

## **OXYGEN INHIBITION AND COATING THICKNESS EFFECTS ON UV RADIATION CURING OF WEATHERFAST CLEARCOATS STUDIED BY PHOTO-DSC**

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### **Abstract**

Radiation curing is an environmentally-friendly technology. Furthermore, radiation curing is a faster, energy saving and more efficient industrial process than the heat-curable process. One of the most important requirements for the widespread application of UV curable coatings in the coating industry is that they are stable *vs.* atmospheric degradation. Today's state of the art in oxidative drying and thermosetting coatings is the use of light stabilizers to protect polymers *vs.* the damage of outdoor exposure. Oxygen has a detrimental effect on the cure response of free radical systems, especially in thin-film coatings. Differential photocalorimetry (photo-DSC) was used to investigate the oxygen effect and the use of light stabilizers on UV curing of photocurable formulations based on acrylate materials. Coating thickness influence was also considered.

**Keywords:** free radical photopolymerization, O<sub>2</sub> inhibition, UV curing

### **Introduction**

Radiation curing of coatings is a high-value technology. Volatile organic compounds (VOC) are near zero [1]. Another important advantage is that heat sensitive substrates can be coated and cured without heating them.

The UV curing process is the conversion of a reactive liquid into a solid through polymerization and crosslinking reactions induced by radiation. The UV formulation components are oligomers, monomers, photoinitiators, pigments and additives. The photoinitiator absorbs the UV radiation, generating free radicals, which start and propagate chemical reactions that convert the reactive compounds into a cured film [2–4].

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UV absorbers are additives, which are incorporated in the formulation to prevent degradation of the cured products when exposed to solar radiation. These additives can absorb UV light competing with the photoinitiator for the photons emitted from the UV lamp. Nevertheless, the photoinitiator and the UV absorber acting at different spectral windows can be included in the same formulation, leaving the photoinitiator to be selectively activated. Another additives that prevent cured film degradation are radical scavengers. These additives are classified as 'hindered amine light stabilizers' (HALS), which do not absorb significant UV radiation [5–7].

The oxygen inhibition of free radical polymerization leads to slower reaction rates and low cure degree. Oxygen interacts with the photoinitiator by quenching effect in which the photoinitiator becomes deactivated. Additionally, oxygen molecules can react with radicals produced from photoinitiator. In this last case peroxide radicals are formed and the initiation activity is lost. Furthermore, oxygen reacts with the polymeric radicals, stopping the polymerization reaction [8].

The influence of the oxygen in the UV cure process is also related to the film thickness such as the thicker the sample is, the larger the differences are between radical generations near the illuminated surface than at the coating/substrate interface. Higher amount of radicals formed greater consumption rates of monomer and oxygen in this region. The competition of oxygen and the monomer in reacting with radicals leads to a non-uniform distribution of these radicals producing a concentration gradient of oxygen and monomer along the depth of the film [9].

The aim of this work was to evaluate the effect of oxygen during UV curing process related to the coating thickness. The influence of light stabilizers in the photocurable formulation was also considered. The photo-DSC technique has been chosen to obtain the information needed for the evaluation of the process parameters studied. Moreover, this technique has provided a monitoring of the curing process, close to actual industrial conditions.

## Experimental

### *Materials and methods*

Two clear coatings named Coating A and Coating B were studied. The coating components were urethane aliphatic diacrylate resin (Ebecryl 270), 1,6-hexanediol diacrylate monomer (HDODA), both supplied by UCB do Brasil Ltda; 2-hydroxy-2-methyl-1-phenyl-propane-1-one photoinitiator (Darocur 1173), the light stabilizer HALS (hindered amine light stabilizer) – Tinuvin 292 and an UV absorber (Tinuvin 400), supplied by Ciba Especialidades Químicas Ltda. Coatings A and B compositions are given in Table 1.

Samples of 2–10 mg of Coatings A or B were poured into graphite pans 5 mm in diameter and 3 mm in depth, resulting in a layer thickness of 110 to 460  $\mu\text{m}$ .

**Table 1** Composition of the formulations of the coatings tested (mass%)

Components	Coating A	Coating B
Resin	63	62.0
Monomer	34	33.5
Photoinitiator	3	2.9
UV absorber	/	0.64
HALS	/	0.96

Measurements of the reaction heat were carried out in a photo-DSC equipment TA Instruments DPC 930/DSC 910, equipped with a medium-pressure mercury lamp (200 W in<sup>-1</sup> and 80 mW cm<sup>-2</sup>). In this equipment the reactions are induced by UV radiation emitted by a medium-pressure mercury lamp. An empty pan was used as a reference. The photopolymerization is an exothermic process and the enthalpy changes are related to the area under the positive peak (exotherm) in photo-DSC curve [10].

All experiments were carried out at 25°C, in air or nitrogen atmosphere (flow rate of 50 mL min<sup>-1</sup>), using a two-minute stabilization time and three-minute exposure time, which was enough to achieve the total coating cure under these experimental conditions.

## Results and discussion

The photo-DSC measurements parameters for Coatings A and B with different layer thicknesses are given in Tables 2 and 3.

**Table 2** Coating A thickness influence – curing in nitrogen and air atmospheres

Thickness/ μm	Nitrogen			Air		
	Enthalpy/ J g <sup>-1</sup>	Induction time/s	Peak maximum/s	Enthalpy/ J g <sup>-1</sup>	Induction time/s	Peak maximum/s
110	208	1.5	5.2	247	2.8	6.8
200	205	1.7	5.4	215	3.3	8.8
300	204	2.0	5.6	219	3.2	8.4
400	205	2.3	7.5	/	/	/
460	207	2.3	7.8	/	/	/

Figure 1 shows the photo-DSC curves of Coatings A and B in air and nitrogen atmosphere, using 2 mg sample mass (~110 μm).

The peak areas of the photo-DSC curves are related to the enthalpy involved in the cure of the material. The values of enthalpy obtained for samples with different thicknesses in photo-DSC are relatively similar, as it was expected, considering that

in this procedure it is possible to reach the highest cure enthalpy of the system due to the long time under UV radiation.

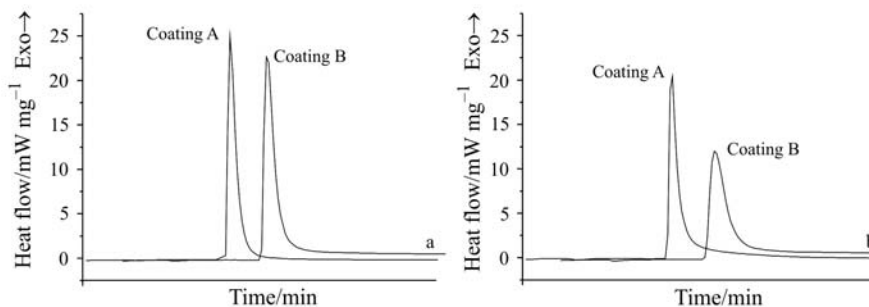
**Table 3** Coating B thickness influence – curing in nitrogen and air atmospheres

Thickness/ $\mu\text{m}$	Nitrogen			Air		
	Enthalpy/ $\text{J g}^{-1}$	Induction time/s	Peak maximum/s	Enthalpy/ $\text{J g}^{-1}$	Induction time/s	Peak maximum/s
110	209	2.2	6.0	114	6.0	10.0
200	200	3.0	9.0	160	9.5	23.2
300	181	3.0	9.0	160	10.8	25.2
400	180	3.6	9.4	/	/	/
460	174	3.6	11.0	/	/	/

However, the induction time (relative to 1% of the conversion of the reactive species), and the peak maximum (time, in seconds, between the opening of the lamp shutter and the peak maximum point in the photo-DSC curve) [11], increases with the coating thickness. Thinner samples have shown higher reaction rates. This effect can be observed in Fig. 1 by the decrease in height and by the expansion of the curves.

The data in Tables 2 and 3 show that, in the presence of oxygen, the induction time of the reaction is greater than in a nitrogen atmosphere. This indicates a lower degree of conversion of the reactive species in the presence of molecular oxygen due to its reaction with the free radicals generated from photoinitiator as well as with the polymeric radicals, leading to the stopping of the polymerization reaction. The reaction rates observed in the presence of oxygen are lower than in nitrogen atmosphere and decrease as the coating thickness increases. Using the Lambert–Beer law this effect can be demonstrated in which the rate of UV absorption in the layers nearer the surface is higher than in those close to the coating/substrate interface.

The experimental results in Table 3 show that the UV absorbers and HALS influence in the cure process related to the Coating A irradiated in nitrogen and oxygen atmospheres. This can be explained considering that the UV absorber absorbs UV



**Fig. 1** Photo-DSC curves – Coatings A and B atmosphere influence: a – nitrogen and b – air – 110  $\mu\text{m}$  thick samples

light in the same electromagnetic spectrum region of the photoinitiator, partly competing with the latter for the photons emitted by the lamp. In oxygen atmosphere therefore, there is a competition among the UV absorber, the reactive species and the oxygen. As a result, there is a reduction in the free radical formation from the photoinitiator; formation of peroxides by reaction of reactive species with oxygen and the action of the UV absorber in the competition with the photoinitiator, which interferes in the total cure of the coating.

Nevertheless, the protection that such additives provide to the UV cured coating when exposed to solar radiation justifies its incorporation. The effect of these additives on the cure degree can be balanced with a rise in the radiation doses applied or in the intensity of the ultraviolet radiation emitted by the lamp [12].

## Conclusions

UV radiation cure process involves various factors that determine the extent of the cure and the properties of the final product. The photopolymerization reactions are carried out in air and, as shown by the results of this study, the presence of oxygen interferes in the cure process, leading to a decrease in the polymerization rate. The film thickness influence is closely related to the inhibition of the polymerization by the diffusion of atmospheric oxygen in the coating as well as by the higher absorption of ultraviolet radiation in the superficial regions as compared to the coating/substrate interface.

The use of the UV absorber and HALS, for the protection of the material *vs.* weathering, leading to the competition, with the photoinitiator, for the absorption of ultraviolet radiation, results in the formation of a lower concentration of free radicals. Moreover, the reactive species may react with the oxygen present in the coating and in the superficial layer, which further reduces the reaction rate. However, the protection *vs.* weathering that these additives provide to the products justifies their addition. Increasing the radiation dose can partially counterbalance the conversion loss of Coating B, which has UV absorber and HALS.

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