

Investigation on the effect of various surface preparations on corrosion performance of powder coated steel by EIS

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Powder coating systems have been considered for different purposes since they have many advantages in use. The performance of the different powder coating systems needs to be examined by various methods. In this paper, a polyester powder coating was applied on various pretreated mild steel panels. Electrochemical Impedance Spectroscopy (EIS) measurements were used to study the durability of the coating on pretreated mild steels upon immersion in 3.5% w/w NaCl solution at ambient temperature for 7 and 50 days. Various

elements of the equivalent circuit are proposed for the different metal/coating systems. The lowest coating and double layer capacitances were measured for acid pickled followed by phosphating pretreated steel panel while the coating and charge transfer resistance were the highest for this system. It revealed an improvement of coating durability on the substrate by phosphating pretreatment. This can be attributed to decreasing ingress of water, dissolved oxygen and ions into the coating.

1 Introduction

Nowadays, powder coating continues to make progress in the competition against conventional organic coating. They do not have solvent and it is the benefit of using them from the environmental point of view. Therefore, it is necessary to study the performance of the different powder coating systems by various methods.

Electrochemical Impedance Spectroscopy (EIS) is a powerful tool to investigate the quality of organic coatings [1–5]. This technique is a non-destructive test to examine corrosion phenomena. Qualitative and quantitative information can be obtained via EIS using applied small magnitude (usually 10–15 mV) AC voltage signal to a sample. Three electrodes are used in this method, namely working electrode (WE), reference electrode (RE) and auxiliary electrode (AE) [6]. With coated metals, the sample area is usually quite large relative to cells for studying bare metal surface and a sample surface area of approximately 1 cm² per 2.5 µm of organic coating thickness was suggested by Kendig and Scully [7]. The purpose of AC impedance is to model the corrosion process in terms of circuit elements such as resistor, capacitance and inductor. In the measurement of impedance, the independent variable is the frequency of the signal [8]. The result is introduced by modulus and phase angle of the impedance or magnitude of the real and imaginary compounds.

There have been many published papers regarding the use of EIS in the study of corrosion problems. A generalized review article by Growcock [9] was published in ChemTech in

1989. A standard practice for EIS, ASTM G106-89 [10] was published in 1989. Especially with respect to analysis of painted surfaces with EIS methods, several papers have been published. The EIS data sets from a slowly degrading coating and change with continual exposure time are presented and correlation of the results were made to the calculated parameters assuming the more popular equivalent circuit model [10–14].

The objective of the investigations reported in this paper was to determine the protective properties of polyester powder coating on steel panels during exposure in 3.5% NaCl solution. Steel panels were coated with a thin layer of polyester. Prior to polyester coating, panels were pretreated by different ways that are described in the following section.

2 Experimental

All the test panels used in this study were cold rolled mild steel (Q-panel). Prior to applying powder coating of polyester on the specimens, four different types of pretreatment were carried out as follows plus water washing and drying;

- 1) Specimens that prior to applying powder coating were just degreased by acetone (SD)
- 2) Specimens that prior to applying polyester powder coating were pickled by a solution of 5% hydrochloric acid (AP)
- 3) Specimens that prior to applying polyester powder coating were degreased by acetone and then phosphated in phosphate bath (DPH)
- 4) Specimens that prior to applying polyester powder coating were pickled in 5% HCl and then phosphated in phosphate bath. (PPH)

Phosphating treatment was carried out in a bath solution containing ZnO, H₃PO₄, HNO₃ and NaClO₄ at 45 °C by immersion method for 35 minutes [15].

After specimen pretreatment, polyester powder coating was applied to a thickness of 45 ± 3 µm using an electrostatic spray gun. The curing schedule used for all powder-coated panels was 20 minutes at 180 °C. Specimens were connected electrically by copper wire. In all experiments a surface area

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of 50 cm^2 was used and the remaining surface area (i.e. back and around the edges) was covered by a 3:1 mixture of beeswax and colophony resin. All the experiments were performed at ambient temperature ($18\text{--}24^\circ\text{C}$). The auxiliary electrode was a platinum rod with a surface area of 2 cm^2 .

The experiments were carried out in 3.5% w/w NaCl solution prepared from analytical grade of NaCl dissolved in deionized water.

The electrochemical impedance measurements were performed at the open circuit potential, E_{corr} , using a sinusoidal AC voltage signal of 20 mV amplitude peak to peak for the samples on 7th and 50th day of immersion. The frequency range was usually from 30 kHz down to 0.01 Hz using an AC Gill potentiostat equipped with a frequency response analyzer manufactured by ACM Instrument. The amplitude of the impedance data was analyzed by the Boukamp EQUIVCRT program [16].

3 Results and discussion

The results of AC impedance of coated specimens after immersion in 3.5% w/w NaCl solution for 7 and 50 days were plotted in Nyquist and Bode plots. A typical Nyquist diagram for the coating systems is shown in Fig. 1.

Figs. 3 to 6 show parameters such as coating resistance, coating capacitance, charge transfer resistance and double layer capacitance for different surface pretreatment methods of coated specimens after 7 and 50 days immersion, analysis by AC impedance data using Boukamp software. In all figures, dimension of resistance and capacitance is Ohm \cdot cm^2 and F/ cm^2 , respectively.

The elements were selected through a model equivalent circuit to represent the systems under study. It was found that the systems were under charge transfer control according to the circuit as it is shown in Fig. 2, where R_s represents the solution resistance, C_c coating capacitance, R_p coating resistance, R_{ct} and C_{dl} charge transfer resistance and double layer capacitance at the metal/coating interface, respectively.

As shown in Fig. 3, the coating resistance for the phosphated specimen is higher than for those specimens that have no phosphate layer. The reason for decreasing coating resistance can be attributed to diffusion of water and ions into the coating during immersion [17–19]. After diffusion of water into the coating, a layer of electrolyte forms at the metal/coating interface and the condition for occurrence of anodic and cathodic reactions on the metal surface is established. Decreasing coating resistance as a result of ingress of ions into its pores causes a greater decreasing in coating resistance of the specimens without phosphate pretreatment due to accommodation of ions from two sources; from electrolyte and ions that were produced from anodic and cathodic reactions at the metal/coating interface.

An intact phosphate layer can act as a barrier to prevent water, dissolved oxygen and ions reaching the metal surface,

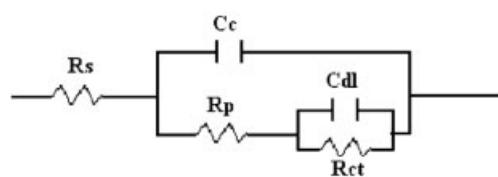


Fig. 2. Proposed electrical equivalent circuit for the polyester powder coating and the different surface treatments of Q-panel mild steel

so protecting the metal surface from corrosion and also limiting the spreading corrosion area in the cases that small areas has suffered from corrosion [20]. Therefore in the case of phosphated specimens due to minimizing incorporation of ions into the coating pores, a small decrease in coating resistance for different pretreatment was observed. In addition, increasing the adhesion of coating on the surface of phosphated specimens due to mechanical locking of the coating into phosphate crystals means that the possibility of coating delamination significantly decreases. Mill scale can affect the phosphate layer formation. Pickling + phosphating pretreatment on specimens has a positive influence on the coating performance due to removing mill scale by acid pickling following good adhesion by the presence of the phosphate layer. Mill scale potential is nobler than bare steel. When cathodic reaction species such as oxygen and water, and also ions reach the interface, galvanic cells can occur between mill scale and bare metal. Corrosion products are the result of electrochemical reactions, which are more voluminous than the original metal. This problem is also applied in the case of an organic coating, which is applied over mill scale and may be delaminated from the metallic substrate [21].

The coating capacitance for the different samples is illustrated in Fig. 4. According to the Kingsbury-Brasher equation, the coating capacitance shows the total amount of water associated with ions in the film. Absorption of water causes an increase in the dielectric constant of the coating with a corresponding increase in the coating capacitance. It is evident that those specimens pretreated by phosphating showed lower coating capacitance than other specimens. It is clear that diffusion of electrolyte and ions into the coating applied on phosphated specimens is much lower than on others. Since coating capacitance is directly affected by ingress of electrolyte and ions into coating pores, improvement of coating adhesion on phosphated surface has significantly decreased the coating capacitance [22, 23].

Specimens with phosphating pretreatment show higher charge transfer resistance in comparison to those specimens that were treated without phosphating pretreatment. Since charge transfer resistance is the resistance of metal surface against electrochemical reactions therefore the barrier of phosphate layer on pretreated specimens has increased the charge transfer resistance as illustrated in Fig. 5 [24]. On the other hand, the easy access of aggressive ionic species

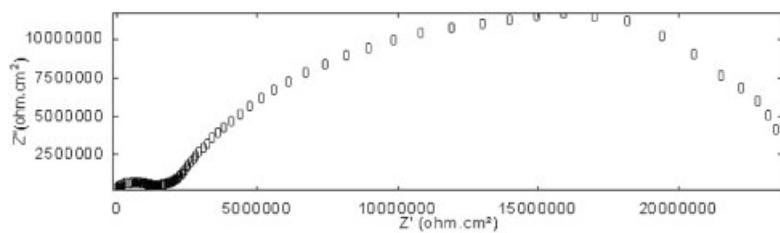


Fig. 1. Typical Nyquist plots

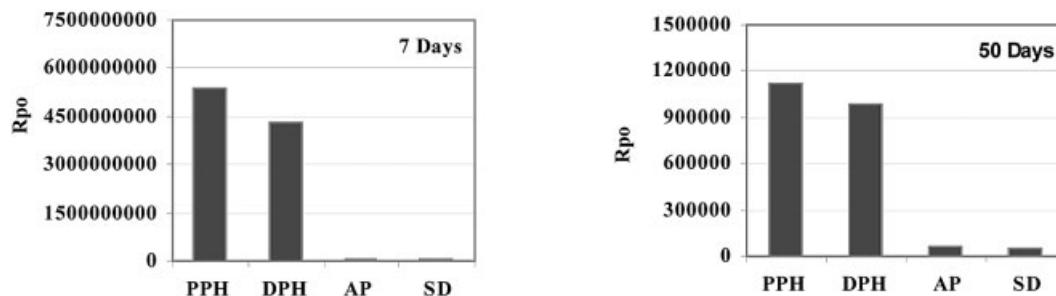


Fig. 3. Coating resistance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days

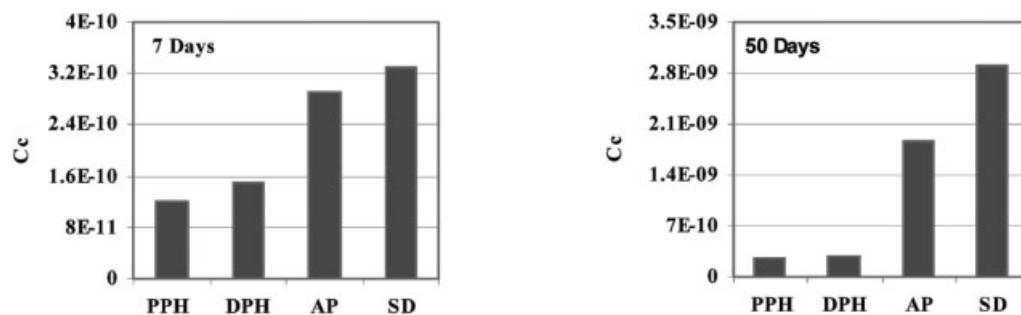


Fig. 4. Coating capacitance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days



Fig. 5. Charge transfer resistance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days

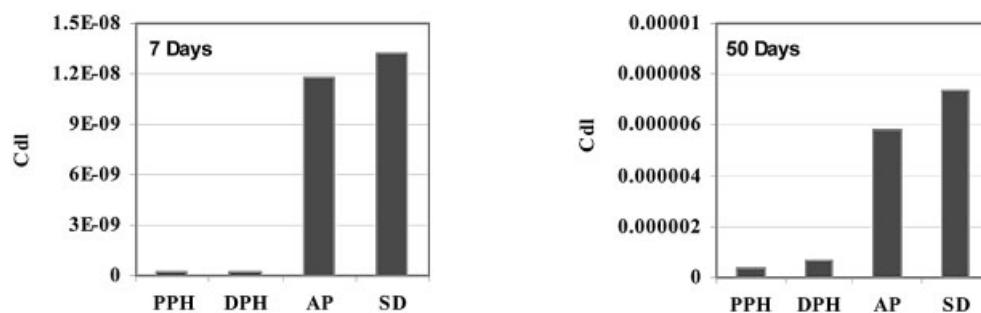


Fig. 6. Double layer capacitance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days

to the interface coating/metal through the pores plus the galvanic cell between mill scale and bare metal could be the reasons to have higher corrosion rates in SD samples.

Double layer capacitance (C_{dl}) is one of the main electrochemical elements of the corroding surface and is approximately constant per unit area. The measured capacitance can be related to the total surface area, which is delaminated due to electrochemical reactions. The higher the double layer capacitance, the higher the disbonded area. Fig. 6 shows double layer capacitance for specimens with different pretreatment and also for different immersion time. Specimens pretreated by phosphating showed much lower double layer capacitance due to corrosion barrier effect and insulating nature of the phosphate layer.

Any factors such as pressure of corrosion products on the film and a chemical gradient across the coating, which can increase the number of defects in the systems which reduced the coating resistance, can also increase the double layer capacitance. Increasing immersion time from 7 to 50 days leads to increasing double layer capacitance increasing the delamination area [25].

4 Conclusion

The electrochemical AC impedance technique can be used to characterize the degradation behaviour and delamination process for organic coatings on steel panels with different pretreatment methods. EIS measurements provided evidence that polyester powder coating on the phosphating treated Q panel mild steel showed the best performance compared to the other treatments. Acid pickling of the mild steel can produce better treatment when an organic coating such as polyester powder coating was applied and this can be attributed to not having mill scale, which produces galvanic cells causing more diffusion of ionic species through the coating. Increasing immersion time of coated specimens in corrosive media cause an increase in surface corrosion area due to further increasing in coating delamination area and opening of new and/or enlargements of existing conductive pathways.

5 References

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