Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Synthetic Metals 157 (2007) 205–213

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Preparation of polyaniline–TiO_2 composite and its comparative corrosion protection performance with polyaniline

S. Sathiyanarayanan, S. Syed Azim, G. Venkatachari *

Central Electrochemical Research Institute, Karaikudi 630006, India

Received 11 September 2006; received in revised form 11 December 2006; accepted 24 January 2007
Available online 6 March 2007

Abstract

Due to strict environmental regulations on the usage of chromate in the coating industries, search for effective inhibitive pigment in replacing those chromate pigments has become necessary. In recent years it has been shown that electrically conducting polymers such as polyaniline (PANI) incorporated coatings are able to protect steel due to their passivating ability similar to that of chromates. This work presents the comparative corrosion protection performance of the coatings containing polyaniline and polyaniline–TiO_2 composite (PTC) on steel in acrylic binder. The PANI and PTC were prepared by chemical oxidative method of aniline by ammonium persulfate. The polymers were characterized by FTIR, XRD and SEM. The corrosion protection performance of the coatings containing PANI and PTC on steel was evaluated by immersion test in 3% NaCl for 60 days and salt fog test for 35 days. The performance of the coatings in both the tests was investigated by open circuit potential measurements and EIS technique. It has been found that the open circuit potential values of PTC containing coating are more nobler by 50–200 mV in comparison to that of coatings with PANI. Besides, the resistance values of the coating containing PTC were more than $10^7\ \Omega\,cm^2$ in the 3% NaCl immersion test after 60 days and $10^9\ \Omega\,cm^2$ in the salt fog test of 35 days which were two orders high in comparison to that of PANI containing coatings. The better performance of PTC containing coatings may be due to uniform distribution of polyaniline which can form uniform passive film on the iron surface.

Keywords: Polyaniline; Polyaniline–TiO_2 composite; Acrylic; EIS; Coating; Corrosion protection; Steel

1. Introduction

In recent years, polyaniline containing organic coatings have been shown to replace the chromate containing primer coatings [1–4]. It has been shown by Wessling et al. [2–4] that samples of mild steel with undoped polyaniline (PANI) and with an epoxy topcoat have exhibited corrosion rates slightly slower in 3.5% NaCl solution and 100 times slower in 0.1N HCl solutions than those of samples coated with epoxy alone. Further it has been shown that an oxide layer has been formed between the PANI coating and the steel surface which is composed mainly of Fe_2O_3 above a very thin Fe_3O_4 layer [2–6], Kinlen et al. [7,8] have shown the occurrence of the redox process in the polymeric layer by scanning reference electrode technique and proposed a model. Santros et al. [9] have shown that the sprayed polyaniline coating on steel is able to protect in 3% NaCl solution due to passive film formation. Wang et al. [10] have shown that conducting polyaniline containing epoxy coating has got antifouling property. Using electrochemical methods, the corrosion resistant properties of polyaniline epoxy blended coating on steel have been reported [11]. It has been shown that emeraldine base is most effective in saline solution while protonated polyaniline is effective in acid media. de Souza et al. [12] have shown that sulfonate doped polyaniline with acrylic coating protects the carbon steel in chloride solutions by forming a passivating complex with dopant anion and also by barrier effect. Samui et al. [13] have studied the protection performance of the paint containing PANI–HCl and shown that lower loading of PANI–HCl has been found to be more effective. da Silva et al. [14] have studied the role of counter-ions on the protection of steel by polyaniline acrylic coating. They have shown that the polyaniline containing coating protects steel by two step protection mechanism. First a redox reaction between Fe and PANI forms a passive layer and a second layer by forming a complex

---

* Corresponding author.
E-mail address: gvchari@gmail.com (G. Venkatachari).

0379-6779/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2007.01.012

salt layer with iron and dopant. Recent studies by the authors [15–17] have shown that polyaniline containing organic coatings are able to protect steel in acid, neutral and alkaline environments. Plesu et al. [18] have shown that the acrylic dispersion based on PANI doped with anions containing phosphonates provides improved corrosion protection of carbon steel. In all the earlier studies, the corrosion protection of polyaniline containing coating have been studied using polyaniline sprayed coating or polyaniline blended resin coating. The most of the paint formulations contain TiO_2 as one of the filler material and it is worthwhile to study the corrosion protection performance of PANI–TiO_2 composite containing coatings. Earlier studies [19–22] on polyaniline–TiO_2 composite (PTC) deal mainly with the properties such as electrical conductivity, thermal stability and spectroscopic characteristics. Hence a comparative study has been made on the corrosion protection performance of PANI and PTC containing coatings on steel in sodium chloride solutions.

2. Experimental

2.1. Preparation of PANI–TiO_2 composite

One molar of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid and 25 g of anataseTiO_2 was added to it. The mixture was stirred well. Pre-cooled 500 ml of 1 M solution of ammonium persulfate was added drop wise to the pre-cooled aniline–acid mixture for about 1.5 h with constant stirring. The reaction was conducted at 5 ± 1 °C. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured PANI–TiO_2 composite thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer was dried in oven at about 80 °C for 2 h. The dried PANI–TiO_2 composite was fine grinded using morter and then used as pigment. The polymerization mechanism of PANI on TiO_2 particles can be explained as follows.

Since the surface of TiO_2 has the point of zero charge (pzc) at pH 5.9 [23], it may be positively charged in the acidic polymerization H_3PO_4 bath. Due to the positive charge on TiO_2, the $H_2PO_4^-$ ions adsorb on TiO_2. These specifically adsorbed anions would work as a charge compensator for positively charged PANI chain in the formation of PTC. Similar reaction mechanism has been put forward for PANI–MnO_2 composite preparation [24].

2.2. Characterization of PANI–TiO_2 composite

The PANI–TiO_2 composite was characterized by the following methods:

(i) *Conductivity measurements*. The conductivities of the PANI and PANI–TiO_2 composite were measured for the palletized pigment using a four probe resistance meter.

(ii) *XRD analysis*. The powder X-ray diffraction of the TiO_2, PANI and the PTC composite were analysed using PHILIPS (Model PW3040/60) X-ray Diffractometer using Cu Kα radiation in the 2θ range 5–75° at the scan rage of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s.

(iii) *FTIR analysis*. The FTIR spectra of TiO_2, PANI and the PTC composite were obtained using Nicolet 380 FTIR Spectrometer in wavenumber range 2000–500 cm^{-1}.

(iv) *SEM analysis*. The scanning electron micrographs of TiO_2, PANI and PANI–TiO_2 composite was analysed using Hitachi (Model S3000 H) instrument. The pigment was spread over a copper block over which gold was sputtered.

2.3. Preparation of PANI–TiO_2 composite containing paint

The primer is formulated using commercial acrylic resin (Kondicryl 166, Pidilite, India). The volume solids of the formulation was kept at 30% with 35% pigment volume concentration (P.V.C.). The main pigments used in this formulation were polyaniline, titanium di oxide and PTC along with mica and silica as extender pigments. Di octyl phosphate (D.O.P.) was used as a plasticizer. This primer coat was top coated with aliphatic polyurethane paint. This paint was formulated with acrylic ployol (Kondicryl SVOL-7, Pidilite, India) as base and poly iso cyanate (Grand Polycoats, India) as curing agent. The paint was formulated with 40% volume solids and 18% P.V.C. Rutile titanium di oxide was used as main pigment along with mica and silica as extender pigments.

The pigments were pre mixed and the paint was prepared in an lab attritor. The attritor was run for 45–50 min. The fineness of dispersion of paint was found using Hegmann gauge and it was found to be between 7 and 8.

The paint was stored in air tight container. The mix ratio of the polyurethane paint was 2:1 by weight. The topcoat was applied over the primer paint applied panels after 24 h of curing at ambient conditions. The specific gravity of the primer was 1.0 and the dry film thickness (DFT) was 40–45 μm. The specific gravity of the top coat was 0.98 and the dry film thickness was 30–35 μm.

2.4. Water uptake studies of coating

The total paint system was applied over 5 cm × 7.5 cm glass plates by means of brush and allowed to cure for 7 days at ambient temperature. These coated glass panels were weighed and immersed in a 500 cm^3 beaker containing 400 cm^3 of distilled water. The panels were reweighed after regular time intervals after removing the surface water by means of a filter paper. The weight gain was measured up to 10 days. The accuracy of the weight measurement is ±0.1 mg.

2.5. Evaluation of corrosion resistant properties of the coating

2.5.1. Salt spray tests

Coated mild steel panels were prepared by coating on sand blasted (Sa 2.5) specimen of size 15 cm × 10 cm × 0.1 cm. The coated panels were exposed to salt spray of 5% NaCl solution as per ASTM B117.