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Performance of polyaniline pigmented vinyl acrylic coating on steel in aqueous solutions

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Abstract

Using electrochemical impedance spectroscopy method, the performance of vinyl acrylic coating containing polyaniline on steel in 0.1 N HCl, 3% NaCl and cement extract (pH 13.0) has been evaluated. The resistance of the paint coating in all the media has been found to decrease initially from 10^8 to $10^6\ \Omega\,cm^2$. On subsequent exposure to the aqueous media, the resistance of the coating has been found to increase steadily. Further, the open circuit potential values have been found to shift in active direction initially and then move in noble direction with longer immersion period due to the passivating effect of polyaniline pigment.

Keywords: EIS; Coating; Polyaniline; Vinyl acrylic; Steel; 0.1 N HCl; 3% NaCl; Cement extract

1. Introduction

Research on corrosion protection of steel by conducting polymers gained momentum in the last few decades. In situ electropolymerised coating on the metal surface and polymer pigmented paint coating have been found to offer corrosion protection. The advantage of protection by conducting polymer coating is that the coatings get more tolerance to pin holes due to the passivation ability of conducting polymer. Electropolymerised coatings such as polyaniline [1–4], polypyrrole [5–7], polythiophene [8] and polyindole [9] on steel have been found to offer corrosion protection. In recent years, studies are being reported on the use of conducting polymer containing paint coatings for the protection of steel. Due to environmental restrictions on the use of heavy metal containing paints, this new class of primers based on polyaniline received much attraction. Mengoli et al. [10] have found that the paints containing polyaniline offer high corrosion resistant coating. Studies by Wrobleski et al. [11] have shown that the doped electrically conducting polyaniline films on steel with epoxy top coat have been found to offer protection in 3.5% NaCl and 0.1 M HCl even at scribed areas. Wessling et al. [12,13] have found that the coating system with polyaniline primer protects the delaminated area in 3% NaCl. Among the conducting and non-conducting polyanilines, it has been reported that the non-conducting polyanilines have performed well [14]. However, the studies of Araujo et al. [15] have shown that the performance of PANI coated system is not good due to poor adhesion. Santos et al. [16] have shown that the steel coated with polyaniline paint gained nearly 100 mV in corrosion potential in 3% NaCl due to the formation of passive film. The formation of passive film on iron by polyaniline coating has been confirmed by SEM and XPS studies [4,12,17–19]. Kinlen et al. [20] have found that the polyaniline paint coatings passivate the pin holes and defects. Samuli et al. [21] have shown that the low loading of PANI–HCl pigment in paint has offered higher corrosion protection of steel in sodium chloride solutions. In a recent study [22], it has been found that a polyaniline pigmented coating is able to protect the steel both in acid and neutral media. In this paper, the corrosion performance of polyaniline pigmented vinyl acrylic coating on steel in acid, neutral and alkaline media is reported.

2. Experimental

2.1. Synthesis of polyaniline pigment

Reagent grade aniline was purified by distillation in the presence of small amount of zinc dust. About 0.1 M of the freshly distilled aniline dissolved in 0.1 M HCl was precooled. To this

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reaction mixture, freshly prepared solution of 0.1 M ammonium persulphate kept at a temperature of 5–10 °C was slowly added with constant stirring for 2 h. Finally polyaniline, a dark green coloured polymer was obtained. The polymer thus obtained was filtered and repeatedly washed with distilled water to remove the excess acid. The polyaniline was characterised by FTIR and UV–vis spectroscopy and molecular weight was determined by GPLC method (Shimadzu, Japan) and was found to be 16,260.

2.2. Preparation of polyaniline pigmented vinyl acrylic paint

The polyaniline containing paint was prepared as per the procedure [23], using vinyl resin (MW: 30,000) and acrylic resin (MW: 45,000) in the ratio 1:2.5 (w/w) as binder and polyaniline as the only pigment. The characteristics of the paint and the coating are as given below:

Touch dry	1.0 h
Complete dry	2 h
Volume solids	30–33%
Thickness/coat	50 ± 5 μm
PVC	3.5%

2.3. Methodology of evaluation of coating

Carbon steel specimens of size 5 cm × 1.5 cm × 0.2 cm were pickled and coated with PANI containing paint. A glass tube of 0.9 cm diameter of length 3 cm was fixed on the coated steel with adhesive (m-seal). The solutions of 0.1 N HCl, 3% NaCl and cement extract (pH 13.0) are taken in the glass tube. Cement extract was prepared using Portland pozzolana cement. At first, 100 g of Portland pozzolana cement was shaken with 100 cm^3 of distilled water in a Microid flask shaker for 1 h. The cement extract was then filtered through no. 1 Wattman filter paper. A platinum foil and a saturated calomel electrode (SCE) were placed inside the glass tube. This assembly was connected to Electrochemical Impedance Analyzer (Model 6310 EG&G). Impedance measurements were carried out for a frequency range of 100 KHz to –0.1 Hz with an ac amplitude of 20 mV for different immersion time. From the impedance plots the resistance (R_c) and capacitance (C_c) of the coating were obtained using Z view software.

3. Results and discussion

3.1. Characterisation of polyaniline pigment

In the UV–vis spectrum (Fig. 1) the absorption peak at 336 nm corresponds to the π–π^* transition in the benzenoid ring and at 578 nm the donor–acceptor interaction of quinonoid ring. The well known cation radicals and localized polaran peaks were observed at 449 and 775 nm. The major IR absorption (Fig. 2) bands at 1555 and 1453 cm^{-1} are the characteristic bands due to nitrogen–quinonoid ring structure and peaks for polyaniline are observed at 1632 cm^{-1} for N–H bending, 1555 and 1494 cm^{-1} for nitrogen benzenoid–quinonoid ring structure. The other IR characteristics are observed at 1126, 1036 cm^{-1}.

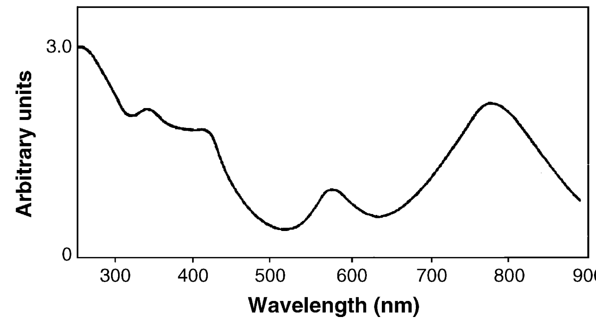


Fig. 1. UV–vis spectrum of polyaniline.

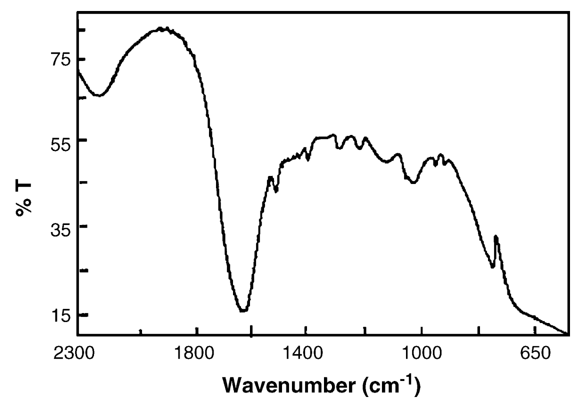


Fig. 2. FTIR spectrum of polyaniline.

3.2. Corrosion performance of coating

3.2.1. Performance of coating in 0.1 N HCl

The impedance behaviour of coated steels of 90 and 120 μm thicknesses in 0.1 N HCl is shown in Figs. 3 and 4. It is observed

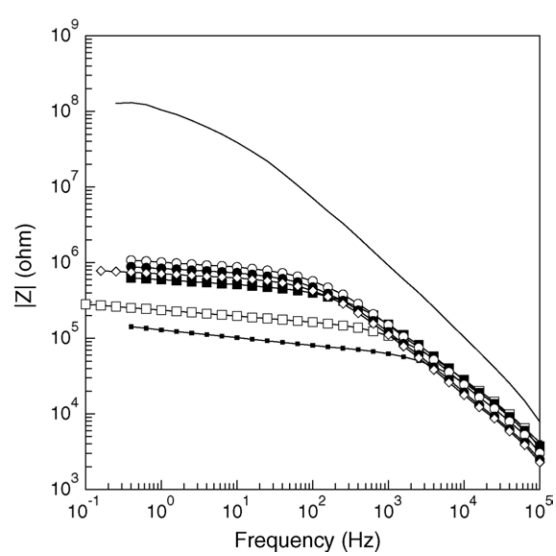


Fig. 3. Impedance plot of 90 μm thick PANI pigmented vinyl acrylic paint coating on steel in 0.1 N HCl: —, initial; ▪, 1 day; □, 3 days; ■, 7 days; ○, 14 days; ●, 35 days; ◊, 100 days.

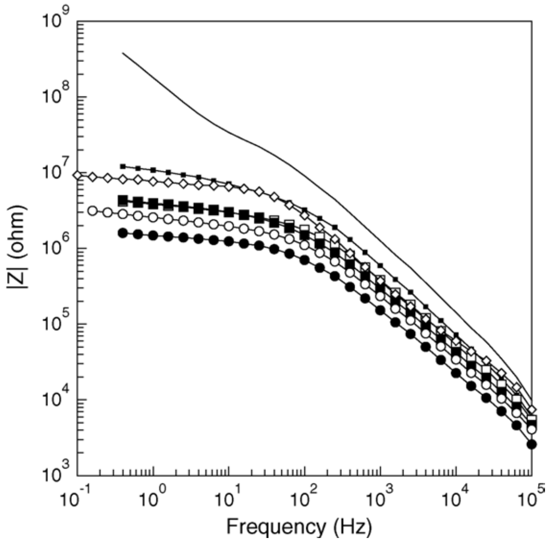
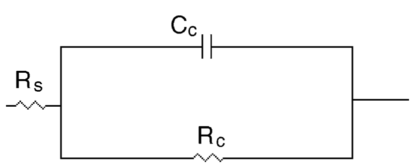


Fig. 4. Impedance plot of 120 μm thick PANI pigmented vinyl acrylic paint coating on steel in 0.1 N HCl: —, initial; ▪, 1 day; □, 3 days; ■, 7 days; ○, 14 days; ●, 35 days; ◊, 100 days.

from the figures that impedance curves have one time constant which may be due to the resistance and capacitance of the coating as reported by Wessling [13]. The equivalent circuit for such behaviour can be represented as



where R_s is the solution resistance, R_c is the coating resistance and C_c is the coating capacitance. Using the above equivalent circuit, the resistance and capacitance values of the coating have been obtained with Z view software. Table 1 gives the impedance parameters for coated steel in 0.1 N HCl for different immersion time. The impedance values are initially at 10^8 to $10^9\,\Omega\,cm^2$ which decrease with exposure time. For 90 μm thick coating, the R_c value is decreased to a low value of 7.8×10^4 in 1 day immersion and it has started increasing steadily by about one order. In the case of higher thickness coated steel, the impedance value decreases steadily up to 35 days of immersion and gained a little after 100 days of immersion. Further the coating capacitance values are in the range of $(0.1–5.0) \times 10^{-10}\,F\,cm^{-2}$ which indicates the protective nature of the coating. These results show that the polyaniline pigmented vinyl acrylic coating offers protection in 0.1 N HCl. However, the open circuit potential values are in the range of −600 to −650 mV for both the thicknesses of the coating. Further it is found that there is no blisters or delamination of coating through out the test period and also the test solution was found to be clear indicating that no corrosion has taken place.

3.2.2. Performance of coating in 3% NaCl

The variations of impedance with different exposure period for steel coated with PANI pigmented vinyl acrylic coatings of 90 and 120 μm thicknesses in 3% NaCl are shown in Figs. 5 and 6.

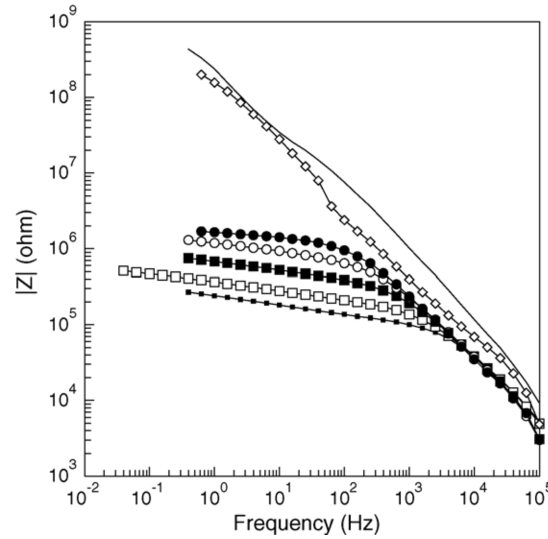


Fig. 5. Impedance plot of 90 μm thick PANI pigmented vinyl acrylic paint coating on steel in 3% NaCl: —, initial; ▪, 1 day; □, 3 days; ■, 7 days; ○, 14 days; ●, 35 days; ◊, 100 days.

As observed in acid media, one time constant is observed in the impedance plots. The paint film resistance and capacitance values have been calculated from the impedance diagrams using the previous equivalent circuit and the results are given in Table 2. The OCP values are found to shift in active direction initially i.e. from −450 to −672 mV on third day of immersion. On subsequent immersion period, the OCP values are found to shift in noble direction and reaches −407 mV on 100th day of immersion. Such type of shifts in open circuit potentials in noble direction for polyaniline pigmented coating on steel in NaCl solution [2,17,24,25] and electropolymerised conducting coating on steel [26–28] have been reported earlier and explained due to the formation of passive layer underneath the film. The paint film resistance values are also decreased initially from

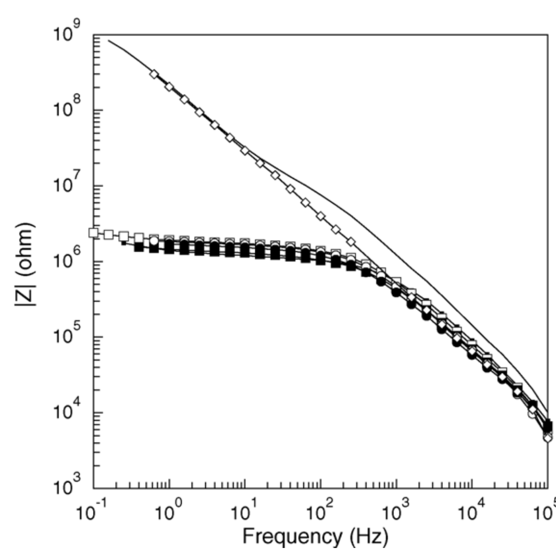


Fig. 6. Impedance plot of 120 μm thick PANI pigmented vinyl acrylic paint coating on steel in 3% NaCl: —, initial; ▪, 1 day; □, 3 days; ■, 7 days; ○, 14 days; ●, 35 days; ◊, 100 days.

Table 1
Impedance values for coated steel in 0.1 N HCl

Duration days	90 μm thick coating			120 μm thick coating		
	OCP (mV) vs. SCE	R_c (Ω cm^2)	C_c (F cm^{-2})	OCP (mV) vs. SCE	R_c (Ω cm^2)	C_c (F cm^{-2})
Initial	−658	1.6×10^8	4.3×10^{-10}	−580	3.4×10^9	1.1×10^{-10}
1	−608	7.8×10^4	6.5×10^{-10}	−592	9.2×10^6	5.9×10^{-10}
3	−661	1.9×10^5	7.5×10^{-10}	−603	3.3×10^6	5.2×10^{-10}
7	−655	5.3×10^5	1.1×10^{-10}	−612	3.6×10^6	8.8×10^{-10}
14	−610	9.3×10^5	1.5×10^{-10}	−616	2.4×10^6	1.0×10^{-9}
35	−629	7.8×10^5	1.9×10^{-10}	−572	1.4×10^6	1.6×10^{-9}
100	−620	6.8×10^5	1.9×10^{-10}	−625	7.3×10^6	5.2×10^{-10}

Table 2
Impedance values for coated steel in 3% NaCl

Duration days	90 μm thick coating			120 μm thick coating		
	OCP (mV) vs. SCE	R_c (Ω cm^2)	C_c (F cm^{-2})	OCP (mV) vs. SCE	R_c (Ω cm^2)	C_c (F cm^{-2})
Initial	−450	1.7×10^9	2.2×10^{-10}	−438	3.3×10^9	2.7×10^{-10}
1	−620	1.4×10^5	4.4×10^{-10}	−661	1.1×10^6	2.3×10^{-10}
3	−672	1.8×10^5	4.7×10^{-10}	−688	1.7×10^6	2.8×10^{-10}
7	−659	4.8×10^5	8.5×10^{-10}	−691	1.3×10^6	3.4×10^{-10}
14	−559	9.8×10^5	8.9×10^{-10}	−681	1.7×10^6	3.5×10^{-9}
35	−569	1.6×10^6	8.6×10^{-10}	−659	1.6×10^6	4.4×10^{-9}
100	−407	3.8×10^8	7.0×10^{-10}	−287	9.6×10^8	2.6×10^{-10}

1.7×10^9 to 1.4×10^5 Ω cm^2 and then increased steadily and reached 3.8×10^8 Ω cm^2 in the case of 90 μm thick coating. Similarly in the case of 120 μm thick coating, the R_c values are decreased by about an order and then increased steadily. However the variation of capacitance values with immersion period is not marked which indicates the absence of any underfilm corrosion by the diffusion of corrosive Cl^- ions and water. This study clearly shows that the polyaniline pigmented coating is able to offer better protection of steel in sodium chloride solution. Visual observation of the coating and the test solution during the test period has shown that the coating is free from blisters and delamination.

3.2.3. Performance of coating in cement extract

Over the two decades, the development of newer type of coatings on steel reinforced inside a concrete gained greater momentum to enhance the corrosion resistance of the steel and to improve the structural life. Evaluation of coated steel in cement extract of pH 13.0 will reflect the performance of the coated steel in real concrete. The impedance behaviour of PANI pigmented vinyl acrylic coating on steel of 90 and 120 μm thicknesses in cement extract (pH 13.0) for various immersion period is shown in Figs. 7 and 8. Here also only one time constant is observed as in the case of acid and neutral media. The values of coating resistance R_c and coating capacitance C_c obtained by using the previous equivalent circuit for different immersion period are given in Table 3.

The open circuit potential values for 90 μm thick coating have been shifted to more negative values i.e. from −223 to −737 mV in the first day of immersion and gradually shifted to the noble direction and attained −291 mV on 100th day immersion. Similarly for 120 μm thick coating, the OCP values have started at −200 mV and reached −613 mV on the first day of immersion and a positive value of −203 mV on the 100th day immersion. As in the case of neutral media, the paint film resistance R_c values are decreased from 10^8 to 10^6 Ω cm^2 with time up to 7 days immersion and subsequently the values increase. But the variation of capacitance values of the film is not significant. These results indicate that the polyaniline pigment in the coating is able to passivate the steel surface in the pinholes, defect spots and under the coated areas in alkaline media also. Moreover, the coating is found to be free from blisters and delamination

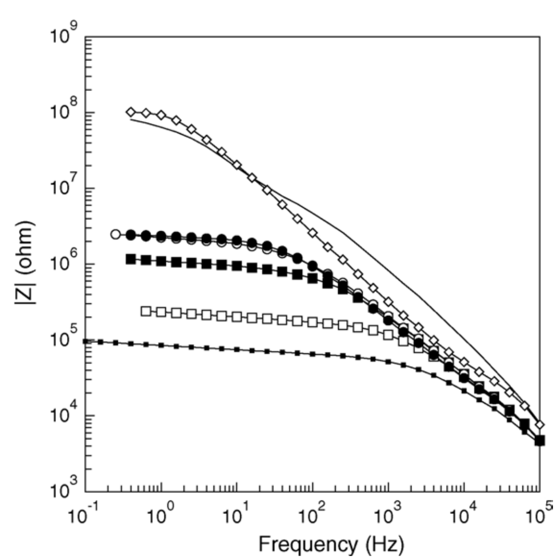


Fig. 7. Impedance plot of 90 μm thick PANI pigmented vinyl acrylic paint coating on steel in cement extract: —, initial; ▪, 1 day; □, 3 days; ■, 7 days; ○, 14 days; ●, 35 days; ◇, 100 days.

Table 3
Impedance values for coated steel in cement extract

Duration days	90 μm thick coating			120 μm thick coating		
	OCP (mV) vs. SCE	R_c (Ω cm^2)	C_c (F cm^{-2})	OCP (mV) vs. SCE	R_c (Ω cm^2)	C_c (F cm^{-2})
Initial	−223	1.1×10^8	1.2×10^{-9}	−200	5.9×10^8	1.3×10^{-9}
1	−737	7.2×10^4	7.3×10^{-10}	−613	1.5×10^8	5.3×10^{-9}
3	−724	1.1×10^5	6.9×10^{-10}	−570	2.0×10^7	6.9×10^{-10}
7	−689	1.1×10^6	1.1×10^{-9}	−587	2.6×10^6	4.3×10^{-10}
14	−659	2.6×10^6	1.3×10^{-9}	−512	5.4×10^7	2.8×10^{-10}
35	−562	2.3×10^6	1.4×10^{-9}	−510	3.8×10^7	1.2×10^{-9}
100	−291	1.1×10^7	1.1×10^{-9}	−203	7.6×10^7	3.9×10^{-9}

and also corrosion of base metal as evinced by the absence of colouration of test solution during the 100 days of immersion.

The mechanism of passivation of steel by PANI coating is schematically shown in Fig. 9.

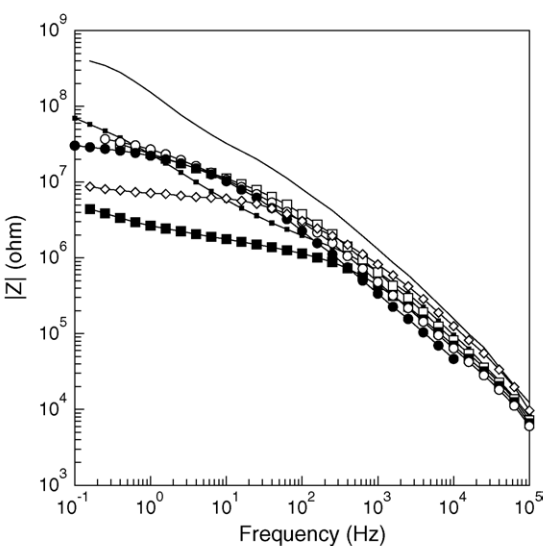


Fig. 8. Impedance plot of 120 μm thick PANI pigmented vinyl acrylic paint coating on steel in cement extract: —, initial; ▪, 1 day; □, 3 days; ■, 7 days; ○, 14 days; ●, 35 days; ◇, 100 days.

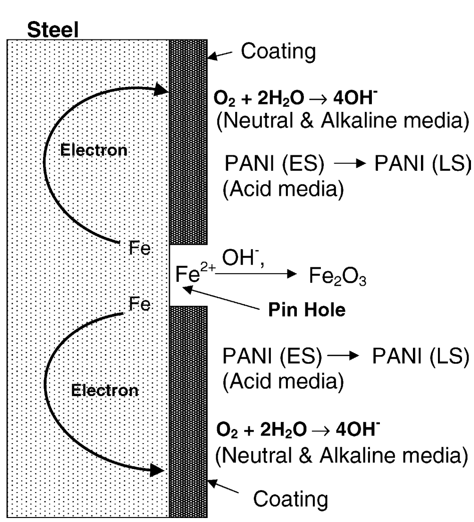


Fig. 9. Schematic diagram of mechanism of iron passivation by PANI pigmented vinyl acrylic paint coating on steel.

Due to the conducting nature of the coating, the oxygen reduction reaction takes place on the coating, while the oxidation of ferrous ions to passive iron oxides takes place on the exposed iron surface at pin hole areas and under the film in neutral and alkaline media. However in acid media, the passivation of pin holes takes place by the cathodic complementary reaction of

PANI(ES) → PANI(LS)

Due to the formation of PANI(LS) in acid media, the coating may be changed from conducting to non-conducting type. Hence in acid media, the OCP values are not shifted to noble direction with time.

But in the case of neutral and alkaline media, the initial decrease of OCP may be due to the initiation of dissolution in the pin holes. The presence of polyaniline in the coating favours oxidation of the ferrous ions to stable passive iron oxide film at the pin hole regions. Due to this reaction, the OCP values have been found to be shifted to noble values after a few days of immersion. The high positive values of OCP indicate the formation of a protective passive film on iron. The presence of Fe_2O_3 layer between PANI coating and steel surface has been confirmed by SEM and ESCA studies [12,17,23]. In all the studied media, it is observed that the surface remained unaffected on removal of coating after 100 days of immersion.

The initial decrease of R_c values in the aqueous media also reflects a small amount of dissolution of iron and subsequent increase in R_c values indicates the formation of passive film. The high R_c values and low C_c values of coating even after 100 days of immersion indicate the protective nature of the coating. After the test period, the glass tubes fitted to the coating in all the three cases were removed and it was found that the coating was intact without any damage at the electrolyte exposed areas.

4. Conclusions

The polyaniline pigmented vinyl acrylic coating is able to protect steel from corrosion in acid, neutral and alkaline media. The coating is found to passivate steel in neutral and alkaline media which is evidenced from the shift of open circuit potential value to noble value and from increase in paint film resistance for longer immersion period. Besides, the lower capacitance values of coating which are not changed with immersion time indicate the absence of corrosion reactions under the coating. Visual observation of the coating indicated blister, delamination free nature of the coating. However in acid media, the protection by the coating may be due to the barrier effect, since the open circuit potential values are not changed markedly with immersion time.

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