



An EIS study of the influence of imperfections on the corrosion behaviour of an organic coated steel system[☆]

V. LAVAERT*, M. MOORS and E. WETTINCK

Laboratory Non-ferrous Metallurgy, Ghent University, Technologiepark 9, B-9052 Zwijnaarde, Ghent, Belgium
(*author for correspondence)

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Abstract

Three different coating conditions influencing the quality of a silicon polyester galvanized steel system were investigated by means of EIS. The first aim was to investigate the influence of different types of pores or discontinuities on the corrosion resistance of the above-mentioned coating system. A second aim was to study the influence of mechanical deformation and damage of the coating on the corrosion behaviour of the coating system. Finally, degradation due to ultraviolet exposure was investigated. In each of these investigations it was possible to distinguish different time constants for different electrochemical events in the Bode phase diagram. Since the difference in magnitude of the values of the resistances was large, they could not be distinguished in the Nyquist plots. Therefore, this type of plot was not used in this work. From the build-up of the coating system and the number of time constants deduced from the EIS measurements, it was possible to model the system. From the model, the physical and electrochemical phenomena occurring during the service life of an imperfect organic coating system was explained.

1. Introduction

The market for silicon polyester-coated, galvanized steel plate increases steadily. These systems give high corrosion protection, provide an appearance with a wide colour spectrum and are moreover not too expensive. In this study, the influence of different types of imperfections for this type of organic coated steel is investigated. The imperfections occur during different stages in the life of the coating, starting with its manufacture. Pores or other discontinuities can be introduced during the curing process of the organic coating. Given the broad range of applications of this coated system, from noise and thermal insulation to structural applications, the plate may intentionally be deformed mechanically.

Once the organic coated steel system is used in outside conditions, it will be exposed to different weather conditions like sunshine, rain and varying temperatures. These elements also speed up the degradation of the coating and diminish its corrosion protection. The influence of the above-mentioned imperfections of the coating on its corrosion behaviour is studied by means of EIS.

By considering the Bode phase graphs, it is possible to distinguish different time constants. In the ideal case [1–3], one or more perfect time constants appear. For

materials departing from this ideal Debye behaviour, a distribution of time constants for a certain frequency range can be distinguished. Each of these groups of time constants represent a different physico-chemical phenomenon taking place in the system and influencing the corrosion behaviour of the coating during its lifetime. The Debye formula has been adapted for nonideal behaviour by Cole and Cole, Cole and Davidson and Havriliak and Negami and others [2]. These formulae, however, describe only one group of time constants.

The aim of this study is to propose an adapted expression to describe the dielectric behaviour of a coating system containing imperfections and defects.

2. Experimental set-up

2.1. Materials

All tested samples were silicon coated galvanized steel plate. The zinc layer had a thickness of about 25 μm . On the phosphated galvanized steel plate, a primer was applied. A 25 μm thick (silicon) polyester film was rolled on top of this. Finally, the coating was cured at 230 °C.

The electrochemical cell was built as follows. On the coated sample a rectangular or round, nonconductive PMMA-cell of 12 cm height was mounted. The coated sample was the working electrode (1.5 \times 8 = 12 cm² for rectangular cells or 2.84 cm² for round cells) in a three

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electrode system. For all the experiments, a platinum counter electrode was used and the reference electrode was a saturated calomel electrode (SCE). The electrolyte was a saline solution as described in ASTM D 1147.

More specific preparation of the samples containing pores and mechanically deformed samples is described in earlier publications [4, 5].

2.2. Method

The impedance spectrum was obtained by imposing a series of a.c. signals with small amplitudes and a wide range of frequencies to the working electrode on the E_{corr} level. The ratio between the applied voltage and the measured current was then calculated to obtain the system impedance $Z(\omega)$. The EIS measurements were carried out with a test set-up containing a potentiostat 273, a two phase lock-in analyser, model 5210 and M398 EIS software (all Perkin-Elmer, former EG&G). The model analysis was done with Boukamp's EquiVCRT [6] and the new ZSimpWin [7] program distributed by Perkin-Elmer.

3. Coating system

3.1. Sources of imperfections

The coating is not homogeneous due to the presence of pores and discontinuities (caused by evaporating gases during the curing process) but also due to the presence of fillers such as pigments and additives. This causes a gradient of quality from the substrate to the surface of the coating.

Different types of pores may be introduced into an organic coating during its processing [5]. The size of these pores is measured by means of optical microscopy. Micropores (dia. $< 2 \mu\text{m}$) are almost always present in the coating without consequences to the corrosion resistance. Macropores can be introduced in the coating when the speed of either the application or the curing (at about $230 \text{ }^\circ\text{C}$) of the coating is increased to increase productivity. Solvents and gases trapped inside the coating do not have time to escape and, hence, form different types of pores or surface discontinuities. This leads to a decrease in quality and a reduced effective thickness of the coating. One can distinguish small ($2 \mu\text{m} < \text{dia.} < 100 \mu\text{m}$) and large (dia. $> 100 \mu\text{m}$) macropores, each with a different impact on the corrosion behaviour of the coating system.

The surface finish of an organic coated steel system is obtained by rolling profiles into a flat-coated steel plate in consecutive steps. During these processing steps, the coated plate is submitted to tensile, compressive and bending stresses. Compared with nonprofiled plates, the profiling provides a higher stiffness to the plate. It is obvious that the coating, even after significant mechanical deformation, still has to provide a good corrosion protection to the underlying galvanized steel plate.

As can be shown easily [4], the strain to which a bent sample is submitted is independent of the bending angle α , but is only influenced by the radius R of the mandrel over which the sample is bent and the thickness of the coated system. For our tests, three series of samples were bent for 60° over a diameter of 11, 6 and 1 mm, imposing an increasing degree of strain to the sample.

When exposed to sunlight, u.v. degradation of the coating will occur. When hygroscopic and thermal stresses are present, they will lead to breaking of bonds in the upper layer of the organic coating.

3.2. Dielectric behaviour of the coating

A simple coating system containing one time constant is characterized by only one semicircle in a Nyquist diagram. The dielectric behaviour of this system follows Debye behaviour and can be represented by [1–3].

$$\varepsilon(\omega) - \varepsilon_\infty \sim \frac{1}{1 + j\omega\tau} \quad (1)$$

with $\varepsilon(\omega)$ the complex permittivity and ε_∞ the permittivity at 'infinite high' frequencies.

Cole and Cole, Davidson and Cole and Havriliak and Negami [2] proposed adaptations to this model for systems with a behaviour departing from the ideal Debye response. Instead of a perfect semicircle, a semi-ellipsoide is then measured. These formulae, however, describe the behaviour of coating systems with only one time constant.

In the study of the corrosion behaviour of organic coatings containing imperfections, several groups of time constants are detected over specific frequency ranges, hence showing separate parts in a Bode phase diagram. We propose the following representation for the frequency response of such a system:

$$\varepsilon(\omega) - \varepsilon_\infty \sim \sum_m \left[\frac{1}{1 + j\omega \frac{1}{\sum_k \left(\frac{1}{\tau_{m,k}} \right)}} \right] \quad (2)$$

Here m can be coating, pores, cracks, fillers, primer, ... The first summation over m then represents two or three major groups of time constants τ_{coating} , τ_{pores} , τ_{cracks} , ... In each group of time constants, k different types and sizes of the coating, pores and fillers can be distinguished.

The measured spectrum is composed of all these time constants $\tau_{m,k}$. Depending on the system being considered, two or three groups of time constants appear, leading to a number of resistances and capacitances in the equivalent electrical circuit. In Figure 1, the equivalent circuit for modelling the organic coating system containing imperfections is shown. Two time constants are present: $\tau_{\text{coating}} = R_c C_c$ and $\tau_m = R_m C_m$. Here, R_c is the ohmic resistance of the coating and C_c the coating capacitance. R_m and C_m represent the resistance and the capacitance of the (intact) coating underneath the

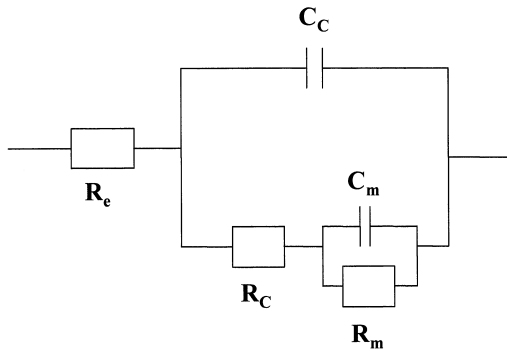


Fig. 1. Equivalent circuit for a nonperfect coating containing different types of imperfections.

imperfections present in the organic coating [5]. In the further text, these parameters will be explained more specifically, depending on the type of imperfection.

Once the electrolyte penetrates the coating and reaches the zinc substrate, a double layer is formed. The parameter τ_m then decreases strongly and a new time constant $\tau_{\text{double layer}} = R_t C_{\text{dl}}$ appears, where R_t is the charge transfer resistance and C_{dl} the double layer capacitance. Each group of time constants that can be characterized by one frequency range will further be noted as one time constant, representing the whole group.

In reality, the system is even more complex since the layer does not behave like a pure capacitance depending on the degradation grade. The capacitance will have to be replaced by a constant phase element (CPE) represented by $Q = (j\omega)^{-n}/Y_0 (0.5 < n < 1)$ as a quality factor. For $n \geq 0.8$, however, Q can be denoted as C . In this investigation this is the case for Q_c and Q_{dl} , further described as C_c and C_{dl} . More detailed fitting results are described in [4, 5].

4. Corrosion behaviour of an organic coated steel system

4.1. EIS measurements

4.1.1. Coating containing small macropores

Since small macropores do not reach the zinc surface, as confirmed by means of microscopy and potential mea-

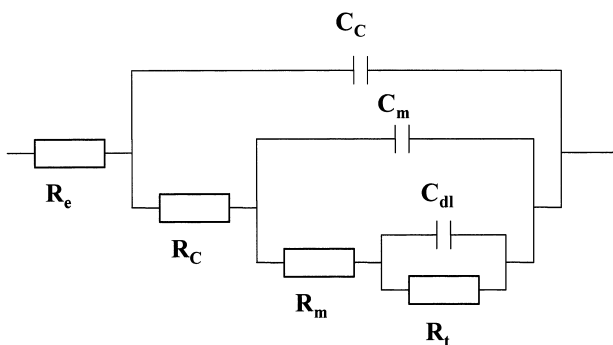


Fig. 2. Equivalent circuit for a nonperfect coating containing different types of imperfections, once a double layer is formed.

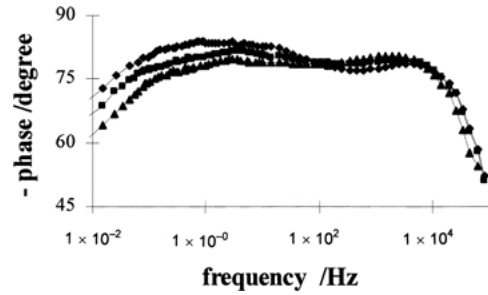


Fig. 3. Bode phase diagram for a coating containing small macropores after immersion in ASTM seawater. Key: (◆) 100 h, (■) 300 h and (▲) 2000 h.

surements, the degradation process during the first 2000 h of exposure to ASTM seawater consists of one phase: water uptake in the coating and filling of the pores. The evolution in the system during this phase is presented in a Bode phase diagram in Figure 3. The equivalent circuit for the interpretation of EIS measurements is presented in Figure 1. Here τ_m represents the time constant $\tau_{\text{pores}} = R_{\text{po}} C_{\text{po}}$ and characterizes the remaining quasi-intact coating under the pores. This time constant appears in the low frequency zone.

The $R_{\text{po}} C_{\text{po}}$ time constant diminishes with time, due to water uptake after the pores are filled with water. The relative dielectric constant of the coating then increases from 4 (air) to 80 (water), while the thickness of the remaining coating under the pores decreases less, so that the parameter C_{po} increases. R_{po} , however, decreases strongly. The overall influence of the water uptake after porefilling is that τ_{pores} decreases, making the maximum frequency of this group higher. This can also be seen in Figure 3. The maximum of the left part of the graph, representing the $R_{\text{po}} C_{\text{po}}$, shifts to the right (to higher frequencies) with longer immersion times, due to water uptake after porefilling.

4.1.2. Coating containing large macropores

The degradation process of an organic coating system containing large macropores includes three phases. These three steps can be distinguished in Figures 4 and 5. During the *first phase* (0–1500 h of immersion), the water penetrates the coating and the pores are filled with electrolyte. Two clearly different time constants are presented in the EIS spectrum. During the *second phase*

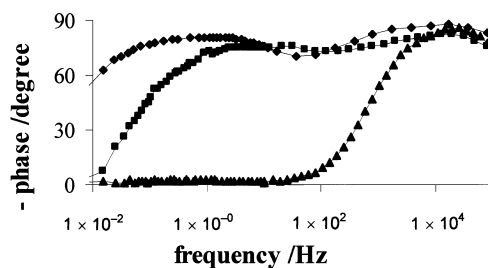


Fig. 4. Bode amplitude diagram for a coating containing large macropores after immersion in ASTM seawater. Key: (◆) phase 1, (■) phase 2 and (▲) phase 3.

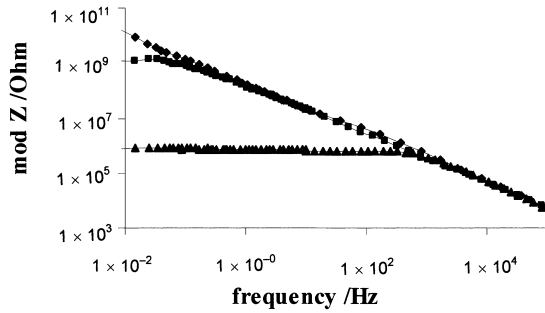


Fig. 5. Bode amplitude diagram for a coating containing large macropores after immersion in ASTM seawater. Key: (◆) phase 1, (■) phase 2 and (▲) phase 3.

(1500–1600 h), ionic contact exists between the electrolyte and the underlying zinc layer and corrosion starts. Comparable with the results for a coating containing small macropores, τ_{pores} decreases strongly, causing a shift in the maximum towards higher frequencies, and a $\tau_{\text{double layer}}$ appears, due to the formation of a double layer. In the *third phase* (>1600 h), the steady corrosion step, severe corrosion occurs τ_{pores} disappears completely, while $\tau_{\text{double layer}}$ increases and decreases cyclically due to the proceeding corrosion process.

4.2. Mechanical deformation

4.2.1. EIS measurements

Mechanical deformation leads immediately to the formation of cracks in the organic coating [4]. In corrosion terms, this means that a double layer is formed immediately after immersion. Hence, immediately after immersion the equivalent circuit represented in, Figure 2 should be used. τ_m is then defined as $\tau_{\text{cracks}} = R_{\text{cr}}C_{\text{cr}}$, present at the lowest frequencies, where also $\tau_{\text{double layer}}$ appears.

Figures 6 and 7 represent the results of EIS measurements on several samples submitted to different degrees of mechanical deformation, and one sample submitted to bending deformation. The bending deformation over a mandrel with diameter 11 mm is less severe than a 1% uniaxial deformation after 100 h of

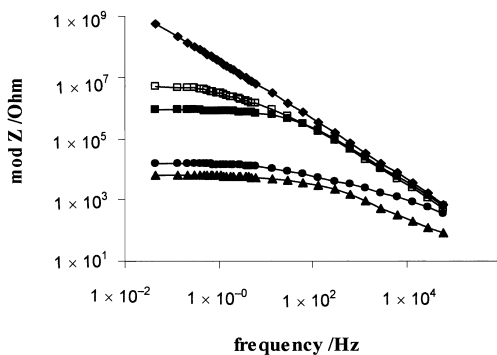


Fig. 6. Influence of mechanical deformation after 100 h of immersion in ASTM seawater. Key: (◆) reference; (■) 1%, (●) 5% and (▲) 10%; (□) $R = 11$ mm.

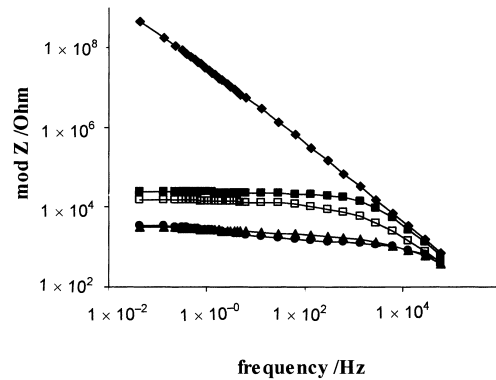


Fig. 7. Influence of mechanical deformation after 1000 h of immersion in ASTM seawater. Key: (◆) references, (■) 1%, (●) 5% and (▲) 10%; (□) $R = 11$ mm.

immersion in seawater. From 5% uniaxial deformation on, a strong influence of the damage can be noticed after this immersion time. After 1000 h of immersion it is clear that all degrees and all types of deformation are harmful to the coating quality. All time constants disappear, and an ohmic level is reached compared with the reference coating. This is clearly visible on Figures 6 and 7.

4.3. Weathering

4.3.1. EIS measurements correlated with alternative tests

By submitting this type of coated sample to accelerated weathering tests, the top layer of the organic coating is affected by breaking bonds. It was possible to observe this phenomenon by measuring the gloss and the static contact angle after the u.v. test. In this test, a drop of distilled water was put on the coating surface. The contact angle, the angle between the liquid and the coating surface, was then measured directly. A decrease in both parameters was measured and the results are shown in Figure 8.

For the QUV 340, the gloss remained almost constant. This could be an indication that the coating is not degraded during the time of the tests. For more severe tests like QUV 313 (continuous u.v. exposure or cyclic test: 8 h u.v. exposure + 4 h condensation) and QUV C (continuous u.v. exposure), a clear indication of deteri-

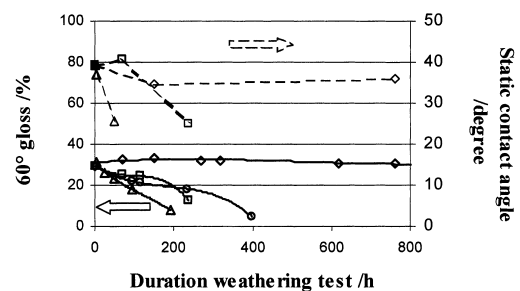


Fig. 8. Deterioration of gloss after different types of weathering tests. (◇) u.v. 340 (4 h u.v. + 4 h condens.); (○) u.v. 313 (cont. u.v.); (□) u.v. 313 (8 h u.v. + 4 h condens.); (△) u.v. C (cont. u.v.).

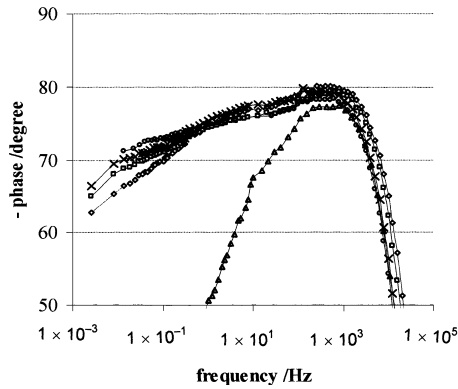


Fig. 9. Bode phase presentation of several samples submitted to different weathering tests after 2000 h of immersion in ASTM seawater. Key: (◆) reference; (□) 70 h u.v. 340 (4 h u.v. + 4 h cond.); (○) 115 h u.v. 313 (8 h u.v. + 4 h cond.); (×) 763 h u.v. 340 (4 h u.v. + 4 h cond.) (△) 48 h u.v. C (cont. u.v.).

oration of the coating appears. It seems that during the first 200 h of a QUV 313 test, continuous exposure to u.v. light is more severe than alternated exposure. This observation needs to be confirmed. For longer exposure times, alternated exposure is more detrimental to the coating. This is expected, since both hygroscopic and thermal stresses are present. The evolution of the contact angle and the gloss are similar. Surface bonds are broken, making the material more rough and more hydrophylic for the most severe u.v. exposures (QUV 313 and QUV C).

The impedance spectra of several u.v. radiated samples after 2000 h of immersion are shown in Figure 9. This graph reveals two groups of time constants, $\tau_{\text{coating}} = R_c C_c$ and $\tau_{\text{uv}} = R_{\text{uv}} C_{\text{uv}}$. For longer u.v. exposure, τ_{coating} increases. This is seen in Figure 9 by a slight decrease of the maximum frequency for this time constant present at the highest frequency range. Moreover, the decrease in phase angle can be explained as a loss of quality for the wetted part of the coating.

Figure 9 shows that the phase angle increases for the lowest frequency zone time constants. This indicates good u.v. resistance of the coating system for the u.v. spectra representative of sunlight after 2000 h immersion. The quality even improves. However, for shorter wavelengths with high intensities in the u.v. C region, the coating is destroyed. This phenomenon will be further investigated.

5. Conclusion

By means of EIS measurements it is possible to detect several groups of time constants in separate frequency ranges. Each time constant characterizes a different physical/electrochemical process. An overall formula for the description of the dielectric behaviour of the imperfect organic coating system is proposed, taking into account the different constituent parts and types of imperfections of the organic coating and their number. For each kind of imperfection, the degradation process can be explained by means of these grouped time constants.

References

1. R. Macdonald and W.B. Johnson, in 'Impedance Spectroscopy, Emphasizing Solid Materials and Systems' (J. Wiley & Sons, New York, 1987) p. 15.
2. A.K. Jonscher, in 'Dielectric Relaxation in Solids', (Chelsea Dielectrics Press, London, 1983) pp. 96–100.
3. F. Geenen, PhD thesis, TU Delft (1991).
4. V. Lavaert, P. Praet, M. Moors, E. Wettinck and B. Verhegghe, *Progr. Org. Coat.* **39** (2000) 157–165.
5. V. Lavaert, M. De Cock, M. Moors and E. Wettinck, *Progr. Org. Coat.* **38** (2000) 213–221.
6. B.A. Boukamp, 'Equivalent Circuit User's Manual', University of Twente (1989).
7. B. Yeum, ZsimpWin 2.00, Electrochemical Impedance Software, Data Analysis Software (2001).