

## Comparative Anti-corrosion Studies of Polyaniline phosphate and Zinc phosphate in Alkyd Base Primer Paints

**V.Rajasekharan,**

Plant Laboratory Bharat Heavy Electrical Limited Tiruchirapalli-620014,  
Tamil Nadu, India

### ABSTRACT

The performance of organic coatings has been researched via electrochemical impedance spectroscopy and many other mechanical techniques. The advantages offered by impedance techniques to analyze different coatings and their corrosion resistance to salt spray test is at the centre of many practical and theoretical research papers. Current studies also detail the importance of impedance interpretation and modeling techniques which have been improved by numerous research groups. Data collected via impedance techniques can be analyzed by modeling the data on known equivalent circuits which can be used to electrically simulate the obtained results; normally these have two time constants, one representing the coated surface and another for the double layer capacitance. In aqueous media water penetration and absorption through a coating will ultimately affect the corrosion properties at the coating metal interface, it is clear that both of these processes are related.

**Keywords:** Polyaniline, Red oxide paint, Red oxide PANI paint, EIS technique, paint.

*Corresponding author:*

Phone: +914312512324,+91 9442502962

Email address: [vrsekar57@gmail.com](mailto:vrsekar57@gmail.com)([V.Rajasekharan](mailto:V.Rajasekharan))

### 1. Introduction:

It is apparent that there is a direct correlation between a paint coating exposed to saline atmosphere at high humidity of condensed water and the adhesion strength which declines considerably on exposure, due to swelling, delamination, corrosion processes, etc; but these effects will ultimately depend on the quality of the coating. Therefore it is possible to draw the conclusion that the corrosion resistance and adhesion of the coating is indirectly related to

corrosion processes which may be occurring at the metal surface. For an electrochemical reaction such as corrosion to take place, water, oxygen and an ionic current flowing between the anodic and cathodic sites is required. Organic substrates generally exhibit very low ionic conductivity, preventing corrosion phenomena by isolating the anodic and cathodic sites. However, there are two separate issues which can affect this, firstly, the presence of pores within the coating, leading to ions reaching the metallic surface through the pores. This process will ultimately lead to adhesion loss, in this instance a layer of water can form at the metal-polymer interface; the contribution of this layer with its corresponding ionic impurities can also lead to a close coupling of anodic and cathodic sites. In this instance the corrosion protection of the coating is effected dramatically.

Careful application of EIS technique[1] in conjunction with other methods of testing can be tremendous aid in quickly selecting good coatings and excluding bad ones. Salt spray testing in accordance to ASTM B 117-03, “Standard Practice for Operating Salt Spray (Fog) Apparatus” [9] or ASTM G 85-02E1, “Standard Practice for Modified Salt Spray (Fog) Testing” [10] is frequently used to measure the corrosion resistance properties of the coating in the presence of corrosive conditions containing chlorides[2-8]. Although salt spray testing accelerates the corrosion attack experienced on coated panels, it can take 5 to 7 days for visible signs of degradation to appear. Changes in the impedance spectrum appear well before such macroscopic degradation, as shown in the following case studies. These techniques are destructive and are used to evaluate the corrosion resistance of the coating but are not necessarily a direct measure of corrosion resistance, primarily providing qualitative information; EIS offers a viable non-destructive alternative to these techniques

## 2. Experimental details

Mild steel type of steel (70x50x0.5mm) was employed as metallic substrate with the chemical composition given in Table.1.1, was obtained commercially. For all electrochemical studies, mild steel specimens coated with red oxide paint with an exposed surface area of  $1.0 \text{ cm}^2$  were used as the working electrode. The specimens were carefully polished with sequence emery papers of various grades (400-800 grit), cleaned as St3 grade (Swedish standard SIS-05 59/00), degreased with ethanol, washed with double distilled water and finally dried in warm air. All the electrochemical experiments were performed in a 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. The electrolyte solution was 3.5% NaCl and all measurements were done at room temperature ( $20 \pm 2^\circ\text{C}$ ). All potentials are reported versus that of the SCE. All purchased chemicals were of analytical reagent grade (Merck) and were used without further purification and double-distilled water was used throughout. These plates are degreased with toluene and are coated with paints whose formulations are shown in Table.1.2. The paint was applied by brush and was dried at a constant temperature ( $25 \pm 2^\circ\text{C}$ ). The dry film thickness was measured by calibrated standard coating thickness gauge and the average value was between 25-27 micron thicknesses.

Table.1.1. The chemical compositions (wt %) of the working electrodes

Mild steel	C	Mn	S	P	Si	Cu	Fe
	0.253	0.729	0.023	0.018	0.202	0.12	Balance

Table.1.2.The chemical compositions (wt %) of the paints

SI No	Description	Paint-A % by mass	Paint-B % by mass
1	Iron oxide ( $\alpha$ Fe <sub>2</sub> O <sub>3</sub> )	50	50
2	Zinc phosphate	4	Nil
3	Volume concentration of the pigments	50	50
4	Poly aniline green polymer	Nil	1%

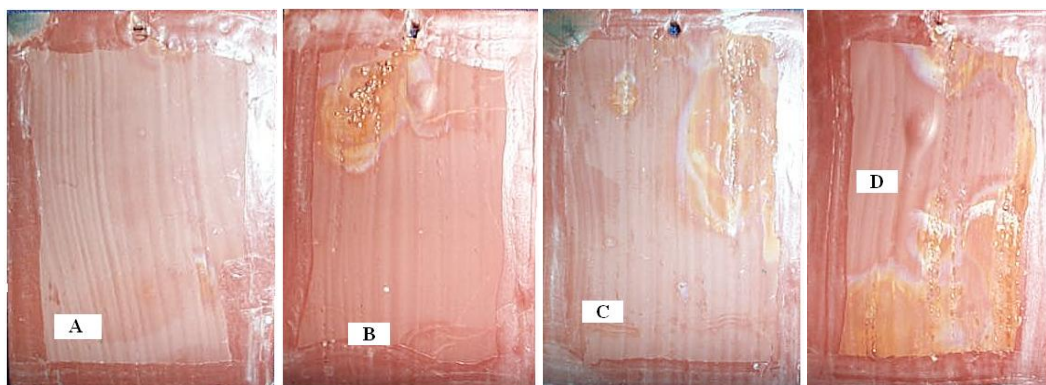


Fig.1.1. of Salt spray testing -exposed Paint-A 4%Zinc phosphate painted panels in accordance to ASTM B 117-03, “Standard Practice for Operating Salt Spray (Fog)” **A**=3days, **B**=5 days, **C**=7 days, **D**=12 days

According to ASTM D610-08 Standard practice for evaluating degree of rusting on painted steel structure the painted panel-B may be evaluated for degree of rusting as in Fig.6.2.

A= less than 1%, B= 10%, C= 16% and D=33% rust

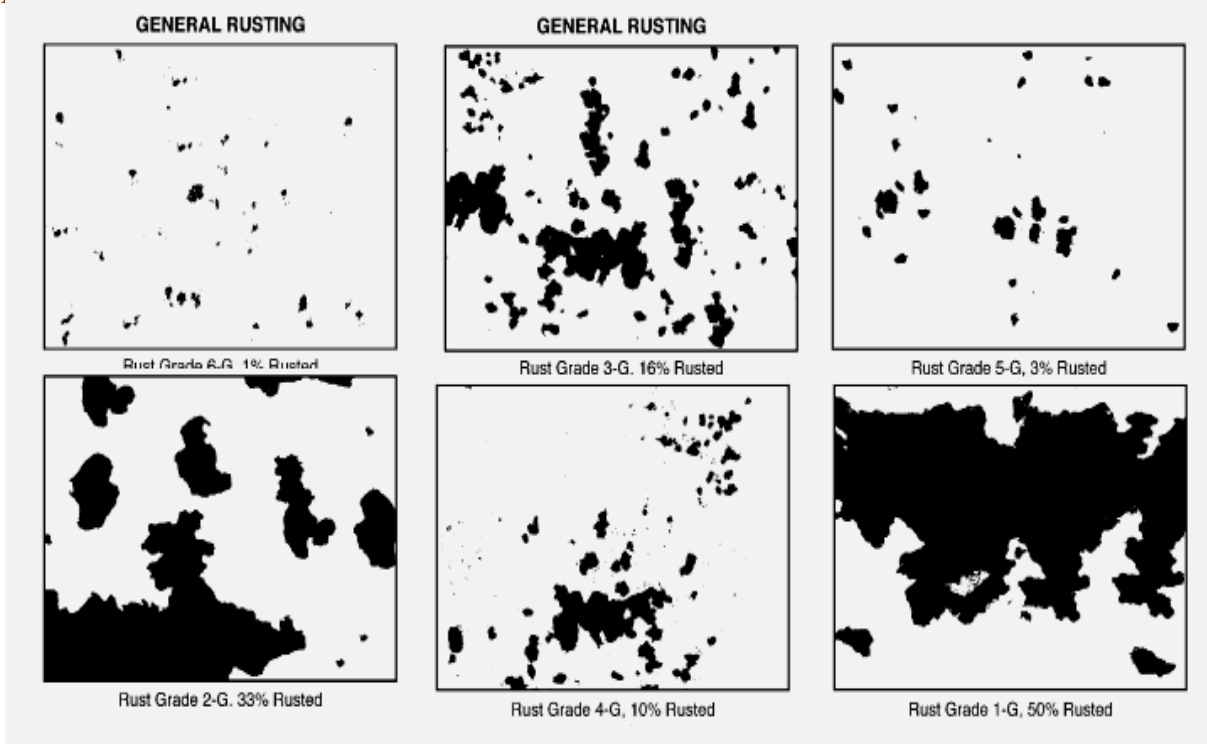


Fig.1.2. “Standard Practice for evaluating degree of rusting on painted steel surfaces”

### 3. Measurements using impedance techniques

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. A computer-controlled potentiostat (PARSTAT Model 2273) with software's powersuiteV.2.58 and the Z SimpWin 3.2 was used. All impedance experiments have been carried out at the frequencies from 100 kHz to 10 MHz. The real and imaginary components of the impedance spectra in the complex plane were analyzed using the ZSimp Win 3.2.1Ink software (Echem Software.) to estimate the parameters of the equivalent electrical models.

Electrochemical Impedance Spectroscopy techniques can be used to determine the quantity of water that has penetrated the coating, from this it is possible to gauge the solubility of

the coating. The data obtained from EIS measurements can be correlated directly to allow analysis of the following phenomena:

- Blister formation [11]
- Water permeation
- Swelling, of the coating
- Loss of adhesion, including delamination.
- Corrosion

The uptake of water in organic coatings can be determined directly from capacitance measurements. The dielectric constants of organic coatings are generally small, and hence it is normal for them to be an order of magnitude smaller than that of water which has a dielectric constant around 80 at ambient temperatures. For this reason the adsorption of a small amount of water can significantly affect the capacitance of the film. The capacitance [1] of the organic coating can be determined directly from the dielectric constant of the coating  $\epsilon$ , the dielectric constant of a vacuum  $\epsilon_0$ , the thickness,  $d$ , of the dielectric and the surface area  $A$ :

$$C = \epsilon \epsilon_0 \frac{A}{d}$$

From the immersion (or exposure) of the coating to water the penetration/adsorption process begins (see Fig.1.3) [12]. This leads to a rapid increase in the film capacitance - shown as phase-I, eventually it is normal for the coating to become saturated leading to a plateau where the capacitance remains constant phase -II. If, however there then follows a further increase in capacitance shown as phase- III, there has been further accumulation of water normally at the



polymer-metal interface indicating adhesion loss and the possible on-set of corrosion. The time period that elapses before the on-set of phase- III is normally related to the coating thickness, electrolyte conditions and strength of adhesion.

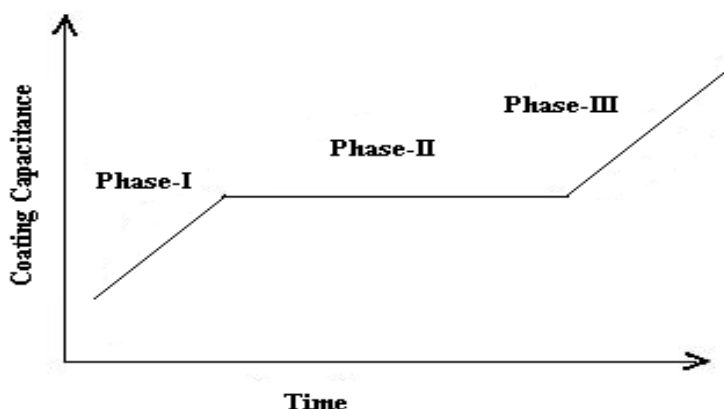


Fig.1.3. Capacitance variation in an organic coating as a function of salt fog exposure time

Low frequency data collected using EIS shows considerable sensitivity and variation to changes in the impedance/phase angle - due to the uptake of water. From the data collected below it is apparent that different coating thickness will affect dramatically the effectiveness of the coating to an aggressive environment. The data shows a series of five similar films of varying immersion time exposed to a saline solution. The Bode plot clearly shows that analysis of the low frequency part of the spectrum indicates which sample provides the most effective protection. The higher the impedance at low frequency the more effective the coating, for the samples with no visible corrosion / adhesion loss the impedance levels remain at around  $10^7$  ohms at 0.1Hz.

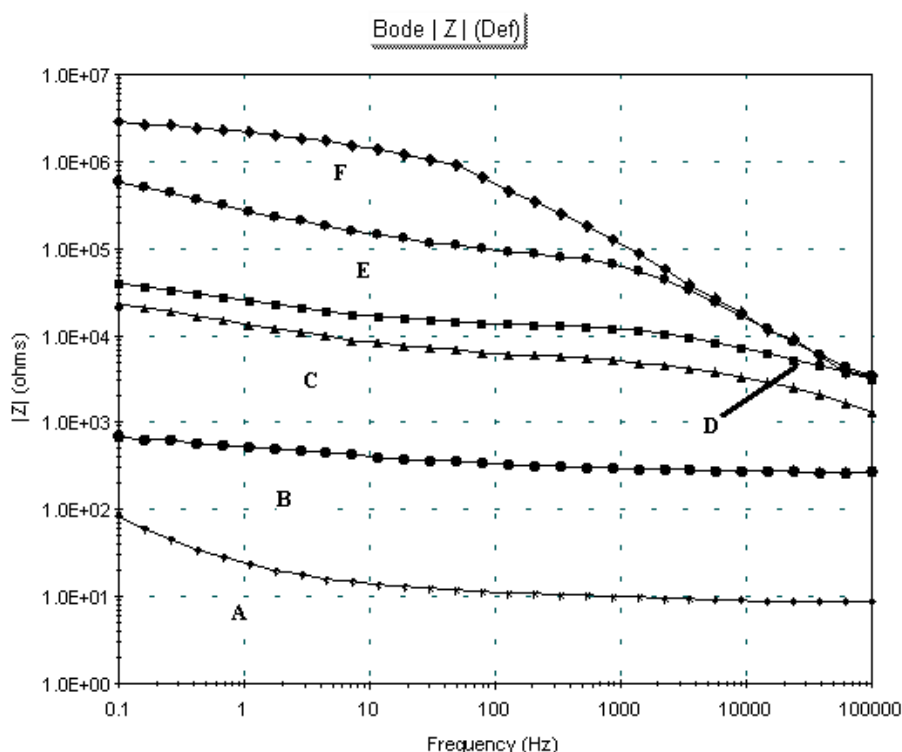


Fig.1.4. Bode diagram showing the difference in electrical properties between different salt spray test exposure times for 4% red oxide zinc phosphate primer paint

A=Bare metal, B=12 days, C=7 days, D=5 days, E=3 days, F=0 days

Equivalent circuit modeling [9] is a standard tool for the interpretation of impedance data. The circuits which are used to model this type of data are usually comprised of  $R_s$ , the electrolyte/solution resistance, followed by a coating capacitance  $C_c$  in parallel with  $R_p$ , the pore resistance. An element called  $Z_w$  (diffusional element) is also included to represent the electrochemical processes taking place at the coating-metal interface. This element  $Z_w$  is often represented as  $C_{dl}$  (the double layer capacitance) in parallel with  $R_{ct}$  (charge transfer resistance) in corroding coated metals. This particular model is extremely popular as it is suitable for many different systems where there is macro coating defects. The coating capacitance  $C_c$  is usually



plotted as a function of the immersion time in solution, as previously discussed. The value of the coating capacitance increases with the uptake of water into the coating. The double layer capacitance  $C_{dl}$  represents the wet area under the coating, which is the area in contact with the electrolyte. It is primarily effected by surface roughness, surface oxidation, accurate measurement of this parameter is easily performed using EIS giving an indication of any delamination which is taking place The pore resistance  $R_p$  relates to the diffusion of electrolyte through the organic coating via the pore, which can affect the barrier properties of the coating; the parameter  $R_p$  is the ionic resistance of the coating which is inversely proportional to the area of surface defects (pores).

#### 4. EIS Parameters

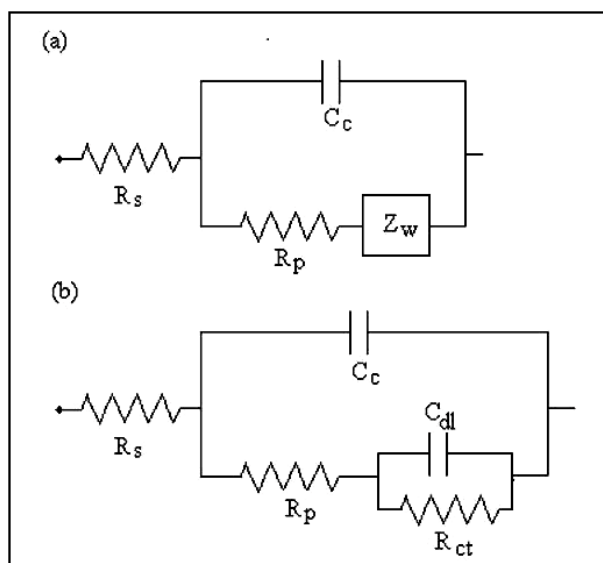


Fig.1.5. Standard equivalent circuit models for coated metals (a) Representing no corrosion,(b) representing a corroding coated metal

$Z_{0.1\text{Hz}}$  is total coating impedance ( $\Omega\text{cm}^2$ ) at an applied signal frequency of 0.1 Hz.  $Z_{0.1\text{Hz}}$  is a good general indicator of the protective capacity of the coating, with higher numbers indicating superior protection. In general, coatings with  $Z_{0.1\text{Hz}} > 10^8 \Omega\text{cm}^2$  are considered excellent

providers of protection and coatings with  $Z_{0.1\text{Hz}} < 10^6 \Omega\text{cm}^2$  are considered poor providers of protection.

**$R_s$**  is the resistance of the test solution.

**$C_c$**  is the coating capacitance ( $\text{F}/\text{cm}^2$ ) produced by the dielectric properties of the coating.  $C_c$  is related to the dielectric strength of the coating and the water absorption by the coating, with higher values indicating higher dielectric strength or higher water content.

**$R_p$**  is the electrical resistance ( $\Omega\text{cm}^2$ ) to current traveling through the pore network in the coating. Higher values indicate higher resistance to penetration of corrosive species

**$R_{ct}$**  is the polarization resistance ( $\Omega\text{cm}^2$ ) of the steel substrate to corrosion (inversely related to corrosion rate of the substrate). Higher values indicate lower rates of corrosion.

**$C_{dl}$**  is the capacitance in  $\text{F}/\text{cm}^2$  produced by the electric double layer at the water/ substrate interface. A measurable  $C_{dl}$  value indicates that water is present at the substrate. Higher values of  $C_{dl}$  indicate a greater wetted area of substrate.

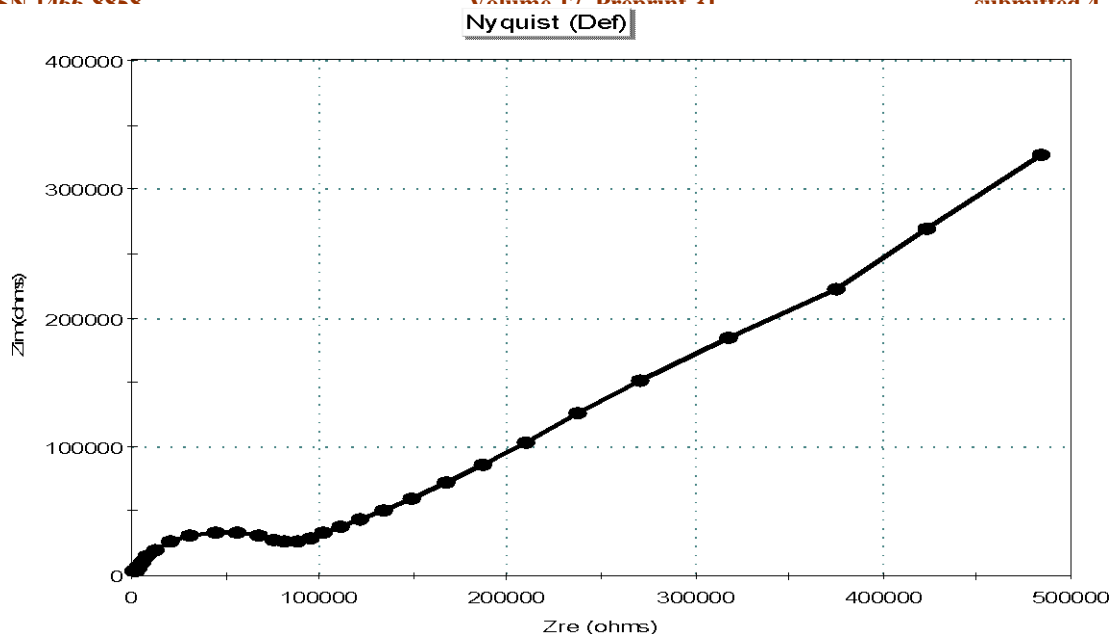


Fig.1.6. Nyquist plot for unexposed 4% Zinc phosphate red oxide alkyd base primer paint coated metals representing non corroded coating

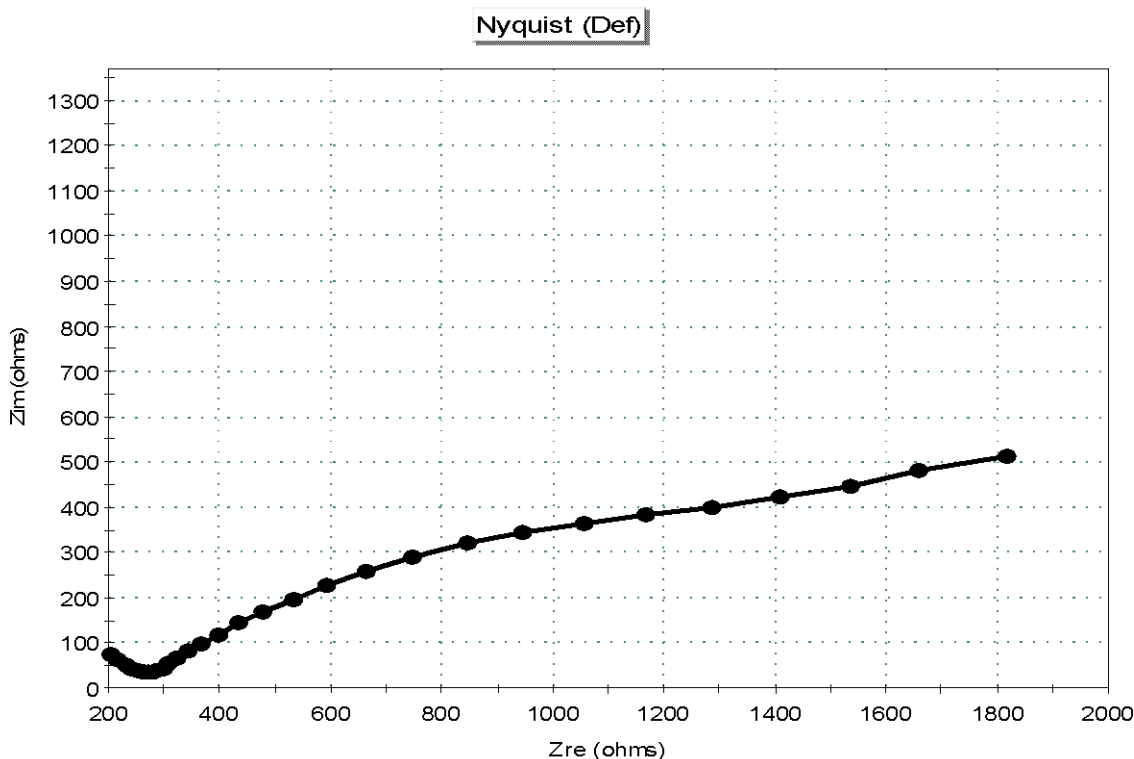


Fig 1.7. Nyquist plot for 3 days exposed 4% Zinc phosphate red oxide alkyd base primer paint coated metals representing a corroding coated metal (10% rust)

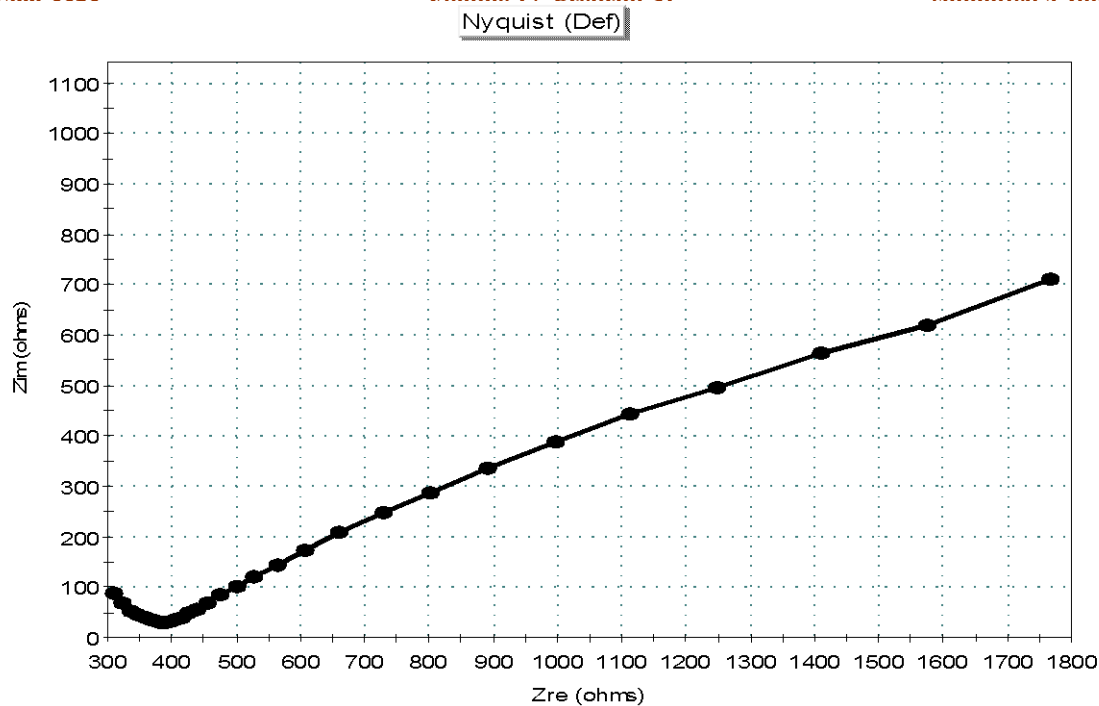


Fig.1.8. Nyquist plot for 3 days exposed 4% Zinc phosphate red oxide alkyd base primer paint coated metals representing a corroding coated metal (16% rust)

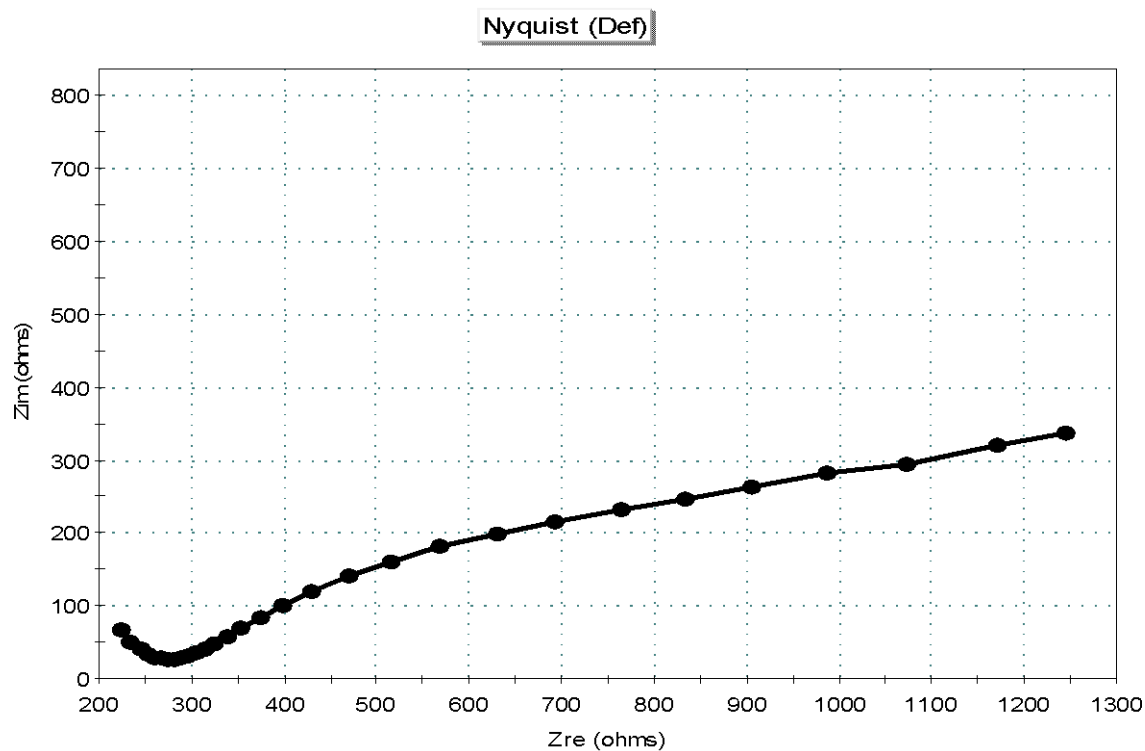


Fig.1.9. Nyquist plot for 7 days exposed 4% Zinc phosphate red oxide alkyd base primer paint coated metals representing a corroding coated metal (33% rust)

Table.1.3. The salt fog exposure parameters for 4% Zinc phosphate red oxide alkyd base primer paint

Exposure Days	Cc	Rpore	Cdl	Rct
3	3.26E-05	9.20E+04	8.99E-07	2.00E+05
5	3.96E-04	8.99E+01	7.67E-03	1.37E+04
7	4.85E-03	4.49E+00	8.49E-02	7.99E+02
12	5.28E-02	7.28E-01	4.03E-01	3.46E+02

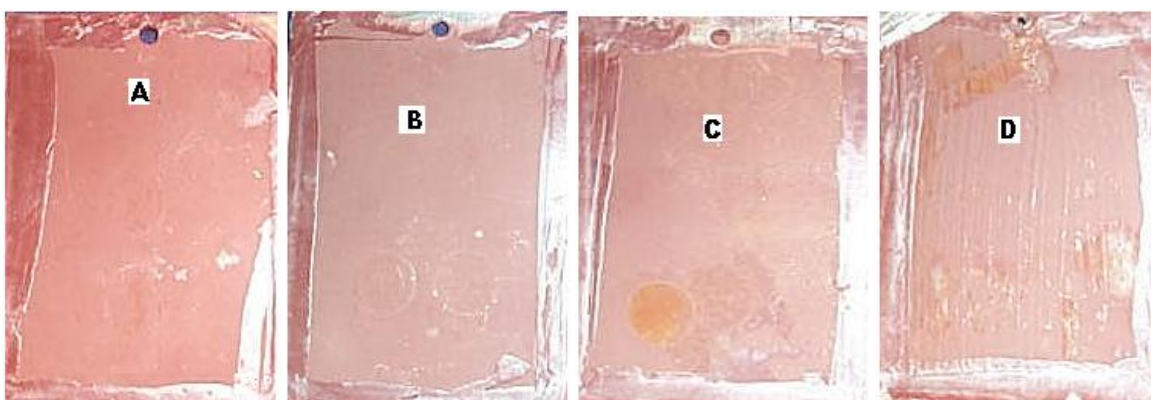


Fig.1.10. of Salt spray testing -exposed Paint-B-1%aniline green polymer painted panels in accordance to ASTM B 117-03, “Standard Practice for Operating Salt Spray. A= less than 1%, B= less than 1%, C= less than 1%, and D= less than 1%, A=3 days, B=5 days, C=7 days, D=12 days

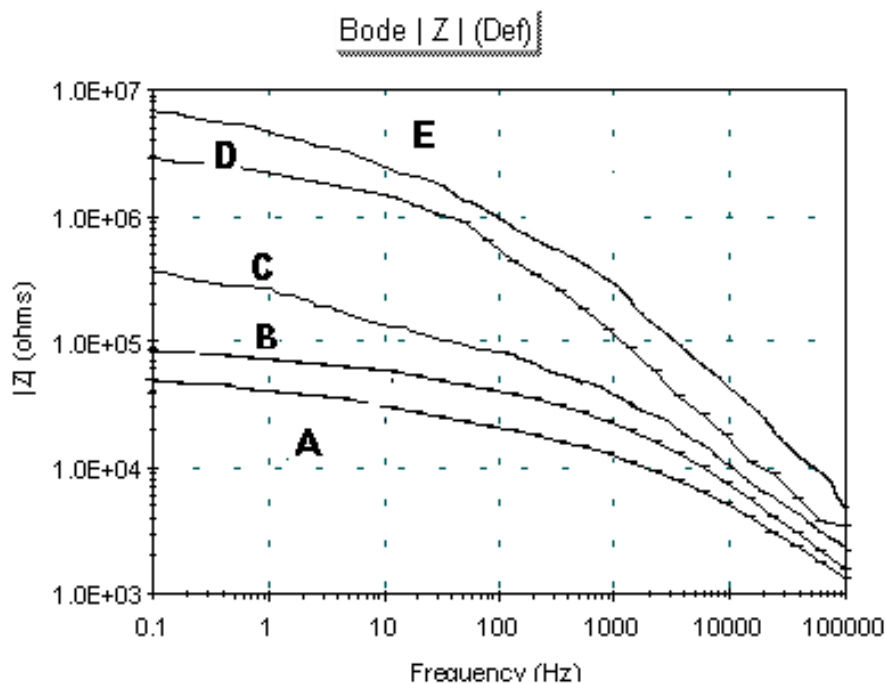


Fig.1.11. Bode diagram showing the difference in electrical properties between different salt spray test exposure time for 1% Aniline green conducting polymer red oxide primer paint, A=12 days, B=7 days, C=5 days, D=3 days, E=0 days

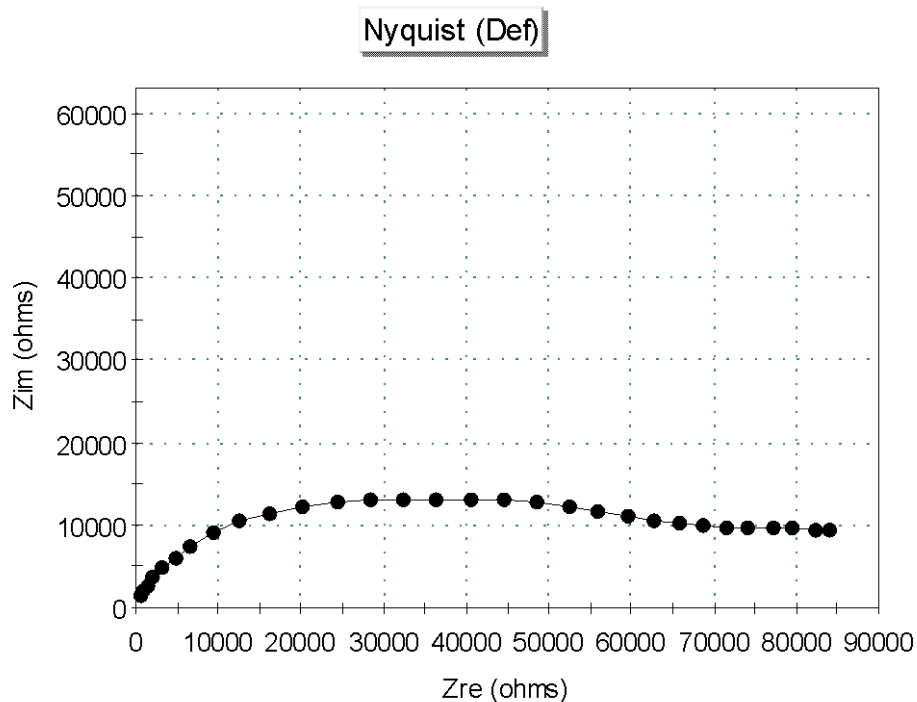


Fig.1.12. Nyquist plot for unexposed for 3 days 1% Aniline green polymer red oxide primer



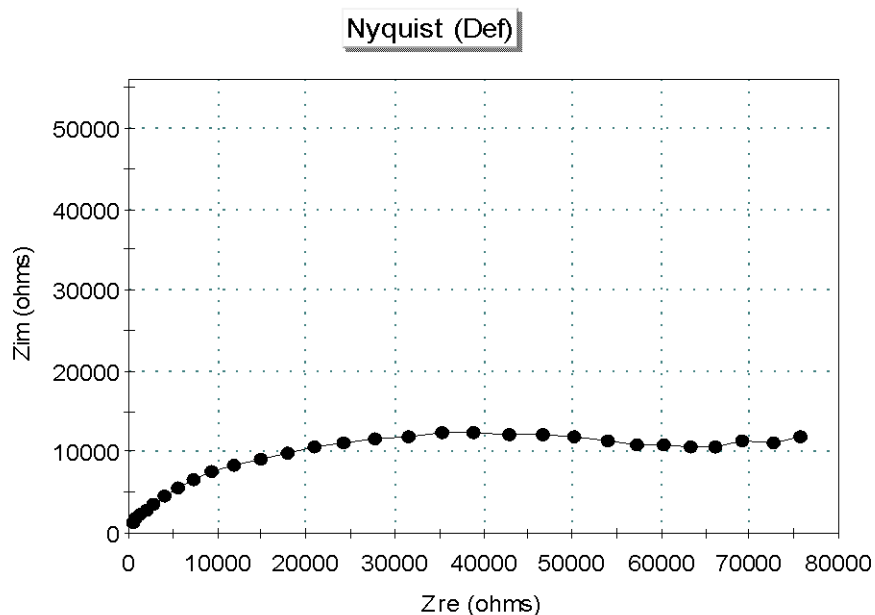


Fig.1.13. Nyquist plot for exposed for 5 days 1% Aniline green polymer red oxide primer paint coated metals representing 1% corroded coating

Table.1.4. The salt fog exposure parameters for 1% poly aniline green polymer red oxide alkyd base primer paint

Exposure Days	Cc	Rpore	Cdl	Rct
3	2.36E-06	3.44E+08	8.22E-08	3.11E+10
5	2.63E-06	6.77E+07	7.80E-08	1.69E+08
7	2.13E-06	4.47E+06	2.45E-06	2.73E+07
12	1.50E-05	1.63E+06	1.16E-06	9.63E+06

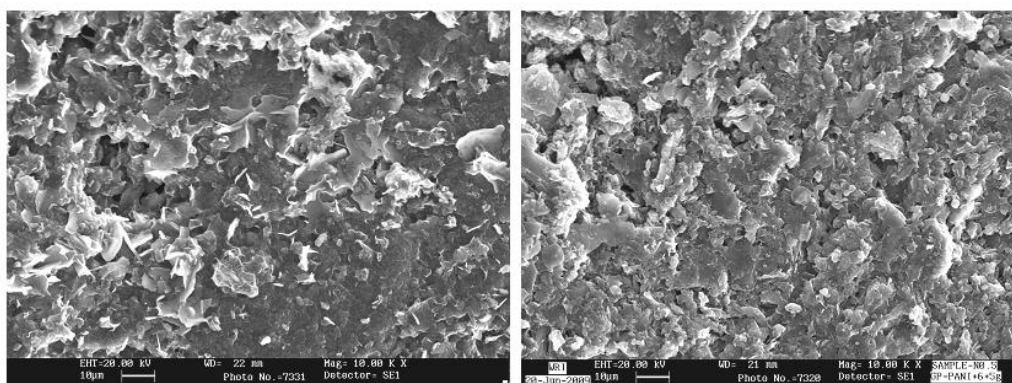


Fig.1.14. SEM photograph of poly aniline green polymer

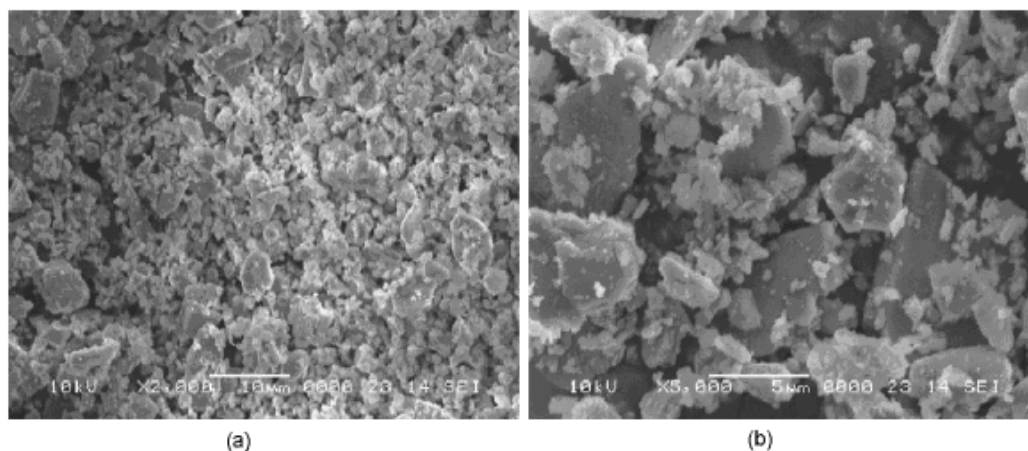


Fig.1.14A SEM images of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  particles at magnifications (a)2000 and (b) 5000

## 5. Discussion

### 5.1. 4% Zinc phosphate red oxide alkyd base primer paint

The 4% Zinc phosphate red oxide alkyd base primer paint (48 h cure) samples showed very poor results during exposure to salt spray test with time.  $R_{\text{pore}}$  values were marginal. The  $R_{\text{pore}}$  and  $C_{\text{dl}}$  values indicated that water was present in the coating and at the substrate

The samples also showed a rapid decrease in protective capacity, with increasing exposure time from 3 days to 12 days as evidenced by large decreases in the  $Z_{0.1\text{Hz}}$ ,  $R_{\text{pore}}$ , and  $R_{\text{ct}}$  values. The decreases indicated water penetration through the pore network to the substrate, with increasing corrosion and large increases in the  $C_{\text{coat}}$  and  $\text{CDL}$  values. The latter indicated water absorption by the coating and its micro-blistering as it detached from the substrate.

### 5.2. 1% Green polyaniline polymer based red oxide alkyd base primer paint

The 1% polyaniline green polymer red oxide primer paint coated metals samples (48 h cure) showed aging behavior typical of a good-quality protective coating. The  $Z_{0.1\text{Hz}}$  ( $R_{\text{ct}}$ )

value decreased slowly with increased exposure time. The Ccoat value slowly increased with time, indicating increasing water absorption. The Rpore value decreased slightly and the Cdl value increased slightly; these changes indicated small increases in corrosion and pore filling at the metal substrate indicating a slow degradation with increasing exposure.

## 6. Conclusion

The salt spray test of log oil alkyd red oxide paint coatings discussed in this study (with zinc phosphate and green polyaniline conducting polymer as corrosion inhibitors) were expected to imbibe water in very different ways. Despite the fact that both were deemed suited for corrosion protection of steel, the question was: which corrosion inhibitor will withstand water uptake prove deleterious to the coating performance and thus undermine the projected in-service life expectancy of the coating.

Imbided water can be absorbed in free-volume elements of polymer segments, condensed in globular clusters at the polymer-substrate interface, or hydrogen-bonded to polar groups on the polymer. Irrespective of the microenvironment for the water in the polymeric matrix, water had a negative impact on coating performance for the alkyd chain.

For the long term protection however Murray [20] found the alkyd coatings to start dropping down after approximately one year. These coatings can show reasonable results but since the protective ingredients are consumed during corrosion protection the protection is limited, but using green conducting polyaniline as corrosion inhibitor, we can extend the life of the coating.

The current experimental data demonstrates that the EIS study for alkyd base primer

paint will indicate, if under certain environmental conditions, the paint is satisfactory if the coating resistance,  $Z_{0.1\text{Hz}} (R_{ct})$  values  $> 10^7$  and  $C_c$  value  $< 10^{-6}$  and the visual values of corrosion ( $< 1\%$ ). The test also will be useful for predicting the behavior of coating in corrosive atmosphere, which will be a quick method to assess the quality of paint

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