An Introduction to UV Cured Solid Resins Applications and Benefits

Michael Knoblauch

Keyland Polymer Material Sciences, LLC

Agenda

- What is cure?
  - Ultra Violet (UV), Electron Beam (EB), Thermal
- Benefits and value proposition of UV curing
  - UV cured solid resin
    - How it is synthesized and produced
    - Properties – benefits and limitations
    - Illustrations of molecular structures
    - Cure testing and evaluation
  - Uses of UV cured solid resins
    - UV cured powder coatings
    - Solubilized or dispersed in liquid materials
    - Binder resin for Li battery cathode
  - Conclusion

DVUV
Wood Powder Coating

Since 2005, DVUV has been producing commercial and industrial medium density fiberboard (MDF) furniture products finished with UVMax® powder coatings.

KEYLAND POLYMER
UV POWDER

Keyland Polymer UV Powder develops, formulates and manufactures UV Cured Powder coatings., sold under the UVMax® brand.

KEYLAND POLYMER
UV RESINS

Keyland Polymer UV Resins' resins are used in powder coatings and as additives in UV and EB cured materials.

KEYLAND POLYMER
UV MATERIALS SPAIN

Keyland Polymer UV Materials Spain develops and manufactures UV curable solid resins used in UV cured powder coatings and other UV/EB materials.

KEYLAND POLYMER
UV APPLICATION TECHNOLOGY

Keyland Polymer UV Application Systems provides system design engineering, installation, and operating consulting assistance to firms building UV powder application systems.

What is Cure?

Cure is the measure of the crosslinked oligomer chains or fully reacted double bonds residing in the coating matrix following exposure to the curing system, which can be ultraviolet (UV) light exposure or thermal energy IR, convection or other types.

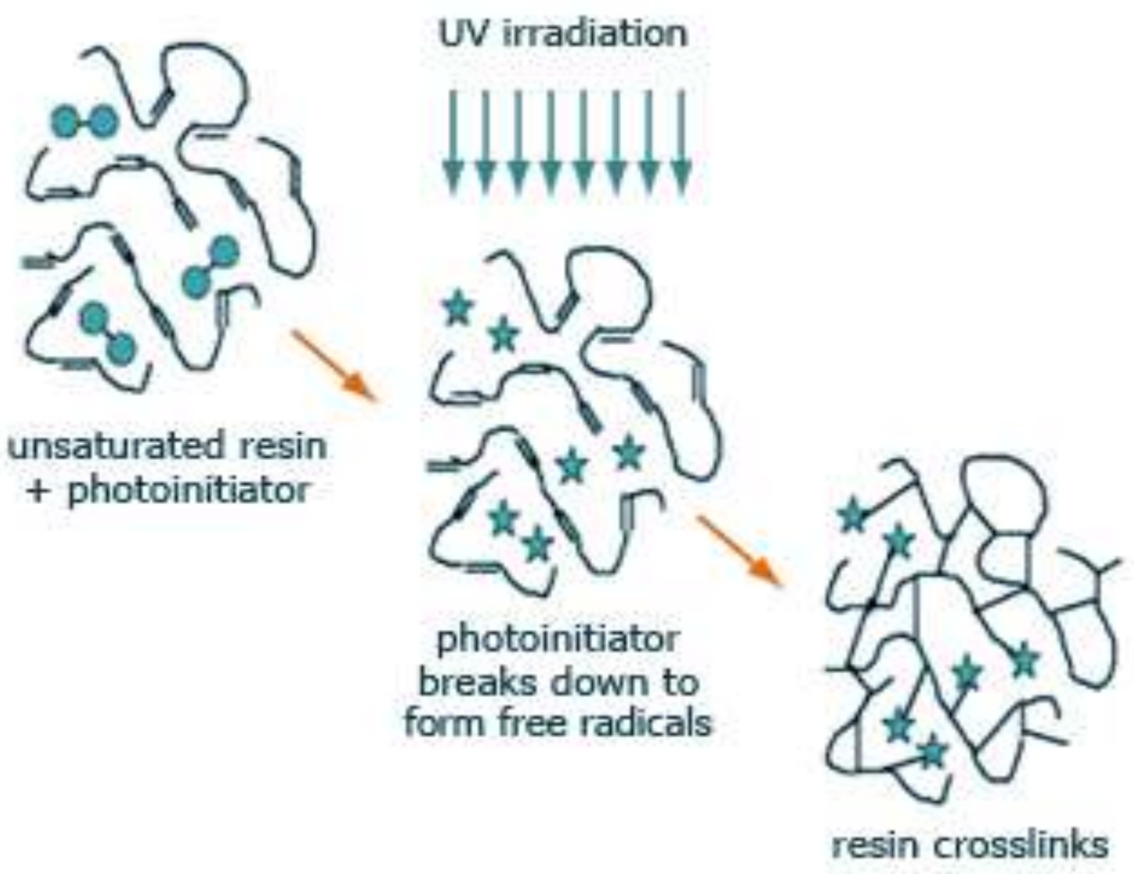
Differential Scanning Calorimetry (DSC) is a scientifically recognized, reliable and repeatable methodology to measure the cure of a coating system.

UV Curing

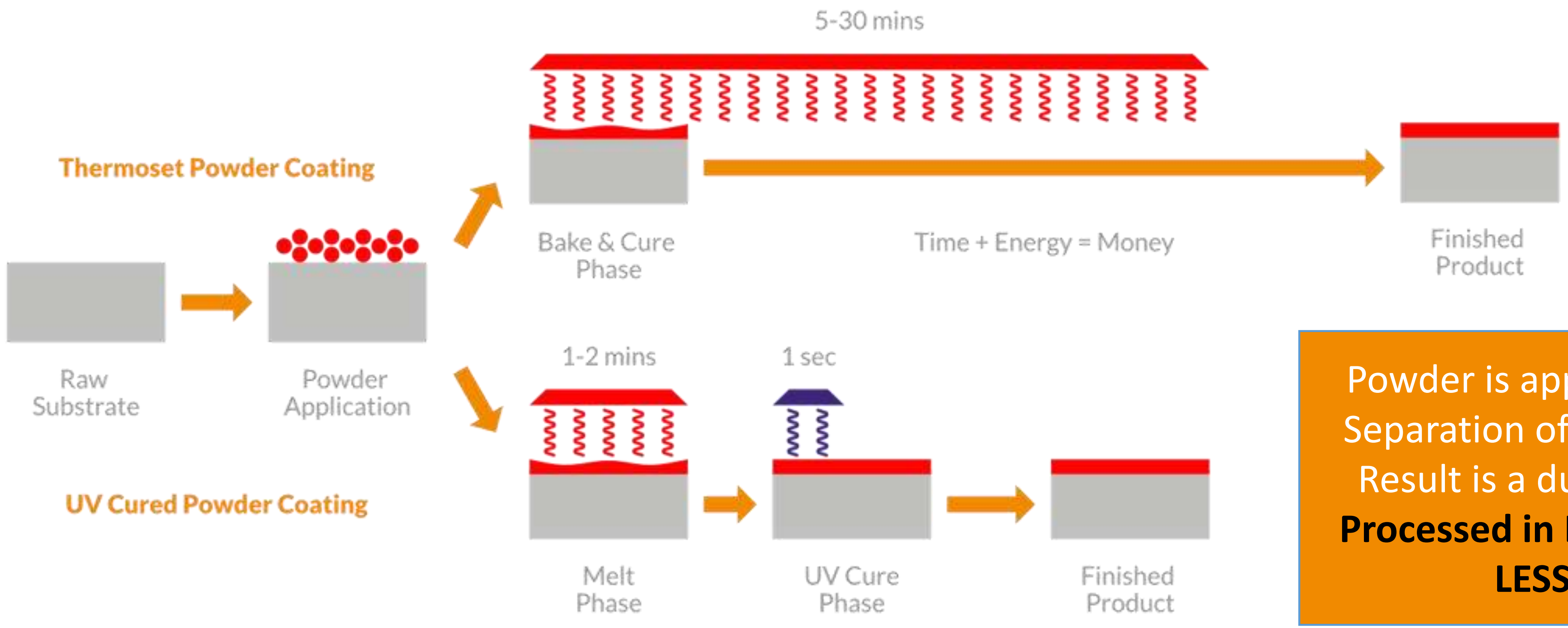
Ultraviolet (UV) powder coatings are photopolymerized coatings containing a chemical photoinitiator that instantly responds to UV light energy initiating a chain reaction and curing the coating.

Post application there are two critical stages, a melt phase followed by UV cure. The purpose of the melt stage is to heat the powder, converting the solid powder to a melted material within temperature range of 110C – 130C.

Once this temperature is reached the coating is instantly cured with UV. The heat source can be IR, convection, or other types.

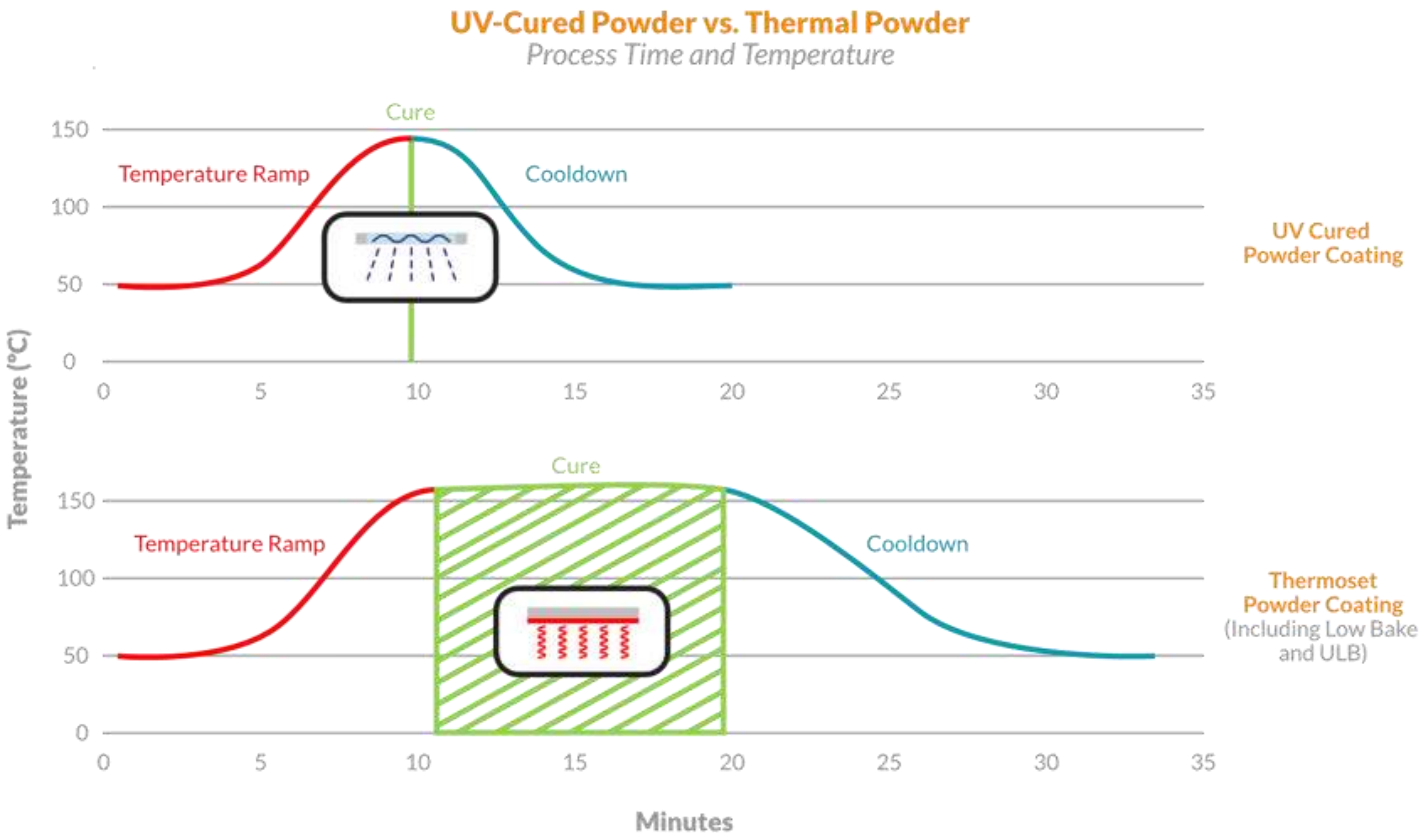


Process Differentiation



Powder is applied the same
Separation of melt and cure
Result is a durable coating
Processed in LESS time with LESS Heat

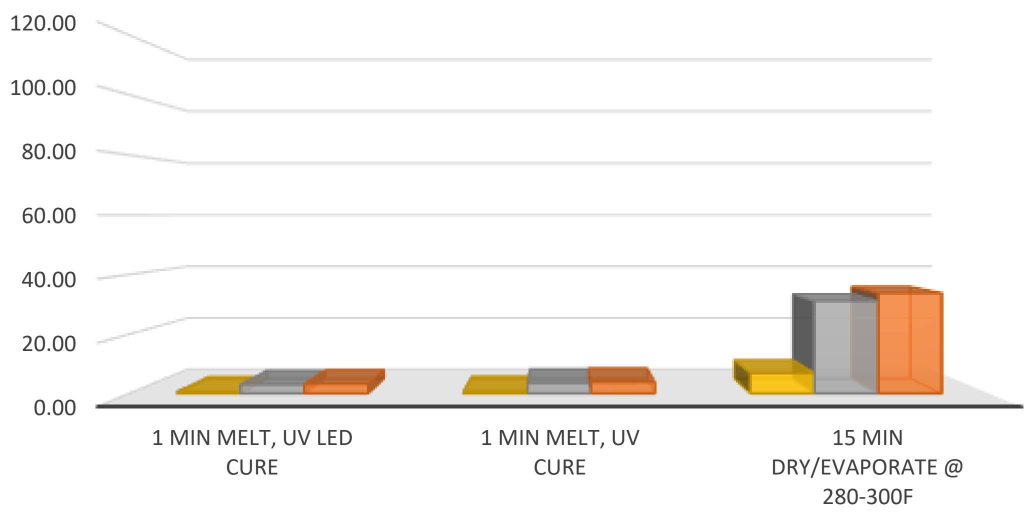
Cure Differentiation - Time & Temperature



GOAL: Melt the powder NOT compromise the substrate

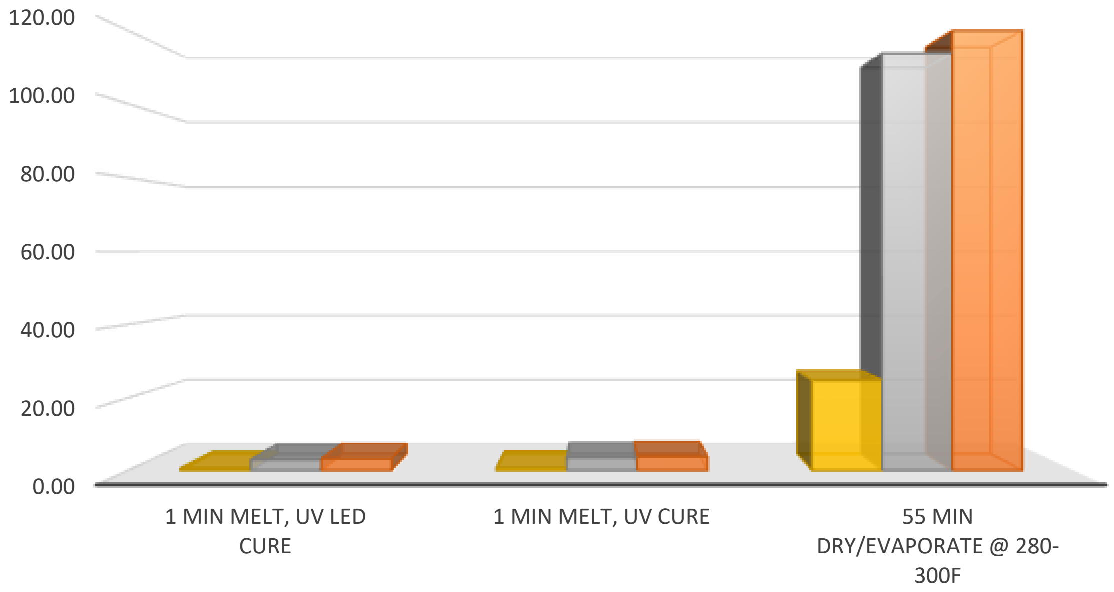
Melt & Cure UV Powder Coating & Drying or Water Evaporation of Waterborne Coating

Energy, Carbon Footprint, & Cost of Energy Comparison



	1 Min Melt, UV LED Cure	1 Min Melt, UV Cure	15 min dry/evaporate @ 280-300F
Energy Cost/Part	$0.64	$0.76	$6.75
Per Part C02	2.94	3.48	31.05
Per Part kWh	3.2	3.8	33.8

Energy, Carbon Footprint, & Cost of Energy Comparison



	1 Min Melt, UV LED Cure	1 Min Melt, UV Cure	55 min dry/evaporate @ 280-300F
Energy Cost/Part	$0.64	$0.76	$24.75
Per Part C02	2.94	3.48	113.85
Per Part kWh	3.2	3.8	123.8

Health and Safety

- High molecular weight – fewer extractables
- Low toxicity
- Low/no odor
- Low/no skin irritation
- 100% solid - easy clean up
- No permits to make or use

Environmental

- No water
- No solvents
- REACH compliant
- Small/low carbon footprint
- Low energy consumption as a % of production

Productivity

- Instant UV cure
- Fast melt for UV cured powder coatings
- Small plant footprint
- High rate of production, one coat finishing
- Quick ROI

Process

- One coat – reclaim – high transfer efficiency
- Uniform coverage
- No edge soak on wood substrates
- Wide variety of materials to finish – woods, plastics, composites, carbon fiber, heat sensitive

Limitations: Line of sight – light must see surface being cured – this can be overcome with robotic movement of UV lamp
Marginally higher capital investment – offset by fast ROI, greater productivity, lower energy and plant costs

Synthesis and Production UV Cured Solid Resins

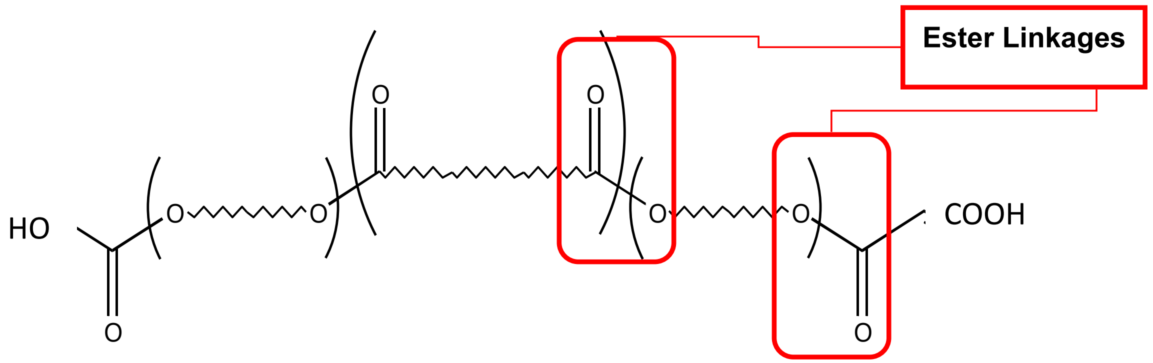
Types of resins and associated crosslinkers

- Properties and limitations
- Illustrations of molecular structure
- Explanation of double bond structures and free radical curing

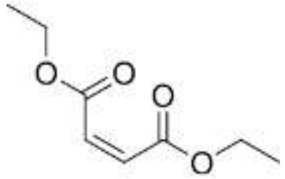
How UV light initiated curing is different from thermal curing

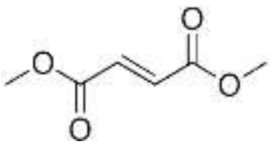
- Explanation of melt phase followed by UV light cure and how this differs from continuous melt and gel phases of thermal curing

Unsaturated Polyester resins



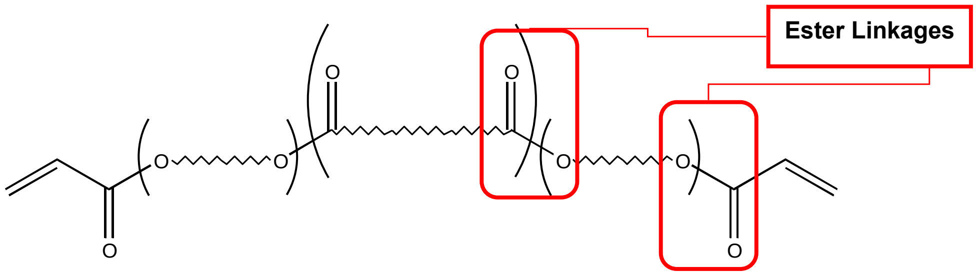
- Reaction products of alcohols with acids with double bond functionality.
- Mainly polyesters based on Maleic anhydride or Fumaric acid





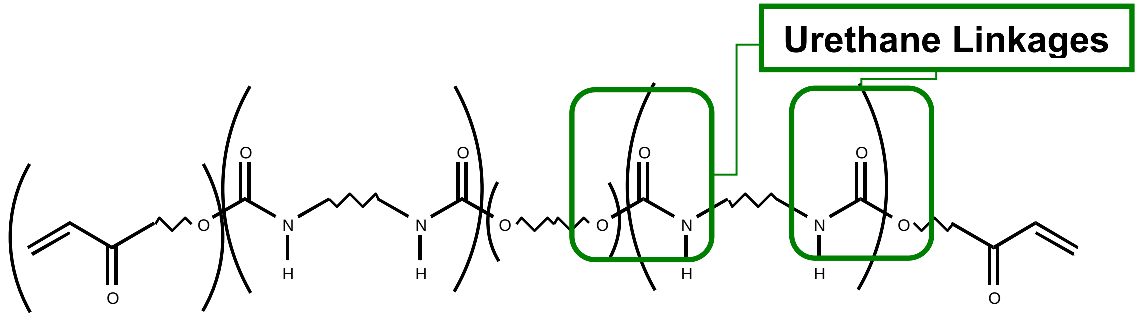
- Two main prepolymer types: carboxyl or hydroxyl types.
- Possibility to be used mixed with Acrylourethane resins or vinylether derivatives.

Polyester (Meth-)Acrylates



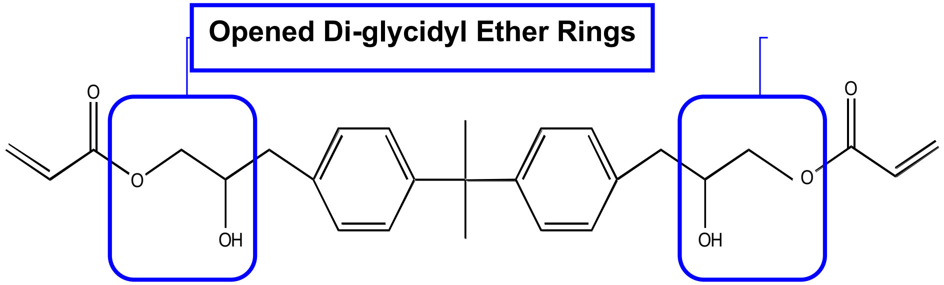
- Based on similar polymer backbone of the Unsaturated polyesters. Possibility to have polyester backbone with saturated dicarboxylic acids or also with unsaturated diacids or anhydrides.
- As indicated two main prepolymer types: carboxyl or hydroxyl types, and then depending on the prepolymer end groups, it is possible to functionalized with acrylic or methacrylic alcohols, acids, or anhydrides and oxirane functional group.
- Amorphous or crystalline types, normally used semicrystalline types or mixed of both, modifying the rheological behavior and chemical and mechanical properties.
- Semicrystalline polymers or combination of amorphous resin with crystalline monomers in the powder coating formulation allows for good storage stability below Tg combined with good flow properties above the melting point.
- Wide range of viscosities, functionalities, and backbone structures
- Properties are variable, depending on the polyester backbone.
- Good outdoor and yellowing performance depending on the polyester backbone.

Urethane (Meth-)Acrylates



- Reaction products of polyols or OH prepolymers with isocyanates and a hydroxy functional acrylate
- Allows for many different molecular weights and backbone structures
- Offer varying properties, depending on the nature of the isocyanate: aromatic or aliphatic.
- Possible to obtain crystalline types
- Low MW difunctional urethanes can be used as reactive diluents into the formulation resulted in a significant reduction in melt viscosity. In general, bifunctional derivatives increased Tg, modulus, crosslink density and impact resistance while monofunctional derivatives increased impact resistance and % elongation at break but decrease Tg and crosslink density.

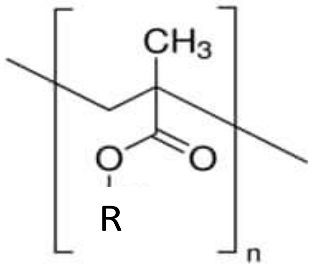
Epoxy (Meth-)Acrylates



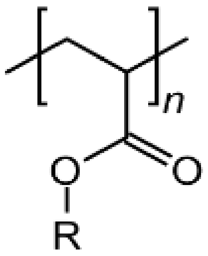
- Reaction products of solid di-glycidyl ethers with (meth-)acrylic acid
- These chemical compounds are based on aromatic groups however it is possible to used aliphatic type epoxy resins e.g. hydrogenated bisphenol, glycidyl acrylate, glycidyl methacrylate
- Tend to be higher in viscosity.
- Offer good hardness, cure speed, chemical resistance.
- Poor outdoor and yellowing performance.
- Addition of hydroxyl polyester contains a terminal hydroxyl group results in better properties of the final UV cured coatings.
- With modified epoxy resins it is possible to formulate UV cationic curing.
- Epoxy resins and vinyl ethers both undergo cationic curing mechanism it is possible to combine them in appropriate ratios. In addition, cationic curing resins can be combined with acrylourethane type resins or unsaturated polyester type resins.
- For cationic curing, photoinitiators used include sulfonium type, ferrocenium type, benzyl dimethyl ketal.

Acrylate and Methacrylate derivatives

The main products are based on an acrylate or methacrylate backbone with the right Tg , modified it to have a solid acrylic resin with the desired functionality for further polymerization by UV radiation.



Polymethacrylate



Polyacrylate

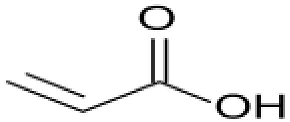
Substitution groups, there are important to obtain the right Tg:

R = - CH_3

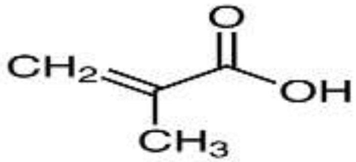
- CH_2 - CH_3 ALKYL GROUPS

- CH_2 - CH_2 - CH_2 - CH_3 ; …..

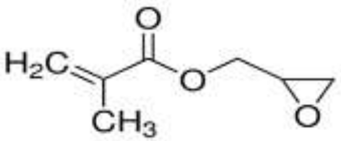
Reactive sites for further functionalization:



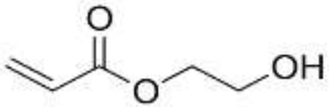
ACRYLIC ACID



METHACRYLIC ACID



GLYCIDYL METHACRYLATE



HYDROXYETHYL ACRYLATE

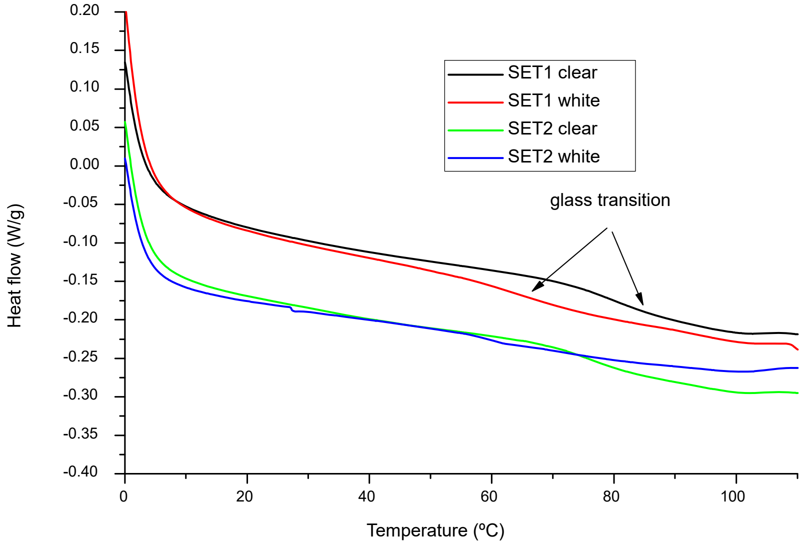
- There is possible to obtain different final coating properties depending the chemical nature of the acrylic back bone.
- With Acrylic based systems we can obtain finish systems with excellent Outdoor properties.
- High hardness and normally poor mechanical properties but with excellent adhesion.

PHOTOCALORIMETRY:

Using a DSC, with an external UV light source to irradiate the sample and reference and measure, the Tg and the exotherm of reaction after dosage of the UV light, energy at a fixed temperature.
The Tg of the cured systems can be used to check the reactivity and the end properties of the cured coatings and use to compare in a practical way that the coating is fully cured. It is used too to check the effectiveness of curing at different lamp distances from the substrate.

In a study of reports the glass transition temperatures (Tg's) of different samples, clear and pigmented and the lamp position. The thermograms are shown below:

It can be observed that both clear coatings have a well- defined Tg with a value of approximately 80ºC, although it is higher in the case of a clear, in case of a closer lamp position indicating better cure, leading to better irradiation throughout the coating thickness. In the case of the white samples, the Tg is not easily determined, as it becomes broader, suggesting a lesser effective irradiation throughout the coating thickness, with regions with a higher Tg (closer to the exposed surface) and lower Tg (closer to the substrate).



In case of evaluating the reactivity:

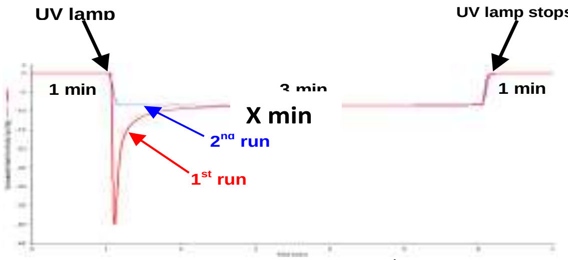


Photo-DSC curves of 1st and 2nd run

The first scan exhibits an exothermic peak which originates from:

- Powder cross-linking reaction's energy
- The energy absorbed by the sample and the reference.

We can evaluate the curing by irradiating several times to check the reactivity.

The second scan is done to estimate the base line and to check if the system is fully cured.

Experiments performed at a defined Temperature, which we consider that the sample is melted.

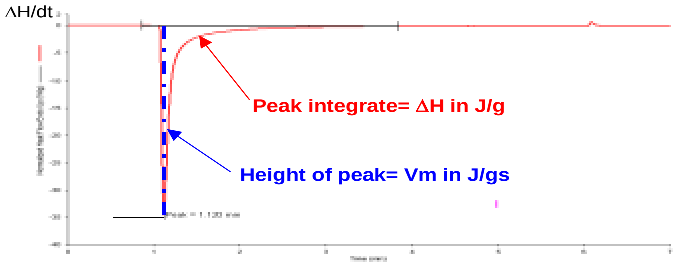


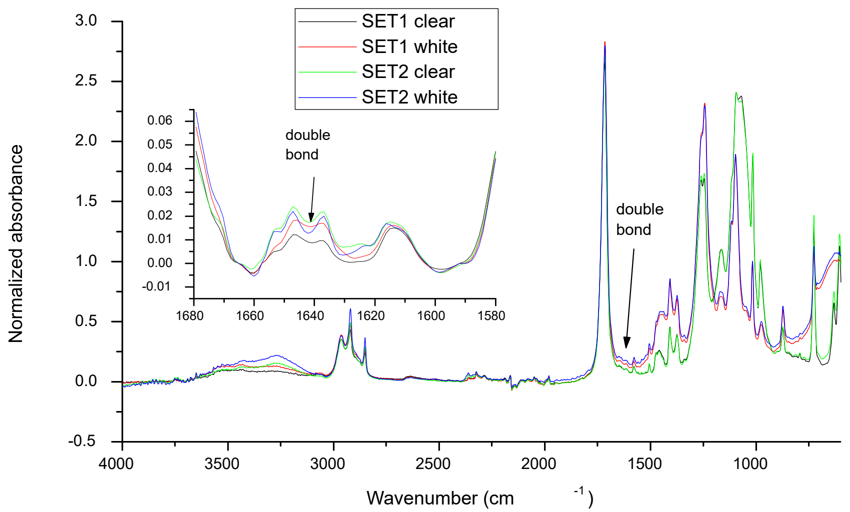
Photo-DSC subtract curve

The energy necessary for the conversion of the monomers is equal to 1st scan - 2nd scan.

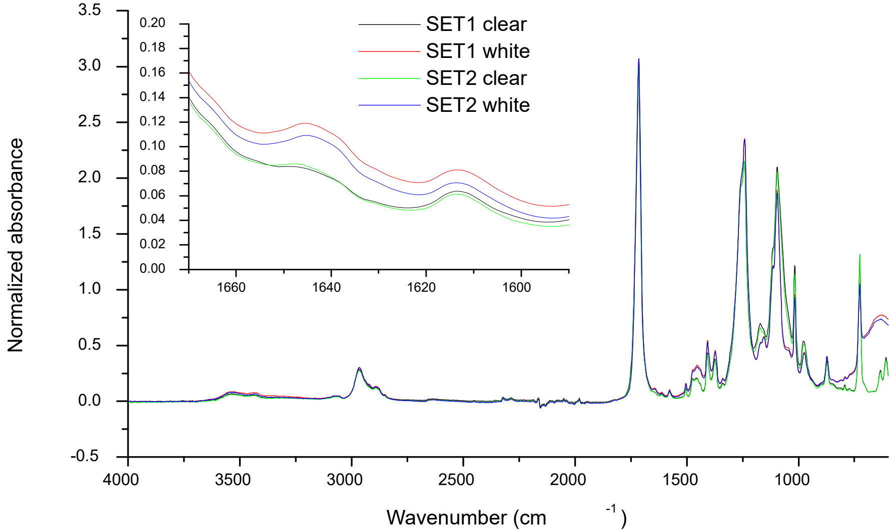
- ΔH: Exothermic energy released by the double bonds crosslinking
- Vm: Maximal crosslinking rate.

FTIR, photocuring.

We can follow the curing of the samples recording the FTIR spectra of them. In the example of comparison of powder coatings below, apparently no relevant differences are observed between the powder coating and T2-T4 samples. If wetake a lok in detail at the region where acrylate bonds are present, at 1636 cm^{-1}, it can be clearly seen a difference between the uncured powder and T2-T4 samples. The acrylate bond peak at 1636 cm^{-1}, decreases significantly after UV-curing, leading to similar degrees of cure in both T2 and T4 samples (no discernible differences can be appreciated), thus confirming the results obtained by photocalorimetry, DSC. It cannot be assured that curing is complete but that the coating has reached the maximum possible extent of cure.



This technique can be used to check the extent of curing at the bottom, that means in contact with the substrate. Below an example showing the spectra of the coating in contact with the substrate, bottom surfaces. We can see clear differences can be observed only in the region corresponding to the double bond at 1640 cm^{-1}. Both white samples, in this example, show a relevant signal corresponding to the amount of unreacted double bonds due to incomplete double bond reaction, while clear samples show a much smaller signal. The values for the white samples are almost identical. These results agree qualitatively with the DSC analysis of the samples, with higher Tg values for clear than for white samples.



Resins and Crosslinkers

As with all polymeric systems the properties are defined by the resin or binder with or without a cross-linker. In case of a binder + x-linker formulation, the x-linker will control the network density for the coating, while the binder determines properties of the coating such as discoloration, outdoor stability, mechanical properties. There are several options for the combination of binder and cross-linker for UV curing powder coating systems.

- Maleic/fumaric polyester combined with a vinyl ester or other crosslinkers
- Acryl/methacryl functional polyesters
- Acrylated/methacrylated urethanes
- Acrylated/methacrylated epoxy
- Unsaturated polyester combined with acrylic functional polyurethane
- Unsaturated polyester combined with acrylic or meth-acrylic functionality
- Acrylic with functional unsaturated groups
- Acrylic functional polyacrylic combined with acrylic functional polyurethane
- Maleic/fumaric polyester combined with allyl functional polyesters

Resin Modification

In general, the base polymer backbone is modified with acrylic or methacrylic groups for additional polymerization. A comparison of end groups:

Acrylic:
- Less Steric Hindrance for Radical Addition
- Faster UV Cure

Methacrylic:
- More Steric Hindrance for Radical Addition
- Harder, Higher Tg
- Lower Toxicity Profile

CERTIFICATE OF ANALYSIS

PRODUCT: **Solid Unsaturated Polyester Resin**

ASPECT: SOLID, granulates

CHARACTERISTIC	Units	Method	Values	Specification
Acid Value	mgKOH/g	EPA-01 REV 01	**9.7**	3 - 10
Hydroxyl Value	mgKOH/g	EPA-02 REV 01	**36.8**	30 - 45
Viscosity Cone Plate at 165ºC	mPa.s	EPA-04 REV 01	**15,663**	13,000 – 25,000
Viscosity Cone Plate at 200ºC	mPa.s	EPA-04 REV 01	**3,300**	3,000 – 6,000
Tg (Ramp 20ºC/min)	ºC	IA-02 REV 01	**46,2**	45 – 49

OTHER ANALYSIS

Molecular Weight Distribution, by GPC:		
	M_n (g/mol)	5,428
	M_w (g/mol)	13,388
	M_p (g/mol)	10,744
	D	2.47

CERTIFICATE OF ANALYSIS

PRODUCT: **Epoxy solid UV cured resin**

ASPECT: SOLID, granulates

CHARACTERISTIC	Units	Method	Values
Acid Value	mgKOH/g	EPA-01 REV 01	**0.6**
Hydroxyl Value	mgKOH/g	EPA-02 REV 01	**194.0**
Viscosity Cone Plate at 165ºC,	mPa.s	EPA-04 REV 01	**2,134**
Viscosity Cone Plate at 200ºC,	mPa.s	EPA-04 REV 01	**633**
Tg (Ramp 20ºC/min)	ºC	IA-03 REV 01	**48.6**

OTHER ANALYSIS

Molecular Weight Distribution, by GPC:		
	M_n	**3,198** g/mol
	M_w	**6,866** g/mol
	D	**2.15**

Resin Properties

Final resin product, the usual controls, or characteristics for the different types of solid reactive polymers indicated, are:

- Acid value
- Viscosity, molten at a fixed T
- Color of the polymer normally as solid or in solution
- Hydroxyl content or value
- % free monomer in finished resin
- Tg, Glass transition T
- Molecular weight distribution, Mn, Mw values and Distribution
- Polymer double bond content in meq/g
- Epoxy equivalent weight or epoxy value for modified epoxy-based types.

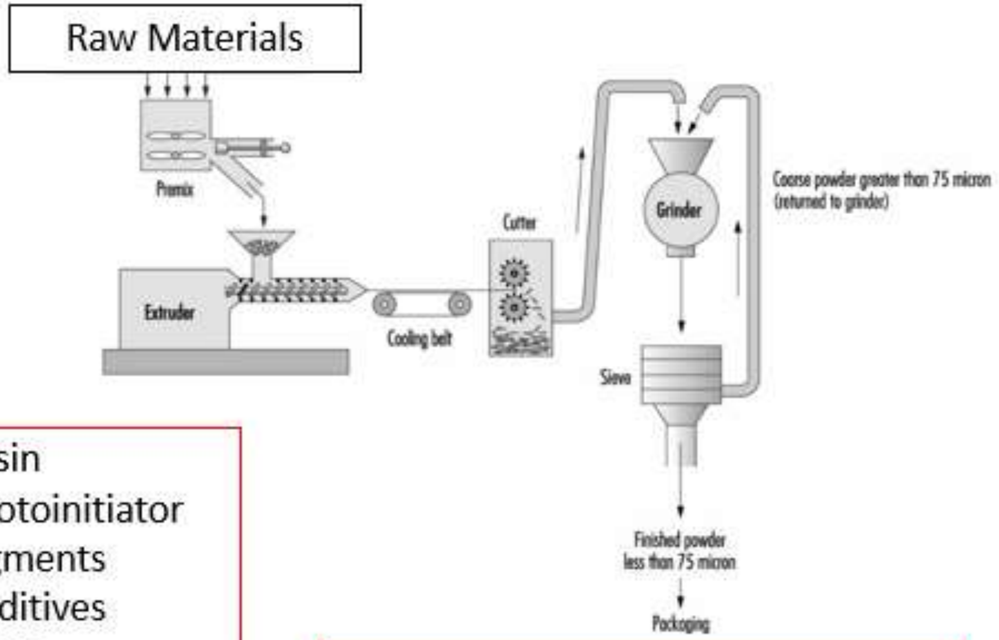
Formulated UV Cured Powder Coating Properties

Control of the powder coating formulated with the solid reactive polymer after preparation of the powder coating by extrusion:

- Coating, after curing (UV radiation)
- Mechanical properties
- Chemical properties
- Storage stability
- Optical and weathering resistance properties
- Tg, (glass transition temperature), of the coating and Tg, of the cured coating
- Photocolorimetry DSC, to determinate the reactivity
- FTIR recording during curing to evaluate the curing, and if there are unreacted double bonds.

UV Cured Powder Coating Manufacturing and Application

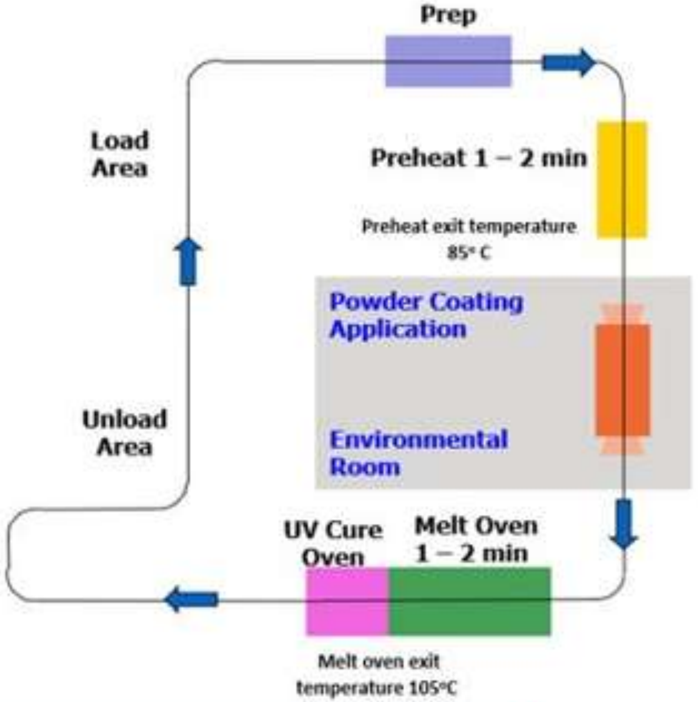
UV cured powder is made on the same equipment as thermoset powder



Resin
Photoinitiator
Pigments
Additives
Filler

No special process control steps required during extrusion or milling

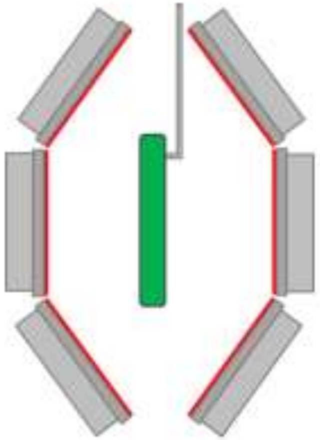
Example of a system layout for a UV cured powder coating line for MDF



200’ in length, 10’/min conveyor speed
20 min to finished component

UV Powder Process Overview
Vertical Hanging Line

1



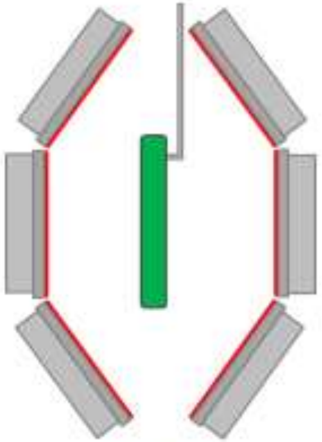
Preheat Preparation
Wood Panel Parts

Non-conductive parts require a conductive primer

2

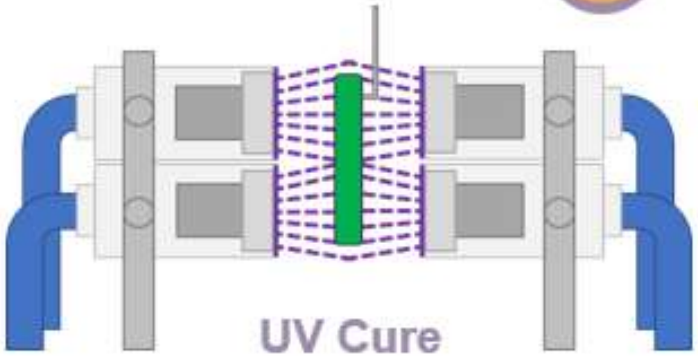
Powder Coating Application

3



Melt

4



UV Cure

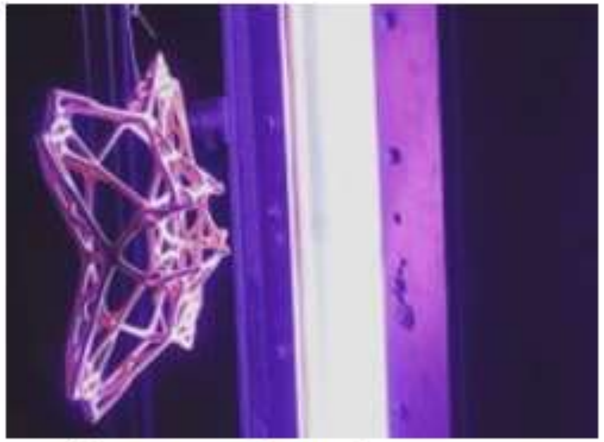
Materials Finished with UV Cured Powder Coatings

Foam core steel door

Carbon Fiber

MDF

Hollow core wood doors & MDF kitchen doors



Additive manufactured components

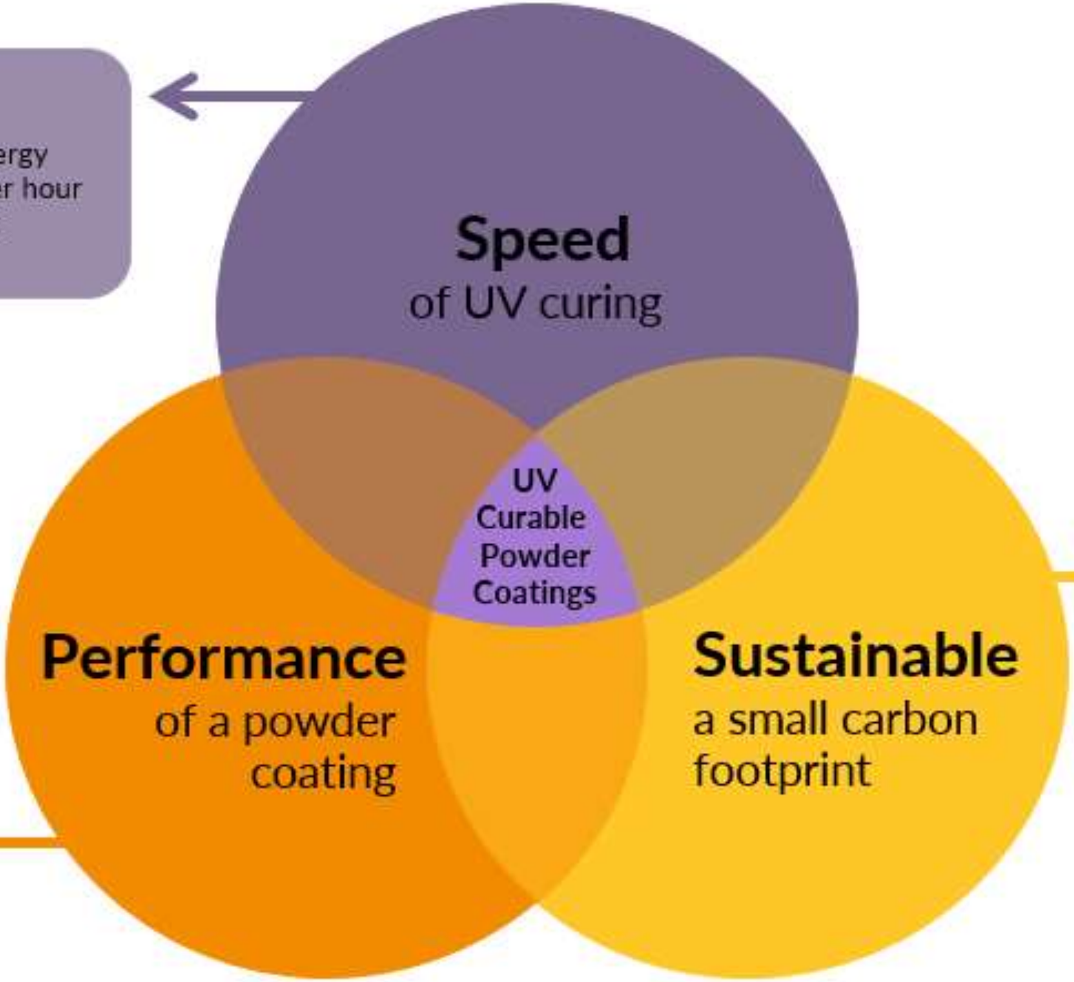
Coatings Trends & Technologies SUMMIT

UV Cured Powder Coating Performance Properties

	Test	Result
60° Gloss	ASTM D523	5 – 90
Film Build	ASTM D4138, Method A Destructive, Tooke Gauge	2.0 – 5 mils – substrate dependent
Adhesion	ASTM D3359, Method B	5B – No loss of adhesion
Pencil Hardness	ASTM D3363-05 Scratch Resistance	H – 3H
MEK Resistance	PCI Test Method #8	No softening after 50 double rubs
Abrasion Resistance	ASTM D4060, CS-17 Wheel 500g, 500 cycles	25 – 35mg Material loss

UV Cured Powder Coatings

- Fastest curing technology
- Saves time & energy
- Higher profits per hour
- High throughput capacity



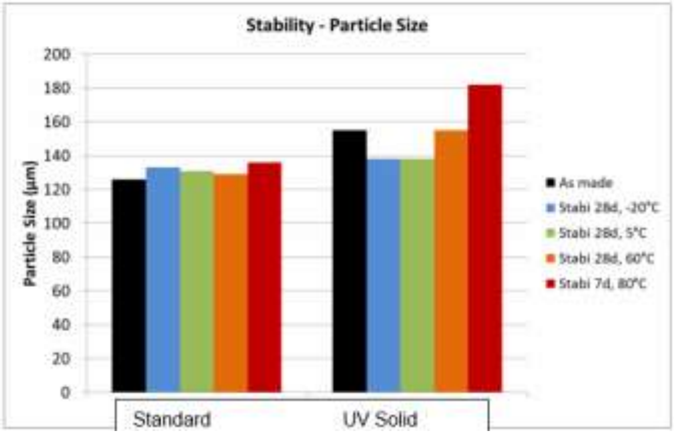
- 100% solid coating
- No Water
- No solvents or VOC's
- Saves energy
- Recyclable

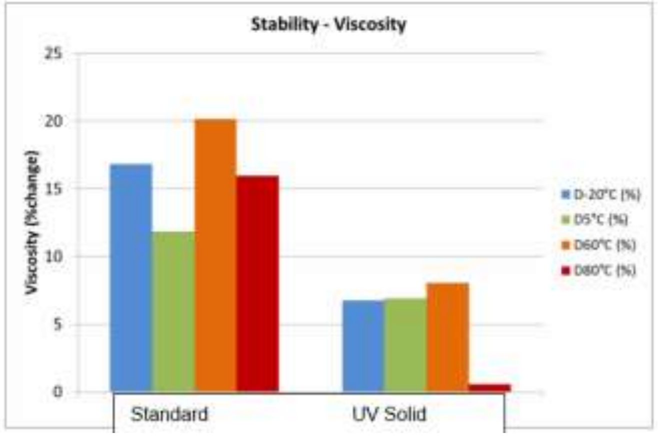
- Functional & decorative coating
- One coat finish
- Superior durability
- Reclaimable coating
- High transfer efficiency
- Reduces system footprint

Use of a UV Cured Solid Resin in Printing Ink

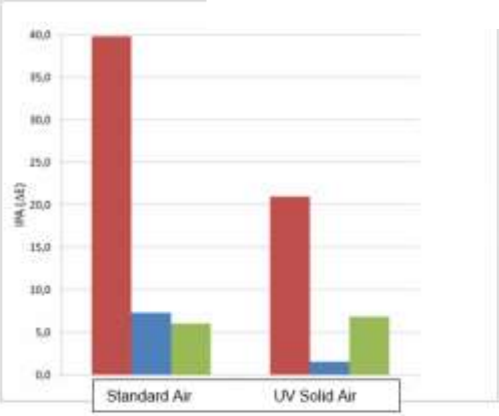
Project intent

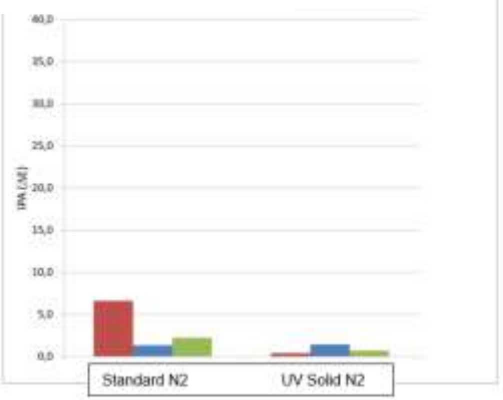
- Viscosity stability
- Viscosity reduction
- Better mechanical properties
- Better/lower migration properties

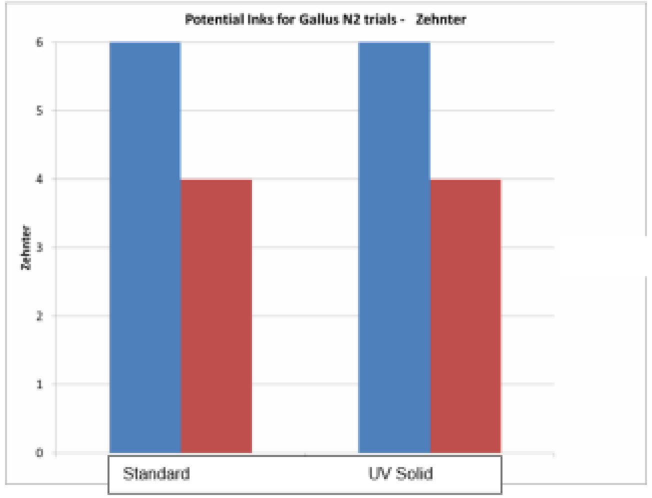

Stability - Particle Size
Particle Size (µm)
As made
Stabi 28d, -20°C
Stabi 28d, 5°C
Stabi 28d, 60°C
Stabi 7d, 80°C
Standard
UV Solid

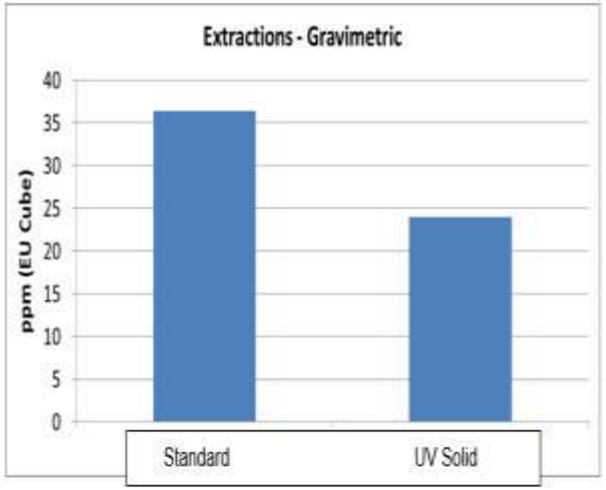

Stability - Viscosity
Viscosity (%change)
D-20°C (%)
D5°C (%)
D60°C (%)
D80°C (%)
Standard
UV Solid

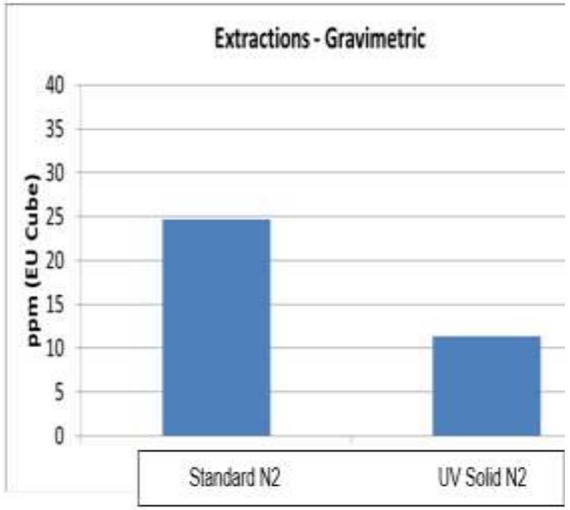
Cure

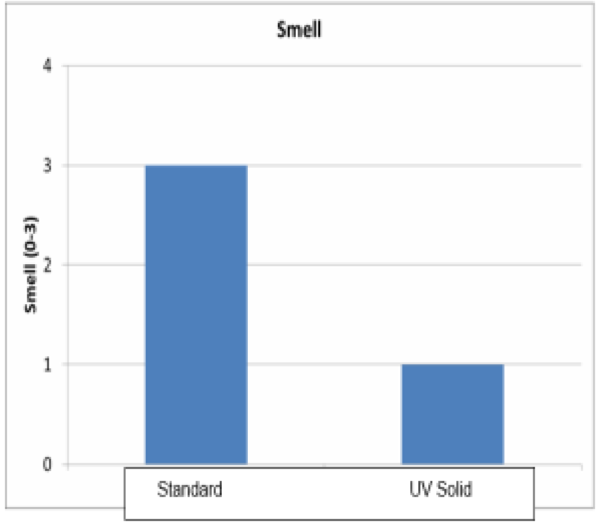

Standard Air
UV Solid Air


Standard N2
UV Solid N2


Potential Inks for Gallus N2 trials - Zehnter
Zehnter
Standard
UV Solid


Extractions - Gravimetric
ppm (EU Cube)
Standard
UV Solid


Extractions - Gravimetric
ppm (EU Cube)
Standard N2
UV Solid N2


Smell
Smell (0-3)
Standard
UV Solid

Project Summary

- Stability – very good storage stability in terms of viscosity in different conditions. There was a slight increase in particle size with time.
- Curing – In some situations the same curing as the standard material, other times better.
- Mechanical Properties – Better mechanical properties than the standard material.
- Compliance – Less extractables than standard materials, better smell.

Use of a UV Cured Solid Resin in Li Battery Cathode

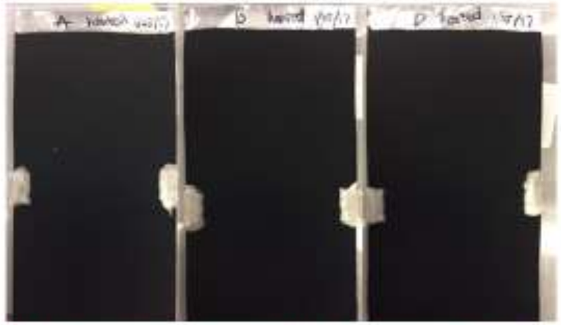
Project intent

- Eliminate the use N-Methyl-2-pyrrolidone (NMP) solvent
- 100% solid components
- Increase battery performance
- Increase productivity and lower cost
- Smaller manufacturing footprint

UV Cured Solid Material in Li Battery

Electrostatic spraying at Keyland Polymer

Collaborators at Keyland Polymer are evaluating electrostatic spraying method for battery coatings.



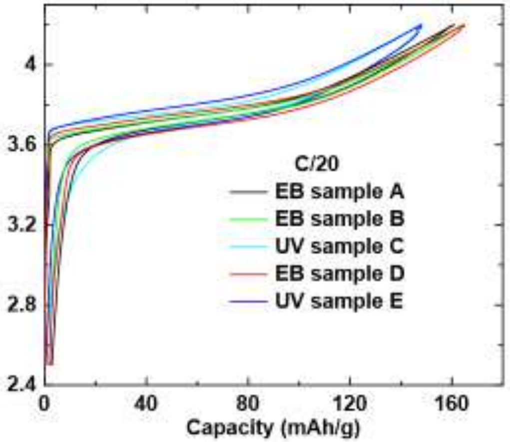
All the powders were well attached to the substrate after electrostatic spraying.

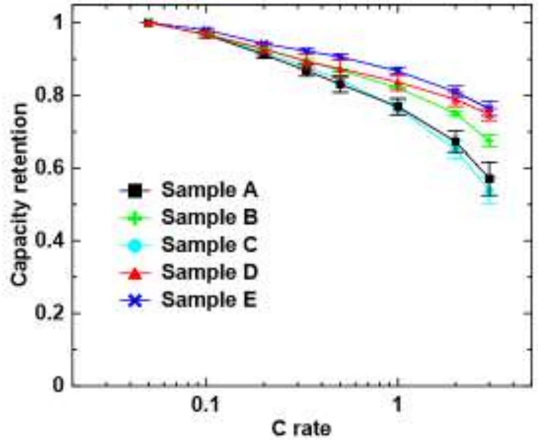
All the samples were calendared and adhesion was improved.

David L. Wood, III, DOE Annual Merit Review, June 8, 2017

OAK RIDGE NATIONAL LABORATORY

Performance of UV cured samples





The sprayed and cured samples shows typical NMC532 lithium intercalation/de-intercalation behavior.
The electrodes have good rate performance up to 3C.

David L. Wood, III, DOE Annual Merit Review, June 8, 2017

OAK RIDGE NATIONAL LABORATORY

Conclusion

UV cured solid resins are a backbone chemistries and performance enhancing additives for a variety of UV cured materials.

- Powder Coatings
- Inks
- Liquid coatings
- 3D printing and additive manufacturing
- Adhesives
- Li batteries

Development initiatives

- Replacement of hydrocarbon materials with bio-based materials
- Development of more robust exterior durable resins for coatings

UV cured solid resin chemistry utilizes the speed of light and intensity of Ultra Violet energy to cure, producing high performing and environmentally beneficial materials and products.

Data provided by: Francesc Williams and Alberto Sarabia, Keyland Polymer UV Materials Spain, SL

Thank you

Michael Knoblauch
Keyland Polymer Material Sciences, LLC
216-849-0342
mfk@keylandpolymer.com

www.keylandpolymer.com