic and inorganic inhibitors in the formulation of a corrosion inhibitive pigment can be considered as one of the effective strategies to control the disadvantages of direct loading of organic inhibitors. Ramezanzadeh et al. [41] introduced hybrid zinc acetate (ZnA)/benzotriazole (BTA) corrosion inhibitor for mild steel in NaCl solution functioning through forming $Zn(OH)_2$, Zn-BTA and Fe-BTA complexes on the active sites. The ZnA/BTA pigment was also shown to have more significant effect on the resistance of epoxy coating to cathodic delamination compared to the conventional ZP pigment.

Recently, researchers have focused on finding green alternatives for toxic organic corrosion inhibitors. Since the plant extracts are cheap, readily available, renewable and contain no dangerous compounds, they have attracted considerable attentions. Although a large number of reports can be found in the literature regarding usability of the plant extracts in acidic solutions, few papers have been published studying the behavior of the green corrosion inhibitors in neutral media [42–44]. In our recent publication [45], the synthesis and characterization of a new hybrid pigment based on zinc acetate and Urtica Dioica (U.D.) was reported. The results obtained from Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), UV–vis analysis, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) revealed that the complex between the organic parts of U.D extract and zinc acetate was successfully created. The inhibition effect of the hybrid pigment was only examined in the solution phase through extracting the hybrid pigment. Visual inspection, open circuit potential (OCP) and polarization measurements indicated the high corrosion inhibition effect of the hybrid pigment in the extracted solution on mild steel. However, the effect of immersion time on the corrosion inhibition of mild steel in chloride solution containing the hybrid pigment extract was not studied. The results in the solution phase could not guarantee the effective function of the hybrid pigment in an organic coating. Therefore, the influence of pigment on the thermal-mechanical and barrier performance of organic coating should be considered to say that it would be a candidate for an effective corrosion inhibitive pigment.

In this research, the synergistic effect of inhibiting species released from the new pigment on the corrosion of mild steel in 3.5% NaCl solution was further analyzed using EIS and surface analysis (SEM/EDX and XPS). To top it off, the role of the ZnA-U.D pigment on the barrier and active protection properties of an epoxy ester coating on mild steel was investigated through taking advantage of EIS, salt spray, SEM/EDX and dynamic mechanical thermal analysis (DMTA).

2. Experimental

2.1. Materials

Analytical grade of zinc acetate ($Zn(O_2CCH_3)_2.(H_2O)_2$) was purchased from Merck Co.. Urtica Dioica leaves collected from north coast of Iran were dried at ambient temperature. It is reported that the U.D plant extract contains flavonal glycosides such as quercitin, carotenoids, chlorophyll, acids, vitamins, histamine, serotonin and minerals [45,46]. The air dried leaves were powdered and used as organic inhibitor in this research. Green organic/inorganic hybrid pigment based on ZnA and U.D was synthesized and denoted as ZnA-U.D. Fig. 1a and b shows the chemical structure of zinc acetate and some important compounds present in Urtica Dioica, respectively. The chemical scheme of possible complexes between the U.D and ZnA present in the ZnA-U.D pigment is shown in Fig. 1c. In order to synthesize ZnA-U.D, 1 g of ZnA and 0.24 g of U.D were individually added to 80 ml deionized water and magnetically stirred for 1 h at room temperature. Then, they were mixed and stirred for 24 h at room temperature. After placing in an oven at 60 °C for 24 h, the residue was centrifuged and washed with deionized water for 3 times. The material was finally dried at 60 °C for 3 h. The details of synthesis and characterization of the pigment is reported elsewhere [45].

For solution phase study, the extracts of ZnA, U.D and ZnA-U.D were individually prepared by stirring 1 g of each material in 1 l of 3.5 wt% NaCl solution, followed by filtration. The stirring period of the solutions containing ZnA, U.D and ZnA-U.D were 24, 24 and 48 h, respectively. A 3.5 wt% NaCl solution with no additive was also used as reference solution. To determine the amount of inorganic and organic inhibitors released from the hybrid pigment in 3.5 wt% NaCl solution, the concentration of Zn and total organic carbon content (TOC) were measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES) [Varian vista pro ICP-OES instrument] and TOC-L model instrument, respectively. According to the ICP-OES analysis result, the hybrid ZnA-U.D complex released 44 ppm of Zn in the sodium chloride solution. The concentration of organic carbon released from Urtica dioica and ZnA-U.D were 513 and 227 ppm, respectively.

To prepare pigmented coatings, 0.2 g of ZnA-U.D particles was added to 30 g of epoxy ester resin (EE-430 CS) and homogenized at 3500 rpm for 45 min. The epoxy ester resin was obtained from Resitan Co., Iran. The solid content and viscosity (at 25 °C) of the resin were 60 ± 2% and 400–600 s, respectively. After filtration, some additives containing defoamer and drier (0.04 g Co, 0.04 g Pb and 1.35 g Ca) were added to the coating formulation. The blank and pigmented coatings were applied on the mild steel panels (composition wt.%: Al: 0.04, S: 0.05, P: 0.05, Mn: 0.32, Si: 0.34, C: 0.19 and Fe: balance) by a film applicator. The coated panels were air-dried at room temperature for 1 week, and then post-cured at 80 °C for 1 h. The thickness of coatings was measured using a digital coating thickness gauge (Elcometer 456 Model B Dual FNF). The dry film thickness was 45 ± 5 µm and 100 ± 5 µm for electrochemical assessment and salt spray test, respectively.

For both solution and coating phases, the mild steel specimens were first abraded using sand papers of 600, 800, 1000 and 1200 grades and degreased by acetone.

2.2. Methods

The electrochemical behavior of the bare metal in the uninhibited and inhibited solutions was further studied using EIS measurement. A three-electrode cell including bare mild steel with an exposure area of 1.0 cm^2, graphite counter electrode and a saturated calomel reference electrode (SCE) was used to perform the tests. The EIS measurements were done over a frequency range of 10 kHz to 10 mHz using 10 mV sinusoidal perturbations. The impedance spectra acquired at OCP (vs. SCE) were analyzed by Zsimpwin software. All EIS test in this research was performed using an Ivium Compactstat-instrument.

The corrosion behavior of coated samples was investigated by EIS and salt spray tests. The cell and procedure designed to

Please cite this article as: E. Salehi et al., Improvement in the protective performance of epoxy ester coating through inclusion of an effective hybrid green corrosion inhibitive pigment, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.09.049