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Scratch Resistance and Weatherfastness of UV-Curable Clearcoats

T. Jung, A. Valet

Ciba Specialty Chemicals Inc., Basle, Switzerland

Summary: UV-cuing has found an increasing number of industry allocations over the past decade due to its unique benefits, e.g. solvent free formulations, high cure speed and low temperature processing. In addition to these benefits two additional properties of uv-cured coatings are of today`s interest, especially in the automotive industry: scratch resistance and resistance against chemicals. One of the most important requirements for a broad use of uv-curable coatings in the coating industry is that coatings are stable against degradation caused by atmospheric influences since coatings for outdoor use are subject to especially harsh weathering conditions, e.g. uv-light, oxygen, moisture and air pollutants. This weathering leads to a degradation of the polymeric binder. Clearcoats containing photoinitiators based on bis-acylphosphinoxide ("BAPO") and a combination of hydroxyphenyl-s-triazine uv-absorber and a sterically hindered amine as a light stabilizer package show a very good curing behavior as well as an improved weatherfastness over a long period of time and a good scratch and chemical resistance.

Keywords: UV curable clearcoat, scratch resistance, durability

1. Introduction

Current state of the art clear coat technology involves heat to initiate cure. Such systems are for example 2P-Polyurethane, acrylic-melamine coatings etc. The UV-curing technology uses UV-light instead of heat to initiate the crosslink mechanism of the coating. The low temperature process and the possibility to formulate zero VOC (Volatile **O**rganic **C**ompounds) made the UV-technology successful over the last years.

In addition to these benefits two additional properties of UV-cured coatings are of today's interest, especially in the automotive industry: scratch resistance and resistance against chemicals. However, before this technology can be broader introduced to the car industry as well as to the general coating industry one major field where UV-curing has to show that it is able to compete with existing coating technologies is the area of outdoor applications [1].

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2. Scratch and Chemical Resistance

The challenge for scratch and chemical resistant coatings seems to be rather simple: to combine the scratch resistance of a 2P-PUR with the chemical resistance like Teflon by keeping cost effectiveness [2]. Coating companies all over the world are currently developing coating systems, which come close to the target, however, there is room for further improvements. One possibility to solve the problems is the use of UV-cured systems [3]. From a cost effectiveness point of view, UV-cured coatings, however, should not only assessed by the raw material costs but also the possible cost savings of the whole coating process have to be taken into consideration.

In recent publications the comparison of the current used coating technologies were discussed with respect to scratch resistance or chemical resistance [18,19]. Clear coat technologies like HS-TSA, 2P-PUR or 1P water based, seam to have only one strong feature either they are chemical resistant or scratch resistant.

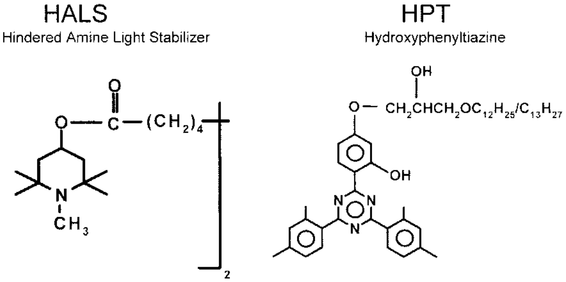
3. Light Stabilization upon Weathering

Coatings for outdoor use are subject to especially harsh weathering conditions, e.g. UV-light, oxygen, moisture and air pollutants. The absorption of UV-light by the polymer backbone or impurities leads to primary photochemical reactions resulting in a photo-oxidative degradation of the polymer. Reactions producing free radicals are particularly harmful. Due to the primary photo physical and photochemical processes, which take place during the interaction of harmful UV-light with absorbing molecules, the possible approaches to the stabilization of coatings can be radically reduced to two types of stabilizers [4]:

- UV-absorbers (UVA), filtering the harmful UV-light in the wavelength range 290-380 nm
- Radical scavengers (Hindered Amine Light Stabilizers = HALS)

Today a stabilizer package utilizing a combination of UV-absorbers and HALS is state of the art.

The filter effect of the UVA protects the substrate against color change and photochemical degradation, which would lead to delamination. However UVA`s do not function as "radical scavengers". Alternately, HALS does not absorb in the UV-area but they trap any radical formed during the outdoor use of a coating [7,8]. HALS protect the coating against loss of gloss and most importantly, against cracking. Figure 1 shows the liquid UV-absorbers and HALS used for this study. The concentrations of UV-absorbers and HALS in the different coating systems correspond to the level used in the European automotive industry.



HALS
Hindered Amine Light Stabilizer

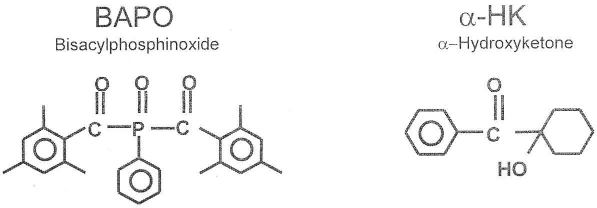
HPT
Hydroxyphenyltiazine

Figure 1. UV-absorber and HALS used in this study

The mode of action of UV-absorbers is the absorption of harmful UV-light and its rapid conversion into harmless energy [5,6], without being destroyed themselves. The four most important UV-absorber classes are the hydroxyphenyl-benzotriazoles (BTZ), hydroxyphenyl-s-triazines (HPT), hydroxy-benzophenones and oxalic anilides. From a technical point of view hydroxyphenyl-benzotriazoles and hydroxyphenyl-s-triazines are the most interesting UV-absorber classes [4].

4. Photoinitiators

The very beginning of the radical curing process of an UV-cured coating involves a photochemical reaction of a molecule within the coating by absorbing a photon, which leads to an excited state of the absorbing molecule. In a second step this molecule is cleaved leading to radicals, which are able to initiate the polymerization reaction. Those molecules are generally called *photo-initiators* and described in detail in the literature [23, 24, 25]. A bisacylphoshine-oxide (BAPO) and a α-hydroxy ketone (α-HK) were used for the present study and are shown in Figure 2.



BAPO
Bisacylphosphinoxide

α-HK
α–Hydroxyketone

Figure 2. Photoinitiators used in this study

5. Results and Discussion

In this study a comparison of the currant coating technologies like 2P-PUR and HS-TSA with the UV-technology regarding durability scratch and chemical resistance is made. The UV-curing technology is one of the most desirable coating technologies for future use in automotive application. In the mean time not only a 100 % UV-Curable coating is discussed. With respect of the complex tree dimensional parts with shadow areas in the automotive application, which are difficult to cure, Dual Cure technology came in place. The Dual Cure system is working with two different cross-link mechanisms: the polyol / isocyanate being responsible for the curing in shadow areas. This mechanism is already used in 2P-PUR coatings today. The second mechanism is based on the radical induced polymerization of acrylate double bounds, which are part of the binder system.

The experiments comparing durability, scratch resistance, chemical resistance, were carried out using the following formulations.

- Commercial 2P-PUR OEM - stabilized with benzotriazole / HALS chemistry. Curing was performed at 130°C for 30 minutes
- Acrylic polyol cross linked with a fully methoxylated melamine resin (high solids thermosetting acrylic = HS TSA). Curing was performed at 130°C for 30 minutes
- Dual Cure coating - starting point formulation from Bayer AG/Germany
- UV-Cure model clear coat - aliph. urethanediacrylate / aliph. urethanetri/teraacrylate / TPGDA / TMPTA

5.1. Stabilization of UV-cured clearcoats

Figure 3 shows that the performance of an *unstabilized* UV-cured clearcoat (depending on the resin system used) can be comparable to commercially available clearcoats, e.g. High Solids (HS) TSA or HS 2P PUR.

The UV-cured coating shows a somewhat better gloss retention, while the conventional coatings show slightly better crack resistance. This led to the expectation that UV-cured clearcoats stabilized with UVA and HALS can also match the performance of stabilized conventional coating systems. Major concern about the use of UVAs in these coatings is their competition with the photoinitiators for UV-light, [1] that could potentially lead to a cure retardation of the coating. However, there are already many literature references to the use of UV-absorbers in UV- cured coatings [9-13], as well as new developments in the area of photoinitiators [14, 15] and UV-absorbers [16, 17] helping to overcome this issue. The chosen

HPT-UVAs have relatively weak absorption at 365 nm, thereby allowing efficient UV-curing to take place as shown in Figure 4. The spectra were taken in chloroform. The concentrations used correspond to an UVA/photoinitiator ratio of 2/3 and 2/5 (similar to a clearcoat stabilized with 2% UVA and UV-cured with 3% or 5% photoinitiator).

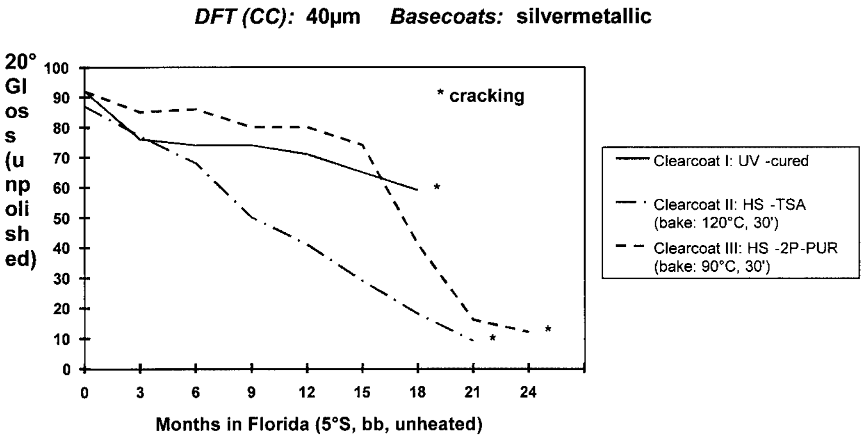


Figure 3. Comparison of gloss retention for conventional clearcoats versus a UV-Cured Clearcoat upon Florida exposure

If the PI contains additionally BAPO it shows a moderate absorption up to 430nm. This means that enough UV-light can be absorbed to impart a sufficient through-cure of the clearcoat.

Figure 5 shows a comparison of the influence of UVA and/or HALS on the performance of a clearcoat. Recent papers [22] reported that a minor influence of UVA on the performance of a UV-clearcoat. The results after 10 years Florida, however, show how important a UVA is regarding the overall stability of a UV cured clearcoat. The UVA/HALS combination shows a significantly improved performance compared to formulations stabilized with HALS or UVA. The proof is shown in Figure 6 which shows the 9 years results of a UV-cured model clearcoat over different basecoats compared to both a HS TSA and a HS-2P-PUR clearcoat over a silver metallic basecoat. No cracking occurred and the gloss retention is rather good. Although the basecoats described in Figure 6 are not the same, it can be concluded that the outdoor behavior of UV-cured systems is at least comparable to the behavior of the thermosetting systems.

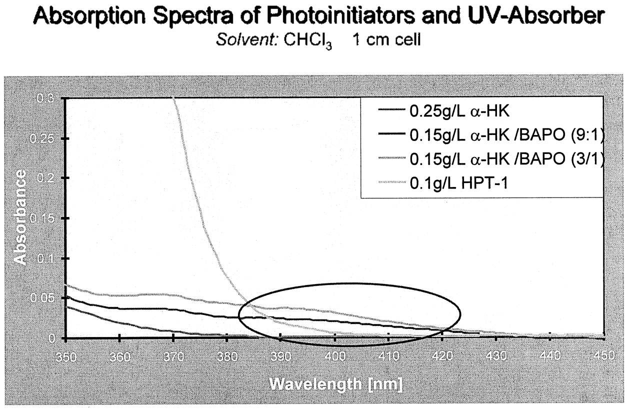


Figure 4. Absorption spectra of photoinitators and UV-absorbers

Under Xenon-WOM conditions (Figure 7) another UV-cured model clearcoat performs similar to UV cured clearcoat mentioned in Figure 6, which shows - as mentioned above - a very good gloss retention during 9 years Florida exposure.

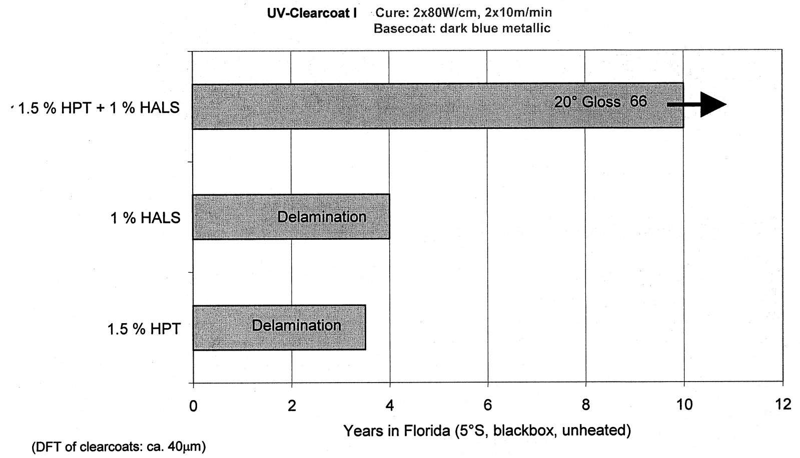


Figure 5. Comparison of the influence of UVA and/or HALS on the performance of a UV-curable clearcoat

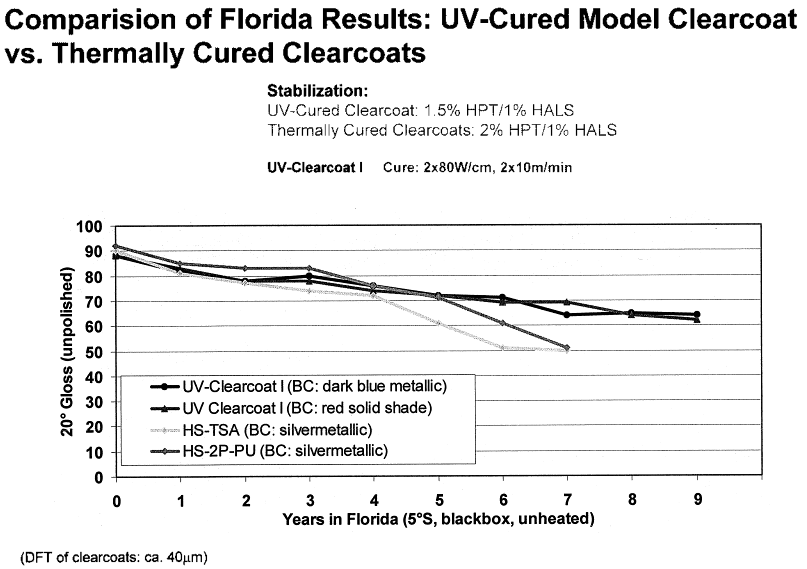


Figure 6. Comparison of UV-cured model clarcoat vs. thermally cured clearcoat after 9 years Florida exposure

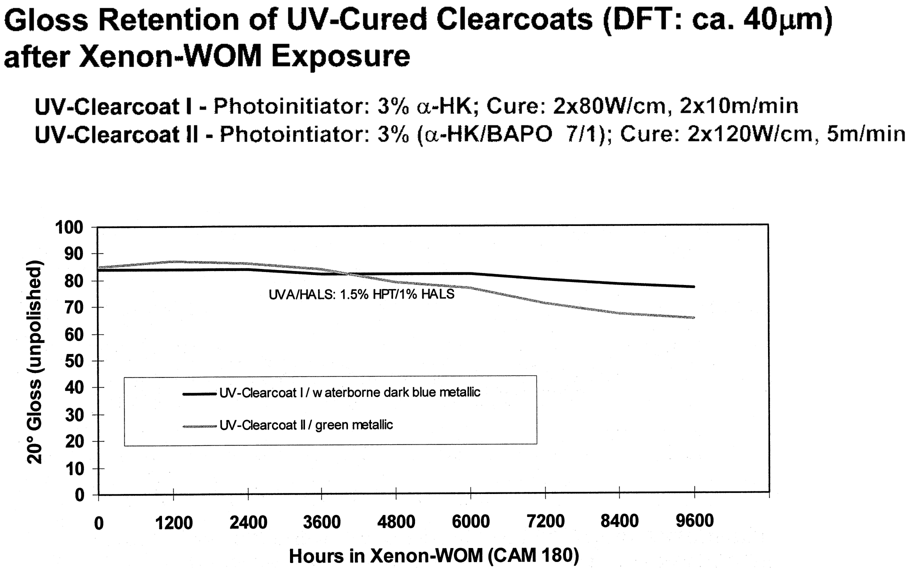


Figure 7. Comparison of two different UV-curable model clearcoats under Xenon Wom Cam 180 conditions

Figure 8 shows the performance of the UV-Cure model clearcoat a Dual Cure and a 2P-PUR clear coat. All coatings were applied over a black basecoat with a dry film thickness of 40µm. The UV-Cure II and the Dual Cure clear coat contain 2.7 % α-HK + 0.3 % BAPO + 1.5 % HPT + 1 % HALS. The concentration of photoinitiator and Light stabilizer are based on resin solids of both formulations.

The UV-cured model Clear coat was cured with two Mercury medium pressure lamps at 120 W/cm with a belt speed of 5 m/min. In case of the Dual Cure a 10 Min bake at 80°C on a heating plate as a thermal cure step and 2 mercury medium pressure lamps with a belt speed of 5 m/min was chosen to cure these coatings.

The UV-Cured model clear coat and the Dual Cure clear coat show by fare a better gloss retention compared to the 2P-PUR clear coat under the Xenon Womb Cam 180 weathering condition.

The crack resistance of the UV-Cured and Dual Cure clear coat is better than with the 2P-PUR clear coat. This result is also confirmed in UVCON weathering.

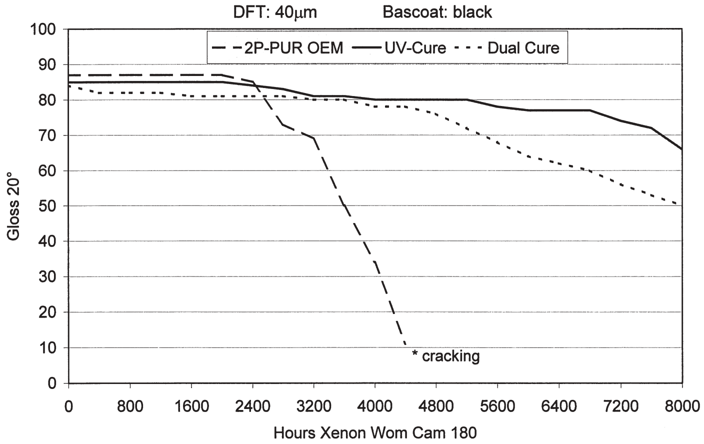


Figure 8. Performance of a UV-cured, Dual Cured clear coat and a 2P-PUR upon Xenon Wom Cam 180 weathering

Color change upon weathering is also a big concern of all paint and car manufactures. Using UV-technologies, including Dual Cure, the color matching is a major concern of the quality control.

Figure 9 show the yellowing behavior of the UV-cured model clear coat in comparison to a 2P-PUR clear coat. Both clear coats were applied over a white basecoat and Cured with the conditions mentioned above. The UV-cured coating shows somewhat better yellowing over time of weathering, while the conventional coating shows a slightly better yellowing after cure.

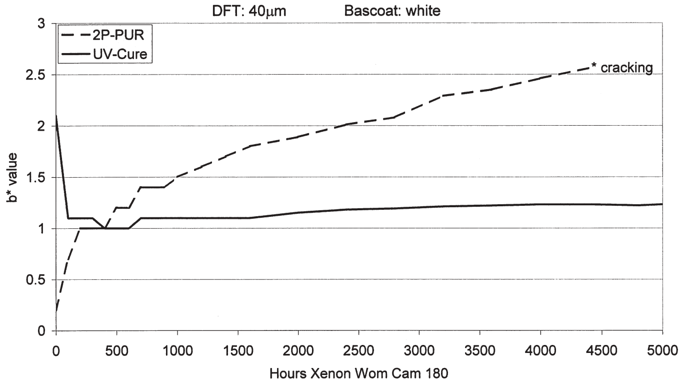


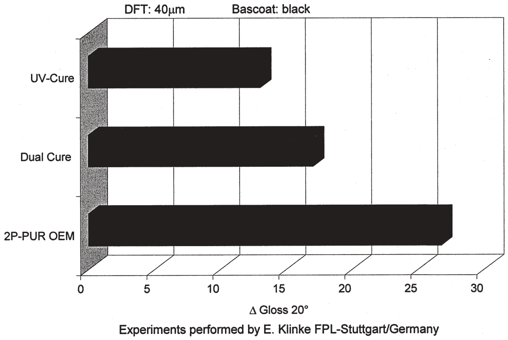
Figure 9. Yellowing behavior of a UV-curable clear coat vs. a 2P-PUR upon weathering.

5.2 Scratch resistance

For high performance coatings the durability is only one criteria to get approved. The Scratch resistance of the coating is also an important parameter. The Rota Hub method was developed by Bayer AG /Germany measuring the scratch resistance under dry conditions. The Gloss data were performed with a reflectometer form Byk-Gardner. The parameter under which the scratch tests were made, are the following: Speed in X and Y direction V_x / V_y = 15/15 mm/min; Speed of rotation ω = 5.0 U/s; Disc radius r= 35 mm; Rub material: paper.

The gloss 20° is determined before and after scratch. Figure 10 shows the Δ Gloss 20° data. The UV-Cure system show the smallest difference of Gloss followed by the Dual Cure clear coat. The Rota Hub scratch test has a big impact on Gloss of conventionally cured clear coat.

The results, which are performed with the Nano Scratch Tester for CSEM Instruments are shown in Figure 11. The figure displays according to Lin [20] the residual depth at 5mN in μm versus the critical Load. The critical load is the load in mN on the indentor at the weight the first crack is visible in the coating. The arrow shows the trend with an increase of scratch resistance. The increase in scratch resistance is in parallels with an increase in acrylate double bounds in the coating systems.

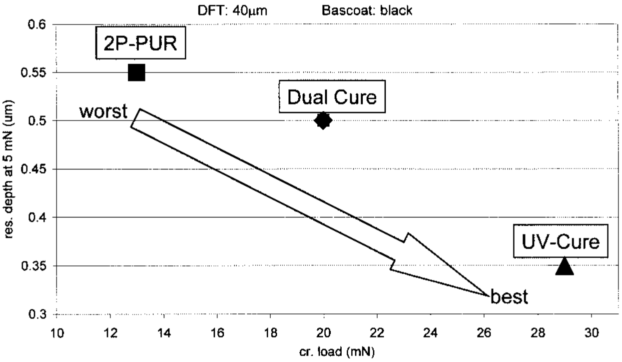


Experiments performed by E. Klinke FPL-Stuttgart/Germany

Figure 10. Scratch resistance of three different clear coats according to Rota Hub

Both methods Rota Hub and Nano Scratch Tester show the same ranking of the tested clear coat. Therefore a good correlation for both methods is shown.

Test Methode: Nano Scratch Tester from CSEM Instruments SA



Experiments performed by E. Klinke FPL-Stuttgart/Germany

Figure 11. Scratch resistance measured with the Nano Scratch Tester of tree different clear coats according. Display according to Lin [20]

5.3 Chemical resistance

Coatings for outdoor use are subjects to especially harsh conditions. For example acid rain or birds shit. The coating used in automotive application should be stabile against these atmospheric and biological influences. Pancratine, soda and chloric acid were selected for the chemical resistance test. The experiment is performed in a gradient oven with a temperature range von from 40-75 °C. The chemical resistance was tested on two sets of panels. The first trial was carried out 4 days after cure, the second one 4 days after cure plus one week QCT (water temperature: 40°C) and one day recovery at room temperature.

Table 1. Chemical resistance of different clear coat technologies

		Pancreatine	**NaOH**	**H_2SO_4**
UV-Cure	After Cure	No impact	Strong impact	No impact
	After 1 week QCT	No impact	Strong impact	No impact
HS-TSA	After Cure	No impact	No impact	Some impact
	After 1 week QCT	Some impact	Some impact	Some impact
2P-PUR	After Cure	No impact	No impact	No impact
	After 1 week QCT	Some impact	Some impact	Some impact

Table 1 shows the results of the chemical resistance of three different coating technologies. The UV-Cured coating is sensitive to soda but stabile against Pancreatine and chloric acid. Even after the storage under wet condition the UV-cured coating show the same good results than before. The thermally cured coatings show instability against acids. Particularly after humidity influence the chemical resistance is weak.

6. Conclusion

The durability of UV-curable clearcoats can be significantly improved by using the correct light stabilizer package and an optimized photoinitiator combination. High performance photoinitiators combinations like BAPO and hydroxyphenyl-s-triazine UV-absorbers (in combination with HALS) are well suited to achieve both through-cure and weatherfastness of the clear coatings, which are at least comparable to those of thermally cured systems. UV-cured clearcoats show a significantly improved scratch resistance as well as chemical resistance. The overall performance characteristics of UV-cured coatings are also determined, as with other coating types, by the components used for the binder system.

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