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# Influence of UV weathering on corrosion resistance of prepainted steel

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## Abstract

It has been observed that UV weathering and corrosion resistance tests are often performed separately, without taking into consideration their reciprocal influence. This is the case in the field of prepainted steel, where the European norm considers either UV durability or corrosion resistance. There is therefore no real evaluation of the global durability of the system. The aim of the present study is to show the influence of the photo-oxidation of painted layers on their barrier effect. This can lead to the formation of small blisters during field exposure. The blistering observed in natural exposure is never observed in individual accelerated corrosion tests. The depth of degradation from the surface of prepainted panels has been determined with infrared spectroscopy. Successive abrasions and FTIR analysis in ATR mode (attenuated total reflectance) allow us to determine oxidation profiles that can be well correlated with the decrease of barrier properties of painted systems measured with electrochemical impedance spectroscopy (EIS). The blistering has then been reproduced by exposing UV-weathered samples in a salt spray device.  
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**Keywords:** Corrosion; UV weathering; Photo-degradation; Protective coating; Barrier properties; Blistering

## 1. Introduction

In the field of construction, aesthetics is the most important criterion for evaluating the quality of a protective coating. The color and gloss retentions of coatings need to be very good, but with metallic products corrosion defects can also degrade considerably the appearance. The European norm EN 10169-2 considers the two types of degradation for samples exposed in separate laboratory accelerated tests, but also in natural outdoor exposure. However, for outdoor exposure, the corrosion and the UV resistance are always evaluated separately and generally on different locations (corrosive sites or UV-rich sites). With regards to this norm (and also many others in the field of coatings evaluation) it is thus noteworthy that the two tests taken separately do not allow an evaluation of the “global durability” (UV resistance + corrosion resistance).

When UV light, water and temperature changes are important factors in the field exposure, then Skerry and Simpson concluded that it should be incorporated into the accelerated corrosion test [1]. Results of their study suggested that UV weathering of

paint and associated substrate corrosion were interrelated phenomena. The cyclic exposure to UV radiations/humidity and to temperature/dilute electrolyte therefore allows integrating more parameters existing in the real-life in a single test. With this consideration in mind, several researchers have tried to compare some tests mixing UV weathering and corrosion [2–6]. However, no consensus exists and combined accelerated/cyclic tests still need to be improved for better correlations with field exposure. There is, for the time being, no universal way of predicting the long-term behaviour of coatings with different chemistries in various locations around the world.

The aim of our study is not to present a substitution test for those already described in norms or in the literature. We aim at confirming that corrosion tests alone are not necessarily representative of the degradation occurring during natural exposure, when UV weathering of coatings can also be significant. Based on results obtained after 10 years of natural exposure in Hendaye (South of France), it indeed appears that one of the main defects for prepainted panels exposed at 5° or 45° South, is their blistering on flat areas. A lot of little blisters start appearing on defective systems after about 6 years exposure. These blisters can degrade the overall appearance of panels as shown in Fig. 1. In some cases blisters can even be “open” and can be considered as small flakes. It is remarkable that the accelerated laboratory

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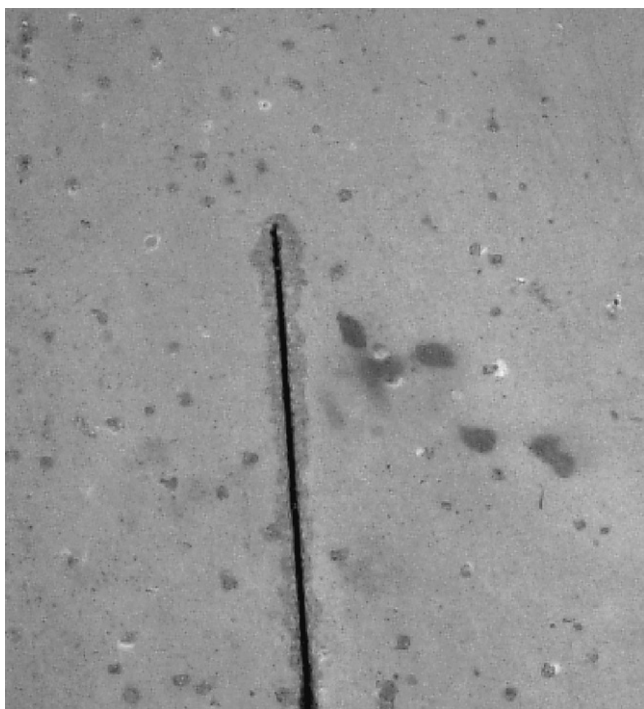


Fig. 1. Example of blistering on a red sample exposed for 10 years on natural exposure site in Hendaye (45° South exposure). The scribe is shown to evidence that corrosion on scribe is not the main visual defect.

tests for corrosion resistance do not lead to this kind of defect. It is thus interesting to wonder what the origin of such defects is.

It is known that the photo-oxidation of organic coatings occurs progressively starting from the surface [7]. The top surface is always more degraded, both because the light is not filtered, and because of oxygen diffusion from the surface. In many systems one can thus observe an oxidation profile in the depth of the coating. Because an oxidation of the polymer network leads to modifications in its chemistry and in its polarity, the solubility of water (and thus the barrier effect) could be modified, as demonstrated by several authors [8]. The role of the barrier layer on the resistance of the system to corrosion is well established, although sometimes not fully understood [9,10]. Electrochemical techniques, and especially impedance spectroscopy (EIS), have been shown to be very useful methods for the study of the performance of protective coatings [6,11–16]. Due to its sensitivity and short testing time, EIS has become more and more used over the last few years. From the analysis of the EIS diagrams with the appropriate electrical equivalent circuit, this method allows obtaining coating properties such as water permeability, coating porosity and delaminated area. These data are often used to predict the long-term behaviour of coatings or to rank various coatings with respect to their corrosion protective properties.

In the present paper, we have tried to reproduce the phenomenon of blistering on flat areas for long-term exposures, and thus to evidence the relationship between UV degradation of paint and corrosion resistance of prepainted steel. For this purpose, panels of nine different paint systems have been exposed to

UV irradiation in QUVA devices, prior to salt spray exposure. The modification of the barrier effect induced by UV degradation has been measured by EIS, and correlated to oxidation profiles appearing in the paint and measured with Fourier transform infrared (FTIR) spectroscopy. The formation of blisters in salt spray exposure is then explained through the evolution of these coating degradations.

## 2. Experimental

### 2.1. Materials

Prepainted steel panels were selected from a range of commercial products. A prepainted panel is constituted of zinc-coated steel with three different layers. A surface treatment converts the surface and promotes the adhesion of the organic layers. The primer is typically about 5–10  $\mu\text{m}$  thick and contains anti-corrosion pigments for corrosion protection. It must also favour the adhesion of the topcoat that is about 20  $\mu\text{m}$  thick. The topcoat brings barrier effect, mechanical resistance and aesthetics to the prepainted panel. Thermoset primers and topcoats are oven-cured in order to evaporate solvents and to allow the crosslinking. The nature of primers and topcoats used here are reported in Table 1. They are based on polyurethane (PUR) or polyester (PES) resins.

Nine polyester-melamine topcoats (PES) have been chosen for this study. In order to estimate the durability of products of different performances, three different kinds of products based on their UV resistance have been selected, which can be called “standard”, “high durability” or “very high durability”.

In order to check the influence of the primer thickness on the barrier effect, two different thicknesses have been tested (samples numbers 2 and 3).

### 2.2. Testing methods and equipment

#### 2.2.1. Accelerated UV weathering

*Test no. 1.* Samples have been studied following EN 10169-2 accelerated testing procedure, which consists in a 2000 h exposure in QUVA with alternated cycles (4 h irradiation/4 h condensation). This test allows obtaining a ranking of samples in terms of UV resistance.

*Test no. 2.* Samples have also been continuously irradiated in a QUVA device (Q-Panel) at a controlled irradiance of 0.89  $\text{W}/\text{m}^2$

Table 1  
Characteristics of samples used in this study

Code	Primer resin	Topcoat	Color	Internal UV ranking <sup>a</sup>
1	PES	PES	Blue	STD
2	PES (5 $\mu\text{m}$ )	PES	Brown	VHD
3	PES (15 $\mu\text{m}$ )	PES	Brown	VHD
4	PES	PES	White	VHD
5	PES	PES	White	STD
6	PUR	PES	White	HD
7	PUR	PES	Green	HD
8	PUR	PES	Ivory	HD
9	PUR	PES	White	VHD

<sup>a</sup> STD, standard; HD, high durability; VHD, very high durability.

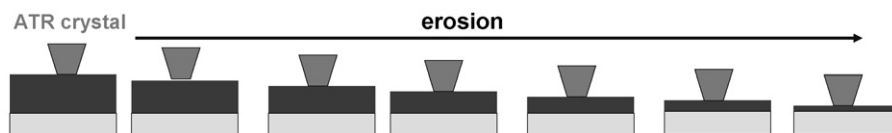


Fig. 2. Scheme for the successive analysis with ATR-FTIR in the depth of the coatings.

for duration up to 2000 h (no condensation cycles). Intermediate hydrolyses were performed every 350 h by immersing samples for 1 h in demineralized water at 60 °C, in order to perform the hydrolysis of oxidation products and to compensate the absence of condensation cycles. This procedure has been shown to be quite efficient for provoking the loss of gloss of oxidized coatings likely to be hydrolyzed. The evolution of the physical and chemical properties was followed as a function of irradiation time: gloss retention, oxidation as measured with ATR-FTIR depth profiling, and change in barrier properties as measured with EIS.

Three different panels of each sample have been exposed in the QUVA, respectively during 500, 750, 1000, 1500 and 2000 h. The first panel was used for gloss, FTIR analysis and EIS measurement, while the two others were used for salt spray testing.

#### 2.2.2. Salt spray testing

After the various exposure periods in QUVA, samples were exposed to a salt spray according to ASTM B117 standard in a Q-Fog cyclic corrosion tester (CCT 600 from Q-Panel) for corrosion testing (NaCl concentration = 5%,  $T = 35$  °C). A systematic observation of the six panels of each sample exposed for various durations in QUVA has been performed. At regular intervals, samples were removed from the salt spray chamber and observed with an optical stereomicroscope. Blisters were counted and their size range was also considered.

#### 2.2.3. Gloss and colorimetry measurements

Gloss was measured at 60° with a Micro-TRI-gloss from BYK-Gardner. Colorimetric measurements have been performed during UV weathering of samples, but because there were very few variations in color, this parameter will not be discussed here. Pigment systems are too stable and resins do not exhibit yellowing. All samples thus exhibited  $\Delta E$  below 1 at the end of the EN 10169-2 test.

#### 2.2.4. Fourier transform infrared (FTIR) spectroscopy

For studying coatings characteristics, FTIR spectroscopy has long been used, as a fast and sensitive method [17,18]. Oxidation profiles can be obtained with different accessories [19–28], at different scales from the micron to hundreds of microns, but with various analytical limitations.

In our study the best results for depth profiling were obtained with the attenuated total reflectance (ATR) mode (ATR-Thunderdome from Thermo Scientific) coupled with a progressive erosion of the surface (MicroLap device from MTEC Photoacoustics Inc.). In the MicroLap, a sample is mounted on an arm, which comes into contact with an abrasive and rotating disk. It enables layer-by-layer FTIR spectroscopy in

samples with a composition gradient, without limit on the depth range that can be probed. The erosion can be controlled quite precisely with the help of the associated micrometric gauge. An analysis of the surface appearing after erosion is made every 3  $\mu\text{m}$ , with the ATR crystal coming into contact with the surface that came apparent (as schematized in Fig. 2). The ATR mode allowed us to analyze the first microns from the surface (the depth of analysis depends on the wavenumber and is around 1.5  $\mu\text{m}$  for wavenumber in the range 1500–1800  $\text{cm}^{-1}$ ).

#### 2.2.5. Electrochemical impedance spectroscopy (EIS)

EIS measurements presented in this paper will only be discussed in terms of the low-frequency impedance modulus (noted  $|Z|_{0.01\text{Hz}}$ ) essentially representative of the coating resistance and thus of the barrier effect of the system. For each experimental condition, the measurements were repeated on six different regions of a same sample, providing a better confidence in the measurements [29]. The presence of application defects, irregular thickness or macro-porosity can in some cases lead to small impedance values not representative of the degradation of the coating itself. To minimize the influence of the presence of coating defects, only  $|Z|_{0.01\text{Hz}}$  values higher than  $10^8 \Omega \text{cm}^2$  were considered for the calculation of the average low-frequency modulus and the standard deviation. The curves are built from the Bode-modulus plots as that represented in Fig. 3 for sample no. 5.

The electrochemical impedance measurements were carried out using a conventional three-electrode cell filled with the electrolytic solution (NaCl 0.5 M). The working electrode is the

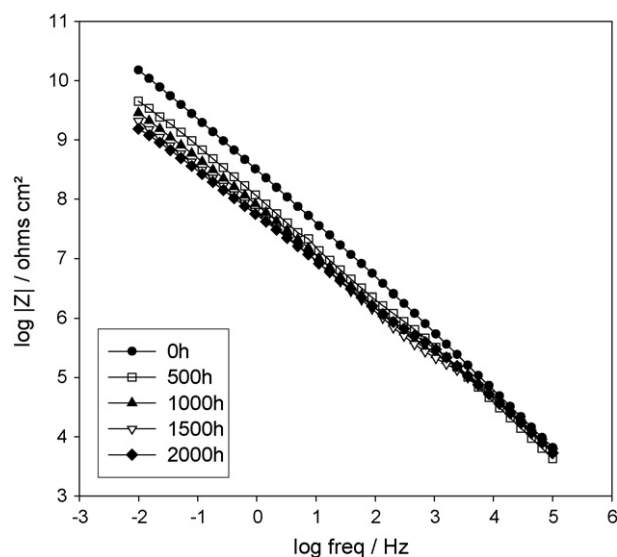


Fig. 3. Example of a Bode-modulus plot for sample no. 5, for different irradiation times (immersion time of 1 h).

sample under study and the counter electrode is a platinum plate. The potentials are measured with respect to an Ag/AgCl reference electrode and the exposed surface area is  $4.5 \text{ cm}^2$ . The electrochemical cell was placed in a Faraday cage in order to minimize external interference on the system. The impedance measurements were performed over frequencies ranging from 100 kHz to 10 mHz using a 20 mV amplitude signal voltage. The spectra were acquired using a frequency response analyzer coupled with a potentiostat (EG&G Parstat 2273). The samples were kept 1 h in contact with the electrolyte solution before performing the EIS measurements.

### 3. Results and discussion

In order to evaluate the relative contribution of the primers and the topcoats, EIS measurements were also carried out on panels covered with primers only. The EIS spectra in the Bode representation of the two PUR and PES primers, measured after 1 h of contact in 0.5 M sodium chloride electrolyte are given in Fig. 4. One can observe that both primers give low barrier effects since the low-frequency region is resistive. The pres-

ence of a second time constant characteristic of metal corrosion (under the coating or at the base of the pores) is also detected. The total resistance of the system represented by  $|Z|_{0.01 \text{ Hz}}$  is rather low and rapidly decreases with time (not shown here) but is however higher for the PES primer than for the PUR one.

Samples have been exposed in QUVA for five different durations and have been analyzed in terms of gloss retention, chemical evolution with infrared analysis and physical evolution with EIS. Values of gloss retention for the various systems are presented in Table 2. The first columns present the time of irradiation in test no. 2 (QUVA without humidity but with hydrolyses every 350 h), while the last column of Table 2 is the gloss retention in the normalized test no. 1 (2000 h of exposure in QUVA with cycles 4 h irradiation/4 h condensation). It can be noted that there are some discrepancies between results obtained with the two different tests, when the gloss is compared after test no. 1 and 1000 h of irradiation with test no. 2 (equivalent total irradiation duration, but different humidity conditions). Differences are mainly visible for sample no. 4 and sample no. 7, where the gloss retention results are largely better with the cyclic test than with the continuous UV exposure. For some painted systems, the condensation step instead of degrading the surface aspect (like for sample no. 1 or no. 5), allows a restoration of surface properties, through migration of some additives towards the surface. For this reason, the standard test no. 1 is not fully reliable when used alone. More data are needed to conclude on the behaviour of the samples and a UV irradiation without condensation phase can complete the evaluation of the surface degradability.

In order to describe the various behaviours observed in this study, the results are detailed for only four samples, namely nos. 2, 4, 5 and 6. These four samples allow seeing the evolution of corrosion resistance in coatings where oxidation profiles are more or less marked. For the series of these four samples, the IRTF spectra are presented as a function of depth for the 2000 h QUV-weathered samples following test no. 2 (Fig. 5a–d).

The spectra in Fig. 5 show that the evolution is very different from the top surface to the bulk of the samples, mainly for those that have not a very good UV resistance. One of the best ways to represent the evolution of a polyester-melamine network is to follow the breakdown of melamine bridges formed during the hardening of the resins. It appears that the decrease of the absorbance related to the melamine band at  $1550 \text{ cm}^{-1}$  (*s*-triazine function) can be used as a good tracer for the photodegradation of these paints. Other tracers like the increase of the carbonyl band at  $1780 \text{ cm}^{-1}$  (oxidation products) could also be used but their absorbance being lower, the precision could be lowered. The decrease of the absorbance at  $1550 \text{ cm}^{-1}$  as a function of depth has been calculated for the six irradiation periods (including 0 h) and is represented in Figs. 6a–9a for the four samples selected. It must be noted that the percentage of residual melamine indicated in these figures must not be considered as absolute and exact. It is only a relative percentage for comparison purpose, since it is calculated from the height of absorption bands and not from an indi-

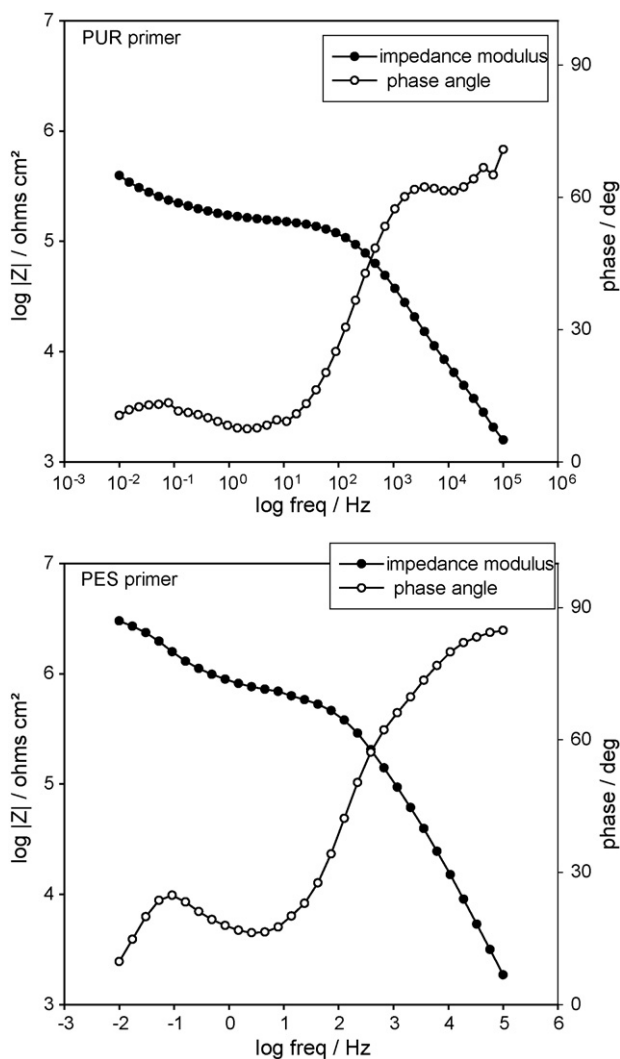


Fig. 4. EIS spectra on primer panels.

Table 2  
Gloss retention (%) of the nine samples as a function of irradiation time in QUVA (test no. 2)

Code	Test no. 2: continuous QUVA irradiation (with hydrolyses every 350 h)						Test no. 1: $T=2000$ h (4 h QUVA/4 h H <sub>2</sub> O)
	$T=0$ h	$T=500$ h	$T=750$ h	$T=1000$ h	$T=1500$ h	$T=2000$ h	
1	100	79	76	75	55	47	58
2	100	88	86	87	85	84	93
3	100	87	86	88	87	79	87
4	100	74	69	58	52	46	80
5	100	72	74	56	48	28	27
6	100	81	65	65	56	44	69
7	100	75	79	73	69	66	139
8	100	85	80	74	67	59	79
9	100	88	91	84	77	84	92

A column is added on the right, which takes into account the gloss retention obtained in the EN10169-2 (test no. 1: 2000 h QUVA with alternation of irradiation/condensation cycles).

vidual and isolated band after complete deconvolution of the spectrum. For the ease of comparison, besides the oxidation profiles, the evolution of the low-frequency impedance modulus as a function of the irradiation time in QUVA is also reported (Figs. 6b–9b).

After irradiation, panel samples were also exposed to a salt spray test. The evolution of panels (number of blisters) as a function of time is reported in Figs. 6c–9c, allowing a direct correlation with oxidation profiles and barrier properties for each sample exemplified here.

### 3.1. Sample no. 2

For sample no. 2, the degree of oxidation remains very low (Fig. 5a). There is apparently a fast but moderate evolution close to the surface during the first 500 h of irradiation, evidenced in Fig. 6a by a decrease in the melamine band absorption up to 6  $\mu\text{m}$  below the surface. But then the oxidation degree does not change significantly. Network remains intact even after 2000 h of exposure as evidenced in oxidation profiles. It can be assumed that the fast evolution at the beginning of the exposure is related to the presence of a small concentration of chromophoric species in the topcoat additives, impurities or formation of photosensitive products during the curing process). These chromophoric species act as sensitizers for the matrix and can start a photo-oxidation reaction. Once these chromophores are consumed, the polymer chains appear to be very resistant to photo-oxidation and there is no further evolution. Because oxidation is quite low and not detected below 7  $\mu\text{m}$  from the surface (Fig. 6a), there is no reason for observing a significant decrease in the barrier effect. This is confirmed in Fig. 6b with the evolution of the low-frequency impedance modulus as a function of UV exposure. There is a slight decrease between the non-exposed sample and the sample irradiated for 500 h, but then no further evolution. As a result of the conservation of the good barrier properties during UV weathering, there is no visible increase in the tendency for blisters during salt spray test (Fig. 6c). The isolated blisters found on the different sample panels likely correspond to macro-defects. These defects do not constitute an evidence of sample degradation through UV exposure.

This behaviour is similar for sample no. 3 and sample no. 9 (not shown here). For sample no. 3, the thicker primer (15  $\mu\text{m}$  instead of 5  $\mu\text{m}$ ) leads to higher impedance values than for sample no. 2. However because the topcoat is very good and conserves its barrier properties upon UV weathering, it is not possible to distinguish the evolution between the two products. It can be assumed that with a topcoat of lower UV resistance losing its barrier property during UV weathering, the thicker primer would be of interest for improving the barrier effect of the system (in addition to an increase of the anti-corrosion pigments concentration).

For sample no. 9 a more pronounced degradation is observed in infrared spectroscopy. However the percentage of melamine band does not decrease below 80% close to the surface, and the profile does not progress deeper than 10  $\mu\text{m}$ .

### 3.2. Sample no. 4

For sample no. 4, the oxidation is more pronounced as seen in Fig. 5b. Furthermore oxidation profiles exhibit after short irradiation times a greater degradation close to the surface (40% of decrease in melamine band after only 500 h of irradiation) (Fig. 7a). However, the oxidation does not occur significantly at depths greater than 10  $\mu\text{m}$  in the coating. It is only after 1000 h of irradiation that the degradation profile becomes evident in the deeper layer (and in almost all the thickness). For samples irradiated for more than 1500 h, the degradation is clearly observed even close to the primer. Parallely, it can be noted from the low-frequency impedance modulus values (Fig. 7b) that the barrier properties only slightly decrease during the first 1000 h of irradiation, but there is then a steep decrease observed after 1500 h of irradiation. This can be explained by a degradation progressing far deeper in the coating than for sample no. 2. The same behaviour has also been observed for samples no. 1 and no. 8.

Results in Fig. 7 show that there is a good correlation between the oxidation profile induced by UV weathering and the loss of barrier properties of the topcoat. The deeper the oxidation is measured, the lower the barrier effect is. This loss of barrier effect interestingly correlates with the formation of blisters in

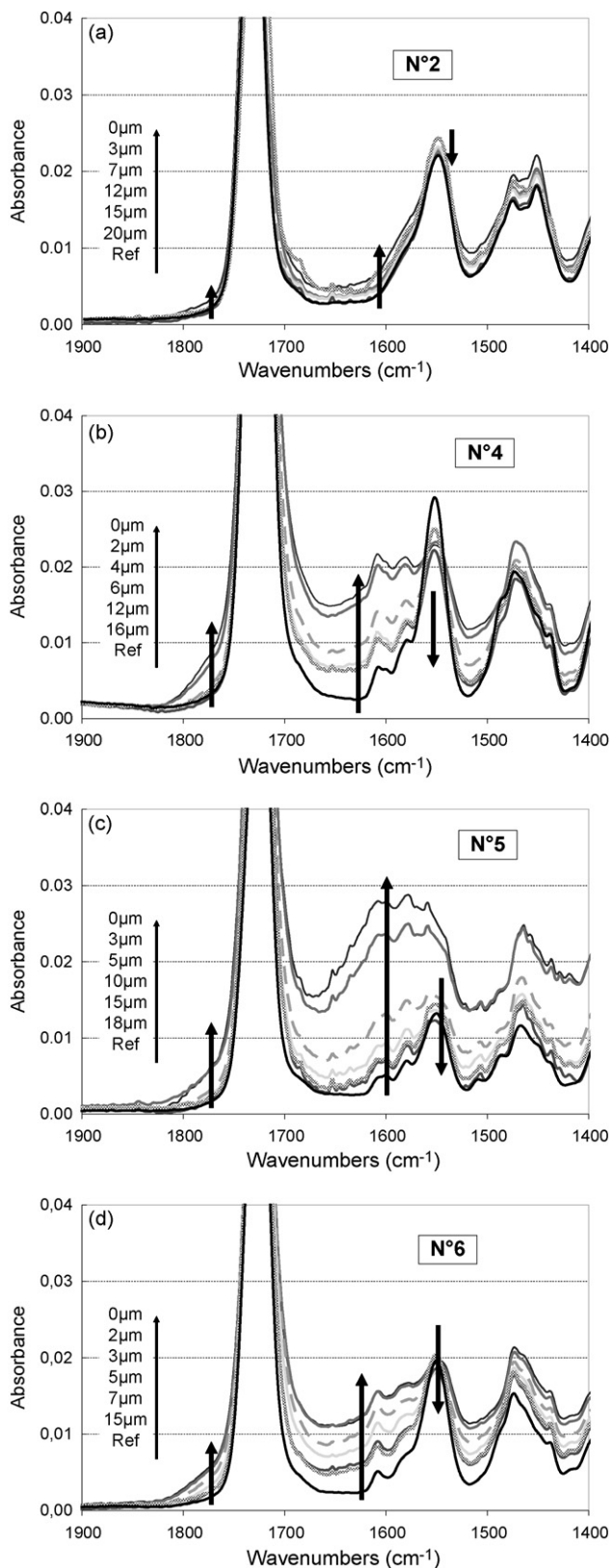


Fig. 5. Infrared spectra of 2000-h irradiated samples at various depths from the surface (zone 1900–1400 cm<sup>-1</sup>): (a) no. 2, (b) no. 4, (c) no. 5, and (d) no. 6.

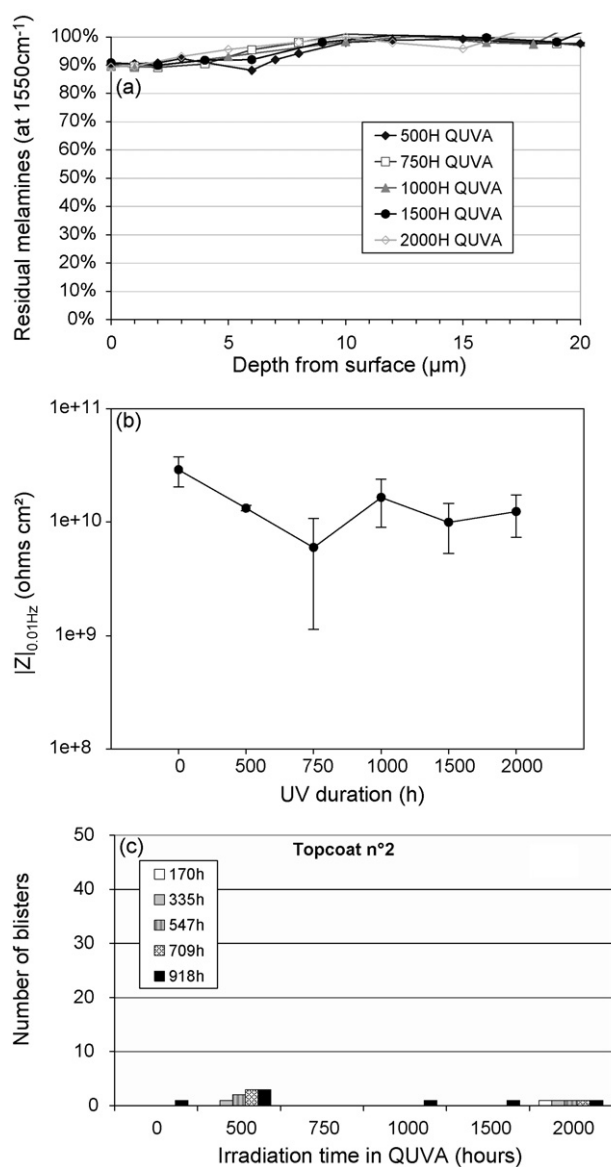


Fig. 6. Topcoat no. 2. (a) Oxidation profiles in samples exposed to UV-A radiation for various durations. (b) Low-frequency modulus as a function of UV exposure. (c) Number of blisters formed after various exposure times in salt spray test as a function of irradiation time in QUVA.

accelerated salt spray testing (Fig. 7c). While a sample non-UV weathered is stable in salt spray (in terms of blister formation), samples exposed to UV irradiation prior to salt spray exhibit a marked tendency towards blistering. This can be explained by an increase in hydrophilicity, which can accelerate general mechanisms of corrosion.

A mechanism of formation of blisters in coatings has been proposed [30] and is based on the diffusion of water and oxygen towards metal interface. This diffusion can obviously be modified when the chemistry of the topcoat changes. This is the case during the photo-oxidation of the resin. This leads to a modification of the sample sensitivity towards corrosion. In the prepainted panels observed here, blisters have a size around 200 μm and more. This is not the same type of blisters that were observed during the weathering of a polyurethane coating

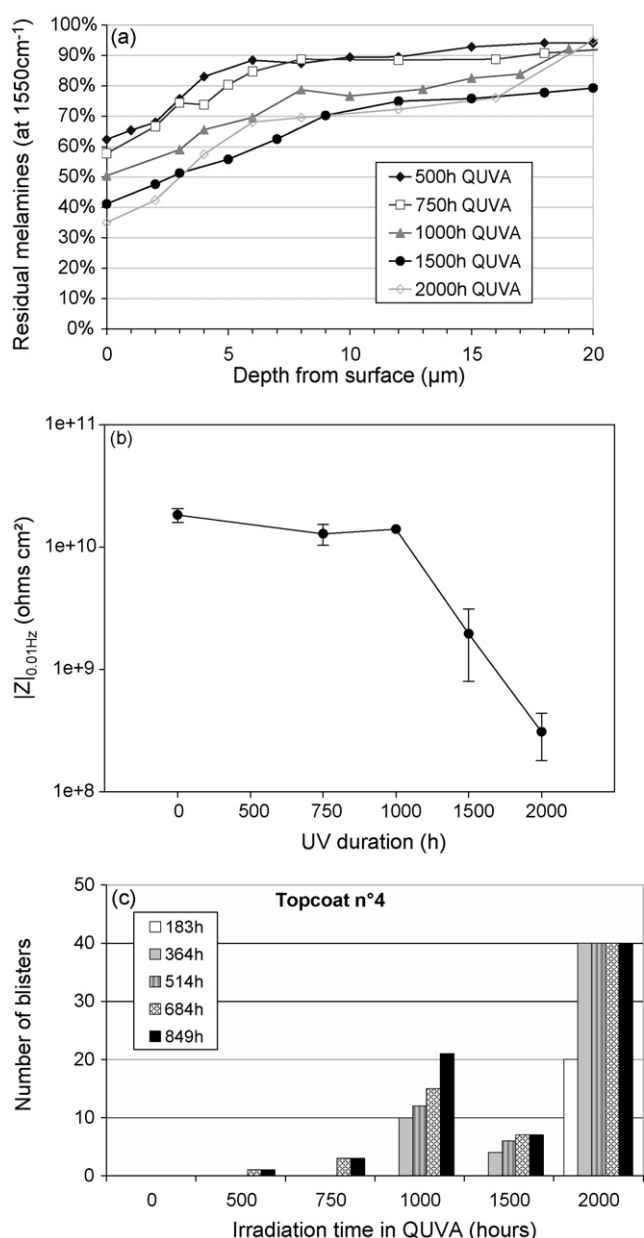


Fig. 7. Topcoat no. 4. (a) Oxidation profiles in samples exposed to UV-A radiation for various durations. (b) Low-frequency modulus as a function of UV exposure. (c) Number of blisters formed after various exposure times in salt spray test as a function of irradiation time in QUVA.

[31,32]. In those cases the blisters of sub-micrometric to micrometric size were attributed to osmotic cells forming in alternation of dry/wet cycles. The greater water absorption induced by the build-up of hydrophilic groups was also assumed to favour the formation of blisters.

Discrepancies between 1000 and 1500 h blistering data in Fig. 7b probably result from the number of local defects in the samples as already discussed before. However, although not mentioned in the graphs, the average size of blisters after 1500 h of QUV exposure is bigger than after 1000 h. One can also observe that the number of blisters increases with the exposure time in salt spray test. This evidences corrosion mechanisms occurring progressively in the system. Furthermore, for

the 2000 h UV-irradiated sample, the number of blisters is more important than for shorter UV exposures. More interestingly, the number of blisters seems to reach a maximum already after 364 h of salt spray exposure. This number is then stable, with only a slight increase in their size. A possible explanation for this “steady state” is that the number of “weak points” in the system (pores in the paint, local poorer adhesion, ...) is revealed by QUV exposure. These local defects are accentuated with the modification of the topcoat structure that is submitted to photo-degradation. After 2000 h of QUV exposure, photo-degradation is such that there is no protective barrier effect and all defects are revealed quite quickly.

The combination of UV/corrosion testing allows us to evidence a poor behaviour for sample no. 4. The sample was classified as a “very high durability” sample since it shows a very good resistance to salt spray test (sample not previously UV-irradiated) and to UV weathering (following test no. 1, which is relevant to EN 10169-2). However, one has to reconsider its ranking in the view of the results obtained in the present study. Although keeping its gloss in test no. 1, the sample no. 4 is not very photo-stable. It can be oxidized even in the deep layers, and this provokes a complete loss of barrier properties. On the medium to long-term, this sample can therefore not be considered as a good performing system.

### 3.3. Sample no. 5

Sample no. 5 is probably the worst sample in terms of photo-degradation (Fig. 5c). The oxidation occurs rapidly and is very pronounced near the surface (Fig. 8a). The topcoat completely lost its barrier properties in the first microns and this is accompanied with a decrease of the modulus already after 500 h of irradiation (Fig. 8b). The oxidation then progressively reaches the deeper layers and accordingly the low-frequency impedance modulus decreases with UV-irradiation time.

For this coating the blisters start to appear after 514 h of salt spray exposure on the sample that has only been exposed to 500 h of QUVA (Fig. 8c). This evidences a quick degradation of the barrier properties related to a fast photo-degradation of the topcoat. For the samples exposed more than 750 h in QUVA, blisters appear only after 183 h of salt spray. The size of blisters being large and the differentiation being made between the samples, salt spray test was not extended further.

### 3.4. Sample no. 6

Sample no. 6 has a relatively low initial value of low-frequency impedance modulus (below 1E+10 Ω cm<sup>2</sup> in Fig. 9b). However, this value does not decrease dramatically as for sample no. 4 for example. After 2000 h of QUV exposure the |Z|<sub>0.01Hz</sub> values are still above 2E+9 Ω cm<sup>2</sup>. This can be correlated with the fact that in sample no. 6, we do not observe a very important oxidation (Figs. 5d and 9a) and oxidation profiles, although quite similar to those of sample no. 4, are about 10% higher in terms of residual melamine. The topcoat shows limited degradation deeper than 10 μm from the surface (Fig. 9a) and melamine percentage remains close to 90% near



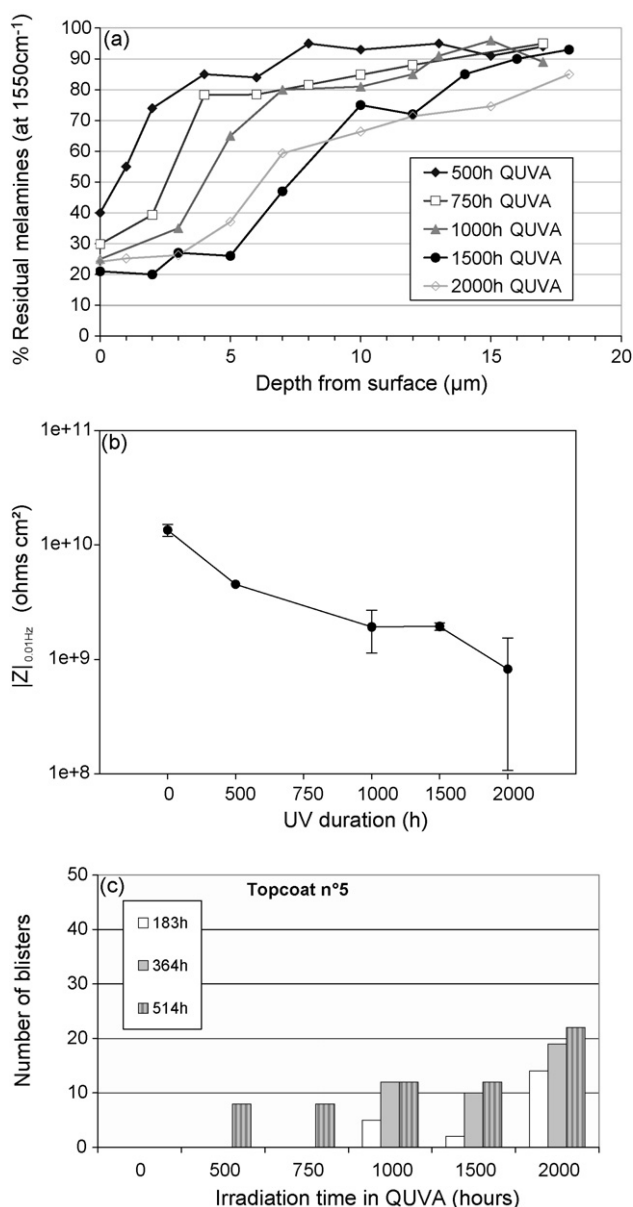


Fig. 8. Topcoat no. 5. (a) Oxidation profiles in samples exposed to UV-A radiation for various durations. (b) Low-frequency modulus as a function of UV exposure. (c) Number of blisters formed after various exposure times in salt spray test as a function of irradiation time in QUVA.

the primer explaining that the barrier properties seem to be maintained.

Another particular behaviour is observed during salt spray exposure (Fig. 9c). There is a progressive increase in the number of blisters, even for the longer UV-irradiation periods. We do not reach a steady state for the number of blisters like for sample no. 4. This is also evidence that the barrier properties are kept and that defects are slowly revealed only after long exposure times in corrosive salt spray. Furthermore, contrary to samples no. 4 and no. 5, which exhibit some large blisters after 1500 or 2000 h of UV exposure (size around 1–2 mm diameter), in sample no. 6 the blisters appearing during salt spray are smaller (size around 400–800 μm) and do not increase significantly in size over time. This coating is therefore different from

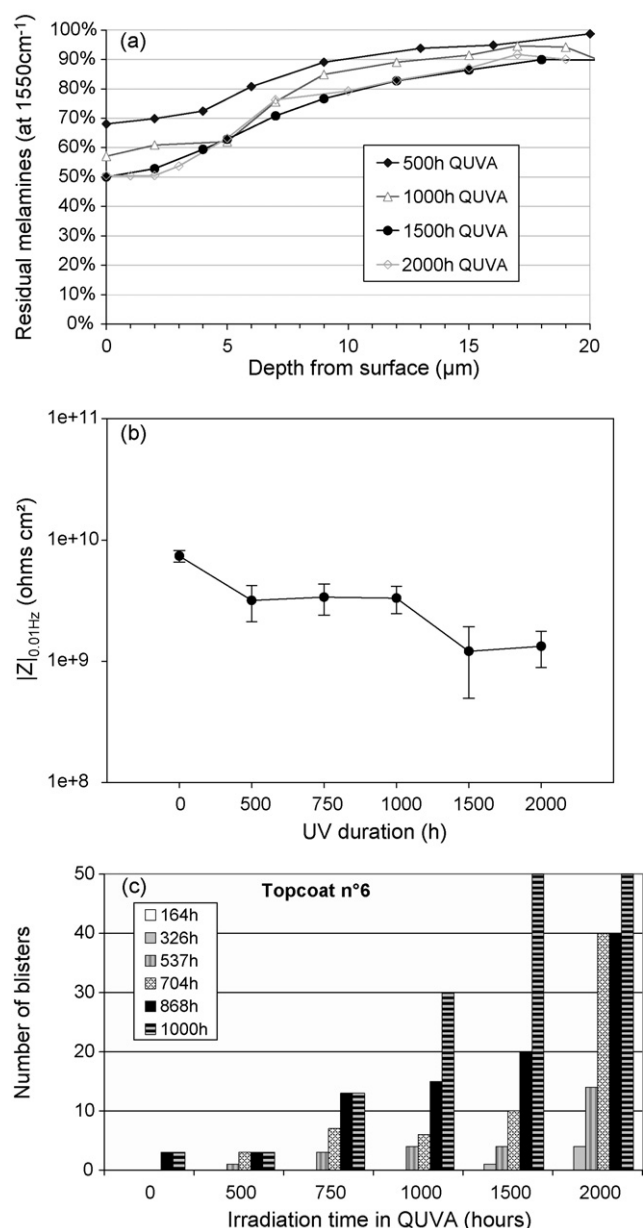


Fig. 9. Topcoat no. 6. (a) Oxidation profiles in samples exposed to UV-A radiation for various durations. (b) Low-frequency modulus as a function of UV exposure. (c) Number of blisters formed after various exposure times in salt spray test as a function of irradiation time in QUVA.

the other ones. The different evolution could obviously be due to different surface treatment and primer that are more resistant to corrosion mechanisms, even when the topcoat shows lower barrier properties. This is under investigation.

To summarize, Fig. 10 represents the low-frequency impedance values measured with the different coatings under study submitted to 2000 h of QUVA exposure. Superposed on the same graph, the blister numbers for the same coatings exposed for 500 h in a salt spray test are also represented. The salt spray test results are also summarized in Table 3 which gives the evolution of blistering in terms of number and size as a function of salt fog duration for the coatings UV-irradiated for 2000 h.

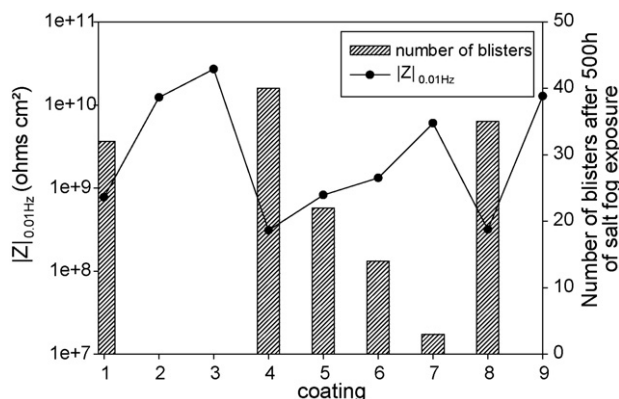


Fig. 10. Low-frequency modulus and number of blisters after 500 h of salt fog exposure for the different coatings exposed to 2000 h of UV irradiation.

Table 3

Number and size range of the blisters observed after different salt fog durations on the different coatings irradiated for 2000 h in QUVA

Coating	Blister number and size range (diameter)		
	300 h	500 h	700 h
1	15 (200–400 $\mu\text{m}$ )	32 (500–1000 $\mu\text{m}$ )	50 (500–1000 $\mu\text{m}$ )
2	0 (–)	0 (–)	0 (–)
3	0 (–)	0 (–)	0 (–)
4	40 (300–1200 $\mu\text{m}$ )	40 (500–1500 $\mu\text{m}$ )	40 (800–2000 $\mu\text{m}$ )
5	19 (700–1000 $\mu\text{m}$ )	22 (1000–1200 $\mu\text{m}$ )	
6	(400–800 $\mu\text{m}$ )	(300–400 $\mu\text{m}$ )	(300–800 $\mu\text{m}$ )
7	0 (–)	3 (100–200 $\mu\text{m}$ )	3 (100–200 $\mu\text{m}$ )
8	15 (200–1000 $\mu\text{m}$ )	35 (300–1000 $\mu\text{m}$ )	40 (800–2000 $\mu\text{m}$ )
9	0 (–)	0 (–)	0 (–)

Coatings with high low-frequency impedance modulus values present a higher barrier effect and a better resistance to salt fog. For example, coatings no. 2, 3 and 9 for which the oxidation, measured from FTIR spectra, is low and essentially superficial, show the highest impedance values and do not exhibit blisters after 500 h of salt fog (except those arising from coating defects). On the contrary coatings 4 and 8 are those presenting the lowest impedance and the highest blisters number and size range. This fast degradation can be explained by the significant photo-oxidation which occurs in the whole coating thickness.

The good correlation between all these experiences is clear, though the experimental conditions slightly differ (salt spray exposure was carried out at 35 °C while EIS measurements were performed at 25 °C).

#### 4. Conclusions

In the present work, a combination of different measurements and methods was envisaged in order to rank the capabilities of different coatings to offer both UV resistance and barrier effect. Nine different coatings were exposed to a QUVA test. The coatings photo-oxidation was determined by FTIR depth profiling and the evolution of the barrier properties was followed both by a standard salt spray test and by EIS. A good correlation was observed between coating photo-oxidation (FTIR depth profiling), loss of protective effect (impedance measurements) and

the resistance to blistering (salt fog exposure) for the different coatings under investigation.

These evidences that a simple measurement of gloss, although very important in terms of aesthetics, does not lead to a good description of the level of degradation of a coating undergoing weathering tests. In terms of durability, the degradation profile in the depth of the coating is also of prime importance. Panels that have lost their barrier effect exhibit a greater tendency to blistering when exposed to salt spray. This is a very interesting result since blister defects were never found on accelerated corrosion tests. One can therefore raise the question of the relevancy of corrosion tests without UV exposure for locations where UV radiation will be quite important. As long as the duration involved is relatively short, one can presume that there will be no reciprocal influence between corrosion and UV weathering, and the outdoor exposure test recommended in the EN 10169-2 should be well adapted (it is only for a 2-year period). However, for mid-term to long-term exposure, the tests included in this norm might be insufficient to safely guarantee the integrity of the coating.

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