Progress in Organic Coatings 64 (2009) 361–364

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Corrosion inhibition of steel in sodium chloride solution by undoped polyaniline epoxy blend coating

E. Akbarinezhad [a,b,*], M. Ebrahimi [b], H.R. Faridi [a]

[a] Corrosion Research Department, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-1998, Tehran, Iran
[b] Polymer Engineering Department, AmirKabir University of Technology, P.O. Box 15875-4413, Tehran, Iran

ARTICLE INFO

Article history:
Received 16 March 2008
Accepted 18 July 2008

Keywords:
Undoped polyaniline
Epoxy
Corrosion inhibitor
Open circuit potential
Electrochemical impedance spectroscopy

ABSTRACT

In this study an undoped polyaniline (PAni) was synthesized by chemical oxidative polymerization with ammonium persulfate as an oxidizing reagent. The synthesized PAni was used as a corrosion inhibitive pigment in an epoxy matrix. The corrosion protection performance of steel coated panels in 3.5% sodium chloride solution was evaluated via determination of open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS). It was found that after 300 days of immersing the resistance of coating was about $4 \times 10^5\ \Omega\,\mathrm{cm}^2$. The OCP was shifted to the noble region due to the passivation effect of PAni pigment. Besides, the phase angle (theta) at 10 kHz was stable around $87 \pm 1^\circ$ during immersion period. Results revealed that PAni pigmented paint showed acceptable protection against the corrosion of carbon steel in 3.5% sodium chloride solution.

1. Introduction

Organic coatings are used to protect metals against corrosion and harsh environments for many years [1]. In recent years, there has been a great interest in using electrically conductive polymers to protect steels, and other metals and alloys [2–5]. Polyaniline (PAni) is the oldest known synthetic electrically conductive polymer. PAni is readily synthesized and it readily participates in redox reactions. It is thermally stable with high corrosion resistance. PAni was first reported in 1862, by H. Letheby in Journal of the Chemical Society [2]. The application of PAni as an inhibitive coating for corrosion protection of active/passive alloys was first reported by DeBerry [6]. PAni can be synthesized by chemical oxidative polymerization and then be used as corrosion inhibitive pigment in paint coatings to protect sensitive alloys, or it can be deposited on the metallic parts through the electro polymerization of aniline from a suitable medium to limit the dissolution of the substrate. PAni helps in protecting against corrosion by forming a protective oxide layer on the surface, and stabilizes metals in a passive region. Both electro-polymerized coating [7–9] and polymer-pigmented paint coating method [10–14] have been found to offer corrosion protection. The advantage of conductive polymer coating is that the coating has more tolerance to pin holes due to its passivation ability.

There are two forms of emeraldine PAni available; doped (conductive) and undoped (non-conductive). There are much fewer studies devoted to the corrosion protection properties of PAni in undoped emeraldine base form. Furthermore, there is some controversy on whether the conducting or non-conductive form of PAni exhibits the best corrosion protection properties [5]. For example, Araujo et al. [15] found that undoped PAni does not present required properties needed to be proposed as anti-corrosive coating, while Spinks et al. [16] by comparison between the emeraldine salt and emeraldine base coatings concluded that the corrosion protection of a steel substrate by emeraldine base coating was superior. Tale et al. [17] and Dominis et al. [18] found that emeraldine base coatings provided a better corrosion protection than the coatings based on a conductive PAni. Meanwhile, Gasparac and Martin [19] found that the corrosion protection properties of PAni were independent of the doping level, and totally undoped emeraldine base coating was equally capable of maintaining the potential of the stainless steel substrate in the passive region. Also Dominis et al. [18] reported that the corrosion protection provided by emeraldine salt primers was strongly influenced by the type of dopant used.

To make a powdery-doped PAni, generally an aqueous acidic medium such as hydrochloric acid is needed. The PAni powder is highly acidic and there are many steps, which is required to be taken to purify the synthesized PAni. Besides, special corrosion resistant reactors are required. In this research, we used a simple method (a non-acidic/non-corrosive medium) to prepare undoped

---

* Corresponding author at: Corrosion Research Department, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-1998, Tehran, Iran. Tel.: +98 21 44739737; fax: +98 21 44739737.
E-mail address: akbarinezhade@ripi.ir (E. Akbarinezhad).

0300-9440/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.porgcoat.2008.07.018

PAni powder according to Subramanian and Deshpande's work [20]. The PAni powder was then used as a corrosion inhibitive pigment in epoxy matrix as a coating to protect carbon steel specimen in 3.5% sodium chloride solution. Protective properties of the prepared coating were evaluated via electrochemical measurements.

2. Experimental

2.1. Synthesize of PAni

All reagents were purchased from Merck and were used without further purifications. Undoped PAni was synthesized by chemical oxidative polymerization of aniline with ammonium persulfate (APS) as an oxidizing agent. The APS agent (10.6 g) was dissolved in 300 ml of distilled water and stirred up for 15 min. The solution was heated up to 40 °C. Aniline monomer (4.08 g) was added to the above solution with constant stirring (50 rpm) for 15 min. The reaction was allowed to proceed for 4 h. The PAni was precipitated by adding the reaction mixture in to the 500 ml of distilled water followed by filtration. The powdery substance was repeatedly washed with distilled water, and then dried at 35 °C in vacuum for 24 h.

2.2. Preparation of PAni pigmented paint

The synthesized PAni powder was added to an epoxy resin solution (Epikote1001 solution 70 wt.% in toluene) and mechanically sized to obtain 50 μm particle size in average. The liquid substance with dispersed PAni powder was mixed with a hardener (polyamide, Crayamid 115) at stoichiometric ratio. The PAni content in the paint was 1 wt.%.

2.3. Evaluation of coating performance by electrochemical methods

Carbon steel panels (SAE 1020) of 100 × 150 × 2 mm in size were used. The specimens were sand blasted to Sa2.5 (according to SIS 055900-67) with a profile of 30–50 μm (according to ASTM D4417) and then degreased with acetone before painting. The paintings were done by air spray method. The thickness of the coating was measured using Minitest 2000, a thickness meter equipment, and was found to be 70 ± 10 μm. The corrosion behavior of coated specimens was determined via measuring the OCP and impedance characteristics in 3.5% sodium chloride solution in several time intervals. The electrochemical measurements were carried out with the Potentiostat/Galvanostat Model 273 A and SI 1255 frequency response analyzer at open circuit potential and frequency ranges of 0.005 Hz to 10 kHz at 10 mV rms AC perturbation. A cell equipped with three electrodes was used for electrochemical measurements. The specimen of coated steel was used as the working electrode (WE) and a pair of graphite rods as counter electrode (CE). A saturated calomel reference electrode (SCE) was brought into the close proximity with working electrode by a luggin capillary. Fig. 1 shows an experimental cell was used in this work. The impedance data were analyzed by using "Zview" software.

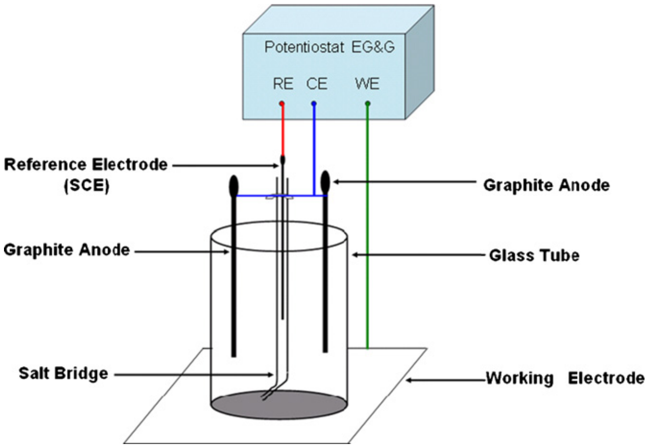

Fig. 1. Schematic of electrochemical cell.

3. Results and discussion

3.1. Open circuit potential measurements

The variations of the open circuit potential (OCP) values for the PAni pigmented paint coating on steel panel are shown in Fig. 2. This figure shows that the OCP values decreased from −567 mV to −622 mV initially and then increased up to −220 mV versus SCE. This behavior could be due to the dissolution of iron at initial time of immersion and formation of the Fe_2O_3 passive layer in second part of the immersion period. Wessling has confirmed the presence of Fe_2O_3 layer between PAni coating and steel surface by SEM and ESCA studies [21–23]. It can be concluded that the PAni in the coating is able to passivate the iron surface in 3.5% sodium chloride solution. Previous studies had shown that the OCP of the PAni coated steel had been higher than uncoated steel sample by 100–500 mV in neutral chloride solutions due to passivation of iron [24–27].

3.2. EIS measurements

Nyquist and Bode plots of the PAni pigmented coating on steel specimen during 300 days of immersion were shown in Fig. 3. The Nyquist diagrams show two capacitive loops, a smaller one at high frequency range followed by a larger one at the low frequencies. This electrochemical behavior corresponds to the interaction between the steel/PAni interface and the electrolyte. The first capacitance loop is attributed to the coating performance and the second one is related to the processes occurring underneath the film [28–29]. This electrochemical behavior is usually modeled with the equivalent electrical circuit (EEC) presented in Fig. 4 [30]. In this circuit R_Ω, R_c, C_c, R_{ct} and C_{dl} are the solution resistance, the coating resistance, the coating capacitance, the charge transfer resistance and the double layer capacitance, respectively. Fig. 5 shows coating resistance and charge transfer resistance of coated steel specimen during the immersion in 3.5% sodium chloride solution. This figure reveals that the coating resistance decreased from 2.325 MΩ cm^2 to 0.45 MΩ cm^2 at the initial 14 days of immersion

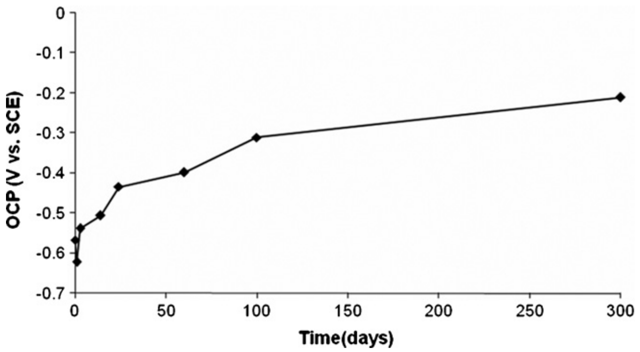

Fig. 2. Variation of open circuit potential of PAni pigmented paint coating on steel in 3.5% sodium chloride solution.