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Natural and artificial weathering characteristics of stabilized acrylic–urethane paints

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Abstract

Depth-profiling by Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical analysis (DMA), microhardness and scanning electron microscopy (SEM) observations have been used to monitor degradation chemistries in two-package acrylic–urethane coatings when exposed to different exposure conditions. Three artificial and three natural weathering protocols (QUV, ASTM D5894, ISO20340, Pipady (south of France), Bandol (south of France) and Kure Beach (USA)) were selected for this study. The same chemical events were found to occur under all conditions, particularly under natural and artificial exposures. Both loss of the amide II band at 1520 cm^{-1} and carbonyl growth occurred but at relatively low rate owing to the presence of hindered-amine light stabilizers in the film. A less typical loss of urea biuret linkages also occurs during all exposures and results in a change in the balance between urethane and urea links across the depth of the film during weathering. The chemical degradation of the polymer matrix involves the formation of species that are readily ablated from the surface and results in loss of gloss, increase in hardness and a rougher topology. The dramatic loss of gloss observed after Pipady and Bandol exposures show that loss of gloss should not be systematically correlated to the advance in chemical degradation.

Keywords: Polyurethane acrylate; Natural weathering; Artificial weathering; FTIR

1. Introduction

The corrosion properties of organic coatings are some of the most important properties of the entire coating system. The testing of corrosion performance is generally achieved by natural outdoor exposure at sites of high corrosivity or accelerated in an exposure cabinet. Although the former requires very long exposure periods (>1 yr), the latter often lacks representativeness leading to misunderstood predictions. In a recent paper [1], physico-chemical changes of the basecoat and primer binders occurring in a multi-layer system have been evaluated. The results have shown that loss of anticorrosive protection is not directly linked to the physico-chemical changes of the basecoat and primer binders.

Urethanes are known for chemical, water and especially abrasion resistance. They can also be designed for high tensile and impact strength, along with excellent low temperature flexibility. Aliphatic polyurethane acrylate (PUA) cured at ambient temperature is used as a single-pack UV-cured system or a two-pack system. The type of reaction to generate crosslinks between the polymer chains is based on a radical-induced polymerization of a difunctional acrylate monomer or oligomer (with internal urethane functions) for the UV-cured PUA while it is based on the condensation reaction between the hydroxyl groups of a polyol-acrylate (and in some cases of atmospheric water) and the isocyanate groups of a crosslinker in the two-pack PUA. The crosslink density of the final network is higher in UV-cured PUA than in two-pack PUA [2]. It is also noteworthy that the network from the two-pack PUA often includes urea functionalities (resulting from the moisture curing of isocyanate groups) that are absent in the case of the photosets.

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Due to the high vapour pressure of hexamethylene diisocyanate (HDI), resins based on either biuret adducts or isocyanurate trimers of HDI are commonly used as crosslinkers for two-pack PUA systems [3]. With such HDI crosslinkers, hydrophobic character of the coating and NCO functionality are reinforced [4].

The light stability of acrylic–urethane coating was found to be improved by HALS and/or UV absorbers [5–12]. Some of these studies were focused on photostabilized two-pack PUA [2,9–12] based mainly on the FTIR analysis on the loss of urethane (1520 cm^{-1}) and CH groups (near 2900 cm^{-1}) that occur during accelerated UV weathering.

In the present work, based on the experimental method previously established [1], the degradation process of an UV-stabilized acrylic–urethane topcoat is proposed. The biuret of 1,6-hexamethylene diisocyanate (HDI-biuret) is used as the crosslinker of the acrylic–urethane. The representativeness of accelerated test methods performed compared to natural degradation is also discussed.

2. Experimental

The system studied consisted of grit blasted mild steel coated with three layers, a 40 μm thick zinc-rich epoxy primer, a 130 μm thick epoxy basecoat in xylene solvent and a 40 μm thick acrylic–urethane topcoat. The biuret of hexamethylene diisocyanate (HDI-biuret) was used as the crosslinker of the acrylic–urethane. Its structure was undoubtedly confirmed by ^{13}C NMR spectroscopy. ^{13}C NMR spectrum notably exhibits a peak at 156 ppm from the biuret that is found downfield in comparison to the triazine ring carbonyl carbon atom of HDI isocyanurate (149.5 ppm), another commonly used polyisocyanate crosslinker. The acrylic copolymer contains styrene as a comonomer besides butyl methacrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl and hydroxypropyl acrylates. The acrylic–urethane coating was formulated in xylene solvent with a hindered-amine light stabilizer (Tinuvin 292 from Ciba Speciality Chemicals) and barium sulphate pigment. The acrylic–urethane topcoat was allowed to crosslink at 21 ± 2 °C under relative humidity condition of $40 \pm 5\%$ for 1 yr. Then, samples were exposed to three different standard artificial cycles, QUV ASTM G 53, ASTM D 5894 and ISO 20340, and to three different natural weathering environments, Pipady, Bandol and Kure Beach. The natural exposures were conducted according to the ASTM G7 standard. Kure Beach is located adjacent to the Atlantic Ocean at latitude 34°N and longitude 77.5°W. Pipady and Bandol are two sites in the south of France at latitude 43°N and longitude 5°E. Only Pipady is located adjacent to the Mediterranean Sea. The test panels for natural weathering were exposed in racks inclined at an angle of 45° from the horizontal, facing south. Duration and sequences are listed in Table 1. Table 2 reports the UV light dose received by the topcoat.

About 1 cm^2 sections (2 μm thick) were cut using a Leica RM 2165 microtome equipped with a tungsten carbide knife. Each sample was analysed with a Continuum IR microscope (Thermo Nicolet) coupled to a Nicolet Nexus spectrometer. The microtomed section was subjected to FTIR analysis by transmitted light through the microscope (100 μm × 100 μm aperture). Averaged spectra were generated from 10 spectra collected from different locations on each sample. All spectra were collected with 32-scan summations and 4 cm^{-1} resolution using MCT detector.

Table 1
Weathering conditions

Weathering code	Procedure
QUV	4 h UV-A at 60 °C + 4 h continuous condensation at 50 °C – 84 days
Cycle 1	168 h QUV (ASTM G53) + 168 h Prohesion (ASTM G85 Annex A5) – 6 months (ASTM D5894)
Cycle 2	72 h QUV + 72 h NSS (ISO 9227) + 24 h at −20 °C – 6 months (ISO 20340)
Pipady (France)	Photochemical and marine atmosphere (C5M) – one sample: 2 yrs
Bandol (France)	Photochemical weathering (C3) – two samples: 3 and 4 yrs
Kure Beach (USA)	Photochemical and marine atmosphere (C5M) – three samples: 1–3 yrs

For natural ageing, the corrosivity categories of the atmosphere according to ISO 9223 standard are indicated in brackets.

The Vickers hardness measurements were performed at room temperature (23 °C) with a FM7 Testwell microhardness tester. The applied load was 10 g for unaged samples and 25 g for aged samples to give a nearly constant indentation depth of about 10 μm for both samples. The indentation time was fixed at 10 s and was considered sufficiently low to minimize for the creep effect. At least 10 indents were used to get the mean value of microhardness and corresponding standard deviation for each material.

Dynamic mechanical analysis (DMA 2980 TA instrument) was carried out to determine the glass transition temperature, T_g, of the acrylic–urethane polymer. The compressive mode was used with a hemispherical tool over a wide temperature range around the T_g. Experimental conditions were as follows:

- Static force: 0.5 N.
- Strain amplitude: 0.5 μm.
- Frequency: 1 Hz.
- Temperature: from 10 °C to 200 °C with a 3 K/min ramp rate.

Table 2
UV light doses received by the aged samples

Weathering conditions	UV light dose (MJ m^{-2})
QUV	142
Cycle 1	142
Cycle 2	120
Pipady (2 yrs)	573
Bandol (3 yrs)	984
Bandol (4 yrs)	1314
Kure Beach (1 yr)	279
Kure Beach (2 yrs)	615
Kure Beach (3 yrs)	930