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UV Refinish Primer and Clear Coat

Hermann Bach, Charles A. Gambino, Larry Galeza, Michael J. Dvorchak, Thomas Fäcke, Christophe Detrembleur, Michael Ehlers*, Holger Mundstock*, Jörg Schmitz*, Jan Weikard*, Bayer Polymers LLC, Pittsburgh, USA and *Bayer Polymers, Bayer AG, Leverkusen, Germany*

UV curable coatings are one of the fastest growing sectors in the coatings industry. In recent years, UV technology has made inroads into a number of market segments like fiber optics, optical and pressure sensitive adhesives, automotive applications like UV cured topcoats, and UV curable powder coatings. The driving force of this development is mostly the quest for an increase in productivity of the coating and curing process. In automotive refinish applications where minor repairs need to be performed swiftly and at ambient temperature, UV technology promises to significantly increase the throughput of cars in a body shop[1-4]. The development of refinish applications breaks new ground in UV technology. Safety concerns associated with the use of UV lamps in body shops as well as economic constraints will likely preclude the use of high intensity light sources. Relatively inexpensive low intensity lamps that emit only in the UV-A region of the electromagnetic spectrum are taking their place thus posing new challenges to resin developers and formulators.

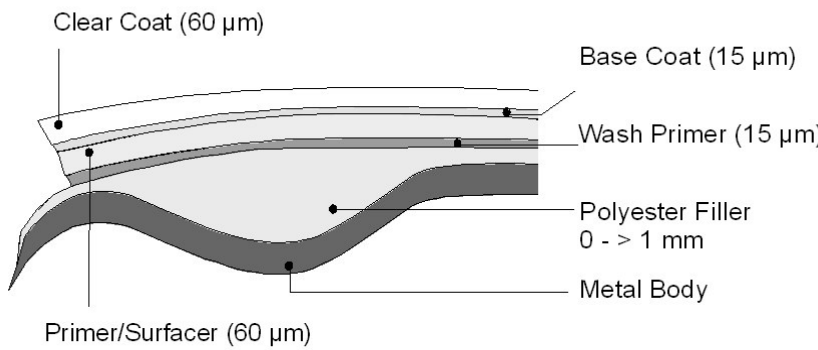

Figure 1: Typical build-up of an automotive refinish system. Total film thickness approx. 150 µm (w/o filler).

A typical build-up of a refinish system consists of wash primer, primer/surfacer, base and clear coat (Figure 1). A UV clear coat system can be either based on Dual Cure[5] or monocure technology. In this paper, we report on our developments of UV refinish primer and clear coat guide formulations based on Bayer Polymers acrylate resin technology. In the primer development, high throughput experimentation[6] was employed to select resin combinations exhibiting optimum UV reactivity under low intensity UV-A irradiation. To this end, 480 combinations of resins, photoinitiators, and reactive diluents were screened for surface cure and through cure at various lamp distances and irradiation times resulting in the testing of more than 25,000 coating films. The clear coat development involved the syntheses of novel flexible urethane acrylates as well as extensive blending studies to yield formulations exhibiting the targeted balance of hardness, flexibility, formulation color, film color, and reactivity. Again, high throughput experimentation tools and statistically guided experimentation to explore the complex parameter space were critical success factors.

UV Refinish Primer

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.

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 2). 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, an 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 experiment 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)[b] from Dr. HOENLE AG[7] under varying conditions with respect to curing 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.

1:1

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 2: 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)[c].

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 3). 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 (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. 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.

Through cure analysis shows that most photoinitiators yield good through cure. IRGACURE® 1300 (blend of α-aminoketone and benzildimethyl ketal) is the best photoinitiator with respect to through cure. This seems to be true for all resins. It is true for the combination R2/R5, which is of particular

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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 yielded a lead formulation containing R2/R5 (1:1) and IRGACURE® 819 (4% on solids). Follow up experiments on larger scale confirmed the lead. 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.

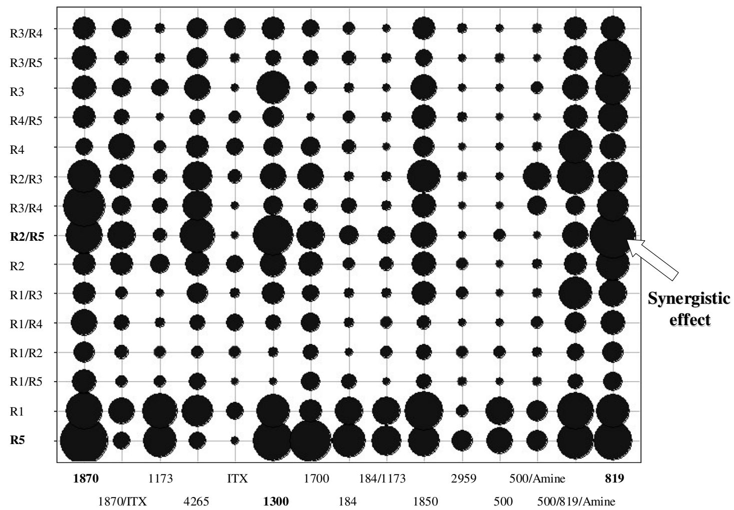

Figure 3: High throughput primary screening results based on the evaluation of ≈ 25,000 films followed by a statistical analysis. Shown is the average predicted surface cure for all resin-photoinitiator combinations after curing using a 250 W UV-A light source. The average is taken over all other parameters 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 lead formulations (pigment/binder-ratio P/B=0.8). Two pigment packages differing by the amount of TiO_2 relative to other fillers (talcs etc.) were tested. Four formulations per reactive diluent were used and were initially applied to cold rolled steel panels in order to identify the most promising adhesion promoters for a subsequent direct to metal trial. Out of 25 reactive diluents, 5 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 (Figure 4). 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).

In Europe, an alternative formulation with a lower VOC content (≤250 g/l) was developed based on urethane acrylate R5, which is the most reactive resin (disregarding blends) according to the screening data in Figure 3. The formulation contains fillers and reactive diluents commonly employed in Europe. We used a combination of an adhesion promoter (EBECRYL® 168)[d] and a mono-functional aromatic reactive diluent (PHOTOMER® 4039)[e] along with a blend of two photoinitiators (IRGACURE® 184 and IRGACURE® 819). This formulation is detailed in Figure 5. It requires higher light intensities to achieve surface cure (e.g. the 900 W UV-A lamp PANACOL UV-F 900 by PANACOL-

[d] EBECRYL is a registered trademark of UCB S.A., Belgium
[e] PHOTOMER is a registered trademark of Cognis Deutschland GmbH & Co. KG, Germany

ELOSOL GmbH, Germany)[8]. The primer exhibits good sandability, excellent adhesion to cold rolled steel, and can be cured at a dry film thickness of up to 90 µm.

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

Figure 4: Highly reactive monocure UV refinish primer guide formulation for spray application. Max. film built ≤ 75 µm dry, 2 min 250 W UV-A lamp, 25 cm distance. Additives and fillers obtained by US suppliers.

Formulation	pbw
Urethane acrylate (R5, Bayer)	55,17
Acidic adhesion promoter (EBECRYL® 168, UCB S.A.)	1,65
Mono-functional aromatic diluent (PHOTOMER® 4039, Cognis)	10,98
Filler (Talkum AT 1, Norwegian Talc)	10,98
Filler (China Clay Grade B, ECC International)	10,98
Pigment HEUCOPHOS® ZPA (Dr. Hans Heubach GmbH&Co KG)[i]	5,49
Pigment (TRONOX® R-KB-2, Kerr McGee Corp.)	1,38
Pigment (BAYFERROX® 303T, Bayer AG)	0,08
Photoinitiator blend (IRGACURE® 184/819, 3:1, Ciba Speciality Chemicals Inc.)	3,29
	100,0
Add butyl acetate for spray viscosity	
VOC [g/l] @ 25 s DIN 4 cup	240

Figure 5: Very high solids monocure UV refinish primer guide formulation for spray application. Max. film built ≤90 µm dry, 5 min 900 W UV-A lamp, 20 cm distance. Additives and fillers obtained by EU suppliers.

UV Refinish Clear Coat

In the UV refinish clear coat development, the following key elements need to be taken into account:

- Hardness – flexibility balance. Lack of flexibility is a well-known shortcoming of polymer networks based on radical polymerization.
- Reactivity under low intensity UV-A. The photoinitiator type and concentration, the double bond density and functionality, and the degree of oxygen inhibition at the surface strongly affect the UV-reactivity. Moreover, in order to obtain a cured film with good weathering stability, unreacted double bonds have to be kept low (ideally ≤10%) after irradiation with low intensity UV-A light.
- Formulation and film color.
- Application properties like clear coat – base coat compatibility, flow, and leveling.

The starting point of our development was an aliphatic urethane acrylate exhibiting excellent weathering characteristics (U1). In addition, a lower viscosity urethane acrylate under development (U2), a flexible version of U1 (U3), the hexafunctional urethane acrylate EBECRYL® 1290 (UCB S.A.) (U4), and a tri-/tetrafunctional reactive diluent (PETIA, UCB S.A.) based on acrylated pentaerythritol providing high functionality were considered. Statistical design of experiment and high throughput experimentation was employed in a multi-step development and optimization of a clear coat guide formulation. Initial screening experiments dealt with formulation color, film color, and film tackiness using U1 – U3 and 8 commercially available photoinitiators. Films were cured using a 450 W UV-A-lamp UV-F 450 from PANACOL-ELOSOL GmbH[10]. The results enabled us to narrow down the choice of photoinitiators to mixtures containing mono acyl phosphine oxide, i.e. DAROCUR® 4265 or ESACURE® KTO[j], and IRGACURE® 184. In these experiments, we observed the phenomenon of postcuring. Films that were subjected to sunlight subsequent to UV irradiation dramatically changed their mechanical behavior. In particular, the pendulum hardness increased. We assigned this phe-

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[g] VICRON is a registered trademark of Specialty Minerals Inc., USA
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[i] HEUCOPHOS is a registered trademark of Dr. Hans Heubach GmbH & Co. KG, Germany
[j] ESACURE is a registered trademark of Fratelli Lamberti SPA, Italy

nomenon to residual photoinitiator as well as unreacted double bonds in the cured films leading to further crosslinking initiated by sunlight.

In a mixture-design experiment the parameter space spanned by resins U1 – U4, PETIA, and the remaining photoinitiators was explored for hardness – flexibility balance. The desired balance of hardness and impact resistance could not be found in this mixture space. As a consequence, we replaced U3 with a further flexibilized resin (U5) of approximately the same functionality. Also, we eliminated resin U2 due to similar performance compared with U1 (formulation viscosity not considered) and U4 due to its high viscosity. Although these experiments did not lead to an optimal resin choice, they did confirm our photoinitiator pre-selection.

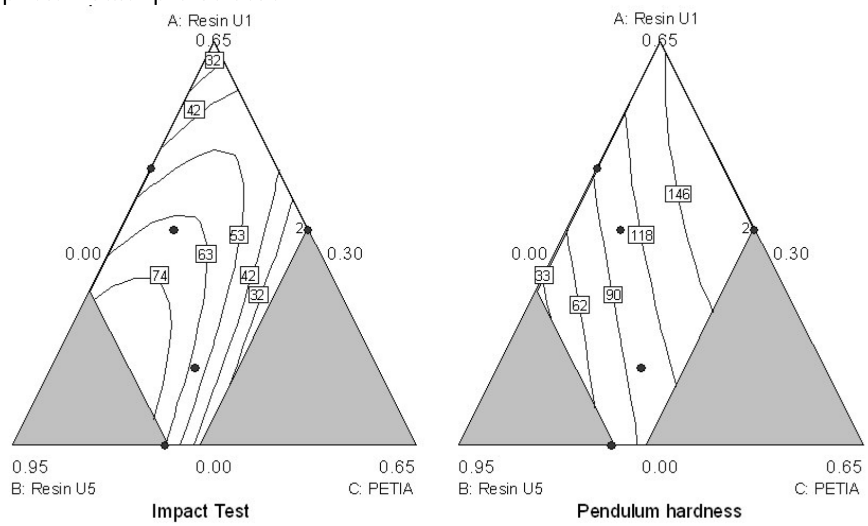

Figure 6: Contour plot of direct impact resistance [inch pounds] and pendulum hardness [s] of a three component mixture design involving U1, U5, and PETIA at DAROCUR® 4265 level of 5%. The contour plots are predictions based on fitting a quadratic statistical model to the data set.

A second mixture design based on a quadratic model and involving 18 formulations of U1, U5, PETIA, and DAROCUR® 4265 was tested for hardness and direct impact resistance. Figure 6 shows two model based contour plots of direct impact resistance and pendulum hardness. Please note that the ratio of U1 and PETIA has a strong nonlinear effect on the direct impact resistance.

Formulation	pbw
Urethane acrylate U1 (Bayer)	29,2
Highly flexible urethane acrylate U5 (Bayer)	23,4
Acrylated pentaerythritol (PETIA, UCB S.A.)	7,0
DAROCUR® 4265 (Ciba Specialty Chemicals)	3,2
IRGACURE® 184 (Ciba Specialty Chemicals)	0,5
UV-Absorber (TINUVIN® 400, Ciba Specialty Chemicals) [k]	1,3
HALS (TINUVIN® 292, Ciba Specialty Chemicals)	0,5
Leveling agent (BAYSILONE® OL 44, Borchers GmbH) [l]	0,03
Butyl acetate	34,8
	99,93
Add butyl acetate for spray viscosity	
VOC [g/l] @ 20 s DIN 4 cup	420

Figure 7: One of the monocure UV refinish clear coat guide-formulations for spray application.

Based on the thorough analysis of these results we selected formulations exhibiting maximum impact resistance and maximum pendulum hardness. As apparent when considering the plots in Figure 6, various mixtures of the two resins and PETIA meet these criteria. We selected three formulations that were significantly different in terms of the component-mixing ratio for further testing. These mixtures were formulated into UV clear coat guide formulations, one of which is detailed in Figure 7. They exhibit a VOC of 420 g/l and contain a flow and leveling agent, a UV absorber, a HALS and another photoinitiator. A 900 W UV-A lamp (H+S AUTOSHOT or PANACOL UV-F 900) at 4 min irradiation

[k] TINUVIN is a registered trademark of Ciba Specialty Chemicals Holding Inc., Switzerland
[l] BAYSILONE is a registered trademark of Bayer AG, Germany

time was used for curing. When fully cured (including UV lamp and some postcuring), films exhibited high gloss, good weathering characteristics, solvent and impact resistance and a pendulum hardness.

Whether this combination of properties would meet the requirements of a commercial UV refinish clear coat will need to be evaluated in collaboration with our customers. Ongoing trials aim at reducing the VOC to 250 g/l.

Outlook: unsaturated polyester (UPE) putties cured by low intensity UV-A lamps

Required properties of putties (polyester fillers in Figure 1) in automotive repair are fast curing even at high film thickness and ambient temperatures and good adhesion to metal. The cured filler has to exhibit good characteristics in dry sanding.

State of the art are rapidly curing putties (potlife ~5 min) based on amine accelerated UPE dissolved in styrene, which are cured by aromatic peroxides. An alternative technology are spray applied putties comprising air drying gloss polyesters dissolved in styrene. Curing of the latter is accomplished by adding cycloaliphatic peroxides/Co-salt mixtures. For both types, the user has to employ the right dosage of the hardener, mix carefully and homogeneously with the putty and apply quickly before the system gels. To extend the pot-life, we investigated the cure of UPE putties by low intensity UV-A lamps and found positive initial results with medium flexible, highly reactive unsaturated polyesters in thick films. Standard talc and barytes-extenders can be used in typical amounts but pigments like TiO_2 and FeO prevent through curing in higher film thickness.

Component	Remarks	pbw
UPE resin (R&D product Bayer)	67% in styrene	32.60
IRGACURE® 184 (Ciba Specialty Chemicals)	Photoinitiator	0.05
IRGACURE® 819 (Ciba Specialty Chemicals)	Photoinitiator	0.10
AEROSIL® 200 (Degussa AG)[m]	Antisettle agent	0.65
FINNTALC® M 40 (Mondo Minerals)[n]	Talc	42.50
LUVOTIX® R- RF (Lehmann & Voss)[o]	Thixotropic agent	0.65
Heavy Spar EWO (Sachtleben Chemie)	Barytes	19.60
Styrene to adjust consistency		3.90
total :		100.05

Binder	32.60 %
Photoinitiators	0.15 %
Inorganic extender	63.40 %
Styrene	14.70 %

Curing: 900 W UV-A lamp 20 cm distance:

film thickness	curing time
0,8 mm	4 min
1,6 mm	6 min
2,4 mm	7 min

Figure 8: Guide formulation of a UV curable UPE putty.

The formulations in Figure 8 exhibit good surface and through curing properties up to 2,5 mm film thickness using a 900 W UV-A lamp (PANACOL UV-F 900). The putty exhibits good sanding properties and good adhesion to cold rolled steel while having no pot-life. Provided the curing time can be reduced to 2 – 5 min, UPE based UV curing putties may have a good chance to be successfully introduced to the automotive refinish market along with UV curing primers and clear coats.

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[m] AEROSIL is a registered trademark of Degussa AG, Germany
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