Acrylate Monomer-Free/ VOC-Compliant Ultraviolet-A Radiation-Curable Technology for Automotive Refinish Clearcoat

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Ultraviolet (UV)-curable coatings have experienced growth in many market areas. However, penetration into the automotive refinish market has been relatively slow. One reason has been the safety concern from the end user about use of UV radiation. RadTech International set up an automotive refinish focus group to help address the issues relating to the use of UV technology for this market area. This included the promotion of UV-A curable technology and its safe use. In 2001, the concept of using UV-A lamps to cure a primer system for the refinish market was introduced.

UVA-curable coatings have since been experiencing growth in automotive refinish applications. They have many advantages over conventional coatings systems in that they can cure fast and are 1K. Current developments in UV-A curable technology have yielded coatings that are highly reactive and also minimize residual unsaturation in the cured coating. Despite this, the use of these resins in automotive refinish clearcoats or spot repair is still limited. The main reason has been the difficulty in the sanding and buffing of the clearcoat due to the difference in coatings properties of the refinish coatings and the OEM coating being repaired. Properties of concern are the hardness and glass transition temperature (T_g). Since 2K polyurethane technology is widely used in the automotive refinish market, if the UV-A curable refinish coating could mimic its properties then the system will blend well. This led to the development of two acrylate monomer-free aliphatic urethane acrylate resins (*Figure* 1).

Urethane Acrylate Resin A was designed as a 100% solids soft resin that has a viscosity of 10,000 mPas at 25°C. The cured film T_g of this resin was 10°C. Urethane Acrylate Resin B is a hard resin that is 60% solids in n butyl acetate and has a viscosity of 200 mPas at 25°C. This resin is hard, as demonstrated by having a cured film T_g of 100°C.

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By blending these two resins the desired combination of T_g and hardness can be achieved for optimum sanding and buffing characteristics.

EXPERIMENTAL

A matrix study was performed using these two resins to determine the optimum blend ratios to achieve superior sanding and buffing performance. The study was conducted by making variations of high and low T_g urethane acrylate resins and blending them in five different ratios. The UVA-curable clearcoat formulations that were made were spray applied over panels prepared from commercial refinish primers and basecoats. For spot repair, the samples were applied over commercial ACT OEM finished panels. Chemical resistance (MEK double rubs), gloss, and appearance testing after sanding and buffing were determined on these samples. UVA-curable paint formulations were also spray applied over glass substrates to determine T_g and pendulum hardness. A commercial UVA-curable refinish system and a commercial 2K polyurethane refinish system were also applied and tested in the same manner for comparison study.

The blend ratios studied are shown in *Table* 1 and a generic coating composition is shown in *Table* 2.

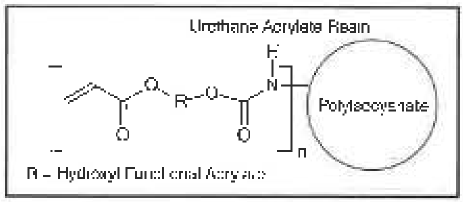
The sprayed clearcoats were flashed at room temperature for 5 min before being cured under an H&S AutoShot 400 UVA lamp (see *Figure* 2) for 4 min at a distance of 12 in. *Figure* 2 shows a picture of curing a clearcoat in a body-shop environment.

RESULTS

Chemical Resistance

Chemical resistance was determined by MEK double rubs and is shown in *Table* 3. The results show that the lower T_g Resin A has very little chemical resistance unblended. The much higher T_g Resin B has very good resistance as well as all of the UA Blends. UA Blend 5 showed a drop in chemical resistance at 14 days but this blend also has the highest amount of UA Resin A in it. This phenomenon has been seen other times when high amounts of UA Resin A are used. It is thought that since UA Resin A is much softer, the polymer relaxes after its initial cure. This allows the MEK to penetrate and soften the polymer network. MEK does not dissolve the coating but softens it to the point that it is being abraded during testing.

Figure 1—Generic structure of urethane acrylate resins.



Glass Transition Temperature (T_g)

The T_g of a clearcoat can be an important contributing factor in the ability to buff out a coating (*Table* 4). During buffing the coating will begin to heat due to friction. If there is a difference between the new coating and the OEM coating, buffing out blend lines and increasing the gloss can be difficult. Typical polyurethane clearcoats have a T_g from 58°C to 65°C.

Hardness

Clearcoat hardness was determined using pendulum hardness. The clearcoat formulations were spray applied over glass panels and cured in the same manner

Table 1—Urethane Acrylate Blend Ratios (Parts by Weight Based on Solids)

	UA Resin A	UA Resin B
UA Blend 1	10	90
UA Blend 2	20	80
UA Blend 3	30	70
UA Blend 4	40	60
UA Blend 5	50	50

Table 2—Urethane Acrylate Clearcoat Generic Formulation

Raw Material	Weight	Volume	Weight Solids	Volume Solids
UA Resin B	54.95	6.46	32.97	3.44
UA Resin A	14.13	1.49	14.13	1.49
Photoinitiator	0.47	0.05	0.47	0.05
Flow agent	1	0.12	1	0.12
Photoinitiator	1.88	0.21	1.88	0.21
Light stabilizer	0.47	0.47	0.47	0.47
Light stabilizer	1.18	1.17	0.94	1.13
Solvent 1	5.76	0.78	0	0
Solvent 2	20.16	3.01	0	0
Total	100	13.75	51.87	6.9

Calculated Properties

Weight solids	51.87	Wt/gal	7.27
Volume solids	50.19	Theoretical VOC	3.5

Table 3—Chemical Resistance as Measured by MEK Double Rubs

Resin	30 M	1 Day	7 Day	14 Day
UA Resin A	14	9	5	15
UA Resin B	100	100	100	100
UA Blend 1	100	100	100	100
UA Blend 2	100	100	100	100
UA Blend 3	100	100	100	100
UA Blend 4	100	100	100	100
UA Blend 5	100	100	100	77
Commercial UV Refinish	100	100	100	100
Commercial 2K Refinish	NA	100	100	100

Figure 2—H&S AutoShot 400 UVA lamp used in body shop and lab.

Figure 3—T_g and hardness with respect to % UA Resin A in the clearcoat.

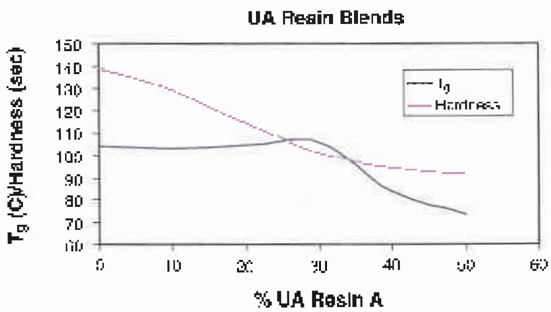


Table 4—Clearcoat Glass Transition Temperature (T_g)

Resin	°C
UA Resin A	10
UA Resin B	104
UA Blend 1	103
UA Blend 2	105
UA Blend 3	106
UA Blend 4	84
UA Blend 5	74
Commercial UV Refinish	101
Commercial 2K Refinish	62

Figure 4—Example of the halo effect.

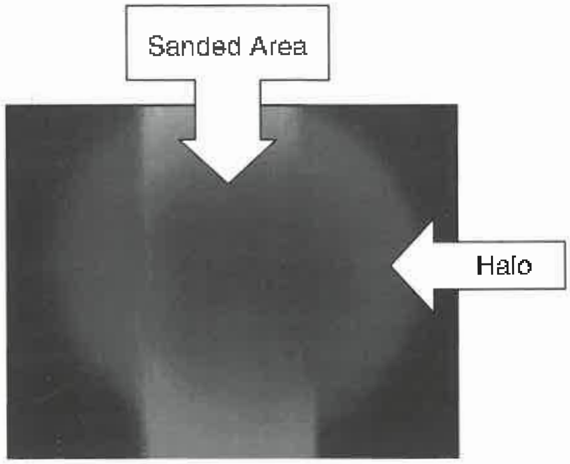


Figure 5—Commercial UV refinish clearcoat blend line.

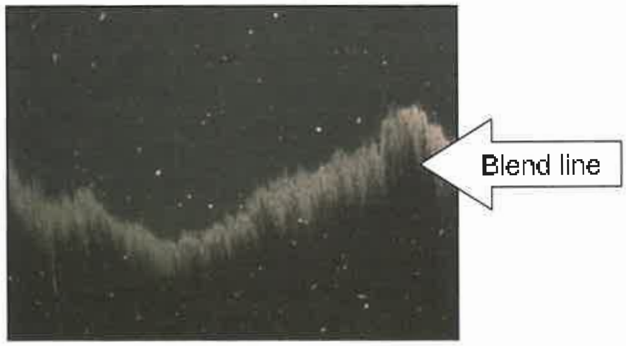


Figure 6—Improved blend line (formulation UA Blend 3).

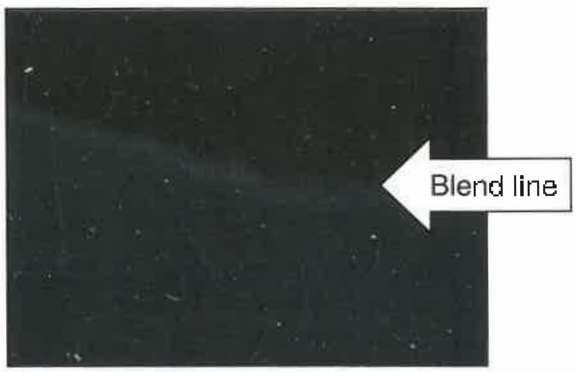
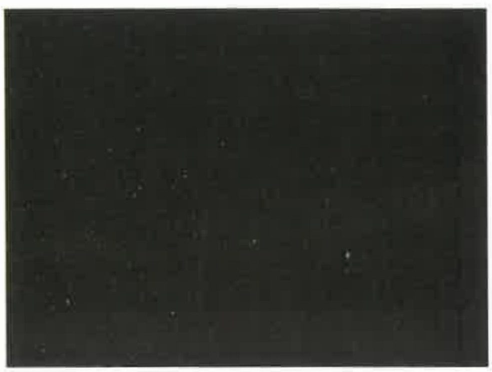


Figure 7—Best blend line (formulation UA Blend 4).



as described previously. Hardness was measured 30 min after cure and also 1, 2, 7, and 14 days after cure. The samples were kept at a constant temperature and humidity to ensure consistency between measurements. Samples were tested according to ASTM D 4366 (*Table* 5).

Current commercial 2K technology is usually sanded and buffed one day after curing to achieve optimum appearance characteristics while maintaining job efficiency. At this time the hardness is 95 sec, whereas the current commercial UV system is much harder at 207 sec. UA Blends achieved a 2K type of hardness 30 min after curing as opposed to one day using the conventional 2K system, thereby increasing efficiency.

Figure 3 illustrates the effect that varying amounts of UA Resin A have on T_g and hardness of the clearcoat (hardness values in *Table* 5 are at 30 min after curing). The T_g appears to remain stable relative to % UA Resin A until more than 30% has been added, at which time it begins to drop sharply. The hardness, however, begins to drop as soon as UA Resin A is introduced.

Appearance Properties

When refinish coatings are discussed it is very important to also discuss appearance properties such as halo and blend lines. Halo is a phenomenon that is common when sanding and buffing refinished parts. Halo is a hazy area of the coating that usually forms around the edges of the unsanded buffed area. To remove this, sometimes the entire body panel section will need to be buffed. *Figure* 4 illustrates the halo effect on a refinished panel. To determine how susceptible a UV coating is to forming a halo, panels were refinished using each system. Thirty minutes later they were sanded using 1000-grit sand paper. A buffer was then placed over the sanded area and that area was buffed for one minute without pressing on the buffer. Panels were ranked as to having halo, medium halo, slight halo, or no halo (*Table* 6). UA Resin A was not determined because by itself it could not be buffed.

Blend lines refer to the area of a refinished part where the new coating meets the OEM coating. This area will typically be sanded and buffed so that the new coating appears to be the same as the original. *Figures* 5 to 7 show the blend line improvements made with the UV formulations.

Table 5—Pendulum Hardness (seconds)

Resin	30 Min	1 Days	2 Days	7 Days	14 Days
UA Resin A	21	18	20	17	17
UA Resin B	139	167	171	167	181
UA Blend 1	130	158	169	189	193
UA Blend 2	115	115	115	137	140
UA Blend 3	102	105	108	112	113
UA Blend 4	95	98	99	104	104
UA Blend 5	92	95	99	102	101
Commercial UV Refinish	207	207	210	221	218
Commercial 2K Refinish	N.D	95	105	112	127

Table 6—Halo Effect in Various UV-Curable Resins

Resin	Halo Effect
UA Resin A	Not Tested
UA Resin B	Halo
UA Blend 1	Medium Halo
UA Blend 2	Slight Halo
UA Blend 3	Slight Halo
UA Blend 4	No Halo
UA Blend 5	Slight Halo
Commercial UV Refinish	No Halo
Commercial 2K Refinish	No Halo

Table 7—DOI and Gloss Before and After Sanding and Buffing

	Initial			After Sanding, Buffing			% Retention After Buffing		
Resin	DOI	20°	60°	DOI	20°	60°	%DOI	%20°	%60°
UA Resin A	ND	ND	ND	ND	ND	ND	ND	ND	ND
UA Resin B	97	86	90	92.2	60	80	95.1	69.8	88.9
UA Blend 1	97	86	91	91.9	75	85	94.7	87.2	93.4
UA Blend 2	97	86	91	89.3	75	86	92.1	87.2	94.5
UA Blend 3	97	87	91	91.1	80	89	93.9	92.0	97.8
UA Blend 4	97	87	91	94	81	89	96.9	93.1	97.8
UA Blend 5	97	86	92	92.4	80	88	95.3	93.0	96.7
Commercial UV Refinish	79.1	71	89	95.5	82	91	120.7	115.5	102.2
Commercial 2K Refinish	96.7	89	93	89.8	65	77	92.9	73.0	82.8

Gloss

Gloss and DOI were determined after curing and also after sanding and buffing. Initial gloss readings of the UA Blends were comparable to the commercial 2K refinish system. After sanding and buffing there was a slight improvement over the 2K system. The commercial UVA refinish system started at a lower gloss compared to the UA Blends. However, it did improve with sanding and buffing to about the same gloss level as the UA Blends (*Table* 7).

CONCLUSIONS

Monomer-free aliphatic urethane acrylate resins with different hardness were successfully synthesized. UV cure coatings were developed by using these resin blends to match the performance of the existing OEM coating, meeting the low VOC requirements. The coatings developed can be sanded and buffed much like a commercial 2K polyurethane system with improved blending capability and near minimal halo effect.

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