1K UV-A Automotive Refinish; Clear Coats and Primers

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Introduction

Over the last decade the automotive refinish industry has been forced to look at new technologies to reduce volatile organic content (VOCs) and hazardous air pollutants (HAPs) while providing a rapid return to service of the consumer's vehicles. UV A cured 1 K auto refinish primers were first introduced in the middle 1990's. UV-A Clear Coats were subsequently introduced in the late 1990's. Materials have continued to be developed and pushed to mimic the classic 2K solvent based polyurethanes (PURs); however, slow acceptance by the auto refinish market over the last decade is indicative of a market that is difficult to change. RADTECH, in conjunction with I-CAR, an industrial training organization for the collision repair professional, developed a web based training module for UV-A Cure 1 K auto refinishing. Over 900 of these module courses have been purchased from I-CAR by the collision repair professional since 2008.

This paper will review the past history of the UV-A cured 1K auto refinish market and formulations for primers and clear coats. It will also attempt to look at current UV-A cured 1K auto refinish primers and clear coats in the NAFTA market as well as new formulations and new developments in UVA equipment.

1.) Changes in the automotive OEM and refinish markets

Over the last several years the automotive OEM and refinish markets have gone through an incredible number of changes in both polymer technologies and substrates. The original markets used nitrocellulose lacquers when the only color you could specify was black. Today, the current number of 2K reactive primers and clear coats as well as base coats has increased pushing the limits of polymer chemistries. With the pressures to lower VOCs and VHAPS, solvent based systems have evolved to water based chemistries. Substrates used by the OEM's have evolved from the traditional steel metals to composites and aluminum.

2.) Introduction of UV A curable auto refinish

a. Early attempts to develop a UV refinish clear coat

The earliest paper [1] that reviews the use of UV cure clear coats for auto refinish was focused around the use of a UV Flash lamp (Xe lamp). The idea was that the fully formulated UV clear coat after application would be flashed several times (by the Xe lamp) to activate the PI for this dual cure system. The dual cure cross linking of this system was done with a polyol that had acrylate and hydroxyl functionality in combination with a dual cure cross-linker that possessed acrylate and polyisocyanate functionality. This system was essentially a 2K system. Due to the Xe lamp wave length occurring around 480 nm, the use of a bis-acyl-phosphine-oxide is specified for this use. Cure was done by using 10 to 20 flashes at 20 °C.

b. Early patents on UV A cure auto refinish primers

Earliest US patent [2] estates (2001)in this technology work space was developed around UV oligomers that were used with bis-acyl-phosphie-oxide PI's and full spectrum 250 W iron doped light sources that were then filtered down to only emit in the UV-A region. The cure time with this configuration was one minute. The reason that the light was filtered was to prevent worker exposure to UV B and UV C wave length. 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 PI's that were used needed to work above the absorption window of the fillers and pigments. The resultant UV-A cured primer needed to have the ability to be sanded immediately after it had cured.

c. Automotive OEM technical paper on UV auto refinish clear coats

One of the OEMs got in on the act of evaluating UV cure clear coating supplied by the OEM paint company to evaluate UV clear coats [3]. In the OEMs evaluation, they talk about the need for HALS and UVAs. It is surprising that an OEM would be evaluating UV clear coats so early in the development cycle. The only possible 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 clear coat technology. It found that the HALS and UVAs slowed this process, but still eventually embrittles to an unacceptable level for an automotive clear coat.

d. 2003 Patent application by a paint company on UV-A cure clear coats

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

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

A report was prepared in 2003 that reviewed the actual use of UV-A primer systems [5] .This report went into great detail as to why the body shops were using the technology. The following list of benefits are compelling arguments explaining why these body shops are using this technology; 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 clear coat.

f. 2006 patent application on dual cure UV clear coat 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 [6] .This clear coat 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/cm^2. After this curing the coating surface was easily polishable without defects.

g. 2006 Patent filed by an automotive OEM paint co. on a UV-A primer that has a high pigmentation levels and extremely low oxygen inhibition.

This 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 [7] .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 400 W UV-A light that is held 10-30 CM away, curing for 1-3 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.

h. Automotive OEM technical paper on scratch performance of three UV automotive refinish clear coats

In 2007, an automotive OEM technical paper reviewed the performance of three UV cure clear coat technologies against a thermally cured acrylic/melamine/silane clear coat [8] .The testing showed that two of the UV clear coats performed better than the thermally cured acrylic/melamine/silane clear coat in the AMTEC-Kistler testing. The AMTEC-Kistler testing simulates the performance of the clear coats to scratches created by running the vehicle through a car wash. The UV clear coats were shown to have superior fracture resistance. With the kind of performance shown in this paper, it is important for everyone to realize that a UV cure clear coat for end of line repair is possible.

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

In 2007 a patent was filed to UV cure a vehicle [9].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.

j. Patent Publication filed in 2009 by an OEM paint company develops a UV cure spot blender for automotive clear coats

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

k. OEM awarded the 2010 RADTECH Emerging Technology Award for the use of in-line UV spot repairs

At the RADTECH conference in 2010 an OEM auto manufacturer was awarded an Emerging Technology Award for in-line spot repairs [11]. 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 if 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.

3.) Current products and innovation in the market

In 2003, two papers really put the ability of a UV cure primer and clear coats to the test [12, 13]. 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 6 independent factors, namely UV curable resins, reactive diluents, photoinitiators, 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, over 15,000 films were evaluated looking for the sweet spot and synergistic effects.

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

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 2.

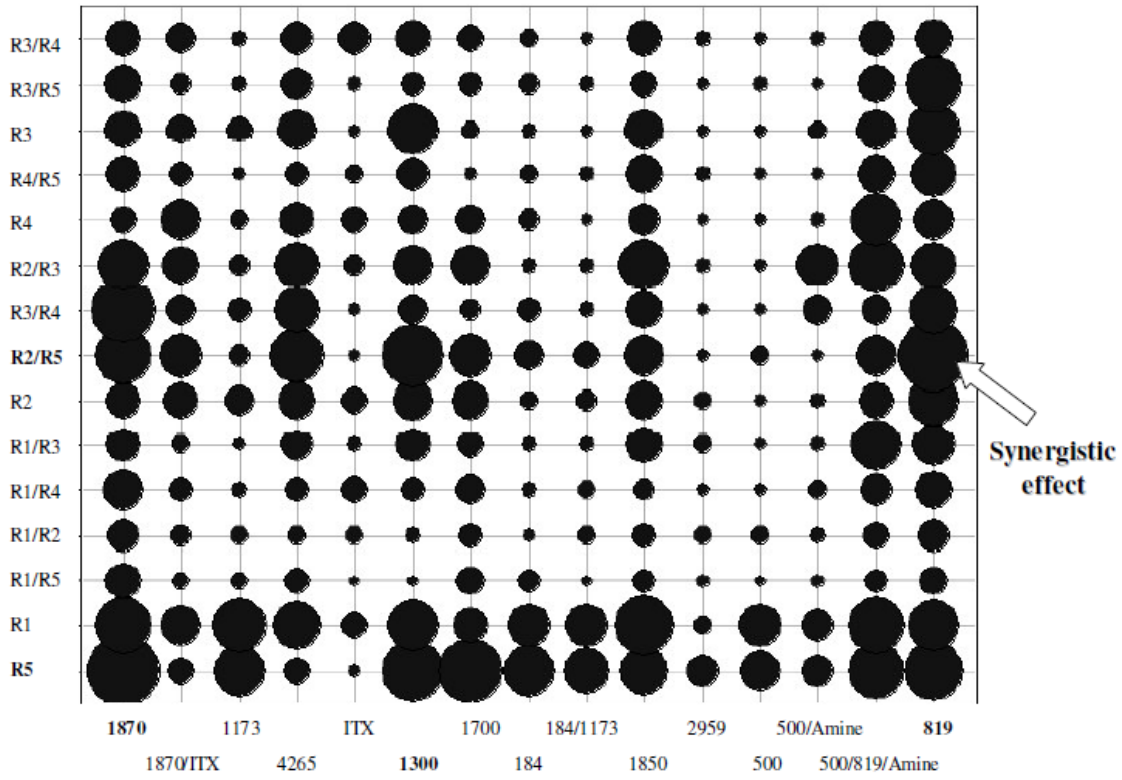


Figure 2: High throughput primary screening results based on the evaluation of over 25,000 films followed by a statistical analysis. Shown is the average predicted surface cure for all resin-photoinitiator combinations after curing using a 250 W UV-A light source. The average is taken over all other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

It is obvious from Figure 2 that the only way to uncover the full surface cure of a UV-A system is to run massive amounts of tests to see if 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, the fact they cured as well as they did without surface tack (i.e. surface inhibition) was a surprise. All of 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, ≤75 µm dry, 2 minutes under a 250 W UV-A lamp and 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 clear coat. Issues that the paper reveals about developing this 1K UV-A curable clear coat are: 1) lack of flexibility on polymers based on radical polymerization, 2) keep the unreacted double bonds very low(≤10%) due to post cure issues, 3) formulation and film color due to visible light photoinitiators and 4) primer, base coat and clear coat compatibility. The testing finally developed a low post curing clear coat that had high gloss, good weathering characteristics, solvent and impact resistance as well as good pendulum hardness. However, future work is needed to look at adjusting these UV cure clear coat systems to the exact performance expected out of a conventional 2K PUR systems.

In 2006, a paper [14] was presented on the development and the use of UV A clear coat technologies in the auto refinish industry. 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 clear coat development. The beauty of the current 2K clear coat 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' 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 can be seen in Graphic 1.

Graphic 1: Photo micrograph of a blend line for a commercially available UV-A curable Clear Coat over a black base coat

It is obvious from this graphic that the appearance of this clear coat is not acceptable. The researchers took a look at commercial 2K systems and measured their Tg's (glass transition temperatures). Then through new UV oligomer development and oligomer blending, they came up with a formulation that would mimic the conventional 2K clear coats.

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 1: This table shows the concept of matching the Tg's of traditional 2K Clear Coat with a UV A Cure Clear Coat.

From Table 1 it is obvious that the current commercially available UV Refinish clear coat is 39 °C over the commercially available Tg 2K refinish system. The commercial 2K system shows the Tg of 62 C while the commercially available UV refinish clear coat is at 101 C. This dramatic difference in Tg will make this product unacceptable in the auto refinish market place. Not only is the Tg

unacceptable, but as was shown in the previous Graphic 1, the blend line would 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 Resin B has a Tg of 104C which is over the commercially 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 Tg of 10 C.

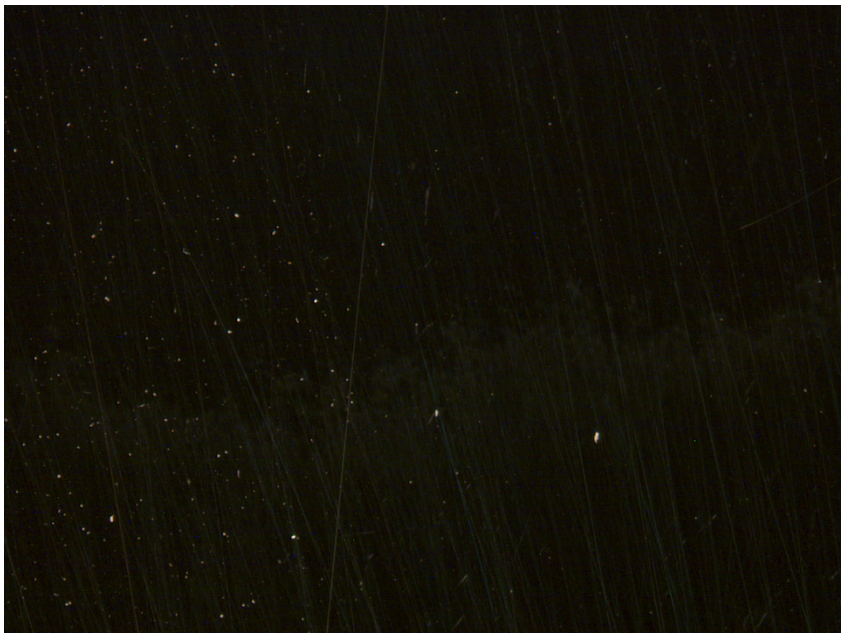
Resin	30 min.	1 Days	2 Days	7 Days	14 Days
UA Resin A	21	18	20	17	17
UA Resin B	139	167	171	167	181
UA Blend 1	130	158	169	189	193
UA Blend 2	115	115	115	137	140
UA Blend 3	102	105	108	112	113
UA Blend 4	95	98	99	104	104
UA Blend 5	92	95	99	102	101
Commercial UV Refinish	207	207	210	221	218
Commercial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

Table 2: Table 2 shows the relationship of cure for the systems tested with Pendulum Hardness reported in seconds.

Tg is not the only variable that needs to be followed in the development of a UA–A clear coat development. 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.

From Table 2 you can see that a commercial 2K System takes at least one day to assume the hardness that would allow the professional body man the ability to rub and buff the cured surface. All of the UV cure system will be ready to rub and polish immediately after cool down 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 Blend 3, 4 and 5 would be good candidates for a potential UV-A cured clear coat.



Graphic 2: Best blend line (formulation UA Blend4).

As was shown in the earlier Graphic 1, the blend line over a black base coat was not acceptable even though the Pendulum Hardness values were the highest of any system as shown in Table 2. 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 Graphic 2.

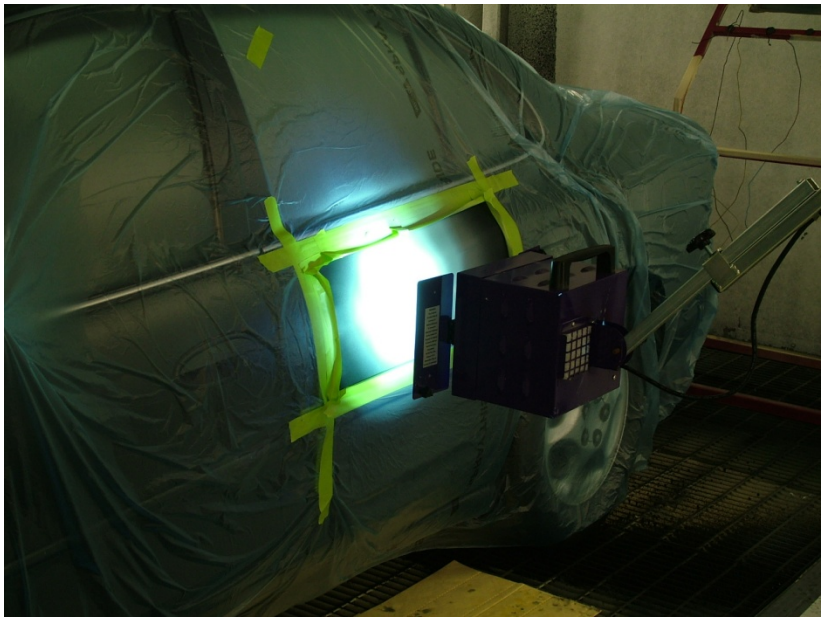


Photo 1: In this photo you can clearly see the use of a UV-A light curing a UV-A based primer with a very high P/B concentration.

With the evolution of the UV-A based primers the ability to cure extremely high P/B systems were developed [7]. 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 show in Photo 1.

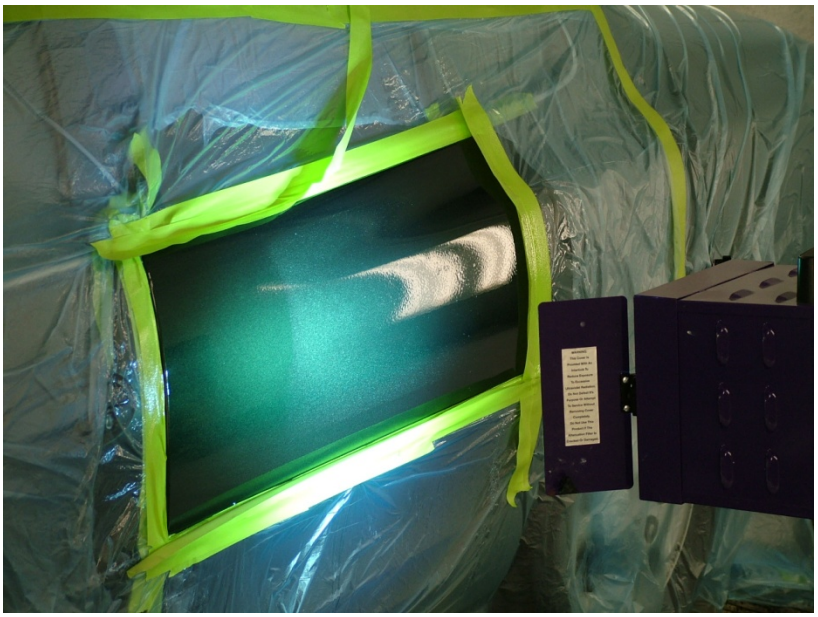


Photo 2: In this photo the small damage repair shows the use of a UV-A light source to cure a 1K UV-A clear coat

The true need in the market was the ability to develop a 1K UV-A clear coat that could meet the rigors of the auto refinish market. In September 2007, an international patent publication [16] reviewed the development of such clear coats. This style of 1K UV clear coat 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 clear coat is depicted in Photo 2.

Photo 3: In this photo you can see the longevity of a 1K UV-A primer and a 1K UV-A Clear Coat after 8 years of service in the Northeastern US.

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. Photo 3 shows a test spot repair using a high P/B non-solvent wiped primer in combination with a conventional black base coat over-coated with a 1K UV-A clear coat. This repair has been in service for over 8 years in the Northeastern US and only shows the stone chip damages that are prevalent in low profile vehicles.

Photo 4: In this photo you can see the longevity of a 2K PUR primer and Clear Coat as the standard for comparing against the 1K UV-A primer and a 1K UV-A clear coat after 8 years of service in the Northeastern US.

For comparison purposes the same vehicle as depicted in Photo 3 was also repaired on the opposite side of the hood with a conventional 2K PUR spot repair. In both cases, the spot repair has shown good service for 8 years.

4.) Future outlook for the UV-A curable refinish market

In September 2003, the RADTECH organization sponsored an event termed Driving Change [15].

The purpose of the event was to bring together all the knowledge that was available on UV cure and automotive exterior coatings technologies. The event was attended by over 130 people. The attendees included OEMs, OEM paint companies, raw material suppliers, academia and many other cross functional specialties in the coating business. The outcome of this 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 UV-A cure clear coat. Attempts to develop and introduce such products have not 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, over 900 professional body repair technicians have paid for and taken this course. This kind of data from the grass root level tells us that this is definitely a developing market and that the professional auto body person are interested in the UV technology. However; even with this interesting data it still doesn't answer why this technology has not developed further into the auto refinishing market. Only major changes in the refinish market will see the evolution and development of the 1K UV-A refinish technology.

5.) Conclusions

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

However, market drivers and technology change are things that this market has seen before but has been slow to move on. When the first 2K reactive systems were introduced to the market to replace the NC 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, this industry is not wanting to change, but as the 1K UV-A primers continue to be used, it is just a matter of time for a 1K UV-A clear coat to become an obvious choice.

References

1.) K. Magg, et al., Progress in Organic Coatings 40 (2000) 93-97
2.) D. Fenn, et al., US 6,838,177 Mar. 27, 2003
3.) M. Nichols, et al., RADTECH Report Nov/DEC 2001
4.) D. Braun, et al., US 2005/0095371 May 5, 2005
5.) D. Maloney, RADTECH Report NOV/DEC 2003
6.) B. Lettmann, et al., US 7,683,105 Mar. 23, 2010
7.) J. O'Neil, US 8,227,050 Jul. 24, 2012
8.) C. Seubert, et al., J. Coat. Technol. Res., 4 (1) 21-30, 2007
9.) K. DeRegge, et al., US 7,704,564 Apr. 27, 2010
10.) M. Bowman, et al., US 2011/0097481 Apr. 28, 2011
11.) Ford Motor Company, 2010 Emerging Technology Award, RADTECH 2010 Conference
12.) H. Bach, et al., RADTECH Europe, Nov. 2003
13.) S. Strazisar, et al., RADTECH Report, Nov. 2003
14.) M. Jeffries, et al., RADTECH 2/5 2006, Apr. 2006
15.) Driving Change Event at the University of Akron, Sept. 2003
16.) H.-B. Gia, WO 2009/039137 Mar. 26, 2009

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