Progress in Organic Coatings 65 (2009) 152–157

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Corrosion protection of galvanized iron by polyaniline containing wash primer coating

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

Central Electrochemical Research Institute, Karaikudi – 630006, India

ARTICLE INFO

Article history:
Received 19 June 2008
Received in revised form 14 August 2008
Accepted 4 November 2008

Keywords:
Galvanized iron
Corrosion protection
Wash primer
Polyaniline

ABSTRACT

Wash primer treatment of galvanized iron (GI) structure is widely used before painting in order to improve adhesion. Traditional wash primer contains zinc tetroxy chromate. Due to hazardous nature of chromate, alternate compounds for chromate replacements have been identified. In recent years polyaniline containing coating has been found to protect GI. In this study, a wash primer based on polyaniline has been formulated and its corrosion protection ability of GI has been compared with that of traditional chromate based wash primer by salt spray and EIS test. It has been found that the polyaniline based wash primer is able to protect GI and its corrosion protection performance is similar to chromate based wash primer coating.

1. Introduction

Surface pretreatment of metals is always important in obtaining satisfactory coating performance. The usual surface treatment of galvanized iron (GI) before painting is chromating and chromate based wash primer treatment [1–5]. Chromating is employed for small sized objects whereas wash primer treatment is applied to large structures. The traditional wash primer is a poly vinyl butyral resin pigmented with zinc tetroxy chromate and phosphoric acid. On treatment of GI surfaces with wash primer, a chromate coating along with the resin coating of thickness of 10–15 μm is formed. The high toxicity of chromate leads to an increasing interest in using non-toxic alternatives. In recent years, it has been shown that polypyrrole and polyaniline containing coatings on zinc are able to protect zinc very effectively [6–12]. Hence a study has been made to formulate polyaniline based wash primer and to compare its corrosion protective property of GI with that of traditional wash primer treatment.

2. Experimental

2.1. Preparation of polyaniline

1 M 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 stirring 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. Dedoping of polyaniline was carried out by mixing the polyaniline powder with 1 M ammonia and stirring for 3 h and the final product was filtered and repeatedly washed with distilled water. The polymer was dried in oven at about 80 °C for 2 h. The dried polyaniline was finely grinded using morter and then used as pigment.

2.2. Preparation of polyaniline based wash primer

The wash primer system consists of two parts. The first part contains 5–15% PANI along with TiO_2, talc and silica in poly vinyl butyral (PVB) resin. The PVC of the first part was 10. The second part contains 5% H_3PO_4 in isopropanol. The parts I and II are mixed in the ratio of 1:1 (w/w) and stirred well. The wash primer paint was applied on the $6'' \times 4''$ GI surface by brush and allowed to dry. The coating thickness was found to be 10 ± 1 μm. The adhesion as per ASTM D 4541 of the coating was found to be 3 N and the flexibility as per ASTM D522–930 was found to pass 1/16th of inch. The top coat was formulated using commercial acrylic resin (Kondicryl 166, Pidilite, India). The volume solids of the formulation was kept at 30% with 35% pigment volume concentration (PVC). The main pigments used in this formulation were titanium dioxide(Rutile),along with mica and silica as extender pigments. Di octyl phosphate (DOP) was used as a plasticizer. The pigments were premixed and the paint was formulated in a lab attritor. The attritor was run for 45–50 min.

---

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227133.
E-mail address: azimcecri@gmail.com (S. Syed Azim).

0300-9440/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2008.11.002

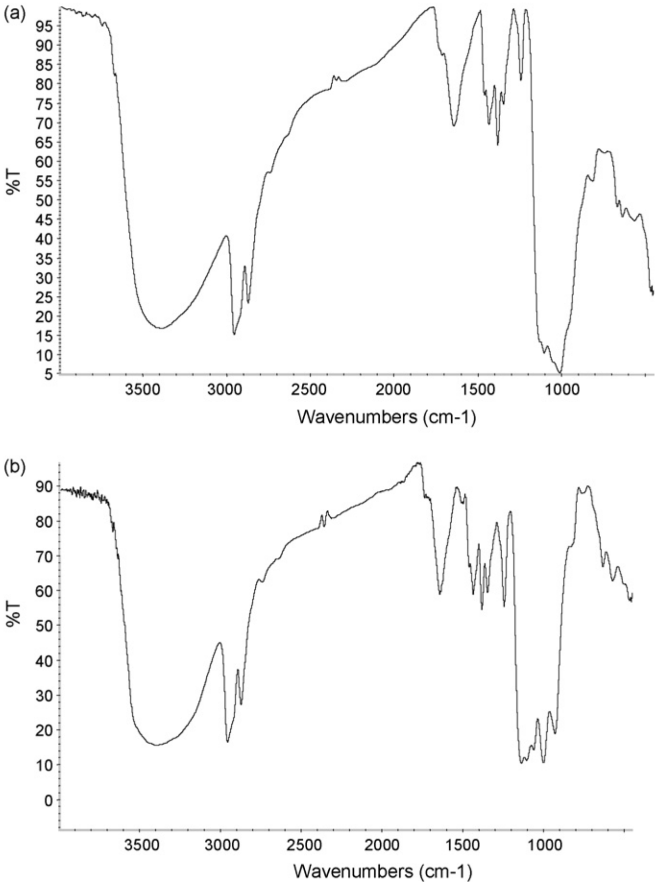


Fig. 1. (a) FTIR spectra of chromate based wash primer; (b) FTIR spectra of PANI based wash primer.

The paint was removed from the container and the fineness of dispersion was found using Hegmann gauge and it was found to be between 7 and 8. The paint was stored in air tight container. The specific gravity of the paint was 1.0 and the dry film thickness (DFT) was 40–45 μm.

2.3. Characterization of wash primer coatings

2.3.1. FTIR analysis

The FTIR spectra of chromate and PANI based wash primers were taken with Nicolet 380 FTIR Spectrometer using ATR attachment in the range 4000–450 cm^{-1}.

2.3.2. XRD analysis

The powder X-ray diffraction of the PANI pigment and wash primer coated GI surface was analyzed using PAN Analytical (Model PW3040/60) X-ray Diffractometer using CuKα radiation in the 2θ range 5–75° at the scan range of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s.

2.3.3. SEM and EDX analysis

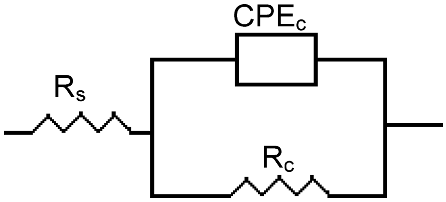
The scanning electron micrograph and EDX analysis of chromate and PANI containing wash primer was analyzed using Hitachi (Model S3000 H) instrument. The pigment was spread over a copper block over which gold was sputtered.

2.3.4. Evaluation of coatings formed on GI by wash primer

2.3.4.1. Salt spray exposure studies. The anticorrosion performance of the wash primer coated GI was found out by exposing the coated panel in a salt spray fog of 5% NaCl for 150 h as per ASTM B117.

2.3.4.2. Electrochemical impedance spectroscopic studies. The salt spray exposed panels were evaluated by EIS by fixing a Teflon tube of diameter 1.15 cm with the help of silicon glue. 3% NaCl solution was poured into the tube and platinum foil and saturated calomel electrode (SCE) were placed into it. The EIS measurements were carried out by making a contact to the base metal after scratching the coating and the platinum foil and SCE as counter and reference electrodes. For the top coated panels, a glass tube of 1.15 cm diameter was fixed with araldite and the three electrode configuration was obtained as above. The assembly was connected to an Advanced Electrochemical System (PAR 2273). Impedance measurements were carried out using Powersine software for a frequency range of 100 kHz to 0.1 Hz with an ac signal of amplitude of 20 mV for different immersion time in 3% NaCl. The impedance values are reproducible ±2–3%.

The bode representations of the impedance data were analyzed with Zsimpwin software. Single slope in the mid frequency range shows the existence of single time constant and hence the impedance data were analyzed using the equivalent circuit.



where R_s is the solution resistance, R_c is the coating resistance and CPE_c is the constant phase element corresponding to the

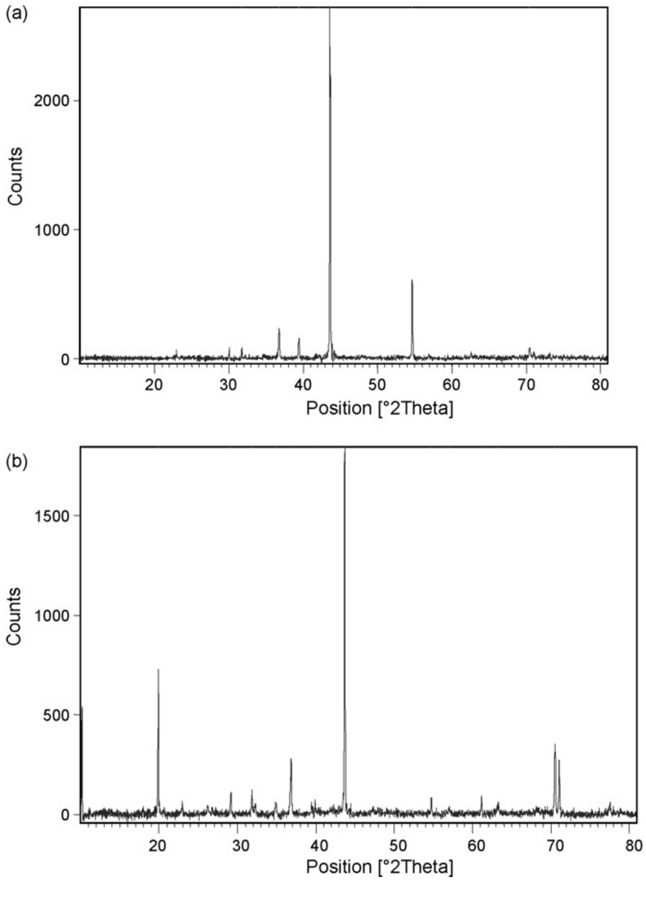


Fig. 2. (a) XRD pattern of chromate based wash primer; (b) XRD pattern of PANI based wash primer.

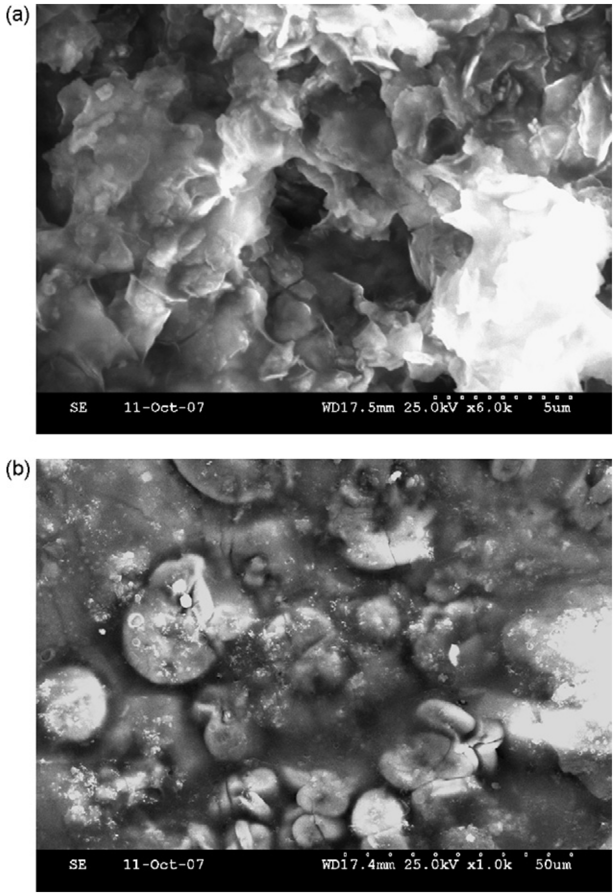


Fig. 3. (a) SEM picture of chromate based wash primer; (b) SEM picture of PANI containing wash primer.

capacitance of the coating. 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

$$Z(\mathrm{CPE}) = Y - 10(j\omega)^{-n}$$

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 $Z(\mathrm{CPE}) = C$, $n = 1$). The following equation is used to convert Y_0 into C_c [13],

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

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

3. Results and discussion

3.1. FTIR spectral characterization

The FTIR spectra of conventional wash primer coated GI and PANI containing wash primer coated GI are shown in Fig. 1a and b. The spectra are found to be similar. The peaks around 2955 cm^{-1}, 2871 cm^{-1} 2358 cm^{-1}, 2319 cm^{-1}, 1434 cm^{-1}, 1380 cm^{-1}, 1344 cm^{-1}, 1247 cm^{-1} and 1136 cm^{-1} are due to poly vinyl butryl [14]. The films in both cases are found to be hydrated by the presence of peak at 3393 cm^{-1} due to O–H absorption band. However in the case of PANI containing wash primer coating shows additional absorptive bands at 1600 and 1496 cm^{-1} due to quinoid and benzenoid of polyaniline and the band at 927.5 cm^{-1} is due to the presence of phosphate in the film [15]. Besides, both the film show the band around 453 cm^{-1} due to the presence of zinc oxide in the film [16].

3.2. XRD characterization

Fig. 2a and b show the X-ray diffraction pattern of conventional wash primer coated GI and PANI containing wash primer coated GI. The peaks at 2θ around 23 and 30 confirms the presence of zinc phosphate hydrate and zinc chromate phosphate in the case of chromate containing wash primer. However, in the case of PANI containing wash primer, peaks at 2θ around 23 and 29 confirms the presence of zinc phosphate and polyaniline is.

3.3. Morphology of the film

Fig. 3a and b show the SEM pictures of conventional chromate wash primer and PANI containing wash primer. It can be seen that the coatings formed by both wash primers are uniform without any defects. It is inferred that the presence of PANI does not interfere with the formation of primer film.

3.4. EDX studies

The EDX spectra of wash primer coating containing chromate and PANI on GI are shown in Fig. 4a and b. Here, the zinc, chromium and oxygen peaks are predominant in the case of chromate containing wash primer coating while the peaks of zinc and oxygen are predominant in the case of PANI containing wash primer coating. The formation of passive ZnO layer on zinc by polyaniline containing coating has been reported by William et al. [12].

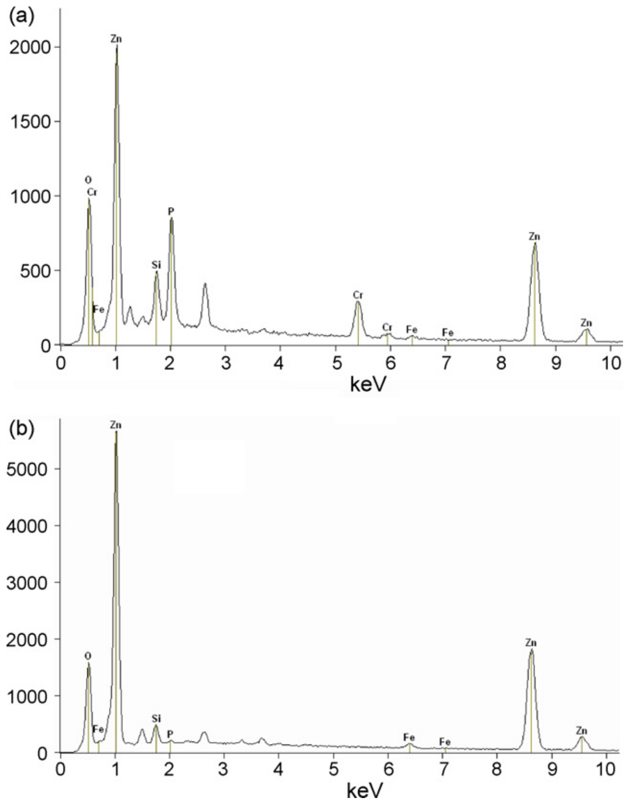


Fig. 4. EDAX spectra of wash primer coated on GI, (a) chromate based wash primer; (b) PANI based wash primer.

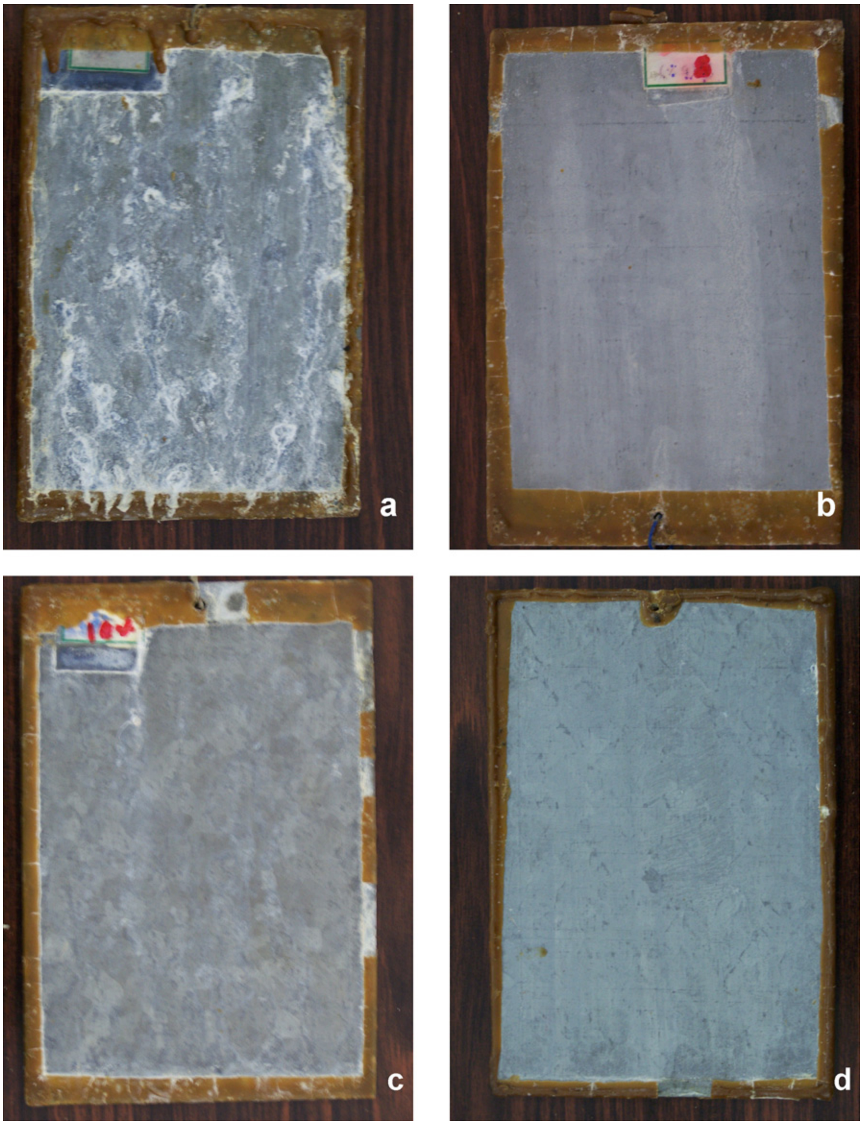


Fig. 5. Photograph of salt spray exposed samples, (a) blank; (b) 5% PANI; (c) 10% PANI; (d) 15% PANI.

3.5. *Salt spray tests*

The appearance of GI and PANI based wash primer coated GI containing 5%, 10% and 15% after salt spray test for 150 h is shown in Fig. 5a–d. It can be seen that the 5% PANI loaded wash primer is found to be free from white rust even after 150 h of exposure.

3.6. *Open circuit potential measurements*

The variation of open circuit potential for chromate and PANI containing wash primer in 3% NaCl is shown in Fig. 6. It can be inferred from the figure that the OCP of both the samples is almost same at the initial instant. The OCP of PANI containing wash primer goes up to −1.115 V in one hour and retraces back to the positive potential, even more positive than its initial value and get stabilized around −1.02 V. This is due to the passivation of GI surface caused by the redox action of PANI. In the case of chromate containing wash primer, even though the OCP goes in the positive direction for a short while, it comes back and stabilizes at the initial value. Thus the OCP measurements clearly shows that PANI containing wash primer offers very good corrosion protection similar to that of conventional chromate containing wash primer.

3.7. *EIS studies of the wash primer coated GI*

3.7.1. *Salt spray exposure*

The impedance behaviour of wash primer coated GI after 150 h of salt spray exposure is shown in Fig. 7. In the case of chromate based wash primer coating, the coating resistance value is $1 \times 10^4\ \Omega\,\text{cm}^2$ after 150 h of salt spray exposure (curve not shown) and for the coatings with 5, 10 and 15% PANI containing wash primer, the coating resistance values are found to be 8739, 5308 and $4362\ \Omega\,\text{cm}^2$ respectively. Because of the high coating resistance value for coating containing 5% PANI, 5% loading of PANI was considered for further immersion tests.

Top coated chromate and PANI (5% loaded) wash primer coated GI samples were exposed to salt spray tests for a period of 20 days. The appearance of both the samples indicate blister free and corrosion free even in the scribed areas. The impedance behaviour of these samples are shown in Fig. 8. The coating resistance and capacitance of these samples are $1.03 \times 10^8\ \Omega\,\text{cm}^2$, $2.3 \times 10^{-10}\ \text{F}\,\text{cm}^2$ and $2.76 \times 10^8\ \Omega\,\text{cm}^2$, $5.61 \times 10^{-10}\ \text{F}\,\text{cm}^2$ respectively. Almost equal values of coating resistance for both the chromate and PANI containing wash primers coated GI indicate that the PANI containing coating is performing equal to that of conventional chromate wash primer.

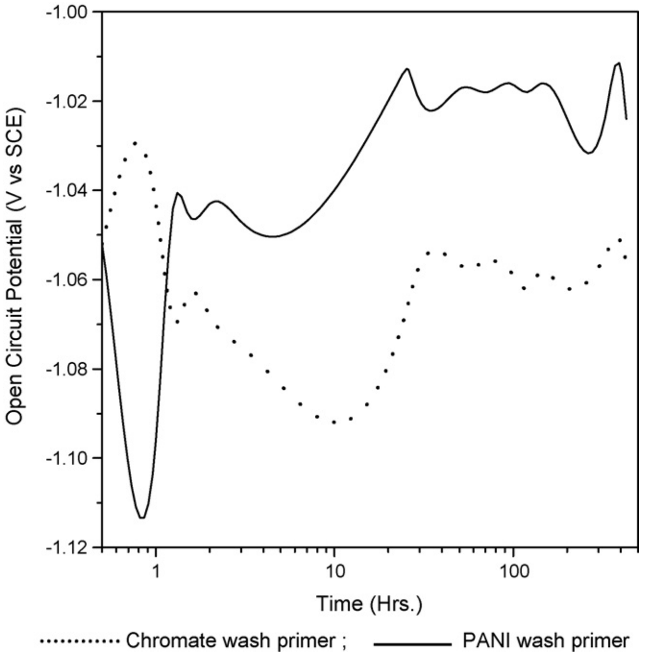


Fig. 6. Variation of open circuit potential with time (···) Chromate wash primer; (—) PANI wash primer.

3.7.2. Immersion tests

The impedance behaviour of chromate and 5% PANI loaded wash primer coated GI in 3% NaCl over a period of 10 days is shown in Figs. 9 and 10. The coating resistance and capacitance values derived from these figures are given in Table 1. In the case of chromate based wash primer coating, the coating resistance values are in the range of $1.4–5.19 \times 10^4\,\Omega\,\text{cm}^2$ and for PANI containing wash primer, the R_c values are in the range of $4 \times 10^3–2.3 \times 10^4\,\Omega\,\text{cm}^2$. These results clearly shows that PANI containing wash primer offers protection of GI similar to that of chromate containing wash primer.

The impedance behaviour of chromate and PANI containing wash primer coated GI with top coat in 3% NaCl is shown in Figs. 11 and 12 and the impedance parameters obtained from these figures are given in Table 2. The coating resistance values of chromate containing wash primer coating are decreased from 2.8×10^{10}

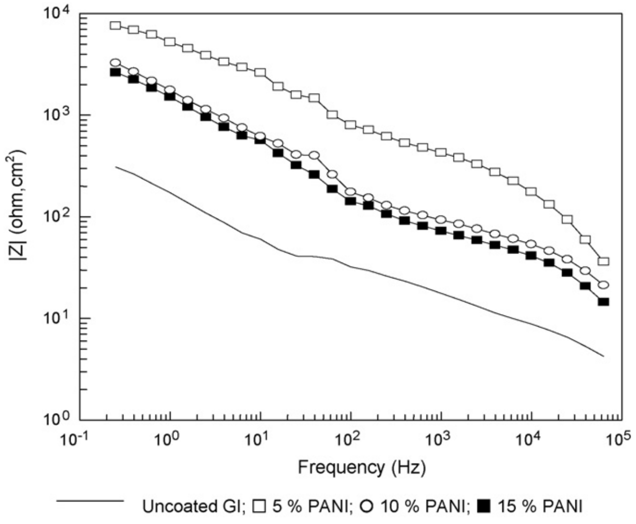


Fig. 7. The impedance behaviour of wash primer after 150 h of salt spray exposure, — Uncoated GI; □ 5% PANI; ○ 10% PANI; ■ 15% PANI.

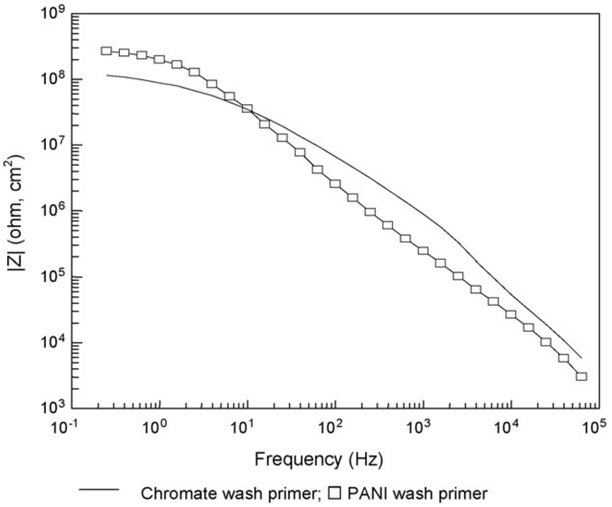


Fig. 8. Impedance behaviour of top coated GI. — Chromate wash primer; □ PANI wash primer.

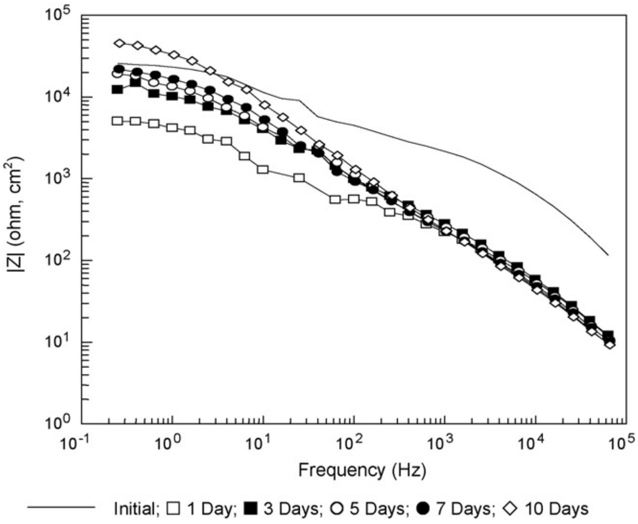


Fig. 9. Impedance behaviour of chromate wash primer in 3% NaCl. — Initial; □ 1 day; ■ 3 days; ○ 5 days; ● 7 days; ◊ 10 days.

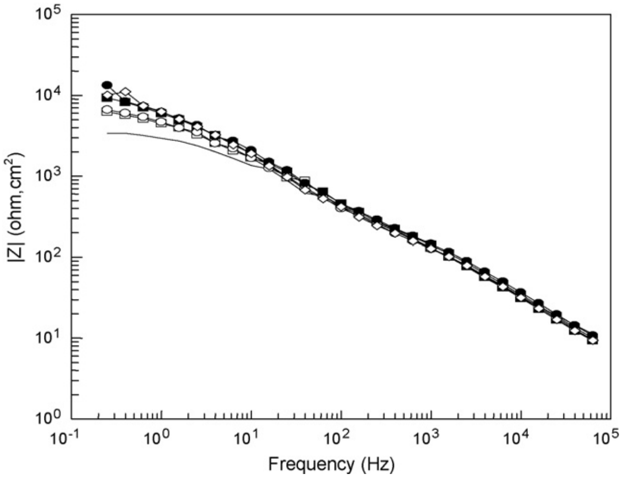


Fig. 10. Impedance behaviour of 5% PANI containing wash primer in 3% NaCl. — Initial; □ 1 day; ■ 3 days; ○ 5 days; ● 7 days; ◊ 10 days.

Table 1
Impedance parameters of chromate and 5% PANI wash primer coated GI in 3% NaCl.

Time days	Chromate wash primer		PANI wash primer	
	R_c (Ω cm^2)	C_c (F cm^{-2})	R_c (Ω cm^2)	C_c (F cm^{-2})
Initial	2.76×10^4	1.67×10^{-6}	4.05×10^3	1.49×10^{-5}
1	1.43×10^4	4.46×10^{-6}	8.39×10^3	2.05×10^{-5}
3	2.63×10^4	3.36×10^{-6}	1.63×10^4	2.86×10^{-5}
5	2.32×10^4	5.38×10^{-6}	9.23×10^3	2.44×10^{-5}
7	1.97×10^4	5.63×10^{-6}	1.98×10^4	3.30×10^{-5}
10	5.19×10^4	3.63×10^{-6}	2.34×10^4	4.13×10^{-5}

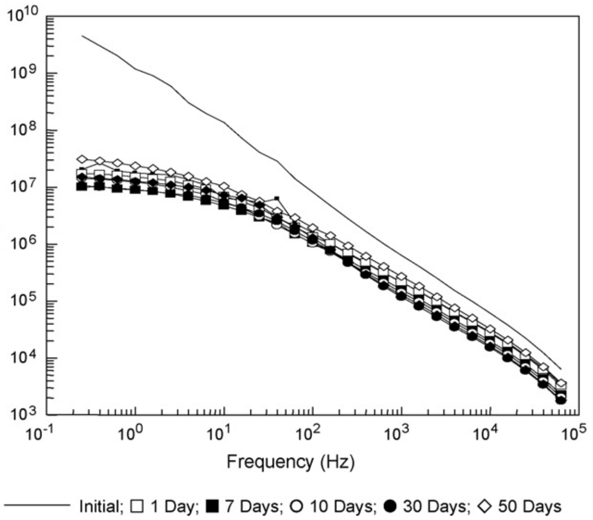


Fig. 11. Impedance behaviour of chromate wash primer and Top coated GI in 3% NaCl. — Initial; □ 1 day; ■ 7 days; ○ 10 days; ● 30 days; ◇ 50 days.

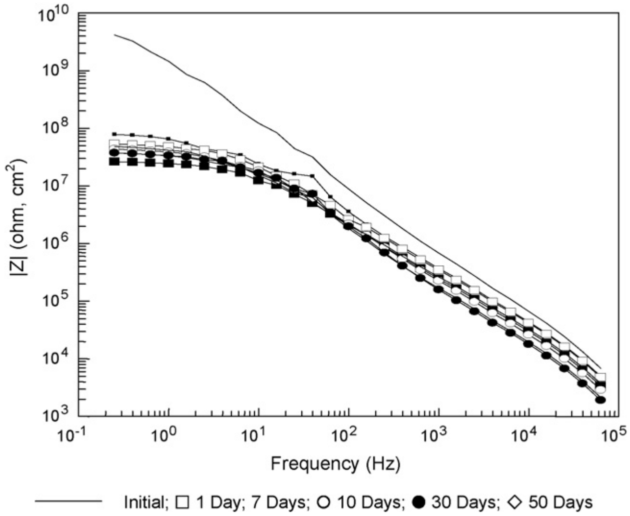


Fig. 12. Impedance behaviour of 5% PANI containing wash primer and top coated GI in 3% NaCl. — Initial; □ 1 day; 7 days; ○ 10 days; ● 30 days; ◇ 50 days.

to $1.4 \times 10^7\ \Omega$ cm^2 after 50 days immersion whereas the R_c values of PANI containing coating are decreased from 2.3×10^{10} to $3.5 \times 10^7\ \Omega$ cm^2 after 50 days immersion. The capacitance values have not much changed for both the coatings.

The above results show that the corrosion protection ability of GI by PANI based wash primer coating is found to be same as that of conventional chromate based wash primer coating.

Table 2
Impedance parameters of chromate and 5% PANI wash primer and top coated GI in 3% NaCl.

Time days	Chromate wash primer		PANI wash primer	
	R_c (Ω cm^2)	C_c (F cm^{-2})	R_c (Ω cm^2)	C_c (F cm^{-2})
Initial	2.83×10^{10}	1.54×10^{-10}	2.33×10^{10}	1.46×10^{-10}
1	2.02×10^7	1.06×10^{-9}	6.97×10^7	4.14×10^{-10}
3	1.97×10^7	1.59×10^{-9}	5.12×10^7	6.00×10^{-10}
5	1.32×10^7	1.69×10^{-9}	2.99×10^7	7.68×10^{-10}
7	9.42×10^6	1.77×10^{-9}	2.48×10^7	8.10×10^{-10}
10	1.36×10^7	2.04×10^{-9}	4.08×10^7	7.35×10^{-10}
20	9.61×10^6	1.59×10^{-9}	3.53×10^7	8.31×10^{-10}
30	2.90×10^7	1.14×10^{-9}	4.51×10^7	6.05×10^{-10}
50	1.37×10^7	1.30×10^{-9}	3.53×10^7	8.60×10^{-10}

The corrosion protection of GI by chromate wash primer coating is due to the formation of a chromate conversion layer on zinc. The chromate conversion coating has an inner layer made of ZnO and an outer layer of Cr_2O_3, $Cr(OH)_3$, $Cr(OH)CrO_4$, $Zn_2(OH)_2CrO_4$ [17]. But in the case of PANI wash primer coating on GI, it is due to the formation of a passivating layer along with a phosphate layer. The formation of passive layer by PANI blended epoxy on Zinc has been established by Silva et al. [8] by Raman microscopic studies. They have proved the existence of galvanic coupling between PANI and zinc surface and the formation of passive layer by redox reaction of PANI. The scanning Kelvin probe studies made by William et al. [12] on PANI–PVB coating on zinc have shown that PANI is able to inhibit the corrosion in coating defect effectively by forming a passive ZnO layer.

4. Conclusions

The corrosion protection performance of GI by PANI based wash primer coating is of the same order as that of conventional chromate based wash primer coating. The PANI based wash primer coating protects the zinc by the formation of phosphate layer along with the passive ZnO layer due to the redox property of PANI.

Acknowledgements

The authors thank The Director, CECRI, Karaikudi – 6 for his keen interest and kind permission. The authors also thank CSIR for research funding through network projects (NWP – 12).

References

[1] ASM Handbook, Vol 13A: Corrosion: Fundamentals, Testing, and Protection, ASM International, USA (2003) p. 720.
[2] V. Lzazuskas, R. Sarnaitos, J. Butkevicius, J. Matulis, Plat. Surf. Fin. 1 (1979) 58.
[3] R. Sarmaitis, A. Suvila, Plat. Surf. Fin. 10 (1998) 64.
[4] T. Belleze, G. Roventi, R. Fratesi, Surf. Coat. Technol. 155 (2002) 221.
[5] A.C. Bastos, M.G. Ferreria, A.M. Simoes, Prog. Org. Coat. 32 (2005) 339.
[6] B. Zaid, S. Aliyach, C.A.M. Takenout, P.I. Lacaze, Electrochim. Acta 43 (1998) 2331.
[7] S. Aliyach, B. Zaid, P.C. Lacaze, Electrochim. Acta 44 (1999) 2889.
[8] J.E.P. Silva, S.I.C. Torresi, R.M. Torresi, Prog. Org. Coat. 58 (2007) 33.
[9] S. Souza, Surf. Coat. Technol. 202 (2007) 7574.
[10] R.M. Torresi, S. Souz, J.E.P. Silva, S.I.C. Torresi, Electrochim. Acta 50 (2005) 2213.
[11] G. Paliwoda–Porebska, M. Rohwerder, M. Stratmann, U. Rammelt, L.M. Due, M. Pleith, J. Solid State Electrochem. 10 (2006) 730.
[12] G. William, R.J. Holness, D.A. Worsley, H.N. McMurray, Electochem. Commun. 6 (2004) 549.
[13] F. Mansfeld, Corrosion 37 (1981) 301.
[14] C.H. Huo, M.S. Cho, J.H. Sung, H.J. Choi, J. Mater. Sci. 39 (2004) 3151.
[15] H.T. Po, L. Qiao, Z. Liu, Z.L. Yang, Eur. Poly. Mater. 41 (2005) 2505.
[16] E.M. Bachari, G. Baud, S. Benarmov, M. Jacquet, Thin Solid Films 348 (1999) 165.
[17] Z.L. Long, Y.C. Znou, L. Xiav, Appl. Surf. Sci. 218 (2003) 123.