Acrylic Urethane Dual-Cure Clearcoats for Three-Dimensional Wood, Metal, and Plastic Substrates: Compliance, Appearance, Productivity and Durability.

Daniel B. Pourreau, Ph.D., Lyondell Chemical Company

Introduction

Acrylic urethane coatings are used in a variety of applications due to their versatility, durability, appearance and superior weatherability compared to most other coating systems.[1] These applications include automotive clearcoats, industrial maintenance topcoats, coatings for plastics, general metal, wood furniture and flooring. The most common are two-component (2K) coatings, where an acrylic polyol solution is mixed with a poly-isocyanate just before use and applied to the substrate. The coating then cures by a combination of solvent evaporation and chemical crosslinking to form a durable urethane bond, Figure 1.

Figure 1. 2K Acrylic Urethane Crosslinking Reaction.

The cure speed and final coating properties are tailored to the application by varying the hardness (Tg) and functionality (EW or OH number) of the acrylic polyol, the isocyanate and solvents used, and by the addition of amine, tin or zirconium catalysts and activators. Heat can also be applied to accelerate cure. Generally, the faster the cure, the shorter the pot life, and the higher the VOCs. This is a limitation of 2K urethane coatings since one often has to trade productivity for compliance, appearance, cost, or ease of use.

UV-curable coatings on the other hand, are one-component (1K) systems that cure by photo-induced polymerization of acrylate functional monomers and oligomers. UV coatings typically do not contain solvents (VOCs) and cure is instantaneous. However, areas not exposed to UV light do not cure and may remain tacky indefinitely. Despite recent advances in this area, this remains a limitation of UV-coatings for three-dimensional substrates. Table 1 highlights other key differences between 2K and UV coatings.

The automotive refinishing market is a prime target for introducing UV-cured clearcoat technology for a number of reasons, including:[2]

- Productivity is key to profitability
- UV-cured spot primers are already in use
- Change is easier than in OEM

Current productive 2K urethanes are tack-free in 15-30 minutes and can be sanded and buffed in 2-4 hours. These coatings rely heavily on exempt solvents to meet the CARB VOC content limit of 2.1 lbs VOC/gallon and often use hard acrylic polyols to provide a lacquer dry effect. This can have a detrimental effect on the coating's appearance, pot life, and flexibility.

Table 1. Key Features of 2K Urethane and UV coatings.

Technology features	2K Urethane	UV-Cured
Raw Material costs	medium	high
Capital costs	low	medium-high
Hazards	isocyanates, solvents	monomers, UV light
Viscosity	low	high
VOC content	low-medium	very low to zero
Solids content	30-60%	~100%
Cure speed	medium-slow	instantaneous
Dark Cure	yes	no
Appearance	very good	very good
Adhesion	very good	variable
Toughness	excellent	variable
Scratch Resistance	OK	excellent
Weatherability	excellent	variable

Because of the superior scratch resistance of UV coatings, their productivity (cure speed and solids content), and low VOC content, there is considerable interest in their possible use as automotive OEM and refinish coatings. However, several inherent limitations of 1K UV systems make it unlikely they will be widely accepted by the automotive industries in their current form:

- High shrinkage resulting in poor adhesion and flexibility
- High viscosity not suitable for HVLP spray
- No dark cure mechanism
- Air inhibition especially with low intensity UV-A lamps

One company has reported on dual-cure coatings that combine the benefits of UV and 2K urethane systems and overcome some of their limitations, Figure 2.[3,4] These coatings are based on acrylated polyisocyanates and unsaturated polyester polyols. The UV-curing step is used to obtain tack-free coatings so the parts can be handled, buffed, or sanded immediately after UV-cure. Another benefit of achieving instantaneous tack-free state is that the coating appearance is improved. This is because fewer airborne impurities have time to contact the wet film and cause defects.

The final coating properties are achieved by the combination of the UV-curing process and chemical crosslinking. The cured films are usually more flexible and adhere better to the substrate than 100% UV-curable systems, presumably because shrinkage is reduced. Also, the dark or thermal cure mechanism provides a means to cure the film in areas not fully exposed to UV light.

However, as is the case with other urethane acrylate oligomers, the base polymer is a polyester, not an acrylic resin. This may limit the ultimate weatherability of the coatings, since polyesters are much more susceptible to hydrolysis than acrylic resins. This chemistry also uses specialty acrylated isocyanate monomers that could add cost to the system.

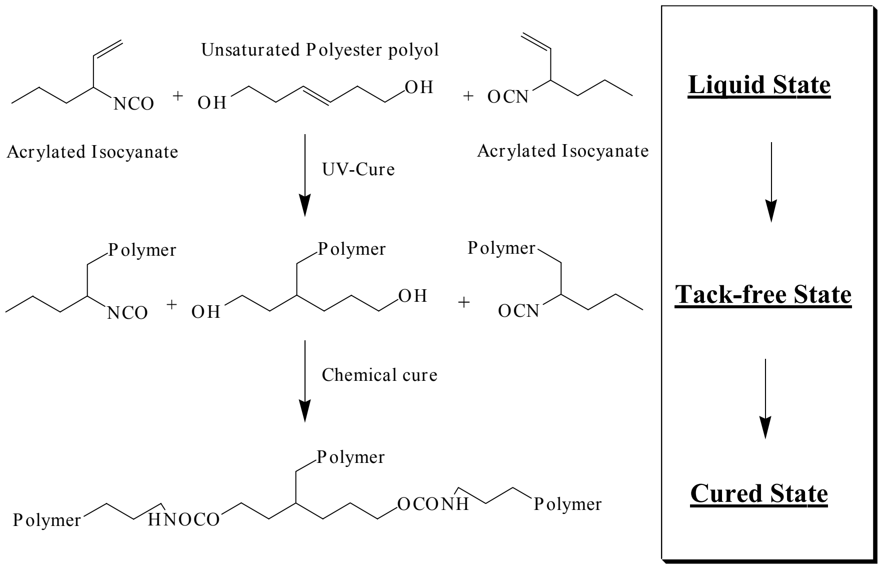

Figure 2. Example of a Dual-cure Coating System.

A simpler, and potentially less expensive, approach is to modify a conventional 2K urethane system with acrylated monomers, Figure 3. This approach does not require the use of acrylated oligomers or specialty isocyanates but uses acrylate monomers to form another acrylic polyol upon irradiation with UV light. This acrylic polyol can then crosslink with conventional polyisocyanates to form an acrylic urethane coating identical to those currently used for automotive refinish clearcoats.

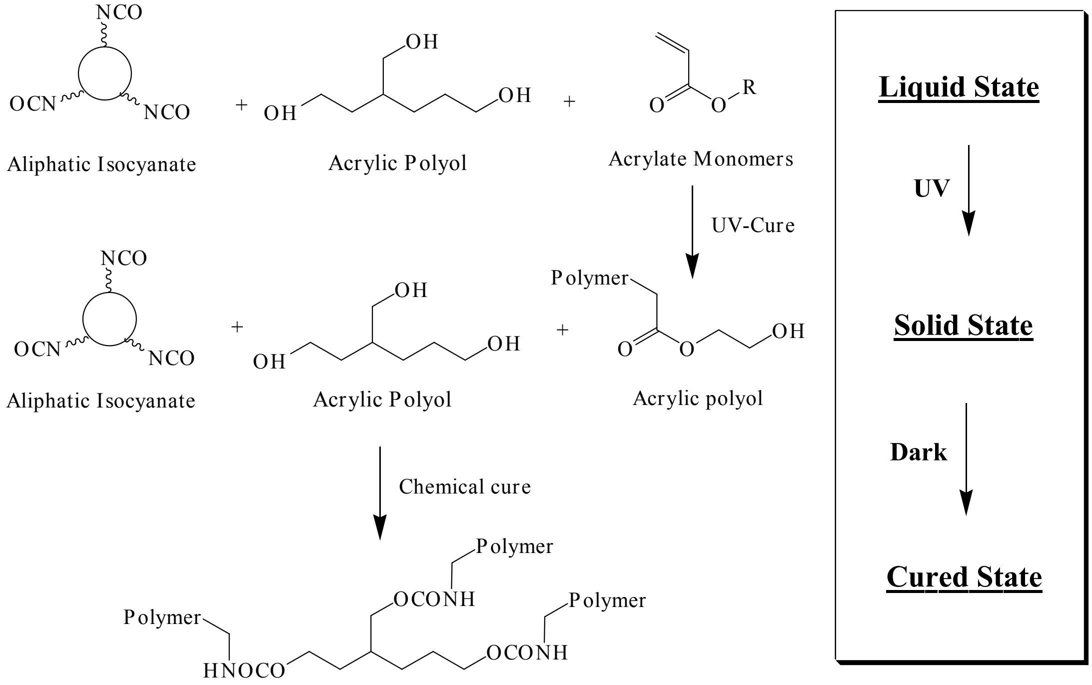

Figure 3. 2K/UV Acrylic Urethane Cure Mechanism.

The following paragraphs describe the preparation and properties of such acrylic urethane coatings for weatherable applications in more detail. These coating systems offer instant cure, and superior properties compared to conventional UV-curable and 2K urethane systems. This may allow UV-curing technology to be used in the most demanding applications such as automotive topcoats.

Results and Discussion

Formulation of 2K/UV Dual-Cure Coatings

Table 2 lists formulation components and coating properties for two dual cure formulations optimized to yield a tack-free coating after UV irradiation and outstanding properties following chemical cure.

Table 2. Composition and Properties of 2K/UV Acrylic-Urethane Coatings.

A-side Components	**2K/UV-1**	**2K/UV-2**
ACRYFLOW A140 (70% in acetone)	16.1	10.7
ACRYFLOW P120	3.75	7.5
IBOA	2.5	2.5
TMPTA	2.5	2.5
HEA	2.5	2.5
SR9008 adhesion promoter	2.5	2.5
B-side components		
HDI Trimer (80% in acetone)	14.5	14.4
9% 819 in 1174 (BAPO/AHK)	0.81	0.81
1% DBTDL (tin catalyst)	0.73	0.73
50% Tinuvin 400 (HALS)	1.1	1.1
50% Tinuvin 292 (UV screener)	1.1	1.1
BYK 358 (flow modifier)	0.5	0.5
Formulation Constants		
% solids	80	83
Viscosity, cps	<100	<100
US VOC content lbs/gal	0.0	0.0
European VOC content grams/Liter	195	166
Pot life, hours	12	12
tack & print-free after UV cure	yes	yes
Film Properties after 7 days		
Film thickness (mil)	1.8	1.8
König Hardness	158	125
Direct Impact	150	160
Reverse Impact	140	160
Adhesion	5B	5B
MEK Rubs	200	200

Raw Material Selection

The final coating properties and cure speed are controlled by the formulation components, their relative amounts and their order of addition. Since neither the polyol nor the isocyanate crosslinker are involved in the UV-curing reaction, the acrylate monomers, acrylic polyols, solvents, and isocyanate crosslinkers must be carefully selected so that a tack-free state is achieved after UV cure.

Solvents

Solvents play a number of roles in coating formulation, application, and performance. Their primary role is to reduce the solvent viscosity so it can be applied to the substrate using spray guns. However, they also play several other important roles which are often overlooked. These include compatibilizing the formulation components, improving adhesion to the substrate, reducing sag, and improving flow and leveling.

For this application, we selected acetone as the primary solvent not only because it is VOC-exempt in the United States, but also because it is an excellent viscosity reducer for the resins and it evaporates rapidly. In dual-cure coatings the acrylate monomer diluents provide some viscosity reduction but are not very good solvents, cf. Figure 4. Since rapid cure and productivity are key benefits of this technology, a fast evaporating solvent is desirable to minimize flash-off time before the coating is UV-cured.

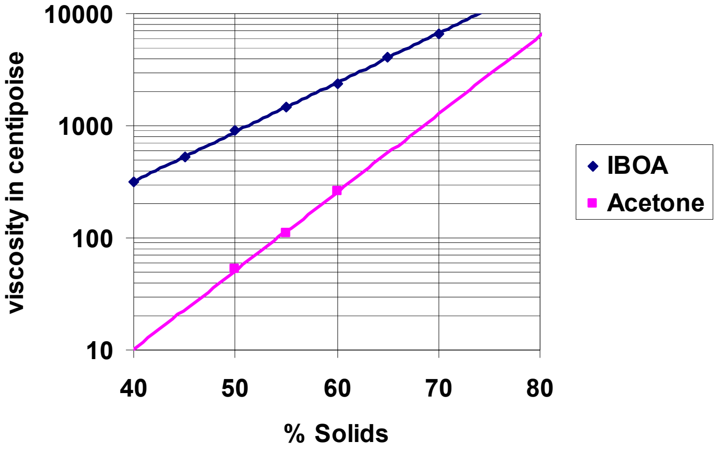

Figure 4. Viscosity Reduction of an Acrylated Oligomer with Acetone and Isobornyl Acrylate (IBOA).

Another important role is sag prevention. In the absence of solvents or rheology modifiers, low viscosity UV coatings would continue to flow until they are UV cured, potentially causing sags and uneven film thickness. Solvents are an excellent tool to reduce the coating viscosity for application, flow and leveling, while minimizing the potential for sag because it evaporates from the coating.

Acrylic Polyols and Isocyanate Crosslinker

We recently developed a family of acrylic polyols based on allylic alcohols.[5,6,7] These new acrylic polyols are unique in that they include hard and soft resins with very low solution viscosities and superior functionality compared to conventional acrylic polyols. These polyols are also designed to be blended together to achieve coating properties for a wide range of applications and coating technologies including high-solids, liquid UV, moisture-curable, and powder coatings, Table 3.

For this study, we chose P120 or P90, two liquid acrylic polyols available solvent-free, and an acetone solution of A140 or A90 to minimize flash-off time and VOC content. By blending these hard and soft acrylic polyols in different ratios, we were able to optimize the formulation to achieve a tack-free state after UV irradiation and a good balance of hardness and flexibility in the final coating.

Table 3. Typical Properties of ACRYFLOW Acrylic Polyols.

ACRYFLOW Polyols	P60*	P90	P120	M100	A90	A140
Tg (measured), ^{o}C	-52	-44	-40	5	55	52
OH# of solids	60	90	120	105	90	140
OH# as supplied	60	90	120	84	63	98
OH EW of solids	900	623	468	534	623	401
OH Functionality/molecule	2.4	5.6	5.6	4.5	4.4	7.0
Mn	2,200	2,900	2,600	2,400	2,200	2,500
Mw	4,700	7,000	5,700	5,900	6,000	6,000
Pd	2.1	2.4	2.2	2.5	2.6	2.4
% solids	100%	100%	100%	80%	70%	70%
Solvent	None	none	none	n-BuAc	n-BuAc	n-BuAc
density as supplied, lbs/gallon	8.53	8.76	8.76	8.43	8.60	8.65
APHA color as supplied	30	30	60	20	25	40
Viscosity, cps, 100% solids	10,000	30,000	35,000	------	solid	solid
Viscosity, cps, as supplied	10,000	30,000	35,000	8,000	5,700	8,000

*Developmental product

We also selected HDI trimer as the isocyanate crosslinker because it is a common crosslinker for automotive coatings and it is available solvent-free. HDI trimer also yields coatings with superior flexibility compared to IPDI trimer.

Acrylate Monomer Selection

Monomer selection was based on a number of considerations including:

- Ready availability and cost
- Low irritancy
- Low volatility
- Minimal shrinkage during polymerization
- High latent hardness
- Good weatherability properties
- High UV reactivity

We chose isobornyl acrylate (IBOA), trimethylopropane triacrylate (TMPTA), based on these factors and hydroxyethyl acrylate (HEA) for its ability to react both with the isocyanate crosslinker and the other acrylates. We also developed similar formulations with less irritating monomers to avoid the European Xi label. These monomers are isooctyl acrylate, di-TMPTA, and caprolactone acrylate.

Additives, Catalysts, and Photoinitiators

Based on prior work on weatherable UV-cured coatings,[8] we selected a combination of a bis-acylphosphine oxide (BAPO) and α-hydroxy ketone (AHK) photoinitiators. The BAPO is an efficient long-wave (up to 440 nm) absorber and is recommended for thick films while the AHK is a liquid with low yellowing potential. These photoinitiators also absorb light in the range where Fe-doped lamps have their highest output (300-450 nm) and do not interfere with hindered amine light stabilizers (HALs) and benzotriazole UV-screeners. Finally, we used a standard tin catalyst for the isocyanate polyol reaction, a flow modifier, and an acrylated phosphate adhesion promoter.

Effect of Formulation Components on Cure Speed and Coating Properties

With only liquid acrylic polyols as the base polyols and HDI-trimer as the isocyanate crosslinker, mono-functional acrylates such as IBOA do not yield a tack-free state after UV cure, unless the HEA is pre-mixed with the isocyanate, Figure 5. In contrast, TMPTA yields a tack-free coating after UV cure, presumably because it is tri-functional and yields a highly crosslinked acrylic polymer. Adding HEA to the B-side caused a further increase in hardness up to 80 Koenig swings after UV cure. We assume the HEA monomer reacts with the isocyanate to generate an acrylated polyisocyanate that can now become involved in the UV-curing process.

Although some tri-functional TMPTA is required to build enough molecular weight, adding too much can lower the flexibility of the coating, Figure 6. We achieved an optimal balance of cure speed and final coating properties by adding a 1:1 ratio of IBOA to TMPTA and adding one equivalent of HEA to the isocyanate side (B-side). Another benefit of adding HEA to the B-side is that the it fully reacts with the isocyanate and is no longer a potential irritant in the formulation.

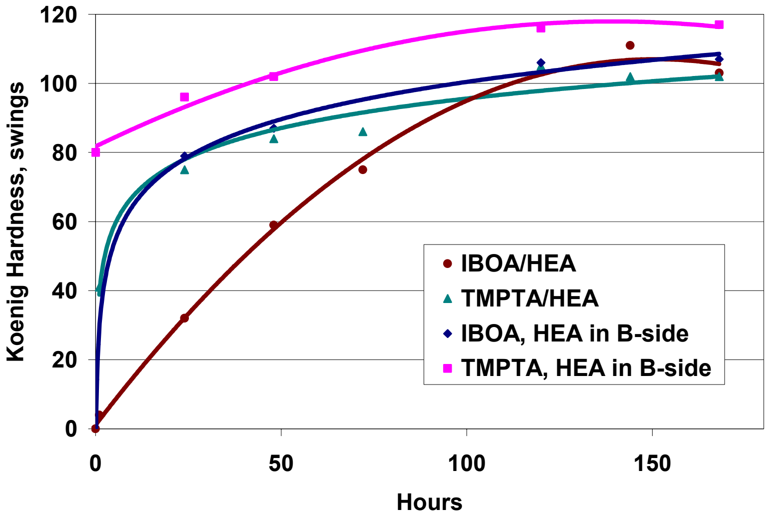

Figure 5. Effect of Acrylate Monomer Selection and Formulation on the Hardness Development of Dual-Cure Coatings with 2K Urethane Components.

Replacing a portion of the liquid polyol with a high-Tg polyol was also effective in achieving a tack-free state immediately after UV-cure. This approach is preferred over the use of TMPTA because the final coating has better impact resistance and flexibility. Zero-VOC formulations sprayable at 80% solids and above were achieved using acetone and acrylate monomers. Film appearance and physical properties were also excellent.

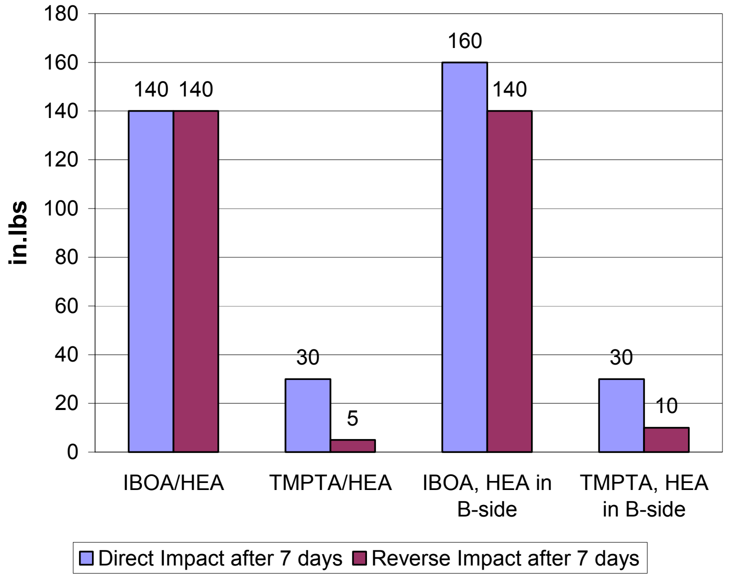

Figure 6. Effect of Acrylate Monomer Selection and Formulation on the Impact Resistance Dual-Cure Coatings with 2K Urethane Components.

Coating Application, Curing, and Properties

The dual cure coatings were mixed prior to application as are conventional 2K urethane coatings. Formulation viscosity was less than 100 cps, which is suitable for conventional or HVLP spray. The pot life, which is the time required to double the initial viscosity, of productive automotive refinish clearcoats is typically in the 1-2 hour range. In contrast, the dual-cure coatings had a pot life of approximately 12 hours.

Coatings were spray applied to basecoated steel panels using conventional spray equipment and were allowed to flash off 10 minutes prior to UV cure with an Fe-doped mercury vapor lamp. The UV light was filtered through borosilicate glass to remove the UV-C and reduce the UV-B components to 9% of the total irradiance between 300 and 445 nm. The majority (91%) of the irradiance was in the 320-445nm range which approximates the output of commercial UV-A lamps. These lamps are now recommended to minimize worker exposure to harmful UV-C and UV-B light. The total energy applied to the coating was ~20 Joules/cm2.

UV and Chemical Cure

Using infrared and Raman spectroscopy, we were able to monitor the conversion of isocyanate groups and acrylate unsaturation. Without UV cure, the NCO reaction was essentially complete (>98%) in 3 days but no curing of the acrylate monomers occurred, Figure 7. If the coating was irradiated after complete chemical cure, approximately 50% of the acrylate monomers polymerized and the conversion of double bonds continued slowly without irradiation.

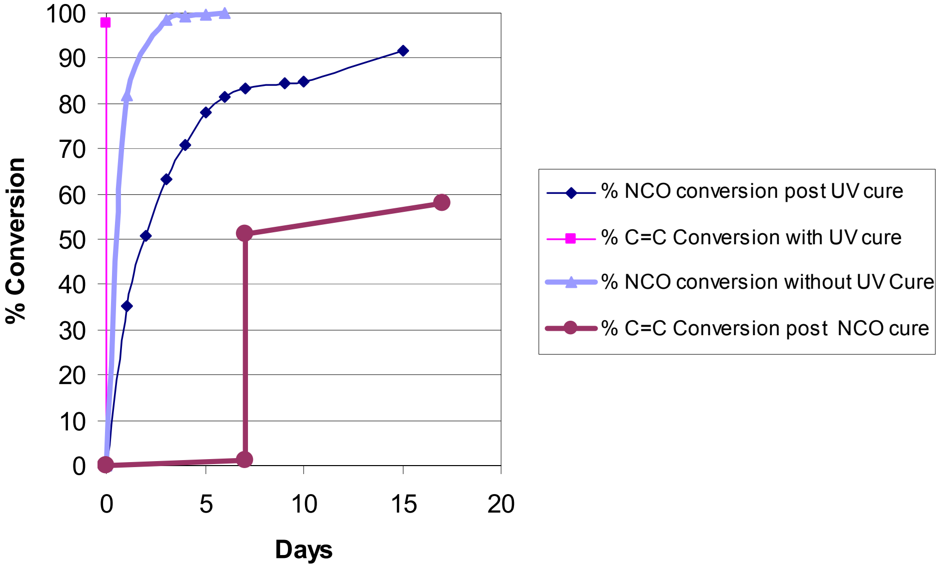

Figure 7. Effect of Cure Schedule on the Conversion of NCO and C=C Functionalities.

In contrast, irradiating the same coating immediately after application resulted in almost quantitative conversion of the acrylate monomers. The NCO-OH reaction, on the other hand, was slower than in the un-irradiated sample and NCO conversion leveled off at 85-90%. These results suggest that coating viscosity affects both the UV and chemical cure processes but that the chemical cure process is less affected by UV curing in these formulations.

Dual Cure Coating Properties

The appearance of the dual cure coatings was excellent, with gloss and DOI values in the 90's, no apparent sag, and a "Class A" appearance over refinish basecoats, Figure 8.

Figure 8. Photograph of a 3-D Form with a Basecoat/Dual Cure Clearcoat Finish.

The physical properties of the cured coatings were superior to both UV and 2K urethane coatings, see Table 1. In particular, the coatings were very hard yet flexible. Koenig hardness usually exceeded 125 swings while impact resistance and adhesion were excellent. Solvent resistance exceeded 200 MEK rubs, suggesting a high degree of crosslinking and cure.

The cured 2K/UV clearcoats were also subjected to accelerated weathering tests under QUVA and QUVB conditions. After 3,300 hours of exposure, all coatings have retained over 80% of their 20°gloss, even under harsh QUVB conditions (automotive cycle), Figure 9.

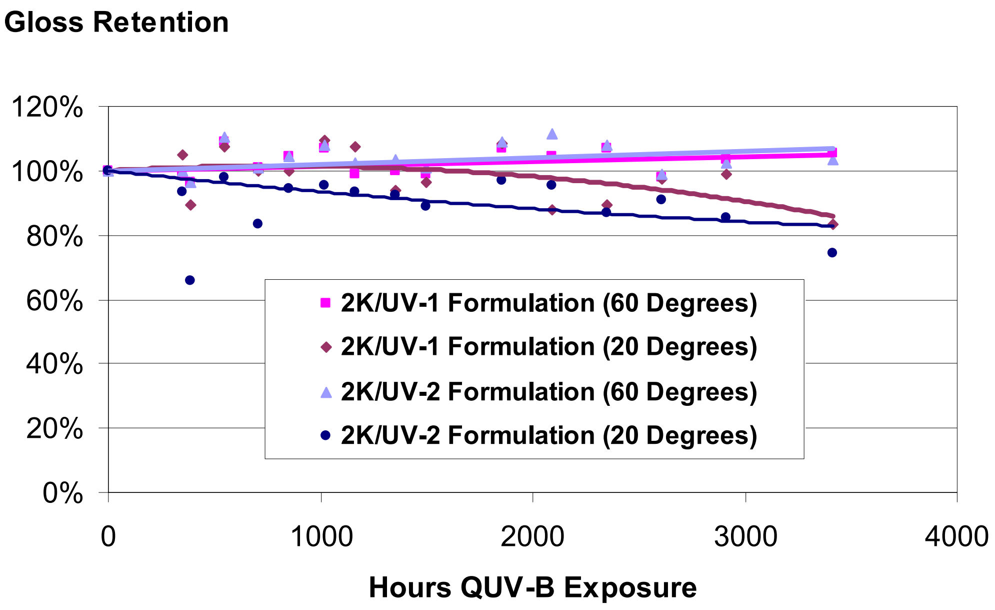

Figure 9. Gloss Retention of 2K/UV Clearcoats under Accelerated Weathering Conditions (QUVB exposure 8/4 automotive cycle).

Conclusions

Low- to zero-VOC acrylic-urethane clearcoats have been developed for weatherable applications. The coatings cure by a combination of solvent evaporation, UV and chemical cure. Unlike conventional UV-curable coatings, these formulations do not require acrylated oligomers but use conventional 2K urethane resins and acrylate monomers as reactive diluents. A wide range of coating properties can be achieved by varying the acrylic polyols, isocyanates, monomers, and component ratios.

These coatings can be spray applied at > 80% solids to three-dimensional forms using conventional spray equipment with minimal sag. The coatings cure to a tack-free solid state in seconds when exposed to low-intensity UV-A light and fully cure in the dark. Un-irradiated coatings also cure to a tack-free state and can be UV-cured after chemical curing has occurred. The cured coatings have excellent appearance, physical properties, chemical resistance, and weatherability, suggesting that this acrylic-urethane UV-curing clearcoat technology could be applied to automotive OEM and refinish applications, as well as wood and plastic parts.

Acknowledgements

The author wishes to acknowledge Ann Good, Bob Good, Dave Pangburn and Mark Smithson for expert technical assistance, Larry Arndt for spectroscopic techniques and data, and Steve Harris for helpful discussions.

Experimental

Coating Formulation and Testing

Panels for accelerated weatherability testing were prepared by applying clearcoats over a white refinish basecoat (PPG Deltron 2000 DBC 4056 Chrysler Bright White) on 3”x6” chromate pretreated aluminum panels. The clearcoat formulations were applied with and without UV Screeners using the following additive package:

Photoinitiators	
Irgacure 819 (%)	0.2
Darocure 1173 (%)	2.0
UV Screeners	
Tinuvin 400 (%)	1.5
Tinuvin 292 (%)	1.5
Flow Aid	
BYK 358 (%)	1.0

Radiometry

All films were cured with 15 passes under a pyrex-filtered Fusion D-Bulb at 2.5 irradiation seconds per pass. The table below lists the average radiometer data recorded per single pass. Total irradiation time was 37.5 seconds and total UV energy was 19.8 Joules/cm^2.

16 ft/min.	Per pass		250-260 nm	280-320 nm	320-390 nm	395-445 nm	Total
Peak intensity	W/cm2	unfiltered	0.018	0.183	0.613	0.404	1.218
Dosage	J/cm2	unfiltered	0.02	0.29	0.79	0.53	1.625
	J/cm2	w/ pyrex filter	0.00	0.13	0.71	0.49	1.323
		% of total light	0%	9%	54%	37%	100%

Weatherability Testing

All coatings were tested with and without UV Screeners using a UV-A Exposure Protocol of 4 hr. UV @ 60º C then 4 hr. Condensation @ 50º C, and a UV-B Exposure Protocol of 8 hr. UV @ 70º C then 4 hr. Condensation @ 50º C.

Raman and Infrared Analysis of Clearcoats

Raman and infrared spectroscopy provide complementary, non-destructive, and rapid analysis of UV clearcoat samples. Although molecular vibration frequencies are nearly identical, relative intensities are quite different. Thus, a weak infrared band such as carbon-

carbon bonds is typically strong in Raman and strong infrared NCO bands are very weak in Raman. In analyzing dual-cure clear-coated panels Raman can be used to measure the conversion of carbon-carbon double bonds during UV cure while infrared can be used to track the conversion of isocyanate bonds.

Raman spectra of 1.5 mil and 3.0 mil clear coat panels were taken using a Bruker 106/s Raman spectrometer with a 1064 nm Nd-YAG laser. The Raman module is connected to a Bruker FT-IR 66 bench equipped with a liquid N_2 Ge detector. Each panel was scanned 120 times with a scanning velocity of 2.2 cm/sec and a resolution of 8 cm^{-1}. Laser strength was set to 1489 mW to obtain maximum signal strength. No scorching was detected on any panel samples.

In order to measure the percent C=C cure for coating samples using the Raman spectrum, the C=C band height at 1632 cm^{-1} was measured and divided by height of the unaffected CH2 band at 1447 cm^{-1}. The same was performed for the uncured sample. Normalizing the Raman peak ratios (cured vs. uncured) provided the percent double bond conversion. In most one component systems complete reaction of all double bonds is rare due to the polymerization hindrance of the radicals during UV curing.

To measure the amount of isocyanate converted to urethane infrared spectroscopy measured the NCO band height at 2263 cm^{-1} and ratioed it against the unaffected CH2 band height at 2930 cm^{-1}. Again normalizing the infrared ratio of NCO to CH2 for the uncured to cured gave the NCO conversion. Infrared spectra were taken of neat coating panels using a Nicolet Nexus 670 interferometer equipped with a 15x Bio-Rad ATR microscope. The liquid N_2 MCT-A detector scanned each sample 120 times at a velocity at 1.9 cm/sec with a resolution of 8 cm^{-1}. Reference spectra were obtained after each sample collection.

References

1. Szycher's Handbook of Polyurethanes, Michael Szycher, CRC Press, 1999, ISBN 0-8493-0602-7.
2. http://www.radtech.org/industry/automotive.html
3. Fischer, W.; Weikard, J.; and Meier-Westhues, U. (2001), "Dual Cure; Combination of Superior Properties", Radtech Report, November/December Issue.
4. US Patent Application US2004/0039103 A1 to BASF Corporation.
5. Larry W. Arndt, L. Joseph Junker, Shanti. P. Patel, Daniel B. Pourreau, and Wei Wang, "UV-Curable Acrylic Urethane Coatings for Weatherable Applications", PCI Magazine, February 2004 issue.
6. Guo, S.-H.; Wang, W.; Harris, S. H.; Patel, S.; Junker, L. J.; Blackwell, R. S.; Fadakar, F.; and Pourreau, D. B., " New Acrylic Polyols for Low-VOC Coatings", PCI Magazine, June 2002 issue.
7. www.acryflow.com
8. A. Valet and C. Decker, "Weatherfast UV-Curable Clearcoats", November/December 2000 Radtech Report, p. 33.