Electrochemical evaluation of a high solid coating in acid media

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Abstract

In the present work a two-component solvent free amine cured epoxy coating was used to protect carbon steel. The coated metal was immersed in an aggressive acid solution and monitored by means of electrochemical techniques: Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise (EN). These techniques were used to evaluate the coating degradation evolution. The values of the pore resistance $R_{po}$, the impedance at 0.1 Hz (calculated by means of both EIS and EN), and noise resistance ($R_n$) were the main parameters calculated with the aim of monitoring the evolution of the system along the immersion time. An excellent correlation among the EIS and EN data was found. Keywords: EIS, ENM, coating, carbon steel, degradation, acidic media.

1 Introduction

Increasing the percentage of solids in conventional solventborne paints has represented one of the first attempts to decrease the volatile organic compounds (VOC) content of a coating formulation and comply with increasingly stringent environmental requirements [1]. Traditional high solid coatings use less paint to achieve the same thickness obtained with other conventional formulations. This results in the volatilization of less solvent into the environment.

By definition, a high solids coating typically contains greater than 60% solids by weight or 80% solids by volume [2]. This technology solution is currently accepted by the automotive, aerospace, and marine industries for use in a variety of formulations. The major advantage associated with the use of this kind of coatings is that the same equipment can be used to apply new high solids and conventional solventborne paints. On the contrary, the major disadvantage with
high solids paint lies in the higher viscosities exhibited by the coating formulations. In addition, although in less content, these coatings still contain a significant amount of traditional solvents and diluents [2].

Nowadays, epoxy solvent free coatings have been adopted in an important way by the marine industry. In this contribution, a two-component solvent free coating, based on epoxy resin and cured with amines, has been studied. This coating, which has excellent resistance to corrosion, chemical products and oil, is usually employed as a monolayer designed for the protection of steel structures and storage tanks.

In order to evaluate the anticorrosive protection of the coating in acid media, electrochemical measurements were recorded and interpreted. On the one hand, Electrochemical Impedance Spectroscopy (EIS) was used to analyse discriminately electrochemical response of the metal-paint system. On the other hand, Electrochemical Noise Measurements (ENM) completed the evaluation. Finally, correlation among all the measurements was intended.

2 Experimental

The behaviour of "Sigmaguard CSF", a commercial high solids content and solvent free epoxy paint produced by Sigma Coatings, has been studied. Table 1 gives the most important technical characteristics of this paint. Naval steel, St 35.8, has been employed as metallic substratum. The samples studied were rectangular test pieces of 100x150x2 mm, dry pressure blasted until a finish of type ISO-Sa 2 1/2 was obtained. The paint was then applied by airless spray to a thickness of approximately 300µm, the optimum thickness recommended in the technical data sheet of the paint.

<table>
<thead>
<tr>
<th>Description</th>
<th>two component solvent free amine cured epoxy coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colours and gloss</td>
<td>green-gloss</td>
</tr>
<tr>
<td>Mass density</td>
<td>approx. 1.3 g/cm³</td>
</tr>
<tr>
<td>Solids content</td>
<td>100% by volume</td>
</tr>
<tr>
<td>VOC (supplied)</td>
<td>max. 17 g/l</td>
</tr>
<tr>
<td>Recommended dry film thickness</td>
<td>300 µm</td>
</tr>
<tr>
<td>Theoretical spreading rate</td>
<td>3.3 m²/l for 300 µm</td>
</tr>
<tr>
<td>Flash point</td>
<td>base and hardener: above 65°C</td>
</tr>
</tbody>
</table>

The coating protective capacity was evaluated by monitoring the painted samples behaviour in immersion tests by means of electrochemical techniques. For this purpose, electrochemical cells were constructed, in which an area of 13 cm² of the painted surfaces was exposed. In some experiments, as ENM or EIS with two electrodes, two electrochemical cells were coupled and joined by a saline bridge. A solution of HCl 3M served as aggressive medium, a saturated calomel electrode was used as reference electrode and a graphite bar, as counter-electrode.

2.1 Electrochemical impedance spectroscopy

A 1287 potentiostat coupled to a 1255 frequency response analyser (FRA), both from Solartron, was used for the impedance measurements. The frequency
measurement range employed for recording the impedance spectra was $10^5$ to $10^2$ Hz and the signal amplitude was 20 mV versus the corrosion potential. Electrical circuits were fitted with Zview software, using non-lineal method of minimum square.

Impedance measurements were recorded separately for both the coupled system and each coated sample (Cell 1 and Cell 2), so that the evolution of the coating degradation could be monitored.

2.2 Electrochemical noise measurements

The Electrochemical Noise potential and current signals were measured simultaneously by means of the classical configuration for this technique [3,4]. A Solartron 1287 potentiostat controlled by the Corrware program was employed to carry out the experiments.

In order to average the values of the parameters analysed, four consecutive Electrochemical Noise records were measured in each exposure time. 2048 points were taken in each record, at a sampling velocity of 2.15 points per second; therefore the time of each record was approximately 15 minutes.

3 Results and discussion

3.1 Electrochemical impedance spectroscopy

A change in the dielectric properties of a coating takes place when they are exposed to a corrosive media. Figure 1 represents some of the impedance spectra corresponding to tests made on painted metals immersed in acid media after being subjected to different periods of time.

![Figure 1: EIS of coated samples immersed in acid media after some days of exposure: a) Nyquist diagrams; b) Bode diagrams.](image-url)

The data obtained on coated steel show a general decrease in the modulus of the impedance (Bode diagrams) along the immersion time, due to the
degradation occurred in the paint (Figure 1). As we can see in the Nyquist diagrams of this figure, spectra are characterised by presenting two semicircles after the day 9. Because of this characteristic, the equivalent circuit selected for simulating the response of the system was the classical for a painted metal (Figure 2). In coated metal samples, the high frequency interval is usually related to dielectric properties of organic coatings; while low frequency gap corresponds to metal performance during the corrosion process.

In the equivalent circuit of Figure 2, each electrical element has a physical meaning [5]. \( R_e \) represents electrolyte resistance, that is, the resistance between the working electrode and the reference electrode. \( C_c \) is the capacity of the coating film and its increase, at the initial moment, is related to absorption of water or the permeability degree of the paint. \( R_{po} \) is pore resistance and is a measure of the degradation level that is suffering the paint.

![Figure 2: Equivalent circuit for painted metals.](image)

Faradaic impedance, related to the second constant time of the spectra, represents electrochemical process taking place in the metal-coating interface. \( C_{dl} \) is the double-layer capacity and is a measure of the paint disbondment. \( R_{ct} \) symbolizes the charge transfer resistance, associated to the corrosion kinetic process. This parameter is proportionally inversed to corrosion rate and to the area where oxidation occurs. Its natural tendency is to decrease along the time of permanence in dissolution.

As a general rule, a metal-coating system that has good performance against corrosion is characterised by presenting high values of \( R_{po} \) and \( R_{ct} \) and low values of \( C_c \) and \( C_{dl} \) [6]. It does not exist a general agreement, but according to some authors [4,7,8], values of pore resistance lower than 10⁷ or 10⁶ Ωcm² reveal that coatings have a bad behaviour in relation to metal protection. Likewise, other authors [9] consider that is more important when the second semicircle appears (electrochemical process), than the values reached by the elements of the circuit.

From fitting of spectra (Fig.1) to selected electrical circuit (Fig.2), values of Table 2 are obtained. For first days, just first semicircle was still defined, so only the elements from first net (\( C_c \) and \( R_{po} \)) were fitted.

As it was expected, elements \( C_c \) and \( C_{dl} \) increase in relation to time evolution, while \( R_{po} \) and \( R_{ct} \) decrease along immersion time; tendencies related to the physical meaning explained before. According to the values of \( R_{po} \) cited and to the time when the second semicircle appears, it can be considered that our coating provides an excellent anticorrosive behaviour for the first two days of
exposure to HCl. It has a questionable protection against corrosion in a period of 9 to 14 days. Meanwhile, after 14 days of immersion in HCl 3M media, the coating does not protect adequately the steel.

Table 2: Evolution of electrical elements from equivalent circuit.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Cc (F/cm$^2$)</th>
<th>Rpo (Ωcm$^2$)</th>
<th>Cdl (F/cm$^2$)</th>
<th>Rct (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>4.17x10$^{-11}$</td>
<td>3.35x10$^9$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.86x10$^{-11}$</td>
<td>7.12x10$^8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.01x10$^{-10}$</td>
<td>4.11x10$^7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.13x10$^{-10}$</td>
<td>2.19x10$^7$</td>
<td>5.02x10$^{-8}$</td>
<td>3.42x10$^{-7}$</td>
</tr>
<tr>
<td>14</td>
<td>1.65x10$^{-10}$</td>
<td>6.62x10$^6$</td>
<td>1.20x10$^{-7}$</td>
<td>5.95x10$^6$</td>
</tr>
<tr>
<td>16</td>
<td>5.01x10$^{-10}$</td>
<td>4.01x10$^5$</td>
<td>5.15x10$^{-7}$</td>
<td>5.01x10$^5$</td>
</tr>
<tr>
<td>21</td>
<td>1.10x10$^{-9}$</td>
<td>2.22x10$^5$</td>
<td>1.01x10$^{-6}$</td>
<td>4.26x10$^5$</td>
</tr>
<tr>
<td>24</td>
<td>2.14x10$^{-9}$</td>
<td>1.33x10$^5$</td>
<td>2.03x10$^{-6}$</td>
<td>3.16x10$^5$</td>
</tr>
<tr>
<td>27</td>
<td>3.59x10$^{-9}$</td>
<td>8.88x10$^4$</td>
<td>3.66x10$^{-6}$</td>
<td>2.29x10$^5$</td>
</tr>
<tr>
<td>29</td>
<td>5.79x10$^{-9}$</td>
<td>5.02x10$^4$</td>
<td>7.81x10$^{-6}$</td>
<td>1.55x10$^5$</td>
</tr>
<tr>
<td>33</td>
<td>5.62x10$^{-9}$</td>
<td>2.27x10$^4$</td>
<td>2.32x10$^{-5}$</td>
<td>9.41x10$^4$</td>
</tr>
<tr>
<td>36</td>
<td>2.22x10$^{-9}$</td>
<td>2.55x10$^4$</td>
<td>3.76x10$^{-5}$</td>
<td>7.76x10$^4$</td>
</tr>
<tr>
<td>43</td>
<td>1.53x10$^{-8}$</td>
<td>6.93x10$^3$</td>
<td>1.60x10$^{-4}$</td>
<td>2.10x10$^4$</td>
</tr>
</tbody>
</table>

On the other hand, parameter $Z_{0.1Hz}$ may be used to obtain a quick evaluation of the status of the coating barrier properties. This measurement represents total impedance of the metal-coating system at frequency 0.1 Hz and some authors consider it as the optimum parameter for evaluating protection properties of coatings [2]. High values of $Z_{0.1Hz}$ are therefore associated to a high protection capacity of the coating. In general, coatings with values of $Z_{0.1Hz} > 10^8 \text{Ωcm}^2$ are considered as providers of an excellent anticorrosive protection; while values of $Z_{0.1Hz} < 10^6 \text{Ωcm}^2$ are presented by coatings with poor anticorrosive protection [10]. Figure 3 includes the evolution of parameter $Z_{0.1Hz}$ for time periods measured. We can observe that it decreases rapidly along exposure time.

According to Figure 3 and taking into consideration the criteria previously mentioned, after the day 14 the coating presents poor anticorrosive protection. As a result, we have reached to a good agreement between criteria of $R_{po}$ element and $Z_{0.1Hz}$ parameter. This because of $Z_{0.1Hz}$ parameter, which is a good measurement for evaluating coating barrier properties applied to metals. In the one hand, if the coating is protecting adequately the metal, $R_{po}$ element from the equivalent circuit can be approximated to $Z_{0.1Hz}$ parameter. On the other hand, when the coating does not provide protection enough to the metallic substratum, the referred parameter is associated to the corrosion process ($R_{ct}$). Since these resistances acquire different values, $Z_{0.1Hz}$ constitutes a good and rapid to obtain parameter of the coating degradation state.
3.2 Electrochemical noise

In Figure 4 the potential and current mean values of the records have been plotted in function of the immersion time. In this figure it can be seen that during the first two days the system has low absolute potential values (about -0.3V), while after seven days the potential suddenly falls to more active values (below -0.6 V), closer to free potential of bare steel. This decrease can be related to a loss in the coating protective properties, since it is usually accepted that the more active the corrosion potential is, the more susceptible to oxidation is the metal surface under the coating [11].

Figure 4 shows the influence of the current mean values (parameter called “coupled current”, $I_c$) versus the immersion time. Although the $I_c$ theoretical value is zero, there are some experimental deviations of this value because of different activities of the two working electrodes. In several papers it can be found that the higher activities of the systems (high corrosion rates), the higher
the $I_c$ values [12-16]. It can be appreciated from plot that $I_c$ values increase notably in relation to the immersion time (see the logarithmic scale). This tendency reflects that the system activity increases according to the exposure time.

In order to verify that the activity of the studied system increases versus the exposure time, noise resistance ($R_n$) values of the time records were estimated. This parameter is one of the most commonly used for the interpretation of electrochemical noise [17,18]. In several cases, $R_n$ is equivalent to the polarisation resistance ($R_p$) measured with linear polarisation [19,20], therefore it is proportionally inversed to the corrosion rate, as $R_{ct}$ element is. $R_n$ can be estimated dividing the standard deviation of the potential by the standard deviation of the current [21-22]:

$$R_n = \frac{\sigma_E}{\sigma_I}$$

Figure 5: Comparison of $R_n$ and $Z_{0.1Hz}$ values measured with EN.

In Figure 5 noise resistance values of the EN records have been included. In this figure the values of the impedance at 0.1 Hz, $Z_{0.1Hz(EN)}$, calculated using EN, have been added with the aim of being compared with the $R_n$ values. $Z_{0.1Hz(EN)}$ parameter was calculated using the estimation of the potential and current PSD (equation 2). PSD were estimated by means of FFT.

$$Z_{0.1Hz(EN)} = \frac{\sqrt{PSD_E}}{\sqrt{PSD_I}} (0.1Hz)$$

$R_n$ values were found to be very similar to $Z_{0.1Hz(EN)}$ values. When these parameters are analysed, the assumption derived from the analysis of the mean current ($I_c$) and potential values can be confirmed. That is, the longer the exposure time is, the lower the values of $R_n$ and $Z_{0.1Hz(EN)}$ are, this means that the activity of the system is higher and the protection provided by the coating is lower.

Values of $R_n$ equal or higher than $10^9 \Omega \cdot \text{cm}^2$ are typically measured for excellent coatings [23-25]. However, the line that divides good and poor
behaviour is not clear. Some authors claim that a coating presenting a \( R_n \) value below \( 10^6 \ \Omega.\text{cm}^2 \) is not protective [25], while others think that the line should be drawn at \( 10^7 \ \Omega.\text{cm}^2 \) [26]. According to these considerations, it can be stated that the coating studied showed excellent anticorrosive behaviour before the second day of immersion, good behaviour in a period of 2 to 7 days and poor behaviour after 14 days of exposure in HCl.

### 3.3 Correlation between EIS and EN

Values of parameters \( Z_{0.1\text{Hz}} \), calculated using both EIS and EN, and \( R_n \) values have been included in Figure 6 to be compared. When these parameters are analysed, the expected tendency is confirmed. Therefore, the higher the exposure time is, the lower the values of all these parameters are. This evolution is related to the higher activity in the system and the lower protection provided by the coating mentioned before. In addition, it can be observed that an excellent agreement exists between the parameters calculated with EIS and EN. In this figure it can be appreciated that \( Z_{0.1\text{Hz}} \) parameter of the double cell (calculated by EIS) is very similar to \( Z_{0.1\text{Hz}} \) values of the cell with lower impedance (Cell 1 when the exposure time is lower than 16 days and Cell 2 when the time of immersion is higher than 16 days). Therefore, the double cell reflects the electrochemical behaviour of the single cell that behaves worse.

![Figure 6: Comparison of Rn and Z\(_{0.1}\) values measured with EIS and EN.](image)

On the other hand, since EN technique needs the double cell to carry out the experiments, this technique measures impedance values similar to the ones calculated in the double cell with EIS. According to the considerations mentioned before, EN measures the electrochemical properties of the electrode with lower impedance, fact that ensures the EN technique as very sensitive to measure decreases of impedance in coated electrodes.
4 Conclusions

In the present work a two-component solvent free amine cured epoxy coating has been used to protect steel. Carbon steel samples were coated with this system and later on immersed in HCl, a very aggressive solution employed to accelerate degradation. Electrochemical Impedance Spectroscopy was used to discriminally analyse the electrochemical response of the metal-paint system. Electrochemical Noise Measurements were also carried out and interpreted. Excellent correlation among EIS and EN data was found.

According to the criteria previously exposed, the coating studied showed excellent anticorrosive behaviour before the second day of immersion, good behaviour in the period of 2 to 7 days, and poor behaviour after 14 days of exposure.

References


