UV Radiation Curable Resin Solutions for Automotive Radtech 2020

By Marcus Hutchins

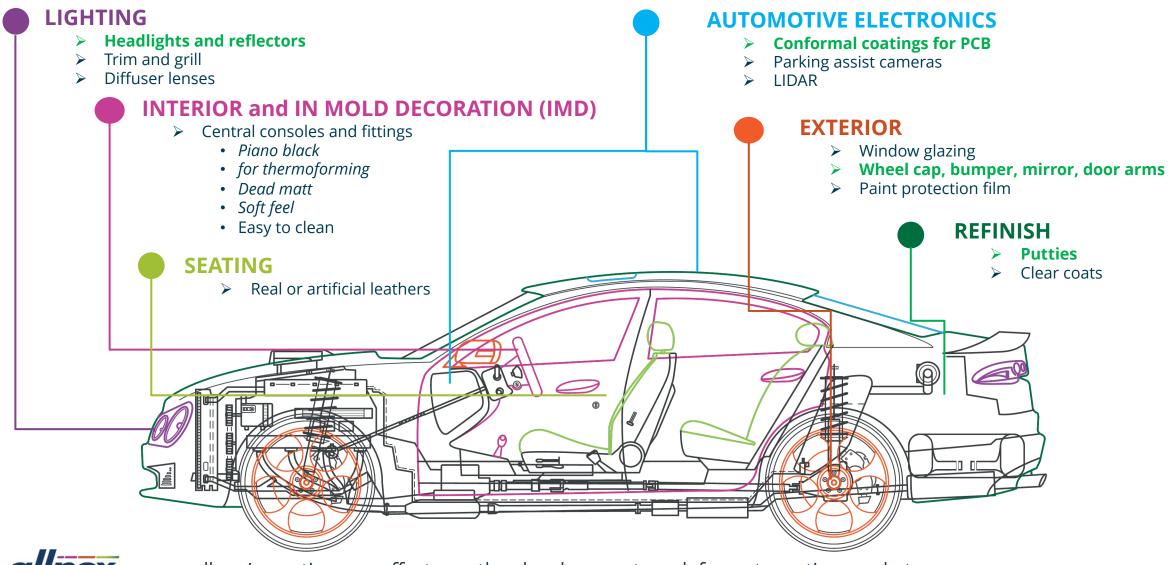
Acknowledgements: Jennifer McClung, Steven Cappelle, Paul Gevaert





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Allnex's diverse UV coating resins for automotive applications



allnex's continuous efforts on the development work for automotive market

UV Coating Chemistry

- The polymerization is induced by UV radiation in fraction of second, immediate after application
- UV radiation penetrate the complete coating layer to get the full polymerization and optimized performance

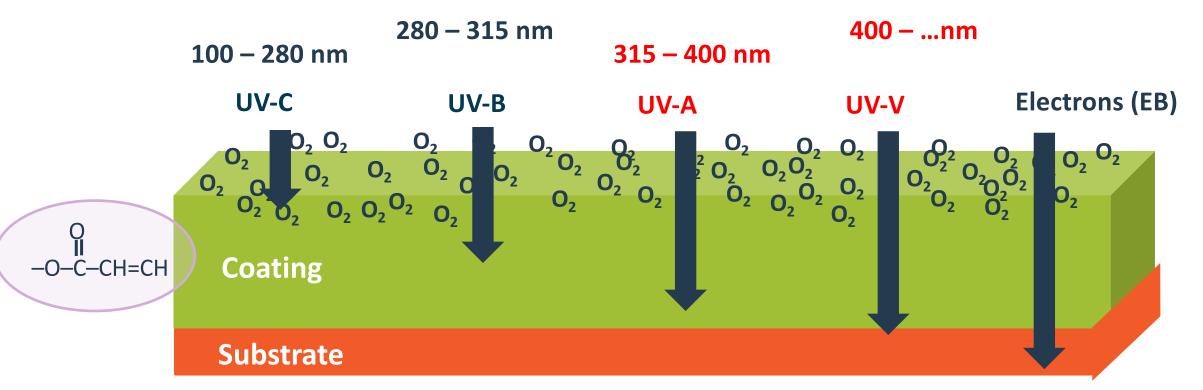
Formulation Mechanism С U Acrylated Resin(s) (oligomers) UV coating layer application basic coating properties R Ε Monofunctional Monomer(s) D viscosity reduction, flexibility UV Ρ Multifunctional Monomer(s) Radiation **UV Radiation** R viscosity reduction, crosslinking 0 D **Additives** U performance fine tuning С **Photoinitiator Package** Т

Polymerization to build crosslinking network

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radical generation

What Is UV Curing



- Different parts of the UV spectrum can penetrate to different depths of the coating.
- The right photoinitiator choice will initiate the reaction in the entire coating.
- UV LED is typically 385 nm, 395 nm, 405 nm. (365 nm is available at low energy output)



Almost Instantons Cure Ready for immediate use

UV Technology

- Energy savings with rapid cure with UV lamp

- Fast throughput with less use of production space

- Excellent for heat sensitive plastics

- UV dual cure for shadow & inaccessible areas

- Achieve harsh auto spec. with enhanced chemical, abrasion & weathering resistances

Conventional Technology

- Long thermal cure time (hours and days)

 Need long curing line or space that consume production space

- Work only in heat resistance plastics

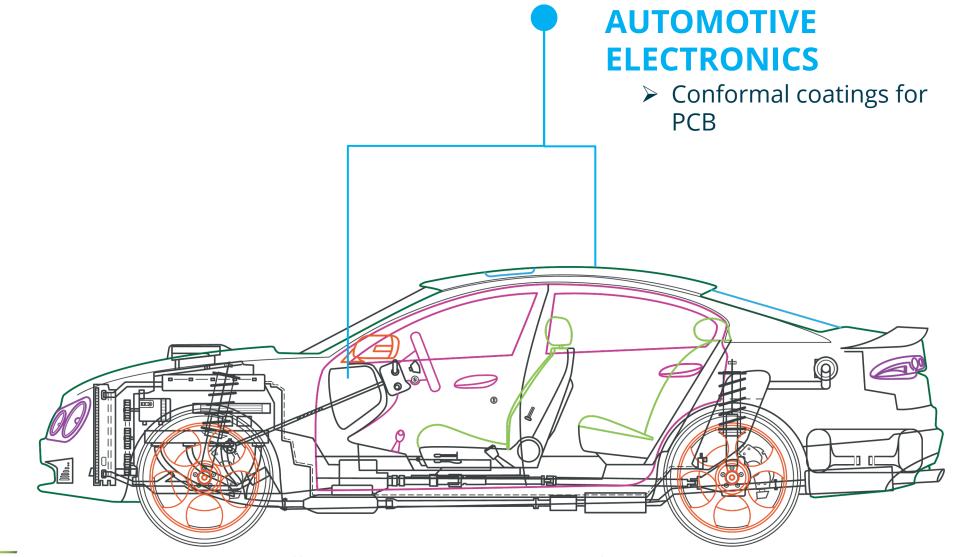
- Allow full cure for difficult shape

- Limitation in chemical resistance performance



UV coating technologies provides an effective solution

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Automotive Electronics: Circuit Boards

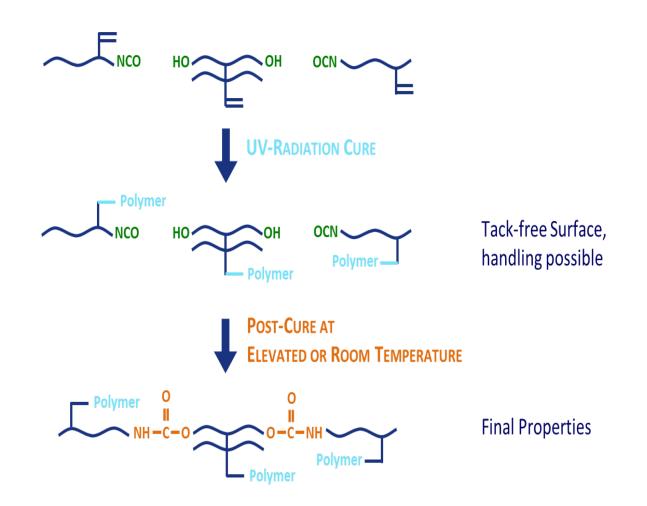
- Conformal coatings conforms to contours of electronic printed circuit boards (PCB) to protect PCB from moisture and contaminants, preventing short circuits and corrosion of conductors and solder joints
 - Minimize dendritic growth and the electromigration of metal between conductors
 - Improves PCB reliability
 - Insulating helps maintains long-term surface insulation resistance (SIR) levels and thus ensures the operational integrity of the assembly
- With UV or LED curing of PCB, there is virtually no pot life limitation, rapid throughput, controlled and low energy consumption, low emission, limited manufacturing footprint, etc. make UV technology a perfect fit for conformal coatings to protect a PCB in an efficient and qualitative way

	UV Light Cure	Solvent Based	2К Ероху
Cure Time	Seconds	Minutes to Hours	Hours to Days
Application Passes	One	Multiple	One
Monitoring of Viscosity	Not needed	Needed	Needed
Material Cost	Medium/High	Medium	Low
Hazardous Shipping Surcharges	No	Yes	Νο



Automotive Electronics: Circuit Boards

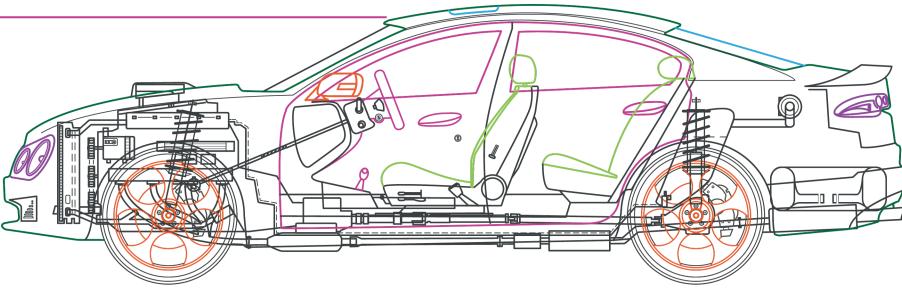
- Why is UV Chemistry optimal for conformal coatings
 - UV chemistry containing both NCO and acrylate functionality
- UV and NCO marries the intrinsic values of UV with reliable gains of having NCO functionality
 - NCO to react with moisture
 - NCO to react with conventional OH polymers
 - Improve workability and removal before UV
- UV can be designed to function at a wide variety of temperatures while offering unique hardness and flexibility





INTERIOR and IN MOLD DECORATION (IMD)

- Central consoles and fittings
 - Piano black
 - for thermoforming
 - Dead matt
 - Soft feel
 - Easy to clean

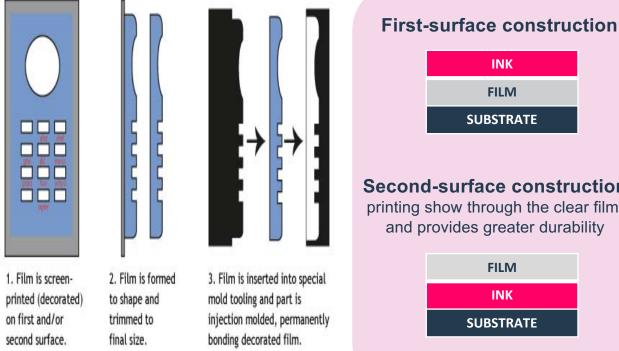




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Automotive Interior: IML and IMD Application

- IMD process can apply design elements during the molding process. A transfer film is carefully placed into the mold before injecting the plastic material.
 - When hot resin is injected into the closed mold the decoration transfers from the film to the molded plastic part.
- Once the part cools, the decoration becomes a permanent part of the piece, resulting in sharp, clear and durable decorations that should last the life of the part.



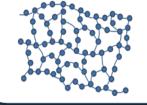
Second-surface construction printing show through the clear film,

and provides greater durability

Coating Requirements:

- Formable to deep draws
- Embossability & 3D forming with thinning performance
- Dimensional stability
- Excellent ink adhesion without pretreatment
- Exceptional optical clarity and high light transmission
- Tintable
- Scratch resistance
- Impact resistance
- Chemical resistance
- Abrasion resistance

High crosslinking density => Excellent surface resistance







Automotive Interior: Solution for IMD and IML

UV initiated free radical polymerization

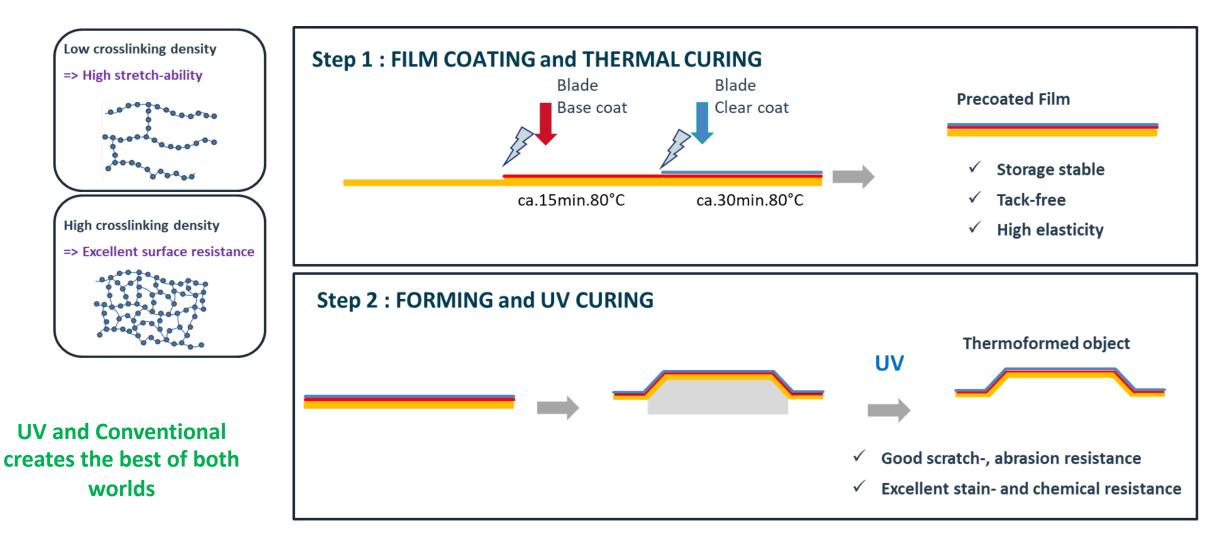
Productivity, fast cure, low temperature processing Excellent scratch & chemical resistance Shorter processing time compared to poly-addition reaction Reduce adhesion and flexibility due to the shrinkage during curing Thermally initiated poly-addition reaction

Full cure of difficult shape such as 3D parts Lower shrinkage Robust adhesion High energy consumption for drying

Improved cure of areas affected by line of sight Lower shrinkage/curl upon cure Robust adhesion Outstanding chemical, scratch, and abrasion resistance Long pot life

Dual cure

Dual Cure Technology for IML and IMD





Automotive Interior: Dual Cure Technology for IML and IMD

Component I	weight %
OH functional urethane acrylate	80.6
Butyl acetate (Solvent)	10
Flow and Leveling agent	0.7
Esacure One (Photoinitiator)	4
DBTL (Catalyst)	200 ppm
Component II	
NCO functional urethane acrylate	19.4
Butyl acetate (Solvent)	7
Viscosity -(mPa.s at 25°C)	288
After 2 hours	342
After 4 hours	486
After 6 hours	573

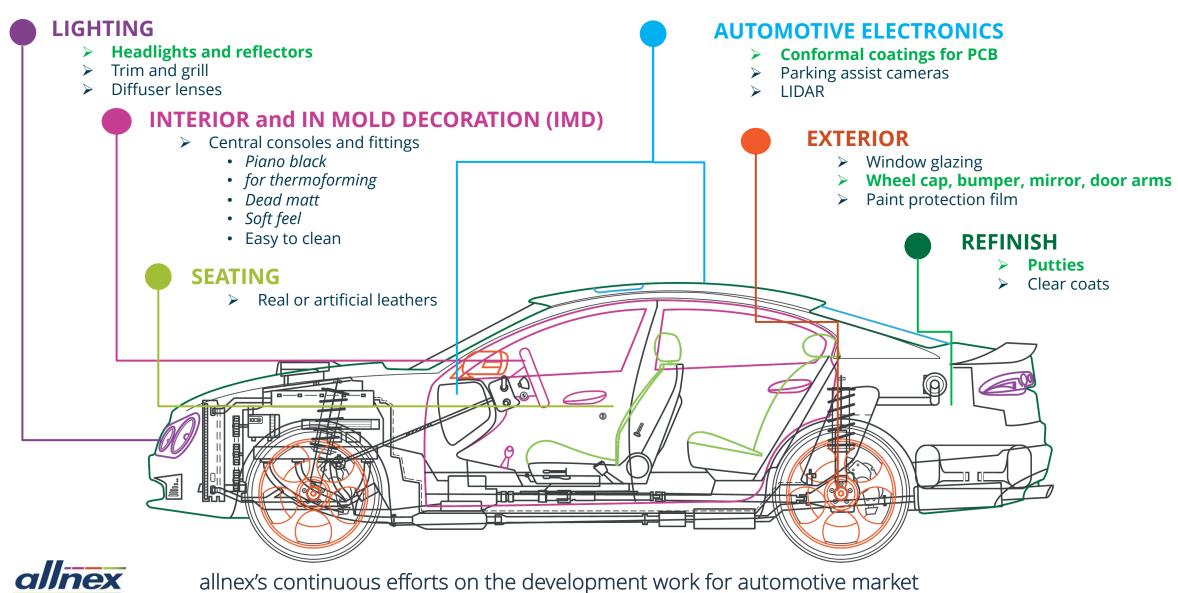
Thermal Cure 30 minutes at 80°C

Tack Free



UV cure 4J/cm ²				
Conditioning one week at RT	Substrate	Results		
Persoz Hardness (seconds)	Glass panel	347		
Mandrel flexibility on PC (mm diam)		4		
Taber haze, % Haze 100 cycles		4.5		
300 cycles	PC	10.6		
500 cycles		16		
Steel wool scratch resistance		4		
Adhesion crosshatch		5 (all substrates)		
Suntan lotion test (PV3964 ,VW, 24H 80ºC) (adhesion/aspect)		5 /pass		
Hand cream test (PV3964 ,VW, 24H 80°C) (adhesion/aspect)	ABS-PC	5 /pass		
Sunscreen/Insect Repellent test (~GMW14445) (adhesion/aspect)	5 /pass			
Humidity resistance (adhesion/aspect)	ABS-PC	5 /pass		
	Thermoformability (Mould - Cylinde different height)			
	1 cn	n (~50 % elongation)	pass	
	3 cn	n (~150 % elongation)	pass	
	<u>5 cn</u>	n (~200 % elongation)	pass	
	8 cm	n (~300 % elongation)	pass	

Allnex's Diverse UV Coating Resins for Automotive Applications: Next Generation UV

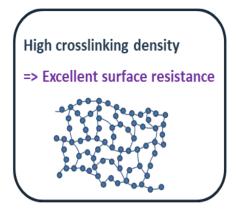


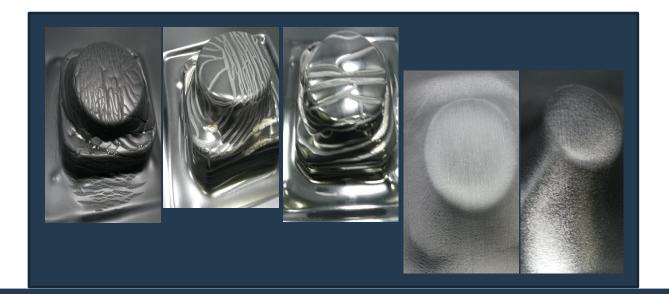
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Automotive Next Generation UV

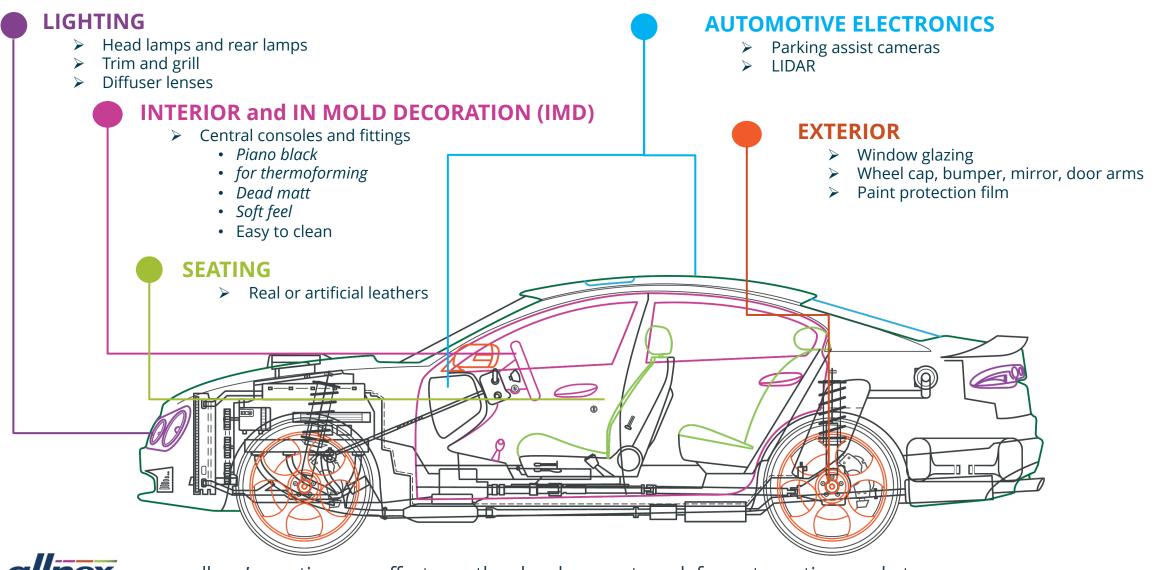
- Dual Cure is an excellent alternative but it works best if you can thermal cure followed by UV cure
 - Learning curve for those not skilled in handling 1K and 2K system
 - > Pot life
 - > Additional handling
 - > Equipment
 - Cannot coat and go
- Challenge remain for a flexible hardcoat for automotive application
 - Tack free after UV cure
 - Chemical resistant
 - Haze after abrasion <15%
 - Elongation >75%
- Weatherable hardcoat
 - Need ductile behavior
 - Improved weatheriability







Allnex's diverse UV coating resins for automotive applications: Next Generation UV



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Automotive Next Generation UV

• How do you get elastomeric and thermoset behavior in a single cure system?

- Traditionally with UV through blending
 - > Low acrylate functional
 - > High MW (>4000 Daltons) oligomers
 - High viscosity
 - > Monofunctioal diluent
 - 20% of the formulation
 - > Glass transition slightly above room temperature
- Result
 - > Soft material with little to no chemical resistance and hardness
 - > Rigid material with limited post UV cure manipulation
- Next generation needs a new structure design
 - Rotational and volumetric hinderance
 - Chain length
 - Acrylate functionality
 - Higher glass transition





- Bridging the gap between flexibility and hardness
 - Materials for Comparison

	RX 20096	Aliphatic Urethane Diacrylate	Aliphatic Urethane Hexaacrylate
Acrylate Functionality	4	2	6
Tg, °C	90	46	50
Viscosity, cPs	~16000	191000	80000
Elongation, %	105	150	<2
Tack free after UV 0=tacky, 5=tack free	5	2	5

- Application
 - Resin + 30% solvent initiated with 4% photoinitiator
 - Solvent was removed at 80oC with a 10 minute dwell time
 - Cured with an energy density of 1000 $\rm mJ/cm^2$
 - Draw film thickness was $12-14\ g/m^2$

Testing

- Hardness: Taber Haze (100-300-500 cycles on PC sheet with 500g load)
- Crosshatch adhesion (CHA)
 - > 0 = no adhesion; 5 = full adhesion
- Tensile
- Sun lotion & hand cream test (Volkswagen test PV3964):
 - Sun lotion and hand cream are applied on a bandage.
 - The sample is put in a ventilated oven for 24 hours at 80°C.
 - Bandage is removed and the remnant of cream/lotion is wiped off with a tissue.
 - The sample is left for 4 hours at room temperature.
 - cross cut adhesion
 - Erichsen (Erichsen pen 318 with tip of 0.75 mm)



Automotive Next Generation UV: Flexible Hardcoat

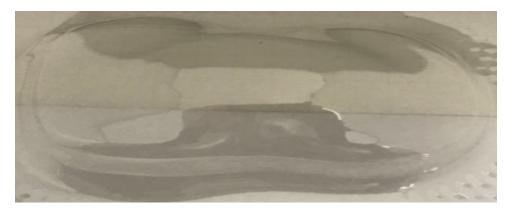
Automotive Stains		RX 20096	Urethane Diacrylate	Urethane Hexaacrylate
	Aspect	ОК	blister	ОК
Suntan lotion	CHA after test	5	1	5
	Erichsen pen	20N	5N	20N
	Aspect	ОК	blister	ОК
Hand lotion	CHA after test	5	1	5
	Erichsen pen	20N	5N	20N
DEET	Aspect	ОК	Blister	ОК
DEET	CHA after test	5	2	5

	RX 20096	Urethane Diacrylate	Urethane Hexaacrylate		
TABER	TABER HAZE (CS10F, 500g, Coating thickness 14 g/m ²				
100 cycles	10.2	23.3	5.7		
300 cycles	16.5	30.2	12.9		
500 cycles	27.5	35.0	19.9		

	Thermoformability after UV (Mould - Cylinder different height)					
RX 20096 Aliphatic Urethane Aliphatic Urethane Hexaacrylate Hexaacrylate						
	1 cm (~50 % elongation)	Pass	Pass	Fail		
	2 cm (~100 % elongation)	Pass	Pass	Fail		
any	5 cm (~150 % elongation)	Fail	Fail	Fail		

Automotive Next Generation UV: Flexible Hardcoat

- RX 20096 offers a unique structure that bridges the performance gap between flexibility and hardcoats
 - With a tensile strength over 5000 psi and elongation over 75% makes RX 20096 first-rate choice for exterior application such as paint protection films
 - > Excepted weatherability over 5000 hours with light stabilizers expected
 - Flexibility, hardness, and chemical resistance makes RX 20096 an excellent choice for automotive interior application
 - > Post cure manipulation
 - Chemical resistance to DEET, sunscreen lotion and hand creams
 - High glass transition temperature
 - > No softening during elevated chemical testing
 - Excellent adhesion to a number of automotive plastics such as PC, PC blends, and ABS







Automotive Next Generation: UV for Glazing

• UV Curing and automotive have had an excellent partnership over many dedicates

- 70 80% of automotive headlights use a UV curable glazing
 - > Outstanding hardness, chemical, abrasion, and chip resistance due to high crosslink density
- Fast reactivity
- Excellent for flat and rigid substrate
- With material advancement comes change
 - Parts no longer flat but elongated
 - Scratch is not longer just surface hardness
 - > Car wash brushes
 - Improve durability
 - > 7-10 years of outdoor durability
 - > 6000+ hours in accelerated weathering
 - Sustainability
 - > Reduced VOC



Automotive Next Generation: UV for Glazing

- Next generation hardcoat for PC glazing and sensors
 - 6000+ hours in accelerated weathering with light stabilizers
 - More ductile system
 - Equivalent hardness to current hardcoat
 - Undiluted viscosity <20,000cP at 25°C

- Testing
 - Hardness: Taber Haze (100-300-500 cycles on PC sheet with 500g load)
 - Taber Abrasion: CS10 wheels, 500 grams

	RX 20383	Traditional Hexa-Functional acrylate for headlamp
Taber Haze (CS10F, 500g) at 14 g/m ²	8.73	6.79
Pencil Hardness (on glass)	ЗН	НВ
Steel wool 0000, 1 kg, double rubs	100	100
Xenon	5,000+ (with light stabilizer)	2500 (with light stabilizer)
Viscosity, cPs at 25°C	10,000 — 15,000	30,000 – 70,000cP

Coatings based on RX 20383 can be formulated to meet a number of OEM specs for water and humidity resistance

- 80 90% high solid builds are possible
 - Excellent adhesion to PC
- Lower crosslink density but equivalent performance
 - Ductile behavior



The seating is usually made by real or artificial leathers. UV coating solutions offer substrates the performance upgrade in scratch & chemical resistances, meanwhile provide a VOC free environment in finishing step

Resin Technology	 ✓ Commercial resin & prototypes available ✓ IRR912 ✓ With 100% UV or Water based UV
Application Technique	 ✓ Air-knife and knife on roll coating ✓ Roller and engraved roller coating ✓ Curtain coating ✓ Spray coating
Performance	 ✓ Matte & High gloss effects ✓ Bally-flex: room temperature 300k times ✓ Taber abrasion: 100 cycles CS10 @ 500g ✓ Stain, denim & hydrolysis tests

Denim test @gloss/matte surface

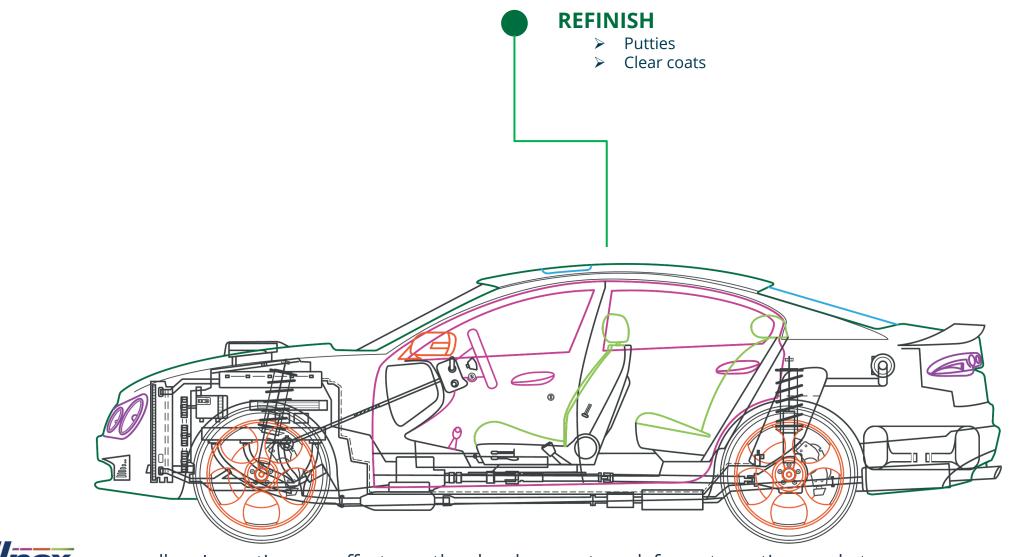


*IRR912 – prototype code



Degree of freedom to determine the best 'performance-sustainability-application' option

Allnex's diverse UV coating resins for automotive applications: Vehicle Refinish

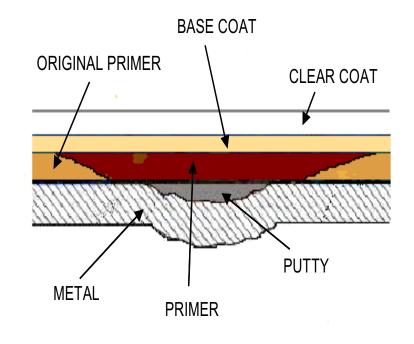




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Automotive Refinish

- UV and automotive refinish has been around for little more than decade
 - Limit growth over that time due to bulky and non standard voltage curing equipment
- New handheld, smaller, more modular units are now available that are battery or use standard voltage
 - Now automotive refinish can capitalize on UV value proposition
 - > Increased vehicle throughput
- How does UV fit within the automotive refinish world?
 - Putties
 - Primer
 - Clear coat
- Why not base or color coats
 - UV system shrinkage upon cure
 - Color generation upon cure





Automotive Refinish: Primer/Putty

Putty/Primer development focus

- Excellent adhesion to refinish substrates
- Excellent pigment wetting
- Reactivity to overcome oxygen inhibition and maximizing cure conditions
- Depth of cure

Ingredients	Function	А	В
		%	%
Aliphatic urethane triacrylate dilated in DPGDA or IBOA	Putty Vehicle	50.0	40.0
CaCO ₃	Filler	40.0	50.0
Mica	Filler	5.0	5.0
Talc	Filler	3.0	3.0
Photoinitiator ⁽¹⁾	UV cure	2.0	2.0

Table X: Putty Film Properties				
Test	Substrate	А	В	
X-hatch Adhesion	cold rolled steel (% retained)	100	100	
aluminum (% retained)		95	100	
Direct Impact cold rolled steel (in·lbs)		75	75	
	aluminum (in·lbs)	70	75	
- Excellent adhesion - Depth of cure of 1/8"				

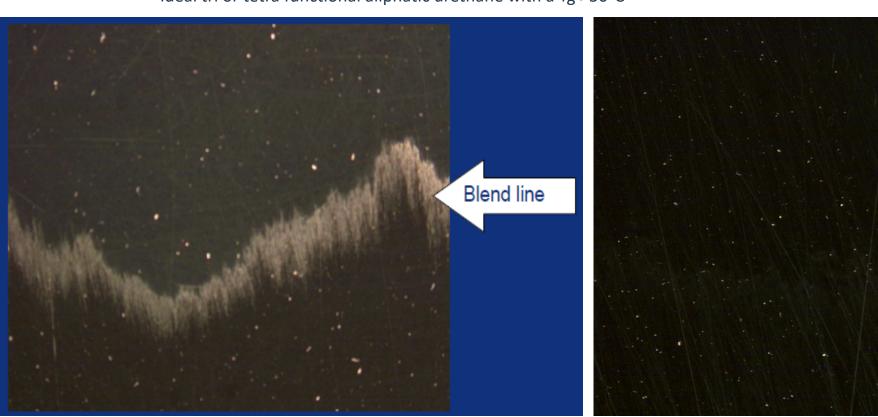
- Excellent pigment wetting
- Outstanding cure response (40-60 mJ/cm²)
 - > Sandable in <2 minutes cured
 - > Fully cured within 5 minutes

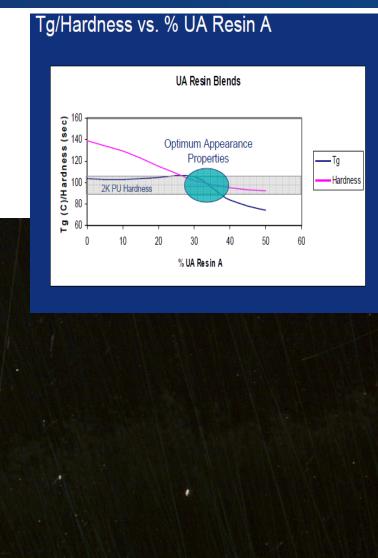
- Good impact resistance
- Can be used on TPO with proper surface prep
- Can be formulated into primer



Automotive Refinish: Clear Coat

- Biggest challenge weatherability
 - UV does not have weathering history compared to automotive clear coat
 - Blending UV cure topcoat with conventional clear
 - > Tg and hardness mismatch
 - Ideal tri or tetra functional aliphatic urethane with a Tg >50°C





Conclusions & Outlook: UV Resin Solution For Automotive Applications

- UV coating technology is well developed for many automotive applications, offering performance to meet many OEM specifications
- Different resin types are available from SB UV, 100% UV to WB UV
- UV coating solution enhance the performance of automotive coating system especially in scratch, chemical and weatherability resistances ve Electronics: Circuit Boards
- allnex, a valuable partner, strived to upgrade UV resin solutions through continuous learning and listening to market needs
- Sustainability and the environment are critical to success factors as allnex strive to improve resin offering to formulators, brand owners, and finishers



Thank You Questions??

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