Evaluation of blistering performance of pigmented and unpigmented alkyd coatings using electrochemical impedance spectroscopy

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Abstract

The influence of pigment on the blistering behaviour of alkyd coating system was investigated using electrochemical impedance spectroscopy, salt spray, visual observation and adhesion techniques. The results showed that the pigment initially enhanced the migration of the environment promoting more number of blisters than the unpigmented system. Over a long period of exposure, however, the unpigmented system was found to be more susceptible to permeation of the environment.

Keywords: Alkyd coating, EIS, Salt spray testing

1. Introduction

Organic coating of metallic materials is one of the most widely employed methods to control corrosion. Good adhesion of the coating to the substrate and the resistance of the coating to permeation of water are the basic requirements to enhance the life of an organic coating. Phosphating of steel structures and pigmentation of the paints are the two important processes that enhance the overall performance of these coatings. In the development of newer paints, it is essential to understand how these two processes affect the coating performance vis-a-vis the mode of failures. In the present study three complementary techniques, viz. electrochemical impedance spectroscopy (EIS), salt spray and adhesion are used to study the nature of coating failures in pigmented and unpigmented conditions. Three different phosphating treatments were used to study the effect of pigment.

2. Experimental details

2.1. Materials and coating

Cold rolled steel panels of size 15 × 10 × 0.3 cm were used in the present study. The surface pre-treatment involved steps, viz. degreasing, water rinsing, derusting, water rinsing, surface activation, phosphating, water rinsing, passivation and oven drying for 10 min. at 110–120°C. The panels were dip phosphated. The temperature of the phosphating bath was kept in the range of 65–70°C and processing time was 3–5 min. Phosphate coatings I, II and III were zinc phosphates with different additives. The weight of the phosphate coatings was 3–5 g/m². The organic top coat used was alkyd system. The pigment part consisted of TiO₂ (anatase) of 0.2 μm sizes and other extenders. The pigment volume concentration was 24%. Application of organic coating was done by spray method. For the study, coating with thicknesses of 20, 40 and 60 μm in the case of unpigmented and 25, 50 and 75 μm in the case of pigmented alkyd coating were chosen. Pigmented and unpigmented coatings of identical thicknesses could not be taken, primarily because of the fact that coating thickness could not be controlled. However, comparison has been made by interpolation of the experimental data.

2.2. Electrochemical impedance

Impedance measurements were carried out after subjecting the samples for salt spray for various intervals of time as described in the subsequent paragraph. Immediately after each impedance test, the samples were...
reloaded in to the salt spray chamber and exposed to salt spray till the commencement of the next impedance experiment. A cylindrical acrylic cell, consisting of a 5% NaCl electrolyte solution (pH: 6.5–7.2; 35 ± 1 °C; freely exposed to air), a platinised platinum counter electrode with an effective area of 4850 cm² and a saturated calomel reference electrode, was used to carry out the impedance tests (Fig. 1). The area of the sample analyzed was 25.5 cm².

The impedance measurements were performed at open circuit potentials using a PAR 273 potentiostat and Schlumberger 1255 frequency response analyser driven by m388 software. Impedance measurements were carried out in the frequency range of 10⁻²–10⁵ Hz. The amplitude of the signal used was ± 5 mV. Ten data per decade of frequency were obtained to get smooth and more reliable curves. Though, the design of the cell enabled evaluation of the same location of the sample for EIS analysis, to continuously monitor the changes in the coating, experiments were conducted in triplicate and mean value of these three data was used for analysis.

The coated panels were exposed inside a standard test chamber (ASTM B117) and were sprayed with 5% sodium chloride solution, at a pH between 6.5 and 7.2, continuously for various intervals of time. The pressure of the compressed air to the nozzle was maintained between 69 and 172 kN/m² (10 and 25 psi). The temperature inside the salt spray was maintained at 35 ± 1 °C.

2.3. Adhesion test

Hatch adhesion test (pull-off tape test), pencil test, scratch test and impact test were carried out to bring out the variation between pigmented and unpigmented alkyd system, in both the as received and after 500 h of exposure to salt spray conditions. This was done for panels treated with phosphate formulation III. Cross hatch test was done with cross hatching having a spacing of 1 mm. Scratch test (BS 3600) was done with a maximum load of 2 kg. Impact test (JISK 4200) was done by dropping a weight of 1 kg from various heights.

3. Results and discussion

A generalised model describing an electrical equivalent circuit of a painted metal/solution interface is shown in Fig. 2(a) [1–3]. The parameters, coating capacitance \( C_c \) and pore resistance \( R_{po} \), represent the basic properties of a coating and, hence, no further modification in \( C_c \) and \( R_{po} \) is proposed. The representation of interfacial impedance, \( Z_i \), has many variations [2,3], the simplest of which, as indicated in Fig. 2(a), involves as its param-

![Fig. 1: Schematic drawing of electrochemical cell used for impedance measurements.](image)

![Fig. 2: Equivalent circuit for painted metal (a); its corresponding schematic Nyquist (b); and Bode (c) plots. The Bode plot illustrates how various coating parameters are extracted. \( R_{po}, C_c, R_{ct}, C_{dl} \) and \( R_{ct} \) represent, solution resistance, coating capacitance, pore resistance of the coating, double layer capacitance and charge transfer resistance, respectively.](image)
eters, a simple charge transfer resistance ($R_{ct}$), a double layer capacitance ($C_{dl}$) and a transmission line-type impedance characterised by the Warburg impedance ($Z_v$). It is necessary to note the facts that the response of interfacial impedance $Z_i$ occurs only in the very low frequency range of the impedance spectrum while the response of the coating parameters $C_c$ and $R_{po}$ appears at the high frequency range [1]. Since the present work concerns monitoring $C_c$ and $R_{po}$ values of the coating as a function of salt spray ageing time, only the high frequency region of Bode plots, where they will be delineated, is used for analysis as follows.

As suggested by Mansfeld et al. [4,5], the value of $C_c$ was obtained by visual extrapolation of the linear region of the high frequency side of log|$Z|$ vs log (frequency) plot to $\omega = 1$ (the corresponding value of frequency $f$ being 0.16 Hz) [4]. That is,

$$\frac{1}{|Z|} = C_c (at \omega = 1) \quad (1)$$

The value of $|Z|$ that corresponded to low frequency plateau region of the log|$Z|$ vs log (frequency) plot was taken as $R_{po}$ value of the coating as the solution resistance was negligible. When the blisters formed, the Nyquist plots clearly reflected the presence of Warburg impedance and the $Z'$ value at the intersection of the $Z'$-axis of the high frequency capacitive loop obtained by manual extrapolation gave $R_{po}$.

Following the earlier work [3,5,6], the parameter break point frequency, $f_{45}$ was determined as the frequency corresponding to a phase angle ($\phi$) of 45° on the descending side of high frequency phase angle plot. These values were further verified using $C_c$ and $R_{po}$ by means of the following equation, which correlates $f_{45}$ to $C_c$ and $R_{po}$ [7]

$$f_{45} = \frac{1}{2\pi R_{po} C_c} \quad (2)$$

Typical Nyquist and Bode plots of a coating system for unexposed and exposed to salt spray for 200 h are given in Figs. 3 and 4 for illustration. The Nyquist plot for the as received coating showed only a single semicircle corresponding to the coating. The Bode magnitude plot also showed the transition of capacitive region to resistive region only once. The occurrence of only one semicircle might be due to a smaller difference between the time constants of the coating and the corrosion reaction at the metal surface [8]. With increase in exposure time, the size of high frequency loop was found to decrease with a simultaneous emergence of a linear region or tail at the low frequency side of Nyquist plot, as shown in Fig. 4(a). The corresponding Bode plots showed a transition from capacitive region to resistive region even at a higher frequency as shown in Fig. 4(b), indicating an appreciable delamination of the coating.

The 45° phase angle exhibited by the low frequency region of the Bode plot (Fig. 4(b)) and the clear low frequency linear region exhibited by the Nyquist plot (Fig. 4(a)), both characteristics of Warburg impedance, indicate that the interfacial impedance, $Z_i$ corresponds to transmission line-type impedance. This particularly occurs when the steel panels are given a phosphating treatment prior to an organic coating [9]. Since the diffusional impedance provides information on the phosphate coating, no further analysis of this part of the spectrum was carried out.

Variation of break point frequency with time of
exposure to salt spray for various combinations of the coating parameters (pigmented and unpigmented alkyd coatings on mild steel panels phosphated with three different phosphating formulations) are shown in Figs. 5 and 6. In all the cases, the break point frequency showed a general increasing trend with exposure time. In the case of thinner coatings, for all the three formulations of phosphating, of thickness 20 μm (unpigmented) or 25 μm (pigmented), the plot of break point frequency with exposure time could be divided into three distinct regions. Here, the break point frequency showed an appreciable increase with the exposure time at very low exposure times, after which it remained nearly constant over a particular period of time, which was followed by a drastic increase with exposure time. On the contrary, in thicker coatings, the initial increase in the break point frequency was not apparent. This may probably be due to the fact that in thicker coatings this transition is expected to occur after longer time of exposure to salt spray and during this stage impedance measurements were performed at longer time intervals. As a result, the expected discontinuity in the break point frequency curve could not be detected. Generally, blisters were observed in coatings of all thicknesses only when the break point frequency started increasing steeply with exposure time (corresponding to the end of region II and start of region III).

Figs. 7 and 8 show the variation of pore resistance values of pigmented and unpigmented systems, respectively, with time for the three different phosphating conditions. Pore resistance of all the coatings followed a general decreasing trend with increasing exposure time as was reported earlier by other investigators [2,9,10]. For all the coating systems, initially there was a steep decline in the pore resistance with exposure time, after which the pore resistance attained more or less a constant value, which was very low in the range of $10^4 - 10^6 \, \Omega \cdot \text{cm}^2$. Pore resistance values were found to increase with thickness of the coatings, thus indicating better performance of thicker coatings, which is expected. This might be due to the reduction in porosity and increase in the diffusion path for the environment migration with increasing thickness.

Variation of coating capacitance with exposure time for different coating systems is given in Figs. 9 and 10, respectively, for pigmented and unpigmented resins. Pigmented and unpigmented systems followed a similar trend irrespective of the type of phosphating. The increase in $C_c$ with exposure time can be attributed to the permeation of environment and formation of blisters. This is because, with water ingress, the dielectric constant of polymeric material which is about 4 [8] is expected to significantly increase as the dielectric constant of water is 80, which is substantially higher than that of the polymer. This increase in dielectric constant of the coating is expected to raise the capacitance of the coating.
Fig. 6. Variation of break point frequency with time of exposure to salt spray for unpigmented alkyd system on mild steel phosphated with (a) Phosphating (I); (b) Phosphating (II); and (c) Phosphating (III) formulations.

Fig. 7. Variation in pore resistance with time of exposure to salt spray for pigmented alkyd system on mild steel phosphated with (a) Phosphating (I); (b) Phosphating (II); and (c) Phosphating (III) formulations.
Fig. 8. Variation in pore resistance with time of exposure to salt spray for unpigmented alkyd system on mild steel phosphated with (a) Phosphating (I); (b) Phosphating (II); and (c) Phosphating (III) formulations. Note that the curves are close to sigmoidal nature.

Fig. 9. Variation of coating capacitance with time of exposure to salt spray for pigmented alkyd on mild steel phosphated with (a) Phosphating (I); (b) Phosphating (II); and (c) Phosphating (III) formulations.
coating according to the following relation:

$$C_i = \frac{\varepsilon_0 \varepsilon_r A}{d},$$

(3)

where $d$ is the coating thickness, $A$ is the area of the coating, $\varepsilon_0$ is the permittivity of the free space and $\varepsilon_r$ is the dielectric constant of the coating.

From Figs. 9 and 10, it is seen that the capacitance of the coating showed a gradual increase and then a step raise followed by a plateau, which is indicative of a near sigmoidal behaviour. If the capacitance variation is assumed to be a consequence water ingress and blister formation, then the sigmoidal behaviour probably reflects the nucleation and growth process of blister formation. Though, quantitatively each curve differs from the other, a qualitative similarity in the trend is observed in all types of coatings.

A quantitative assessment of the blister formation kinetics to compare with the impedance data will be more useful. The area fraction of the sample covered by blisters was determined by physically measuring the diameter of each blister for all the coating systems, for different times of exposures to the salt spray. As an illustration, data for the phosphating formulation 1 in pigmented and unpigmented conditions are given in Figs. 11 and 12, respectively. Typical appearance of blisters in pigmented and unpigmented coatings for two different exposures time intervals are brought in Figs. 13 and 14, respectively. What distinguishes the pigmented alkyd system from that of the unpigmented system, as seen from Figs. 13 and 14, is the fact that the former exhibits more number of blisters with smaller sizes, while the latter, on the contrary, shows larger sized blisters with smaller population. The large size of the blisters, due to faster growth, observed in the unpigmented system has led to their bursting and consequent direct
The continuous increase in the number of nuclei and the size of the blisters with time will give rise to sigmoidal trend in the overall blister formation. Interestingly, blister formation kinetics determined by direct observation (Figs. 11 and 12) are in close agreement with capacitance data (Figs. 9 and 10). This is not surprising in the sense that blister formation and capacitance changes of a coating are primarily due to water permeation with in the coating. It would be worthwhile to make a detailed investigation from the point of view of blister formation kinetics, which is not dealt in the literature.

The other data that seems to provide some information on the effect of pigment is the variation in break point frequency of the unexposed pigmented and unpigmented coating with thickness (Fig. 15). According to Eq. (1), the break point frequency depends on the $C_c$ and $R_{po}$ of the coating. These parameters in turn depend on the coating thickness. However, it should be noted that the capacitance is inversely related to thickness and directly related to area as given by the Eq. (2). Resistance, on the other hand, is directly related to thickness and indirectly related to area by the relation

$$R_{po} = \frac{\rho d}{A}$$

Therefore, the break point frequency of an unexposed coating is given by

$$f_{45} = \frac{1}{2\pi R_{po} \varepsilon}$$

From the above equation it becomes clear that $f_{45}$ does not depend on thickness of the coating. For this reason,
Fig. 14. Visual observation of unpigmented alkyd system of thickness 20 μm on mild steel phosphated with phosphating formulation III after (a) 400 h and (b) 600 h of exposure. The blisters are relatively large in size and smaller in numbers as compared to Fig. 13.

Fig. 15. Variation of break point frequency values with thickness of dropping the weight from the heights of 25 and 20 cm pigmented and unpigmented coatings on mild steel (for phosphated in the as received and exposed to 500 h of salt spray with phosphating formulations I and III). Note the variation is more rapid in the case of unpigmented coating.

Mansfeld and Tsai [5] have shown that the break point frequency of even a failed coating depends only on the degree of delamination, which equals the fraction of the blistered area, and not the thickness. However, it is seen from Fig. 15 that $f_{45}$ of unpigmented coating does significantly vary with thickness, while that of pigmented coating vary only marginally with thickness. Presuming that the bulk property of unpigmented coating does not vary as the coating thickness is increased, the apparent variation in $f_{45}$ with thickness can be attributed to the effect of interface between the coating and the metallic substrate in the case of unpigmented system. This may be reflected in the poor adhesion and delamination characteristics of the unpigmented coating over the pigmented coating.

The influence of pigment on coating adhesion to substrate was evaluated with various adhesion tests like cross hatch adhesion test (pull-off tape test), scratch test, pencil test and impact test. Both pigmented and unpigmented systems behaved similarly for cross hatch adhesion test. Furthermore, both the systems passed the 2H pencil. However, scratch test done with a load of 2 kg gave raise to a mild scratch in pigmented system and a relatively deep scratch in unpigmented system, even though scratch did not reach the base metal in both the cases. Dropping impact test with 1 kg of weight, have brought out the influence of pigment. This was examined with regards to pigmented and unpigmented coatings of steel panels treated with phosphate formulation III. In this, the unpigmented systems failed for dropping the weight from the heights of 25 and 20 cm in the as received and exposed to 500 h of salt spray conditions. On the other hand, the as received pigmented system did not fail even when the weight was dropped from a height of 50 cm and with respect to samples exposed to 500 h, only wrinkles were seen, when the weight was dropped at an height of 40 cm. Based on the above observations it was suggested that pigment enhances both the adhesion as well as the impact strength of the coatings. This observation, in the following way, can explain why $f_{45}$ of unpigmented coating is thickness dependent, while that of pigmented coating is not dependent (Fig. 15). The contribution from the interface to the overall capacitance and resistivity of a more adherent coating will be less significant owing to its compactness. On the contrary, a weakly adherent interface might appreciably alter the overall capacitance.
and resistivity of the coating as it is a less compact interface. In this regard, as the thickness of the coating is increased the contribution from the interface towards capacitance and resistivity becomes less significant and as a consequence \( f_{\text{max}} \) is thickness dependent in the case of a less adherent coating. For this reason, it is proposed that the pigmented coating did not show thickness dependence with respect \( f_{\text{max}} \) as it is more adherent than that of unpigmented coatings.

In order to bring out the effect of pigment on the performance of alkyl system, it is essential that data on identical coating thicknesses are compared. Since it was not possible to obtain the same thickness in pigmented and unpigmented conditions, interpolation of the data was resorted to and the data so obtained were compared.

Table 1 compares the \( f_{\text{max}} \), \( R_{\text{p}} \) and \( C_{\text{c}} \) of pigmented and unpigmented systems for identical thicknesses of 40 and 60 \( \mu m \) for the steel panels treated with Type II phosphate formulation. \( R_{\text{p}} \) and \( C_{\text{c}} \) values of the coatings exposed to 0, 50 and 300 h of salt spray are given in the table. These time intervals were chosen because, they represent various stages of coating failure with no water in the coating at 0 h, a little ingress of water at 50 h and an appreciable blistering at 300 h. Also seen from the table is that the break point frequency values for pigmented system were found to be relatively higher than that of the unpigmented system at all time intervals, for a given thickness, indicating apparently an inferior performance of pigmented coating as compared to the unpigmented coating. Pore resistance values also indicate more or less the same trend. However, the coating capacitance values of pigmented system were found to be higher than that of unpigmented system at 50 h of exposure and less than that of the unpigmented system at 300 h of exposure.

To understand this, it is necessary to examine the factors responsible for the variation in capacitance.

It can be seen from Table 1 that the capacitance values of the pigmented and unpigmented coatings in the unexposed condition are similar. This is possibly because the presence of the pigment does not change the dielectric constant of the coating perceptibly. However, the variation in capacitance of the pigmented and unpigmented systems upon exposure to salt spray differs notably. Table 1 shows that the capacitance ratios of pigmented to unpigmented systems of corresponding thicknesses are higher for 50 h exposure and lower for 300 h of exposure. Since change in capacitance is directly related to water content of a coating, this reversal in trend implies that water ingress into the pigmented system is higher at 50 h and lower at 300 h exposure in comparison to the unpigmented system. As a consequence, nucleation of more blisters takes place in pigmented system than that of unpigmented system (cf. Figs. 13 and 14). These results were not surprising in the sense that TiO

\[ \text{Table 1} \]

Coating parameters of pigmented and unpigmented alkyl system on mild steel phosphated with phosphating II

<table>
<thead>
<tr>
<th>Type</th>
<th>Exposure time (h)</th>
<th>Coating thickness (µm)</th>
<th>( f_{\text{max}} ) (Hz)</th>
<th>( R_{\text{p}} ) (Ω cm²)</th>
<th>( C_{\text{c}} ) (F cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigmented</td>
<td>0</td>
<td>40</td>
<td>33</td>
<td>( 1.2 \times 10^5 )</td>
<td>( 6.73 \times 10^{-9} )</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>40</td>
<td>15</td>
<td>( 3.2 \times 10^6 )</td>
<td>( 4.6 \times 10^{-14} )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>90</td>
<td>( 5 \times 10^7 )</td>
<td>( 9.2 \times 10^{-15} )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>18</td>
<td>( 1.7 \times 10^8 )</td>
<td>( 5.4 \times 10^{-19} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>40</td>
<td>1500</td>
<td>( 2 \times 10^9 )</td>
<td>( 1.3 \times 10^{-7} )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>250</td>
<td>( 9 \times 10^{10} )</td>
<td>( 0.43 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>Unpigmented</td>
<td>0</td>
<td>40</td>
<td>29.97</td>
<td>( 1.63 \times 10^8 )</td>
<td>( 7.04 \times 10^{-9} )</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>40</td>
<td>10.86</td>
<td>( 3.7 \times 10^9 )</td>
<td>( 3.7 \times 10^{-15} )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>51.25</td>
<td>( 0.63 \times 10^{10} )</td>
<td>( 6.7 \times 10^{-19} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>40</td>
<td>31.87</td>
<td>( 1.95 \times 10^{10} )</td>
<td>( 3.6 \times 10^{-14} )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>89.65</td>
<td>( 2.7 \times 10^{10} )</td>
<td>( 1.6 \times 10^{-7} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>89.65</td>
<td>( 17.6 \times 10^{10} )</td>
<td>( 1.2 \times 10^{-7} )</td>
<td></td>
</tr>
</tbody>
</table>
A study involving a systematic variation of pigment volume concentration on the blistering kinetics on the one hand and the effect of interfacial characteristics, namely, the adhesion on the break point frequency on the other hand will be valuable. (4) It will be worthwhile examining, in detail, the blistering kinetics in terms of nucleation and growth, processes using a simple paint system to understand whether they are dependent on the constituents of a paint such as pigment.

4. Conclusions

(1) Capacitance and visual observation are complementary to each other in following blistering kinetics of organic coatings.

(2) Presence of TiO$_2$ pigment in the resin has been found to enhance the uptake of water in the initial stages of salt spray test as compared to the stage involving growth of blisters.

(3) Coating failure in the case of pigmented system has been primarily due to the existence of more blister nucleation centres created by the presence of pigment particles, while in the case of unpigmented system it has been predominantly due to weaker interfacial adhesion.

References