

# Weathering Performance of Thermoset And Photoset Acrylate Coatings

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## INTRODUCTION

The surface properties of polymer materials can be substantially improved by protective coatings, in particular their resistance to weathering in exterior applications. Such coatings must not only have the required mechanical and optical properties, but they must also withstand durably environmental factors by showing a great resistance to UV-radiation, oxygen, moisture, pollutants, and heat. They are usually made of highly crosslinked polymers which show superior weathering performance to their linear counterparts, because chain scissions have less dramatic effects on the polymer durability. For automotive finishes, most of today's topcoats consist of thermosetting acrylate polymers which contain light stabilizers to protect the painted basecoat and avoid photobleaching and delamination upon outdoor exposure.<sup>1-5</sup>

The growing concern for the protection of the environment has urged polymer chemists to develop solvent-free systems, in particular in the coating industry. In this respect, UV-radiation curing appears to be a valuable alternative to the conventional thermal curing of solvent-based clearcoats. Despite the presence of small amounts of residual photoinitiator, it has been shown that some UV-cured acrylate clearcoats can exhibit an excellent resistance to weathering in the presence of adequate light stabilizers.<sup>6-9</sup> By using UV-radiation to initiate the crosslinking polymerization of multifunctional monomers, one can transform almost instantly a liquid resin into a solid polymer material. Therefore, such solvent-free formulations can be cured at ambient temperature with minimal energy consumption.

UV-cured coatings need to have mechanical properties and exterior durability at least equal to that of the thermoset polymers, if they are to be used as automotive finishes. The scratch and abrasion resistance of some UV-cured polyurethane-acrylate clearcoats has been shown to be as high as that of two-pack-polyurethane/acrylate thermoset clearcoats.<sup>10</sup> In the present work, we compare the performance of thermoset and photoset acrylate polymers, with respect to both the curing process and the weather-

*Thermosetting and photosetting acrylate polymers have been tested for their resistance to accelerated weathering. The chemical changes occurring both upon curing and upon photoaging have been followed by infrared spectroscopy. In the photodegraded polymers some functional groups are lost (ether, amide, CH groups) and oxidation products are formed (carbonyl and hydroxyl groups). The UV-cured polyurethane-acrylate coatings were found to be more resistant to accelerated weathering than the melamine/acrylate thermosets currently used as automotive finishes. The light stability of both thermoset and photoset acrylate clearcoats was substantially increased by the addition of a hydroxy-phenyltriazine UV-absorber and a HALS radical scavenger. The weathering resistance of painted metallic panels has been markedly enhanced by means of properly stabilized UV-cured acrylic coatings.*

ing resistance of well-stabilized clearcoats. We have tried to prevent color fading of a painted metallic panel by means of such UV-cured acrylate coatings.

## EXPERIMENTAL

### Materials

The solvent-based thermoset resins used in this study consisted of a mixture of an acrylate polyol copolymer (Joncryl 510 from SC Johnson & Sons or Macrymal SM-510 from Hoescht) and a crosslinking agent which was either a methoxylated melamine (Cymel 327 from American Cy-

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anamid Corp.) or a trifunctional isocyanate (Desmodur N75 from Bayer). Both types of formulations contain equal amounts of hydroxy groups and methoxy or isocyanate groups. The thermosetting melamine/acrylate (TMA) and urethane/acrylate (TUA) were cured by a 30 min bake at 130°C. The solvent-free UV-curable resin (PUA) contained three components: an aliphatic urethane-acrylate telechelic oligomer (Ebecryl 284 from UCB), hexanediol diacrylate (HDDA from UCB) as reactive diluent (30 mass %) and a bisacylphosphine oxide (BAPO) photoinitiator (Irgacure 819 from Ciba Specialty Chemicals) at a concentration of 0.75 mass %. A hydroxyphenyl ketone (HPK) photo-initiator (Darocur 1173 from Ciba Specialty Chemicals) was added to achieve a better surface cure, at a concentration of 2.25 mass %.

The formulation was cured by a two-second exposure to the UV-radiation of a medium pressure mercury lamp (120 W/cm) at ambient temperature. Two types of light stabilizers were added to the liquid resins: a hydroxyphenyl-s-triazine (HPT), Tinuvin 400 from Ciba Specialty Chemicals as UV-absorber (UVA) at a concentration of 2 mass %, and an N-alkoxy substituted hindered amine (HALS), Tinuvin 123 from Ciba Specialty Chemicals, as radical scavenger at a concentration of 1 mass %. The chemical formulas of these additives are given in Scheme 1.

### Weathering

The liquid formulations of TMA, TUA, and PUA samples were applied on a BaF<sub>2</sub> crystal as a uniform layer, to get after curing a 35 µm thick dry film. For evaluation of their resistance to accelerated weathering, the cured samples were placed in a QUV-accelerated weatherometer equipped with UV-B-313 or UV-A-340 fluorescent lamps and operated under wet cycle conditions: eight hours UV irradiation at 70°C, followed by four hours in the dark with water condensation at 50°C. All the weathering experiments have been carried out in duplicate.

### Analysis

Infrared spectroscopy was used to monitor both the curing process and coating photodegradation after QUV-

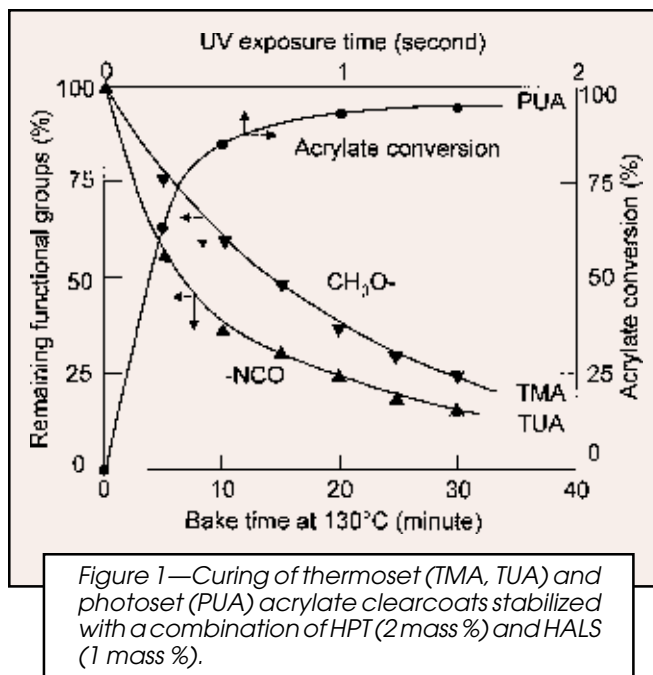


Figure 1—Curing of thermoset (TMA, TUA) and photoresin (PUA) acrylate clearcoats stabilized with a combination of HPT (2 mass %) and HALS (1 mass %).

exposure. The disappearance of the TMA methoxy groups and the TUA isocyanate groups was followed during the 130°C cure; the disappearance of the PUA acrylate double bonds was followed during the intense UV-irradiation. The chemical modifications occurring upon QUV weathering were monitored quantitatively through the decrease of the binder structural groups: the ether bond of TMA at 1072 cm<sup>-1</sup>, the carbamate CNH bond of TUA and PUA at 1521 cm<sup>-1</sup>, and the CH bond of the three polymers in the 2930-2960 cm<sup>-1</sup> region.

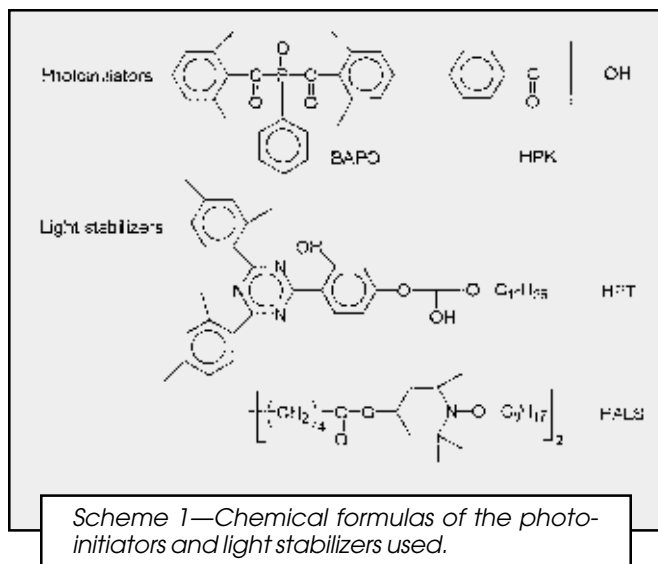
## RESULTS AND DISCUSSION

### Curing of Acrylate Clearcoats

Crosslinking of the two types of thermoset acrylate polymers occurs either by transesterification (melamine/acrylate) or by polycondensation (urethane/acrylate) according to the following reactions between the trifunctional methoxylated melamine or isocyanate crosslinker and the hydroxylated polyacrylate (P~OH):

### Insert Scan

The crosslinking reaction in thermosetting acrylate polymers was found to proceed readily upon heating at 130°C. Figure 1 shows how the TUA isocyanate double bond and the TMA methoxy group disappear with cure time. In both samples, the hydroxy groups disappeared according to the same kinetics as the methoxy or isocyanate groups. These thermoset coatings were found to reach their final hardness (Persoz value of 310 sec) after a 15 min heating, once about half of the functional groups have reacted. The molecular mobility restrictions resulting from the hardening are mainly responsible for slowing down the rate of cure observed upon further heating. After 30 min, the usual bake time, the two thermoset coatings still contained about 20% unreacted isocyanate and



Scheme 1—Chemical formulas of the photoinitiators and light stabilizers used.

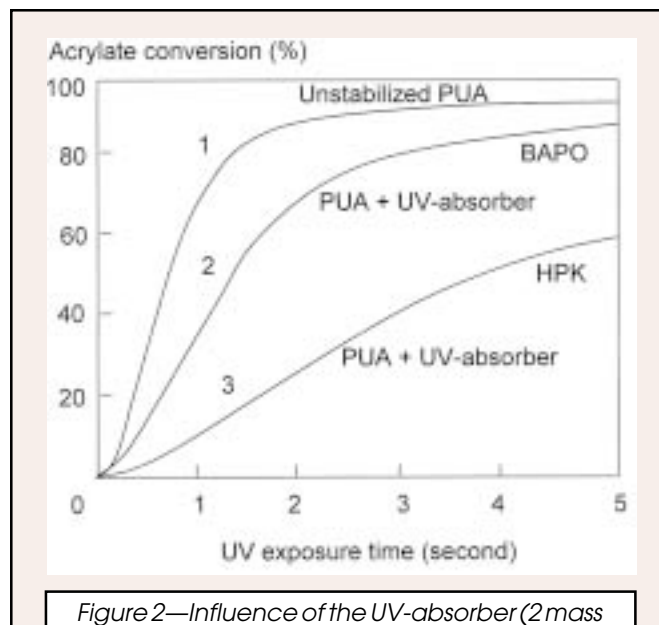


Figure 2—Influence of the UV-absorber (2 mass % HPT) and the photoinitiator on the UV-curing of a polyurethane-acrylate (PUA) clearcoat. (1) HPK (2.25 mass %) + BAPO (0.75 mass %); (2) HPK (2.25 mass %) + BAPO (0.75 mass %) + HPT (2 mass %); (3) HPK (3 mass %) + HPT (2 mass %). Light intensity:  $120 \text{ mW cm}^{-2}$ .

methoxy groups. To get completely cured polymers, the thermal treatment at  $130^\circ\text{C}$  had to be extended for two hours. The presence of the HALS and HPT light stabilizers was not found to have any effect on the curing reaction.

The photoinitiated crosslinking polymerization of the PUA urethane acrylate coating proceeds within a fraction of a second upon intense illumination at ambient temperature. Figure 1 shows the polymerization profile obtained by monitoring by infrared spectroscopy the disappearance of the acrylate double bond in the stabilized sample (HPT + HALS). As expected, the UV absorber was found to slow down the rate of initiation by interfering with the photoinitiator for the scavenging of the incident photons (radiation inner filter effect). This leads to a top to bottom cure depth gradient within the coating, which may have a detrimental effect on its adhesion to the substrate. The slowing down effect of the UV absorber on the photocuring process is illustrated in Figure 2 which shows the polymerization profiles recorded by real-time infrared spectroscopy for unstabilized and stabilized PUA samples, with BAPO or HPK as photoinitiators. Because the BAPO photoinitiator has an absorption in the near UV region (370–400 nm) where the UV-absorber is nearly transparent, photopolymerization proceeds faster and more extensively than with the HPK photoinitiator which absorbs below 340 nm, just like the UV absorber. To reach the same acrylate conversion as in the unstabilized sample, the UV exposure time had to be doubled for the stabilized sample containing the BAPO photoinitiator.

When compared to a number of photoinitiator/UV-absorber combinations, the selected BAPO/HPT association was found to have the less pronounced inner filter effect, thus allowing the chain reaction to proceed fast and extensively, up to 90% conversion, as shown in Figure 1.

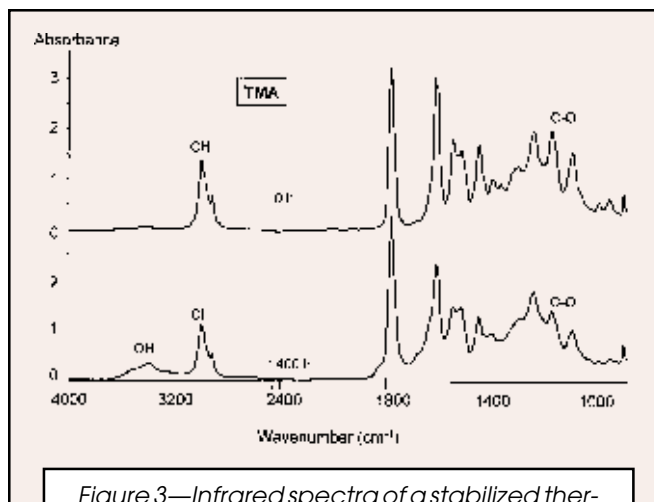


Figure 3—Infrared spectra of a stabilized thermosetting melamine/acrylate (TMA) clearcoat, before and after QUV-B aging. Film thickness:  $35 \mu\text{m}$ .

Such an extensive curing is generally sufficient to ensure a proper adhesion of the coating to the substrate. If necessary, the coating adherence to organic substrates can be enhanced by performing a two-step photografting which creates chemical bonds at the interface.<sup>9</sup> A diacrylate monomer (HDDA) is first grafted onto the organic substrate by a short UV-irradiation in the presence of benzophenone. The UV-curable formulation is then applied onto this sample and exposed to UV light. Adhesion is achieved through the covalent bonding of the coating to the substrate, which results from copolymerization of the PUA acrylate double bonds with the unreacted acrylate double bonds of the grafted HDDA.

A short heating at  $80^\circ\text{C}$  of the UV-cured coating was also found to be beneficial to adhesion, by causing the residual acrylate double bonds to further polymerize. In this respect, it should be mentioned that dual-cure systems combining thermal and photochemical-induced crosslinking have been recently developed, in particular to address the issue of the curing in shadow areas on 3D substrates.<sup>11</sup> By using a urethane-diacrylate telechelic oligomer bearing pendent isocyanate groups as crosslinker,

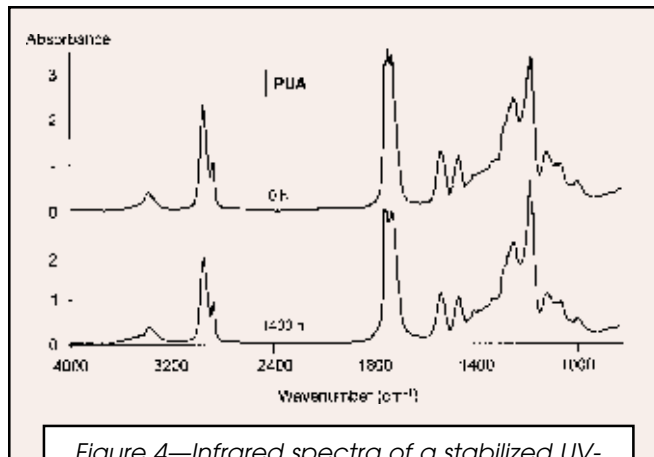


Figure 4—Infrared spectra of a stabilized UV-cured PUA coating, before and after QUV-B aging. Film thickness:  $35 \mu\text{m}$ .

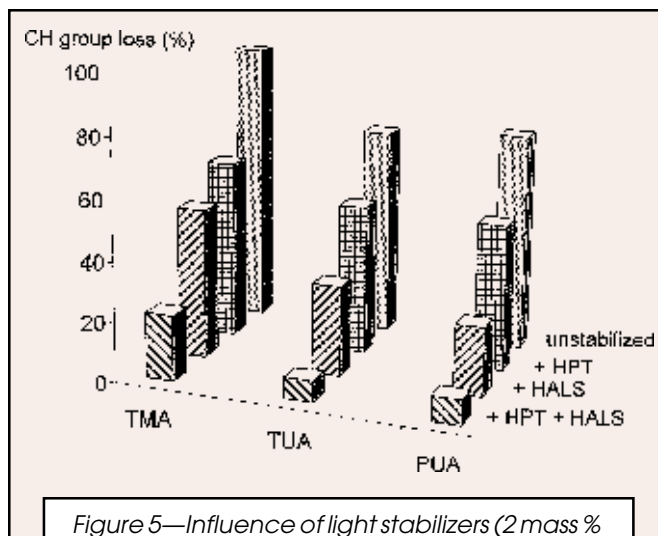


Figure 5—Influence of light stabilizers (2 mass % HPT and 1 mass % HALS) on the photodegradation of thermoset (TMA, TUA) and photoset (PUA) acrylate clearcoats after 1400 hr QUV-B exposure.

the curing of the acrylate polyol polymer is achieved first by a thermal treatment and second by a short UV exposure to polymerize the acrylate double bonds.

### Accelerated Weathering of Acrylate Clearcoats

**PHOTODEGRADATION AND PHOTOSTABILIZATION:** The photodegradation of thermoset and photoset acrylate polymers was monitored by FTIR spectroscopy because this technique gives quantitative information on the chemical modifications which have occurred at an early stage of the photodegradation process, well before physical and optical changes can be observed.<sup>6,12</sup> The infrared spectra of

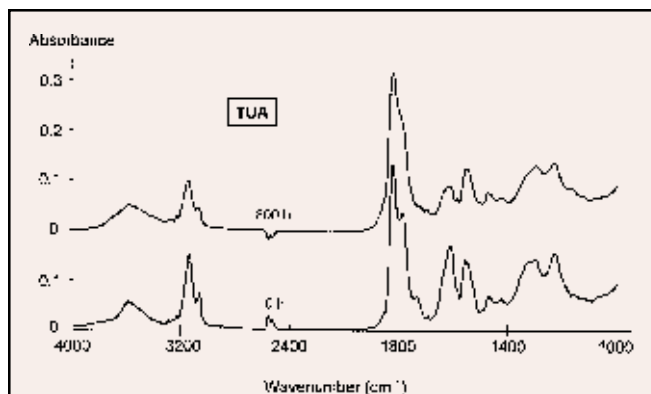


Figure 7—Infrared spectra of an unstabilized TUA clearcoat, before and after QUV-A aging for 800 hr. Film thickness: 3  $\mu$ m.

the 35  $\mu$ m thick stabilized coatings were recorded before and after wet cycle QUV-B exposure. Figures 3 and 4 show some typical IR spectra obtained for the TMA and PUA clearcoats, respectively. It is clearly apparent that the urethane acrylate photoset has been much less modified chemically upon QUV aging than the melamine/acrylate thermoset, currently used as automotive topcoat.

In a well stabilized TMA coating, the production of hydroxyl groups ( $3500\text{ cm}^{-1}$ ) and amide carbonyl groups ( $1650\text{ cm}^{-1}$ ) is accompanied by a destruction of the ether crosslinks ( $1072\text{ cm}^{-1}$ ) and of the CH groups ( $2956\text{ cm}^{-1}$ ). By contrast, the IR spectrum of the stabilized PUA coating hardly changes after a 1400 hr QUV exposure, the most photodegradable structure being the carbamate group ( $1521\text{ cm}^{-1}$ ). This is also the case for the two-pack polyurethane TUA coating which shows a weathering resistance as strong as that of the PUA coating,<sup>13</sup> and which is

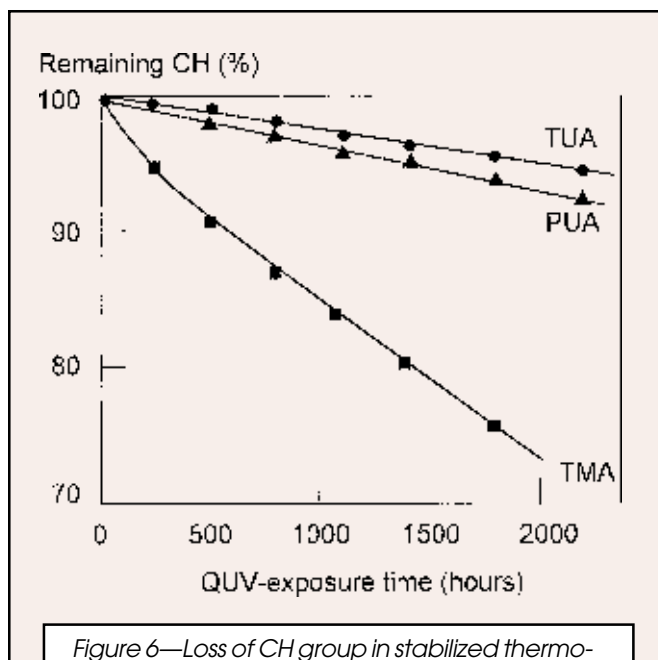


Figure 6—Loss of CH group in stabilized thermoset and photoset acrylate clearcoats exposed to QUV-B aging. Light stabilizers: (HPT) = 2 mass %; (HALS) = 1 mass %. Film thickness: 35  $\mu$ m.

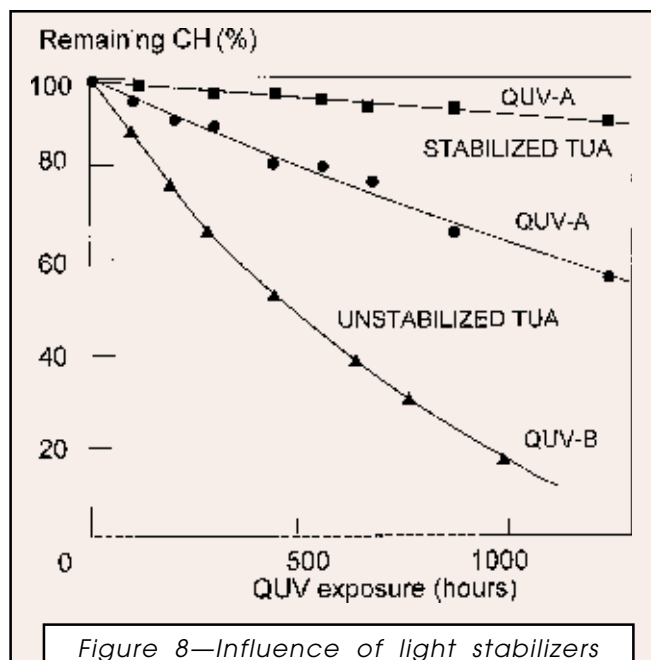


Figure 8—Influence of light stabilizers (HPT+HALS) on the photodegradation of a 3  $\mu$ m thick TUA coating exposed to QUV-A or QUV-B aging.



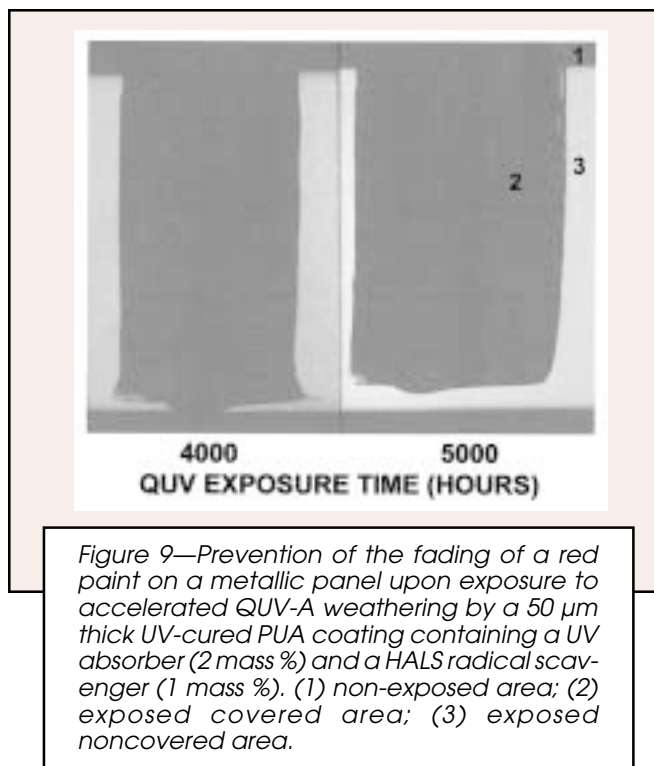
generally considered as the state of the art for automotive finishes. It is still not as widely used in today's applications as TMA coatings because of the inconvenience of a two-pack formulation and its higher cost.

In both thermoset and photoset acrylate polymers, the HALS and HPT additives proved to be very efficient light stabilizers, as shown in Figure 5 where we have reported the relative loss of the CH group after 1400 hr QUV-B aging of TMA, TUA, and PUA clearcoats. With the HALS + HPT combination, the stabilization efficiency, defined as the ratio  $(\text{CH loss})_{\text{unstabilized}} / (\text{CH loss})_{\text{stabilized}}$ , was found to reach values superior to 10 for the two urethane-based polymers, compared to a factor of 4 only for the melamine/acrylate thermoset. Figure 6 shows the CH decay curves for the three properly stabilized samples upon wet cycle QUV-A exposure for up to 2000 hr. According to these results, one would expect the outdoor durability of urethane/acrylate polymers to be quite remarkable. This prediction has been fully confirmed by natural weathering experiments, carried out in Florida for up to seven years, which show the superior performance of the light stabilizer combination used in this study, for both thermoset and photoset urethane/acrylate clearcoats.

It should be noted that some of the CH group loss measured by IR spectroscopy is due to an erosion process which reduces the thickness of the photodegraded coating. Photoaging experiments performed on very thin coatings (3  $\mu\text{m}$ ) have shown that these thermoset and photoset acrylate coatings are quite resistant to erosion, a process which accounts for less than 10% of the CH loss measured in 35  $\mu\text{m}$  thick coatings after extensive photodegradation. Figure 7 shows the infrared spectra of an unstabilized 3  $\mu\text{m}$  thick TUA film, before and after exposure to QUV-A aging for 800 hr. A kinetic study of the photodegradation process in such very thin coating has revealed that the intensity of the CH infrared band of the unstabilized TUA film is cut by half after 500 hr of QUV-B and 1200 hr of QUV-A aging, as shown in Figure 8. Even if this loss were solely due to erosion, it would correspond to only a 1.5  $\mu\text{m}$  thick layer erased from the sample surface upon accelerated weathering during that time. For a 35  $\mu\text{m}$  thick coating, it would represent a 4% decrease of the sample thickness, a value to be compared to the observed 45% drop of the CH infrared band after a 500 hr or 1200 hr QUV-B or QUV-A exposure, respectively.

With respect to the optical properties, the UV-cured coating showed similar performance upon accelerated weathering as the thermoset TUA and TMA coatings. The stabilized PUA clearcoat remained noncolored, transparent, and glossy for up to 3000 hr QUV-A aging.<sup>8</sup> It should be noted that the chemical modifications detected by IR spectroscopy appear well before the gloss starts to drop. The weathering resistance of thermoset and photoset coatings can therefore be predicted at an earlier stage of the photodegradation by monitoring the light-induced chemical changes. Infrared spectroscopy proved to be a particularly useful method to assess rapidly the performance of new light stabilizers in polymers exposed to accelerated weathering and to help elucidate the mechanism of the degradation.

The outstanding weathering resistance of well-stabilized UV-cured polyurethane-acrylate clearcoats has been



confirmed by outdoor exposure tests in Florida.<sup>10</sup> Based on gloss retention data, their lightfastness was found to be superior to that of TMA automotive topcoats, and quite comparable to that of two-pack TUA thermosets stabilized with the same UVA + HALS combination.

**PHOTOPROTECTION OF ORGANIC MATERIALS:** The efficiency of photoset urethane-acrylate coatings to protect organic materials against photodegradation has been tested on painted metallic panels exposed to QUV-A aging for up to 5000 hr. Their weathering resistance, evaluated by

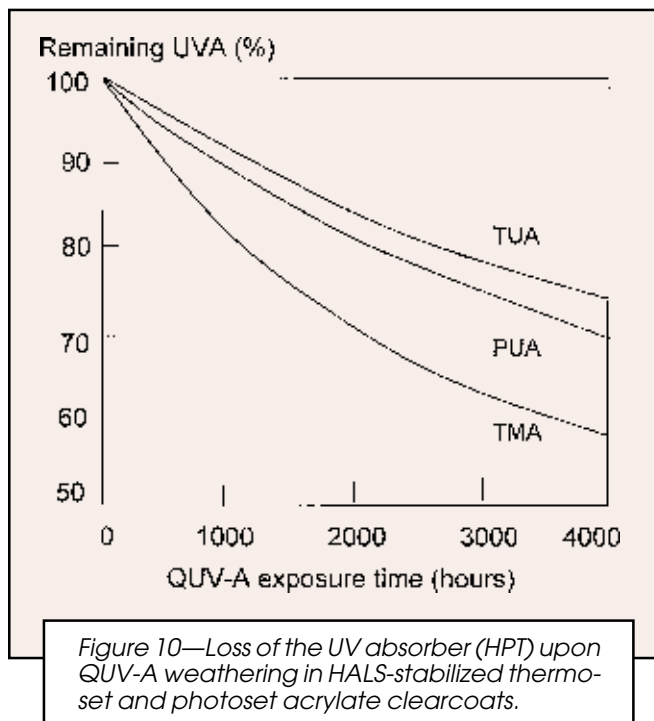


Table 1—Curing and Weathering Performance of Stabilized Thermosetting and Photosetting Acrylic Polymers

Acrylate Clearcoat	Thermoset		Photoset
	Melamine/Acrylate	Urethane/Acrylate	Urethane-Acrylate
Formulation .....	Solvent-based	Solvent-based	Solvent-free
Cure time .....	30 min at 130°C	30 min at 130°C	2 sec
Residual functionality (%) .....	20 (OCH <sub>3</sub> )	20 (NCO)	6 (C=C)
Crosslink density (mol kg <sup>-1</sup> ) .....	1.5	1.5	5
Persoz hardness (s) .....	310	300	270
Weathering resistance .....	High	Excellent	Excellent
Loss of CH group <sup>a</sup> (%) .....	20	4	3
Loss of ether or urethane <sup>a</sup> (%) .....	48	8	10
Gloss retention (%) after 3000 hr QUV-A aging .....	70	95	92

(a) After 1400 hr wet cycle QUV-A aging of 35 µm thick coatings stabilized with HPT (2 wt%) + HALS (1 wt%).

photobleaching measurements, was improved tenfold by means of a 50 µm thick UV-cured PUA topcoat containing 2 mass % HPT, which remained clear and glossy and did not delaminate after this extensive exposure. Figure 9 shows a typical picture of such a red painted panel, which was exposed in an accelerated QUV-A weatherometer for 5000 hr. It can be seen that the color of the area covered by the coating has hardly changed after photoaging, while the unprotected area of the panel has been completely bleached out. This result clearly demonstrates that the UV absorber is still present after a 5000 hr exposure and is capable of screening efficiently the sunlight which is responsible for the paint fading. This is partly due to the presence of the HALS radical scavenger which was shown to increase substantially the UVA lifetime<sup>14</sup> by preventing its attack by free radicals.

The UV absorber retention upon weathering can be directly followed quantitatively by UV-spectroscopy. Figure 10 shows some typical UVA loss profiles in the three types of HALS stabilized coatings exposed to accelerated QUV-A aging. While the HPT light stabilizer disappeared faster in the TMA coating, probably because of the higher flux of free radicals, its lifetime was essentially the same in TUA and PUA coatings. Consequently, the thermoset urethane/acrylate proved to be equally effective for color protection as the photoset urethane/acrylate.

A performance analysis of the thermoset and photoset acrylate polymers examined in this study is given in Table 1, with respect to both curing and weathering data. The main advantage of the UV-technology, besides providing a much faster and more complete cure, is that the coating is obtained from a one-pack solvent-free formulation cured at ambient temperature.

## CONCLUSION

The photoinitiated polymerization of multifunctional monomers and oligomers is one of the fastest and most efficient methods for producing tridimensional polymer networks. The UV-cured polyurethane-acrylate coatings were found to be more resistant to accelerated weathering than the melamine/acrylate thermosets currently used as automotive finishes, in particular when using a hydroxyphenyl-s-triazine UV absorber and HALS radical scavengers as light stabilizers. Such well stabilized urethane-acrylate clearcoats were shown to be very effective for improving the weathering resistance of painted metals

and for preventing color fading upon prolonged exposure. Based on such performance, one can expect UV-radiation curing to be increasingly used in the manufacturing of organic coatings employed in exterior applications, for which outstanding light-stability and superior mechanical and surface properties are required to ensure long-term protection of the coated material.

## ACKNOWLEDGMENTS

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