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Electrochemical Evaluation of Anticorrosive Performance of Organic Acid Doped Polyaniline Based Coatings

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In this work we examine the performance of the organic acid doped polyaniline to impart protection against corrosion when it is used as additive of long oil alkyd based red oxide primer paint. For this purpose, polyaniline doped with tartaric acid, oxalic acid and citric acid were characterized through FTIR and SEM studies. Cyclic voltammetry studies showed that doped polyaniline shown the electrochemical activity of the paints. Accelerated corrosion experiments (salt water chamber) revealed a significant improvement in the performance of the paint formulation which contained the aliphatic organic acid doped polyaniline coatings. These results were verified by evaluation of the electrical resistance and capacitance measurements of the films using electrochemical impedance spectroscopy. The results of this study reinforce the anticorrosive properties of long oil alkyd based red oxide primer paint through the formation of a protective layer of oxides using coatings which contain tartaric acid doped polyaniline..

Keywords: Polyaniline, Anticorrosive additive, Conducting polymer, Organic coating, Red oxide paint.

1. INTRODUCTION

Polyaniline (PANI) is a conducting polymer that has been investigated for applications in batteries, sensors, membranes and protection of metals against corrosion [1-4]. The polymer can be prepared by chemical and electrochemical methods from aqueous or organic media. The electrolytic species can participate as dopant and incorporate into the polymeric films [5]. The anions are indispensable to compensate the conducting polymer charges. The structure and the concentration of these anions affect the conductivity, the stability and the morphology of the PANI films [6]. It was found that the films doped with aromatic organic anions are electrically more conductive than those doped with inorganic anions. This behavior has been ascribed to a better superposition of the molecular orbitals of the dopant with the π atomic orbitals of the carbon in the polymeric chain. It was also observed that PANI films doped with organic species are more adherent and uniform than those doped with inorganic anions [7].

Among the popular conducting polymers PANI has gained greater interest over the past two decades owing to their electronic applications and their potential use as anti-corrosion coatings. Polyaniline is one of the most easily prepared conducting polymers, it has controllable electrical conductivity, excellent environmental stability and easy processability. It has several oxidation forms, namely emeraldine salt, emeraldine base, pernigraniline and leucoemeraldine, but only the emeraldine salt form is conductive. Its conductivity is enabled by the presence of cations-radicals in its structure. Such emeraldine "salt" can be obtained by the polymerization of aniline in the presence of an appropriate acid [8]. Most often, inorganic acids are used for this purpose of polymerization of aniline [9]. Thus PANI is insoluble in all kinds of solvents except in concentrated sulfuric acid. The conductivity of emeraldine salt is substantially affected by the concentration of the acid.

The possible mechanisms proposed to explain the anti-corrosion behavior of polyaniline on ferrous surfaces are many; however, most researchers agree that the passivation of iron and its alloys is promoted by the formation of adjacent layers of iron oxides [10-14] or nitride [15]. Wessling et al. [11] and Lu et al [12] observed that the emeraldine salt is immediately reduced on contact with iron in the presence of water, with consequent oxidation of the metal and formation of a double layer of oxides. In the presence of oxygen, PANI oxidizes and enables the reconstitution of the oxide layer if the coating is damaged.

In many applications of paints, it is convenient to formulate a composite made up of inorganic particles (a pigment) with a suitable chemical composition and that are coated with a functional layer of a conductive polymer. A binder pigmented with such particles forms a composite with excellent properties [10]. Hence any modification in the formulation of paints which will lead to improved properties assumes significance. Since the introduction of PANI anticorrosive pigment instead of inorganic pigments has many advantages, three types of doped PANI are selected for this study.

In this work, the of long oil alkyd based red oxide paint with aliphatic organic acids such as tartaric, oxalic or citric acid doped PANI was formulated and their influence on the film formed on mild steel surfaces was studied. The surface morphology of the films was characterized by Scanning electron microscopy (SEM). The anticorrosive action of the formulated paint was evaluated by electrochemical methods.

2. EXPERIMENTAL

2.1 Synthesis of the conducting polymer

PANI was synthesized by solid–solid reaction according to the procedure given by Huang et al. [21]; anilinium chloride and $(NH_4)_2S_2O_8$ with variable molar ratios (0.5-4.0) were ground in an agate mortar until the colour changed to dark green which is the characteristic colour of emeraldine polyaniline. The polymerization lasted for 24 h at room temperature. Afterward the dark green product was washed with distilled water until a colorless wash solution without oligomers was obtained. Then the PANI was neutralized and dopped with selected organic acid such us tartaric/oxalic/citric acid.

2.2 Paint formulation

The anticorrosion pigments were dispersed in a solution of long oil alkyd resin used for the production of red oxide primer paint. The quantity of pigments maintained in all the tested paints was 50% by volume. The various ingredients used for the preparation of the primer paint was as follows: Iron oxide 50 kg, Aluminium stearate 0.6 kg, Mineral turpentine oil, 27 liters, Long oil alkyd resin, 35 kg, Formaldehyde, 500 g, Cobalt napthianate, 0.1%(V/V), Lead napthinate 0.1% (V/V), PANI 1.5 to 2%(V/V). The paints were dispersed in an attrition mill. During dispersion and right before preparing the paints, the long oil alkyd resin was homogenized with a polyamine at a ratio of 100:27 by mass. If needed, all the paints were diluted to an appropriate application viscosity immediately before use.

2.3 Preparation of the test specimens

Mild steel with, chemical composition (wt %) is: 0.25 C, 0.20 Si, 0.73 Mn, 0.023 P, 0.018 S, 0.05 Cr, 0.03 Mo, 0.02 Ni, is used for all electrochemical studies, mild steel specimens embedded in red oxide paint with an exposed surface area of 1.0 cm2 were used as the working electrode. The specimens were carefully polished with sequence emery papers of various grades (400-800 grit), degreased with ethanol, washed with double distilled water and finally dried in warm air.

2.4 Infrared spectroscopy

FT-IR spectrometer, model Thermo Nickolite 6700 (Thermo Scientific) was used for the characterization of PANI. The analysis conditions were: wave number range of 4000-400 cm^{-1}, 4 cm^{-1} resolution, 40 scans, and room temperature (25°C), using diamond ATR.

2.5 SEM analysis

Scanning electron microscopy (SEM) was employed to study the type of surface morphology of the blends. A JEOL 5410 SEM was used for this purpose.

2.6 Electrochemical studies

A computer-controlled potentiostat (PARSTAT Model 2273) with software PowersuiteV.2.58 and Power CORR V2.47 was used. All the electrochemical experiments were performed at room temperature in a cell containing standard three-electrode assembly. The reference electrode was a Saturated Calomel Electrode (SCE) and the counter electrode was a platinum sheet with high surface area. All potentials are reported versus that of the SCE. Impedance measurements were carried out at open circuit potentials with sufficiently small excitation signal amplitude to remain within the quasi-linear response region of the systems. All impedance experiments have been carried out at the frequencies from 100 kHz to 100 MHz. The real and imaginary components of the impedance spectra in the complex plane were analyzed using the Z-Simp Win (Ink software) to estimate the parameters of the equivalent electrical analogous.

All purchased chemicals were of analytical reagent grade (Merck) and were used without further purification and double-distilled water was used throughout.

3. RESULTS AND DISCUSSION

3.1. Analysis of PANI composition

Infrared analysis was carried out on all three paint samples to verify the stability of the organic acid PANI polymer chain after the processing, and also to identify for possible spectral effects of interactions between the paint standard constituents and doped PANI.

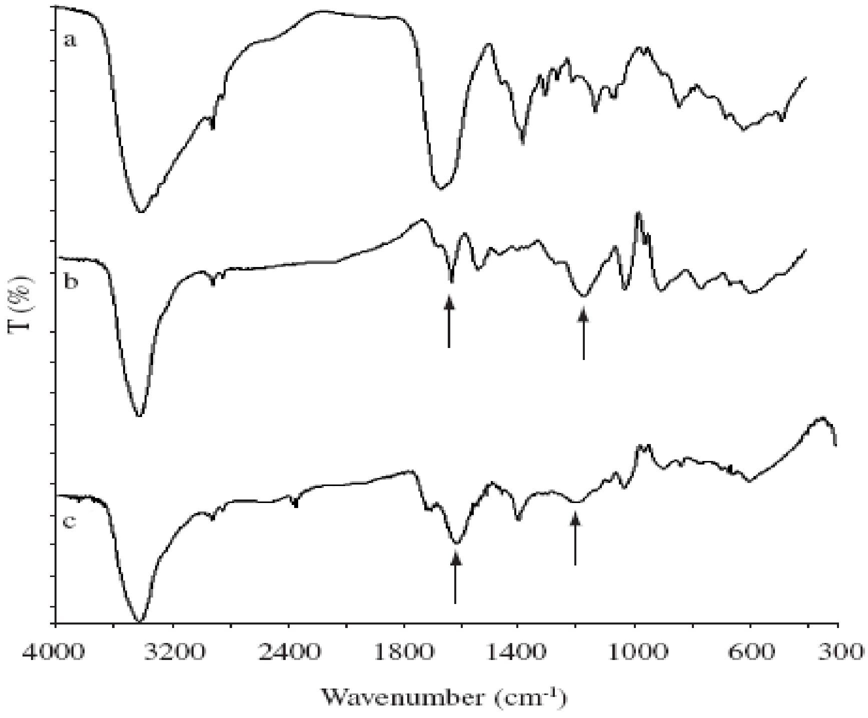


Figure 1. FT-IR spectra of PANI doped with a) tartaric acid, b) oxalic acid, and c) citric acid.

Figure 1 presents the FT IR spectra of PANI doped with tartaric acid, oxalic acid and citric acid. All three kinds doped PANI show a strong peak at 3400 cm^{-1} due to the stretching frequencies of OH and NH groups. The peak observed around 1650 cm^{-1} attributes to the stretching frequency of carboxyl carbonyl group present in the dopant. The peak around 1200 cm^{-1} may be due to the stretching frequency of C-O. These peaks suggest the presence of organic acids in the PANI film.

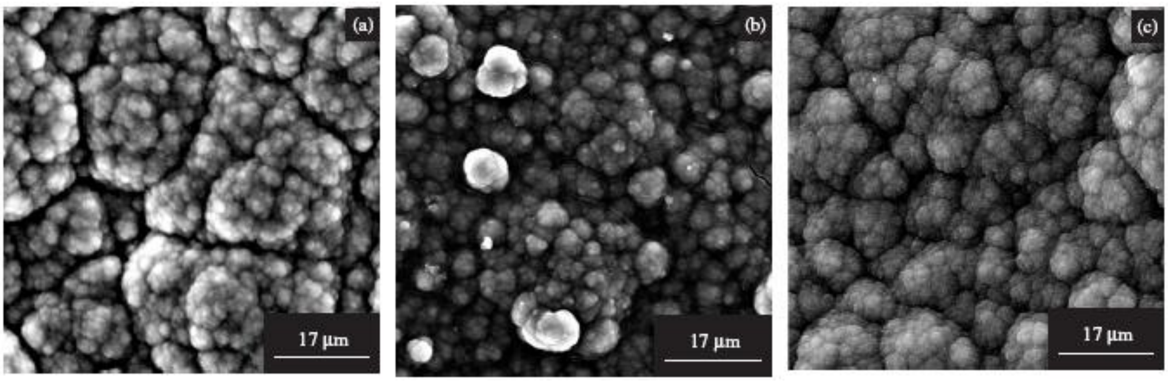


Figure 2. SEM micrographs of a) tartaric acid b) oxalic acid and c) citric acid doped PANI

Fig.2 shows the SEM images of PANI doped with tartaric acid, oxalic acid and citric acid. All three images exhibit granular morphology. On comparison of the all the three images, it is concluded that the PANI doped with tartaric acid (Fig.2a) has uniform surface characteristics with lesser granular size than other two.

3.2 Potentiodynamic polarization studies of paint film

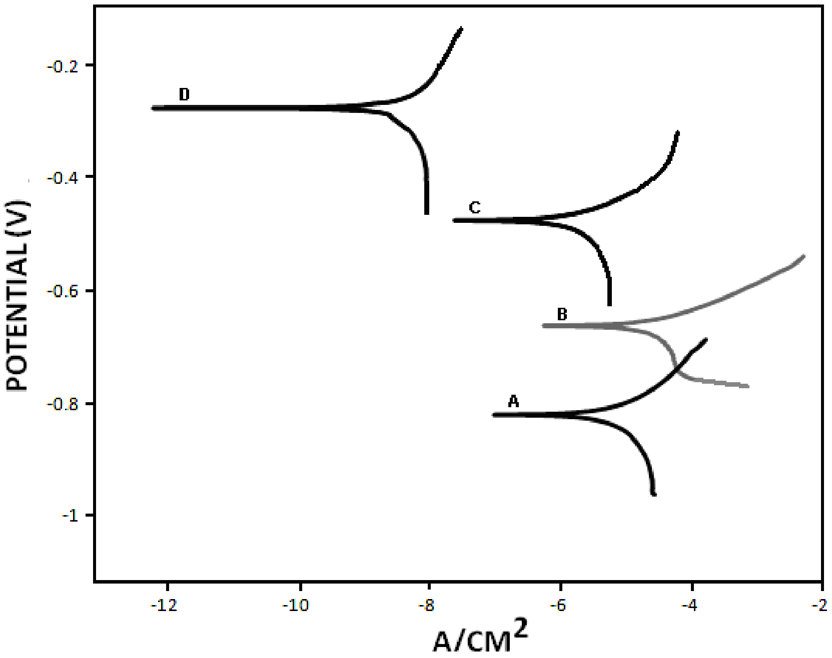


Figure 3. (A) Tafel plot for the polished mild steel in 3.5 % NaCl; Tafel plots for (B) Citric acid, (C) Oxalic acid and (D) Tartaric doped PANI/red oxide dispersed alkyd painted mild steel in 3.5 % NaCl.

The potentiodynamic technique is used to examine the passivation of a metal in an electrochemical system. The behaviour of the potentiodynamic polarization curves for metal covered with anticorrosion coatings indicates whether the metal is cathodically protected (sacrificial anode principle) or anodically protected (passivation principle) [18]. The corrosion resistance of long oil alkyd base red oxide primer painted surfaces was investigated using the potentiodynamic polarization technique. The surfaces were exposed to a 3.5% NaCl aqueous solution (pH 6.8), without stirring and kept open in the atmosphere. The polarization curves were obtained starting from the open circuit potential (OCP) and varying the potential, respectively, up to 400 mV (anodic branch of the Tafel plot) and down to –400 mV (cathodic branch of the Tafel plot). The potential scan rate was 5 mV s^{-1}. The corrosion potential (E_{corr}) and the corrosion current density (j_{corr}) were obtained from the Tafel plots. The Ecorr is the potential at which the current density is zero. The j_{corr} was determined by extrapolation, to Ecorr, from linear parts of the anodic and cathodic branches of the Tafel plots.

Fig. 3 shows the potentiodynamic polarization curves, 3.5% NaCl aqueous solutions, without stirring at pH 6.8. The potential scan rate was 5 mVs^{-1}. The corrosion potential of steel surfaces coated with paint shifted to lesser negative values and the anodic current densities of these surfaces were smaller than those observed to just polish steel surfaces. These observations can be taken as an indication that steel surfaces coated with PANI paint are more resistant to corrosion than uncoated surfaces. Furthermore, after polarisation curves, pits were observed on the uncoated steel surface, which presented pit potential at –0.69 V (Fig. 3). Pit potential was not observed in polarisation curves for steel surfaces coated by PANI paint coating. Before testing, samples were immersed into the solution and the open circuit potential (OCP) was monitored until a constant value was reached. The cathodic current densities, however, were higher for steel surfaces coated with PANI paint than for uncoated steel surfaces. The cathodic current densities increased in the sequence: uncoated surfaces < surface coated with PANI paint coated with dopant citric acid < surface coated with PANI paint with dopant tartaric acid < surface coated with PANI paint coated with dopant oxalic acid. Similar results have been shown in literature and have been associated to the reduction reaction of polymeric matrix, which contributes in increasing the cathodic currents [19, 20]. So, compared to the uncoated steel, a shift in the corrosion potential to more positive value (ΔE=545mV) occurs when the sample surface is covered by the tartaric acid doped PANI red oxide paint coating and a shift to (ΔE=345 mV), (ΔE=159 mV), when it is covered by the oxalic and citric acid doped red oxide paint respectively. This shows that the tartaric acid doped paint coating enables the metal by more passivation effect compare to other coatings.

The presence of the voids among the cauliflower structure of the films deposited in oxalic and citric acid allows the penetration of chloride ions (aggressive species) favouring the corrosion process. It was also observed that the steel surfaces coated by PANI red oxide paint with tartaric acid presented smaller amount of pits after polarisation experiments in chloride medium.

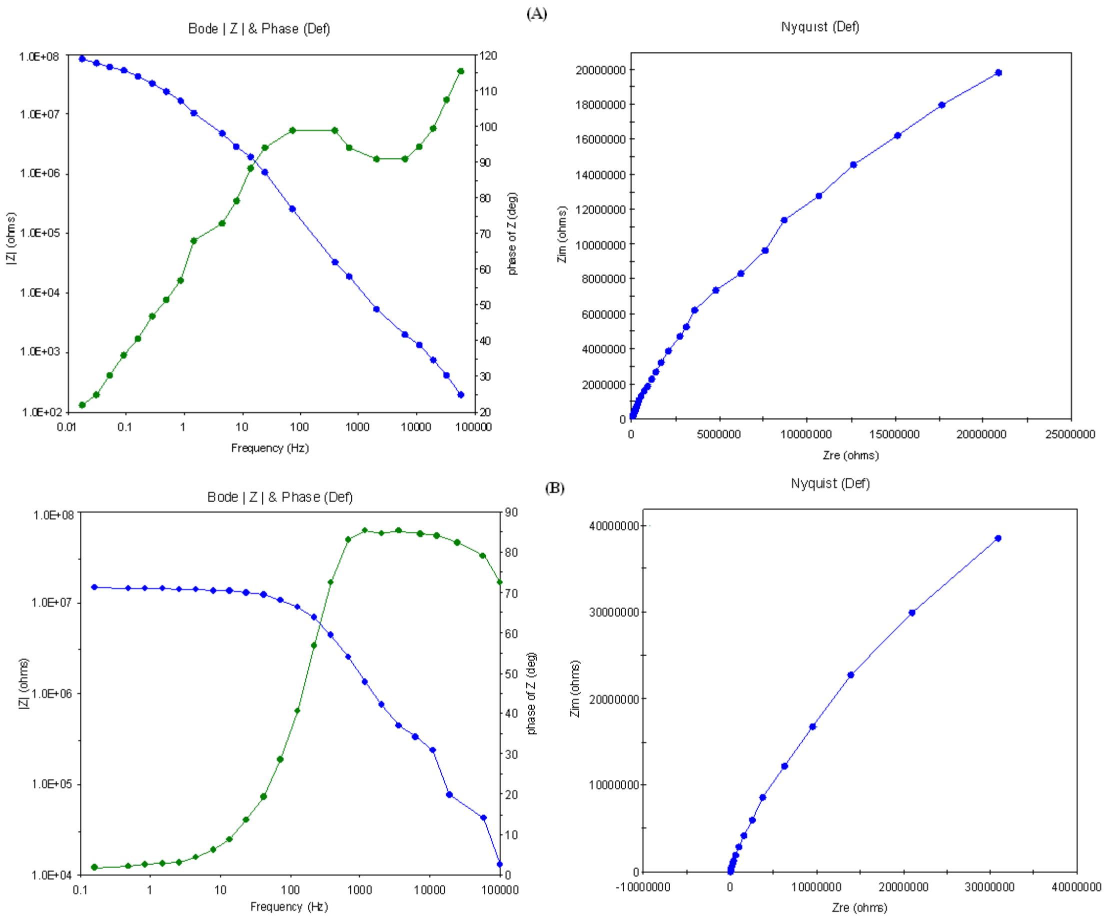
3.3. Electrochemical Impedance Spectroscopic studies of paint film

In the Electrochemical Impedance Spectroscopic (EIS) measurement, an alternating voltage is applied to the metal, and the impedance, Z, is measured. In an EIS experiment, the impedance is measured for a number of frequencies that span a range from 0.001 Hertz to 100 K-Hertz. EIS is useful in the evaluation of coatings, the elucidation of transport phenomena in electrochemical systems, and the determination of corrosion mechanisms and rates. If ΔE is the perturbation brought to the impressed potential between the working electrode and the reference electrode, the theoretical expression of the total Faradaic impedance Z_f is:

$$\frac{1}{Z_f}=\left(\frac{\partial I}{\partial E}\right)_{\theta_i,C_j}+\sum_i\left(\frac{\partial I}{\partial \theta_i}\right)_{C_j}\frac{\Delta\theta_i}{\Delta E}+\sum_j\left(\frac{\partial I}{\partial C_j}\right)_{\theta_i}\frac{\Delta C_j}{\Delta E} \quad \text{---------} \quad (1)$$

Where, θ_i is the covering factor, C_j is the concentration of the j specie. Bode and Nyquist plots are the most common data output formats. At very high frequency, the imaginary component, Z", disappears, leaving only the solution resistance, R_s. At very low frequency, Z" again disappears, leaving a sum of R_s and the faradic reaction resistance or polarisation resistance, R_p, which is inversely proportional to the corrosion rate.

The tendency which doesn't allow ions (salts and corrosion products) can be quantitatively described by the coating resistance (R_{ct}). From the Nyquist plots (Fig. 4), the difference existing between the semicircles of the impedance diagrams for the studied samples immersed during 1 hour in the saline solution are seen.



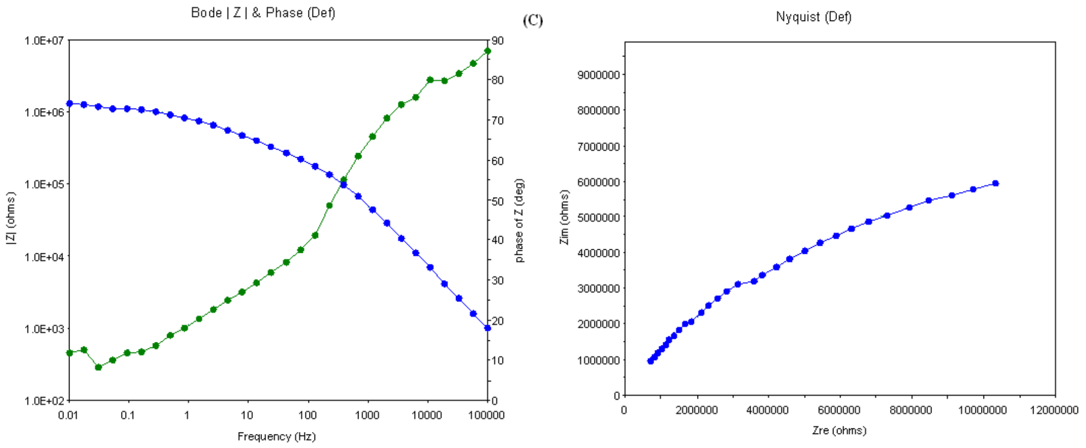


Figure 4. Bode and Nyquist plots for the (A) Tartaric acid, (B) Citric acid and (C) Oxalic acid doped PANI/red oxide dispersed alkyd painted samples immersed during 1 hour in 3.5% NaCl.

By fitting curves, a coating resistance value of the PANI coating higher than that of the conventional one and as a direct consequence, an increase of the metal protection against corrosion by a factor of 10 have been obtained.

The R_{ct} values for PANI- tartaric acid based paint are relatively higher than that of the other citric and oxalic doped PANI coated sample (Fig 4a and Fig 4c). This accounts for the fact that the rate of charge transfer reactions on metal surface has been limited because of the cooperative formation of a primary protective passive layer and a barrier polymer layer as well. During all the exposure times, the citric and oxalic acid doped coating has shown lower coating resistance. This serves for the fact that the paint coating has a higher degree of oxidation because of the incorporation of the dopants and also dopants with high negative charges. As long as, the polymeric material during the process of oxidization, the citrate and oxalate ion diffuses through the polymer film in order to compensate the charge resulting from the polymer oxidation. Thus, it can influence the ease of oxidation as well as the doping level of the polymer. Therefore, the presence of the excess species (*e.g.* oxalate and citrate) in the solution increases the entrance of dopant species in the polymer chain that will indirectly increase the degree of doping. Moreover, it appears that the extra negative charges of the above ion facilitate and promote its entrance rate compared with the tartrate ions. Tartrate ion is heavier and geometrically bigger than oxalate and citrate ions. It must also be noted that contrary to oxalate and citrate anions, tartrate anion has tetrahedral space geometry, owing to its lower possibility to release from the polymer chain into the aggressive media. The highest value of double layer capacitance (C_{dl}) was obtained for PANI / tartrate (273 mF / cm^2) than citrate (C_{dl} = 84.2 mF / cm^2) and oxalate (21.5 mF / cm^2) from equivalent circuit model [21]. Thus, stored charges of the coating is held for more prolonged times. Increasing of stored charges of the tartrate paint due to doping the tartrate ions was also verified by increasing of its capacitance even in prolonged immersion times.

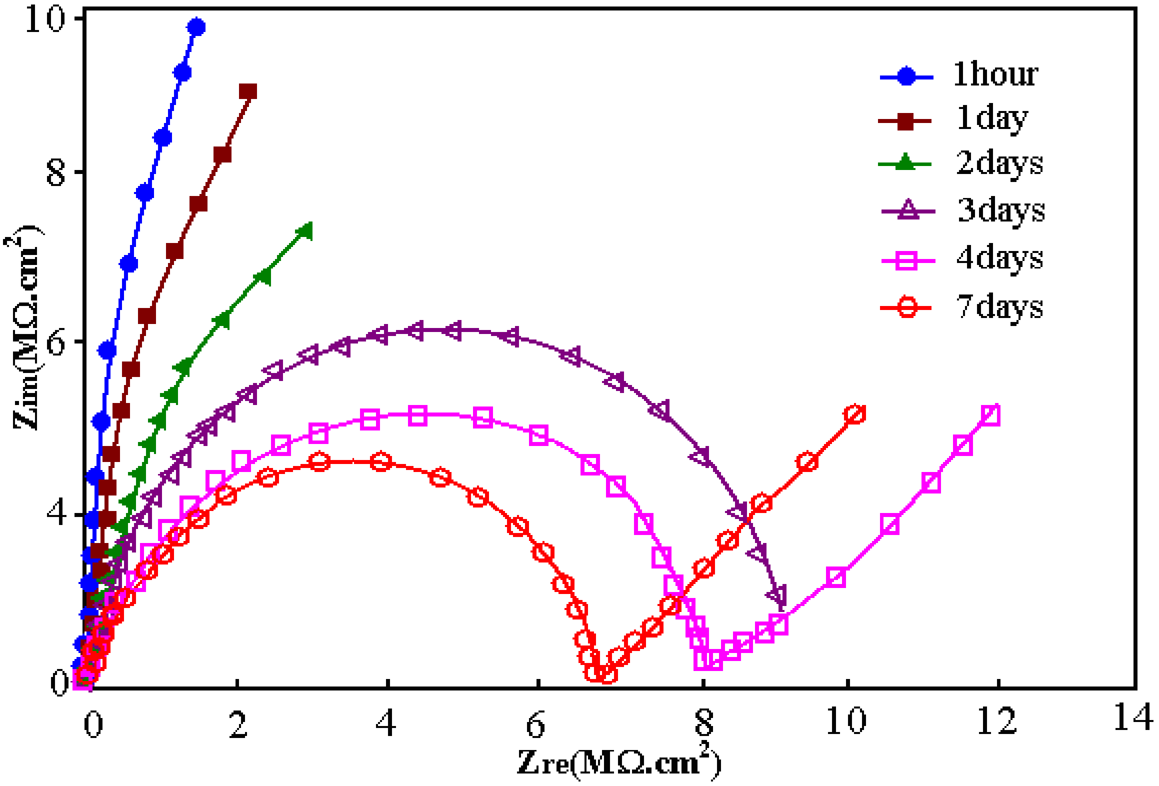


Figure 5. Nyquist plots of polished steel surface coated with Tartaric Acid doped PANI red oxide paint after immersion in 3.5% NaCl.

EIS measurements were periodically monitored and the results obtained from the Nyquist plots of coating resistance Rct (ohm) is 2.27E+08 1hr, 1.27E+08 1day, 9.27E+07 2days, 5.62E+07 3days, 6.41E+06 4 days and 4.11 E+05 for 7 days. After 7 days exposure in salt spray chamber, Tartaric Acid doped PANI red oxide paint coating revealed the highest impedance value of the coatings tested and showed protection ability in 3.5% NaCl. The coating resistance values indicate that the conventional coating fails faster than the PANI coating. This fact is clearly shown in fig 5, where the coating resistance decreases with immersion time in saline environment. It was accepted by some researchers [22] that the value of coating resistance, Rct, which can be found from semi-circle diameter of the Nyquist plot [23], is the best for the measurement of coating degradation,.

Considering the anodic current densities in the potentiodynamic polarisation curves, as a criterion in determining the corrosion protection afforded by the PANI films, it would be possible to affirm that steel surfaces coated with the polymeric films are less susceptible to corrosion process than just polished ones [24,25]. Additionally, it could be also said that tartaric acid doped PANI based paint coatings are the ones that offer better corrosion performance. This result can be explained by the highest homogeneity of the polymeric films formed in this medium.

4. CONCLUSION

The results clearly indicate that the selection of corrosion inhibitor used in the coating formulations is a crucial factor for corrosion protection. The tartaric acid doped PANI based corrosion inhibitor is outperforming the conventional alkyd base red oxide primer paint coating. Both chemical and physical properties of this polymer and the ease of its synthesis, allow us to preserve the natural environment. It should be noted, that this developed coating can also lead to a significant cost reduction for oil and gas industries because of the new ennobling and passivation technology.

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