Journal of Applied Electrochemistry (2007) 37:353–358
DOI 10.1007/s10800-006-9265-1

Interlayer defect evolution in an organic coating system on steel under hydromechanical loading

A. MISZCZYK*, M. SZOCIŃSKI and K. DAROWICKI
Department of Electrochemistry, Corrosion and Material Engineering, Faculty of Chemistry, Gdansk University of Technology, 11/12 Narutowicza St., Gdansk, 80-952, Poland
*(*author for correspondence, tel.: + 48-58-3471915, fax: + 48-58-3471092, e-mail: misa@chem.pg.gda.pl)*

Received 17 March 2006; accepted in revised form 15 October 2006

Key words: hydromechanical loading, interface defects, impedance spectroscopy, organic coating

Abstract

Impedance measurements on the interlayer region in an organic coating system subjected to cyclic mechanical stress are presented. A novel impedance sensor capable of detecting contact imperfections between adjacent coating layers has been developed. A bilayered coating system designated to serve in a marine environment has been subjected to conditions simulating synergistic impact of fatigue effects due to repetitive mechanical stress and immersion in 3% NaCl aqueous solution. The results revealed the detrimental influence of cyclic stress and water ingress on the quality of the interlayer adhesion. The proposed method of interlayer impedance evaluation can be employed to interlayer defect monitoring in multi-coating systems.

1. Introduction

Fatigue phenomena have been identified as an important cause of many component failures in engineering systems subjected to a repeated or fluctuating mechanical load [1]. In practice, many industrial constructions undergo repeated undercritical mechanical loads connected with e.g., engine vibration (cars, aircraft), wind activity (masts), vehicular traffic (bridges). Usually, paint systems are applied on the metal surface in order to protect against corrosion. They are now usually multilayer. The weak points of such a system are situated at the interlayer region. Fatigue damage generated by the load are caused by the development and growth of microscopic defects in these areas. Propagation results in the loss of adhesion between layers and failure of the protective function. Engineering systems exposed to atmospheric conditions also undergo humidity and temperature cyclic fluctuations [2–4], that generate additional stresses at the interfaces. These localize at the interlayer imperfections, defects and cracks. Additionally, such systems undergo ageing changes, which strongly decrease the resistance to fatigue due to making the polymer material stiffer [5]. Multilayer systems are now extensively used in practice and the mechanical resistance of the interfaces is a critical factor for reliability demands [6, 7]. For these reasons, in order to improve the performance, non-destructive methods capable of testing and monitoring of the interface mechanical integrity during system formulation and service life are needed.

In this paper we have proposed a new method for continuous, non-destructive testing or monitoring of protective system interfaces using impedance spectroscopy. This technique is widely used for studying the properties of electrochemical and corrosion systems [8–11]. Information on interface integrity is obtained by using a special electrode arrangement situated between the coating layers and made of conductive ink. Using this system we observed the changes in interface integrity as a function of the number of applied cycles under different exposure conditions.

2. Experimental procedure

A high-performance coating system used in ship applications from the Polish Paint Factory “Oliva” in Gdansk was studied. The naval coating samples consisted of a steel substrate, a solvent based epoxy primer (ca. 80 μm in thickness) and solvent based polyurethane topcoat (ca. 80 μm in thickness). To provide representative results, four samples were tested at the same time. Due to the fact that all samples behaved in a similar way presented results relate to one exemplary representative specimen, which was examined with great care. A special sensor was developed. Two 7($\pm$3) μm thick, 3 mm wide and 8 cm long stripes of the conductive ink (Orgacon, E1-P1030, Agfa-Gevaert, Belgium) were applied on the primer layer 1 cm apart from each other and then overcoated with a topcoat and used as sensor electrodes in impedance measurements, as shown in Figure 1.

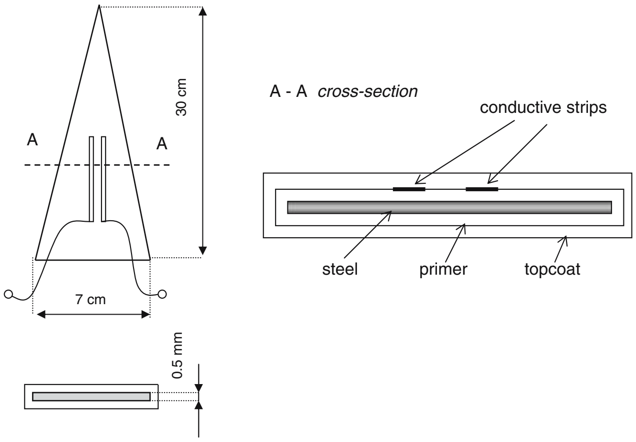

Fig. 1. Schematic representation of a sample with sensor electrodes.

In order to provide uniform stress distribution over the specimen a beam in the form of an isosceles triangle was used, Figure 2. The bending of such a triangle with a force applied to its vertex and with its base fixed results in an equal mechanical load, independent of distance to the axis [12]. The strain ε applied may be expressed as [12]:

$$\varepsilon = (6FL)/(Ebh^2) \quad (1)$$

where h, E, L and b are the thickness, Young's modulus, bisector length, and the width of the base of the triangular cantilever beam respectively and F is the force applied on the vertex of the beam. The displacement z of the vertex of the cantilever beam along the z direction under force F can be expressed as [12]:

$$z = (6FL^3)/(Ebh^3) \quad (2)$$

Combining Equations (1) and (2) leads to a relationship between ε and z:

$$\varepsilon = (h/L^2)z \quad (3)$$

Thus, the strain ε is directly proportional to the displacement z. Thus the triangular beam subjected to the force naturally develops a uniform curvature. As a consequence, the film on the top surface of the beam is subjected to uniform state of plain strain as the beam is deflected. In the same situation the rectangular beam geometry gives various state of plain strain, the greatest at the support.

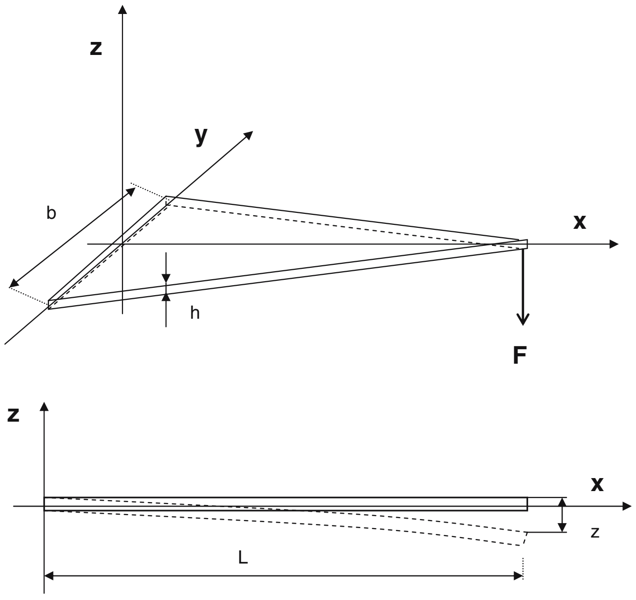

Fig. 2. Triangular cantilever beam notations.

In order to estimate stress caused by mechanical cycling the mathematical expression derived by Corcoran [13, 14] was adopted. Originally this equation was derived for determining stress in coating using the cantilever beam deflection method. In the case presented forcing defined deflection causes a development of defined stress.

Using the Concoran equation [13, 14]:

$$\sigma = (zE_s h_s^3)/\{3h_c L(h_s + h_c)(1 - \nu_s)\} + \{zE_c(h_s + h_c)\}/\{L^2(1 - \nu_c)\} \quad (4)$$

where: σ – the coating stress, h – the thickness, ν – Poisson's ratio, the subscripts s and c refer to the substrate and coating, respectively, it was estimated that for selected deflection (9 cm) maximum stress during cycling was ca. 135 MPa. The obtained value seems to be high compared to the weathering-induced stress (this stress is of the order of 20 MPa [15]). Although high for acceleration reasons this stress is undercritical for the tested systems. This was checked using impedance measurements through the coating in immersion by comparison of impedance spectra recorded before and after single mechanical cycles. Possible irreversible effects are detected by changes in the impedance spectrum.

Coated panels were exposed in the laboratory to immersion in 3% NaCl aqueous solution at 22(±1) °C. This simulated conditions similar to those in naval coating systems. Figure 3 shows a schematic diagram of

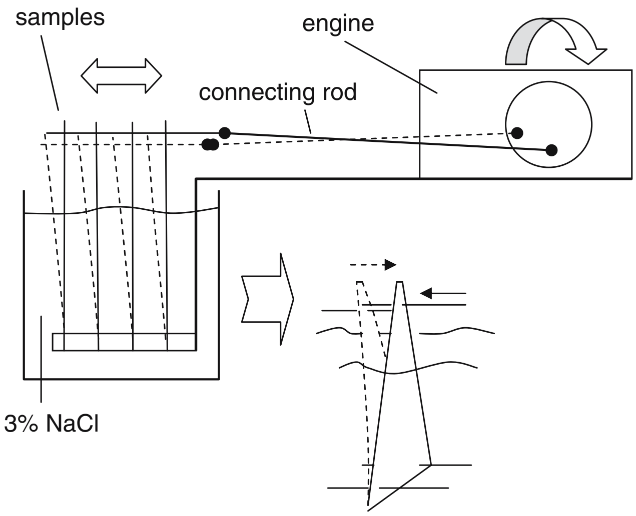

Fig. 3. Schematic diagram of an experimental set-up utilized in the test.

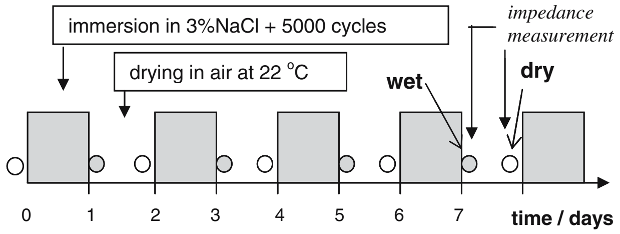

Fig. 4. Schematic diagram of the testing procedure.

the sample loading due to mechanical cycling under immersion conditions. Usually four samples were tested simultaneously in order to check the reproducibility of the measurements. After each immersion-cycling period (24 h immersion and 5000 mechanical cycles) the sample was taken from the bath for 24 h and dried naturally in laboratory air at ca. 22 °C and 30–35% RH. Results were obtained at a mechanical cycling frequency of 0.07 Hz. Figure 4 shows a schematic schedule of the sample loading.

The impedance measurements were performed using a two electrode system, with a frequency response analyser (Solartron 1255) connected to a high impedance interface (Atlas 9181). The two electrode system was preferred because there should be no potential difference applied between two identical electrodes, which could influence the tested system. The impedance measurements were carried out registering 10 points/decade over a frequency range from 1 MHz to 0.1 Hz and 5 points/decade over a range from 0.1 Hz to 0.001 Hz with 60–20 mV signal amplitude depending on the order of the measured impedance value. The selected amplitude allowed reliable measurements due to the improved signal to noise ratio. As the system under investigation was a dielectric one and exhibited very high impedance, the amplitude applied was slightly higher than in conventional electrochemical systems. Some impedance measurements were carried out employing commonly used assembly. A glued cylinder was used, filled with 3% NaCl solution and platinum mesh immersed in electrolyte as a counter electrode and coated steel as a working electrode ("through-the-coating" measurements). Figure 5 shows a schematic diagram of both electrode arrangements and expected capabilities for detection of defects along the intercoat region (a) or through the coating (b). The Boukamp program was used for fitting of impedance data [16].

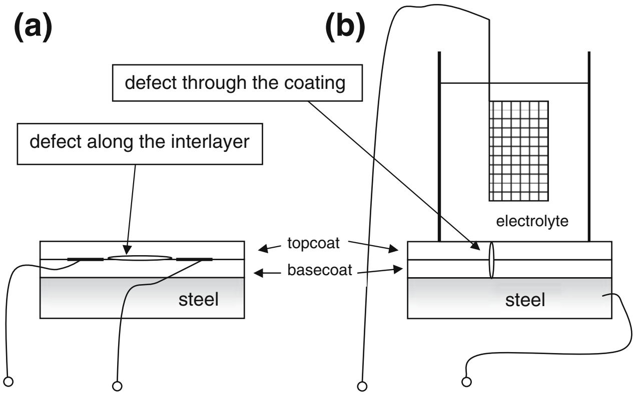

Fig. 5. Diagram showing a schematic view of new (a) and traditional electrode arrangement (b) with type of defects detected in each case.

3. Results and discussion

Figure 6 presents impedance spectra for a high-performance naval system on steel subjected to cyclic mechanical deformation and immersion in 3% NaCl aqueous solution after different numbers of cycles. They were recorded in the wet state, immediately following cycling. A gradual degradation of the interlayer region with number of mechanical cycles is evident. Conduction through the topcoat was excluded using the procedures described in [17]. Each series of mechanical cycles produces a decrease in interlayer impedance. Such behaviour suggests fatigue damage. According to fatigue theory [1] the stress suffered by the system is

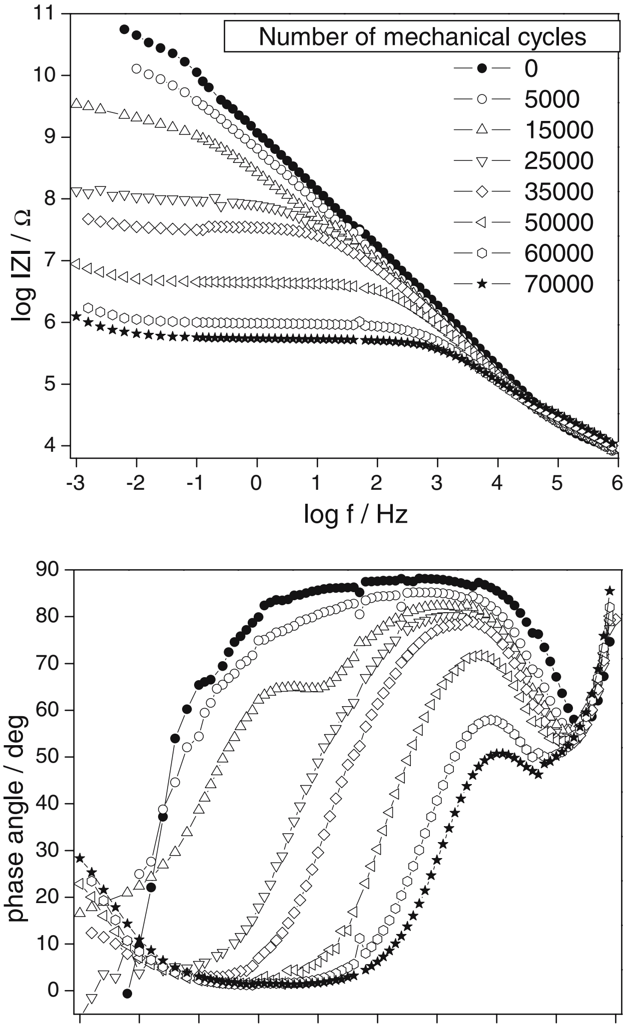

Fig. 6. Impedance spectra (in Bode format) for the interlayer region of the tested coating system as a function of an applied number of mechanical cycles.

undercritical in nature. This means that it is not the magnitude of a single deformation that causes coating failure. The repetitiveness and number of stress cycles imposed is a key factor. It seems that the area of contact between epoxy primer and polyurethane topcoat gradually becomes non-uniform. This is confirmed by the behaviour of the high frequency part of the impedance spectra presented in Figure 6. A linear part with a slope lower than −1 on the log $|Z|$ vs. log f plot is typical for transmission line systems [18, 19]. It is very likely that each set of mechanical deformations applied resulted in increased contact imperfections manifested by local debonding between successive coating layers. The progress of this process is a function of the number of applied cycles. If the interface between coating layers is locally weak enough, coating stress leads to local delamination [15, 20]. Therefore, further mechanical cycling contributes to the formation of new defects and the propagation of already existing defects [15]. Such discontinuities within the interlayer region become the preferred sites of electrolyte ingress. The gaps formed between the primer and topcoat are progressively filled with water [21]. Wapner et al. [22] have shown, using FT-IR and Kelvin probe techniques, that the interfacial diffusion of water is about two orders of magnitude faster than transport through the coating itself. Leng et al. [23] presented a model considering a threshold ionic concentration at the interface which develops the delamination front. The process of water incorporation was found to be reversible, at least in the initial stages of the experiment.

Figure 7 depicts the impedance spectra for the tested coating system in the wet and dry state after 40,000 mechanical cycles. The two spectra were registered after a fixed number of mechanical cycles, one just after cycling and immersion and a second after moisture desorption for ca. 23 h of drying in ambient laboratory conditions. Impedance after water desorption remains high throughout most of the experiment. It is so until 50,000 cycles, when dry state impedance does not come back to the previous level and drops by order of magnitude. This can be seen in Figure 8, which shows the evolution of log $|Z|$ value at 0.001 Hz for samples subjected to various conditions. This suggests that the damage to interlayer adhesion by the cyclic mechanical stress is so significant that it is also reflected in the dry state parameters.

In order to show that gradual degradation of the interlayer region was exclusively due to cyclic mechanical stress experienced by the specimen, a reference sample was also included in the test. It was nominally the same coating system subjected to cyclic immersion in 3% NaCl solution and drying under ambient laboratory conditions. Figure 8 shows sample impedance values obtained for the reference sample in the wet and dry state, respectively. There is no significant deterioration of dielectric bulk properties in such a system. Thus it is the repetitive mechanical stress that is responsible for interlayer impedance impairment.

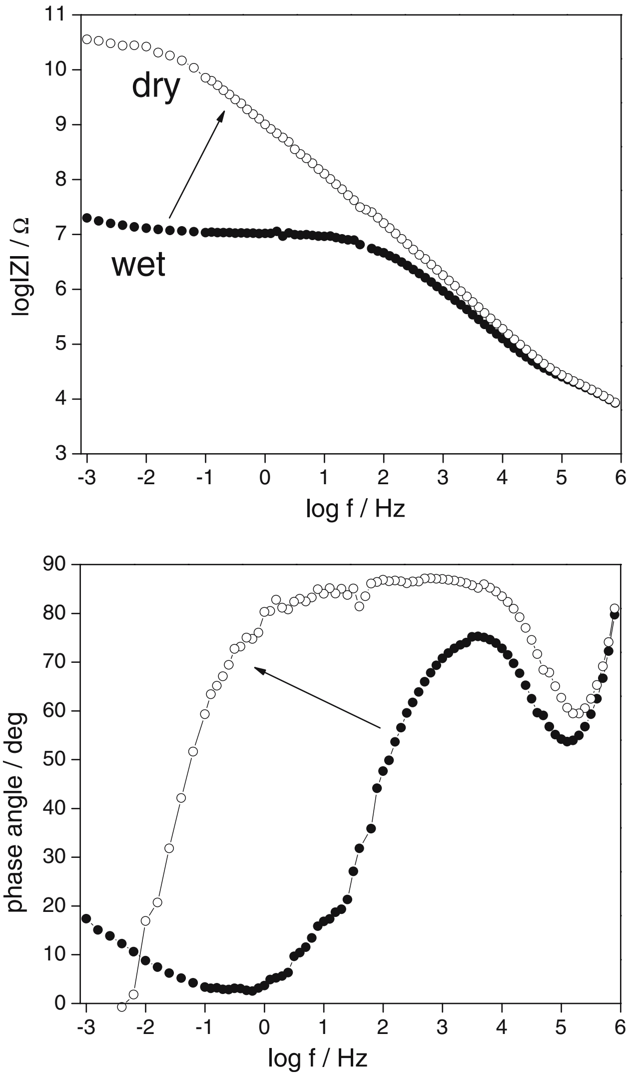

Fig. 7. Impedance spectra (in Bode format) for the tested coating system in wet and dry states after 40,000 mechanical cycles.

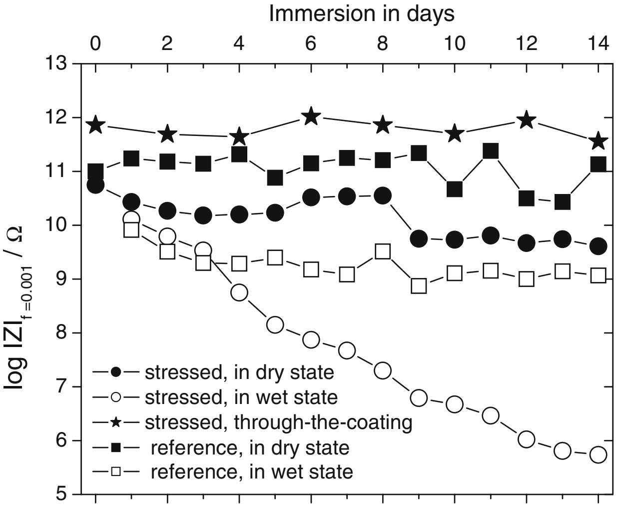

Fig. 8. Impedance modulus at a frequency of f = 0.001 Hz as a function of the number of mechanical cycles or immersion time for tested coating samples.

A comparison of the two systems (stressed and reference ones), provided in Figure 8, shows that the sample subjected to deformation exhibits a gradual fall in impedance, especially in the wet state.

Apart from revealing the detrimental impact of cyclic mechanical stress on the quality of interlayer adhesion, the experiment proved the usefulness and capability of the new electrode arrangement to detect damage in the interlayer region. Its advantages become clear when compared with the traditional approach to impedance measurement of coating systems. Figure 9 shows impedance spectra recorded for the stressed specimen after a fixed number of cycles, but acquired using the traditional technique ("through-the-coating"). These spectra suggest excellent protective properties of the coating but do not reveal any problems at the interlayer region. Thus the novel methodology proposed by the authors can lead to reliable assessment of interlayer defects and allows continuous monitoring. Detailed analysis of changes in impedance spectra with temperature enables the determination of adhesion durability in the interlayer region [17, 24]. Thus appropriate tests can characterize the durability of coating systems with respect to interlayer defect growth and adhesion loss in conditions similar to real exposure of automotive, aircraft or naval coating systems.

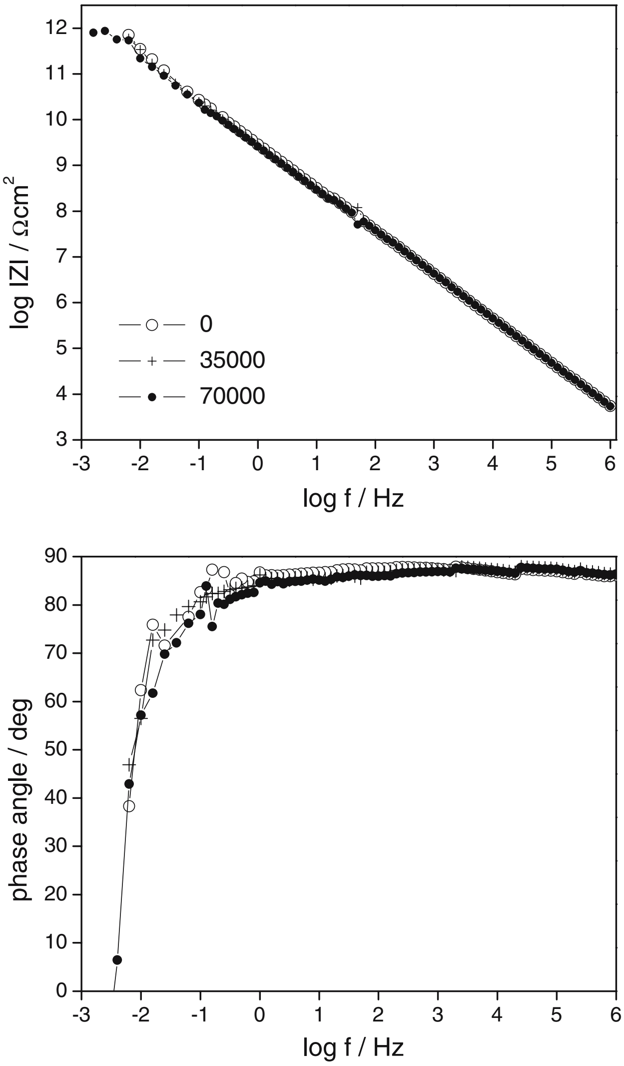

Fig. 9. Impedance spectra (in Bode format) for the tested sample after a different number of mechanical cycles measured in the traditional manner (cross coating).

4. Conclusions

(1) A new electrode arrangement has been proposed for the evaluation of interface integrity in multilayer coating systems subjected to fatigue load using an impedance spectroscopy method.
(2) According to the well known detrimental effect of water on adhesion, the proposed approach enables the quantification of bond degradation due to environmental moisture attack accompanied by cycling mechanical stress.
(3) Interlayer impedance is very sensitive to outer conditions (immersion or dry atmosphere).
(4) In the investigated case, using the proposed approach, it was shown that mechanical cycling (vibration) of a coated system causes degradation of the interlayer bond. Using the traditional impedance measurement method it was simultaneously found that barrier properties were not significantly altered.

References

1. S. Suresh, *Fatigue of Materials* (Cambridge University Press, Cambridge, 1998).
2. D.Y. Perera, *Prog. Org. Coat.* **28** (1996) 21.
3. D.Y. Perera, *Prog. Org. Coat.* **44** (2002) 55.
4. A. Miszczyk and K. Darowicki, *Prog. Org. Coat.* **46** (2003) 49.
5. M.E. Nichols, J.L. Gerlock, C.A. Smith and C.A. Darr, *Prog. Org. Coat.* **35** (1999) 153.
6. S.J. Bull and A.M. Jones, *Surf. Coat. Technol.* **78** (1996) 173.
7. R. Zou, L. Li and Z. Gui, *Ceramic Int.* **27** (2001) 889.
8. ‚Impedance Spectroscopy: Theory, Experiment, and Applications', E. Barsoukov and J. Ross Macdonald (eds), (New York, Wiley & Sons, 2005).
9. A. Amirudin and D. Thierry, *Prog. Org. Coat.* **26** (1995) 1.
10. J.N. Murray, *Prog. Org. Coat.* **30** (1997) 225, **31** (1997) 255, **31** (1997) 375.
11. D.D. Macdonald, E. Sikora and G. Engelhardt, *Electrochim. Acta* **43** (1998) 87.
12. W.C. Young, *Roark*'s Formulas for Stress and Strain, 6th ed., (McGraw-Hill, New York, 1989).
13. E.M. Corcoran, *J. Paint Technol.* **41** (1969) 635.
14. L.F. Francis, A.V. McCormick, D.M. Vaessen and J.A. Payne, *J. Mater. Sci.* **37** (2002) 4717.
15. M.E. Nichols, J.L. Gerlock, C.A. Smith and C.A. Darr, *Prog. Org. Coat.* **35** (1999) 153.
16. B.A. Boukamp, *AC-Immitance Data Analysis System ‚Equivalent Circuit'* (Twente University of Technology, Enschede, The Netherlands, 1989).
17. A. Miszczyk and T. Schauer, *Prog. Org. Coat.* **52** (2005) 298.
18. R. de Levie. *in* P. Delahay (ed.), Advances in Electrochemistry and Electrochemical Engineering 6, (Wiley, New York, 1967).
19. D.D. Macdonald, *Electrochim. Acta* **51** (2006) 1376.

20. M.E. Nichols, C.A. Darr, C.A. Smith, M.D. Thouless and E.R. Fischer, *Polym. Deg. Stab.* **40** (1998) 291.
21. A.A. Korzhenko, M. Tabellout and J.R. Emery, *Mater. Chem. Phys.* **65** (2000) 253.
22. K. Wapner, M. Stratmann and G. Grundmeier, *Electrochim. Acta* **51** (2006) 3303.
23. A. Leng, H. Streckel and M. Stratman, *Corros. Sci.* **41** (1999) 579.
24. A. Miszczyk, K. Darowicki and T. Schauer, *J. Solid State Electrochem.* **9** (2005) 909.