

Protective properties of multilayer coatings containing inhibitive primer

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ABSTRACT

The protective properties of multilayer coatings on mild steel substrate were evaluated in 3% NaCl solution at ambient temperature (21oC) and 50oC using the electrochemical impedance spectroscopy technique. In this work the investigation was performed on coated panels mostly at 50oC with data also taken at elevated temperature to understand better in terms of protection mechanism given by multilayer coatings with inhibitive primer to the metal substrate. Result obtained from this work show those multilayer coatings at 21oC exhibit excellent protective properties even after prolonged immersion in sodium chloride solution up to ten months duration. At elevated temperatures, impedance changes with temperature whereby at 50oC low impedance was observed. However, upon cooling to ambient temperature the impedance value increases by about two orders of magnitude which indicates that low impedance at 50oC is not really a good indicator of coating condition. Elevated temperature test was also unable to distinguish this multilayer coating resistance from charge transfer resistance but there is a high possibility that the high resistance is related to the charge transfer resistance.

Keywords:

Organic coating, Electrochemical impedance spectroscopy, Thermal testing, Inhibitive pigments, Zinc phosphate pigmented

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1. Introduction

In the field, multilayer coatings are generally used for corrosion protection. Multilayer coatings often have a thickness more than 250µm and a typical stacking sequence would consist of a metal substrate, primer, intermediate and top coat layers as shown in Fig. 1. The primer layer may provide inhibition or provide galvanic protection, while the intermediate may provide barrier protection. The top coats normally provide the gloss, colour and UV protection.

The most effective inhibitor is one that works well in a wide range of environments. Pigment solubility and pH are important factors in the corrosion inhibiting process. In addition, the amount of

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soluble inhibiting species should be in sufficient concentrations to inhibit the corrosion process [1]. Among the different kinds of inhibitive pigment, red lead and zinc chromate were historically the best for steel due to their excellent anti-corrosion resistance. However, both of them are highly toxic and not environmentally-friendly. Thus, on-going research is still being carried out globally to find non-toxic and environmentally-friendly pigments which are as good as chromate pigments. At present, of the available non-toxic and environmentally friendly pigments, zinc phosphate is the most frequently used anti-corrosive pigment for steel [2-4].

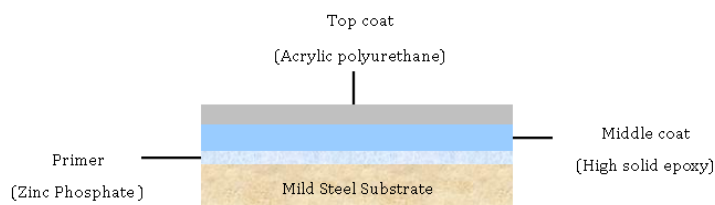


Fig. 1. Schematic diagram of a multilayer coatings consisting of primer, middle and top coating [23]

Generally, zinc phosphate gives good protective performance in industrial environments due to its high solubility in acidic media [5]. The protection offered by zinc phosphate on steel is said to rely on the formation of an iron oxyhydroxides film that passivates the steel surface [6, 7]. The mechanism of protection would also involve polarization of the cathodic areas due to precipitation of basic insoluble salts on the steel surface [6, 8]. Ghaffari et. al. observed an improved corrosion protection and adhesion strength for coated metal with zinc phosphate and suggested that they were connected to the deposition of a protective layer at the coating metal interface which might limit active zones for electrochemical reactions [9].

Contradictory results were reported regarding the performance of zinc phosphate as an anticorrosion pigment when exposed to accelerated tests [3, 10]. Samples in an accelerated test show a very much lower corrosion protection than in field tests. Some suggested that this is due to the low solubility and a coarse crystallinity of the zinc phosphate [11, 12]. Gimeno et. al. compared anti-corrosion performance for alkyd coating with zinc phosphate using neutral salt spray test and accelerated cyclic electrochemical test which showed good correlation between the two methods. They observed higher polarisation resistance for coated metal with zinc phosphate [25]. Romagnoli and Vetere [13] observed that the penetration rate of aggressive ions is increased in an accelerated test, but not the solubility of zinc phosphate. This resulted in unbalanced protection as more ions penetrate into the coating but the protective capacity of both the phosphate anion and the iron oxide layer on the metal substrate remained unchanged. Some authors maintain that zinc phosphate increases barrier properties of organic coatings [11], while others disagreed [14].

Thermal effects on coating properties as well as the reaction involved at the coating/metal interface must be taken into account when considering the performance of the organic coating. Bierwagen et al. [15] investigated the acceleration of coating failure by high temperature and suggested that an increase in temperature increases the rate of diffusion of the electrolyte into the coating. This reduced the barrier properties of the coating and enhanced the chemical and physical ageing effect from attack by the electrolyte. Work by Rezaei et al. [16] on polyurethane coatings exposed at two different temperatures (25°C and 75°C) showed that the higher temperature without the presence of ions has a considerable impact on the reduction of coating performance. The impact on coating resistance is more severe, as their test results show that the presence of ions reduces the service life of the coating and higher temperature accelerates the degradation process. Oliveira and Ferreira [17] reported that high temperature testing only affects the transport phenomena of active

species through the paint coating and does not introduce forms and mechanisms of degradation different from those that occur at room temperature. Li et al. [18] have shown that the barrier properties of the organic coatings are remarkably affected by high temperatures or thermal cycling. Coatings become more permeable and less protective which facilitates the transportation of the permeating species through the coating films. In return this initiates corrosion at the coating/metal interface.

This paper reports on experimental investigation on the use of electrochemical impedance spectroscopy for multilayer coatings exposed at ambient (21°C) and high temperatures (50°C). Test at elevated temperatures were also carried out to determine whether there is a link between multilayer coating resistance containing inhibitive primer and the corrosion process at the interface between coating and metal substrate.

2. Experimental procedures

Multilayer coatings consisting of zinc-phosphate-pigmented 2-component epoxy primer (50 μm), a low-VOC high-solid high-build epoxy barrier coat pigmented with micaceous iron oxide (180 μm) and 2-component acrylic-urethane topcoat (60 μm) were tested. Coatings were applied to grit-blasted mild steel panel by air spraying. Exposure test were conducted by immersion of the coated panels in 3% NaCl solution at 50°C and compared with tests at ambient condition (21°C). All tests were conducted in duplicates. The impedance measurements using electrochemical impedance spectroscopy (EIS) were conducted at free corrosion potential using a Gill AC computer controlled potentiostat, using 20 mV sine amplitude and a frequency range from 0.1 Hz to 30 kHz at 21°C, 50°C and at intermediate temperatures down to ambient temperature. After the coated panels had been tested, it was put back into the hot water bath and kept constant at 50°C until the time for the next measurement. The electrochemical measurements were made using a three-electrode cell with a vertical working electrode of area of 40 cm². The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum electrode with an area of 9 cm². The EIS spectra from attached films were analyzed using non-linear least squares fitting (with ZSimWin 2.0) to a R[Q[R[QR]]] model circuit.

3. Results and discussion

Figure 2 shows result for tests in NaCl at 21°C for the multilayer coatings. Throughout the 30 days of immersion, the impedance modulus $|Z|$ at the low frequency limit displayed very high values ($>10^9$ ohm.cm²).

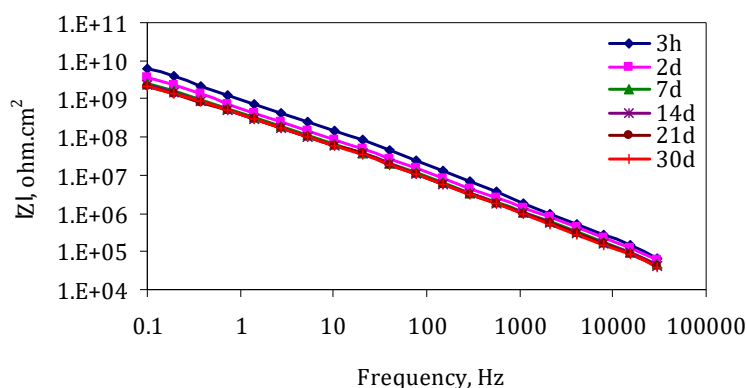


Fig. 2. Bode plot for multilayer coatings in 3% NaCl at 21°C after various periods

This kind of impedance response is characteristic of a coating system in very good condition [19]. Since a period of 30 days immersion show excellent protective properties, longer monitoring has been conducted where the coatings were exposed to 3% NaCl up to ten months period at room temperature and the result is shown in Fig. 3.

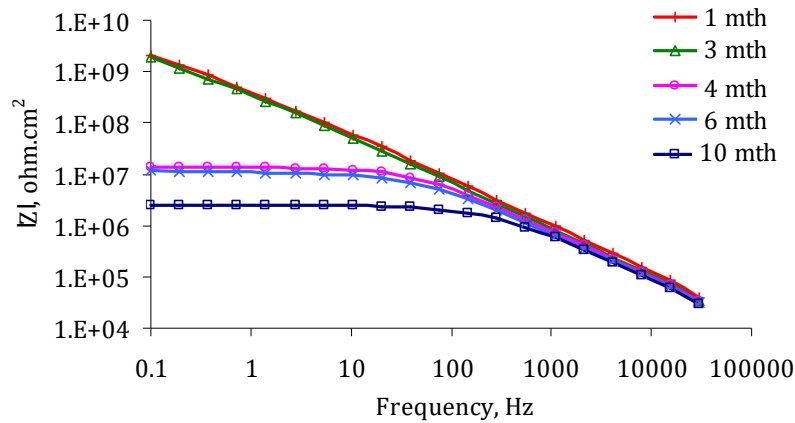


Fig. 3. Bode plot for multilayers coating in 3% NaCl at 21°C after various periods

The coating only starts to degrade after 4 month exposure as shown in Fig. 3 where the impedance modulus drop from 10^9ohm.cm^2 to 10^7ohm.cm^2 which motivates us to speed up the coating degradation process by exposing the coated panels in a solution at higher temperature. Fig. 4 shows result of multilayer coatings after various periods of exposure at 50°C. Degradation is very much faster at 50°C; the impedance drops from 10^8ohm.cm^2 down to 10^6ohm.cm^2 over a 30 days period. This indicates that the protective properties of coating system gradually decreased due to a faster degradation process upon exposure at higher temperature. Impedance spectra from Fig. 2 and 4 were then fitted with an equivalent circuit $R[Q[R[QR]]]$ to gain detail values on coating resistance.

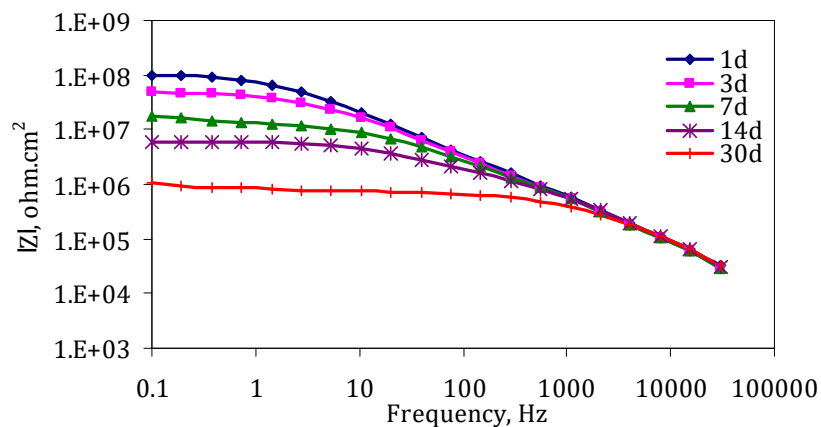


Fig. 4. Bode plot for multilayer coatings in 3% NaCl at 50°C after various periods

Figure 5 shows the evolution with time of coating resistances and open circuit potential (OCP) values for the multilayer coatings tested at 21 and 50°C. As expected, the values of coating resistance for coating exposed at 50°C drop faster than coating exposed at 21°C. The evolution with time of open circuit potential (OCP) as shown in Fig. 5b displays a good resemblance to Fig. 5a. For coating tested at 50°C, as the coating resistances drop, the OCP values also drop. According to Mahdavian

and Attar, OCP values drop when the surface becomes active or any passive layer start to break down thus the coating becomes more permeable to OH⁻ and Cl⁻ ions [12].

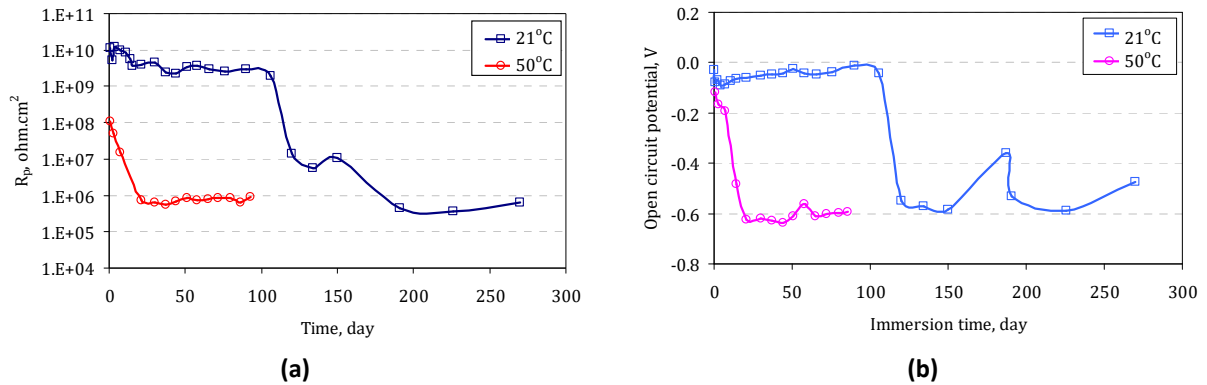


Fig. 5. Coating resistance (a) and OCP values (b) against immersion time for multilayer coatings in 3% NaCl at various temperatures

Figures 6 and 7 show the effect of temperature on impedance response of multilayer coating exposed in 3% NaCl solution after 14 and 180 days at 50°C. Nyquist plot shows an obvious influence of high temperature where a higher temperature generates a much smaller semi-circle size which indicates that lower impedance. However, no second semi-circle can be observed even after 6 months of immersion at 50°C.

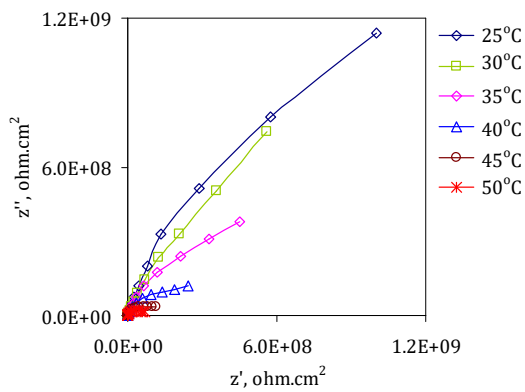


Fig. 6. Nyquist plot for multilayer coatings after 14 days at 50°C in 3% NaCl

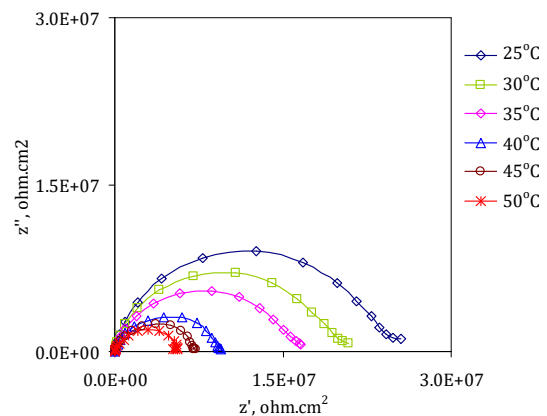


Fig. 7. Nyquist plots for multilayer coatings after 180 days at 50°C in 3% NaCl

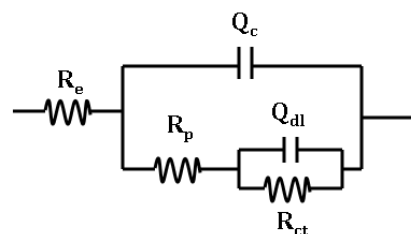


Fig. 8. Equivalent circuit (R[Q[R[QR]]) used for fitting [24]

Due to the absence of the second semi-circle, it is very difficult to distinguish whether the curves represent ionic diffusion through the coating or corrosion reaction at interface or both. Tamilselvi et.al also facing similar results whereby their semicircles are not well defined nevertheless they

relates this to frequency dispersion [26]. Impedance spectra from Fig. 6 and 7 were then fitted with an equivalent circuit (Fig. 8) and the fitted parameters are summarized in Tables 1 and 2.

Table 1

Parameters for multilayer coatings from fitting of EIS after 14 days at 50°C

T (°C)	Q_c (Ss ⁿ cm ⁻²)	n	R_p (Ωcm ²)	Q_{dl} (Ss ⁿ cm ⁻²)	n	R_{ct} (Ωcm ²)
25	1.30E-10	1	1.17E+06	6.97E-10	0.72	4.34E+09
30	1.39E-10	1	9.27E+05	1.17E-09	0.68	3.94E+09
35	1.42E-10	1	7.77E+05	1.37E-09	0.68	1.19E+09
40	1.56E-10	1	6.74E+05	1.94E-09	0.68	3.49E+08
45	1.88E-10	0.99	6.07E+05	2.11E-09	0.71	1.04E+08
50	1.75E-10	1	4.22E+05	2.84E-09	0.69	7.00E+07

Table 2

Parameters for multilayer coatings from fitting of EIS after 180 days at 50°C

T (°C)	Q_c (Ss ⁿ cm ⁻²)	n	R_p (Ωcm ²)	Q_{dl} (Ss ⁿ cm ⁻²)	n	R_{ct} (Ωcm ²)
25	5.09E-10	0.90	1.19E+07	2.19E-09	0.87	2.46E+07
30	5.82E-10	0.89	7.88E+06	1.95E-09	0.87	2.01E+07
35	6.65E-10	0.91	3.50E+06	1.48E-09	0.87	1.60E+07
40	7.67E-10	0.91	1.58E+06	1.59E-09	0.86	9.23E+06
45	7.96E-10	0.91	9.20E+05	1.62E-09	0.85	7.08E+06
50	1.35E-09	0.88	5.07E+05	1.96E-09	0.83	5.57E+06

According to Table 1, the coating resistances, R_p are about 10^5 – 10^6 ohm.cm² and this is unlikely as the coating tested here is a very thick coating (290 μm). On the other hand, the charge transfers resistance values, R_{ct} is very high (10^7 – 10^9 ohm.cm²). It can be suggested that the curve is being dominated by the charge transfer resistance that the coating resistance value is a small fraction but that seems unlikely. Plotting logarithm of charge transfer resistance, R_{ct} against $1/T$ may perhaps give some answers. Fig. 9 displays the Arrhenius plots in which activation energy is calculated by multiplying the slope by the gas constant.

As presented in Table 3, the activation energies calculated from ' R_{ct} ' are giving large values. From this study, only the larger resistance can be measured with certainty from the impedance spectra and it is uncertain whether it is the coating or corrosion reaction at the interface (only one semi-circle is presence in the impedance spectra). According to the work by Sharer and Sykes [20, 21], high activation energy was generated from the charge transfer resistance. So there is a possibility that since the activation energies generated in this test were high that the response of the impedance spectra is being dominated by the charge transfer resistance. High activation energies were generated from the high resistance value and this would be evidence that this high resistance is related to the charge transfer resistance. However, Ochs and Vogelsang [22] have shown increasing values of activation energy with coating thickness, based on values of 'coating resistance' of coated panels. As this study is unable to distinguish for certain between the coating and the corrosion at the interface, it is unable to test the link between them. Nevertheless, the activation energy generated from this test is larger than before and in agreement with Ochs and Vogelsang's [22] observation, but from this study we link the behaviour to the electrochemical process rather than to ion transport in the coating.

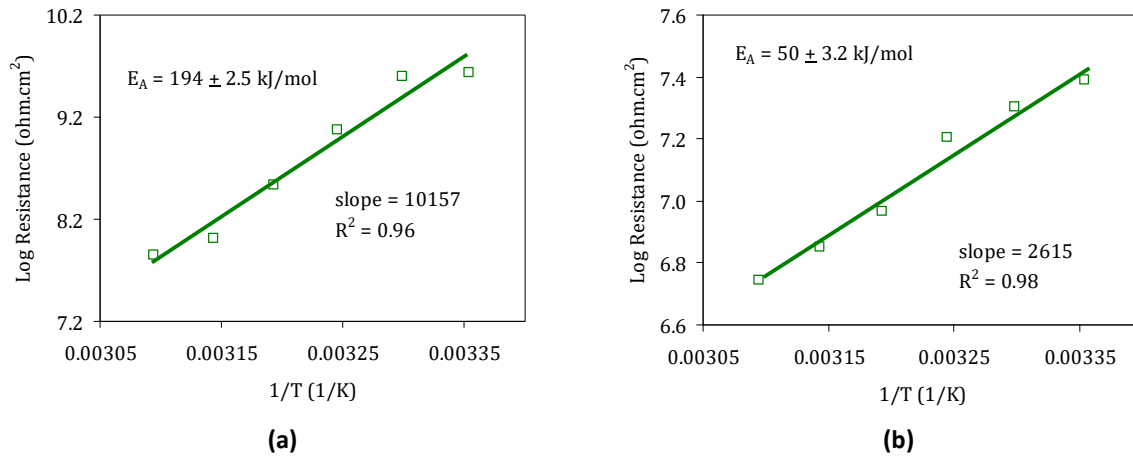


Fig. 9. Arrhenius plot of R_{ct} for multilayer coatings after (a) 14 days and (b) 180 days of exposure

Table 3

Summary of activation energy, E_A values, calculated from ' R_{ct} '

Time, day	7	14	30	46	70	180
E_A , kJmol ⁻¹	191	194	124	96	44	50
Error, ±	7.5	2.5	3.3	6.3	1.6	3.2

4. Conclusion

Coating resistances (R_p) determined from fitting of EIS, are about 10^5 – 10^6 ohm.cm² and this is unlikely as the coating tested here is very thick (290µm) which is expected to have larger coating resistance values (> 10^8 ohm.cm²). But high charge transfer resistance (R_{ct}) values were observed thus the activation energies determined from charge transfer resistance were used instead and gave large values (44–191 kJmol⁻¹). There is a possibility that since the activation energies from this work were high that the response of the impedance spectra is being dominated by the charge transfer resistance. However as only one semicircle is apparent in the impedance spectra, this work is unable to distinguish for certain between the coating and the corrosion at the interface; it is unable to test any link between them. But the activation energy generated from this work is reasonably high so we link the behaviour to the electrochemical process rather than to ion transport in the paint.

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