

UV CURE AUTOMOTIVE REFINISH, CLEARCOATS, AND PRIMERS



A T T H E S P E E D

“The automotive-refinish coatings market is forecast to surpass U.S. \$6.3 billion globally in 2021.”

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INTRODUCTION

Over the past decade, the automotive-refinish industry has been forced to look at innovative technologies to reduce volatile organic compound (VOC) content and hazardous air pollutants (HAPs) while providing a rapid return to service of the consumer’s vehicle.

UV-A-cured one-component (1K) auto-refinish primers were first introduced in the mid-1990s. UV-A clearcoats were subsequently introduced in the late 1990s.

Materials have continued to be developed and pushed to mimic the classic two-component (2K) solvent-based polyurethanes (PURs); however, slow acceptance by the auto-refinish market over the past two decades is indicative of a market that is difficult to change.

The automotive-refinish coatings market is forecast to surpass U.S. \$6.3 billion

globally in 2021.¹ This market is expected to increase by 5.4% CAGR between 2021 and 2031. The main technology types are solventborne, waterborne, and UV cure. The classic coating layers are primers, basecoats, topcoats, and clearcoats.¹ A specific parameter in the refinish area that must be addressed is the bottleneck of a 2-hour cure for the primer before it can be sanded. Current UV-cure primers can be sanded within 2 minutes. The need to lower VOCs and VHAPs is among the current constraints for all technologies. A hurdle that has recently been cleared in the UV-cure sector is the price barrier for UV light equipment. Reports for the market have UV LED units being priced under \$1,000.² This market continues to consolidate and will be required to decrease refinishing speeds to remain competitive.

This article will review the history of the UV-cured 1K and 2K auto-refinish market and formulations for primers and clearcoats. It will also attempt to look at current UV-cured 1K and 2K auto-refinish primers and clearcoats in the global market, new formulations, and new developments in UV equipment.



O F P H O T O N S

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CHANGES IN THE AUTOMOTIVE OEM AND REFINISH MARKETS

The automotive OEM and refinish markets have undergone incredible changes in both polymer technologies and substrates over the past several years. The original markets used nitrocellulose lacquers when the only color you could specify was black. Today, the number of 2K reactive primers and clearcoats, as well as basecoats, has pushed the limits of polymer chemistries. With the pressures to lower VOCs and VHAPS, solvent-based systems have shifted to water-based chemistries. The OEM's substrates have evolved from the traditional steel metals to composites and aluminum.

INTRODUCTION OF UV-A-CURABLE AUTO REFINISH

Early attempts to develop a UV refinish clearcoat

The earliest paper that reviews the use of UV-cure clearcoats for auto refinish

was focused on the use of a UV Flash lamp (Xe lamp).³ The idea was that after application, the fully formulated UV clearcoat would be flashed several times (by the Xe lamp) to activate the photoinitiator (PI) for this dual-cure system. The dual-cure crosslinking of this system was done with a polyol that had acrylate and hydroxyl functionality in combination with a dual-cure crosslinker that possessed acrylate and polyisocyanate functionality. This system was a 2K system. Due to the Xe lamp wavelength occurring around 480 nm, the use of a bis-acylphosphine oxide photoinitiator was specified for this use. Cure was done by using 10 to 20 flashes at 20 °C.

Early patents on UV-A cure auto-refinish primers

The earliest U.S. patent estates in this technology workspace, which date to 2001, were developed around UV oligomers that were used with bis-acylphosphine oxide PIs and full spectrum 250W iron-doped light sources that were then filtered down to only emit in

the UV-A region.⁴ The cure time with this configuration was 1 minute. The reason that the light was filtered was to prevent worker exposure to UV-B and UV-C wavelengths. An issue with this system was the need for a solvent wipe due to the surface of the film that had become inhibited by oxygen. This surface-inhibition issue would plague this technology. Future work would lead to keeping high levels of oligomers, low levels on acrylates monomers, and new developments in light sources. In addition, the PIs that were used needed to work above the absorption window of the fillers and pigments. The resultant UV-A-cured primer had to be able to be sanded immediately after it had cured.

Technology Insight: Matching the PI with the UV light source and pigments absorption/ transmission

When selecting a PI, it is important that every effort is made to match the PI to the wavelength of the UV light source to obtain maximum crosslinking of the coating. In pigmented coatings, this becomes even more important due to the

absorption of UV light by most pigments. *Figure 1* shows the absorption/transmission spectrum for a rutile version of titanium dioxide (TiO_2).

This absorption/transmission spectrum is critical when using certain PIs. In fact, UV light sources that are in the UV-B and UV-C ranges cannot fully activate the PIs through to the bottom of the applied coating. The formulator then needs to find a light source that operates in the UV-A wavelength since the rutile (TiO_2) will block the absorption of the UV light.

Figure 2 shows the proper source of UV-A wavelength that operates above 365nm using gallium to spectrally shift a traditional low-wattage long-wavelength fluorescent (FL) bulb to be above the absorbance of the rutile (TiO_2).

It is important to utilize PIs that are not blocked by the rutile (TiO_2), as shown in *Figure 3*. Typically, PIs, such as PIs a, b, and c shown in *Figure 3*, that are used in unpigmented coatings will not work with pigmented systems because the UV light is not able to

penetrate the coating and will result in a cured upper surface and an uncured lower surface. However, to resolve this issue, PIs that operate in the 380nm and above cut-off will activate and fully cure

the coating all the way to the substrate as illustrated by PI d in *Figure 3*.

UV light sources and their intensities also play a significant role in curing and through-curing the pigmented coating.

FIGURE 3—Absorption curves for photoinitiators used. a=Benzoine ether absorbs in the 280 to 360 nm range, b=Irgacure 651 absorbs in the 280 to 360 nm range, c=Darocur 1173 absorbs in the 280 to 360 nm range and is blocked by the rutile (TiO_2). d=Lucirin TPO absorbs above 365 nm to allow proper through-cure of the coating due to high pigment loading by rutile (TiO_2).

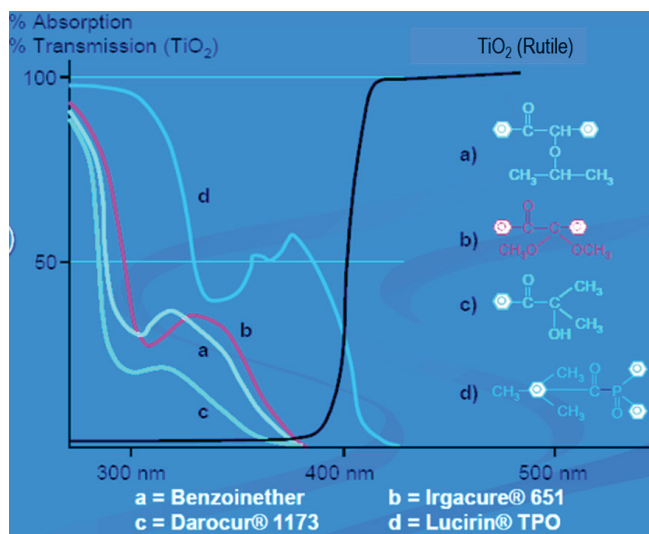


FIGURE 1—Absorption/transmission spectrum of rutile (TiO_2) that is important to consider when attempting to cure pigmented UV nail gel formulations.

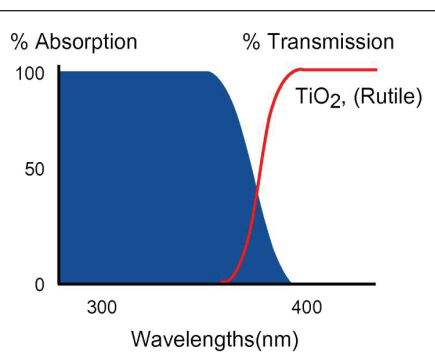


FIGURE 2—Proper source of UV-A wavelength.

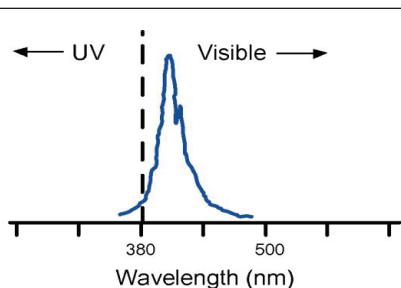


FIGURE 4—UV through-cure of various rutile (TiO_2) formulations; pendulum hardness values, sec vs P/B (pigment to binder) ratio vs. thickness, μm . These formulations were compared against A.) UV Arc @ 200W; B.) 300W; C.) TLO3 (GA-FL; 60W) @ 200W, and D.) TLO3 (GA-FL; 60W) @ 300W; E.) Electrodeless V (GA) and D (Fe) @ 300W; and F.) Electrodeless V (GA) and D (Fe) @ 600W UV light sources.

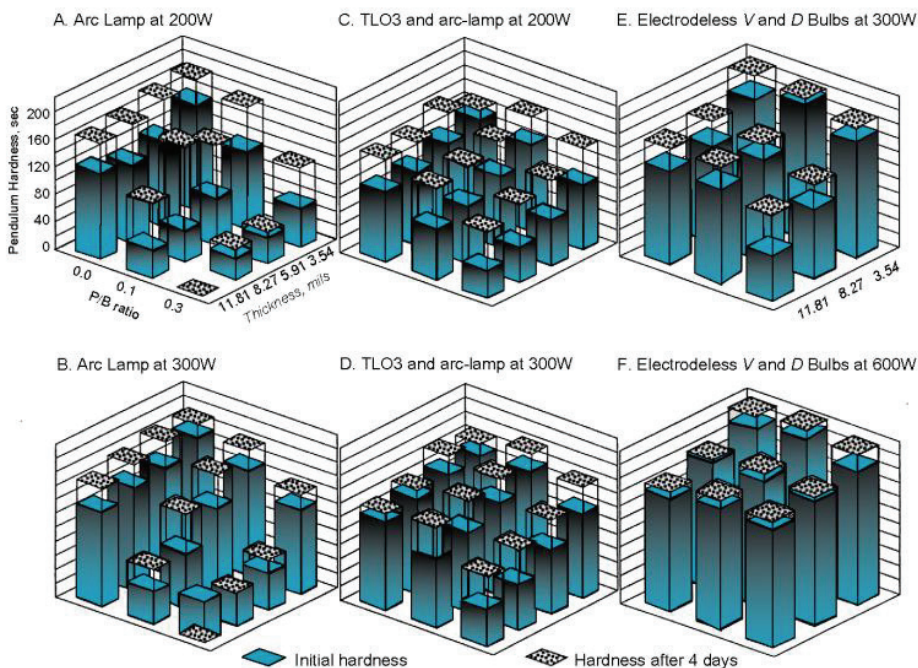


Figure 4 shows how pendulum hardness values vary greatly depending on the UV light source used.

The ability to cure coatings that contain up to 30% rutile (TiO_2) has an impact on through-cure. The higher the pigmentation, the less the chance for through-cure. In addition, a thicker pigmented coating also results in no through-cure. Using the same UV-cure formulation, researchers have shown that by just increasing the energy density, one can get better through-cure as shown in Figure 4 (A and B) using UV arc lamps at 200W and 300W. By using the addition of TL03 UV Lamp (gallium-doped, low-wattage, long-wavelength fluorescent; Phillips 60W), one enhances the deep penetration of the UV light into the coating, which results in better through-cure and hardness development. Even better performance results are shown in Figure 4 (E-gallium doped and F-iron doped) and the use of high-performance (300W and 600W) UV light sources results in the best through-cure and hardness development.⁵

In the UV-A auto-refinish market, the first UV light sources were gallium-doped mercury high-wattage long-wavelength sources that are close to Figure 4 (C and D). Early work with these gallium-doped mercury high-wattage, long-wavelength sources allowed the formulator to cure highly pigmented oligomeric chemistries in about 2 to 3 minutes.

Automotive OEM technical paper on UV auto-refinish clearcoats

One of the OEMs got in on the act of evaluating UV-cured clearcoating supplied by the OEM paint company to evaluate UV clearcoats.⁶ In the OEM's, evaluation, they talk about the need for hindered amine light stabilizers (HALS) and UV absorbers (UVAs). It is surprising that an OEM would be evaluating UV clearcoats so early in the development cycle. The only plausible reason for this interest would be the ever-increasing need to evaluate the best technology for the automotive OEM environment. This early evaluation uncovered the issues with unacceptable brittleness of the UV-cured clearcoat technology. It found that the HALS and UVAs slowed this process, but still eventually embrittles to an unacceptable level for an automotive clearcoat.

2003–2010: Timeline of the UV-cured 1K and 2K auto-refinish market and formulations for primers and clearcoats

03

2003 patent application by a paint company on UV-A-cure clearcoats

In 2003, a UV cure paint company filed a patent application on the development of a UV-A-cure clearcoat.⁷ In this application, references are made to the system being 1K, UV-A/UVB and UV-A-only curable. The cure time is reported to be 4 minutes with no gloss reduction or cracking when subjected to weathering via SAEJ1960. This was a better performance than what was reported earlier by the automotive OEM during its testing of UV-A-cure clearcoat prototypes.

03

2003 RADTECH report on use of UV-A-cure primer systems in body shops

A 2003 report reviewed the actual use of UV-A primer systems.⁸ The report detailed why the body shops were using the technology. The following list of benefits are compelling arguments: 1) saving 25% to 88% time on each job; 2) less preparation time; 3) disposable utensils use is reduced; 4) less masking; 5) no flash times required between layers; and 6) less waste over a 2K system. All four body shops interviewed did not see any downside to the technology. However, the article states the need for a UV-A auto-refinish clearcoat.

05

2005 investigation of a UV and UV-A flash lamp for a UV-cure primer

This investigation into the use of a UV flash lamp showed that flashing 10 to 40 times the UV primer formulation without extender/pigment had a residual double bond content of 1% or less. However, when the UV primer utilized extender/pigments, the relative double-bond conversion ranged from 22.8% to 7.1% when subjected to flashing 10 to 40 times. This is the expected result due to the mismatch of photoinitiator in response to extender/pigment that has been previously studied.⁹ However, the researchers did adjust the photoinitiator from one designed for clearcoatings to one that is optimized for pigmented coatings, and the result was they did obtain bulk cure but suffered poor surface cure due to oxygen inhibition.

06

2006 patent application on dual-cure UV clearcoat spot repair

The concept in this patent application is to use a dual-functional oligomer that has acrylate as well as polyisocyanate to develop a spot blender in automotive refinishing with a focus on spot repair.¹⁰ This clearcoat spot repair would be done by applying the coating after preparation of the surface, then applying a shortwave infrared radiation for three minutes. UV-A radiation would then be applied at a dose of 4,000 mJ/cm². After this curing, the coating surface was easily polished without defects.

06

2006 patent filed by an automotive OEM paint company on a UV-A primer that has high pigmentation levels and extremely low oxygen inhibition

A 2006 patent pushed the level of the technology away from systems that needed to be solvent-wiped after UV-A cure to remove materials that had become inhibited by oxygen.¹¹ This technology also pushed the primer to a level of pigmentation that is traditionally found in conventional 2K primer systems. The technology reports on the use of a 400W UV-A light that is held 10-30 cm away, curing for 1 to 3 minutes at a thickness of 200 microns. The patent reports the ability to sand the primer right after UV curing and the panel has had time to cool.

07

Automotive OEM technical paper on scratch performance of three UV-cure clearcoats

In 2007, an automotive OEM technical paper reviewed the performance of three UV-cure clearcoat technologies against a thermally cured acrylic/melamine/silane clearcoat.¹² The testing showed that two of the UV clearcoats performed better than the thermally cured acrylic/melamine/silane clearcoat in the AMTEC-Kistler testing. The AMTEC-Kistler testing simulates the performance of the clearcoats to scratches created by running the vehicle through a carwash. The UV clearcoats were shown to have superior fracture resistance. With the kind of performance shown in this article, it is important to understand that a UV-cure clearcoat for an end-of-line repair is possible.

07

Patent filed in 2007 that uses a structure to UV cure a vehicle

In 2007, a patent was filed to UV cure paint on automobiles.¹³ The structure would be used to apply UV-curable paints and when completed, allow the use of natural sunlight to cure the paint. This structure is particularly suited for the use with UV-cured paints for the automotive market. The concept of only using natural sunlight is intriguing.

09

Patent application filed in 2009 by an OEM paint company develops a UV-cure spot blender for automotive clearcoats

This patent application is developed around the use of a spot blender using a 2K dual-cure and 3K dual-cure thiol-ene based system.¹⁴ The system after applied to the substrate is subjected to an AutoShot UV-A 400 curing lamp for 5 minutes at a distance of 10 inches.

10

OEM awarded the 2010 RADTECH Emerging Technology Award for in-line UV spot repairs

At the 2010 RADTECH conference, an OEM auto manufacturer was awarded an Emerging Technology Award for in-line spot repairs.¹⁵ This in-line repair by UV-cure material is reported to reduce the cycle time by 50% as compared to the traditional catalyzed materials. At that point in time, the OEM was evaluating this process to determine whether this UV-cure system will meet the OEM's durability specifications and test procedures. Once the UV systems pass all submission requirements, it would be implemented after facilities modifications were made.

PRODUCTS AND INNOVATION IN THE MARKET

Combinatorial chemistry approach to identify the best non-air-inhibited formulation

Technology Insight: UV-cure oxygen-inhibition Issues

As mentioned earlier, oxygen inhibition issues with UV cure will result in coatings that have poor surface cure. Work done on early UV-cure systems looked at the depth of penetration that ambient air had on the problem of oxygen inhibition.

It is obvious from *Figure 5* that oxygen in the uncured coating will result in less-favorable cure—potentially all the way down to 50 μm .¹⁶ This potential problem resulted in development of several new techniques to solve this issue of oxygen inhibition. Some of the earliest techniques utilized paraffinic waxes that were of low density and would rise from within the coating to the surface, blocking the ambient oxygen. This technique works, but the paraffinic wax needs to be ground and polished to result in a high-gloss finish.

Another old technique shown in *Figure 5* was the use of free radical PIs in combination with allyl ethers in the presence of oxygen to form hydroperoxides to prevent oxygen inhibition at the surface. Amines and thiol-enes will also work in mitigating oxygen inhibition. However, amines result in yellow color shades especially in light-colored

coatings. Thiol-ene based coatings emit strong odor before, during and after UV curing and are not a preferred chemistry for UV-cured nail gels. Another method to prevent oxygen inhibition is the use of inert gases such as nitrogen, argon, and carbon dioxide.

Technology Insight: UV cure and free radical oxygen inhibition

To overcome these issues, the formulator can look at the several chemical techniques to override the oxygen inhibition. As seen in *Figure 6*, when the free radicals are formed, oxygen in the environment quenches the PI to an unexcited non-reactive state. This quenching lowers the number of polymeric chains and thus lowers crosslinking within the system. As the first step of *Figure 6* shows, the reaction forms an oxygen-based free radical that then seeks another free radical, and the chain terminates as shown in the second step. This classically results in an uncured coating surface.¹⁷

Technology Insight: Methods for mitigating oxygen inhibition during UV cure

Numerous techniques have been used to mitigate oxygen inhibition. As shown in *Table 1*, these oxygen mitigation techniques offer several methods that work only to a certain degree.¹⁸

Inert gases work quite well since the coating is absent of oxygen so no oxygen inhibition can occur. In fact, electron beam curing will only work when done

in an inert atmosphere. Paraffinic waxes work well also but complicate the issue with gloss because paraffinic waxes migrate to the surface and result in low gloss. Two additional steps are needed to bring the UV-cured coating back to its original gloss by first grinding away the wax and then buffing and polishing the surface back to a high gloss. Barrier coatings work but add an additional step in the process and are problematic on contoured surfaces. Increasing the PI concentration is also an easy fix, but it is costly and can reduce the coating properties. Also increasing the UV light intensity can help override the oxygen inhibition issues but could result in coating degradation. Thiol-ene based acrylate (mercapto acrylate) is currently being used in the UV-cure industry but results in “post odor” of the UV-cured coating. Amines are also used but result in yellowing and “post odor” of the UV-cured coating. Ether acrylate-based chemistries are used but might result in poor performance properties of the cured coating.

In 2003, two articles put the ability of a UV-cure primer and clearcoats to the test.¹⁹⁻²⁰ These papers looked at the UV technology and its ability to have good hiding, sand-ability, and good adhesion to all substrates. Another requirement of the primer was that it needed to have a tack-free surface without a solvent wipe. A screening was done using six independent factors, namely UV-curable resins, reactive diluents, photoinitiators,

FIGURE 5—Depth of penetration by ambient oxygen in a UV-cure coating. This oxygen migration into the coating is the source of oxygen inhibition by quenching the chain propagation of the free radical. The depth of oxygen penetration can be as high as 50 μm .

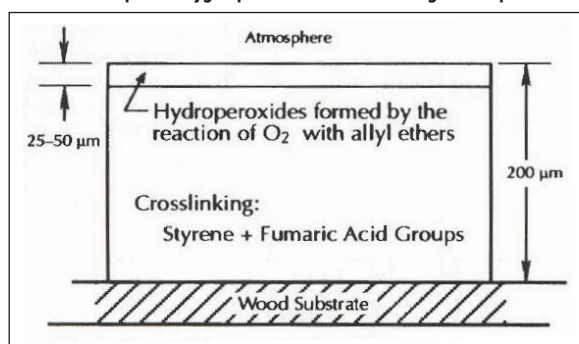
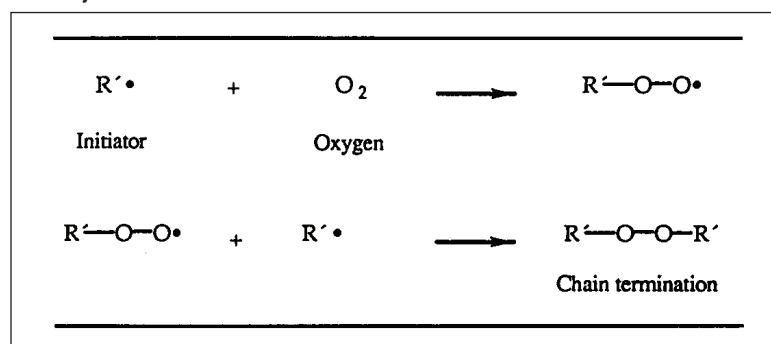


FIGURE 6—Chain termination of the free radical initiator by oxygen. When the free radical is formed, oxygen in the environment quenches the PI to an unexcited non-reactive state. This quenching lowers the number of polymeric chains and crosslinking within the system. As can be seen in the first step, the reaction forms an oxygen-based free radical that then seeks another free radical and then chain terminates as shown in the second step. This classically results in the formation of an uncured surface.



“Numerous techniques have been used to mitigate oxygen inhibition.”

TABLE 1—Methods to Mitigate Oxygen Inhibition Showing Advantages and Disadvantages.
(These techniques can include, but are not limited to, the following methods: uses of inert gases, waxes, coatings, increased PI concentration, increased light intensity, and use of, thiols, amines, and ethers.)

METHOD	ADVANTAGES	DISADVANTAGES
Inert Gas	Does not adversely affect coating properties	Expensive; difficult to implement
Waxes	Inexpensive	Affects final coating properties; time needed for migration
Films	Good solution when film becomes part of product	Cost/disposal of film when not part of product
Increase PI Concentration	Easy to implement	Increased residuals/by-products; reduced coating properties
Increase Light Intensity	May no affect coating properties	Part of existing equipment; cost
Thiols	Improved thermal resistance; reduced moisture absorption; improved adhesion	Odor
Amines	Inexpensive; possible improved adhesion	Yellowing upon after cure; residual odor; moisture sensitivity
Ethers	Can be used in large quantities	Affects coating properties; reduced temperature resistance; possible reduced water resistance



FIGURE 7—Factors and levels covered in the search for formulations exhibiting tack-free surfaces when cured using low-intensity 250W UV-A lamp. (*Bayer, # Ciba Specialty Chemicals Inc.; Rahn AG)

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 #				

photoinitiator levels, irradiation time, and distance from the lamp. In this evaluation, the so-called Edisonian method meets the combinatorial world of chemistry.

In this analysis, more than 15,000 films were evaluated to identify synergistic effects.

Additional development work eventually led to the evaluation of more than 500 formulations and 25,000 films that were evaluated in about 6 weeks. The results of this testing led to a specific graphic as shown in Figure 8.

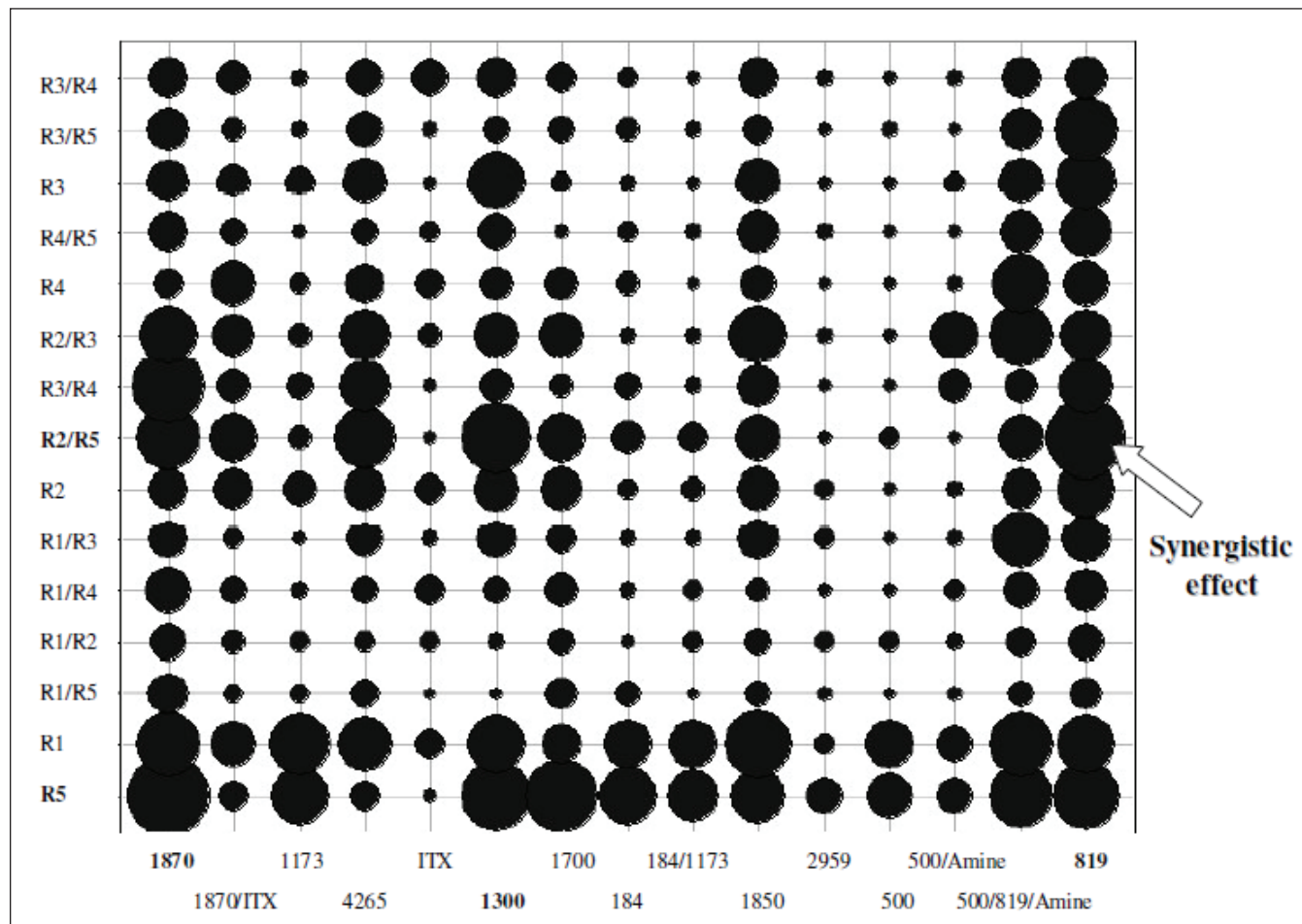
Figure 8 shows the only way to uncover the full surface cure of a UV-A system is to run massive amounts of tests to determine whether a combination or synergistic effect could be

uncovered. In this test protocol, the R2/R5 along with IRGACURE®819 showed a synergistic effect. Even though the test resins were evaluated in the past, it was surprising that they cured as well as they did without surface tack (i.e., surface inhibition). All this testing was done in clears but were then further evaluated in pigments systems. The pigmented systems were evaluated at a P/B=0.8, $\leq 75 \mu\text{m}$ dry-film thickness, 2 minutes under a 250W UV-A lamp at 25 cm distance. The resultant primers had no surface tack and required no surface solvent wipe before the traditional sanding step.

Development work was also revealed in these papers that showed the development of a 1K UV-A-curable clearcoat.

Issues that the paper reveals about developing this 1K UV-A curable clearcoat are: 1) lack of flexibility of polymers based on radical polymerization, 2) keep the unreacted double bonds very low ($\leq 10\%$) due to post-cure issues, 3) formulation and film color due to visible light photoinitiators, and 4) primer, basecoat, and clearcoat compatibility. The testing finally developed a low post-curing clearcoat that had high gloss, good weathering characteristics, solvent resistance and impact resistance, as well as good pendulum hardness. However, future work is needed to look at adjusting these UV-cure clearcoat systems to the exact performance expected out of a conventional 2K PUR system.

FIGURE 8—High-throughput primary screening results based on the evaluation of more than 25,000 films followed by a statistical analysis. Shown is the average predicted surface cure for all resin-photoinitiator combinations after curing using a 250W 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, and 2 lamp distances). The bigger the circle, the better the surface cure.



Mimicking a 2K polyurethane clearcoat with a 1K UV-A-cure clearcoat via T_g values

In 2006, research was presented on the development and the use of UV-A clearcoat technologies in the auto-refinish industry.²¹ Up to that point in time, it was assumed that the UV polymer technology could not meet the rigors of the automotive industry. Several issues plagued the clearcoat development. The beauty of the current 2K clearcoat technology was that it is both a thermoset and thermoplastic. What this did for the auto refinisher was that when a repair had to be made the repairing system needed to “need” (blending) into the existing fully cured and aged coating. The importance of this was this “needing” of the two technologies (different systems) could not show a blend line. An example of this is shown in *Figure 9*.

It is obvious from *Figure 9* that the appearance of this clearcoat is not acceptable. The researchers looked at commercial 2K systems and measured their glass transition temperatures (T_g s). Then through new UV oligomer development and oligomer blending, they produced a formulation that would mimic the conventional 2K clearcoats.

Table 2 shows that the current commercially available UV refinish clearcoat is 39 °C over the commercially available T_g 2K refinish system. The commercial 2K system shows the T_g of 62 °C while

the commercially available UV refinish clearcoat is at 101 °C. This dramatic difference in T_g will make this product unacceptable in the auto-refinish marketplace. Not only is the T_g unacceptable, but as the previous *Figure 9* shows, the blend line would also not be acceptable for the auto-refinish market. The researchers were able to first develop a new oligomer that was very hard and would physically dry prior to UV. This is important since it would allow the solvent to evaporate and become dust free. This new oligomer listed as UA

FIGURE 9—Photo micrograph of a blend line for a commercially available UV-A-curable clearcoat over a black basecoat.

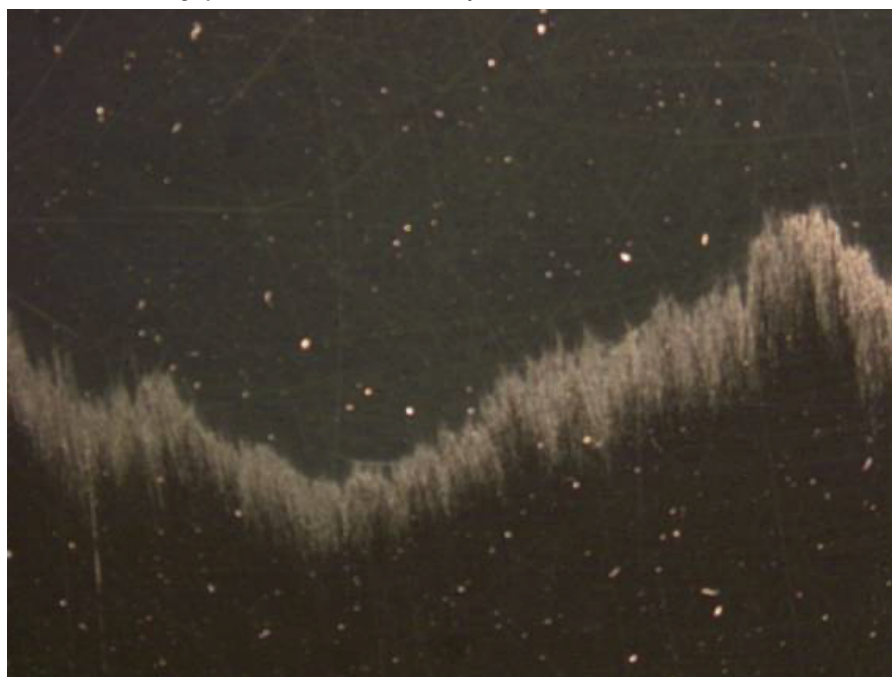


TABLE 2—Concept of Matching the T_g s of Traditional 2K Clearcoat with a UV-A-cure Clearcoat

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

TABLE 3—The Relationship of Cure for the Systems Tested with Pendulum Hardness, Reported in Seconds.

RESIN	30 MIN.	1 DAY	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

Resin B has a T_g of 104 °C, which is over the commercial UV refinish system. To be able to mimic the commercial 2K refinish system, the researchers used an extremely low blending partner UA Resin A which has a T_g of 10 °C. The addition of the low blending partner (UA Resin A) did not affect early dust-free resistance because the UA Resin B percentage was kept within levels that still allowed the physical dry characteristic to dominate the coating.

T_g is not the only variable that needs to be followed in the development of a UA-A clearcoat. Another variable that was studied was the hardness development. Hardness development is important because it determines when the auto body refinisher will be able to rub and buff the repair.

Table 3 shows that a commercial 2K System takes at least one day to assume the hardness that would allow the professional body technician the ability to rub and buff the cured surface. All the UV-cure system will be ready to rub and polish immediately after cooldown from the UV cure. This immediate return to service is what the market is demanding.

Also, from this table we can see the distinct results of the blending of UA Resin B and UA Resin A. Just from the Pendulum Hardness values you can see that UA Blends 3, 4, and 5 would be good candidates for a potential UV-A-cured clearcoat.

As shown earlier in Figure 9, the blend line over a black basecoat was not acceptable even though the Pendulum Hardness values were the highest of any system as shown in Table 3. The blending option formulation UA Blend 4 shows very little blend line; it is acceptable for the auto-refinish market. This lack of blend line can be seen in Figure 10.

With the evolution of the UV-A based primers, the ability to cure extremely high P/B systems were developed.²¹ These systems now mimicked the conventional 2K primers and had the major attribute to be able to be sanded right after cooling without any solvent wipe. These current styles of products are in major use within the UV-A auto-refinish market. The use of these high P/B products is shown in Figure 11.

2K UV-A-curable clearcoat that uses a photo latent amine catalyst

In 2006, research was published reviewing the development of a 2K UV-A-curable clearcoat. This technology utilized a photo latent amine in combination with a thiol-polyisocyanate. This system is reported to give a 5-minute cure, is not affected by oxygen inhibition, and exhibits no shrinkage. This obvious speed rivals a conventional 2K polyurethane clearcoat that takes 30 to 60 minutes to cure at 140 °F.²²

1K and 2K UV-A-curable clearcoat

The true need in the market was to develop a 1K and 2K UV-A clearcoat that could meet the rigors of the auto-refinish market. In September 2007, an international patent publication reviewed the development of such clearcoats.²³ This style of 1K and 2K UV-A clearcoat is what the auto-refinish market has been pushing to be developed to take this technology to the next level. This style of 1K UV-A clearcoat is depicted in Figure 12.

The chemistry of the 1K UV-A clearcoat was based on a IPDI trimer that has the added benefit of physically drying before UV-A cure. This added benefit allows the surface of the coating to become “dust free” prior to the UV-A cure. UV-A cure time is 1 to 3 minutes.

With the concerns of UV “shadow cure,” the 2K UV-A technology was developed based on a polyester polyol that also had acrylate double bonds incorporated. In addition, an aliphatic polyisocyanate is used that also includes an acrylate double bond. These two components when mixed react in the classic 2K polyurethane scenario and then have the added benefit of UV-A curing. The cure speeds of the 2K UV-A technology are 3 minutes. Reported pot life after the two components are mixed showed minimal viscosity increase after 24 hours.

1K UV-A clearcoat and primer field study to evaluate long-term performance

As with any new development in the automotive coatings industry, the lab testing is only a part of finding if the technology will meet the rigors of this market. Figure 13 shows a test-spot repair using a high P/B, non-solvent wiped primer in combination with a

conventional black basecoat over-coated with a 1K UV-A clearcoat. This repair has been in service for more than 8 years in the northeastern United States and only shows the stone-chip damages that are prevalent in low-profile vehicles.

For comparison purposes, the same vehicle depicted in Figure 13 was also repaired on the opposite side of the hood with a conventional 2K PUR spot repair as shown in Figure 14. In both cases, the spot repair has shown good service for 8 years.

Current RADTECH automotive refinish project

The RADTECH Automotive Focus Group has developed a program with the Ford Motor Company to answer the questions about the development of a 1K UV-A clearcoat.

The study is intended to follow up on a 2003 study that included an in-depth chemical and physical analyses on what was at the time, state-of-the-art UV-curable clearcoats to determine if they performed well enough for automotive industry. Cracking/embrittlement during service proved to be significant issue of the UV-A clearcoat materials that were evaluated. The latest Ford Motor Company study is currently evaluating seven clearcoats submitted by UV-cure material suppliers. The test results will be presented in a future RADTECH conference.²⁴

Continued development of a 1K UV-A cure clearcoat

Development continues in 1K UV-A-clearcoat technology for automotive refinish. One recent patent application shows the development in the technology shows the use formulations that are contained in an aerosol.²⁵

Considering this information, it is important to review the UV-A-cure putty, glazes, and primers that exist in the market today.

Table 4 shows a list of these products and the major manufacturers that have these products in the market today. These products are all designed to work as a putty, filler, or primer. This is not an exhaustive list of products; an exhaustive list of all the current products will be a subject of a future article.

FIGURE 10—Best blend line (formulation UA Blend 4).

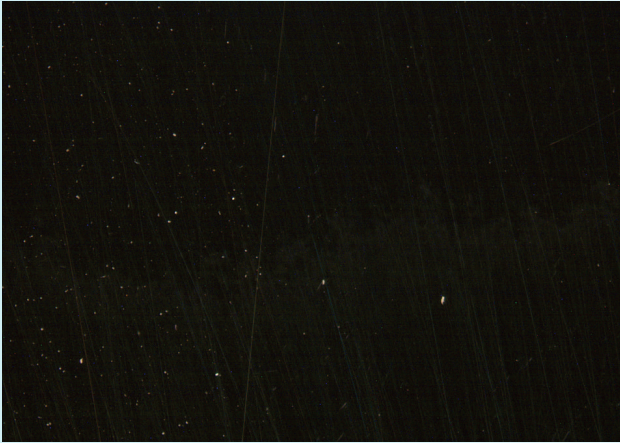


FIGURE 11—The use of a UV-A light curing a UV-A-based primer with a very high P/B concentration.

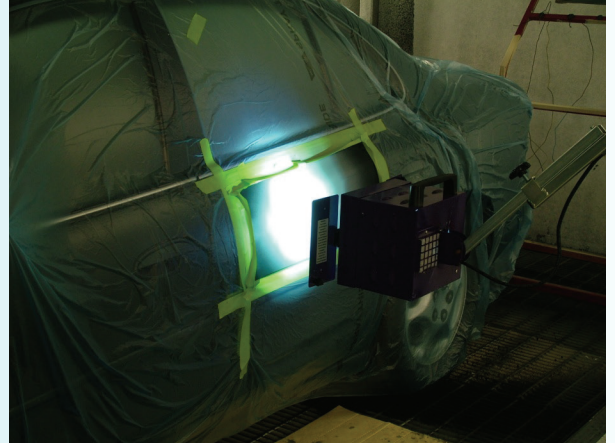


FIGURE 12—This small-damage repair shows the use of a UV-A light source to cure a 1K UV-A clearcoat.

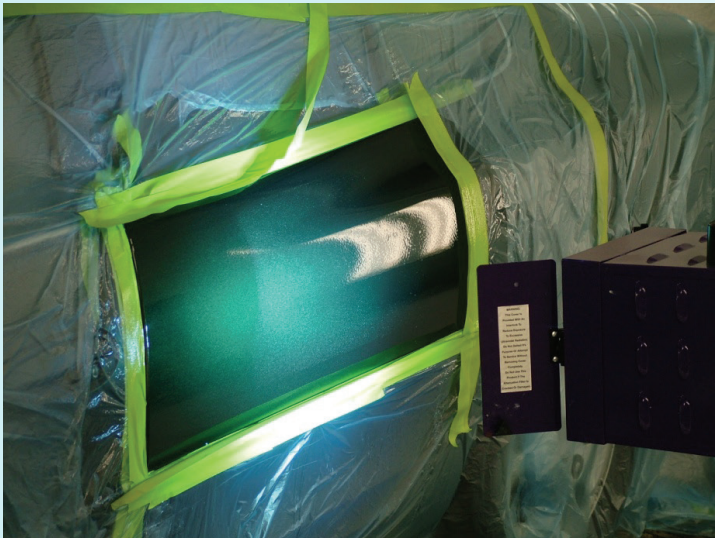


FIGURE 13—This image shows the longevity of a 1K UV-A primer and a 1K UV-A clearcoat after 8 years of service in the northeastern United States.



FIGURE 14—This image illustrates the longevity of a 2K PUR primer and clearcoat as the standard for comparing against the 1K UV-A primer and a 1K UV-A clearcoat after 8 years of service in the northeastern United States.



TABLE 4—Current Automotive Refinish UV-A Products in the Market

TRADE NAME	COMPANY	1K
ONECHOICE® UV Primer	PPG Industrial Coatings	1K
Permasolid UV Primer	Axalta Spies Hecker	1K
UV-A PRIMER-SURFACER	Axalta Cromax	1K
Glasurit UV Primer	BASF Corporation	1K
Aero-MAX Flash UV Primer	BASF Corporation	1K
Autosurfacers UV	Akzo Nobel Sikkens/Lesonal	1 K
UV Fast Fill	UV Fast Lane	1K
UV Buildable Putty Glaze	UV Fast Lane	1K

FIGURE 15—A 1K UV-A clearcoat has been introduced to the market, but it is currently difficult to find such products. Technical articles have been written on the 1K UV-A clearcoat technology and have shown some of the performance considerations that are needed to meet the automotive-refinish industry performance requirements.



TABLE 5—Current UV Light Sources Available to the Automotive Industry

TRADE NAME	COMPANY	OUTPUT, WATTS
CURE-TEK	H & S Auto Shot	400, 1200
UVAHAND LED	Honle	250
UV Power Shot 2400	CUREUV	2400
Mini UV Power Shot	CUREUV	—
IRT	IRT UV Lamps	200
UV-F900	Panacol	900

TODAY'S UV-A CURE LIGHT SOURCES FOR THE 1K UV-A-CURE AUTOMOTIVE-REFINISH MARKET

Table 5 lists some of the potential UV light sources available today for automotive refinishing. The list is not complete but will be developed further in a future technical review.

Figure 16 shows a recent introduction into the UV-A-cure-unit world is the Integration Technology AC-500 battery-powered portable UV LED handset for small-area damage repair. The unit's unique features are that it operates as a UV-A LED at the following wavelengths: 365nm, 395nm, and 405nm. Its cure footprint is 90 mm x 200 mm, and it has a 26-minute battery life. This technology innovation hits the sweet spot for small-damage repair in the automotive refinish industry.²⁶

FORECAST FOR THE UV-A-CURABLE REFINISH MARKET

In September 2003, the RADTECH organization sponsored an event called Driving Change.²⁷

The purpose of the event was to bring together all the knowledge that was available on UV-cure and automotive exterior coatings technologies. Among the more than 130 attendees were OEMs, OEM paint companies, raw material suppliers, academia, and many other cross-functional specialties in the coating business.

The conference predicted a bright future for UV technology and automotive industry; however, the future of this market is really tied to the introduction of a 1K or 2K UV-A-cure clearcoat. Attempts to develop and introduce such products have not been met with a lot of success.

In 2007, the RADTECH Transportation Focus group developed a web-based training seminar in conjunction with I-CAR. Since its inception, more than 3,000 professional body-repair technicians have taken this course. This kind of data from the grass-root level shows this is a developing market and that the professional auto body technicians are interested in the UV technology.²⁸ However, even with this interesting data, it still does not answer why this technology has not developed further into the auto-refinishing

FIGURE 16—Integration Technology AC-500 battery-powered portable UV LED handset for small-damage repair.



market. Only major changes in the refinish market will see the evolution and development of the 1K UV-A refinish technology.

CONCLUSIONS

During the research and development of this article, it became evident that a lot of work has been completed in trying to push the auto-refinish market to 1K and 2K UV-A primers and clearcoats.

However, market drivers and technology change are things that this market has seen before but has been slow to embrace. When the first 2K reactive systems were introduced to the market to replace the nitrocellulose lacquers, there was a lot of resistance to the change. One of the biggest issues was repair of the new 2K reactive systems, which were much more difficult to handle. In time, acceptance of the 2K reactive systems became the standard. Again, the industry appears reluctant to change, but as the 1K UV-A primers continue to be used, it is just a matter of time for a 1K or 2K UV-A clearcoat to become an obvious choice. ❖

References

- Future Market Insights website. "Automotive Refinish Coatings Market Snapshot." <https://www.futuremarketinsights.com/reports/automotive-refinish-coatings-market> (accessed Oct 25, 2022).
- Body Shop Business website. "UV Products Making a Resurgence in the Auto Body Industry." <https://www.bodyshopbusiness.com/uv-products-a-resurgence-in-the-auto-body-industry/> (accessed Oct 25, 2022).
- Magg, K., et al. New UV curing systems for automotive applications. *Progress in Organic Coatings*, 2000, Volume 40(1-4), 93-97.
- Fenn, D., et al. Process for Priming a Surface and Article. U.S. Patent 6,838,177, Mar. 27, 2003.
- Dvorchak, M.J. UV curing of pigmented high-build wood coatings based on non-air-inhibited unsaturated polyesters. *J. Coatings Technol.* 1995. 67 (842), 49-54.
- Nichols, M., et al. Weathering and Crosslinking Behavior on UV-Curable Automotive Clearcoats. RADTECH Report. Nov-Dec 2001.
- Braun, D., et al. Coatings composition curable with ultra-violet radiation. U.S. Patent 2005/0095371, May 5, 2005.
- Maloney, D. UV-Coating and Curing System Receives 'Thumbs Up' from Customers. RADTECH Report, Nov-Dec 2003, pp 29-32.
- Stropp, J.P., et al. UV curing systems for automotive refinish applications. *Progress in Organic Coatings*. 2006. 55(2), 201-205.
- Lettmann, B., et al. UV-A Curable, Solvent-Containing Composition, Process for Preparing It, and Use Thereof. U.S. Patent 7,683,105, Mar 23, 2010.
- O'Neil, J. Coating Composition and Method for Coating Substrates. U.S. Patent 8,227,050, Jul. 24, 2012.
- Seubert, C., et al. Scaling behavior in the scratching of automotive clearcoats. *J. Coat. Technol. Res.* March 2007. 4 (1), 21-30.
- DeRegge, K., et al. UV Curing Structure and Process. U.S. Patent 7,704,564, Apr. 27, 2010.
- Bowman, M. et al. Coating compositions and methods for using the same as a spot blender. U.S. Patent, 2011/0097481, Apr. 28, 2011.
- Ford Motor Company. 2010 Emerging Technology Award, RADTECH 2010 Conference.
- Traenckner, H.J.; Pohl, H.U., Untersuchungen zum Trocknungsmechanismus lufttrocknender ungesättigter Polyesterharze. *Angew. Makromol. Chem.* Nov 1982. 108(1), 61-78.
- Dvorchak, M.J.; Riberi, B.H. Water-reducible, unsaturated polyesters as binders and clearcoatings for UV-curable furniture coatings. *J. Coatings Technol.* 1992. 64(808), 43-49.
- Arceneaux, J.A. Mitigation of oxygen inhibition in UV LED, UVA and low intensity UV cure. Proceedings RADTECH International North America Conference 2014.
- Bach, H., et al. UV Refinish Primers & Clearcoats. RADTECH Europe, Nov 2003.
- Strazisar, S., et al. Development of Low Energy UV Refinish Formulations. RADTECH Report, Nov 2003.
- Jeffries, M., et al. Urethane Acrylates for Automotive Refinish Clearcoats. RADTECH, Apr 2006.
- Dogan, N., et al. Fast UV-A Curable Clearcoat. RADTECH Report, March-April 2006, pp 43-52.
- Gia, H.B. Radiation and chemical curable coating composition. WO 2009039137, Mar 26, 2009.
- Seubert, C. The RadTech UV Clearcoat Durability Study: How Paint Performance is Assessed by Ford Motor Company. *UV+EB Tech*, May 28, 2019.
- Guo, X. Low-Energy UV Automotive Refinishing paint, as well as method of application and use thereof. WO 2017177674, Oct 19, 2017.
- Integration Technology website. UV-A LED Battery-powered portable handset for small automotive refinish repair. <https://www.integrationtechnology.com/en/products/portable-uv-curing> (accessed Oct 25, 2022).
- RADTECH Driving Change Event, University of Akron, Sept 2003.
- Dvorchak, M.J. I-Car Automotive Refinish at the Speed of Photons. *UV + EB Technology*, Q2, 2022, pp 42-47.

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