Low Energy UVA Radiation-Curable Refinish Primers and Clearcoats

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In recent years, the major emphasis in the coatings industry has been adapting to environmentally friendly technology that has all the key performance attributes of traditional solventborne systems. Lately, automotive OEMs have suggested the use of "greener coatings technologies" for the "end of line" repair and body-shop refinish applications. This "market pull" effect has rejuvenated interest among innovative resin manufacturers to bring novel concepts into this field. One such approach is the use of Ultraviolet-A (UVA) radiation-curable raw materials for primers and clearcoats.

Various aliphatic urethane acrylates were screened for the right combination of coatings properties using high throughput screening. The few predicted formulations were subjected to rigorous performance tests to identify combinations that have fast dry time, adhesion, and sanding characteristics. The details of the formulations, evaluation methods, and the coatings properties will be presented.

INTRODUCTION

The automotive refinish industry is poised for a radical change. Of the major technological changes in the last three decades, the adaptation of 2K-urethane technology from lacquer technology is noteworthy. This big leap revolutionized the coatings industry, which transformed from the old simple polyester technology to the superior performance urethanes. Subsequently, the 2K-urethane system has been accepted as the industry standard. Another innovative concept that was launched a few years ago was the use of IR lamps for refinish cure. This fast-cure technology had a mixed response with end users due to the requirement of new capital investment and its justification in terms of the advantages seen.

The launch of UVA curable refinish primer by a major coatings manufacturer a few years ago was a milestone in the automotive refinish business.[1]

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Table 1—UV-Curable Primer Formulation

Pigmented Formulation	Weight (g) A	B	C	D	E	F
Component A—urethane acrylate	50	50	50	50	50	50
Component B—epoxy acrylate	50	50	50	50	50	50
Pigment—TiO_2	3.4	3.4	3.4	3.4	3.4	3.4
Calcium carbonate filler	41.1	41.1	41.1	41.1	41.1	41.1
Extender pigment—talc	59	59	59	59	59	59
Pigment—Bayferrox 318M	0.58	0.58	0.58	0.58	0.58	0.58
Adhesion promoter (Trifunctional acid ester) – Sartomer CD9052	0	10	30	0	10	30
Photoinitiator—Irgacure 2020	7.8	7.8	7.8	7.8	7.8	7.8
Solvent—butylacetate	0	0	0	30	30	30

Its unique advantages motivated various resin and coatings manufacturers to work in this area. During that period, the lamp technology was not as advanced as the resin and coatings technology. A significant breakthrough in this field was achieved when a range of low intensity UVA lamps (radiation output in the range of 320 nm–400 nm) with different design and power output started emerging into the market. This kindled interest in the "refinish" and "end of line" market segments that helped steer UVA technology toward commercialization. The recent developments like the introduction of 400 to 450 watts/in. lamps with easy to use assembly will encourage more end users to evaluate and adapt this technology.

The driving factors of UVA technology are:

- Faster cure time and increased productivity
- Reduced waiting time between coats (primer, basecoat, and topcoat)
- Operator safety
- Lower VOC and VHAPs wherever possible

These advantages encouraged the OEM and coating manufacturers to adapt to this environmentally friendly greener technology as opposed to the traditional high VOC and VHAPs solventborne systems. In response to these market developments, major innovative resin and coatings suppliers focused their research efforts on developing products that were robust and could cure under low intensity UVA radiation.

With these requirements in the background, an extensive investigation was conducted in our laboratory using the combinatorial approach.[2-3] Miniaturization, Automation, and Parallelization (MAP) is a wonderful tool to screen different resins and formulations for optimum properties. A D-optical design with second order interaction was used to evaluate ~25,000 coatings in a period of three months versus a two-year timeframe required for traditional testing. This initial study gave an excellent boost to our developmental efforts and provided the capability to select resin combinations that are beneficial for refinish applications. Our prior knowledge of the 2K-urethane refinish market also helped us compare this new technology with the current industry standard. This article deals with the recent developments and new opportunities available in the emerging market.

UV-CURABLE 100% SOLIDS AND SOLVENTBORNE PRIMERS

Preparation and Evaluation of Optimized Formulations

The MAP study pointed toward a few formulations that could yield good coatings properties. Our further

Table 2—Salt-Fog Evaluation of UV-Curable Primer

Treated Steel Panel	500 hr Creepage from scribe (mm) read in 5 places					Average	Rating
UV Control W	0.1	1	0.5	5.5	4	2.22	6
#1 white	5	3.5	3.5	5	6	4.6	5
#2 white	0.5	0.5	3	3.5	3.5	2.2	6
#3 white	0.5	4	4	5	4	3.5	6
#4 white	1	2.5	3	3	3.5	2.6	6
EpoxyW	0.1	0.1	0.5	0.8	3	0.9	8
Untreated Steel Panel	**Creepage from scribe (mm) read in 5 places**					**Average**	**Rating**
UV Control Y	1.2	2	1	0.5	1	1.14	7
#1 yellow	2	2	2	0.5	0.3	1.36	7
#2 yellow	1	1	7	9	8	5.2	4
#3 yellow	1	0.3	0.3	0.3	1.1	0.6	8
#4 yellow	1.2	0.5	1.2	0.5	0.5	0.78	8
EpoxyY	0.2	0.2	0.2	0.3	0.3	0.24	9

Rating based on standard test for evaluation degree of blistering in paints ASTM D 714-87.

Table 3—Salt-Fog Evaluation of UV-Curable Primer

Treated Steel Panel	1000 hr Creepage from scribe (mm) read in 5 places					Average	Rating
UV Control W	9	9	8	11	12	9.8	3
#1	12	11	7	13	16	11.8	2
#2	5	6	7	7	10	7	4
#3	4.5	3	4	6	8	5.1	4
#4	5	6	8	10	22	10.2	2
Epoxy	4.5	5.5	5	5	5	5	5

Table 4—Humidity Resistance of UV-Curable Primers

Untreated Steel	500 hr Cleveland Condenser ASTM D 1654-79A Rating Based on Blistering
Panel	
UV Control W	3
#1 White	4
#2 White	6
#3 White	7
#4 White	6
EpoxyW	9
Panel	
UV Control Y	6
#1 Yellow	6
#2 Yellow	2
#3 Yellow	8
#4 Yellow	6
Epoxy Y	9

Table 5—UV-Curable Clearcoat Formulation

Raw Material	Weight, g A	B	C
Urethane acrylate—hard	350.47	—	104.82
Urethane acrylate—soft	—	350.47	83.86
Pentaerythritol tetraacrylate	—	-	25.16
Sanduvor 3058 liquid	3.5	3.5	1.93
Sanduvor 3206 liquid	8.76	8.76	4.82
Irgacure 184	3.5	3.5	1.93
Darocur 4265	21.03	21.03	11.57
Baysilone OL 44	0.35	0.35	0.96
Butyl Acetate, n-	348.25	348.25	164.95
Total	735.86	735.86	400.00

Table 6—Solvent Resistance of Clearcoats

Systems	MEK Rubs Initial	Day 1	Day 7	14 Days
Urethane acrylate—hard (A)	100	100	100	100
Urethane acrylate—soft (B)	90	70	60	20
Urethane acrylate (hard + soft) (C)	100	100	100	100

investigation and testing using the traditional test protocol resulted in a formulation that had the best overall performance. It was a combination of an aliphatic urethane acrylate and an epoxy acrylate. The details of the formulation are shown in *Table* 1.

The formulations were prepared both as 100% solids and also in a solvent depending on the type of application. The resins (urethane acrylate and epoxy acrylate) were mixed together along with the photoinitiator using a mixer. The additives and pigments were then added slowly with continued stirring. The formulations prepared were kept overnight to de-aerate. The coatings were then applied on the substrate by using either a drawdown bar, putty knife, squeegee, or sprayed to a wet film thickness of ~5 mils.

Curing the formulations under low intensity UVA light sources, e.g., H&S Autoshot UVA-400 lamp at a distance of 10 inches for two minutes, resulted in a tack-free surface. The primer had excellent adhesion to cold rolled steel. It can be sanded with a 320-grit sandpaper and then base-coated right after curing. The primer exhibited excellent hiding.

The primer formulation F was then evaluated for salt-fog and humidity resistance. A commercial epoxy primer was used as the control. The test protocol consists of applying the primer followed by a commercially available basecoat (white and yellow) and 2K-urethane top clearcoat. The evaluation was done according to ASTM D 714-87 and the details are shown in *Table* 2 (with higher ratings indicating better coatings performance).

Test results from *Tables* 2–4 show that there are differences in the performance based on the type and color of the basecoat selected for the evaluation, which is typical even in a 2K-urethane system. The tests were based on a standard textbook primer formulation without any special pigments or anticorrosion

Table 7—Hardness of Clearcoat

Systems	Initial	Pendulum Hardness Day 1	Day 7	14 Days
Urethane acrylate—hard (A)	72.8	91	110.6	100
Urethane acrylate—soft (B)	49	30.8	19.6	19.6
Urethane acrylate (hard + soft) (C)	147	159.6	170.8	163

pigment package. This was done mainly to study the effect of resins in the formulation. The coatings performance could be significantly improved by adjusting the formulation further. Salt-fog and humidity tests show that the UV-curable primer developed performed very well compared to the standard epoxy primer system.

UV-CURABLE SOLVENTBORNE CLEARCOAT

Aliphatic urethane acrylates are ideal resins for UV-curable clearcoat applications. They have superior weathering characteristics along with excellent chemical resistance and toughness. The development efforts were focused on achieving the right hardness and flexibility along with good solvent resistance. The urethane acrylate clearcoat formulations are shown in *Table* 5. The formulation A was based on a hard urethane acrylate that had eight years of proven outdoor weathering data, formulation B was based on a flexible soft urethane acrylate, and formulation C was a combination of hard and flexible urethane acrylates.

UV Clearcoat Evaluation

The clearcoats were evaluated for their solvent resistance and hardness. *Table* 6 shows the resistance to solvent as determined by MEK double rubs and *Table* 7 shows the hardness of the coatings as determined by Konig pendulum hardness.

The test data show that the hard urethane acrylate coating A had good solvent resistance and pendulum hardness. The soft urethane acrylate coating B was able to develop the initial MEK resistance but over a period of time became soft. However, by using both hard and soft urethane acrylates (formulation C), the resulting coating had good hardness along with excellent chemical resistance.

CONCLUSION

An ultraviolet-A curable refinish solventborne primer was successfully developed and evaluated. The primers have fast cure time combined with good solvent resistance and sanding characteristics. The initial salt-fog and humidity resistance evaluation show excellent performance compared to the traditional epoxy primer system. A combination of hard and soft urethane acrylates resulted in a UV-curable refinish clearcoat with good coating performance. CT

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