Synthesis of tungstate doped polyaniline and its usefulness in corrosion protective coatings

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ABSTRACT

A study has been made on the corrosion protection performance of tungstate doped polyaniline containing vinyl coating on steel. The tungstate doped polyaniline was chemically synthesized and characterized by FTIR, XRD, UV-VIS and TGA studies. The corrosion protection performance of vinyl coating containing tungstate doped polyaniline on steel was assessed in 3% NaCl by electrochemical impedance studies (EIS). The coating has been found to offer protection more than 60 days in salt spray and immersion in 3% NaCl. FTIR studies have shown that the formation of iron–tungstate complex along with the passive film on steel.

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1. Introduction

Intrinsic conducting polymers were identified as promising candidate materials for chromate free corrosion protection [1–5]. Coatings based on polyaniline have been found to offer superior corrosion protection in comparison to the coatings of conventional inhibitive primers like zinc phosphate primer [6]. Kinlen et al. [7,8] have shown that PANI emeraldine salt dispersed in polymeric matrix is able to protect pinholes due to its redox activity. Further they have shown the importance of dopants such as phosphonate and sulfonate on corrosion protection of iron. Dominis et al. [9] have compared the corrosion protection performance of primer coatings containing polyaniline with different dopants using Raman spectroscopy. Silva et al. [10,11] have established the formation of secondary iron–dopant complex protects iron along with the primary passive film formed by the redox processes of PANI. PANI acts as an anion reservoir which releases dopant anions when it undergoes redox transition. Thus, when corrosion manifests at pin holes or at coating damaged areas, PANI undergoes reduction and oxidizes the metal. During this action, PANI releases the dopant anions (corrosion inhibitors) in a smarter way. This facilitates the formation of secondary physical barrier by forming iron-dopent complex which can avoid further penetration of aggressive ions [12]. This warrants the need of a systematic research study on the corrosion protection performance of inhibitive ions doped polyaniline. It has been found that benzoate, sulfonate and oxalate doped polyaniline containing coatings have been found to offer corrosion protection for steel in neutral media [13–15]. Tungstate ions have been reported as good corrosion inhibitor at low concentrations for iron and steel neutral media [17–21]. Sabouri et al. [16] have studied the influence of tungstate dopants in corrosion protection behavior of electropolymerised polyaniline coating on mild steel. They have reported that tungstate ions improved the undercoat passive layer by primary passivation process before polymerization of aniline monomer. It could be a better choice to have tungstate doped polyaniline dispersed in an organic coating instead of electropolymerised coating so that the primary barrier protection of the coating will be achieved. Besides, polyaniline blended organic coating can be used for protection of large industrial structures. In addition, PANI will bring self healing of pinholes by its redox activity and the released tungstate dopant ion is expected to strengthen the passivity. Hence a study has been conducted on the chemical oxidative synthesis of tungstate doped PANI and evaluating its corrosion protection ability for iron in neutral medium.

2. Experimental

2.1. Synthesis of tungstate doped PANI

One molar distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid or 1 M solution of hydrochloric acid. Pre-cooled 1 M solution of ammonium persulphate was added drop

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wise to the precooled aniline-acid mixture for about 90 min. The reaction was conducted at $5 \pm 1\,°C$. After the addition, the stirring was continued for 2 h. A dark green coloured conducting polyaniline thus formed was filtered and washed repeatedly with distilled water to remove residual acid. The synthesized polyaniline was dedoped by dispersing it and stirring in 1 M NH_4OH for 5 h. The dedoped polyaniline was filtered and dried at 60 °C. Tungstate doping of polyaniline was made by dispersing the polyaniline in 0.001 M tungstic acid and stirring for 4 h. The tungstate doped polyaniline was filtered, washed with distilled water and acetone and dried in oven at 60 °C for 2 h.

2.2. Characterization of tungstate doped polyaniline pigment

2.2.1. FTIR analysis

The FTIR spectra of doped polyaniline and coated panels before exposure to corrosive media were recorded on a NICOLET 380 FTIR spectrometer using ATR at room temperature. In the case of coated panels exposed to the corrosive media, localized FTIR measurements have been carried out using NICOLET CENTRAUµS microscope attached with the FTIR instrument.

2.2.2. TGA analysis

The TGA analysis of tungstate doped PANI has been found out using thermal analyzer (STA, 1500), Polymer laboratory, Thermon Science Ltd.

2.2.3. Morphology studies

A scanning electron microscope (SEM) (Hitachi, model: S3000H, Canada) was used to characterize the surface morphology of tungstate doped PANI.

2.2.4. XPS analysis

X-ray Photoelectron Spectra (XPS) of the samples were recorded on MultiLab 2000 (Thermofisher Scientific, UK) fitted with a twin anode X-ray source using MgKα radiation (1253.6 eV). The sample pellets were mounted on the SS sample holder (stub) using conducting silver paint (Agar Scientific Ltd, UK). The stub was initially kept in the preparatory chamber overnight for desorbing any volatile species at 10^{-9} mbar and was then introduced into the analysis chamber having a base pressure of 9.8×10^{-10} mbar for recording the spectra. High-Resolution spectra averaged over 5 scans with a dwell time of 100 ms in steps of 0.05 eV were obtained at pass energy of 20 eV in Constant Analyzer Energy Mode. The binding energy was referenced with C (1s) at 284.98 eV within accuracy of ±0.05 eV.

2.3. Preparation of paint with tungstate doped PANI

The primer is formulated using commercial vinyl resin (VMCH, Vimal Agencies, India) which is a high molecular weight co-polymer of vinyl chloride (VC), vinyl acetate (VAc) and a dicarboxylic acid (Maleic acid) with a number average molecular weight 27,000. The volume solids of the formulation were kept at 30% with 35% pigment volume concentration (P.V.C.). The main pigments used in this formulation were tungstate doped polyaniline/zinc phosphate, titanium dioxide along with mica and silica as extender pigments. This primer coat was top coated with vinyl paint using the same vinyl resin having 30% volume solids and 18% P.V.C. Rutile titanium dioxide was used as main pigment along with mica and silica as extender pigments.

The pigments were pre-mixed and the paint was formulated in a 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 7–8 µm. The paint was stored in an air tight container. The topcoat was applied over the primer applied panels
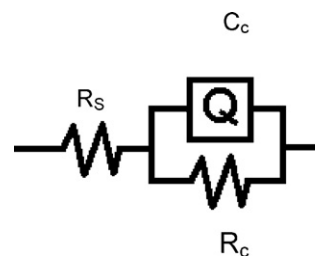

Fig. 1. Equivalent circuit for coated mild steel panel.

after 24 h of curing at ambient conditions. The specific gravity of the primer paint was 1.01 and the dry film thickness (DFT) was 30–35 µm. The specific gravity of the top coat paint was 0.98 and the dry film thickness (DFT) was 30–35 µm.

2.4. Evaluation of corrosion resistant properties of the coating

2.4.1. Open circuit potential measurements

A glass tube of 1.2 cm diameter was fixed on the coated steel panels with epoxy adhesive (m-seal). 3% NaCl solution was poured into the glass tube and the saturated calomel reference electrode was immersed in the solution inside the glass tube. Coating was removed at one of the edges for making electrical contact. The open circuit potential (OCP) of the coated steel was measured with respect to saturated calomel electrode (SCE) using a high input impedance voltmeter (HP 973 A).

2.4.2. EIS studies

The electrochemical cell as described in Section 2.4.1 with a platinum auxillary electrode inside the glass tube along with SCE reference electrode was used for EIS measurements. The assembly was connected to an Advanced Electrochemical System (PARSTAT 2273). Impedance measurements were carried out using Power-sine software for a frequency range of 100 kHz to 0.1 Hz with an AC signal of rms amplitude of 20 mV for different exposure time in 3% NaCl. Higher AC amplitude was used since the impedance of the coating was very high. The impedance values are reproducible up to ±2 to 3%. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using ZsimpWin 3.21 software using the equivalent circuit (Fig. 1) for impedance data with one time constant.

In Fig. 1 R_s is the solution resistance, R_c is the coating resistance and Q is the constant phase element of the coating capacitance.

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 representation as

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

where Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and n is the CPE exponent ($n > 0$, for ideal capacitance Z(CPE) = C, $n = 1$). The following equation is used to convert Y_0 into C_c [22],

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

where C_c is the coating capacitance and ω_m'' is the angular frequency corresponding to a measurement at which Z'' is maximum.

2.4.3. Salt spray test

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 for 1000 h. The samples were removed periodically
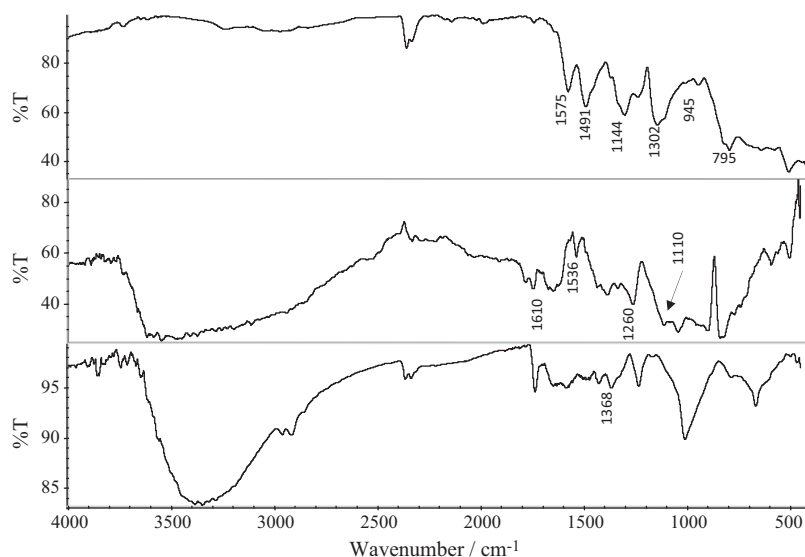
Fig. 2. FTIR spectra of (a) tungstate doped PANI pigment; (b) FTIR spectra of scribed area after salt spray test; (c) FTIR spectra taken at the paint removed area of steel surface.

from the salt spray chamber and the EIS measurements were carried out by fixing a Teflon tube of diameter 1.2 cm on the salt spray exposed sample using silicon grease. 3% NaCl solution was poured inside the teflon tube and platinum counter electrode and SCE reference electrode were inserted which constituted conventional three electrode cell for electrochemical measurements.

3. Results and discussion

3.1. Characterization of tungstate doped PANI

3.1.1. FTIR spectroscopic studies of polyaniline pigment

The characteristic FTIR spectra of tungstate doped PANI is shown in Fig. 2(a). The peaks at 1575 and 1491 cm^{-1} correspond to quinone and benzene stretching ring deformation. The band at 1302 cm^{-1} belongs to C–N stretching of a secondary amine stretched due to protonation of PANI [23]. The band at 1245 cm^{-1} is due to protonation and corresponds to C–N$^+$ stretching vibration. The band at 1144 cm^{-1} is assigned to vibration mode of the –NH$^+$= structure which is formed during protonation [24]. Besides the bands at 945.5 and 795 cm^{-1} are due to tungstate dopant [25].

3.1.2. XPS studies of polyaniline pigment

Fig. 3 shows the survey scan spectrum of the tungstate doped PANI which confirms the presence of C,N,O and W atoms. XPS core level spectra of C 1s, N 1s and W 4f of tungstate doped PANI pigment are shown in Fig. 4a–c. The C 1s core level spectra (Fig. 4a) can be deconvoluted into four peaks 284.1, 284.6, 285.2, 285.8 eV. The first two peaks at ~284.4 eV and 284.6 are attributed to the neutral C–C or C–H bonds in the backbone of the polymer. The contribution at 285.2 eV can be assigned to the carbon bonded to the neutral nitrogen atoms C–N and C=N. The fourth peak at 285.9 eV can be attributed to the carbon atoms bonded to polaronic-type and bipolaronic-type nitrogen atoms [26].

In Fig. 4b, the core level spectrum of N 1s spectrum can be deconvulated into four peaks centered around 398, 399.0, 399.7 and 400.3 eV correspond to neutral imine (–N=), amine (–NH–), and protonated amine and imine nitrogen atoms [27,28]. Fig. 4c shows the XPS W 4f core level spectra and this spectrum can be resolved into spin-orbit pairs (splitting 2.14 eV) with a 4f$^{7/2}$ binding energy (BE) of 35.35 eV [29].

3.1.3. Conductivity studies of PANI pigment

The conductivity of the tungstate doped PANI pigment is found to be 0.0139 S cm^{-1}. Conducting PANI is expected to have conductivity in the range of 4–7 S cm^{-1} [30]. The reduction in conductivity of tungstate doped PANI may be due to very low concentration of tungstic acid used during redoping process. However, it has been reported by R. Gasparac et al. [31] that the mechanism by which PANI protects the underlying metal surface from corrosion is independent of doping level.

3.1.4. TGA analysis of tungstate doped PANI pigment

The thermal stability of PANI has been found out by thermogravimetric analysis and the results are shown in Fig. 5. As reported earlier [32,33], the thermal analysis exhibits a three stage decomposition pattern. The first weight loss up to 90 °C is due to dehydration of polymer in which PANI loses its moisture content. The second weight loss observed from 92 °C to 389 °C is attributed to the loss of dopant from the polymer. The weight loss from 389 °C onwards is due to the decomposition of polymer chain.
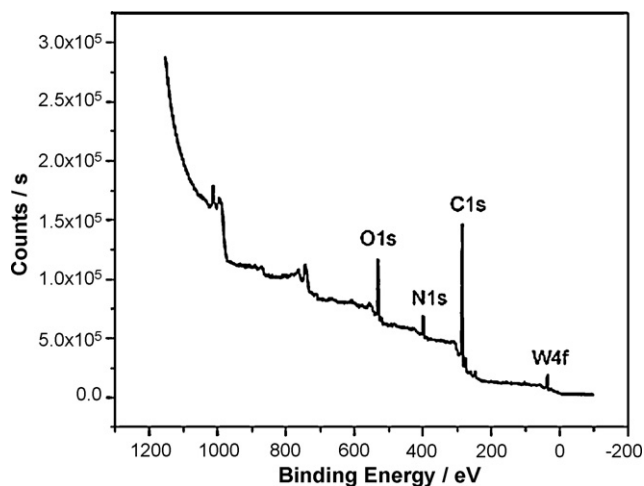

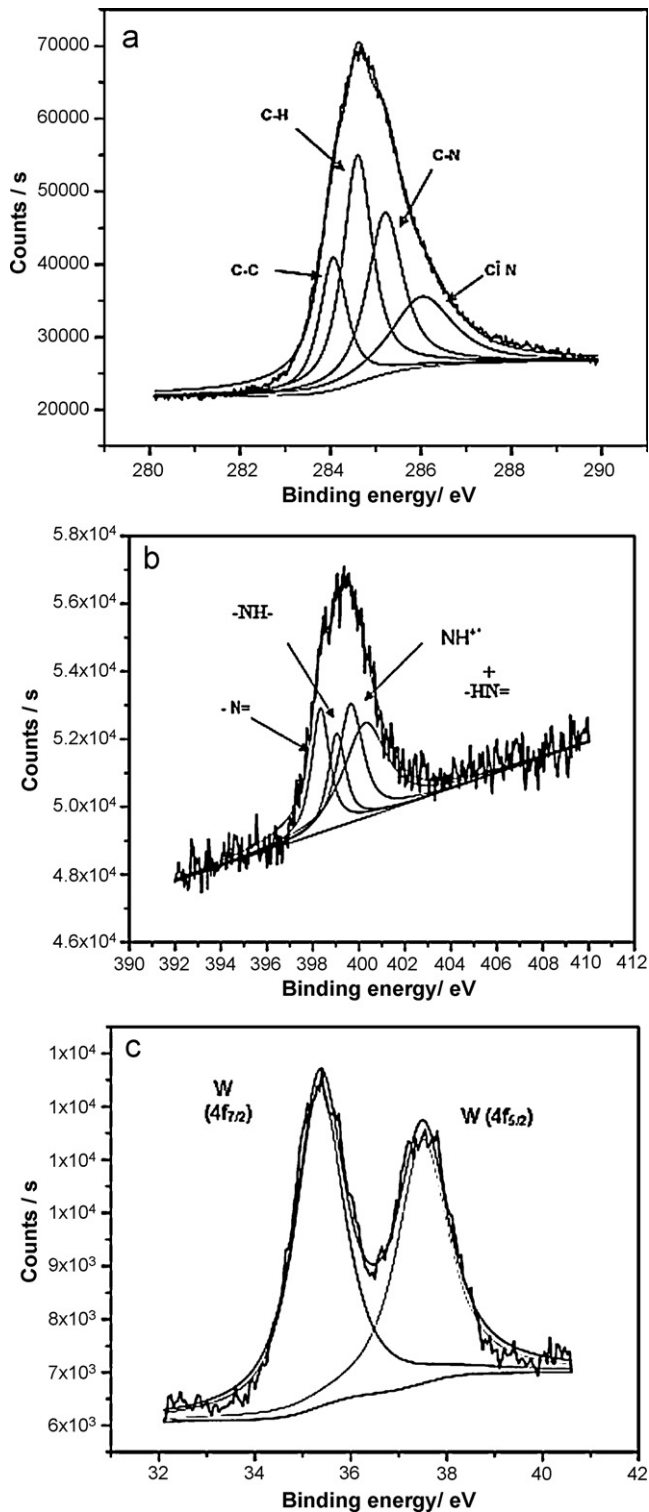**Fig. 3.** XPS survey spectra of tungstate doped PANI pigment.

Fig. 5. Themogravimetric analysis curve of tungstate doped PANI.

3.1.6. Corrosion studies of PANI pigmented coating

The corrosion behavior of tungstate doped PANI pigmented primer coating with top coating has been studied by EIS and salt spray tests.

The results of EIS studies of PANI primer with top coated steel in 3% NaCl solution for different immersion period are shown in Fig. 7. The impedance parameters derived from these figures are given in Table 1. It is found that the resistance value of the coating is found to be decreased slightly up to two days immersion in 3% NaCl solution and then the values are found to be increased. At the end of 45 days immersion, the resistance value of the coating is found to be 3.9 GΩ cm². The capacitance values of the coating are found to be low and in the range of 68 nF cm^{-2} in 3% NaCl solution. In order to compare the corrosion resistance behavior of PANI containing coating with that of conventional coating containing inhibitive zinc phosphate pigmented primer coat and top coat, EIS studies have been made with steel sample coated with zinc phosphate primer along with a top coat in 3% NaCl solution. Fig. 8 shows the impedance behavior of zinc phosphate primer along with top coating on steel in 3% NaCl solution. The variation of resistance and capacitance values of the coating is given in Table 1. It is found that the resistance values of the coating are remained above 0.8 GΩ cm² up to 45 days immersion. These studies indicate that the corrosion protection performance of PANI primer over steel is comparable

Fig. 4. (a) XPS C 1s core level spectra of tungstate doped PANI pigment. (b) XPS N 1s spectrum of tungstate doped PANI pigment. (c) XPS W 4f core level spectra of tungstate doped PANI pigment.

3.1.5. SEM studies of tungstate doped PANI pigment

The SEM micrograph of tungstate doped PANI pigment is shown in Fig. 6. It is reported that conducting polymers synthesized by chemical route may have fibrillar or globular or filmlike structure [34]. The morphology of PANI in this study is found to be globular structure of 5–10 μm in size.
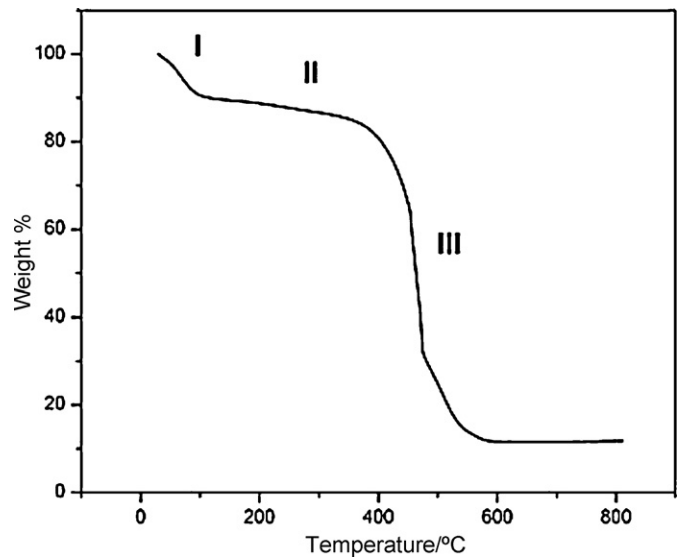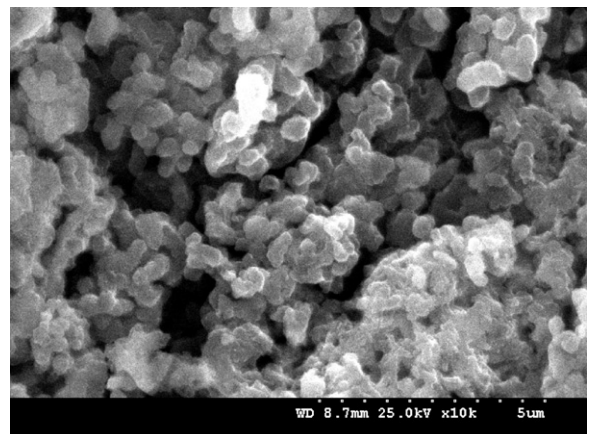

Fig. 6. Scanning electron micrograph of tungstate doped PANI pigment.

Table 1
Impedance parameters of coated steel in 3% NaCl.

Period (days)	Coating containing tungstate doped PANI		Coating containing Zinc phosphate	
	Coating resistance, R_c ($\Omega\,cm^2$)	Coating capacitance, C_c ($F\,cm^{-2}$)	Coating resistance, R_c ($\Omega\,cm^2$)	Coating capacitance, C_c ($F\,cm^{-2}$)
Initial	8.13×10^8	1.53×10^{-10}	2.52×10^9	2.03×10^{-10}
1	5.47×10^8	2.11×10^{-10}	8.70×10^8	4.84×10^{-10}
3	1.96×10^9	2.21×10^{-10}	1.86×10^9	2.72×10^{-10}
7	1.02×10^9	2.45×10^{-10}	4.07×10^8	2.91×10^{-10}
15	3.48×10^9	3.11×10^{-10}	7.94×10^8	3.60×10^{-10}
30	2.35×10^9	8.49×10^{-10}	1.03×10^8	1.71×10^{-10}
45	3.90×10^9	6.86×10^{-10}	8.95×10^8	5.34×10^{-10}

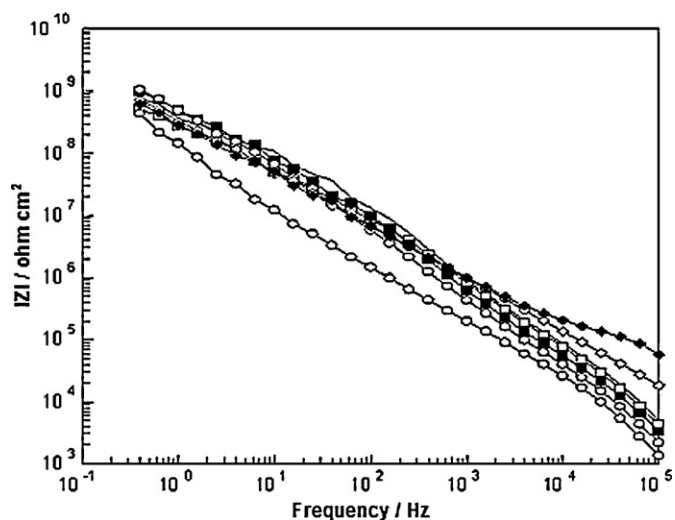**Fig. 7.** Impedance plots of tungstate doped PANI incorporated paint with top coated steel exposed to 3% NaCl. Initial; □ 1 Day; ■ 3 Days; ○ 7 Days; ● 15 Days; ◇ 30 Days; ♦ 60 Days.

Fig. 9. Photograph of tungstate doped PANI incorporated paint coated with top coated panels exposed to salt spray.

and slightly better than that of zinc phosphate primer along with top coat.

The salt spray exposure test on PANI primer with top coated steel has been conducted for a period of 45 days and periodic impedance measurements have been made. The appearance of the coated samples after salt spray exposure test is shown in Fig. 9. It can be seen from the photograph that the coating is able to withstand the salt spray exposure test and no spreading of rust is observed. In addi-

tion, no blisters were observed after the exposure to salt spray fog. The results of the impedance behavior of PANI primer with top coating on steel after salt spray exposure are shown in Fig. 10. The variation of impedance values of the coating for different exposure period is given in Table 2. It can be seen that the coating resistance values of specimen are found to be mostly above 0.1 GΩ cm² up to

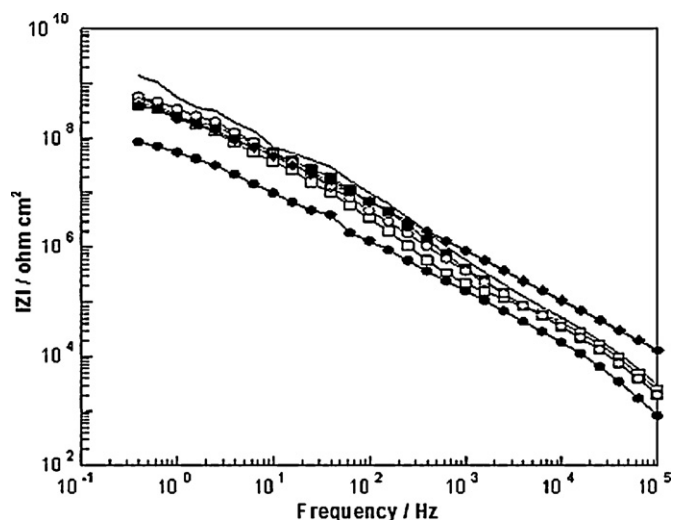**Fig. 8.** Impedance plots of conventional inhibitor (zinc phosphate) containing paint with top coated steel exposed to 3% NaCl. Initial; □ 1 Day; ■ 3 Days; ○7 Days; ● 15 Days; ◇ 30 Days; ♦ 45 Days.
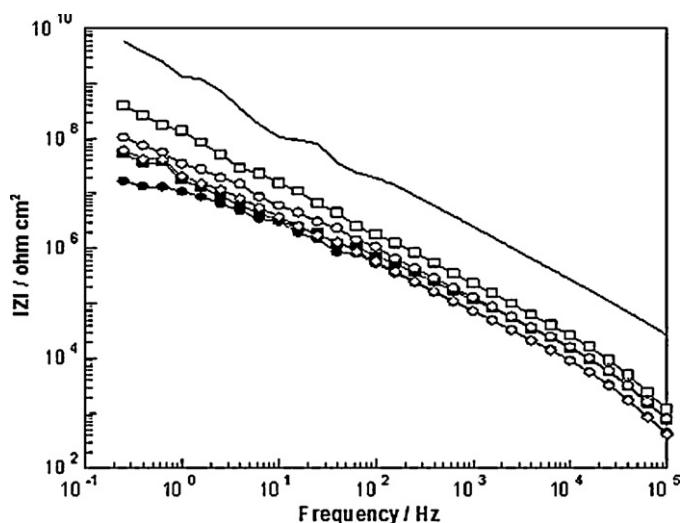

Fig. 10. Impedance plots of tungstate doped PANI incorporated paint with top coated steel exposed to salt spray. Initial; □ 1 Day; ■ 3 Days; ○ 7 Days; ● 15 Days; ◇ 30 Days; ♦ 45 Days.
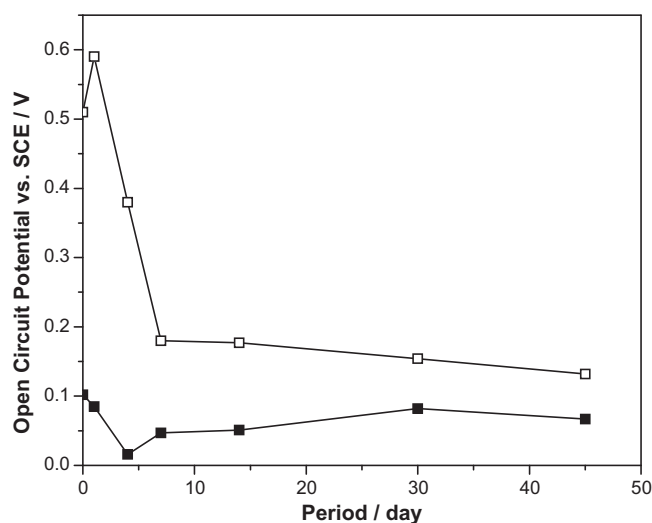
Fig. 11. The open circuit potential behavior of coated steel in 3% NaCl □ Immersion in 3% NaCl; ● Exposure to salt spray test.

45 days of salt spray exposure. Besides, the capacitance values of the coatings are found to be less than $1\,\mathrm{nF\,cm^{-2}}$. The higher coating resistance and lower capacitance values indicate the protective nature of the coating.

The nature of protection by PANI pigmented coating of iron has been examined by FTIR studies on scribed area (in Fig. 9) and by EDAX and FTIR studies of paint removed surface after salt spray exposure tests. The FTIR spectra taken on the scribed area after salt spray exposure tests are shown in Fig. 2(b). The spectra show the characteristic bands of polyaniline at 1610, 1536, 1260 and $1110\,\mathrm{cm^{-1}}$ due to emeraldine salt formation. Besides a new band at $1384\,\mathrm{cm^{-1}}$ is observed due to the presence of non-conducting PANI base [35]. The FTIR spectra (Fig. 2(c)) of paint removed area after salt spray test show the presence of new band at $1368\,\mathrm{cm^{-1}}$ which is due to non-conducting state of PANI. These spectral studies show that the PANI has changed from conducting state to non-conducting state due to its redox reaction. This redox transition facilitates the passivation of iron at exposed areas.

The open circuit potential behavior of tungstate doped PANI containing coated steel in 3% NaCl solution is shown in Fig. 11. Mostly, the potential values are found to be in noble region in both immersions in 3% NaCl and also in salt spray exposure studies. Earlier studies have also shown that the PANI containing coating is able to maintain the potential of iron in noble region due to the formation of passive film on iron [36–42].

It has been established that the mechanism of corrosion protection of iron by PANI containing coating is by formation of passive film due to redox reaction of iron and PANI. This passivation is followed by the secondary reaction between iron oxide and dopant i.e. tungstate ion resulting in the formation of dopant–iron complex [8,10,11,13,14,41]. Hence the protection of iron at pin-

Table 2
Impedance parameters of tungstate doped PANI incorporated paint coated steel exposed to salt spray.

Period (days)	Coating resistance, R_c ($\Omega\,\mathrm{cm^2}$)	Coating capacitance, C_c ($\mathrm{F\,cm^{-2}}$)
Initial	1.18×10^{10}	6.31×10^{-10}
1	1.34×10^{9}	1.18×10^{-9}
3	1.08×10^{9}	3.17×10^{-9}
7	2.11×10^{8}	4.41×10^{-9}
15	3.16×10^{8}	6.67×10^{-9}
30	2.00×10^{7}	6.28×10^{-9}
45	1.08×10^{8}	4.41×10^{-9}

holes takes place through the oxidation of iron by the reduction of PANI (emeraldine salt (PANI–ES) to PANI lecuemeraldine salt (PANI–LS)) with simultaneous release of dopant tungstate anions These released tungstate ions even in low level form iron–tungstate complex along with the passive film formed by PANI offer higher corrosion protection of iron. Unlike the improvement of primary passivation by tungstate ions as reported by Sabouri et al. [16], it has been visualized in this study that iron gets oxidized to iron oxide by the redox activity of polyaniline and the released tungstate ion assists in strengthening, completing and repairing of passive layer as reported [43].

4. Conclusions

The tungsted doped PANI was synthesized by chemical oxidative polymerization. It has been found by FTIR studies that tungstate doped PANI contains both benzenoid and quinoid moieties. TGA studies indicate that tungstate doped PANI undergoes three staged thermal decomposition. Vinyl coatings were formulated with tungstate doped polyaniline and are found to offer corrosion protection for steel in sodium chloride solutions. The open circuit potential values remain in noble region which indicates the formation of passive film by the redox activity of PANI as confirmed by the FTIR studies. Besides, the formation of iron–tungstate complex has also been found to reinforce the corrosion protection of iron.

Acknowledgements

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