Durability Prediction of p-Urethane Clearcoats Using Infrared P(hoto) A(coustic) S(pectroscopy)

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Summary: The durability of topcoats is dependent on a large number of factors as polymer composition, stabilization package and the conditions during the weathering process.
For obvious reasons prediction of the long-term (5-10 year) durability of coatings is very important. The rate-determining factor for the degradation of PUR coatings is photo-oxidation. The photo-oxidation rate is controlled by the polymer structure but also stabilizers as HALS has a large influence.
The prediction of the durability of clearcoats is based on tracing of the photo-oxidation rate and of the HALS longevity during exposure.
The photo-oxidation rate is measured using FTIR-PAS. The results show that degradation can be detected much earlier compared with classical methods as gloss loss. Moreover detection of differences between systems after short exposure times as well as prediction of the long-term durability are possible.

Keywords: clearcoat, durability, polyurethane, photo acoustic spectroscopy, infrared spectroscopy

Introduction

Durability prediction is in the coating industry a main issue. A lot of effort is put in research focussed on correlation between short-term artificial weathering methods and long term outdoor weathering. The idea behind these programs is the assumption that the process of degradation during weathering is only accelerated and that the mechanism does not change during the artificial exposure.

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Polyurethane clearcoats are applied mainly for cars. But also new areas like the aerospace industry show interests to use these clearcoat systems. Furthermore, the warranty demands (aircraft's 8 years) are becoming more stringent. Also new environmental stresses, as acid pollution, become of more influence on the durability behavior of coatings.

To make the prediction of the long-term durability of clearcoats more reliable the classical approach of comparison artificial and outdoor weathering is not anymore sufficient. The main problem is the non-linearity of e.g. gloss loss in time (Figure 1). Cracking or gloss loss starts after already a reasonable chemical attack has been taken place.

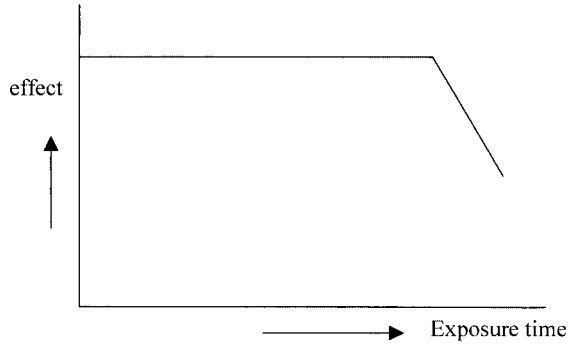

Figure 1. Non linearity effect of e.g. gloss loss/cracking in time

More knowledge about the background of the degradation is needed to overcome this dilemma.

This knowledge could be of great help to develop a service life prediction model [1].

The durability of clearcoats can be described by the following factors:

a. Photo-oxidation rate of the surface
b. Longevity of hindered amine stabilizers (HALS)
c. Longevity of UV-absorbers

These factors are related to gloss/cracking (a, b) and delamination (c). Photo-oxidation causes a more hydrophilic film, which will be more sensitive for hydrothermal stress [2].

The polymer design as well as the presence of HALS is of strong influence on this process.

This paper focuses on the measurement of the photo-oxidation rate by photo-acoustic spectroscopy. The prediction capability of this method has been investigated using several types of polyurethane clearcoats.

Experimental

Photo Acoustic FTIR Spectroscopy (PAS) was performed with an accessory of METC model 300, at 2.5 kHz using disks of 10-mm diameter. The spectra were evaluated in two ways. The relative changes of the bands in the whole spectrum were determined and the photo-oxidation product (POP) was measured. The definition of the POP value is given in Figure 2.

$$\left(\frac{(NH + OH + CH) - (CH)}{CH}\right)_{t=t} - \left(\frac{(NH + OH + CH) - (CH)}{CH}\right)_{t=0}$$

Figure 2. Definition of the Photo-Oxidation Product (POP),

The systems were exposed in the WOM (ISO 11341 Q/B as well as B/B filters), UVCON (ISO 11507, UVB-313) and in the BAT test. The BAT is a cyclic test consisting of 5 cycles of condensation/SO_2 according to ISO 3231, 16 h ventilation at ambient conditions and 100 hrs WOM according to ISO 11341 B/Q.

Two PUR clearcoats and one PUR solid color were investigated:

PUR 1 solid color (white)

PUR 2 MS clearcoat on light blue basecoat

PUR 3 HS clearcoat on HS light blue basecoat; both p-ester based

The stabilization with UV-absorber and HALS were varied.

Results and discussion

Influence of filters in WOM

The spectral distribution of using Boro/Boro or Quartz/Boro is very equal. The only difference is the short wavelength part. The Quartz/Boro filter transmits more of the wavelength between 290-310 nm. This part of the spectrum can have a big influence on the degradation rate as well as on the mechanism [3] since many polymers and crosslinker or formed crosslinks start to absorb light in this region. Figure 3 shows some results of a comparison of the two filter sets for PUR 3.

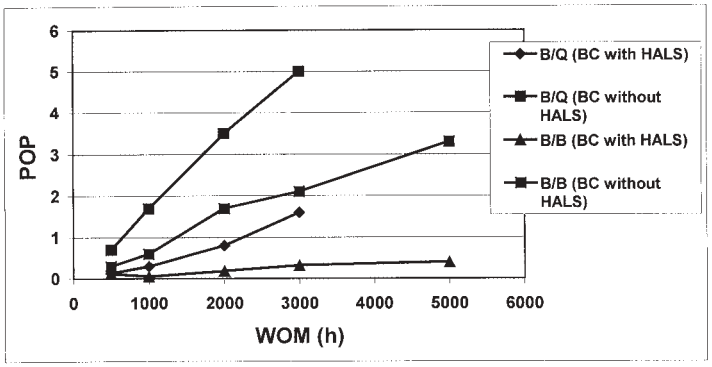

Figure 3. Comparison Quartz/Boro and Boro/Boro filters in WOM for stabilized and unstabilized PUR 3.

The photo-oxidation rate (POR) of the films exposed in the Q/B is faster as in the B/B exposure. More experiments show that the order of stability of the several systems does not change. So, the mechanism of degradation is not influenced by the filter system for these paint films.

Stabilization with HALS

Figure 4 shows the results of PUR 2 and PUR 3 with and without HALS. The protection of HALS against photo-oxidation of the clearcoat surface is obvious. Without HALS the photo-oxidation starts immediately. The stability of the p-urethane clearcoats with HALS is very good. After more than 8000 hrs of WOM exposure the POP start to increase

somewhat. This can be explained by the fact that the HALS is becoming inactive during exposure which results in less protection to photo-oxidation [4]. This point is the start of a more severe degradation of the clearcoat and an indication that gloss loss/cracking will occur in the next period.

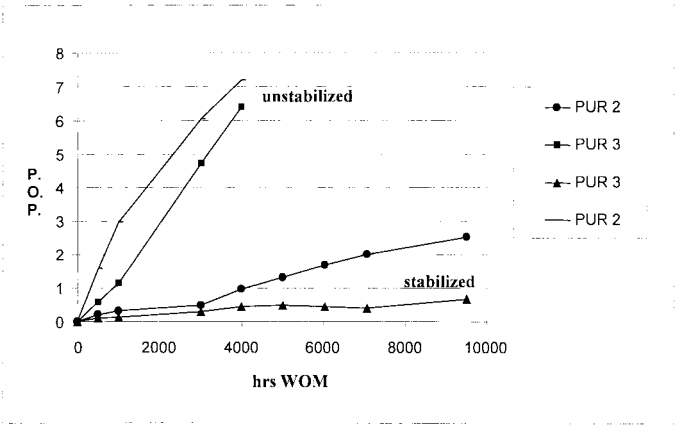

Figure 4. Influence of HALS on photo-oxidation rate of PUR 2 and PUR 3.

Comparison exposure methods

The rate of degradation has been compared for the three exposure methods. The variation is on one hand acid environment versus neutral conditions (BAT versus WOM/UVCON) and on the other hand a comparison between hard UV light (UVCON with UV-B bulbs) and soft UV-light (WOM B/Q). Figure 5 shows the POR of PUR 3.

The BAT test appears to be very aggressive. The photo-oxidation rate is very close to an unstabilized system (Fig. 4). The results suggest that either the acidic attack of the polymer is very severe or more likely, considering the same POR as the unstabilized system, the HALS activity is strongly diminished by the strong acid. ESR measurements [4] show indeed that no nitroxyl radicals are present anymore in the films exposed in the BAT test. A second conclusion from figure 5 is that for this system the difference between the WOM and the UVCON is only small.

Comparison PUR systems

Figure 6 shows the POR's of the three PUR systems during the WOM exposure. As expected the two clearcoats differ only to a less extent since the durability is dominated by the presence of the HALS. The solid color system reaches within short time a rather high level of POP and keep than constant. Several reasons can be mentioned for this behavior. Firstly the pigment particles keep the light in the upper few microns of the film. Secondly after already short time there is an equilibrium reached between the degradation of the polymer and the removal (e.g. rinsing with water) of degraded material. Thirdly the depth information of the PAS measurements could be smaller than in the case of clearcoats, since the pigments will influence the thermal diffusion of the film.

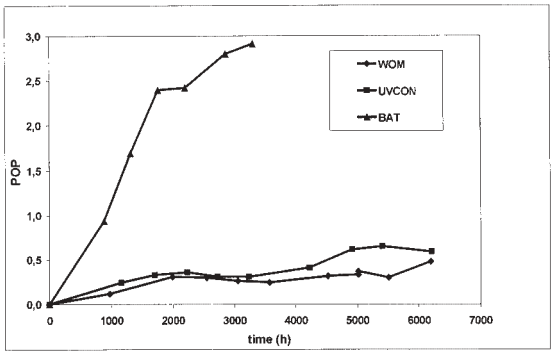

Figure 5. Comparison of exposure methods for PUR 3.

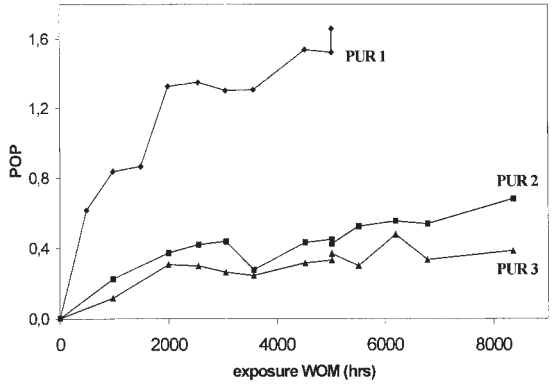

Figure 6. Comparison of three PUR systems; WOM exposure.

Relation POP and conventional parameters (gloss/cracking)

In figure 7 the POP values and the measurements of the conventional parameters gloss and cracking are plotted for the unstabilized PUR 3.

The predicting value of the POP method is clearly demonstrated. The gloss and cracking show the typical non-linear behavior whereas the POP increases from the start of the exposure indicating that the chemical degradation starts immediately. A comparison of this initial POR between systems will give a faster insight in the weathering behavior.

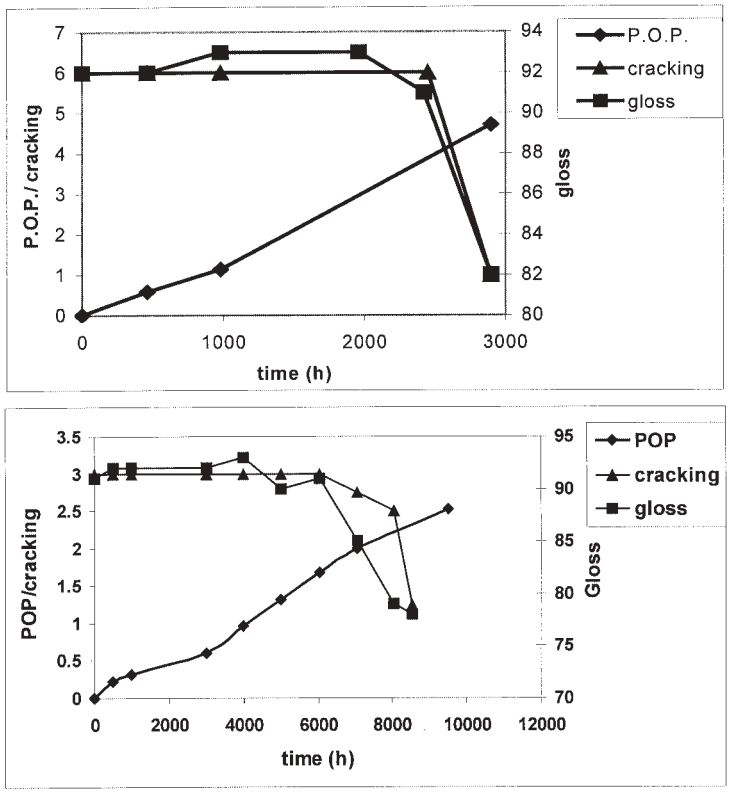

Figure 7. Comparison of POP with gloss and cracking of PUR 3; top unstabilized; bottom stabilized.

Conclusions

PAS measurements during weathering of p-urethane clearcoats are very useful to obtain in an early stage of the exposure information about the photo-oxidation sensitivity of clearcoats.

Differences between weathering methods, clearcoats, stabilization etc. can be quantified.

Moreover, determination of the photo-oxidation rate seems a tool to overcome the problem of non-linearity behavior of conventional parameters as gloss and cracking.

In the case of solid color p-urethane paint films the PAS method has no advantages since the photo-oxidation products reaches after short exposure time already its maximum value.

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