

UV-A Curable Automotive Refinish Coatings: Utilizing High-Throughput Experimentation as a Tool in the Discovery Process

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Introduction

In 2001 the concept of using a UV-A lamp to cure a primer system for the automotive refinish market was introduced. There is the perception, real or imagined, that radiation cure of coatings presents a safety risk to the worker. Overexposure to UV-A radiation can be harmful, but there is much less risk associated with UV-A radiation versus shorter wavelength UV light. However, the lower energy and shifted spectral output of UV-A lamps introduce limitations to the coating's formulator. Oxygen inhibition of the coating's surface and pigmentation preventing through-cure are two concerns. Since the concept was introduced, paint suppliers to the refinish market have worked to formulate materials tailored to UV-A light sources. RADTECH International has set up an Automotive Refinish Focus group to help address issues with the use of this technology, which includes the development of safe and effective light sources. As safety issues for radiation cure come to the forefront, it is likely that even more products will be introduced for the UV refinish primer market area to take advantage of the UV-A light source.

To gain widespread acceptance within the automotive refinish market, the reactivity of UV-A curing clear coat resins must be relatively high. High reactivity insures process efficiency, and also minimizes residual unsaturation. Residual unsaturated acrylate functionality can lead to post-curing, with negative effects on adhesion. Because UV-A lamps impart less energy to the coating than traditional bulbs, the aforementioned requirements present a challenge. Another test for UV-A radical cure involves the need for colorless clear coat formulations and films. The difficulty to resolve is that curing with UV-A radiation requires photoinitiators that absorb UV-A light. These materials are typically yellow.

For any clearcoat to make significant inroads into the market, it must be flexible. Lack of flexibility is a well-known shortcoming of polymer networks based on radical polymerization. Typical two component polyurethane clear coats exhibit values of 180s pendulum hardness and 100 inch pounds impact resistance. It would be difficult to match this benchmark with the radical cure of low molecular weight oligomers. However, it is feasible that good application properties would be obtained for more intermediate values of pendulum hardness and impact resistance.

High Throughput Experimentation vs. Traditional Methods

In the Bayer Polymers' laboratories the search for UV-A curable coatings proceeded in part with high-throughput experimentation. These techniques permitted rapid synthesis and analysis of more than 24,000 films, and yielded results that were consistent with more traditional methods. Coatings are prepared by combining many components (resins, photoinitiators, adhesion promoters, etc.) in some ideal ratio to generate a desired property set. The formulation chemist has not only a large number of component choices available to him/her, but also an unlimited ratio space in which to find the perfect system. The use of high

throughput and combinatorial chemistry techniques in the field of coatings science allows for extensive coverage of formulation component space. This high-throughput workflow allows the chemist to streamline the discovery process.^{1,2}

The development of refinish formulations offered an ideal opportunity to utilize high-throughput methodology. There are many material and process variables that contribute to the properties of a UV-A curable coating, making the parameter space quite extensive. Arrays of formulations can be rapidly assessed for one or two key properties that determine the success or failure of a particular combination of variables. With the UV primer for example, these key tests were for surface and through cure. The best candidates from the large primary screening were then optimized via traditional techniques for other important characteristics.

Results and Discussion

UV Refinish Primer

Issues with the original UV-A curable system can be explained by the problem of oxygen inhibition. The original evaluation done at Bayer looked at the best way to override this chemistry by the selection of base oligomer.

As in all primer developments, one wants to achieve good hiding, sandability, and good adhesion to cold rolled steel (direct to metal), e-coat, and aged coatings. The objective of a UV refinish system is quick cure with no oxygen inhibition, which typically generates a more open network structure with reduced crosslink density at the surface of the coating versus in the bulk. This is truly a surface phenomenon, due to the limited solubility and diffusivity of oxygen.³

First, we aimed at selecting a UV curable resin or resin combination exhibiting a tack free surface after curing employing a low intensity UV-A lamp (250 W). To this end, a screening was performed involving 6 independent factors, namely *UV curable resins*, *reactive diluents*, *photoinitiators*, *photoinitiator level*, *irradiation time*, and *distance from the lamp* (**Figure 1**). The selection of resins covers two aliphatic urethane acrylates (R1 and R5), an epoxy acrylate (R2), and a polyether acrylate (R4). These systems were selected because they are solvent and reactive diluent-free (100% solid) and exhibit relatively low viscosity. In addition, a urethane acrylate based on a polyisocyanate diluted in hexanediol diacrylate (HDDA) (R3) was included. 50:50 mixtures of the resins were also included. Difunctional and trifunctional reactive diluents were considered. Fifteen photoinitiators and photoinitiator blends covering three major classes (α -hydroxyketones, α -aminoketones, bis-acylphosphine oxides) were included. Based on a D-optimal design of experiments including second order interaction terms we selected 480 formulations. The process parameters *distance from lamp* (2 levels) and *irradiation time* (4 levels) were screened in a full factorial design whereby 4 repeats were prepared for each process parameter. Four hundred and eighty formulations thus translate into 15,360 films (480*2 distances*4 times*4 repeats). Replicates of some formulations were included also. Therefore, roughly 25,000 films were prepared and tested in this experiment. Stock solutions of all formulations were prepared and a liquid handler was used to cast films of ca. 1 mm thickness into flat bottom glass vials. All samples were cured using a 250 W UV- A lamp (UVAHAND[®] 250)ⁱ from Dr. HOENLE AGⁱⁱ under varying conditions with respect to curing

ⁱ UVAHAND is a registered trademark of Dr. K. Hönle GmbH, Germany

time and distance from the lamp. Two methods were employed to determine the degree of surface cure as well as the degree of through cure. Surface cure was visually assessed as “cured” or “not cured”. The degree of through cure was determined using an environment sensitive optical charge transfer probe, which exhibits a blue shift of its fluorescence spectrum upon increasing rigidity and/or decreasing polarity of its matrix. The spectral shift can thus be used as a measure of the degree of curing. All films were tested for through cure using a fluorescence reader. The visual assessment of surface cure was only performed for one repeat resulting in roughly 6,000 visual assessments.

Resin/ 50:50 blend Symplex lattice design	Reactive diluent	Photoinitiator / blend	[Photoinitiator]	Irradiation time [sec]	Distance from lamp [in]
R1 * (urethane acrylate)	HDDA	IRGACURE® 184 #		4%	0 8
R2 * (epoxy acrylate)	TPGDA	IRGACURE® 500 #		1%	20 4
R3 * (urethane acrylate)	TMPTA	IRGACURE® 500 #/Amine synergist			60
R4 * (polyether acrylate)		DAROCUR® 1173 #			180
R5 * (urethane acrylate)		CGI 1870 #			
R1 */R2 *		IRGACURE® 819 #			
R1 */R3 *		IRGACURE® 1850 #			
R1 */R4 *		DAROCUR® 4265 #			
R1 */R5 *		IRGACURE® 184/DAROCUR® 1173			
R2 */R3 *		GENOCURE® ITX +			
R2 */R4 *		IRGACURE® 500/Amine synergist/IRGACURE® 819			
R2 */R5 *		GENOCURE® ITX +/ CGI 1870 #			
R3 */R4 *		IRGACURE® 1300 #			
R3 */R5 *		IRGACURE® 1700 #			
R4 */R5 *		IRGACURE® 2959 #			

Figure 1: Factors and levels covered in the search for formulations exhibiting tack free surfaces when cured using a low intensity 250 W UV-A lamp. (*Bayer, #Ciba Specialty Chemicals Inc., +Rahn AG)ⁱⁱⁱ.

According to high throughput experimentation and analyses, the blend of R5 (a flexible urethane acrylate) and R2 (an epoxy acrylate) in combination with IRGACURE® 819 (a BAPO type photoinitiator) yields the best surface cure (**Figure 2**). It is worth noting that the surface cure value for the R2/R5 combination is higher than the values for the individual resins, which hints at a synergistic effect. The urethane acrylate seems to make a major contribution since good surface cure is observed for many photoinitiators. Interestingly, good surface cure is observed for phosphine oxide type photoinitiators (BAPO, e.g. IRGACURE® 819) while the α -hydroxyketone-type IRGACURE® 184 does not yield good results. Traditionally, IRGACURE® 819 has been recommended for through cure and IRGACURE® 184 for surface cure. α -hydroxyketone-type photoinitiators can serve as hydrogen atom donors. The hydroperoxide yielded from this reaction can decompose to form more reactive radicals than the peroxide formed from oxygen inhibition. Thus, prevailing wisdom would suggest this type of photoinitiator would serve to suppress oxygen inhibition. We assign these at first surprising observations to spectral features of the lamp, which exclusively emits UV-A light. IRGACURE® 184 has almost no absorption in the UV-A range while the absorption spectra of phosphine oxide type photoinitiators extend up to 450 nm. More recent high-throughput screening studies in Bayer Polymers’ laboratories have shown that UV-A transparent α -hydroxyketone photoinitiators can still offer some benefit when used in blends with bis-acyl phosphine oxide photoinitiators.⁴

ⁱⁱ www.hoenle.de

ⁱⁱⁱ IRGACURE and DAROCUR are registered trademarks of Ciba Specialty Chemicals Holding Inc., Switzerland, GENOCURE is a registered trademark of Rahn AG, Switzerland

Analysis shows that most photoinitiators yield acceptable through cure. IRGACURE® 1300 (a blend of α -aminoketone and benzildimethyl ketal) is the best photoinitiator for promoting through cure for all resins. It is true for the combination R2/R5, which is of particular interest to us. However, IRGACURE® 1300 is not much better than IRGACURE® 819, which yielded favorable results with respect to surface cure.

Summarizing, more than 500 formulations and about 25,000 films were screened in about 6 weeks. The screening suggested a formulation containing R2/R5 (1:1) and IRGACURE® 819 (4% on solids). Follow up experiments on larger scale confirmed the hit. Even with no reactive diluent and with pigment loading tack free surfaces with good sanding characteristics could be obtained that outperformed anything that had been looked at before in our laboratory.

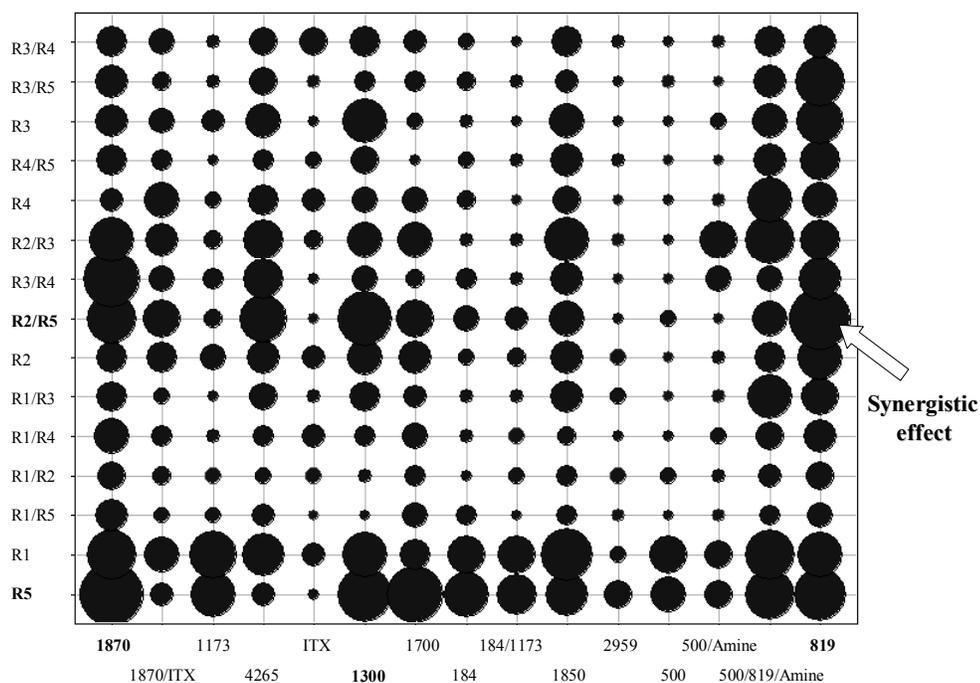


Figure 2: High throughput primary screening results based on the evaluation of \approx 25,000 films followed by a statistical analysis. Shown is the average predicted surface cure for all resin-photoinitiator combinations after curing using a 250 W UV-A light source. The average is taken over all other parameters screened in this experiment. Thus, each circle represents an average of 48 values (3 reactive diluents * 2 photoinitiator concentrations * 4 irradiation times * 2 lamp distances). The bigger the circle the better the surface cure.

Adhesion of this formulation to cold rolled steel was poor though, and we addressed this issue in a secondary screening. About 25 reactive diluents – most of them mono-functional – were tested at two levels (20%, 40% on resin solids) in pigmented formulations based on the original hit (pigment/binder-ratio P/B=0.8). Out of 25 reactive diluents, five exhibited promising results.

The tertiary screening was based on the optimization of the secondary screening. The parameter space spanned by the factors reactive diluent (6 levels), P/B ratio (2 levels), photoinitiator concentration (2 levels), film thickness (2 levels), irradiation time (2 levels), and substrate (2 levels) was explored and 48 films were tested. After further optimization of the

formulation we obtained a mono-cure UV refinish primer formulation exhibiting good performance as a UV primer (**Table 1**). Its properties include good sanding characteristics, excellent hiding, and a tack free surface. Butyl acetate was added to reach spray viscosity and to meet the current US VOC standard of 3.5 pounds/gallon (~420g/l).

Table 1: Highly reactive monocure UV refinish primer guide formulation for spray application. Max. film build ≤ 75 μm dry, 2 min 250 W UV-A lamp, 25 cm distance.

Formulation	pbw
Urethane acrylate (R5, Bayer)	20.6
Epoxy acrylate (R2, Bayer)	20.6
Tri-functional adhesion promoter (CD 9052, Sartomer Company, Inc.)	12.4
Filler (Talc 399, Whittaker, Clark & Daniels, Inc.)	24.5
Filler (VICRON [®] 15-15, Whittaker, Clark & Daniels, Inc.) ^f	17.0
Pigment (TRONOX [®] R-KB-2, Kerr McGee Corp.) ^g	1.4
Pigment (BAYFERROX [®] 303T, Bayer AG) ^h	0.3
BAPO-type photoinitiator (IRGACURE [®] 819, Ciba Specialty Chemicals Inc.)	3.2
	100.0
Add butyl acetate to meet US standard (3.5 pounds/gallon)	
VOC [g/l] (3.5 pounds/gallon ~ 420 g/l)	420

UV Refinish Clear Coat

The development of the UV-A cured clear coat involved an initial photoinitiator screening followed by a series of experimental designs with increasingly narrowing focus. A high-throughput workflow and statistical design of experiments were utilized in the development process. The material variables in the study included urethane acrylate resins, high-functional oligomers, and photoinitiators. Component ratios were also kept variable. The urethane acrylates in this study were analogues of a material with superior weathering resistance. All material variables involved in the development of the clear coat are shown in **Table 2**.

Table 2: Variables involved in the formulation of a UV Refinish Clear Coat (a) all photoinitiators from Ciba Specialty Chemicals, Inc., except Lucerin TPO-L from BASF Corp. (b) experimental products developed by Bayer Polymers, LLC (c) Oligomers obtained from UCB S.A.

Photoinitiator ^a	Urethane Acrylate ^b	High-functional Oligomers ^c
IRGACURE [®] 819	A	Ebecryl 1290
IRGACURE [®] 1850	B	PETIA
IRGACURE [®] 1870	C	

IRGACURE [®] 1700	D
DAROCUR [®] MBF	
DAROCUR [®] 4265	
ESACURE [®] KTO	
LUCERIN [®] TPO-L	
IRGACURE [®] 184	
IRGACURE [®] 907	

At loading levels appropriate for UV-A cure, a series of photoinitiators were tested for formulation color, film color, and surface cure after exposure to a 450W UV-A lamp (UV-F 450) from Panacol-Elosol GmbH.^{iv} Sample preparation included automated methods, and all experiments were conducted on small size samples. The response analysis involved rapid sequential measurements, some of which were also automated. As a result of this screening, IRGACURE[®] 819, IRGACURE[®] 1850, IRGACURE[®] 1870, and IRGACURE[®] 1700 (BAPO products) were deemed non-ideal due to formulation/film yellowing. DAROCUR[®] MBF was eliminated due to surface inhibition. Of the non-yellowing photoinitiators, LUCERIN[®] TPO-L yielded films with the least tacky surfaces, followed by DAROCUR[®] 4265 and ESACURE[®] KTO.

A selection of these UV-A cured films were also analyzed for pendulum hardness and impact resistance. In many cases, the properties of these films were observed to change after three days of exterior post-curing. This is undesirable as it may lead to film shrinkage and delamination. This post-cure phenomenon probably results from the presence of unreacted photoinitiator in the film and/or residual solvent evaporation. It was also determined that film properties for a UV-A cured material were often different from the same film cured with a high intensity light source.^v It would appear that in these cases the UV-A lamp has not completely cured the film.

All of the variables in **Table 2** were used for the first generation screening except for IRGACURE[®] 1850, IRGACURE[®] 1870, IRGACURE[®] 1700, and urethane acrylate D. All formulations suggested by a D-optimal mixture design were assessed for film color, pendulum hardness, and impact resistance.^{vi} Each film was assessed immediately after curing under UV-A and also after three days of exterior post-cure. **Figure 3** shows one way of visualizing the results from this primary screening. This visualization indicates that the increase in hardness upon post-cure is more pronounced for soft, flexible films. Markers for the harder films fall closer to a diagonal line through origin whereas markers for softer films fall above this line. The hardness of films that delaminated upon post-cure is misleading; air entrapment probably resulted in erroneous readings.

^{iv} www.panacol.com

^v High intensity light source was H bulb from Fusion UV Systems, Inc. Energy output measured as UV-V 0.30 J/cm², UV-A 0.40 J/cm², UV-B 0.35 J/cm², UV-C 0.039 J/cm²

^{vi} Mixture designs were generated from Design-Expert software from Stat-Ease, Inc.

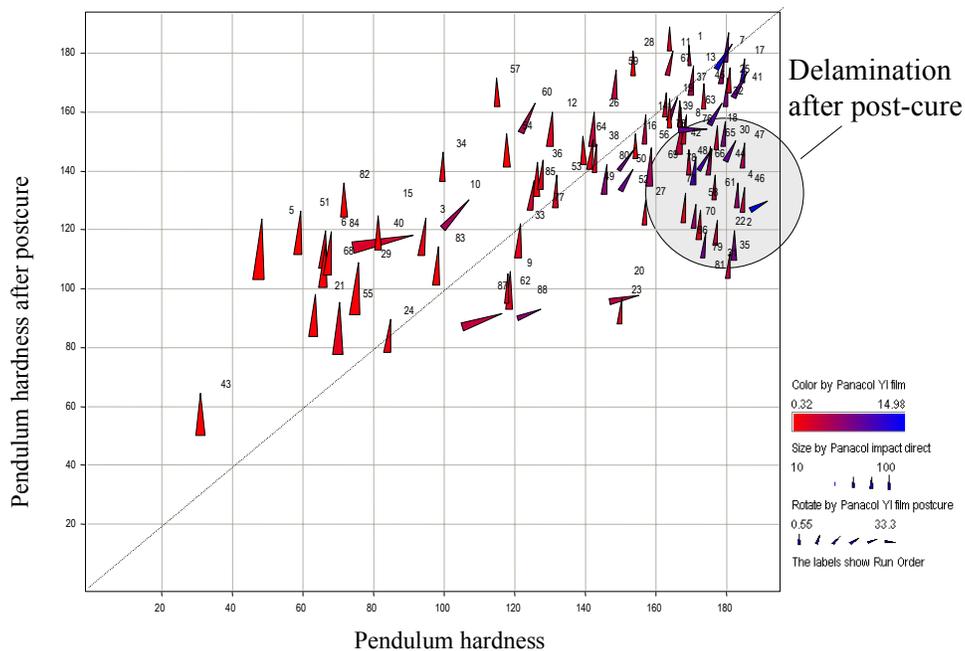


Figure 3: First generation screening results. Pendulum hardness [s] (abscissa), impact resistance [inch pounds] (symbol size), and yellowness index (color) right after UV curing and pendulum hardness [s] (ordinate) and film color (symbol orientation) after postcure.

The results from this primary screening and from the initial photoinitiator screening were used to determine the parameters for the next experimental design.

The second level experimental design generated 32 more formulations, which were assessed in the same manner as those in the primary screening. This screening pointed to a photoinitiator blend involving DAROCUR[®] 4265 and IRGACURE[®] 184. However, the appropriate resin/reactive diluent combination was not found in this mixture space when curing was effected with the UV-F 450. Once again, the information gained from the previous screenings was used to design the next level screening. Given the results in the aforementioned screenings, a switch to a different UV-A source was necessitated. A 415 W H&S Autoshot was used to cure the formulations in the third level screening. A quadratic model was fitted to the impact resistance and pendulum hardness data. This model was used to theoretically optimize for formulations with maximum hardness and flexibility. Several of these predictions were prepared experimentally, and found to exhibit impact resistance of 50 inch pounds and pendulum hardness of 130s. It remains to be seen if these systems, one of which is shown in **Table 3**, will be successful in the automotive refinish market.

Table 3: One suggested guide formulation for monocure UV refinish clear coat. Typical film build is 25 – 50µm dry film thickness, VOC [g/l] @ 20 s DIN 4 cup is 420.

Component	Characteristic	Supplier	pbw
Urethane acrylate B	resin	Bayer Polymers, LLC	29.2
Urethane acrylate D	flexible resin	Bayer Polymers, LLC	23.4

PETIA	high-functional	UCB S.A.	7.0
DAROCUR [®] 4265	photoinitiator	Ciba Specialty Chemicals,	3.2
IRGACURE [®] 184	photoinitiator	Ciba Specialty Chemicals,	0.5
TINUVIN [®] 400	UV absorber	Ciba Specialty Chemicals,	1.3
TINUVIN [®] 292	HALS	Ciba Specialty Chemicals,	0.5
BAYSILONE [®] OL	leveling agent	Borchers GmbH	0.03
Butyl Acetate	solvent		34.8

Conclusions

- The development and use of UV-A lights with tailored binders/photoinitiator combinations will allow the growth of a new automotive refinish market.
- There are significant market drivers for the ultimate “fast cure” technology: auto auctions need something faster, mobile repair units require speed, consolidators have productivity issues, and OEM require end of line repair along with better scratch and mar resistance.
- Introduction of a UV-A primer system will require a UV-A curable clear coat for total market acceptance.
- With the continuous development of lower viscosity oligomers for the primer and clear coats, VOC values should be able to meet current and future standards.

References

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