

Weathering of coil-coatings: UV radiation and thermal effects

A.S. Castela*, A.M. Simões*, G. Davies** and M.G.S. Ferreira*

Abstract The effect of heat and of QUV ageing on coil coatings was tested by electrochemical impedance, and the results compared with surface analysis of the polymers by FTIR and XPS. It was shown that UV radiation is more relevant than heat to chemical degradation. A different correlation between water permeation and chemical degradation was observed depending on the coating thickness: for the thinner coatings, the higher UV degradation has corresponded to increased water absorption, whereas in the thicker coating, the bulk effect of heat was more relevant to water permeation.

Keywords Organic coatings. Electrochemical impedance. XPS. FTIR.

Degradación de recubrimientos de bobinas: radiación UV y efectos térmicos

Resumen El efecto del calor y del envejecimiento, QUV, sobre recubrimientos de bobinas se probó mediante la impedancia electroquímica, y los resultados se compararon con análisis superficiales de los polímeros usando FTIR y XPS. Se encontró que la radiación UV es más importante que el calor en la degradación química. Una correlación diferente, entre agua infiltrada y degradación química, se observó, dependiendo del espesor del recubrimiento: para los recubrimientos más delgados, mayor degradación UV correspondió a un incremento de absorción de agua; en cambio, para los recubrimientos más gruesos, el efecto del calor fue más importante para la infiltración del agua.

Palabras clave Recubrimientos orgánicos. Impedancia electroquímica. XPS. FTIR.

1. INTRODUCTION

Coil coatings are widely used for many applications, namely in architecture. Weathering, however, is a major problem in outdoor exposure. Weathering results from the joint action of ultraviolet (UV) radiation, heat, oxygen, humidity and chemical species. These agents induce chemical and physical changes in the polymer, which may vary depending on the nature and intensity of the aggressive agent, but which all result in degradation. Industrially, this degradation is usually assessed by the changes in the optical properties, namely gloss and colour. Although it has been demonstrated that the water barrier properties of a polyester coating decreased with the exposure to UV radiation^[1], not much attention is paid in the literature to the loss of corrosion protection provided by the coating to the substrate. In this respect, electrochemical impedance is a powerful technique. It can be used to determine the rate of delamination, the electrical properties of the

coating and also to estimate the water uptake from a solution, a parameter of relevance since the permeation of water is the first step in the process of aqueous corrosion of the substrate. Estimation of water uptake is frequently made using the Brasher-Kingsbury equation, which gives the volume fraction of water, ϕ as:

$$\phi = \frac{\log(C_t / C_0)}{\log(\epsilon_w)} \quad (1)$$

In this correlation, C_t and C_0 represent the capacitance of the coating at an instant t and extrapolated to $t = 0$, respectively, and ϵ_w is the dielectric constant of bulk water (taken as ≈ 80 at ambient temperature). The coating capacitance can be determined from the imaginary impedance at high frequency:

$$C = \frac{1}{(2\pi Z_{\text{imag}})} \quad (2)$$

(*) Instituto Superior Técnico. Chemical Eng. Department. Av. Rovisco Pais, 1096 Lisboa Codex (Portugal).

(**) Corus, WTC, Port Talbot, U.K.

In a previous study it was concluded that the Brasher-Kingsbury equation gives higher values of the water content than those estimated from gravimetry, but that qualitatively the information obtained is quite reasonable, since the relative order of water absorption obtained with different formulations was confirmed by gravimetry^[2 and 3]. In this work the degradation of coil coatings was assessed by electrochemical impedance, in order to determine the effect of elevated temperature and of UV radiation combined with water. The results are interpreted based upon surface analysis (FTIR and XPS).

2. EXPERIMENTAL

2.1. Materials

The study was made using three commercial coil coatings: polyvinylidene fluorine (PVDF), an architectural polyester (outdoor polyester) and a PVC based coating (PVC *plastisol*). The coatings were applied on a substrate of (hot-dip) galvanized steel (20 μm zinc layer), primed with an acrylic primer ($\approx 5 \mu\text{m}$). All the coatings had red pigment, and the total coating thickness (primer + topcoat) was as follows:

PVDF: 20 μm , Polyester: 25 μm and PVC: 200 μm .

For the surface analysis, model coatings (grey pigment) were prepared with the following proportions:

Polymer	Quantity	Others
PVDF	29 %	8.6 % Acrylic (PMMA)
Polyester	28 %	7 % Melamine
PVC	57 %	24 % Dioctyl Phthalate

Coatings were tested as-produced (after curing) and also after accelerated ageing by two different processes:

- Continuous heating at 125 °C during 2 weeks
- QUV ageing. This was made in a standard QUV-weatherometer by a cyclic treatment consisting of 4 h UV-A at 70 °C, alternating with 4 h of condensation at 50 °C. The total time was 3000 h of ageing.

2.2. Electrochemical measurements

Electrochemical measurements were made with the sample held vertically against an o-ring, leaving

an exposed area of 3.14 cm², during continuous immersion in 3 % NaCl. The measurements were made using a 1255 Solartron frequency response analyser and a 1256 Solartron electrochemical interface. A sine wave of 30 mV (rms) was applied across the cell, in a 3-electrode arrangement. The capacitance measurements were made at a constant frequency of 50 kHz.

2.3. FTIR

Spectrum acquisition was made using micro-ATR (Attenuated Total Reflectance). This is an accessory of the FTIR microscope by which an attenuated reflectance spectrum can be acquired from a very small area (area of the micro-ATR crystal, diameter about 100 μm). Since the information depth of this technique is $\approx 1 \mu\text{m}$, it is used to acquire chemical information from the topmost surface layer of the coating and not from the bulk. The measurements were repeated a few times to obtain a representative spectrum from each sample. The instrument used was a Perkin Elmer System 2000 Spectrometer with Autoimage microscopy and ATR Accessory.

2.4. X-Ray photoelectron spectroscopy (XPS)

XPS was used with the aim of characterising the outermost atomic layers of the polymers. The surface is excited by x-ray radiation, causing ionisation of the atoms, and analysis of the kinetic energy of the emitted electrons leads to the determination of their binding energy. The technique has excellent energy resolution, allowing chemical analysis. The tests were made using a 310 F Microlab (VG Scientific) equipped with a concentric hemispherical analyser, a differentially pumped ion gun and a non-monochromated Mg mode ($K\alpha = 1253.6 \text{ eV}$). Spectra were obtained in the Constant Analyser Energy mode (CAE = 30 eV).

3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance

Under the conditions of the tests, no signs of corrosion were detected on any of the systems. The capacitance values are significantly different for the various coatings, mainly as a result of the different thickness, since the capacitance is inversely

proportional to the thickness d (ϵ_0 : permittivity of vacuum):

$$C = \frac{\epsilon \cdot \epsilon_0}{d} \quad (3)$$

The coating capacitance rises significantly in the first 10 h of immersion, becoming nearly stable after that period. This corresponds to absorption of water and ions from solution, which leads to an increase of the dielectric constant of the coating.

The values of capacitance for the "dry" coating, C_0 , can be obtained by extrapolation of the first part of the curve to $t = 0$. Once the capacitance C_0 is known, the volume fraction of water can be estimated from the Brasher-Kingsbury equation (Fig. 1).

For PVC plastisol a fraction of 10 % of water in the coating was estimated, a value that is approximately twice that of the polyester and five

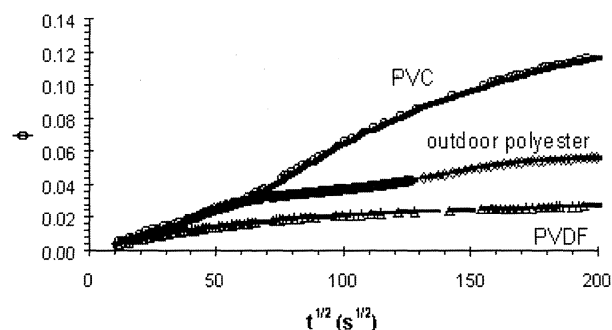


Figure 1. Water uptake of the various coatings, estimated from impedance measurements.

Figura 1. Contenido acuoso de varios recubrimientos, estimado de medidas de impedancia.

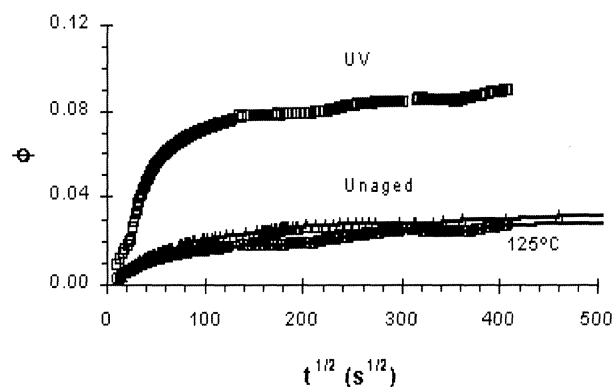


Figure 2. Effect of ageing tests on the water absorption of commercial PVDF.

Figura 2. Pruebas de efecto de envejecimiento sobre la absorción de agua de un PVDF comercial.

times that of PVDF. Also a difference in the shape of the curve is observed, with an inflection after a linear portion of the curve, followed by an acceleration of the permeation processes. This difference can be attributed to the closed porosity of PVC plastisol^[2]. This coating has internal gas bubbles that form in the cure stage, and which lead to closed pores in the bulk of the polymer. Once this water reaches these pores, they tend to absorb quickly, accelerating the process.

Impedance tests were then performed on samples of the same batch, but aged by one of the methods described above (Figs. 2 to 4).

In the PVDF and the polyester, the absorption curve remained practically unaffected by the heat treatment, whereas the QUV treatment enhanced the water permeation. Surprisingly, however, the results with PVC were opposite: no effect of QUV

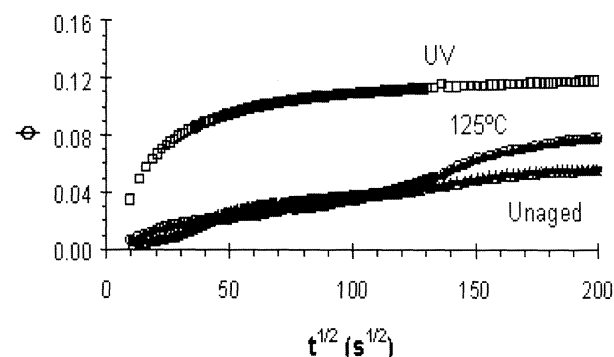


Figure 3. Effect of ageing tests on the water absorption of commercial polyester.

Figura 3. Pruebas de efecto de envejecimiento sobre la absorción de agua en un poliéster comercial.

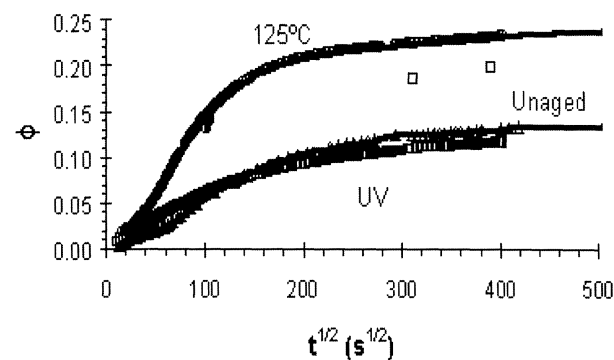


Figure 4. Effect of ageing tests on the water absorption of commercial PVC.

Figura 4. Pruebas de efecto de envejecimiento sobre la absorción de agua en un PVC comercial.

ageing, but an enhancement of water permeation by the treatment at 125 °C.

3.2. Surface analysis

Both FTIR and XPS were made using the model samples. The infrared spectra of these coatings are complex, and total identification was not possible.

3.2.1. PVDF

In the FTIR spectra (Fig. 5) several peaks were identified^[4] the $\nu_a(\text{CH}_2)$, $\nu[(\text{O})\text{CH}_3]$ and $\nu[(\text{C})\text{CH}_3]$ of PMMA at $\sim 2954 \text{ cm}^{-1}$ and the $\nu(\text{C}=\text{O})$ at 1725 cm^{-1} ^[5] also of the PMMA. For the PVDF molecule, the characteristic peaks at 1401, 1182 and 1065 cm^{-1} were also observed.

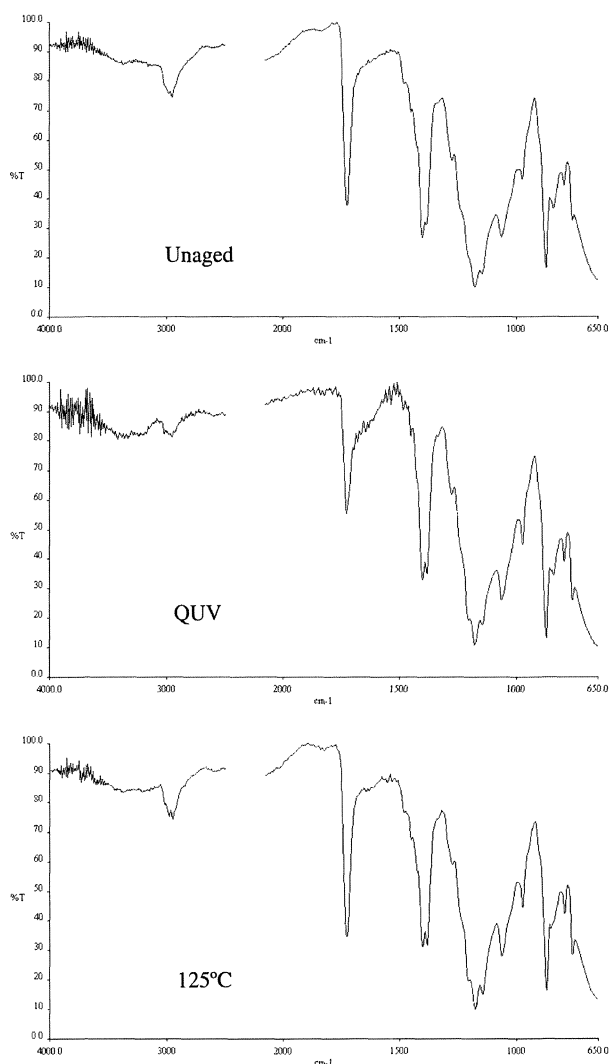


Figure 5. FTIR spectra of model PVDF.

Figura 5. Espectro FTIR de un PVDF modelo.

The heat treatment did not introduce any relevant changes in the spectrum, with the peaks practically in the same positions and with the same intensity. With the QUV, only a very slight degradation was detected, consisting of the formation of weak peaks at 1681 and 1616 cm^{-1} , and a rise of intensity in the region $3000\text{-}3300 \text{ cm}^{-1}$ (formation of OH groups). Finally, the peak at $1725\text{-}1730 \text{ cm}^{-1}$, assigned to the $\text{C}=\text{O}$, has become smaller after the QUV test, revealing some degradation of the PMMA.

3.2.2. Polyester

The peaks at 1545 cm^{-1} and 813 cm^{-1} correspond to the out-of-plane and in-plane vibration of the triazine bond in the melamine molecule, respectively (Fig. 6)^[6 and 7]. The 1545 cm^{-1} peak becomes

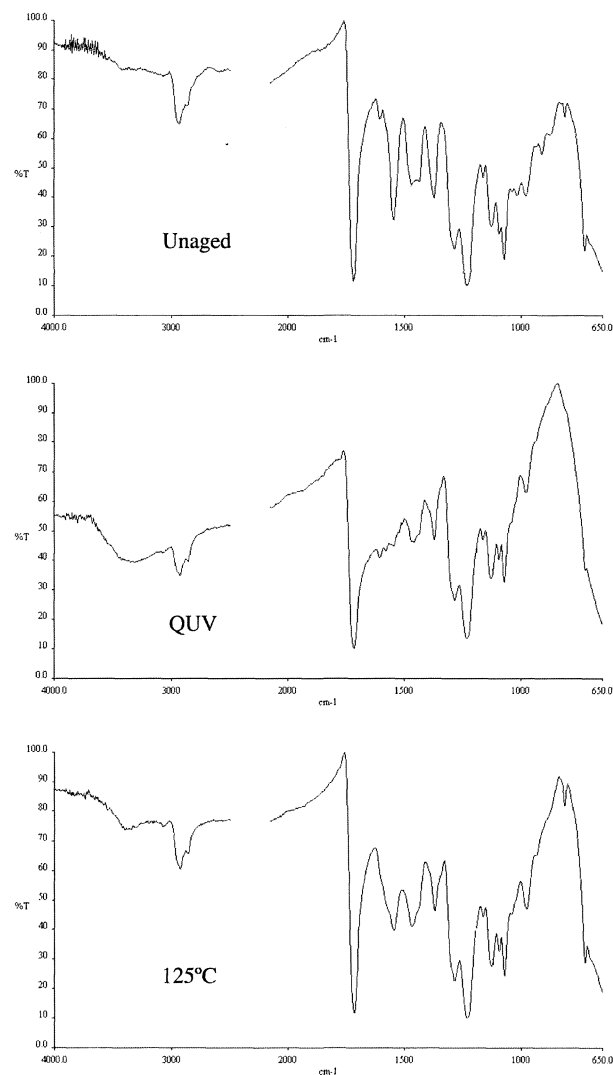


Figure 6. FTIR spectra of model Polyester.

Figura 6. Espectro FTIR de un poliester modelo.

weaker and broadened both by UV and by heat, whereas the 813 cm^{-1} peak remains unchanged. With the QUV, however, both peaks disappear. This can be interpreted as a breakdown of the bonds in the substituents of the triazine ring and is consistent with the literature^[6 and 7], where it is stated that the out-of-plane vibrations is more sensitive to small degradations, whereas the 813 cm^{-1} peak is affected only by severe degradation. The methoxy group, at $911\text{-}913\text{ cm}^{-1}$, was also affected, having disappeared with both the ageing treatments. This is consistent with the formation of a broader band at $\sim 3300\text{ cm}^{-1}$, that corresponds to the region of the O-H and N-H peaks. According to the literature^[6 and 7] the degradation of polyester – melamine system may lead to the formation of amines, alcohols, formates and formamides, as a consequence of the breakdown of the ether and N-C bonds of the cross-linking.

The atomic ratios at the surface of the polyester coating estimated by XPS analysis (Table I) support the FTIR since they suggest some loss of nitrogen at the surface.

3.2.3. PVC

Several characteristic peaks are observed in the reference samples (Fig. 7). From the DOP, the $\nu(\text{C}=\text{O})$ at 1721 cm^{-1} ^[5] the in-plane vibrations of the ring at 1599 and 1579 cm^{-1} and the $\delta(\text{CH}_3)$ at 1328 cm^{-1} were identified^[8]. For the PVC molecule, only the $\delta(\text{CH}_3)$ at 1425 cm^{-1} and the stretching $\nu(\text{CH})$ at 2970 cm^{-1} were identified. The C-Cl vibrations appear below 800 cm^{-1} , where identification was not possible.

The $125\text{ }^\circ\text{C}$ aged coating revealed a spectrum very similar to the unaged one, except for slight reduction in the 1425 cm^{-1} peak and an increased intensity of the $3280\text{-}3400\text{ cm}^{-1}$ peaks, suggesting an increase of OH bonds^[5 and 9].

The QUV ageing induced relevant degradation, with an increase of the peaks at $1550\text{-}1700\text{ cm}^{-1}$, including one peak at 1619 cm^{-1} . This region has

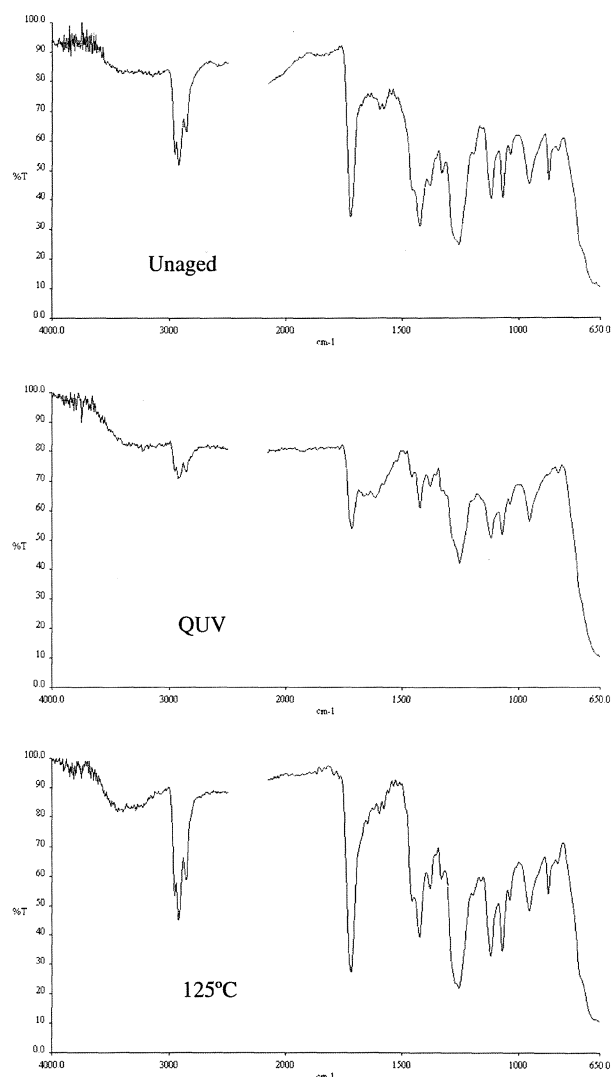


Figure 7. FTIR spectra of model PVC.

Figura 7. Espectro FTIR de un PVC modelo.

been assigned to C=C double bonds. A significant reduction of the 1425 cm^{-1} peak was detected, as well as a general increase of the absorption below 1250 cm^{-1} . Also relevant is the extinction of peaks, namely at 873 cm^{-1} , revealing the disappearance of chemical bonds.

Elemental quantification of the XPS spectra allowed estimation of atomic ratios (Table II).

Table I. Atomic ratios in Polyester

Table I. Razones atómicas en el poliéster

Treatment	O/C	N/C
Unaged	0.32	0.10
Heat, $125\text{ }^\circ\text{C}$	0.36	0.06
QUV	0.29	0.03

Table II. Atomic ratios in PVC plastisol

Table II. Razones atómicas en el plastisol PVC

Treatment	O/C	Cl/C
Unaged	0.25	0.26
Heat, $125\text{ }^\circ\text{C}$	0.25	0.08
QUV	0.60	0.12

The results suggest surface oxidation induced by UV radiation, but not heat. Loss of chlorine occurred at the surface with both ageing treatments, although it was more pronounced with the 125 °C treatment.

Deconvolution of the C_{1s} peak was made accounting for 4 peaks. Following the decreasing order of the binding energy, the peaks are: C_1 corresponding to C=O, C_2 to C-Cl in the PVC molecule, C_3 to CH_2 in PVC plus the C-O in the phthalate and finally C_4 corresponding to the aromatic and aliphatic carbon in the phthalate (plasticizer). The C_2/C_3 ratio, together with the percentage of C=O bond, was selected as reflecting the most relevant chemical changes in the polymer (Table III). The decrease of the C_2/C_3 ratio reveals de-chlorination. This phenomenon was observed in both ageing treatments, but with higher intensity after 125 °C treatment. The C=O content was significantly increased under the UV radiation, confirming oxidation of the polymer at the surface.

4. DISCUSSION

The surface analysis has shown that for all the coatings, the QUV ageing has produced higher degradation than the heating to 125 °C.

Of the 3 coatings tested, PVDF was clearly the more resistant to degradation. Nevertheless, some degradation of the co-polymer (PMMA) occurred under de QUV ageing. In this treatment, UV radiation plays a major role, inducing breakdown of chemical bonds with the formation of light compounds, and loss of elements at the surface, whereas the water washes the surface, leaching some of these light compounds away from the surface.

A direct correlation between chemical degradation and water absorption was thus observed in PVDF and polyester coatings. In fact, the more intense degradation corresponded to the QUV ageing, and it was accompanied by a rise in permeability.

Table III. Carbon distribution in PVC plastisol

Tabla III. Distribución de carbón el el plastisol PVC

Coating	C_2/C_3	C=O (%)
Unaged	0.89	2.9
125 °C	0.52	3.9
QUV	0.69	7.9

The PVC coating revealed a different behaviour. Although the spectroscopic analysis revealed a more severe degradation in the QUV, the rise in water absorption was detected in the samples aged by temperature. The mechanism of ageing explains this difference. As observed before^[10], the effects of UV radiation are felt only in a thin layer at the outermost part of the film. With the PVDF and polyester, which are very thin, the effect of UV radiation is felt across a thickness that corresponds to a significant portion of the film. Since PVC plastisol is a thick coating, the surface effect of UV radiation affects only a minor fraction of the film. This coating was, however, the most sensitive of the three to degradation, and the only one degraded by heat. The effect of heat, although less effective in terms of chemical degradation, affects the bulk of the polymer.

From the point of view of corrosion performance, the good performance of the PVC plastisol is greatly dictated by its large thickness.

5. CONCLUSIONS

The joint use of electrochemical impedance to assess the loss of water barrier properties and of spectroscopic surface analysis to determine the degradation mechanisms has proved to be an interesting way of studying the ageing processes of organic coatings.

From the two ageing treatments tested – QUV and heating at 125 °C – QUV was the one that produced a higher chemical degradation. For PVDF and polyester, which are thin coatings, this higher degradation had led to an increase of permeability.

For thick coatings, such as PVC plastisol, although the effect of UV radiation was severe, it was felt only at the surface, and consequently did not affect the water permeability of the film. The effect of heat was in this case more significant in terms of water absorption, because it is felt across the entire thickness of the coating.

Acknowledgements

This work was made under EU /DGXII/ ECSC contract 7210.TS/ 941.

We also express our gratitude to our colleagues in the project, T. Heatley (Corus,UK) and K.Jyrkas (Rautaruukki, Finland) and also to Gary Williams

(Akzo Nobel) with whom we had many useful discussions.

REFERENCES

- [1] F. DEFLORIAN, L. FEDRIZZI and P. BONORA, *Corros. Sci.* 38 (1996) 1697.
- [2] A.S. CASTELA, A.M. SIMÕES and M.G.S. FERREIRA, *Prog. Org. Coat.* 38 1 (2000).
- [3] A.S. CASTELA, A.M. SIMÕES and M.G.S. FERREIRA, Paper presented at EMCR2000, Budapest, Hungary, May 2000.
- [4] *Vibrational Spectroscopy of Molecules and Macromolecules on Surfaces*, Marek W. Urban, John Wiley & Sons (Eds.), 1993.
- [5] F.W. BILLMEYER, J.R., *Textbook of Polymer Science*, 3rd edition, Chapter 4, John Wiley & Sons (Eds.), 1984.
- [6] E. MUSEAU, G. SEYTRE, R. HELLOUIN and C. BONNEBAT, *53rd Int. Meeting of Physical Chemistry*, Paris, American Institute of Physics, 1995.
- [7] P. DELORME, J. LEMAIRE, F. CARRARA and C. BONNEBAT, *53rd Int. Meeting of Physical Chemistry*, Paris, American Institute of Physics, 1995.
- [8] S. KRIMM HARRISON, V.L. FOLT, J.J. SHIPMAN and A.R. BERENS, *J. Polym. Sci. Part A 1* (1963) 2621.
- [9] J.F. RABEL, G. CANBÄCK, J. LUCKY and B. RÅNBY, *J. Polym. Sci. Chem.* 14 (1976) 1447.
- [10] ECSC report, contract 7210.TS/809, 941, 902, DGXII (2000).