Performance Studies of Phosphate-Doped Polyaniline Containing Paint Coating for Corrosion Protection of Aluminium Alloy

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ABSTRACT: Polyaniline-phosphate polymer was prepared chemically by oxidation polymerization of aniline in phosphoric acid medium using ammonium persulphate. The PANI-phosphate polymer was characterized by FTIR, XRD, and SEM. The paints using PANI-phosphate as pigment in acrylic and epoxy binder were prepared. The protective performance of the coating formed on aluminum alloy AA 2024 T3 was studied by electrochemical impedance spectroscopy in 0.5% NaCl solution. Both the coating systems have exhibited the coating resistance values above 1*M* Ω cm^2 even after 50-days exposure in 0.5% NaCl solution. Besides the anticorrosion performance of PANI-containing coating is comparable with that of chromate-containing coating. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2224–2230, 2008

Key words: polyaniline; acrylic; epoxy; aluminum; EIS; corrosion

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INTRODUCTION

Chromates are commonly used as pigments in the primer coating of aluminum and its alloys for corrosion protection.[1,2] Even though chromates are highly efficient, the use of chromate in the coating system has been limited since 1982 due to their carcinogenic effects.[3] The alternative nontoxic pigments such as zinc molybdate, zinc phosphates, and zinc benzoates have been used in the primers.[4,5] This system provided only fair protection comparable with the military specification air craft primers.[2] In recent years, studies have shown that the intrinsically conducting polymers such as polyaniline and polypyrrole found to offer corrosion protection of metals. Recent reviews[6–8] summarize the studies on the protection of metals by conducting polymers. Such type of coatings have been found to passivate the metal substrates similar to the chromate-containing coating.[9–12]

The anticorrosion property of electrodeposited conducting polymer coatings on aluminum is studied by Tallman et al.,[13] Breslin et al.,[14] Shah and Iroh.[15] The use of conducting polymer as pigment in primer coating of aluminum alloys is little studied. Seegmillar et al.[16] studied the corrosion protection mechanism of polyaniline-poly[metylmethaacrylic] coating on AA 2024 T3 alloy and showed that polyaniline was able to protect scribed areas due to its electrochemical activity. In this article, the anticorrosion property of polyaniline pigmented acrylic and epoxy coatings on aluminum alloy is reported.

EXPERIMENTAL

Synthesis of PANI-phosphate pigment

About 1*M* of distilled aniline was dissolved in 500 mL of 1*M* solution of phosphoric acid. Precooled 1*M* solution of ammonium persulfate was added drop wise to the precooled 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 colored conducting polyaniline 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 polyaniline was ground to a fine powder using a pestle and mortar and then used as pigment.

Characterization of PANI-phosphate pigment

The infrared spectra of the polymer were recorded on NICOLET 380 FTIR spectrometer in KBr medium at room temperature in the region of 2000–500 cm^{-1}. X-ray diffraction pattern of PANI-phosphate pigment was taken with Analytical (Model PW3040/60) X-ray diffractometer using Cu Kα radiation. The morphology

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TABLE I
Details of the Coating Systems

Sl no.	System	Volume solids (%)	Pigment volume concentration (PVC) (%)	Paint constituents wt %	Specific gravity of paint	Dry film thickness (DFT) (μm)
1.	Epoxy primer	30	35	Epoxy resin: 25; Pani-PO_4: 1–6; TiO_2 (Anatase): 12; Talc: 4; Silica: 1; Aluminum sterate: 0.5; Polyaminde: 10; Solvent: Balance	1.2	60 ± 2
2.	Acrylic primer	30	35	Acrylic resin (30%): 63; Pani-PO_4: 3; TiO_2 (Anatase): 10; Talc: 4; Silica: 2; Aluminum sterate: 0.5; Solvent: Balance	1.01	55 ± 2
3.	Acrylic-Polyurethane top coat	40	18	Acrylic polyol: 25; TiO_2 (Rutile): 5; Talc: 2; Silica: 3; Aluminium state: 0.5; Mica: 3; Additives: 0.5; Aliphatic isocyanate: 10; Solvent: Balance	1.08	35 ± 2

of the pigment was analyzed using Hitachi (Model S3000 H) scanning electron microscope by spreading the pigment over a copper block over which gold was sputtered. The electrical conductivity of the pigment was measured by the standard four-probe resistivity method.

The paint system was applied over 5 cm × 7.5 cm^2 glass plates by means of brush and allowed to cure for 7 days at ambient temperature. These glass panels along with the paint films were weighed and immersed in a 500 cm^3 beaker containing 400 cm^3 of distilled water. The panels were reweighed at regular intervals after removing the surface water by means of a filter paper. The weight gain was measured up to 50 days.

Preparation of PANI-phosphate pigmented paint

Epoxy resin (Epoxy equivalent 500) of 30% volume solids was prepared by refluxing 30 g of epoxy resin with 70 c.c. of solvent mixture of xylene, MIBK, and butyl cellosolve. The paint was prepared in a lab attritor. The pigments were premixed before mixing it with the resin solution. The attritor was run for 45 min. The paint was transferred to an airtight container. The paint was mixed with polyamide hardener (amine value 210–230 mg KOH/g) in the mix ratio of 7 : 3 and applied over the aluminum surface by spray.

A commercially available acrylic resin (Kondicryl 166, Pidilite, India) is used for formulating acrylic primer. The primer was formulated with 30% volume solids and 35% pigment volume concentration using titanium dioxide and polyaniline-conducting polymer doped with phosphate as main pigments.

Polyurethane topcoat was prepared by taking acrylic polyol (Pidilite, India) as base. The paint was prepared in a lab attritor with 40% volume solids. The pigments were premixed before mixing it with the resin. The mixture of xylene and butyl acetate was taken as solvent. The attritor was run for 45 min at room temperature. The paint was transferred to an airtight container. The paint was mixed with aliphatic polyisocyante curing agent in the mix ratio of 2 : 1 and applied over the primer after 24 h as topcoat.

The formulation details of the primers and the topcoats are given in Table I along with the physical properties of formulated paints.

Evaluation of anticorrosion properties of the coating

Aluminum alloy specimens (AA 2024 T3) of size 15 × 10 × 0.1 cm^3 were polished and degreased with trichloroethylene and coated with PANI-phosphate pigment containing paints. The thickness of the total coating system (primer and topcoat) was 100 ± 5 μm. A glass tube of 0.9-cm diameter and of length 3 cm was fixed on the coated aluminum with adhesive (m seal). The solution of 0.5% NaCl was taken in the glass tube. A platinum foil and a saturated calomel

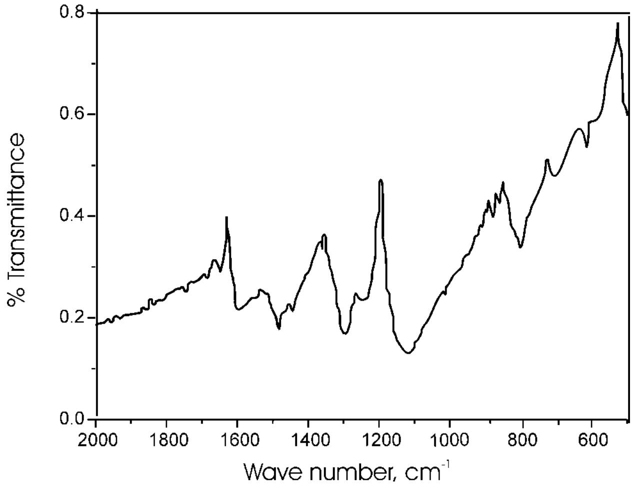


Figure 1 FTIR spectrum of PANI-phosphate pigment.

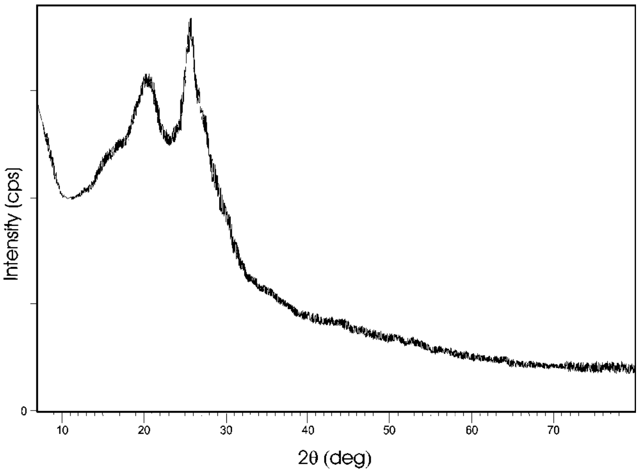


Figure 2 X-ray diffraction pattern of PANI-phosphate pigment.

electrode were placed inside the glass tube. The assembly was connected to electrochemical impedance analyzer (Model 6310, EG and G). Impedance measurements were carried out for a frequency range of 100 KHz to 0.01 Hz with an AC amplitude of 20 mV for different immersion time up to 50 days. The impedance data were analyzed using Z Plot software.

RESULTS AND DISCUSSION

Characterization of PANI-phosphate pigment

Infrared analysis

Figure 1 shows the infrared spectrum for PANI-phosphate pigment. The peak at 820 cm^{-1} is due to the 1,4 para substituted benzene ring. The peaks at 1120 and 620 cm^{-1} are due to in-plane and out of plane C—H bending motion of quinoid and benzenoid rings, respectively. The peaks at 1250 and 1350 cm^{-1} are characteristic of aromatic amines. The peaks at 1560 and 1490 cm^{-1} are due to C=N stretching of quinoid and benzenoid groups, respectively.[17,18] The peak around 1000 cm^{-1} has been assigned to $H_2PO_4^-$ peak.[19] Further it has been reported that the dopant anions present on PANI/H_3PO_4 are dihydrogen phosphate anions $H_2PO_4^-$.[20,21]

XRD analysis

The XRD pattern of the PANI-phosphate pigment is shown in Figure 2. The intense peak at 2θ around 25° has a similar profile as that of free polyaniline reported in literature.[22,23] The diffraction pattern also matches well with the PANI standard pattern (00-053-1890).

Conductivity measurement

The conductivity of the pigment is 2.5 S cm^{-1} as measured by four probe resistivity method. This value is some what less from the value reported in literature, ~ 15.5.[24]

SEM studies

Figure 3 shows the morphology of the PANI-phosphate pigment. It is found that PANI-phosphate pigment shows a globular structure consisting of small globules and pores. Earlier studies[25] have shown that the morphology of polyaniline-phosphate polymer is dependent on the pH of the solution from which the polymer is prepared.

Water uptake studies

The results obtained in the water uptake studies of polyaniline-pigmented acrylic and epoxy coatings is given in Table II. It can be seen that the amount of

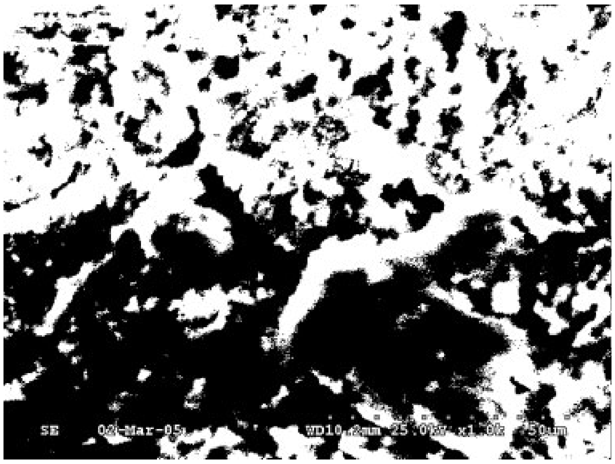


Figure 3 Scanning electron micrograph of PANI-phosphate pigment.

TABLE II
Water Uptake Values for PANI-Phosphate Pigmented Acrylic and Epoxy Coatings

	Weight gain (mg)	
Time (days)	Acrylic coating	Epoxy coating
1	0.018	0.095
4	0.045	0.093
7	0.077	0.090
15	0.080	0.097
28	0.113	0.104
38	0.119	0.106
50	0.128	0.098

uptake of water is not significantly varying with time for both the coatings.

Open circuit potential measurements

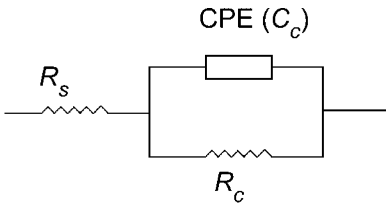
Open circuit potential measurements were made on the coated aluminum alloy in 0.5% NaCl with respect to saturated calomel electrode (SCE) for different immersion period. Table III shows the variation of open circuit potential values with immersion time of the epoxy and acrylic coatings containing PANI-phosphate. In both the cases, there is a shift of potential in noble direction after 7 days of immersion period. But in the case of bare aluminum the OCP values were in the range −0.690 ± 0.020 V. This shows that the PANI present in the coating is able to passivate the aluminum substrate.

TABLE III
Variation of Open Circuit Potentials of PANI-Phosphate Pigmented Coating on AA 2024 T3 Alloy in 0.5% NaCl

	Open circuit potential V vs. SCE		
Time (days)	Acrylic coating	Epoxy coating	Bare aluminium
Initial	−0.344	−0.516	−0.710
1	−0.496	−0.495	−0.690
2	−0.748	−0.554	−0.730
3	−0.860	−0.560	−0.720
4	−0.772	−0.560	−0.720
7	−0.760	−0.531	−0.730
15	−0.725	−0.476	−0.715
28	−0.625	−0.349	−0.705
38	−0.619	−0.376	−0.690
50	−0.597	−0.391	−0.695

EIS studies

The anticorrosion performance of polyaniline phosphate pigmented paint coating on aluminum alloy has been evaluated by electrochemical impedance spectroscopy in 0.5% NaCl solution for a period of 50-days exposure. Figure 4 shows the impedance behavior of acrylic coating containing PANI-phosphate. It can be seen that the impedance values decrease with exposure time. However, the spectra show a single time constant due to coating behavior. Absence of second time constant indicates the absence of any corrosion reaction. The following equivalent circuit was used to obtain the resistance (R_c) and capacitance (C_c) of the coating.



where R_s is the solution resistance, CPE is the constant phase element of the capacitance of the coating, and R_c is the resistance of the coating. The impedance of the metal/coating interface did not behave as an ideal capacitor. A constant phase element (CPE) was used as a substitute for the equivalent circuit to fit more accurately the impedance behavior of coating capacitance. The admittance of CPE is described as

$$Z(\mathrm{CPE}) = Y_0^{-1} \ (j\omega)^{-n} \tag{1}$$

where Y_0 represents the modulus, ω the angular frequency, and n the phase.[26,27] The correct equation to convert Y_0 into C_c is,[28]

$$C_c = Y_0 \ \left(\omega''_m\right)^{n-1} \tag{2}$$

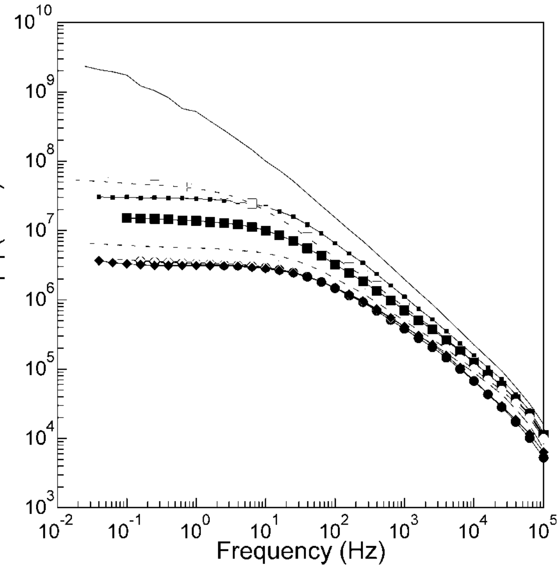


Figure 4 Impedance plots of PANI-phosphate pigmented acrylic coated AA2024-T3 alloy in 0.5% NaCl; ——— Initial; ■ 1 day; □ 4 days; ■ 7 days; ○ 15 days; ● 28 days; ◇ 38 days; ◆ 50 days.

TABLE IV
Impedance Parameters of PANI-Phosphate Pigmented Acrylic Coated AA2024-T3 Alloy in 0.5% NaCl

Duration (days)	Coating resistance R_c (Ω cm^2)	Y_0 Ω^{-1} s^n cm^{-2}	n	Coating capacitance C_c (F cm^{-2})
Initial	4.1×10^9	2.45×10^{-10}	0.80	1.28×10^{-10}
1	3.0×10^7	2.88×10^{-10}	0.80	1.13×10^{-10}
4	5.3×10^7	6.63×10^{-10}	0.80	3.45×10^{-10}
7	1.5×10^7	6.78×10^{-10}	0.80	3.82×10^{-10}
15	6.4×10^6	6.88×10^{-10}	0.80	2.33×10^{-10}
28	3.4×10^6	8.27×10^{-10}	0.80	2.61×10^{-10}
38	3.0×10^6	8.04×10^{-10}	0.80	2.55×10^{-10}
50	3.2×10^6	7.29×10^{-10}	0.80	2.24×10^{-10}

TABLE V
Impedance Parameters of PANI-Phosphate Pigmented Epoxy Coated AA2024-T3 Alloy in 0.5 % NaCl

Duration (days)	Coating resistance R_c (Ω cm^2)	Y_0 Ω^{-1} s^n cm^{-2}	n	Coating capacitance C_c (F cm^{-2})
Initial	1.2×10^9	4.64×10^{-10}	0.80	4.24×10^{-10}
1	1.4×10^8	3.58×10^{-10}	0.80	1.72×10^{-10}
4	4.2×10^7	8.67×10^{-10}	0.80	4.32×10^{-10}
7	2.6×10^7	9.79×10^{-10}	0.80	4.66×10^{-10}
15	1.5×10^7	10.05×10^{-10}	0.80	4.34×10^{-10}
28	8.4×10^6	12.16×10^{-10}	0.80	4.91×10^{-10}
38	9.7×10^6	10.60×10^{-10}	0.80	4.52×10^{-10}
50	9.7×10^6	9.10×10^{-10}	0.80	3.70×10^{-10}

The resistance (R_c) and capacitance (C_c) values of the coating derived from Figure 4 are given in Table IV. Initially the coating resistance is 4.1×10^9 Ω cm^2. On prolonged exposure period, the coating resistance is decreased to 6.4×10^6 Ω cm^2 after 15-days exposure and after words there is not much change in the resistance value of the coating. The coating resistance remained constant in the range of 3.2 to 3.4×10^6 Ω cm^2, which shows the stability of the coating. The capacitance values of the coating are in the range of 2.8 to 6.6×10^{-10} F cm^{-2} in most of the cases which again confirms the absence of any delamination of the coating.

The impedance behavior of epoxy containing PANI-phosphate coated aluminum in 0.5% NaCl is shown in Figure 5. The impedance parameters obtained from the studies are given in Table V. The resistance of the coating is changed from 1.2×10^9 Ω cm^2 to 1.4×10^8 Ω cm^2 after 1-day immersion. After words, the resistance of the coating decreases gradually and has reached a value of 9.7×10^6 Ω cm^2 after 50-days exposure. The capacitance values remained in the range of 1.7 to 4.9×10^{-10} F cm^{-2} from 1-day exposure to 50-days exposure which indicate the absence of any delamination of the coating. Besides, the impedance spectra show a single time constant as observed in the case of acrylic-coated aluminum, which indicates the absence of any corrosion reaction. Also the constant value of 0.80 for "n" in both the coating systems for the entire period of study indicates the absence of any change in surface state due to corrosion reaction.[29] A similar EIS study with strontium chromate pigmented acrylic primer coating with acrylic polyurethane top coat showed that the initial coating resistance and capacitance values were 7.28×10^8 Ω cm^2 and 8.27×10^{-11} F cm^{-2}. After 28-days exposure, the resistance and capacitance

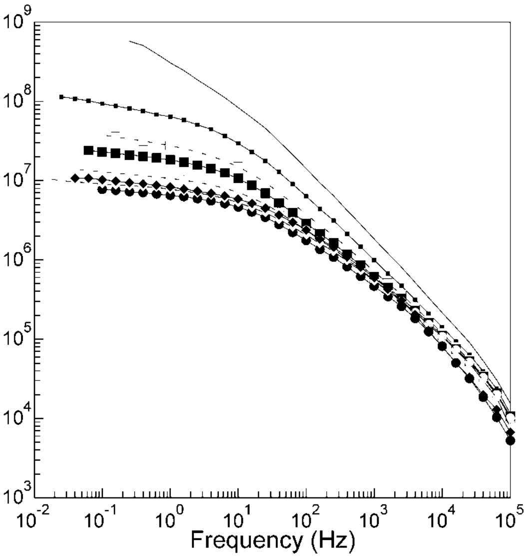


Figure 5 Impedance plots of PANI-phosphate pigmented epoxy coated AA2024-T3 alloy in 0.5% NaCl; ——— Initial; ■ 1 day; □ 4 days; ■ 7 days ; ○ 15 days; ● 28 days; ◇ 38 days; ◆ 50 days.

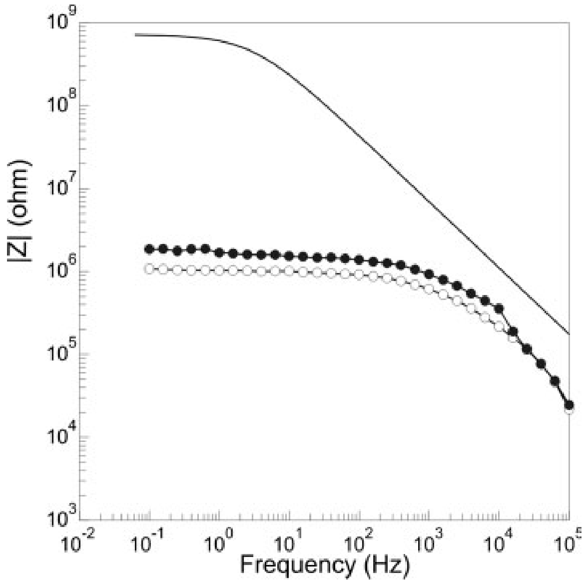


Figure 6 Impedance plots of strontium chromate pigmented acrylic coated A2024-T3 alloy in 0.5% NaCl; ——— Initial; ○ 15 days; ● 28 days.

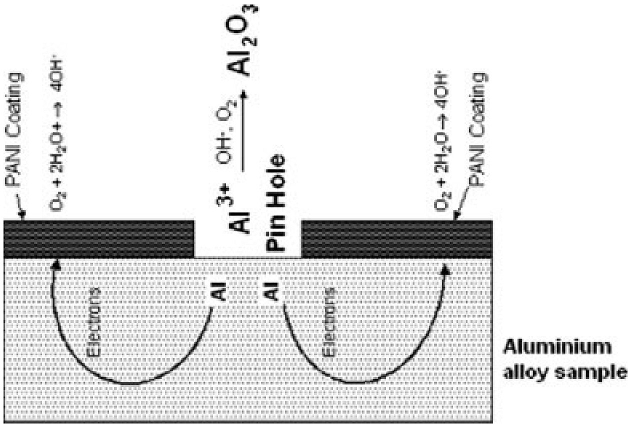


Figure 7 Schematic diagram of mechanism of AA2024-T3 alloy passivation by PANI-blended paint coating.

values were found to be 1.69 × 10^6 Ω cm^2 and 1.50 × 10^{-10} F cm^{-2} (Fig. 6). On comparing these values with that of PANI containing coatings, it is clear that the performance of PANI containing coating is of the same order as that of chromate pigmented coating.

Visual inspection of the coated panels after 50-days exposure has indicated no white rust formation and the coating is highly intact. Besides, the color of the solution remained unchanged.

In a recent study by Gui and Kelly[30] on the performance of corrosion protection coatings on AA 2024-T3 aluminum alloy by EIS, it has been shown that the coating with impedance value above 0.1*M* Ω cm^2 or capacitance values below 7.6 × 10^{-8} F cm^{-2} exhibit excellent protection. In this study it is found that both the coatings exhibit resistance values above 3*M* Ω cm^2 and capacitance values below 1.0 × 10^{-8} F cm^{-2}. This shows that the PANI-phosphate containing coatings are able to protect aluminum from corrosion.

Mechanism of action of PANI-blended coatings

The PANI blended coatings on aluminum alloy have been found to suppress the anodic dissolution reaction by forming passive layer on the metal surface. This has been found by Tallman et al.[13] and Seegmiller et al.[16] in their studies on the protection of PANI-containing coating on AA 2024 alloy. They showed that the PANI-coated alloy has a more positive open circuit potential than that of bare alloy. They proposed that the positive OCP value was due to the redox communication between the alloy and the PANI film. In the present study also, it has been observed that the open circuit potential values have been shifted to positive value after 7 days of immersion which indicates the growth of oxide film. Further, the coating resistance values also are increased slightly after 28-days immersion, which also indicate the protective nature of the film. Similar increase in resistance values have been reported by Tallman et al.[13] On the basis of these observations, the protection mechanism of PANI-blended coating is schematically shown in Figure 7. Because of the conducting nature of the coating, the oxygen–reduction reaction takes place over the coating, while the oxidation of aluminum ions to aluminum oxide takes place on the exposed aluminum alloy surface at pin hole areas and under the film.

CONCLUSIONS

PANI-phosphate polymer has been chemically synthesized and characterized by FTIR and XRD. The PANI-phosphate polymer containing acrylic and epoxy coatings are able to protect the aluminum alloy from corrosion due to the passivation ability of the polyaniline which is evidenced from the shift of open circuit potential in noble direction with time of exposure. The corrosion protection performance of PANI-containing coating is comparable with that of chromate-containing coating.

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