

New 100% Solids, Acrylated Allophanate Oligomers Offer Low Viscosity and High Functionality while Maximizing UV-Coating System Performance

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The coatings industry's desire for 100% solids, low viscosity, high functionality and exterior performance has resulted in a new class of oligomers based on acrylated allophanates.¹ These new polyurethane products offer viscosities in ranges from 8,000 to 60,000 cPs; functionalities as high as 4; T_g s from 30 to 80 °C; and pendulum hardness values from 60 to 180 seconds. This unique class of oligomers gives UV formulators the ability to minimize the amount of acrylated monomer and maximize coating performance.

Background

Ultraviolet (UV)- or radiation-cured coatings is one of the fastest growing segments in the coatings industry today due to its many competitive advantages. The key advantages include fast cure speed (cutting the overall cost of coating operations), lower energy costs, extremely long pot life and reduced environmental impact.

UV-curable formulations typically contain acrylated oligomers based on a polyether, polyester or epoxy resin. Each resin offers distinct

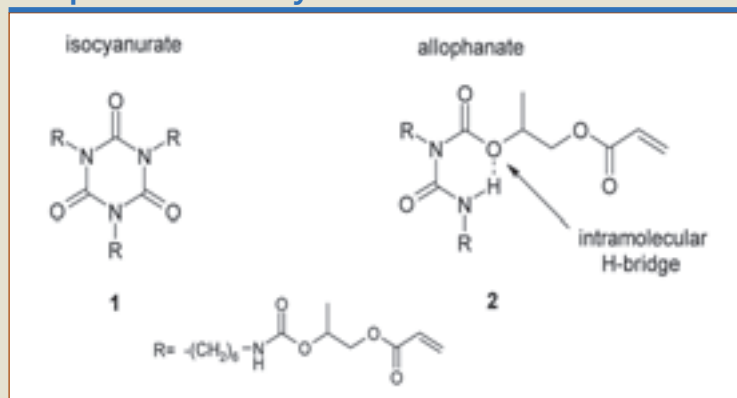
advantages depending upon the performance requirements of the end-user. While most radiation-cured coatings are high solids or 100% solids formulations, they can also be solvent-based and waterborne. The versatility, durability and performance of urethane-based coatings allow the UV formulator to tailor the coating system to meet the current market drivers. A new generation or class of polyisocyanates (termed *allophanate polyisocyanates*) was developed, and these new products give continued improvements in alternatives to meet the demanding challenges of better performance and environmental compliance. These new acrylated products offer the advantage of low viscosity and reduced crosslink density due to the reduced isocyanate functionality, thus allowing greater freedom in designing new high-solid systems.

Chemistry

The key to the market success of polyurethane films is their superior optical characteristics such as gloss and "wet look," as well as the remarkable weathering, chemical and mechanical resistance. Dedicated research has refined polyurethane chemistry and delivered a next-

FIGURE 1

Ideal structures of an acrylated allophanate compared to an isocyanurate



generation product for the field of UV coatings—acrylated allophanate oligomers.

Urethane acrylates are reaction products of isocyanates, hydroxyalkyl acrylates and polyols. Polyurethane coatings intrinsically have a high proportion of hydrogen bonds which can enhance thermoplastic properties of a cured film; however, these hydrogen bridges are also responsible for the high viscosity of most urethane acrylates. While other parameters must be taken into account, careful design of the polyurethane raw materials and chemistry architecture can achieve a balance between viscosity effects and application property profile.

Allophanate chemistry was developed in the 1990s and initially used to produce low-viscosity resins, thereby allowing for a higher solids formulation. Different routes were attempted in the early allophanate urethane acrylate oligomer developments that yielded low viscosity and no need for reactive diluents or organic solvents.⁵ Low-viscosity resins are environmentally friendly because there is no need for reactive diluents or organic solvents. Compared to isocyanurate structures,

allophanates possess a reduced NCO-functionality and, consequently, reduce the crosslink density of the cured polyurethane product. However, reduced crosslink density leads to lower UV reactivity and less robust coating properties.²

The functionality of UV-curing polyurethane resins can be adjusted by adding a double bond-bearing alcohol to the allophanate reaction. This leads to a comparable functionality and to a higher crosslink density of the cured films as only two hexamethylene diisocyanate (HDI) molecules are necessary to bear three hydroxyl alkylacrylates, rather than three HDI molecules in case of an isocyanurate structure (Figure 1). At the same functionality, the viscosity of allophanate urethane acrylates is reduced to less than 10% compared to the isocyanurate-based materials.² Additional viscosity adjustments can be achieved by using a selective allophanate catalyst or by introducing irregular structures into the molecule (such as a suitable blend of hydroxyl functional acrylates).

Three new binders based on this novel chemistry are shown Table 1. These new 100% solids, low-viscosity

aliphatic urethane acrylates are free of reactive thinner and are weather stable. UV-Resin A was the first acrylated allophanate for an outdoor application and it has good barrier properties. UV-Allophanate Resin B has the advantage of curing exceptionally quick. UV-Allophanate Resin C may be used as a co-binder with other urethane acrylates to enhance flexibility and elasticity. While these versatile new raw materials may be used on a variety of substrates, Resin C improves adhesion on metal and plastic due to its low shrinkage and elasticity.

Application on Engineered Plastics and Outdoor Stability of Isocyanurate-Based Oligomers versus Allophanate-Based Oligomers

With any new development, it is very difficult to speculate without doing the testing on a new UV oligomer's exterior weathering performance. Most current exterior-grade urethane oligomers have been based on isocyanurate building blocks as shown in Figure 1. With the advent of the new allophanate-based oligomers, it is important to compare their performance via accelerated techniques so that hardcoat product failures do not occur again. It would be nice to think that the traditional accelerated weathering will uncover all potential problems over a potential 10-year life span, but recent automotive hardcoat failures cannot be ignored since many of these systems were tested via the traditional techniques.

Many requests have been made over the years for a hardcoat to protect engineered plastics. These products have typically been applied to polycarbonate (PC) to protect the PC from UV degradation. Application areas have normally been in the automotive headlight areas and for external PC sheeting. Degradation of these hardcoats have been described in past

TABLE 1

Resin data

UV Resin	AA Resin A	AA Resin B	AA Resin C
Form Supplied	100 %	100 %	100 %
Type	aliphatic	aliphatic	aliphatic
Viscosity (23°C, mPas)	ca. 60,000	ca. 35,000	ca. 8,000
Hazen color value	< 100	< 100	< 100
Molecular weight, g/mol (GPC)	ca. 1,100	ca. 800	ca. 1,250
Functionality cal.	ca. 4	ca. 3	ca. 3
Double bond Density, Val/kg	ca. 3.8	ca. 4.1	ca. 2.8
UV Reactivity (3%, Dar. 1173, 1 lamp 80 W/cm)	ca. 25 m/min ca. 140 mJ/cm ²	ca. 10 m/min ca. 450 mJ/cm ²	ca. 7.5 m/min ca. 450 mJ/cm ²
Pendulum hardness, sec.	ca. 140	ca. 170	ca. 60
T _g in °C	ca. 65	ca. 80	ca. 30
Elongation at break, %	ca. 4	ca. 3	ca. 17
Tensile strength, N / mm ²	ca. 65	ca. 40	ca. 22
Special properties	Balanced properties, high scratch resistance combined with high functional oligomers. High UV reactivity.	Well-balanced properties, good barrier against water and corrosive environment, standard type.	Product is designed to adjust flexibility combined with the other allophanate urethane acrylates.

papers showing that the incorrect choice of oligomers, monomers and fillers can have a dramatic detrimental effect on the hardcoats' weathering performance.

UV degradation occurs over time due to ambient UV light, as well as environmental conditions (Figure 2).⁶ This particular case showed only 3,000 candela on low beam and 7,000 candela on high beam. The obvious degradation of the hardcoat on the polycarbonate is actually blocking light from the bulb making it to the outside where it is needed. When the headlight was refinished with the proper oligomer, monomer and filler, the headlight survey showed the following results—7,000 candela and 17,000 candela, respectively. This remarkable difference in candela performance needs a system that can withstand up to 10 years of exterior weathering performance. Most hardcoat coatings

manufacturers will utilize performance tests as described in Table 2.

There has been a considerable effort to try to artificially weather coat plastic substrates and duplicate the 10-year weathering performance in a much

shorter time. A recent study by National Renewable Energy Laboratory's Ultra-Accelerated Weathering System (UAWS) has shown a positive response to weathering of 1-K UV-cured coating that is used for hardcoats

FIGURE 2

Automotive headlight with degraded UV-cure hardcoat

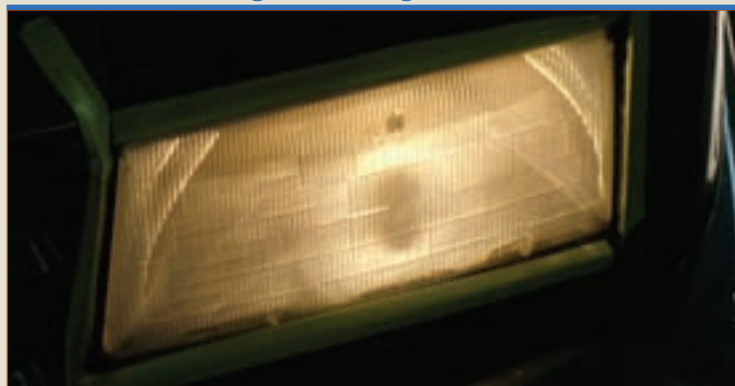


TABLE 2

Weathering data of different allophanate products compared to an isocyanurate-based type products

Method	ISO 11341 Xenon test	CAM180	UV-B
Isocyanurate-based resin	3,000h ongoing	3,000h ongoing	2,500h
Optimised allophanate-based resin	3,000h ongoing	3,000h ongoing	2,500h
Scratch-resistant, allophanate-based resin	3,000h ongoing	3,000h ongoing	2,500h
Elastic allophanate-based resin	3,000h ongoing	3,000h ongoing	2,500h

The following formulation was applied on Makrolon AL 2647 and tested using the weatherometer methods described below.

Formulation	Function	% By Weight
UV-curing allophanate	Resin	80
Reactive thinner	Reactive thinner	80
Photoinitiator	UV initiator	4.9
Leveling agent	Flow and leveling	1.6
UV absorber	UV absorber	3.8
HALS amine	Light stabilizer	1.7
Curing conditions	1,800 mJ/cm ² , HG bulb	
DFT	Approximately 25 microns	
Substrate	Makrolon AL 2647	

Weathering results

UV Resin	ISO 11341 Xenon Test, Hours	SAE J2527 Hours	UV-B Hours
*Standard trimer	<5,000	5,000	2,500
Flexible UV resin	3,750	3,250	2,500
AA Resin A	Testing in Progress	Testing in Progress	Testing in Progress
AA Resin B	5,000	5,000	2,500
AA Resin C	3,000	3,000	2,500

Test parameters—chalking, adhesion, cracks and blisters

*The standard trimer UV resin and Acrylated Allophanate Resin C perform at the same level with regard to outdoor resistance.

for the protection of polycarbonate head lamps.³ This technique allows simulated weathering of polycarbonate coated substrate in weeks versus years of actual exposure. Another aspect of the UAWS is the ability to keep temperatures constant at expected service temperatures. In the UAWS test at 70°C, the 1K UV aliphatic hardcoat

passed approximately seven years of weathering, while the 2K aliphatic PUR exhibited approximately 10 years. In the UAWS test at 30°C, both the 1K UV aliphatic urethane and the 2K aliphatic PUR survived just past 10 years exposure.

This data is quite relevant since testing by Bayer MaterialScience

(Table 2) shows that the isocyanurate-based product passed 3,000 hours in the Xenon Arc and Cam 180 4 on polycarbonate substrate. In addition, the isocyanurate-based system completed 2,500 hours of weathering testing. It is also shown that the allophanate-based resin systems can also obtain this distinct weathering performance.

TABLE 3

Adhesion of allophanate and urethane acrylate oligomers with acidic adhesion promoter

	Acrylated Allophanate Resin C		Aliphatic Urethane Acrylate	
	2	5	2	5
Wt. % adhesion promoter				
Substrate:				
Aluminum chromate treated	X	X	X	X
Aluminum untreated	X	X	X	X
B1000 (iron phosphate)	-	X	X	X
B952 (phosphate-treated steel)	X	X	X	X

X = 4B adhesion or greater

FIGURE 3

UV direct-to-metal application examples



Direct-to-Metal Application

It can be a challenging task to get a coating to stick to a variety of metal substrates, such as galvanized steel, untreated and phosphate treated steel, and treated and untreated aluminum. Bonding of the coating to the metal substrate is of significant importance for the corrosion protective performance of the coating. One of the main coating performance requirements for metal substrates is salt-fog resistance (ASTM B117). This test is used as a measure of corrosion resistance, and the formulator normally

adds an adhesion promoter to the formulation in order to obtain adhesion. However, adhesion promoters are usually acidic in nature and, under the

harsh salt-fog, conditions can cause water-sensitivity issues.

Table 3 demonstrates two UV resins where it is possible to use less adhesion promoter and still get good adhesion on several metal substrate examples. While the adhesion for the aliphatic-urethane acrylate is excellent, the low viscosity and flexibility of Resin C brings improved overall properties to the final coating. Another advantage of Resin C is that it exhibits low film shrinkage which is an important factor for adhesion to the metal substrate.

Moreover, by blending these two resins together, good adhesion is achieved in many cases without an adhesion promoter added to the formulation.

A formulation using a combination of acrylated allophanate Resin C with the urethane acrylate gives remarkable

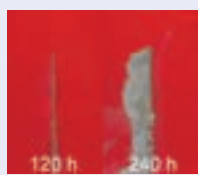


FIGURE 4

UV clearcoated galvanized steel panels



TABLE 4

Salt spray test results of a polyester acrylate compared to two allophanate-based resins

Substrate: Bonder Wh 60 OC, ca. 40µm DFT, curing with 1 UV lamp, Hg, 80 W/cm ca. 1100 mJ/cm ²			
Formulation FWO 5721	polyester acrylate	allophanate, optimised	allophanate, elastified
Adhesion 1 mm (Cross batch, best)	2	1	0-1
Erichsen indentation in mm	5	3	3
Salt spray result 72h, corrosion creep in mm	9	0	0
Salt spray result 240h, corrosion creep in mm	14	7	6
Samples			

adhesion to the untreated steel parts shown in Figure 3. The motorcycle fender and gas tank are not normally used for a direct-to-metal application. It is now possible to eliminate a layer in the paint sandwich for many metal applications resulting in a cost savings for the customer.

Figure 4 shows a coated galvanized steel panel that failed the mandrel bend when using standard UV resins. The panel on the right is coated with the new acrylated allophanate/urethane-acrylate blend and has both good adhesion and good mandrel bend.

Salt Fog Example

The performance data of three formulations are shown in Table 4. This work was reported previously at the Radtech Europe 2009 proceedings. Please refer to this paper for more information on the formulations used in the testing. Initially, all the coatings had good to excellent adhesion. According to the procedure, the salt fog spray test is begun after the coating is scratched down to the metal substrate. Although the salt water creeps under the

polyesteracrylate coating quite quickly, the allophanate-based coatings remain largely undamaged.²

Conclusions

New acrylated allophanate resins give the formulator more opportunities to meet the challenges of better performance and environmental compliance due to their low viscosity and high functionality. The acrylated allophanate resins show good stability in accelerated weathering tests and can endure more than 240 hours in the salt fog test. The performance benefits were demonstrated using the new acrylated allophanate materials alone, as well as in blends with an aliphatic urethane acrylate on various substrates.

Acknowledgement

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References

1. M. Ludewig, N. Stöckel, J. Weikard; RadTech Europe 2005, Conference Proceedings Vol 1. 261-268

2. Acrylated Allophanates—Low-viscous Alternatives for Outdoor Applications, Michael Ludewig, Helmut Kuczewski and Wolfgang Fischer, Radtech Europe 2009 Proceedings.
3. C. Bingham, G. Jorgensen, and A. Wylie, "Exposure of Polymeric Glazing Materials Using NREL's Ultra-Accelerated Weathering System (UAWS)," ASME ES2010, Proceedings of the Fourth International Conference on Energy Sustainability, May 17-22, 2010, Phoenix, Arizona
4. CAM 180 Weathering Test
5. US 5,739,251; Low Viscosity Ethylenically Unsaturated Polyurethanes Containing Allophanate Groups, Lanny D. Venham, Art W. Mason, Mike Jeffries and Michael J. Dvorchak; Apr. 14, 1998
6. UV Refinish of Plastic Headlamps, Ramesh Subramanian, Charles Gambino and Michael Dvorchak, Coatings 2005 Indianapolis Show Proceedings.

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