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Effect of UV aging on electrochemical behavior of an anticorrosion paint

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Abstract

The effect of the photochemical artificial ageing (UVA) on the electrochemical behavior of an anticorrosion paint has been studied by electrochemical impedance spectroscopy (EIS). Two types of coatings have been tested: a formulated tri coat system (FS) formed by a primer (epoxy), an intermediate coat (epoxy) and a topcoat (alkyd) which presents a total film thickness of 240 μm and, on the other hand, a non-formulated varnish (NFV) which presents a total film thickness of 70 μm. Panels have been aged in a QUV chamber and the maximal exposure's time was about 1000 h. EIS testing were carried out with a naturally aerated 3% NaCl solution.

Results present Nyquist diagrams for formulated system (FS) and corresponding varnish (NFV) versus UV exposure time after immersion. Evolutions of water uptake for the FS system and the NFV varnish are also presented. In the two cases, we can observe that UV treatment generates a decrease of up taken volume water due to a post-reticulation process. The post-reticulation process concerns both the varnish and the formulated system but its effects are different in the two cases because of the thickness and formulation influences.

In order to precise that result, water uptake evolutions according to UV exposure time have been studied for formulated system and NFV varnish, looking at saturation stage. A post reticulation stage followed by a degradation stage is observed. The evolution of the coefficient of diffusion to half sorption according to UV exposure time completes the previous interpretation.

Keywords: Coatings; EIS; UV aging; Water uptake

1. Introduction

Organic coatings are widely used to prevent corrosion of atmospheric marine structures. The coating efficiency is dependent on the properties of the organic film and on its resistance to the environment aggressiveness. Anticorrosion paint for marine environment are degraded due to different type of weathering parameters, mainly water (rain, condensation or seawater aspersion), UV and temperature [1–3]. Therefore, damages occurring in anticorrosive organic coatings after weathering are complex because of the synergic effects between the different parameters on the degradation process.

UV is an important weathering parameter which induces specific degradations [4–6] but which is always associated with temperature during natural and artificial ageing (60 °C in most standards like ASTM G 154-00, ASTM D 4587-01, ASTM D 5894-96 or ISO 11507-97). Moreover, in these standards, UV is often associated with condensation or artificial rain in order to simulate water influence: synergic effect of water by leaching products from photochemical degradation and also modification of water diffusion due to UV exposure.

So this paper presents some results concerning the effect of artificial UV degradation on the barrier properties of two coatings, evaluated by EIS. The aim of that paper is to study the influence of UV and temperature on the barrier properties. For that, the behaviour of a tri-coat anticorrosion system (FS) used by the French Navy is studied and compared to the varnish (NFV) corresponding to the FS topcoat.

2. Experimental

2.1. Paint samples and exposure conditions

Two types of coatings have been tested. The description of these paints is given Table 1.

The primer and the intermediate coat of the formulated system are chemical curing paints (two components react with each other). On the other hand, the silicon alkyd topcoat is an oxida-

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Table 1
Description of studied coatings

	Primer	Intermediate coat	Topcoat	Thickness (μm)
Formulated system (FS)	Vinyl epoxy (with pigments and fillers)	Vinyl epoxy (with pigments and fillers)	Silicon alkyd (with pigments and fillers)	240
Non-formulated varnish (NFV)	–	–	Silicon alkyd (without pigments and fillers)	70

tive drying paint for which drying is due to a reaction between the binder and the oxygen in the air and the simultaneous evaporation of the solvents.

All panels have been aged in a UV chamber ($T = 60\,^\circ$C, irradiance = 0.77 W/m^2 nm, $\lambda_{\text{UVA}} = 340$ nm) and the maximal exposure's time was about 1000 h.

2.2. EIS measurements

The influence of the photochemical degradation on water uptake has been characterized by electrochemical impedance spectroscopy (EIS) testing on several samples removed from the UV chamber after different UV exposure times. After UV exposition, samples are immerged during 6–8 months depending on the samples.

EIS testing were carried out with a naturally aerated 3% NaCl solution. The electrochemical cell is a three electrodes setting including a platinum counter electrode, a saturated calomel reference electrode and a painted steel panel as working electrode.

The impedance measurement was made as a function of frequency between 100 kHz and 1 mHz using a sinusoidal voltage modulation of 20 mV. Twenty points per decade frequency were collected. All measurements were made under laboratory conditions ($T \cong 23\,^\circ$C). The experiments were conducted using a princeton applied research (PAR) model 273A potentiostat/galvanostat and a model 1025 Frequency Response Detector.

Capacitance and resistance measurements as a function of immersion time in the test solution and UV exposure's time have been used to study the water uptake through protective films.

The volume fraction of up taken water in the coatings (ϕ_t) was calculated following Brasher and Kingsbury's formula [7–9]:

$$\phi_t = \frac{\log C_t/C_0}{\log 80} \tag{1}$$

where C_t is the capacitance of protective film at time t, C_0 the capacitance of protective film at time $t = 0$ and 80 is the relative permittivity of water at 20 °C.

The capacitance of coating (C) was calculated following the formula:

$$C = \frac{Z''}{2\pi f[(Z' - R_e)^2 + Z''^2]} \tag{2}$$

where Z' and Z'' are respectively real and imaginary components of impedance, f is the corresponding frequency and R_e the electrolyte resistance.

The measurements have been carried out at the frequency of 20 kHz which is an optimized value determined for getting reproducible and stabilized answer of the electrochemical system. That value is used by different authors [10].

2.3. Glass transition temperature measurements by the pin-point method

For characterizing polymeric materials by DMTA, different modes of deformation are possible. The pin-point method uses a compression mode adapted in order to allow T_g measurement on a coating applied on a metallic substrate. This test is based on the vibration of a pin, placed on a paint surface. The pin is a pyramidal indentor, built from a 4 mm steel cylinder, as described in Fig. 1. The apparatus used is a RSA2 solid viscoanalyser form rheometrics. The vibration frequency has been fixed at 1 Hz. The pre-tension load and the amplitude of deformation have been optimised respectively to 0.05 N and about 5 μm. Those values do not depend on the material under investigation, and have been used throughout. A temperature ramp of 5 K/min has been used for all samples. T_g is measured at the maximum of the damping peak.

Previous studies have validated this method. An excellent agreement was observed between T_g measured by means of the pin-point method and by means of the dual cantilever [11]. Moreover, T_g measurements were compared to Vickers micro hardness [12]. Then, the pin-point test has proved to be a reliable technique to study T_g of material, and especially to study the surface properties of the same materials.

With the consideration that this technique has been developed to study surface properties of materials, the sample thickness effect on the pin-point response was also investigated. It was observed that the relaxation temperature is poorly sensitive to the material thickness [11].

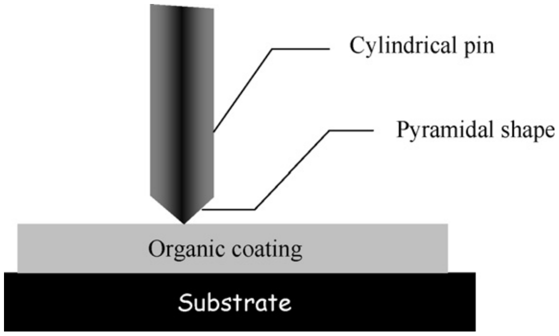

Fig. 1. Schematic of the pin-point method.