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Evaluation of Relative Humidity Effects on Interfacial Impedance at Inter-Coat Interfaces*

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Impedance spectroscopy has been applied as potentially non-destructive method for the evaluation of adhesion at the interface between two polymer layers in protective coating system. The aim was to examine the effect of the outdoor humidity on the interfacial impedance. A automotive basecoat/clearcoat system has been investigated. A new electrode sensor has been employed to detect the changes caused by adhesive debonding and accumulation of water at the interface. The electrode comprising two thin stripes of an electroconductive ink was placed between two coating layers. Large changes in the impedance were observed when humidity conditions were altered. The obtained data were indicative for strong sensitivity of the interlayer impedance to the outdoor humidity. Water accumulation in the interlayer and the formation of conductive paths led to the worsening of adhesion and deamination of the coating layers.

Key words: coatings, adhesion, corrosion

Polymeric coatings are commonly used for anticorrosion protection of metals. Modern coating systems are multilayered and each layer plays a distinct function. Interlayer spacing is potentially weak point of the protective system.

Degradation mechanism of polymer coatings on metals has been extensively studied using electrochemical impedance spectroscopy (EIS) [1–3]. Detection of defects in the coatings and their expansion in time has received a special interest. These investigations provided important information on the protective properties of the coating systems. However, some defects could not be readily identified using typical methods, since they did not connect bulk solution with the metal substrate through the coating, but along the interlayer area. These defects can be serious and lead to the interlayer de-cohesion, when the coating system is placed in a humid environment. Moisture penetrates the coating and diffuses along the interfaces, reduces dipolar and dispersive interactions between the layers, and breaks chemical bonds at the interface

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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by initializing hydrolysis reactions. All this results in the lowering of polymer adhesion (wet adhesion) and is considered as the main reason of the adhesion loss.

Bulk diffusion into the coating system has been studied using impedance spectroscopy [4–6]. However, interfacial diffusion [7–9] was rarely investigated by this technique. In this work, impedance spectroscopy has been utilized to study the effect of water absorption at the interface of two polymer layers in the coating system.

EXPERIMENTAL

Waterborne polyurethane-polyacrylate-dispersion basecoat and a two-component waterborne polyurethane clearcoat were investigated using standard steel panels (190 mm×105 mm×1 mm) of the thickness of 25 μm and 30 μm, respectively. Two 10 μm-thick, 3 mm-wide and 8 cm-long stripes of electroconductive ink (Orgacon, E1-P1030, Agfa-Gevaert, Belgium) were applied on the basecoat 1 cm apart from each other, covered with a clearcoat, and used as sensor in the impedance measurements (Fig. 1).

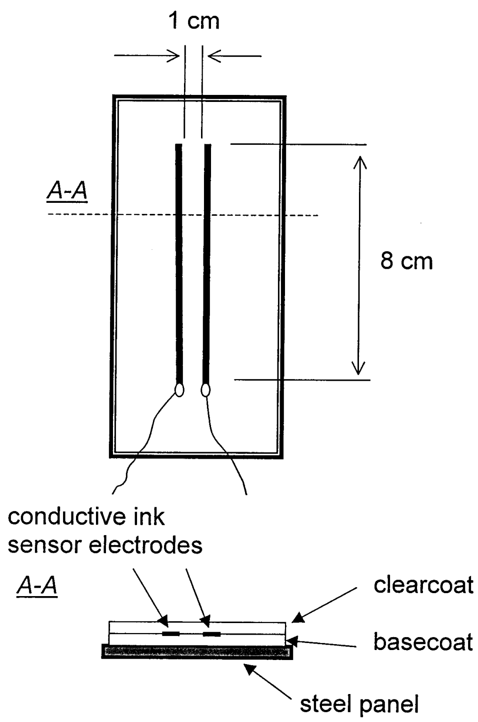


Figure 1. A scheme of a new sensor.

The temperature of the sample was controlled using programmed PID heating device. Before EIS measurements the samples were exposed to air of the known relative humidity (rh), which was adjusted with saturated solutions of potassium carbonate (43% rh), potassium chloride (84% rh) and potassium sulphate (97% rh). The impedance measurements were obtained using two-electrode system. A Solartron 1255 Frequency Response Analyser and a high impedance buffer Atlas 9881 was utilized in the frequency range 64 kHz÷1 mHz applying the sinusoidal signal of a 60 mV amplitude.

RESULTS AND DISCUSSION

In Fig. 2 the results of impedance investigations of the sample conditioned in exsiccator under *ca*. 4% relative humidity (rh) are presented. The results are typical of dielectric materials of very high impedance.

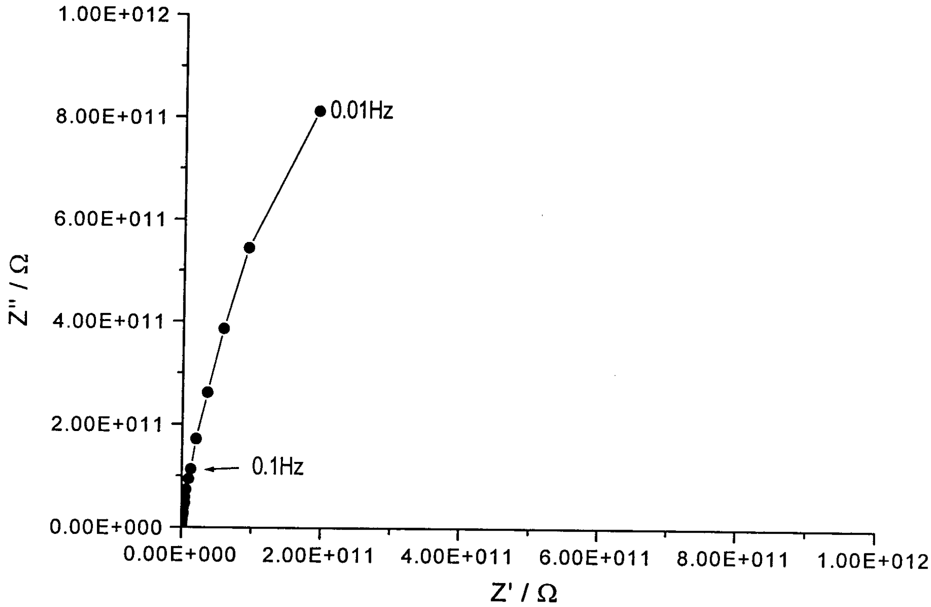


Figure 2. Impedance spectrum of the interlayer region in the basecoat/clearcoat system at the exposure to the air of 4% rh.

The sample was exposed for two consecutive days to the air of 43% rh, 97% rh, 43% rh, and 84% rh (Fig. 3). Impedance spectra were taken after various times of exposure to the air of different humidity (36 hours after each humidity change) – see Fig. 4. For the comparison purpose, the results obtained for the same sample after its immer-

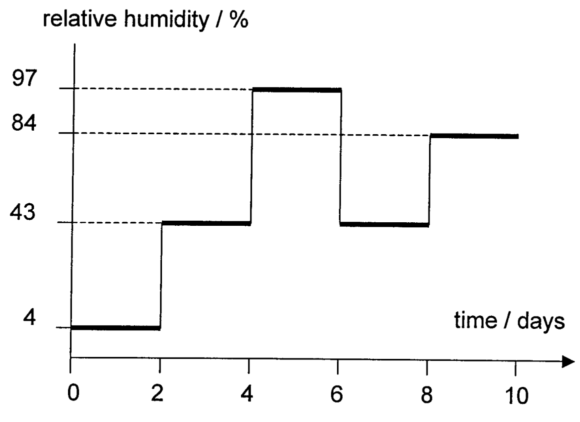


Figure 3. Schematic diagram of the humidity variations.

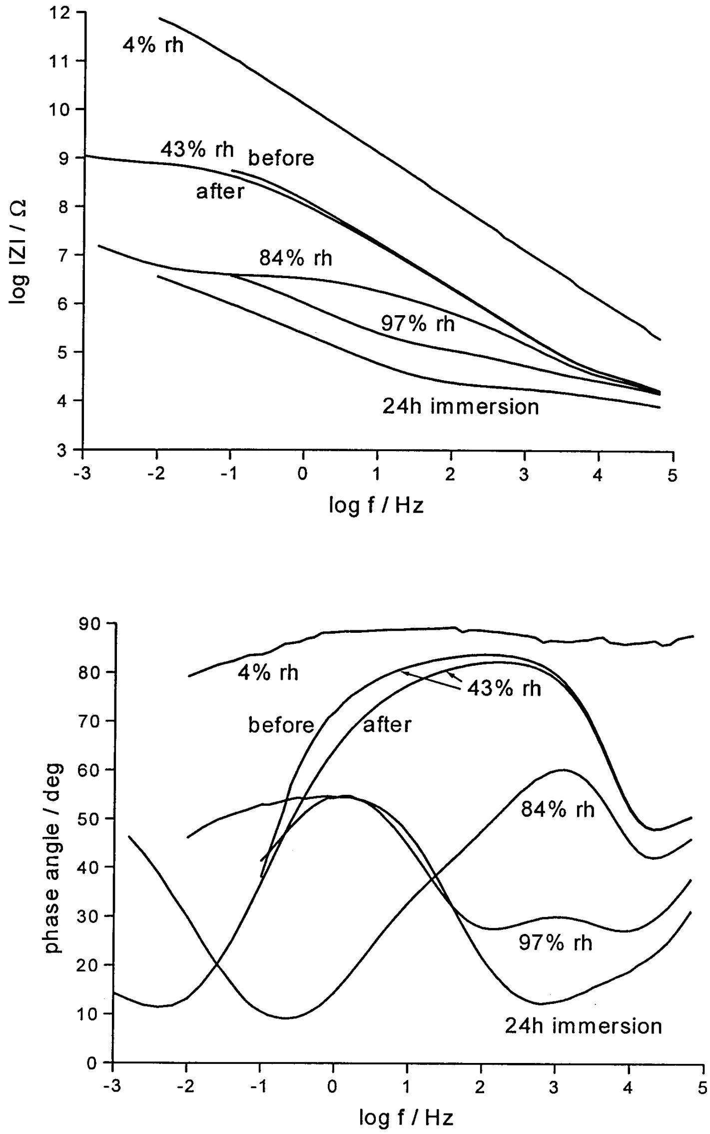


Figure 4. Impedance spectra of the interlayer region in the basecoat/clearcoat system after its exposure to the air of different humidity and after 24 h-long immersion in water.

sion in water for 24 h are also shown. One easily notices a strong dependence of the interlayer impedance on the air humidity. Moreover, impedance tends to decrease with the increasing humidity. This tendency is more pronounced in the middle-frequency spectrum range. This behaviour can be attributed to the water ingress into the coating and interlayer area, and the formation of water conductive paths. Regeneration of the interlayer impedance is observed when humidity is being changed in the opposite direction – from high to low values. This is an evidence for the almost reversible transport of water into and out of the coating.

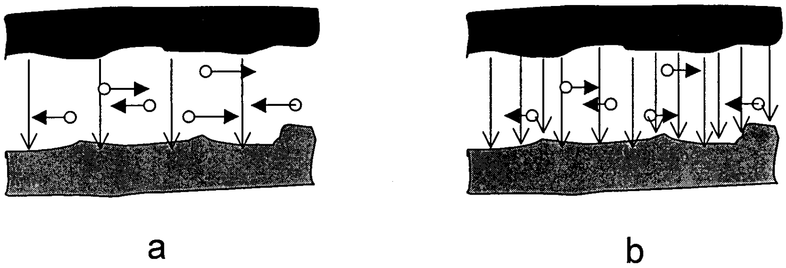
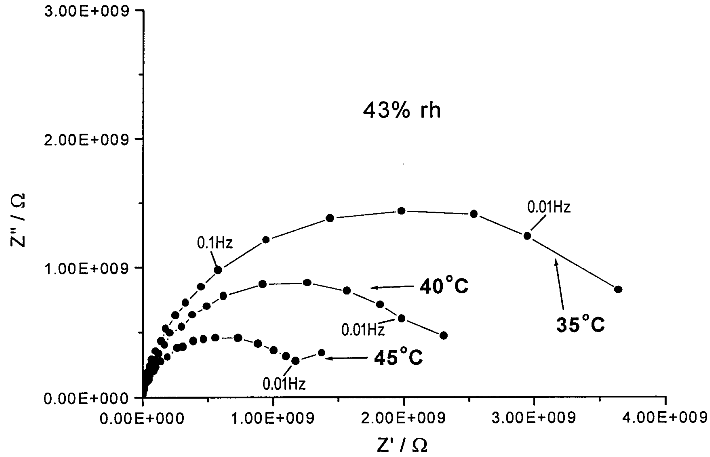


Figure 5. Schematic representation of mass transport in the interlayer region at weak (a) and strong (b) attractive forces (poor and strong adhesion, respectively).



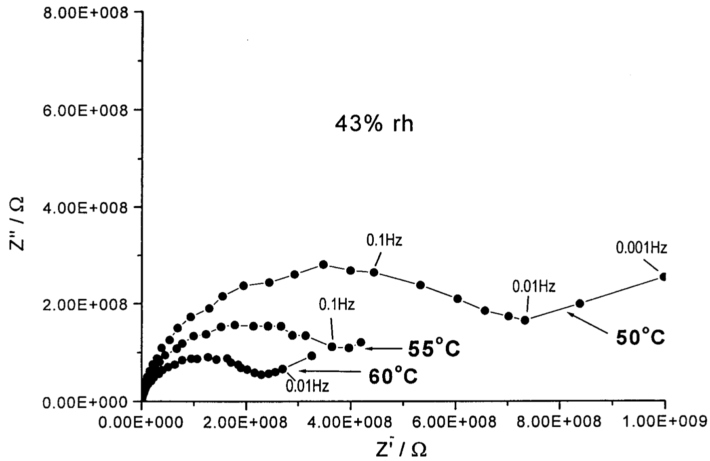


Figure 6. Impedance spectra of the interlayer region in the basecoat/clearcoat system after its exposure to the air of 43% rh at different temperatures.

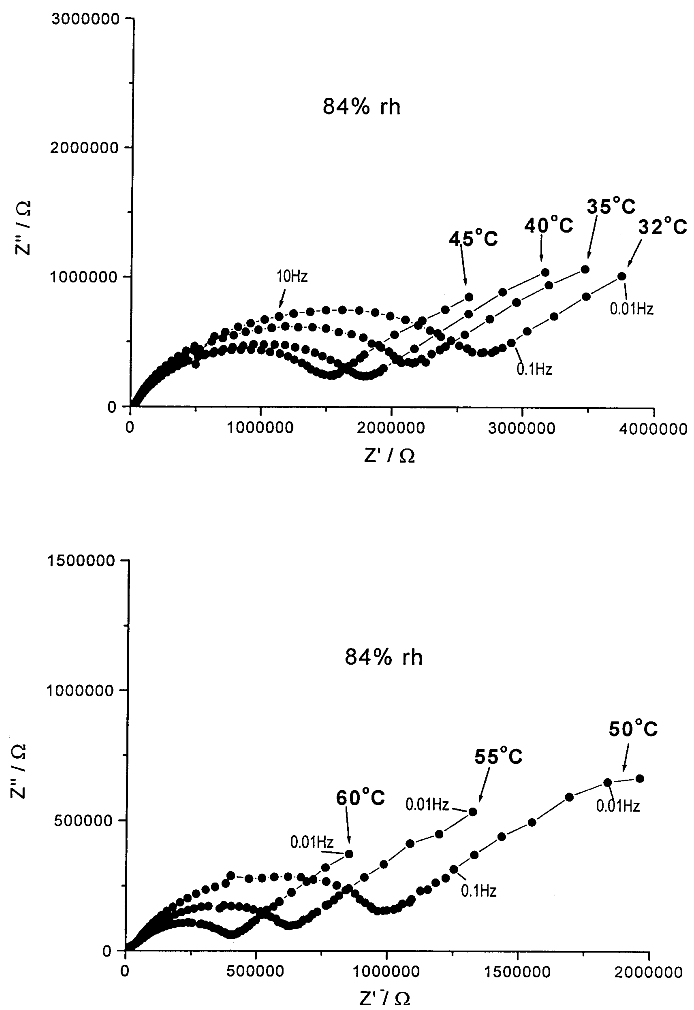


Figure 7. Impedance spectra of the interlayer region in the basecoat/clearcoat system after its exposure to the air of 84% rh at different temperatures.

In order to compare the interlayer impedance with the impedance of the entire coating, the measurement with the conventional working electrode/auxiliary electrode system was carried out under the same humidity conditions. The obtained impedance data were at least one order of magnitude higher than those obtained for the interlayer [10]. This is indicative for the stronger accumulation of water in the interlayer area and development of conductive paths. Obviously, the interlayer region predominantly contributes to the measured impedance.

The ingress of water vapour into the coating caused a decrease of the impedance modulus, as well as the shift of the time constant to lower frequencies. Such behaviour can be related to the presence of some defects (electrolytic contacts) between the layers. Water penetrating the layers fills up these defects and activates them dielectri-

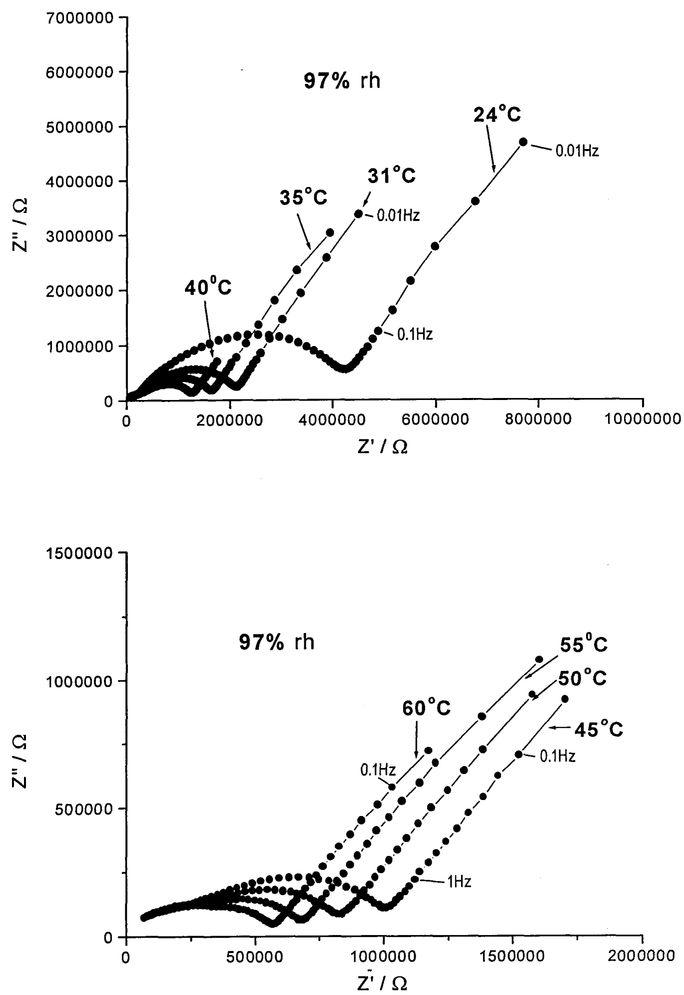


Figure 8. Impedance spectra of the interlayer region in the basecoat/clearcoat system after its exposure to the air of 97% rh at different temperatures.

cally/ionically. Ionic mobility within the interlayer region depends on the magnitude of attractive forces between the layers. Strong attractive forces between the layers (good adhesion) decrease ionic mobility, which is schematically shown in Fig. 5. In Figures 6–8 the impedance spectra of the interlayer region obtained at different temperatures and rh of 43%, 84% and 97% are presented. Strong influence of both the humidity and the temperature on the impedance of the interlayer spacing is evident. To quantify the influence of air humidity on ionic mobility in this region semicircle diameters from Figures 6–8 were plotted *vs.* 1/T to obtain Arrhenius plots, Fig. 9. The slopes of the plots are proportional to the activation energy of ionic mobility and progressively decrease as the humidity increases. Consequently, the slopes of the logR *vs.* 1/T plots can be used for the quantification of the interlayer adhesion.

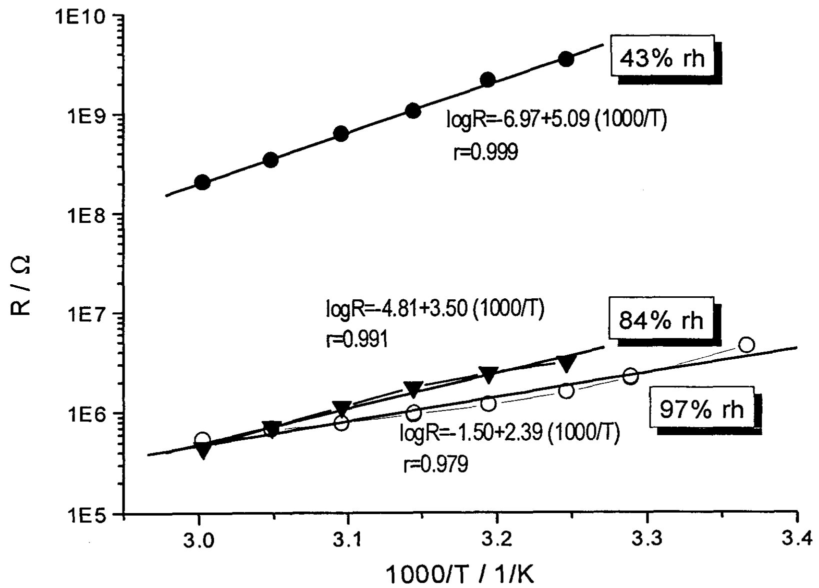


Figure 9. logR *vs.* 1000/T plots obtained for different air humidity (rh); R stands for semicircle diameters from Figures 6–8.

In order to support this prediction, the blister test was employed to directly evaluate the interlayer adhesion [9]. The results were similar to and correlated with the previous ones. One may conclude that the higher the slope, the better the adhesion [9].

CONCLUSIONS

A new sensor was used to monitor the interlayer adhesion in the coating system exposed to different humidity conditions. A new design of the electrode sensor was proposed. The sensor comprised thin conductive-ink stripes applied on the basecoat, which were subsequently covered with the top coating. The sensor was used in the impedance measurements.

Ion transport and water accumulation in the interlayer region were proved to affect the interlayer adhesion. The interlayer resistance, R was measured from the impedance spectra and plotted against the reciprocal of the temperature, 1/T (Arrhenius plot). The slope of the obtained dependence corresponded to the activation energy of the ion/water diffusion in the interlayer region, and can be regarded as the measure of the interlayer adhesion.

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