

Enhanced Surface Roughness of Organic Coatings Due to UV – Degradation; an Unknown Source of EIS – Artifacts

OCHS, Hartmut; VOGELSANG, Jörg; MEYER, Gabriela
SIKA Chemie GmbH, Kornwestheimer Str. 107, D-70439 Stuttgart, Germany

Abstract:

Coatings can be destroyed by UV radiation causing polymer degradation resulting in an increased surface roughness. In conditions of high humidity or after contact with electrolyte solution water is accumulated in the rough surface. The process of monitoring the degradation of coatings with Electrochemical Impedance Spectroscopy (EIS) may be effected by severe misinterpretation of EIS – spectra, because of stray currents through the water film to a coating disruption (scribe or unpainted area), even if the measured area is sealed. This superficial humidity is hardly removed by drying with a towel or similar measures. Only by air – drying the water evaporates and it is possible to measure the coating properties and not any kind of artifact. This mistake, reported here the first time, is not only limited to EIS measurements, moreover all other electrochemical techniques may be affected accordingly.

Introduction:

UV – degradation is an important aging process of coatings exposed to atmospheric weathering conditions. Many different standards are available for lab testing and several companies offer services for outdoor weathering of coated samples in quite distinctive environments.

Further, cyclic weathering tests become more important due to sometimes poor correlation of single accelerated weathering tests, like salt spray cabinet or constant condensation. These cyclic weathering tests are developed to simulate several different aggressive environmental impacts like humidity, salt fog, changing climatic conditions or UV.

The monitoring of the degradation of coatings with electrochemical techniques, such as Electrochemical Impedance Spectroscopy (EIS) or Electrochemical Noise Analysis (ENA), became more and more popular over the last decade. So it was a logical consequence to check the suitability of EIS for the monitoring of UV degradation.

The idea was to measure EIS spectra series with increasing irradiation time in order to follow the changes of water uptake and coating resistance. The ongoing polymer degradation should lead to less dense paint films with lowered barrier properties. As a result increasing water uptake and decreasing coating resistance could be expected.

Experimental

Coatings

Two chemically different coatings were used: two layers of a one-component physically drying and oxidatively cross-linking alkyd paint and a two-component polyurethane top coat on an epoxy primer with micaceous iron oxide. The coatings were applied according to their technical data sheets, on smooth and grit blasted panels. After application the samples were conditioned for two weeks at 23°C/50% r.h. in order to allow sufficient curing. A scratch was applied according to the draft of standard ISO/CD 20340 “Performance Requirements for Protective Paint Systems for Off-shore and related Structures” and then exposed to a cyclic test as described in Fig. 1: over a period of 80h 10 cycles were performed with 4hours humidity and 4 hours UV – irradiation. Thereafter 72 hours of salt fog exposure and 16 hours of dry conditioning at ambient temperature were added to complete one macro-cycle of one week. This procedure was followed as closely as possible in order to meet annex A part B “optional climatic cycle” of the committee draft of ISO 20340. But during the experiments the cycle has been changed twice by the responsible ISO – committee. Now the cycle is 72 hours

of salt fog, followed by 24 hours of thermal shock or dry and ambient climate, finalized by 72 hours of UV/condensation.

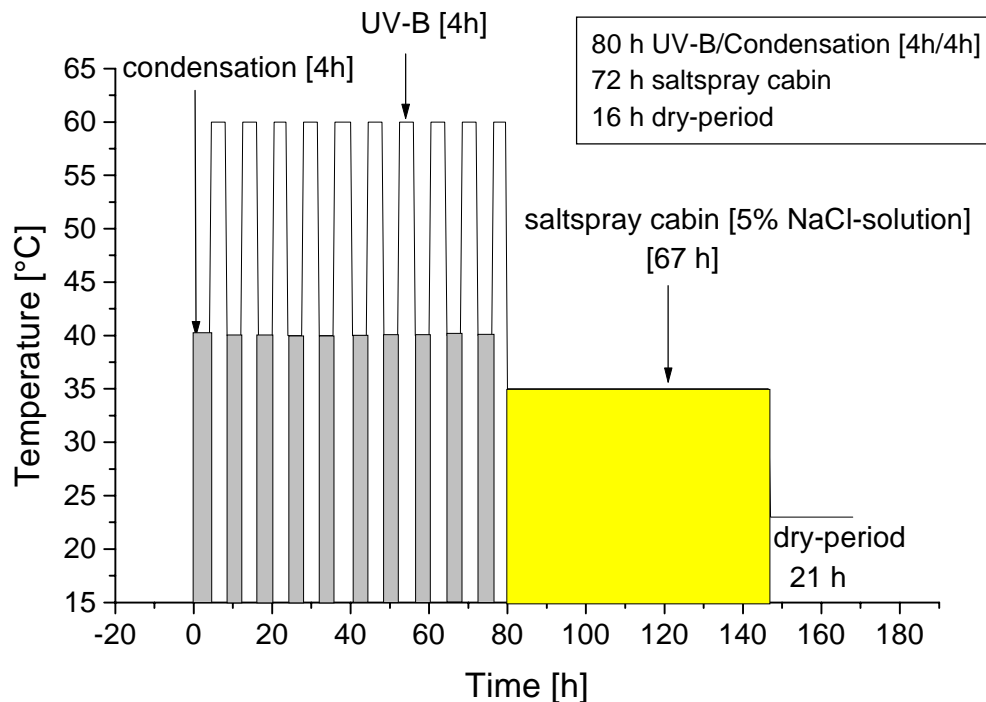


Fig. 1: Schematic plot of weathering procedure according to ISO/CD 20340 “Performance Requirements for Protective Paint Systems for Off-shore and related Structures”; 10 cycles were performed (4hours humidity and 4 hours UV – irradiation) over a period of 80h. Thereafter 72 hours of salt fog exposure and 16 hours were added to complete one macro-cycle of one week.

Measuring

After each cycle (ergo once a week) EIS – spectra were recorded with a Zahner IM6 Impedance Spectrometer equipped with a “HighZ” – preamplifier. The frequency range was 0.1 Hz to 100kHz with an amplitude of 20mV. In order to have comparable conditions the measurements were performed directly after salt spray exposure. The spectra were recorded after rinsing with de-ionized water and removal of excess water from the surface by using a towel. Thereafter the samples were mounted in a sample holder, as described in Fig. 2, where the coated steel panel was fixed with a rubber seal between PVC – tube and coating. The measured area was 4.9 cm².

The electrolyte was a 0.01molar KNO₃ – solution. All data were analyzed with Thales SIM, a simulation software package developed by Zahner.

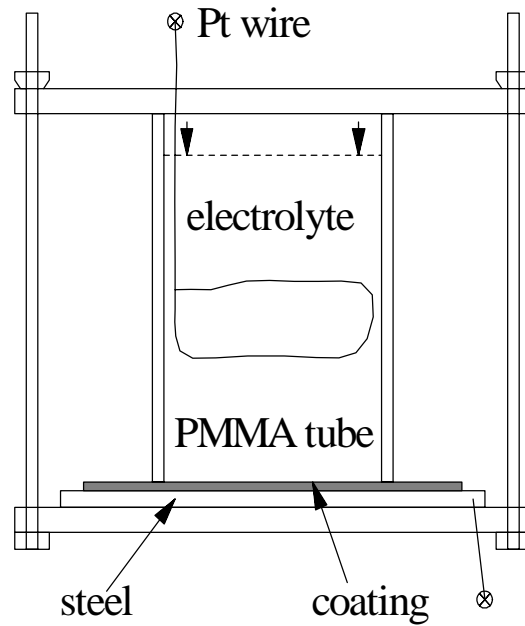


Fig. 2: Principle plot of the sample holder. The measured area was 4.9 cm^2 . The coated steel panel was fixed with a rubber seal between PVC – tube and coating.

Results

In Fig. 3 an EIS- spectra of the alkyd paint is shown after 4 days of immersion. The coating is in a pseudo stationary state, where no significant changes occur for a certain time. In Figure 4 the respective graph is shown for the polyurethane top coat. Both show the state of the coating after sufficient time of swelling under immersion condition. Both graphs have been fitted with model M1, as displayed in the figures.

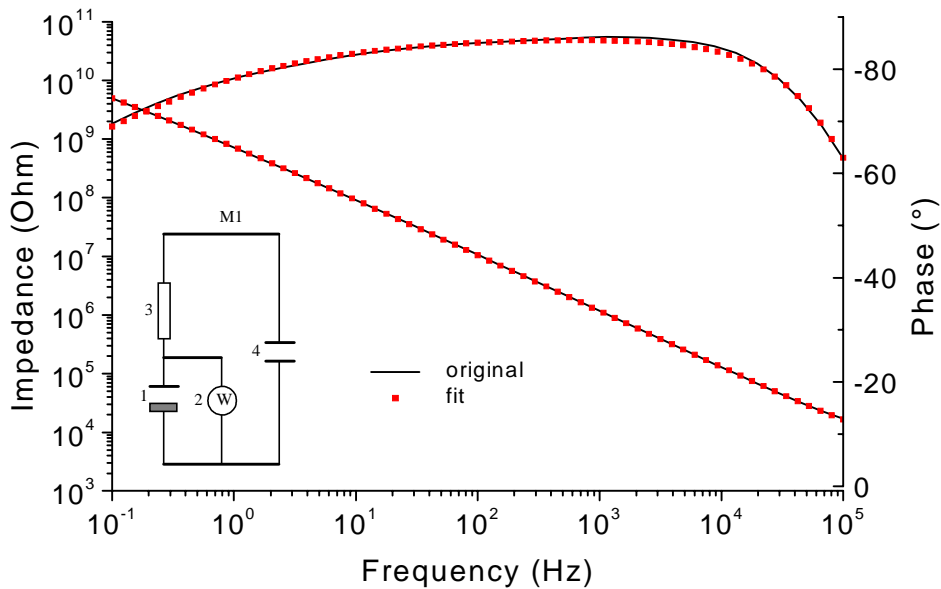


Fig. 3. EIS- spectra of alkyd paint after 4 days of immersion; solid line: measurement, dots: fit with “reduced” model (see fig. 5)

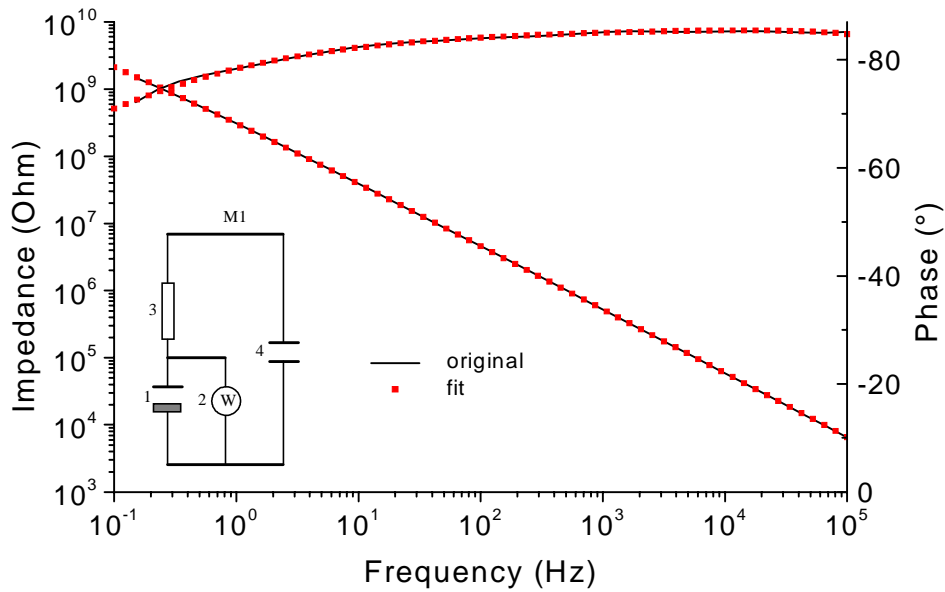


Fig. 4. EIS – spectra of epoxy/PU coating after 4 days of immersion; solid line measurement, dots: fit with “reduced” model (see fig. 5)

This model M1 was derived from basic considerations (Fig. 5): the total signal from impedance measurements of barrier coatings is effected by the coating properties and the input impedance of the spectrometer. The coating itself shows a Constant Phase Element (CPE) which should be called “loss capacity”*, a Warburg impedance as a first approximation for the description of diffusion processes in the coating and the coating resistance R_C . The input impedance Z_I was considered via a RC – couple in parallel to the coating properties (R_I and C_I as input resistance and capacitance). But it turned out that in the limited frequency range of 0.1Hz to 100kHz the R_C and R_I are hardly detectable and showed only slightest significance during the fitting algorithm. Therefore only the model M1, where R_C and R_I were omitted, was used for the further fitting procedure.

* The loss capacity is defined as $Z_{CPE} = \frac{1}{\omega_o \cdot V \cdot \left(j \cdot \left(\frac{\omega}{\omega_o} \right) \right)^\alpha}$ with the normalization frequency $\omega_o = 1000$ Hz.

1: loss capacity of coating; 2: Warburg – diffusion; 3: electrolyte resistance
 4: input impedance of spectrometer (R and C) 5: coating resistance

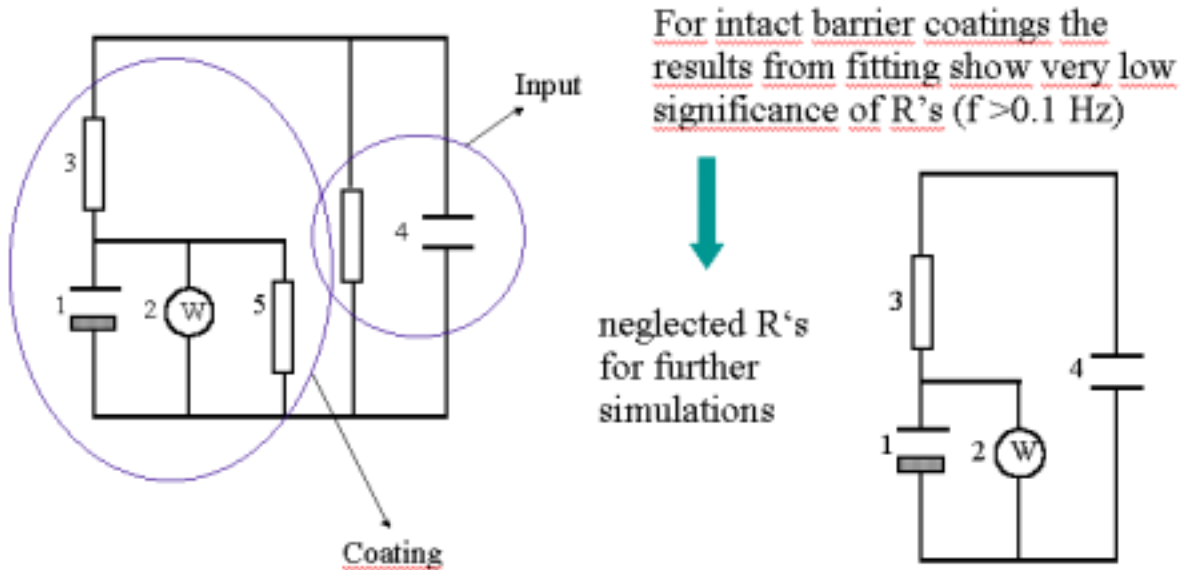


Fig. 5. Model for EIS – data interpretation; left model describing coating properties and input impedance, model on the right hand side was reduced due to limited frequency range leading to not significant R – values.

As can be seen from Fig. 3 and 4 model M1 is sufficient for the description of both types of coatings.

In Fig. 6 two different spectra of the alkyd paint are shown. The spectra with solid lines was obtained directly after the salt fog exposure whereas the spectra with the dashed line was recorded after two hours of air drying. This drying took place under immersion condition, that means the coating remained in the measuring cell. Although the measured area was still under the electrolyte, the surrounding coatings surface was able to dry because of the evaporation of the water/electrolyte. This lead to an increase of the measured impedance (dashed line).

In order to check the influence of different immersion periods the samples were measured during 48hours of immersion. The EIS – spectra are plotted in Fig. 7.

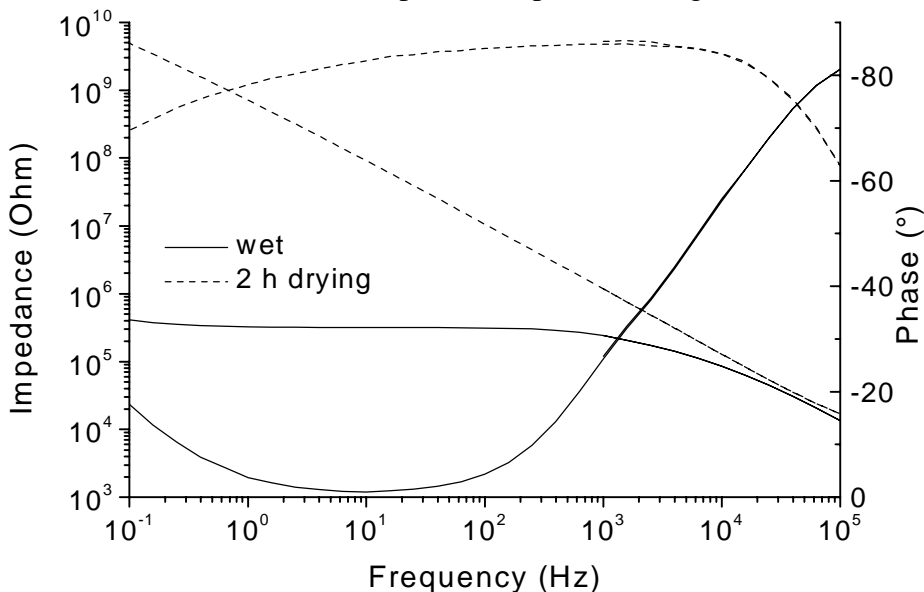


Fig. 6. Spectra of an alkyd paint directly measured after salt fog exposure (wet) and after two hours of air drying of the surface around the measuring cell.

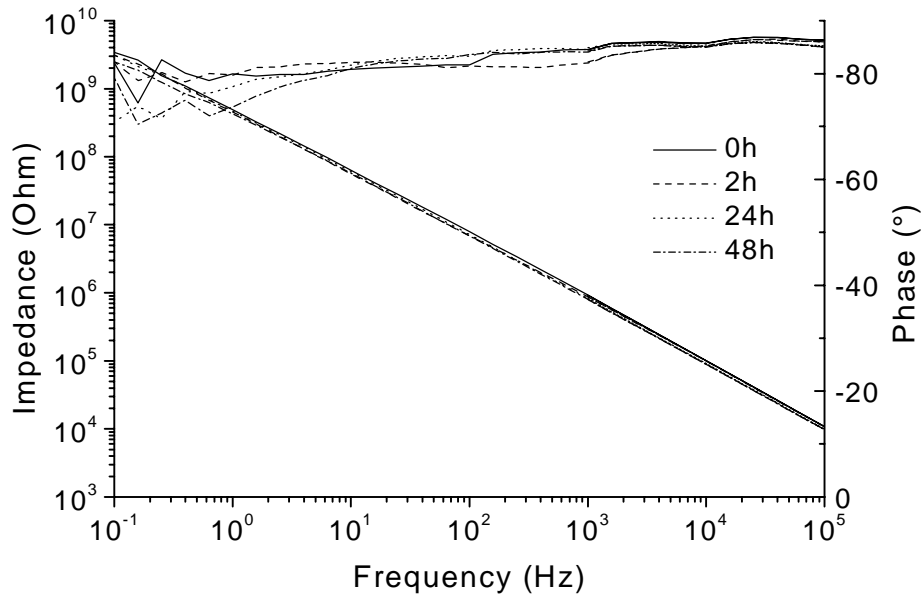


Fig. 7. Spectra of an alkyd paint recorded with increasing immersion time

Basically the same was done with the PU/epoxy coating. The results are shown in Fig. 8 and 9 respectively. The corresponding behavior was found to be independent from the type of binder.

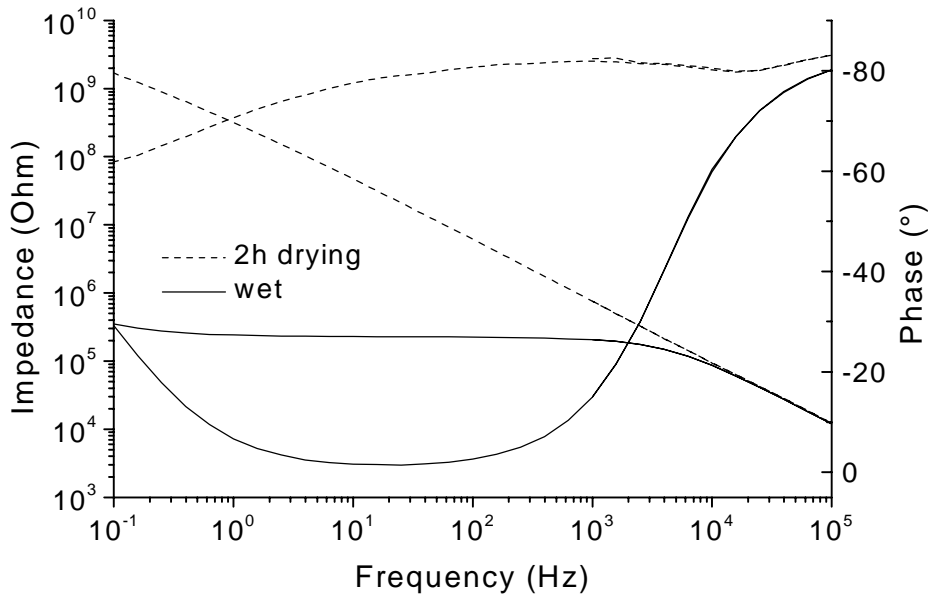


Fig. 8. Spectra of PU/Epoxy coating directly measured after salt fog exposure (wet) and after two hours of air drying of the surface around the measuring cell.

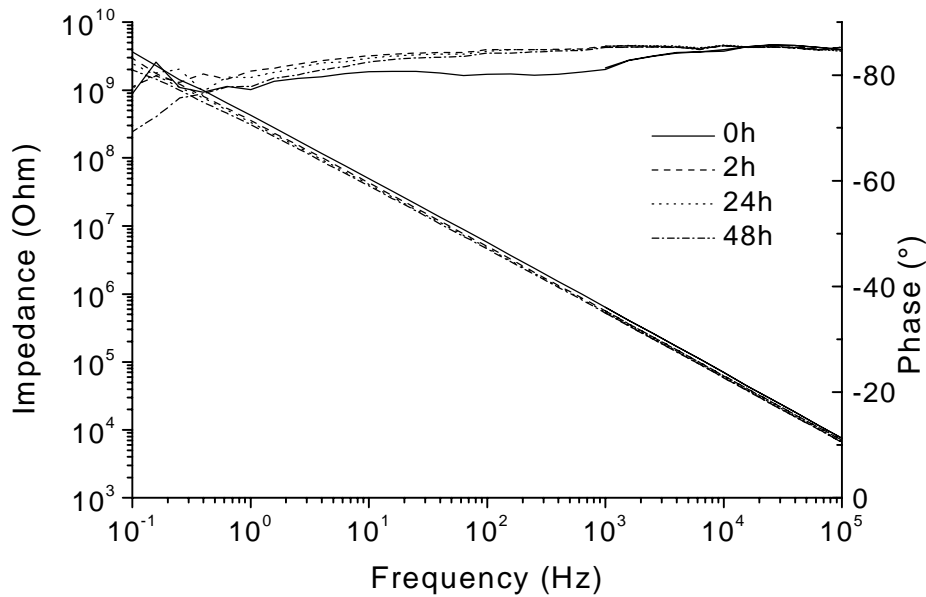


Fig. 9: Spectra of PU/epoxy coating recorded with increasing immersion time

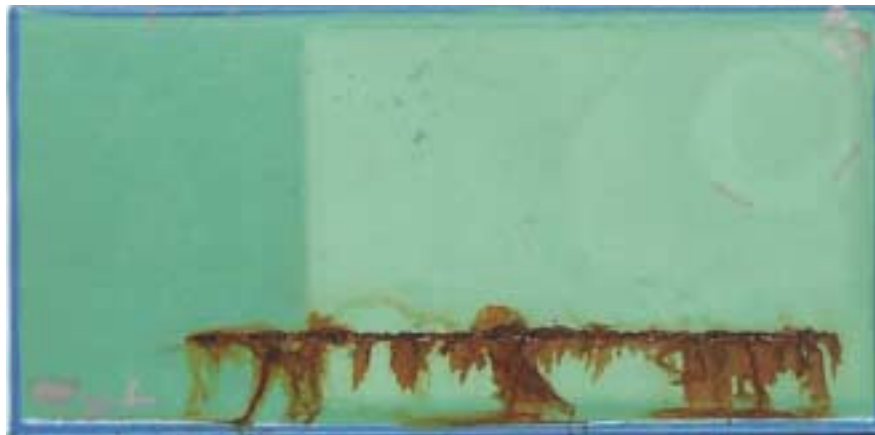


Fig. 10. Photograph of a sample plate with scribe after 15 weeks in the weathering cycles.

Discussion, Modeling

The results from above are easy to be understood, if a conductive path is assumed, which vanishes after a certain drying time. This source of stray currents can be generated by water adsorbed on the rough coating surface. In Fig. 11 a photograph of a typical sample plate is shown after 15 weeks of exposure, where the scribe is clearly visible because of rusty traces. Except of rust at the scribe the plate seems to be undamaged and the barrier properties are still present. Chalking has already started on the UV – exposed area of the sample plate.

A rough surface is formed by UV - degradation of the coating and becomes evident from gloss loss measurements. The rough surface is illustrated in Fig. 11, where micrographs of the surface are shown, which are taken from samples before and after UV – exposure by using direct illumination. On the left side of Fig. 11 the more glossy and not irradiated surface with a lighter appearance is shown in comparison to the right side, where the UV – degradation caused a rougher surface being visible by a darker micrograph, indicating that more light has been scattered.

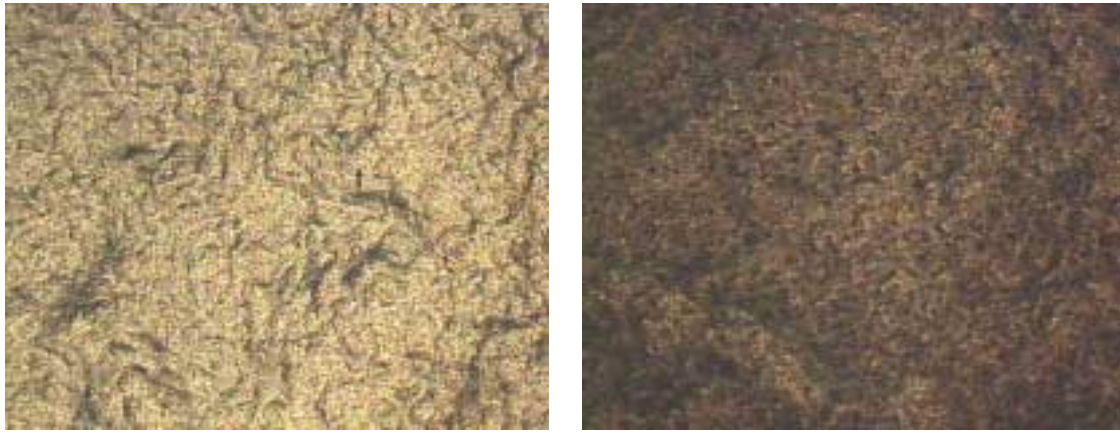


Fig. 11. Micrographs of a smooth and glossy surface without UV – irradiation (left) and after intensive weathering in a QUV – chamber with condensation which lead to a rough and less glossy surface (right). Picture taken with 50x magnification in direct illumination.

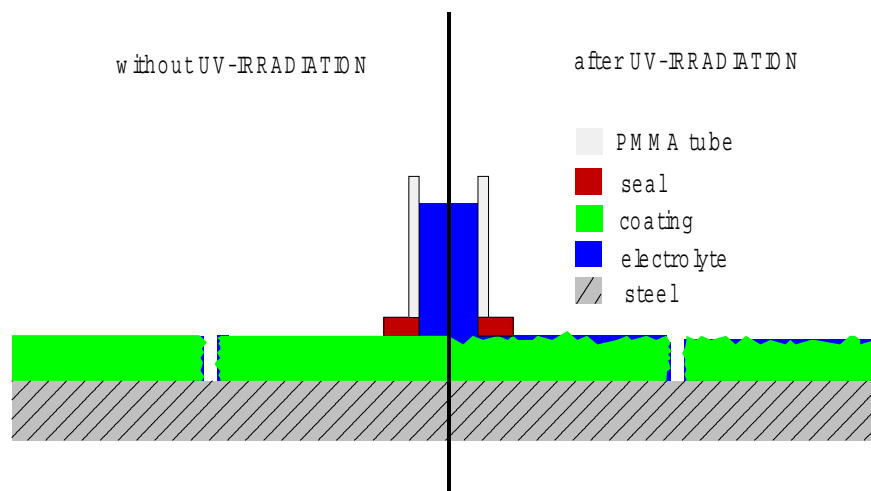


Fig. 12. Basic idea of imperfect seal leads to stray current over rough surface, whereas a smooth surface does not show this problem due to perfect sealing (no microscopic gaps between rubber seal and coating).

In order to prove the assumption of stray currents the model used for the intact coating was modified. Therefore two modifications of model M1 were used. The modifications started with the most simple approximation of stray currents via a simple resistor (Fig. 13A) and on the next level with a double layer time constant, taking into account the metallic surface at the bottom of the scribe (Fig. 13B).

Further, for a first check the parameters obtained from curve fitting of Fig. 3 and 4, using model M1, were kept constant and only the values of the part representing the stray current were adjusted. In a second step all parameters of Model A and B were fitted to the measured curve. The results of all the fitting efforts are given in Table 1.

Fig. 13A+B: Two modifications of the reduced model from figure 5.

A: stray current represented via a resistor describing the limited conductivity of the path:
counter electrode – seal – rough surface – scribe – substrate.

B: this modification takes into account that a double layer may be formed at the substrate below the scribe. This is considered with a RC – couple representing the double layer in serial connection with a resistor describing the resistance in the conductive path (like A).

Fig. 14. Results from both types of coatings fitted with model A. Square dots: only R(5) was fitted, triangular dots: parameters 1 – 5 were fitted.

Tab. 1. Three different models were used to fit the measured data. The first letter in the first row denotes the type of coating: k: alkyd paint, a: polyurethane coating. The results of model M1 (*k2dry* and *a2dry*) belong to figure 3 and 4. *A2wet1* and *a2wet2* belong to figure 14a, *k2wet1* and *k2wet2* correspond with figure 14b. The fitting results of model B correspond with figure 15, (15a with *a2wet3* and *a2wet4*, 15b with *k2wet3* and *k2wet4*). For files with the last digit 1 or 3 the initial fitting values were kept constantly like obtained from M1 after the fitting of the undamaged sample (results from Fig. 3 and 4), only the parameters higher than order number 5 were adjusted. For 2 and 4 all parameters were fitted in order to obtain an optimum representation of the measured curves.

In Fig. 14 results of both materials are shown, the solid line was the originally measured curve and the square dots belong to the fit where the coating parameters were kept constant. The triangular dots represent the fit where all parameters have been adjusted. Even if some significant deviations from the measured curve are obtained for the squared dots the trend is found to be in the right direction. By fitting all parameters a nearly optimal representation of the measured curve was found. The only deviation was found at the low frequency part, where a second time constant becomes visible. This was taken into account in Fig. 15. Model B shows a second time constant which may be related to a double layer formed on the metal – electrolyte – interface at the bottom of the scribe. For Fig. 15 the same procedure was used as for Fig. 14, the solid lines are the measured curves and the square dots are obtained from fitting only the stray current branch, whereas the triangular dots show the fitting of all parameters.

These results can easily justify the interpretation of the unexpected early failure of the coatings by stray currents, yielding in a spectra quite similar to a degraded coating. But drying of the surface around the measuring cell “improves” the spectra in such an extent that the coating is still in perfect shape.

Fig. 15. Results from both types of coatings fitted with model B. Square dots: only $5a+b$, 6 and 7 were fitted, whereas the triangular dots represent the fitting of all parameters.

Conclusions

An explanation was given for the interpretation of the erroneously measured poor results of coatings during the monitoring process. From the results and their discussion it becomes obvious, that stray currents can occur unexpectedly under such conditions where no directly visible leakage is present. This was checked via modeling of the EIS – data considering two different physical descriptions of the stray current.

As a consequence, and in order to avoid misinterpretations, special emphasis has to be put on the cell design, conditioning of samples and detailed measuring procedure. A clear hint for problems with stray currents is present, when curves change very abruptly from “bad” to “good” coatings, and vice versa, without any clear reason.