

# Corrosion protection of steel by polyaniline blended coating

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## Abstract

Phosphate doped polyaniline was synthesized from aqueous phosphoric acid containing aniline by chemical oxidation method using ammonium persulfate as oxidant. The polymer was characterized by UV–vis and FT-IR spectroscopic techniques. Using this polymer, a paint with 1% polyaniline was prepared with epoxy binder. The corrosion resistant property of the polymer containing coating on steel was found out by open circuit potential measurements and electrochemical impedance spectroscopic method in 0.1 N HCl, 0.1 N H<sub>3</sub>PO<sub>4</sub> and 3% NaCl for a duration of 50 days. The coating was able to protect the steel more in 0.1 N H<sub>3</sub>PO<sub>4</sub> and 3% NaCl media than in 0.1 N HCl.

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**Keywords:** Polyaniline; Coating; Epoxy; Electrochemical impedance spectroscopy; Corrosion

## 1. Introduction

The chemical and electrochemical synthesis of polyaniline has received considerable attention in recent years by various researchers in corrosion science. Polyaniline containing organic coatings have been found to offer corrosion protection of steel in acid and saline media [1–16]. In most of the studies, polyaniline is doped with hydrochloric acid, sulphonic acid, phosphonic acid, dioctyl phosphate and camphor sulfonic acid and the doped polyaniline is used in the coating. The mechanism of corrosion protection of steel by polyaniline coating has been studied by Kinlen et al. [1,9,12] and Jain et al. [17]. They have reported that doped polyaniline coatings passivate the pin hole defects in the coatings. Further, it has been reported that steel coated with polyaniline has gained 100–200 mV in corrosion potential in 3% NaCl due to decrease in iron dissolution reaction by passive film formation [7,9,11,14] and shift the potential in passive region.

The studies by SEM and XPS techniques have revealed that a passive oxide layer has been formed between polyaniline coating and the steel surface and the oxide is composed mainly of Fe<sub>2</sub>O<sub>3</sub> above a very thin Fe<sub>3</sub>O<sub>4</sub> layer [18–20]. Since phosphate compounds are known to be corrosion inhibitors for steel, the

polyaniline polymer with phosphate dopant may be more effective in corrosion protection. Recently, Moraes et al. [21] have synthesized the polyaniline–phosphate polymer electrochemically and characterized the polymer. In this paper, the corrosion resistant property of steel coated with phosphate doped polyaniline in epoxy binder is reported.

## 2. Experimental

### 2.1. Chemicals

All chemicals were of high purity commercially available: aniline (Sd-fine chemicals, 99.5%), ammonium persulfate (Sd-fine chemicals, 99.5%); sodium chloride NaCl (Fisher, 99.9%), phosphoric acid H<sub>3</sub>PO<sub>4</sub> (Fischer, 99.9%), hydrochloric acid HCl (Fischer, 99.9%), epoxy resin with epoxy equivalent 450–500 (Ciba Geigy) and polyamine hardener with amine value 210–230 mg KOH/gm (Sympol 115). Aqueous solutions were prepared from double distilled water.

### 2.2. Preparation of phosphate doped polyaniline (PANI)

One molar of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid. Pre-cooled 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 stir-

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ring was continued for 2 h for ensuring complete polymerization. A dark green coloured 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 fine grinded using mortar and then used as pigment.

### 2.3. Instrumentation

#### 2.3.1. FT-IR analysis

The FT-IR spectra of PANI–phosphate pigment were taken with KBr pellets using Nicolet 380 FT-IR Spectrometer in the range 2000–500  $\text{cm}^{-1}$ .

#### 2.3.2. UV spectra analysis

The UV–vis spectra of the PANI–phosphate pigment in the wavelength range 250–900 nm was recorded with Hitachi (Model U 3400) spectrophotometer.

#### 2.3.3. SEM analysis

The scanning electron micrograph of PANI–phosphate pigment was analyzed using Hitachi (Model S3000 H) instrument. The pigment was spread over a copper block over which gold was sputtered.

#### 2.3.4. XRD analysis

The powder X-ray diffraction of the PANI–phosphate pigment was analysed using PAN Analytical (Model PW3040/60) X ray diffractometer.

#### 2.3.5. Conductivity measurements

The conductivity of the PANI–phosphate pigment was measured for the palletized pigment using a four probe resistance meter.

#### 2.3.6. Electrochemical measurements

The open circuit potential measurements were made with digital multi meter and the impedance studies of the coated panels were made using the impedance analyzer (6310 EG&G).

#### 2.3.7. Coating thickness measurements

The thickness of the coating was measured by the Elcometer thickness meter (Model No. 456).

### 2.4. Preparation of PANI containing paint

The epoxy resin solution was prepared by dissolving solid epoxy having epoxy equivalent weight 450–500 in xylene. The conducting PANI pigment was completely dispersed in the resin by using attritor. The PANI pigmented epoxy resin solution was cured with polyamide having amine value 210–230 mg. The paint was prepared in such a way that it had the volume solids 65–70%. The polyaniline content in the paint was 1%.

The PANI pigmented paint was applied over sand blasted (SA 2.5) mild steel panels. The coatings were evaluated after 10 days of curing at room temperature.

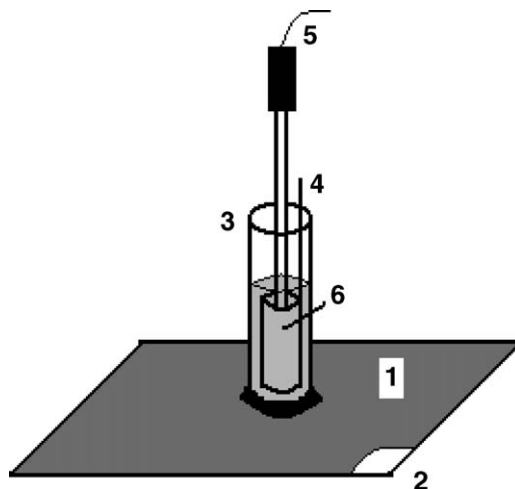


Fig. 1. Experimental cell set-up. (1): painted steel panel; (2): paint removed area for making working electrode contact; (3): glass tube; (4): platinum counter electrode; (5): SCE reference electrode; (6): test electrolyte.

### 2.5. Evaluation of coating by total immersion test

Coated panels of 10 cm × 15 cm were exposed to 3% NaCl, 0.1 N  $\text{H}_3\text{PO}_4$  and 0.1 N HCl for a period of 50 days. The performance of the coating was examined visually.

### 2.6. Evaluation of corrosion resistant property of coating by electrochemical methods

The coated mild steel panels were prepared by coating on sand blasted (SA 2.5) specimen of size 15 cm × 10 cm. The dry film thickness was  $100 \pm 5 \mu\text{m}$ . A glass tube of 1.2 cm diameter was fixed on the coated steel with m-seal adhesive. Solutions of 3% NaCl, 0.1 N  $\text{H}_3\text{PO}_4$  and 0.1 N HCl were taken in the glass tube and the platinum electrode and SCE were placed inside the tube (Fig. 1). This assembly was connected to impedance analyzer and impedance spectra were obtained for a frequency range of 100 mHz–100 KHz with an a.c. amplitude of 20 mV. The impedance values are reproducible  $\pm 2$ –3%. From the impedance plots, the coating resistance ( $R_c$ ) and the coating capacitance ( $C_c$ ) values were calculated using the equivalent circuit shown in Fig. 2. In the equivalent circuit,  $R_s$  is the solution resistance,  $R_c$  is the coating resistance and CPE is the constant phase element of the coating capacitance ( $C_c$ ).

Assumption of a simple  $R_c$ – $C_c$  is usually a poor approximation. For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used which is defined in impedance

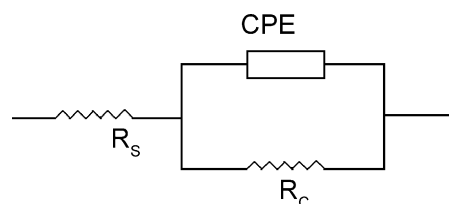


Fig. 2. Equivalent circuit for painted steel panel.

representation as:

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

Where  $Y_0$  is the CPE constant,  $\omega$  is the angular frequency (in  $\text{rad s}^{-1}$ ),  $j^2 = -1$  is the imaginary number and  $n$  is the CPE exponent. Depending on  $n$ , CPE can represent resistance ( $Z(\text{CPE}) = R$ ,  $n = 0$ ), capacitance ( $Z(\text{CPE}) = C$ ,  $n = 1$ ), inductance ( $Z(\text{CPE}) = L$ ,  $n = -1$ ) or Warburg impedance for ( $n = 0.5$ ) [22]. The following equation is used to convert  $Y_0$  into  $C_{dl}$  is [23],

$$C_c = Y_0 (\omega_m'')^{n-1}$$

where  $C_c$  is the coating capacitance and  $\omega_m''$  is the angular frequency at which  $Z''$  is maximum. The experiments were carried out for a period of 50 days.

### 3. Results and discussion

#### 3.1. Characterization of polyaniline–phosphate pigment

The synthesized pigment has been characterized by spectroscopic techniques. The FT-IR spectrum of the synthesized phosphate doped polyaniline is shown in Fig. 3. The presence of two bands in the vicinity of  $1500$  and  $1600\text{ cm}^{-1}$  are assigned to the non symmetric  $C_6$  ring stretching modes. The higher frequency vibration at  $1600\text{ cm}^{-1}$  is for the quinoid rings, while the lower frequency mode at  $1500\text{ cm}^{-1}$  depicts the presence of benzenoid ring units. The peak around  $1000\text{ cm}^{-1}$  has been assigned to  $\text{H}_2\text{PO}_4^-$  peaks [24]. Further it has been reported that the dopant anions present on PANI/ $\text{H}_3\text{PO}_4$  are dihydrogen phosphate anions,  $\text{H}_2\text{PO}_4^-$  [25,26]. Further more, the peaks at  $1250\text{ cm}^{-1}$  and at  $800\text{ cm}^{-1}$  are assigned to vibrations associated with the C–N stretching vibration of aromatic amine and out-of-plane deformation of C–H of 1,4 disubstituted rings. The aromatic C–H bending in the plane ( $1167\text{ cm}^{-1}$ ) and out of plane ( $831\text{ cm}^{-1}$ ) for a 1, 4 disubstituted aromatic ring [27,28] indicates a linear structure. The UV–vis spectra of the phosphate doped polyaniline (Fig. 4) showed peaks at  $330\text{ nm}$  for the  $\pi-\pi^*$  benzenoid transition and  $630\text{ nm}$  for benzenoid to quinoid exci-

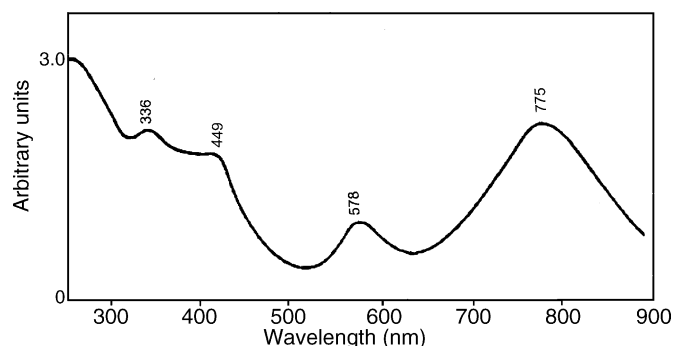


Fig. 4. UV–vis spectra of PANI–phosphate pigment.

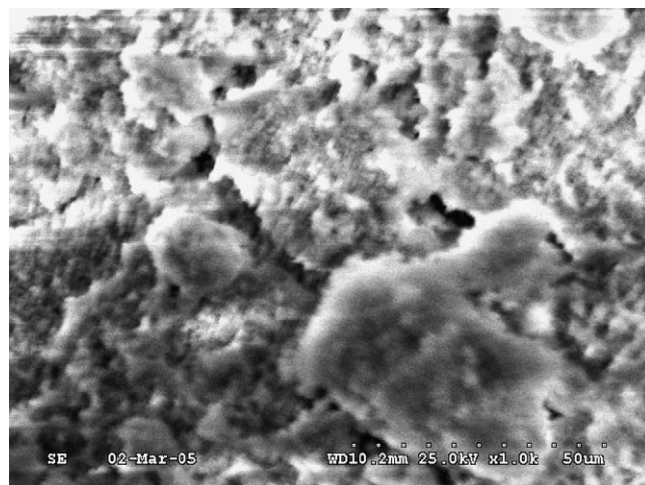


Fig. 5. Scanning electron micrograph of PANI–phosphate pigment.

tonic transition in agreement with literature [29,30]. From the IR and UV spectra it can be concluded that the synthesized polymer pigment is polyaniline in the oxidized form.

The morphology of the phosphate doped polyaniline is shown in Fig. 5. It is found that PANI–phosphate showed globular structures with small globules and pores.

The X-ray diffraction patterns of the phosphate doped polyaniline is shown in Fig. 6. The intense peak at a  $2\theta$  value of

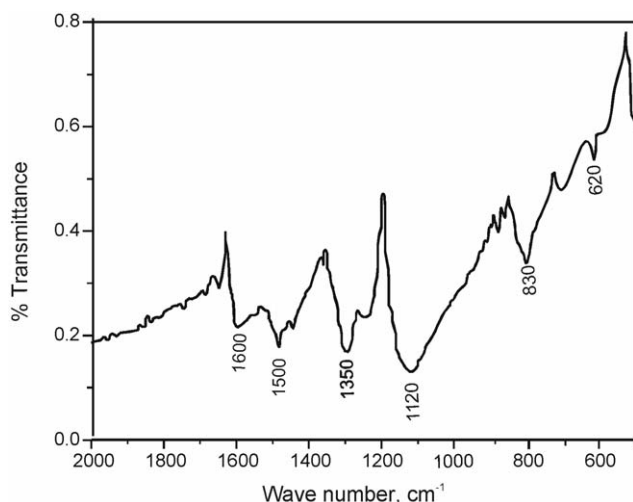


Fig. 3. FT-IR spectra of PANI–phosphate pigment.

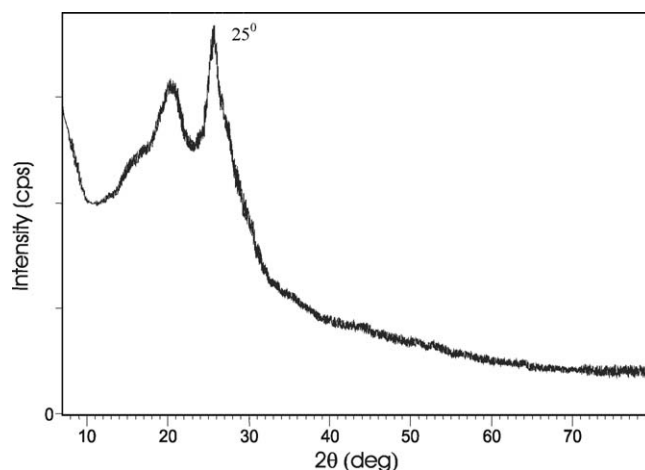


Fig. 6. X-ray diffraction pattern of PANI–phosphate pigment.

25<sup>0</sup> has a similar profile as reported in the literature for polyaniline [31–33]. The conductivity of the palletised PANI–phosphate pigment was  $2.17 \text{ S cm}^{-1}$ . This conductivity value shows that the synthesized polymer pigment is of conductive in nature.

### 3.2. Evaluation of corrosion resistant property of the coating containing phosphate doped polyaniline

#### 3.2.1. Total immersion studies

The coated panels were immersed in 3% NaCl, 0.1 N HCl and 0.1 N H<sub>3</sub>PO<sub>4</sub> solutions for a period of 50 days. On examining the panels after 50 days of immersion, it has been found that there are no rust spots and also the paint films are intact. Besides there were no spreading of corrosion along the scribed area.

#### 3.2.2. Open circuit potential measurements

The open circuit potential values of the bare steel in 3% NaCl, 0.1 N H<sub>3</sub>PO<sub>4</sub> and 0.1 N HCl are  $-0.574$ ,  $-0.551$  and  $-0.549 \text{ mV}$  versus SCE, respectively. The variation of OCP of coated steel with period of immersion in 3% NaCl, 0.1 N H<sub>3</sub>PO<sub>4</sub> and 0.1 N HCl is shown in Fig. 7. The OCP values of coated steel in 3% NaCl and in 0.1 N H<sub>3</sub>PO<sub>4</sub> are decreased initially and shifted to noble direction after 28 days immersion. This shows that the polyaniline in the coating is able to passivate the iron surface in 3% NaCl and in 0.1 N H<sub>3</sub>PO<sub>4</sub> media after longer exposure period. However, in 0.1 N HCl medium, the OCP values are shifted to more negative values with immersion time and passivation effect is not noticed. Many earlier studies have shown that the OCP of PANI coated steel is higher than bare metal by 100–500 mV in neutral chloride solution due to passivation of iron [5,7,34–37].

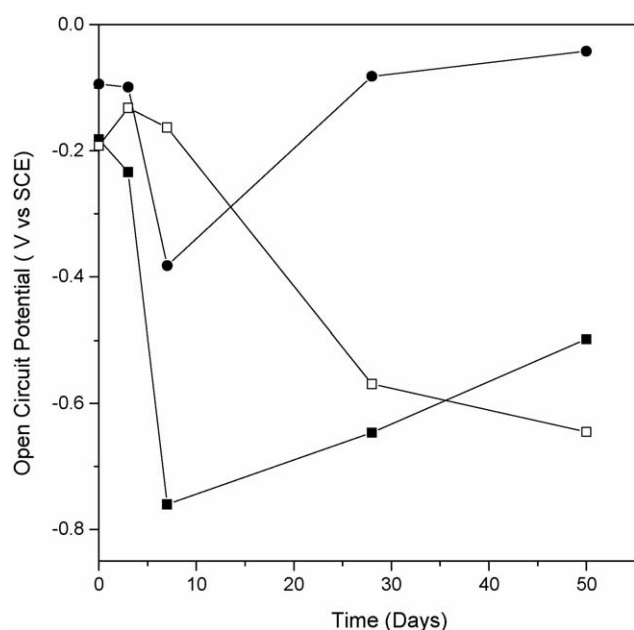


Fig. 7. Open circuit potential of PANI–phosphate pigment coated steel. (■) 3% NaCl; (●) 0.1 N H<sub>3</sub>PO<sub>4</sub>; (□) 0.1 N HCl.

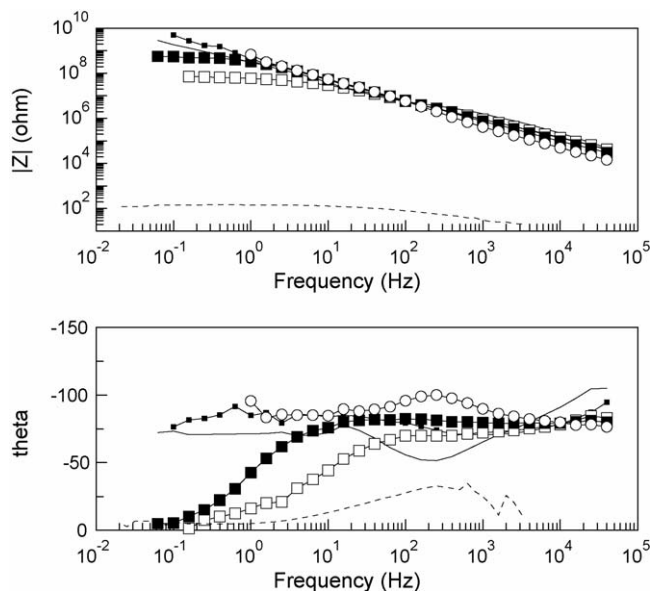


Fig. 8. Impedance plots of bare steel and PANI–phosphate coated steel in 3% NaCl. (---) bare steel; coated steel: (—) initial; (■) 3 days; (□) 7 days; (●) 28 days; (○) 50 days.

#### 3.2.3. EIS studies

The electrochemical impedance spectroscopy is used to find out the protective nature of the coating by measuring the resistance ( $R_c$ ) and capacitance ( $C_c$ ) of the coating.  $R_c$  can be attributed to the electric resistance of ionic transfer through coating pores. Normally,  $R_c$  decreases with time due to the penetration of electrolyte through the coating pres. The coating capacitance  $C_c = \epsilon \epsilon_0 A/d$ , where  $\epsilon$  denotes the relative dielectric constant of paint film,  $\epsilon_0$  is the permittivity of the vacuum ( $=8.85 \times 10^{-14} \text{ F cm}^{-1}$ ),  $A$  the active area and  $d$  the coating thickness. The effect of increase in dielectric constant with the permeation of water may increase  $C_c$  value. Hence variation in capacitance values indicate the water uptake by the film.

#### 3.2.4. Studies in 3% NaCl

The impedance studies have been made for different immersion periods and the results are shown in Fig. 8. The Bode plot shows the presence of single time constant which indicates the absence of corrosion reaction. The impedance values derived from these curves are given in Table 1. The paint film resistance is  $8.75 \times 10^{10} \Omega \text{ cm}^2$  initially. After 7 days immersion, the resistance of the film is decreased to  $7.41 \times 10^7 \Omega \text{ cm}^2$ . After 28 days immersion, the resistance value is increased to

Table 1  
Impedance parameters of PANI–phosphate pigmented coating on steel in 3% NaCl

Time days	$R_c (\Omega \text{ cm}^2)$	$Y_0 (\Omega^{-1} \text{ s}^n)$	$n$	$C_c (\text{F cm}^{-2})$
Bare steel	143.66	$1.73 \times 10^{-5}$	0.80	$5.39 \times 10^{-6}$
Initial	$8.75 \times 10^{10}$	$3.05 \times 10^{-11}$	0.80	$2.78 \times 10^{-11}$
3	$2.88 \times 10^8$	$5.51 \times 10^{-11}$	0.80	$5.50 \times 10^{-11}$
7	$7.41 \times 10^7$	$4.43 \times 10^{-10}$	0.80	$2.29 \times 10^{-11}$
28	$5.59 \times 10^8$	$3.23 \times 10^{-10}$	0.80	$2.29 \times 10^{-10}$
50	$9.39 \times 10^9$	$6.69 \times 10^{-10}$	0.80	$3.39 \times 10^{-10}$



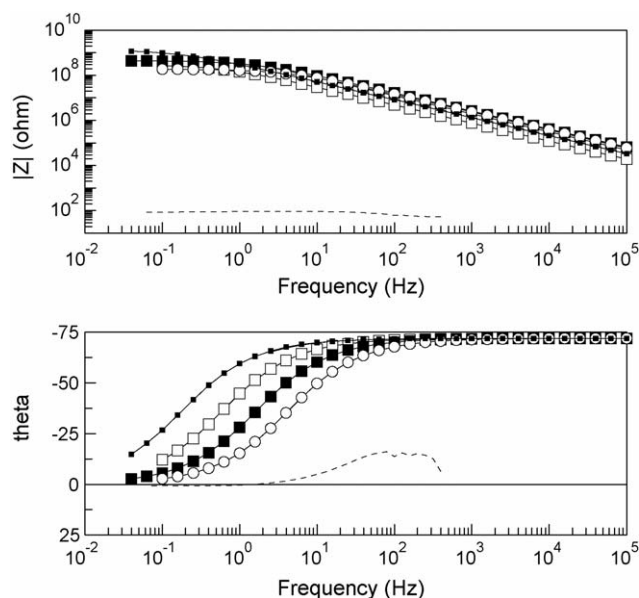


Fig. 9. Impedance plots of bare steel and PANI-phosphate coated steel in 0.1 N  $\text{H}_3\text{PO}_4$ . (---) bare steel; coated steel: (—) initial; (■) 3 days; (□) 7 days (■) 28 days; (○) 50 days.

$5.59 \times 10^8 \Omega \text{ cm}^2$  and reached  $9.39 \times 10^8 \Omega \text{ cm}^2$  at 50 days. The increased resistance value after an initial decrease may be due to the passivation effect of polyaniline, which is also evident from the shift of OCP values to noble direction after longer immersion period. Besides, the capacitance values of the film remained at  $0.3\text{--}3.85 \times 10^{-10} \text{ F cm}^{-2}$  during the test period, which indicate that water uptake of the coating is not increased. Since the coating resistance is higher than  $10^7 \Omega \text{ cm}^2$  and the low capacitance values during the study period, indicate that the coating is of protective nature in 3% NaCl solution.

### 3.2.5. Studies in 0.1 N $\text{H}_3\text{PO}_4$

The impedance behaviour of PANI-phosphate containing coating of steel in 0.1 N  $\text{H}_3\text{PO}_4$  is shown in Fig. 9 and the impedance values obtained from the figure are given in Table 2. Initially the resistance of the coating is  $1.89 \times 10^9 \Omega \text{ cm}^2$ . The resistance value is decreased to  $2.985 \times 10^8 \Omega \text{ cm}^2$  after 7 days immersion. Afterwards, there is a gain in the resistance values after 28 days immersion and reached  $4.91 \times 10^8 \Omega \text{ cm}^2$  after 50 days of immersion. The increase in resistance value may be due to the passivation of iron surface by polyaniline pigment. The passive film formation after longer exposure period is sup-

Table 2  
Impedance parameters of PANI-phosphate pigmented coating steel in 0.1 N  $\text{H}_3\text{PO}_4$

Time days	$R_c (\Omega \text{ cm}^2)$	$Y_0 (\Omega^{-1} \text{ s}^n)$	$n$	$C_c (\text{F cm}^{-2})$
Bare steel	42.15	$7.04 \times 10^{-5}$	0.95	$7.39 \times 10^{-5}$
Initial	$1.89 \times 10^9$	$4.90 \times 10^{-10}$	0.80	$4.90 \times 10^{-10}$
3	$1.33 \times 10^9$	$6.92 \times 10^{-10}$	0.80	$6.76 \times 10^{-10}$
7	$2.99 \times 10^8$	$1.19 \times 10^{-9}$	0.79	$9.82 \times 10^{-10}$
28	$4.51 \times 10^8$	$3.46 \times 10^{-10}$	0.80	$2.40 \times 10^{-10}$
50	$1.91 \times 10^8$	$3.84 \times 10^{-10}$	0.80	$2.28 \times 10^{-10}$

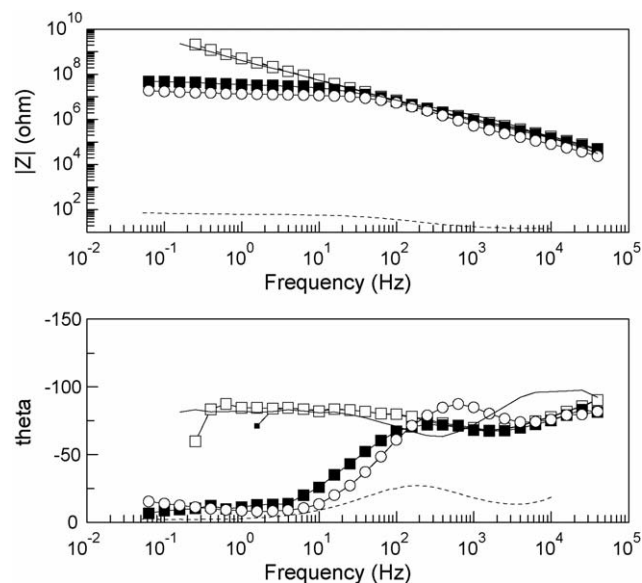


Fig. 10. Impedance plots of bare steel and PANI-phosphate coated steel in 0.1 N HCl. (---) bare steel; coated steel: (—) initial; (■) 3 days; (□) 7 days (■) 28 days; (○) 50 days.

ported by the shift of OCP values in noble direction as shown in Fig. 6. The capacitance values of the paint film are remained constant which are in the range  $2.28\text{--}9.82 \times 10^{-10} \text{ F cm}^{-2}$ . The low capacitance values of the coating indicate negligible water uptake by the coating and the corrosion protective nature of the coating in 0.1 N  $\text{H}_3\text{PO}_4$ .

### 3.2.6. Studies in 0.1 N HCl

Fig. 10 shows the impedance behaviour of steel coated with polyaniline containing paint in 0.1 N HCl. The impedance values are given in Table 3. The impedance curves show one time constant which indicate the absence of corrosion reaction. Initially, the resistance of the coating is  $1.31 \times 10^9 \Omega \text{ cm}^2$ . On subsequent exposure, the resistance of the paint film is decreased gradually and reached to  $1.30 \times 10^7 \Omega \text{ cm}^2$  after 50 days immersion. The capacitance values are remained at very low values of the order of  $10^{-10} \text{ F cm}^{-2}$  due to low permeation of water through the coating. The corrosion protective ability of the coating is found to be good in this media also due to the high coating resistance and low capacitance values even after 50 days exposure.

Coatings with high resistance values ( $>10^7 \Omega \text{ cm}^2$ ) and low capacitance values ( $<10^{-9} \text{ F cm}^{-2}$ ) have been found to offer corrosion protection of steel [38]. Earlier studies [39–42] have shown that the corrosion protection ability of the coating on steel

Table 3  
Impedance parameters of PANI-phosphate pigmented coating steel in 0.1 N HCl

Time days	$R_c (\Omega \text{ cm}^2)$	$Y_0 (\Omega^{-1} \text{ s}^n)$	$n$	$C_c (\text{F cm}^{-2})$
Bare steel	54.46	$4.22 \times 10^{-5}$	0.68	$31.9 \times 10^{-5}$
Initial	$1.31 \times 10^9$	$7.34 \times 10^{-11}$	0.80	$6.35 \times 10^{-11}$
3	$1.27 \times 10^9$	$7.93 \times 10^{-11}$	0.80	$5.01 \times 10^{-11}$
7	$8.31 \times 10^9$	$3.00 \times 10^{-11}$	0.80	$2.28 \times 10^{-11}$
28	$3.23 \times 10^7$	$2.66 \times 10^{-10}$	0.80	$1.03 \times 10^{-10}$
50	$1.30 \times 10^7$	$2.52 \times 10^{-10}$	0.80	$0.82 \times 10^{-10}$

is found to be high if the impedance of the coating is greater than  $10^7 \Omega \text{ cm}^2$ .

This study has shown that the coating containing 1% polyaniline is able to offer protection in saline and acid media. Wang et al. [43] have shown from their studies that epoxy coating containing 1% polyaniline is able to protect steel in 3.5% NaCl and 0.1 N HCl solution effectively.

### 3.3. Protection mechanism of polyaniline containing coating

Wessling [18] has stated that polyaniline behaves like a noble metal since its redox potential is close to silver. Hence it ennobles the surface of metals and forms a thin but dense passive oxide layer on the surface. The formation of  $\text{Fe}_2\text{O}_3$  film on iron surface by polyaniline has been found by XPS studies. Talo et al. [5] observed a light grey oxide layer on mild steel after coating with PANI – epoxy blend and immersion in salt water or HCl. The oxide was found to be iron oxide by XPS. Schauer et al. [44] used reflectance IR spectroscopy and found that the oxide layer was stable  $\gamma$   $\text{Fe}_2\text{O}_3$  and  $\alpha$   $\text{Fe}_2\text{O}_3$  when iron was coated with PANI containing polymer binder. The formation of passive iron oxide on iron by PANI containing coating has been found out by Lu et al. [2], Epstein et al. [45] and Fahlman et al. [46].

The mechanism of protection of steel by PANI is schematically shown in Fig. 11. Due to conducting nature of the coating, the oxygen reduction reaction takes place on the polyaniline coating while the oxidation of iron to passive oxides takes place on the exposed iron surface at pin hole areas and under the film in neutral media. However in acid media, the protection of pin holes takes place by the cathodic reaction  $\text{PANI (ES)} \leftrightarrow \text{PANI (LS)}$  where PANI (ES) is polyaniline emeraldine salt and PANI (LS) is polyaniline leuco salt. Similar type of mechanism of pro-

tection has been postulated by Wessling [18] and Kinlen et al. [9,12].

## 4. Conclusions

Phosphate doped polyaniline has been prepared by chemical oxidative method using ammonium persulphate as oxidant. FT-IR study has shown that phosphate dopant is present as  $\text{H}_2\text{PO}_4^-$  ion in polyaniline. Conductivity measurements indicated that the polymer has got good conductivity. The epoxy coating with the phosphate doped polyaniline is able to offer protection in saline and acid media. The coating on steel has been found to be more protective in 3% NaCl and 0.1 N  $\text{H}_3\text{PO}_4$  than in 0.1 N HCl.

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## References

- [1] P.J. Kinler, D.C. Silverman, C.R. Jeffreys, *Synth. Met.* 85 (1997) 1327.
- [2] W.K. Lu, R.L. Elsenbaumer, B. Wessling, *Synth. Met.* 71 (1995) 2163.
- [3] B. Wessling, J. Posdorfer, *Electrochim. Acta* 44 (1999) 2139.
- [4] D.E. Tallmen, Y. Pae, G.P. Bierwagen, *Corrosion* 55 (1999) 779.
- [5] A. Talo, P. Passiniemi, O. Forsen, S. Ylasaari, *Synth. Met.* 85 (1997) 1333.
- [6] S.P. Sitarum, J.O. Stoffer, T.J. O'Keefe, *J. Coat. Technol.* 69 (1997) 65.
- [7] J.R. Santos Jr., L.H.C. Mattoso, A.J. Mothed, *Electrochim. Acta* 43 (1998) 309.
- [8] W.S. Araujo, I.C.P. Margarit, M. Ferreira, O.R. Mattos, P. Lima Neto, *Electrochim. Acta* 46 (2001) 1307.
- [9] P.J. Kinlen, V. Menon, Y. Ding, *J. Electrochem. Soc.* 146 (1999) 3690.
- [10] A.B. Samui, A.S. Patenkar, J. Rengarajan, P.C. Deb, *Prog. Org. Coatings* 47 (2003) 1.
- [11] S. Sathiyarayanan, S. Muthukrishnan, G. Venkatachari, D.C. Trivedi, *Prog. Org. Coat.* 53 (2005) 297.
- [12] P.J. Kinlen, J. Ding, D.C. Silverman, *Corrosion* 58 (2002) 490.
- [13] A.B. Samui, S.M. Phadnis, *Prog. Org. Coat.* 54 (2005) 263.
- [14] S. Sathiyarayanan, S. Muthukrishnan, G. Venkatachari, *Prog. Org. Coat.* 54 (2006) 5.
- [15] S. de Souza, J.E.P. da Silva, S.I.C. de Torresi, M.L.A. Temperini, P.M. Torresi, *Electrochem. Solid State Lett.* 4 (2001) B27.
- [16] A.J. Dominis, G.M. Spinks, G.G. Wallade, *Prog. Org. Coat.* 48 (2003) 43.
- [17] F.C. Jain, J.J. Rosala, K.S. Kalonia, V.S. Agarcale, *Corrosion* 42 (1986) 700.
- [18] B. Wessling, *Synth. Met.* 85 (1997) 1313.
- [19] B. Wessling, *Adv. Mater.* 6 (1994) 226.
- [20] D.A. Wroblewski, B.C. Benicewit, K.G. Thompson, C.I. Bryan, *Polym. Chem.* 35 (1994) 265.
- [21] S.R. Moraes, D.H. Vilca, A.J. Motheo, *Eur. Polym. J.* 40 (2004) 2055.
- [22] F. Mansfeld, *Corrosion* 37 (1981) 301.
- [23] C.H. Hsu, F. Mansfeld, *Corrosion* 57 (2001) 747.
- [24] H.T. Pu, L. Qiao, Q.Z. Liu, Z.L. Yang, *Eur. Polym. J.* 41 (2005) 2505.
- [25] J. Stejskal, D. Heavata, D. Hollar, P. Trchora, M. Prokes, J. Sapurina, *Polym. Int.* 53 (2004) 294.
- [26] A.H. Gemeay, I.A. Mansour, R.G. El. Sharkar, A.B. Zaki, *Eur. Polym. J.* 41 (2005) 2575.
- [27] Z. Ping, G.E. Nauer, H. Neugebauer, J. Theiner, A. Neckel, *J. Chem. Soc. Faraday Trans.* 93 (1997) 121.
- [28] Y.M. Lee, J.H. Kim, J.S. Kang, S. Ha, *Macromolecules* 33 (2000) 7431.
- [29] Y. Wei, F.K. Hsueh, G.W. Tang, *Macromolecules* 27 (1994) 518.
- [30] P. Prori, P. Rannoa, *Prog. Polym. Sci.* 27 (2002) 135.

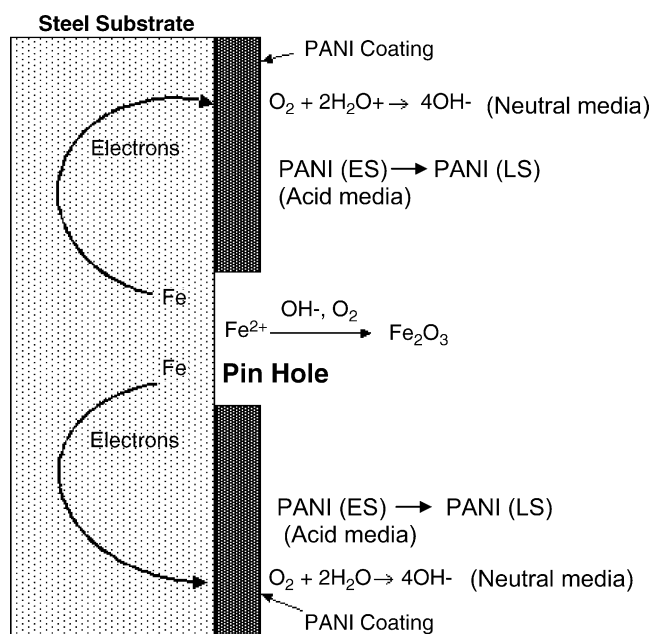


Fig. 11. Schematic diagram of mechanism of iron passivation by PANI-phosphate coated steel.

- [31] T. Abdiryim, Z.X. Gang, R. Jamal, *Mater. Chem. Phys.* 90 (2005) 367.
- [32] M. Wan, J. Li, *J. Polym. Sci. A36* (1998) 2799.
- [33] M. Wan, M. Li, Z. Liu, *J. Appl. Polym. Sci.* 53 (1994) 131.
- [34] A.A. Pud, G.S. Shapoval, P. Kamarchik, N.A. Ogurtsov, V.F. Gromoraya, I.E. Myronyuk, Y.V. Konstur, *Synth. Met.* 107 (1999) 111.
- [35] M. Fahlman, H. Guan, J.A.O. Smallfield, A.T. Epstein, *Chem. Abs.* 130 (1998) 44596.
- [36] M.M. Attar, J.D. Scantelbury, J. Marsh, *Proc. Electrochem. Soc.*, 97–41: 1.
- [37] T.P. Mc Andrew, S.A. Miller, A.G. Gilicinski, L.M. Robeson, *Polym. Mater. Sci. Eng.* 721 (1996) 204.
- [38] J.R. Scully, S.T. Hensley, *Corrosion* 50 (1994) 702.
- [39] J.R. Scully, *J. Electrochem. Soc.* 136 (1989) 979.
- [40] W.S. Tait, K.A. Handrich, S.W. Tait, J.W. Martin, in: J.R. Scully, D.C. Silaman, M.W. Kending (Eds.), *ASTM STP 1188*, ASTM, Philadelphia, PA, 1993, 428.
- [41] H. Leidheiser Jr., *J. Coat. Technol.* 63 (1991) 21.
- [42] C.C. Lee, F. Mansfeld, *Corros. Sci.* 41 (1999) 439.
- [43] X.H. Wang, J. Li, J.Y. Zhang, L. Yu, X.B. Jing, F.S. Wang, Z.-X. Sun, Z.-J. Ye, *Synth. Met.* 102 (1999) 1377.
- [44] T. Schauer, A. Joos, L. Dulog, C.D. Einsenbach, *Prog. Org. Coat.* 33 (1998) 20.
- [45] A.J. Epstein, J.A.O. Smallfield, H. Guan, M. Fahlman, *Synth. Met.* 102 (1999) 1374.
- [46] M. Fahlman, S. Jasty, A.J. Epstein, *Synth. Met.* 85 (1997) 1326.