EVALUATION OF THE PROTECTIVE PERFORMANCE OF EPOXY COATED MILD STEEL BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

By

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Abstract

Electrochemical Impedance Spectroscopy (EIS) and open circuit potential (o.c.p) measurement were employed to study the protective action of epoxy based paint coating on mild steel (AISI 1020) in artificial sea water (3.5% NaCl). From EIS data such as Pore resistance (R_{pore}), coating capacitance (C_c), and by polarization resistance (R_p), double layer capacitance (C_{dl}) it was possible to obtain information regarding the corrosion performance of paint coating. The presence of micro-porosity or cracks in the coating initiated the corrosion process at the interface very earlier after 24Hrs of exposure. The variation of the pre-described parameters defined the actual mechanism of coating failure and corrosion process at the interface.

Introduction

Protective coatings are probably the most widely used products for corrosion control. They are used to provide long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions. Protective coatings in themselves provide little or no structural strength, yet they protect other materials to preserve their strength and integrity. **[1]**

It is generally accepted that the coating efficiency is dependant on the intrinsic properties of the organic film (barrier properties), on the substrate/coating interface in terms of adherence, on the inhibitive or sacrificial pigments used and on the degree of environment aggressiveness. **[2]**

Epoxy based paints are within the best organic coatings employed as insulating from a marine medium to protect mild steel against corrosion. When a metal surface is covered with a polymeric film and then immersed in an electrolytic solution, an interaction is produced between the film and the solution. Water with electrolyte ions is transported through the coating by two simultaneous mechanisms: convection through the pores and coating imperfections (fast step) and by diffusion through the polymeric matrix (low step). In continuous and defect-free films, only the transport of ionic species through the polymer is favored. **[3]**

Electrochemical impedance spectroscopy (EIS) provides a rapid and convenient technique to evaluate the performance of organic coated metals. One of the most successful applications of this technique has been in the evaluation of the properties of polymer coated metals and their performance variation during exposure to corrosive environments. **[4]**

Experimental Methodology

For the epoxy based paint integrity evaluation, the mild steel (AISI 1020) was selected as a substrate.

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Surface Preparation

The steel substrate was grit blasted in an automatic grit blasting unit to a near white surface (SSPS-SP-10). The grit size was of 960µm (Ave), mesh USS* 16 (G # 20). The surface profile of the panel was taken through surface profilometer Mitutoyo SURFTEST SJ.201P/M following the ISO standard. The surface profile parameters measured are given in **table I**. The prepared surface was washed with acetone to remove any oil, grease or contamination.

Paint Application

The epoxy based paint primary coat (Resin: Hardener = 3: 1) was applied on the surface by spraying technique. It was kept at room temperature for 15 min and then the top coat was similarly applied over the surface. The 120 hours curing time was given at room temperature. The dried paint film thickness was about 150-170 µm.

EIS Measurements

The electrochemical cell having an area 6.28cm^2 and 100cm deep polymethyl methacrylate (PMMA) cylinder was bounded to a painted metal substrate with a silicon adhesive. Graphite Rod was used as counter electrode and Saturated Calomel Electrode (SCE) as reference electrode, while the grit blasted painted panel served as working electrode. A representative cell for EIS measurement was similar, as shown in figure 1.

EIS measurement was carried out with the help of Gamry EIS 300 Potentiostat. The ac impedance measurements were performed at the open circuit potential (OCP) between SCE reference electrode and working electrode in artificial sea water (3.5% w/v NaCl) before each scan within a 50 seconds initial delay. The impedance measurements were performed at the OCP using a sine wave of 10 mV amplitude peak to peak. The frequency range was usually from 100 kHz down to 10 mHz. The impedance spectrum was analyzed with Echem Analyst version 5.30 to determine the operating parameters of the system.

Results & Discussion

Open Circuit Potential (OCP)

The OCP measurement is a simple additional tool that provides complementary information to EIS results regarding the corrosion undergone by the steel substrate after exposure to aggressive solutions. Figure 2 presents the OCP variation over time for the paint panel. The evolution of the curve trend was clearly related to the performance of paint film protectiveness. The initial OCP value was the representation of paint film protectiveness but the decrease in OCP value, shift of potential towards more negative values indicates a fast damage produced by an accelerated corrosion process due to the loss of adherence of the paint from substrate. The increasing trend (less –ve) may be due to the corrosion product layer formed at the paint /metal interface hence lowering the corrosion acceleration process.

EIS Data analysis

The EIS spectrums of painted panel after exposure to electrolyte are shown in figures 3 to 6. Initially the coating pore resistance was 10^9 Ohms and the EIS data was very scattered, which may be due to the initial barrier effect of coating. The increase in pore resistance and decrease in coating capacitance as a function constant Phase Element $(CPE)_c$ are shown in figures 7 & 8 respectively. Capacitors in EIS experiments often do not behave ideally because

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* USS - United States Standard Sieve screen size

of it may be due to surface roughness of working electrode, inhomogeneous reaction rates on a surface, varying thickness or composition of a coating. Instead of perfect capacitors, they act like a constant phase element (CEP) as defined by an equation.

$$\mathbf{CPE = 1/Z\ (2\pi f)^{\alpha}} \quad \text{----------} \quad \mathbf{(1)}$$

Where $0 < \boldsymbol{\alpha} < 1$ depends on phase angle. For an ideal capacitor the phase angle in bode plot is -90° and $\alpha = 1$**. [1-2]**

The presence of second time constant shown in the Bode and Nyquist plots just after 24 hrs of exposure suggested that the solution has penetrated through the defects caused by the coating porosity and not by the diffusion through the polymeric paint matrix (Figure 3). The coating may be damaged locally due to micro-porosity or cracks in its uniformity. From EIS data before 96 hrs showed the lower values of R_{pore}, were the conformation of this fact. Apparently, double layer capacitance at paint metal interface was responsible for the formation of second time constant. Double layer capacitance, C_{dl} can be related to the delamination of the coating and polarization resistance, R_p to the corrosion process **[3-5].** This variation may be observed in figure 9 & 10 respectively.

EIS has also been used to determine the amount of delamination of coating exposed to an electrolyte. The double layer capacitance is proportional to the area of the substrate exposed to the electrolyte i.e the delaminated area. This occurs after the electrolyte has penetrated through the coating to the substrate. The polarization resistance, R_p, also provide assistance to estimate delaminated area. The polarization resistance (charge transfer resistance) is inversely proportional to the corrosion rate which is, in turn, related to corroding area. **[6]**

After 96 hrs (figure 4) of exposure the third time constant appearing in the spectrum was due to on going corrosion process and formation of the corrosion product at the interface of coating. The corrosion product layer tends to grow, inhibited the further corrosion process. This may be evaluated from the increase of oxide film resistance R_{of} as presented in figure 11 and polarization resistance R_p as described earlier. The increase in corrosion product layer thickness is also directly proportional to oxide film resistance. Oxide film resistance was increased after 216 hrs of exposure in electrolyte as shown in fig 11 with the increase in the layer of corrosion product.. Also the increase in R_p is the direct indication of decrease in corrosion rate due to the formation of corrosion product layer at the interface according to equation 2.

$$\mathbf{Rp = d/kNA_p} \quad \text{----------} \quad \mathbf{(2)}$$

Where k is the solution conductivity ($W^{-1}cm^{-1}$), N the number of coating pores and A_p the mean pore area. Thus, the impedance increases when d increases. **[7]**

With 168 hrs of exposure the continuous corrosive reactions taking place at the interface developed a corrosion product layer which provided hindrance to further corrosion. Hence the EIS spectrum in figure 5 is showing the prominent development of third time constant defining the oxide film resistance and oxide film capacitance. As shown in figure 11 the oxide film resistance started to develop after 96hrs of exposure, initially the oxide film resistance was lower in the time span of 216 hrs and then increased to about 20.58 k-Ohms after 288 hrs. This was an indication of the slow corrosion reactions due to the formation of oxide film having high resistance.

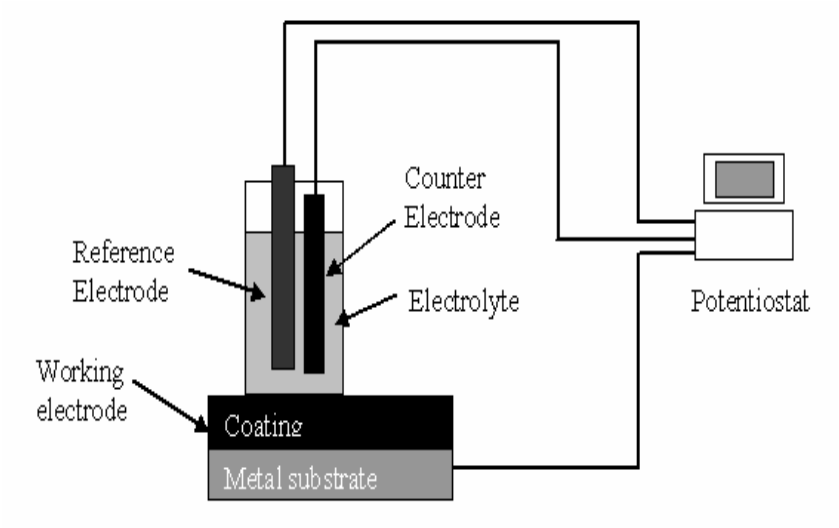


Figure .1 A representative EIS Cell

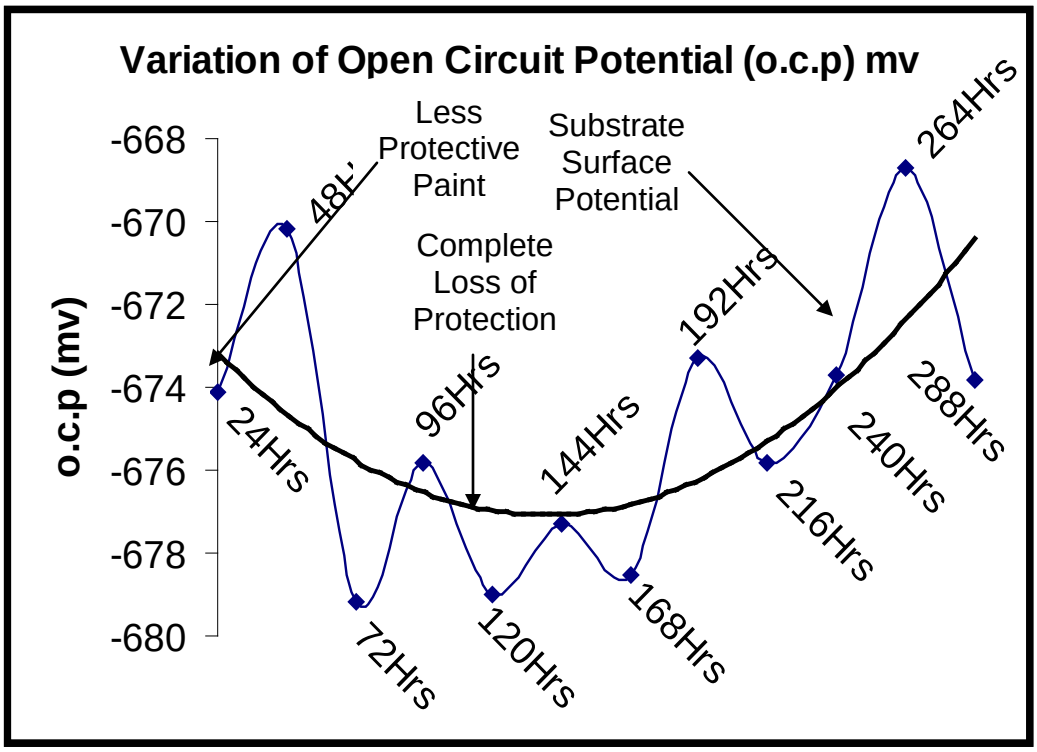
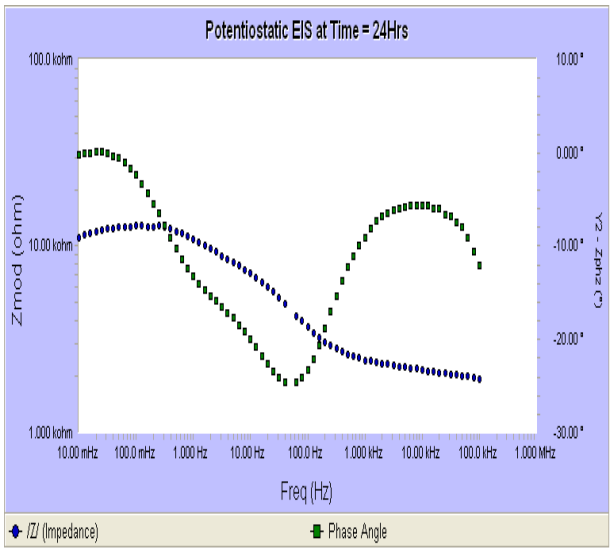


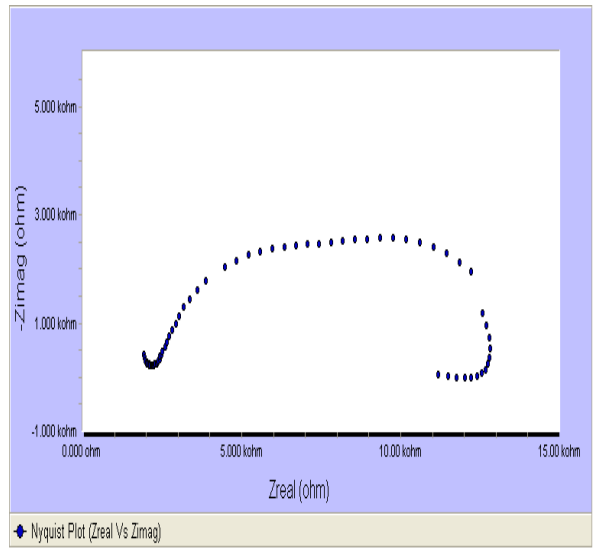
Figure .2 Variation of Open Circuit Potential (o.c.p) over time

Parameter	R_a(µm)	R_y(µm)	R_z(µm)	R_q(µm)	R_t(µm)	R_p(µm)	R_{pc}(µm)
(G-20)	12.41	0.000	32.96	4.46	48.11	11.82	113.03

Table -1 Surface Parameters of Grit blasted steel surface

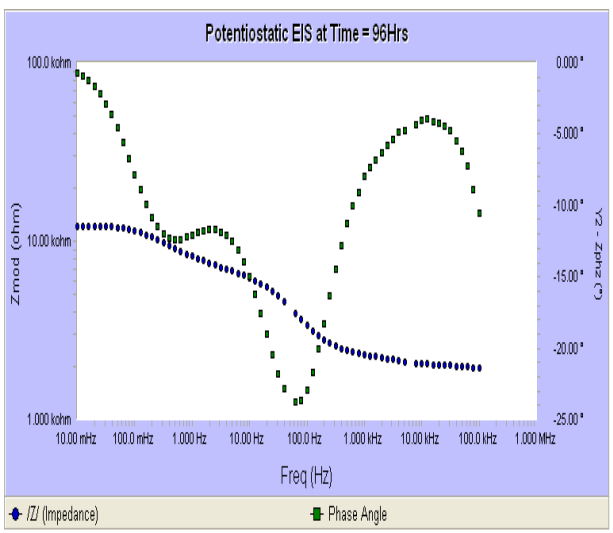


a) Bode Plot



b) Nyquist Plot

Figure 3 Time = 24Hrs: The spectrums showing two time constants, the higher frequency zone representing the Coating protectiveness behavior and lower frequency region of curve is the evidence of corrosion process.



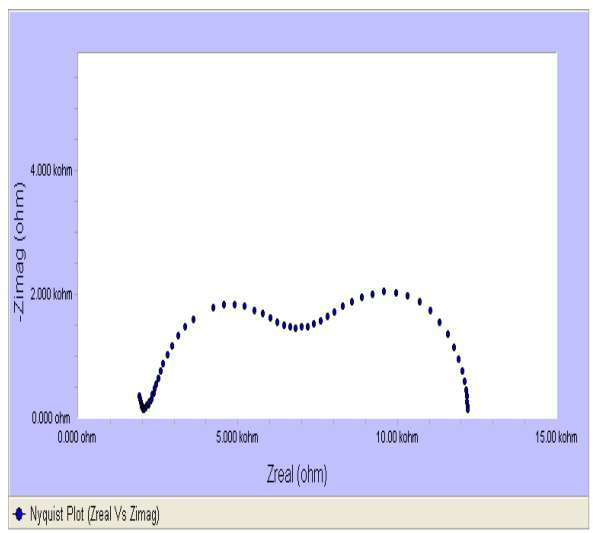


Figure 4 Time = 96Hrs: The spectrums showing the appearance of third time constant, which was the initiation of corrosion product formation at the Coating/Metal interface.

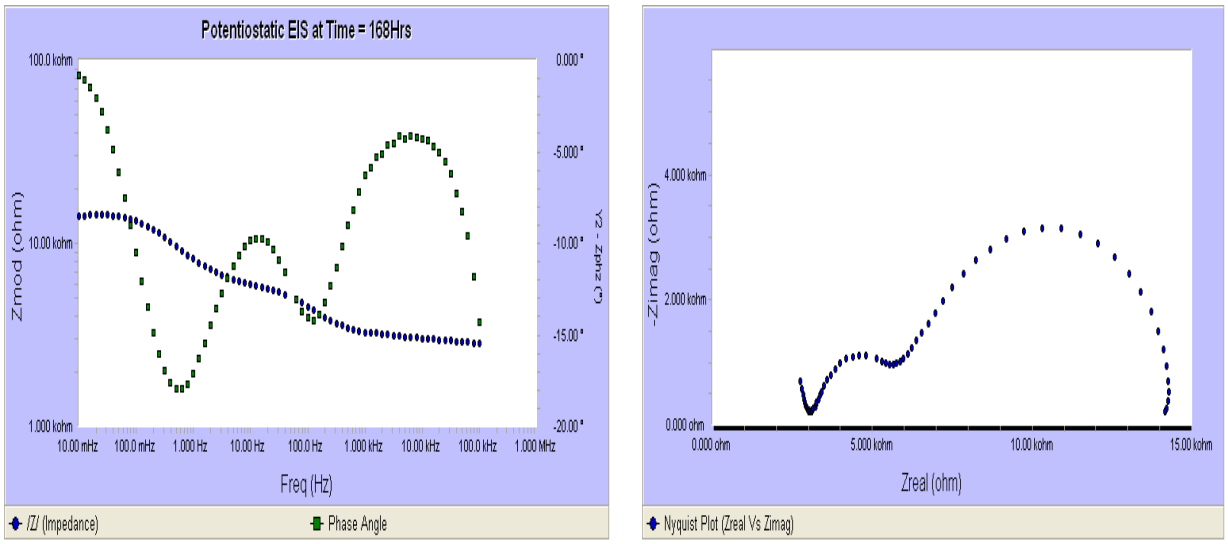


Figure 5 Time = 168Hrs: The third time constant is predicting the corrosion product layer at the Coating/Metal interface slowing down the further corrosion reactions as indicated by high polarization resistance, R_p value.

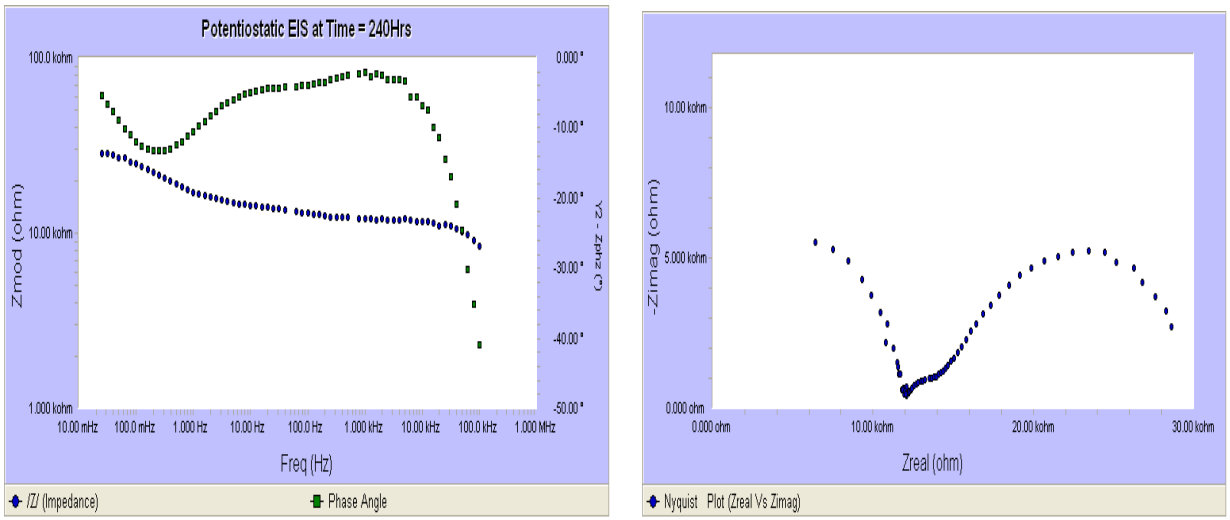


Figure 6 Time = 240Hrs: The spectrums showing the complete failure of coating protectiveness as the 1st time constant representing coating protective behavior is completely vanished from the curve and was similar to a rusted surface type behavior.

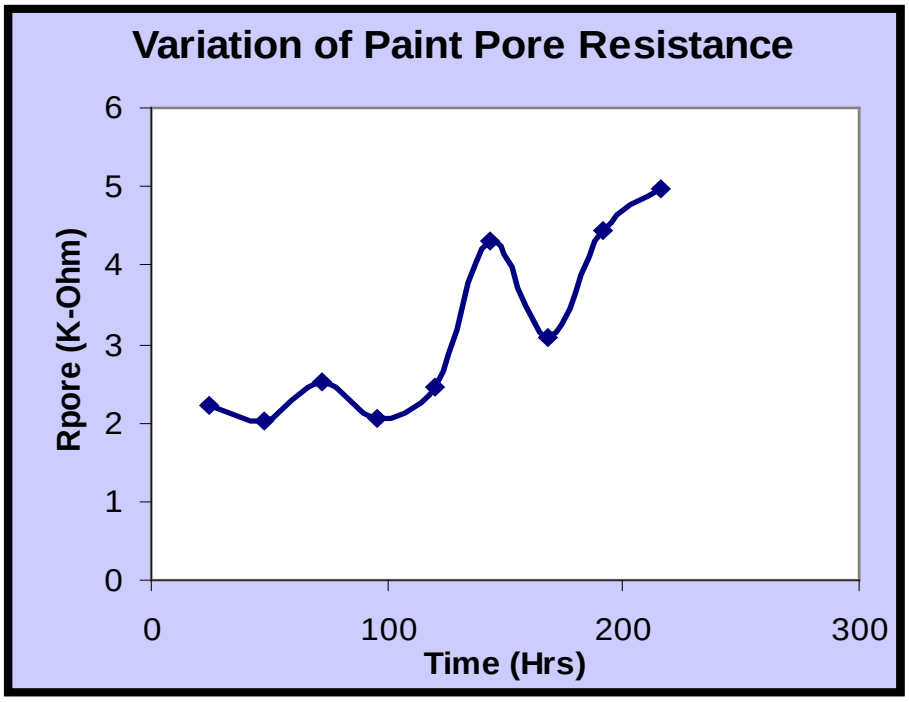


Figure 7 Pore Resistance; increasing trend

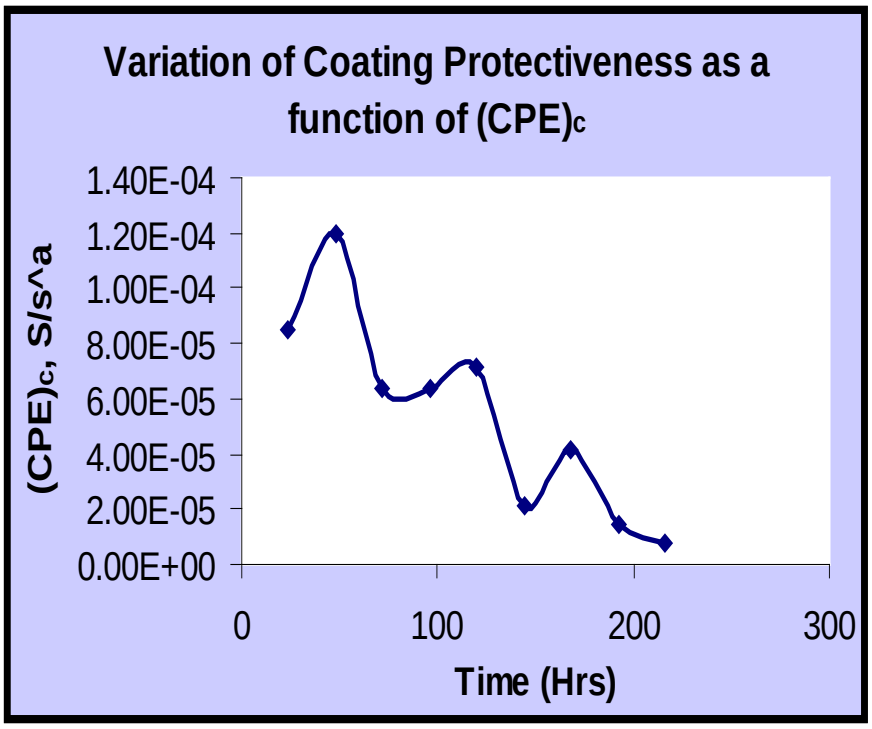


Figure 8 Coating Capacitance as a function of (CPE)c; Decreasing trend

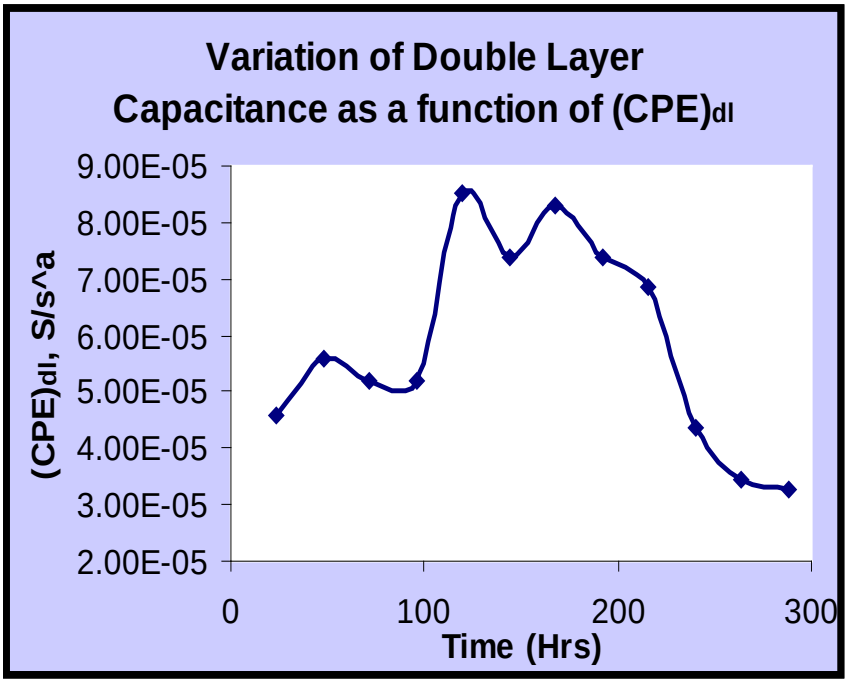


Figure 9 Double Layer Capacitance as a function of $(CPE)_{dl}$

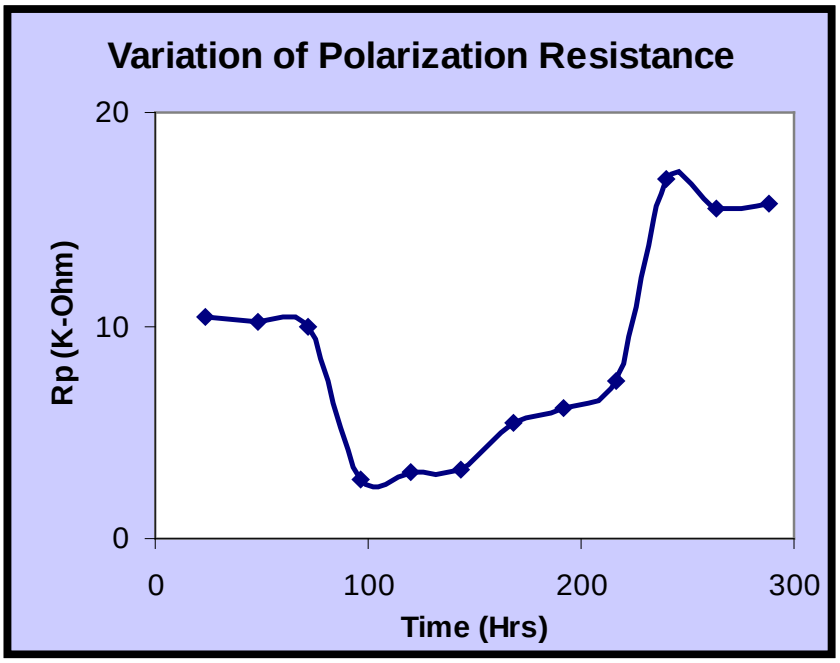


Figure 10 Variation of Polarization Resistance (R_p)

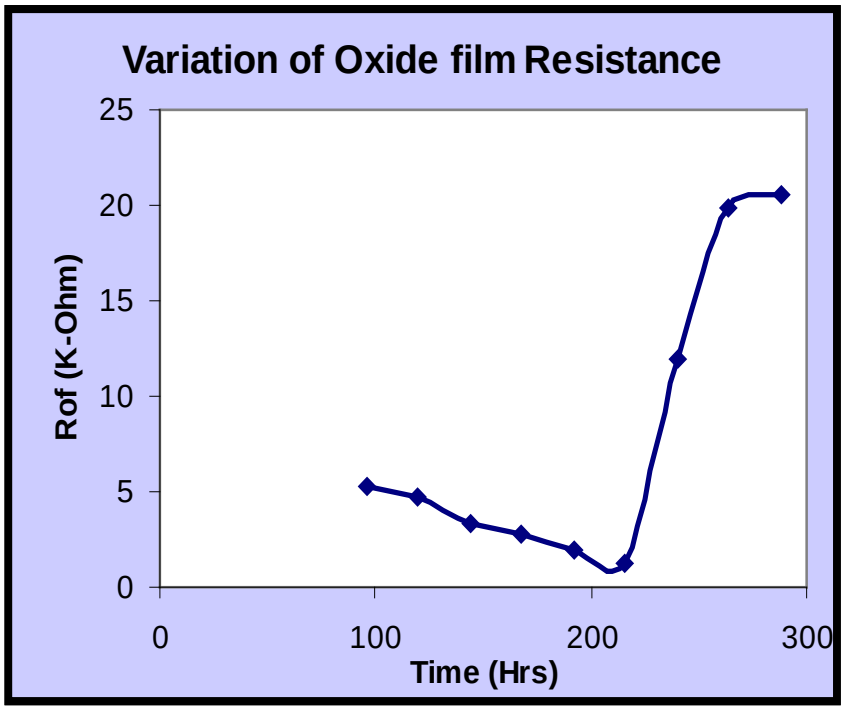


Figure 11 Variation of Oxide Film Resistance (R_{of})

Conclusion

In this work, the influence of the electrolyte (artificial sea water) on the Protective Efficiency of paint coating, when applied onto pretreated steel test panel was studied.

The anticorrosion Performance and the Electrochemical Properties of this coated test were evaluated by EIS & OCP (open circuit potential).

The following conclusions were drawn.

- The epoxy paint film exhibited poor protective performance after 24 hrs of exposure owing to the effect of micro pores or cracks within its uniformity.

- The anticorrosion performance of coating appraised by visual observations of the coated test panels, exposed to artificial sea water. This could be acknowledged as an excellent performance since no rusting, blistering or delaminate was observed during whole period of exposure.

- The corrosion product initiated underneath the coating may cause delamination but growth of this corrosion product film may decrease the further corrosion at the interface as observed in EIS spectrum after 168 hrs of exposure.

- After 288 hrs of exposure, the EIS spectrum showed the rusted surface like behavior. This indicates the complete failure of protective layer after this time period.

17 18 19 20

References

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