Low Temperature Crosslinking for Powder Coatings

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Abstract:
This paper will focus on low temperature cure of hydroxyl polyesters with polymeric blocked isocyanate crosslinkers, carboxyl polyesters cured with TGIC and a discussion about the future of IR/UV cured powder coatings.

Specific polymeric blocked isocyanates have been formulated for low temperature cure of various hydroxyl polyesters. Cure capabilities in the range of 130 C have been achieved. Polymeric isocyanate crosslinkers blocked with ε-caprolactam and ε-caprolactam free crosslinkers will be described.

A novel approach to low temperature cure carboxyl terminated polyesters is described.The use of specific raw materials combined with selected catalysts has resulted in polyesters for triglycidyl isocyanurate,TGIC, cure which have cure capabilities at 121 C. Polymers and powder coating formulations which exhibit low temperature cure properties are described. This technology pushes conventional polyester powder resin raw material capabilities to the apparent limit of performance for low temperature cure.

For lower temperature cure than 120 C, ultraviolet, UV, cured powder coatings seem to be most feasible. Powder coating formulations melted with IR and cured with UV will be discussed.

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Introduction:

The powder coatings industry has continuously sought the reduction of cure temperature. Twenty-five years ago, low temperature cure for decorative powder coatings was considered to be temperatures below 200 C (392 F).

Today, low temperature cure products can be generally classified as products which cure at relatively short times at temperatures at or below 160 C (320 F).

Hydroxyl polyesters and specific polymeric blocked isocyanate curing agents have been developed for low temperature cure. It has been observed that as the functionality of the hydroxyl polyester increases, the temperature required for cure decreases. Crosslinkers based on more reactive isocyanates like HDI, hexamethylene diisocyanate, and Desmodur®W, methylene-bis-4-cyclohexyl diisocyanate, H_{12} MDI, have shown better low temperature cure capability than other isocyanates like IPDI, isophorone diisocyanate. Crosslinkers formulated with more reactive isocyanates and low temperature blocking agents have shown cure activity at 130 C (266 F).

Typical approaches to low temperature cure carboxyl polyesters have focused on the use of catalysts which accelerate the reaction between the acid functionality on the polyester with the epoxy functionality on the TGIC,triglycidyl isocyanurate curative. This standard approach results in powder coatings with flow decreasing as the cure temperature is reduced. The utilization of a more reactive polymer structure and a latent catalyst [1] in combination, is the essence of the invention described in this paper.[2] The optimized product described here has resulted in powder coatings which cure at 121 C (250 F).

Formulation of a polyester with low melt viscosity to provide good flow at low temperature cure conditions and a glass transition temperature, Tg high enough to prevent sintering, is a goal of the polymer chemist. These properties are often in conflict and present challenges to the polymer chemist. For hydroxyl polyesters cured with polymeric blocked isocyanates, flow is maintained even at very low temperatures because the crosslinking does not begin to any extent until the blocking agent has left the polymeric diisocyanate. This is usually enough time to permit good flow to occur before crosslinking increases the viscosity of the powder coating.

Low temperature curing systems can give faster cure at elevated temperatures. This can result in optimum coatings performance properties and permit faster line speeds.

Normal cure versus low temperature cure

The maximum temperature that an oven can attain, or the heat stability limitations of the substrate may require specification of a low temperature cure powder coating. Typically, low temperature cure powder coatings have a baking temperature 20-40 degrees C below the equivalent normal curing powder coating. Powder coating suppliers do not recommend that the normal powder coating be cured at temperatures 20-40 C below what is typically recommended because an under cure situation would most likely be created or very long cure times would be needed.

Low temperature curing powder coatings are often cured at higher temperatures, near typical baking temperatures, to induce faster cure. This is commonly done when an applicator has a short oven and wants to increase the production rate. If a standard cure powder is used in this manner, under cured parts would result from the short bake times.

Low temperature curing powder coatings may be used to:

- Permit powder coating of temperature sensitive substrates or components. This may include assembled parts with temperature sensitive seals etc., wood components, certain plastic parts or components.

- Reduce energy costs by lowering baking temperatures.

- Provide a means of increasing the rate of production by baking at higher temperatures or normal temperatures for shorter periods of time.

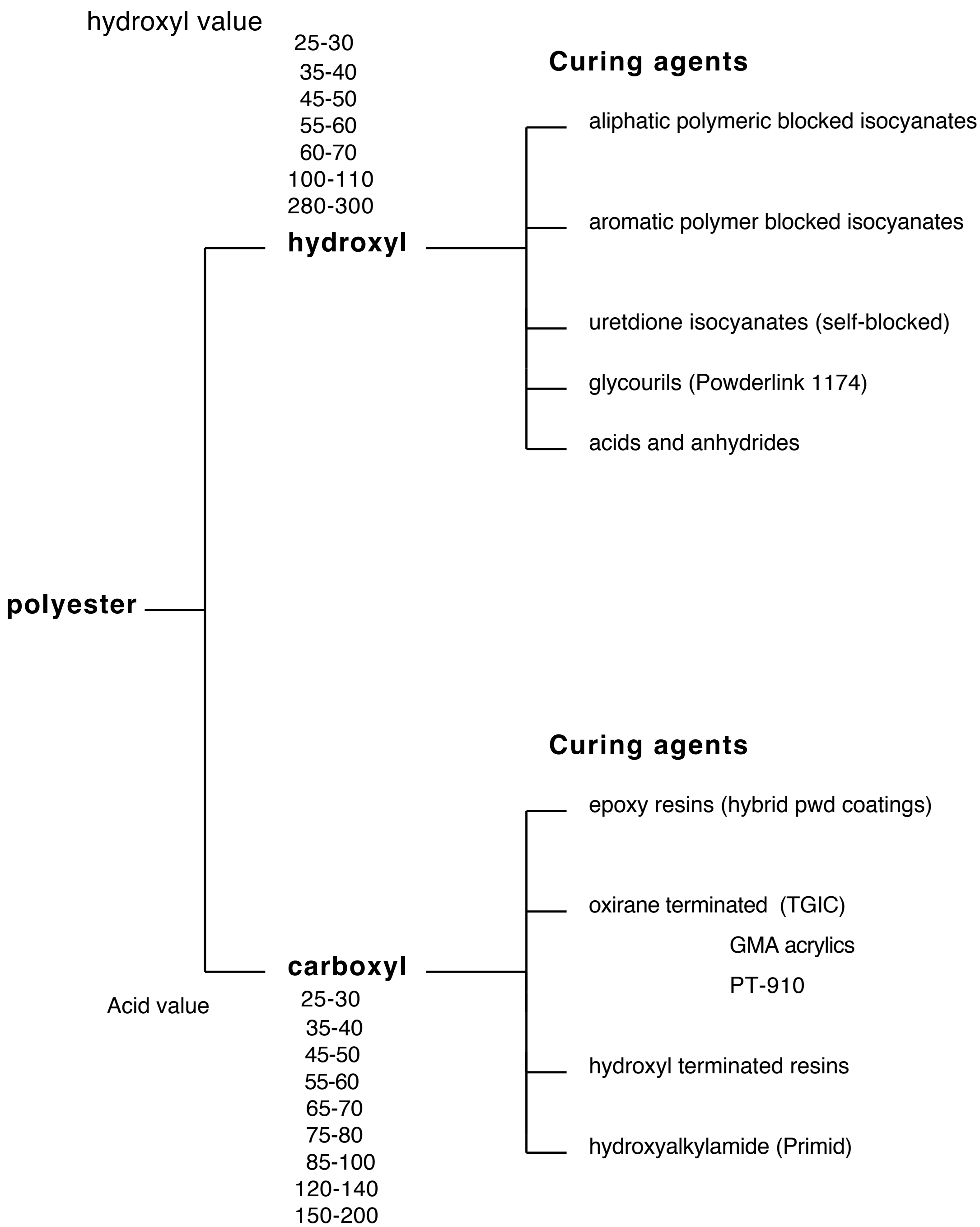
Limitations of low temperature cure powder coatings:

- Extremely high levels of catalyst in some low temperature curing powder coatings may cause powder package stability problems due to premature curing of the powder coating even at room temperature. (This instability could be measured by a change in gel time, a decrease in gel plate flow, GPF, and increased orange peel of the cured powder coating.)

- Lower softening point or glass transition temperature,Tg, associated with low temperature cure powder coatings often limit their use to regions that do not have high ambient temperatures. This is to prevent caking/sintering of the powder during transport, storage and application.

- Refrigerated storage or transport may allow low temperature curing powders to be used in regions with high ambient temperatures or to extend the low temperature powder shelf life.

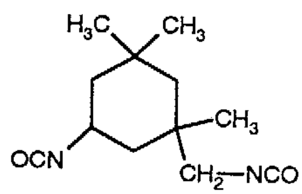
Range of Polyesters With Crosslinker Options



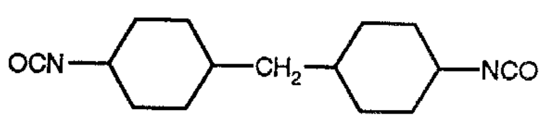
Crosslinking Hydroxyl Polyesters with Polyisocyanates

Polyester/urethanes provide advantages to the powder coatings formulator. Polyester/urethanes can be described as achieving the ideal attributes of a thermosetting coating; namely to be a highly reactive system during cure conditions and to be virtually unreactive during manufacture, storage and application. These ideals are achieved by the blocked polymeric isocyanate curing agents or ring opening reaction associated with uretdione curing agents used with hydroxyl terminated polyesters.

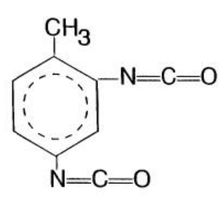
Polymeric blocked isocyanate curing agents are well known in the powder coating industry. These compounds have been used for many years to produce polyester/urethane powder coating compositions. The most widely used polymeric blocked isocyanate curing agents are based on IPDI, isophorone diisocyanate and its higher functional adducts.[4]



Some other commonly used polymeric blocked diisocyanate curing agents are based on blocked methylene-bis-4-cyclohexyl diisocyanate, Desmodur ®W,



and toluene diisocyanate, TDI.



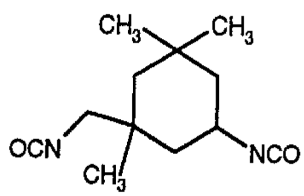
note: Desmodur is a registered trade mark of the Bayer Corporation

Crosslinking Hydroxyl Polyesters with Polyisocyanates

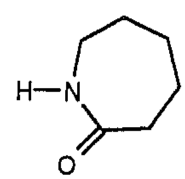
Blocking agents have been selected to present minimum risks to health and safety. The Powder Coatings Institute, PCI, has published a "white paper" covering Polyester/urethane health and safety information. The conclusion is reached that polyester/urethane powder coatings are inherently safe when used properly.[3]

Polyester/urethane powder coatings, used in the thin-film decorative market, represent approximately 25-30 percent of the total powder coatings volume in the North American market.

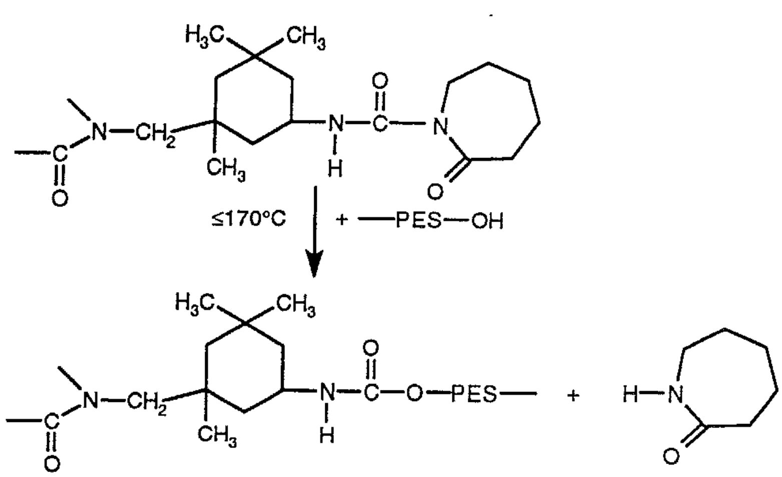
isophorone diisocyanate



ε-caprolactam



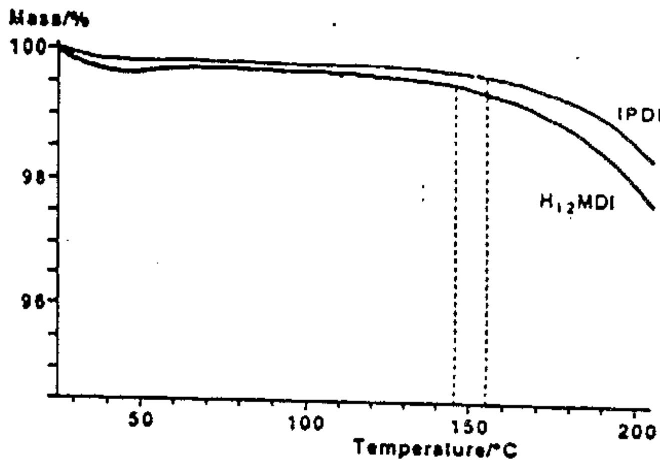
blocked polymeric isocyanate reaction with hydroxyl polyester



Typically, IPDI is reacted with a polyol like TMP, trimethylolpropane, and blocked with a blocking agent like ε-caprolactam.[4]

Crosslinking Hydroxyl Polyesters with Polyisocyanates

TGA Analysis of ε-caprolactam blocked powder coatings [5]

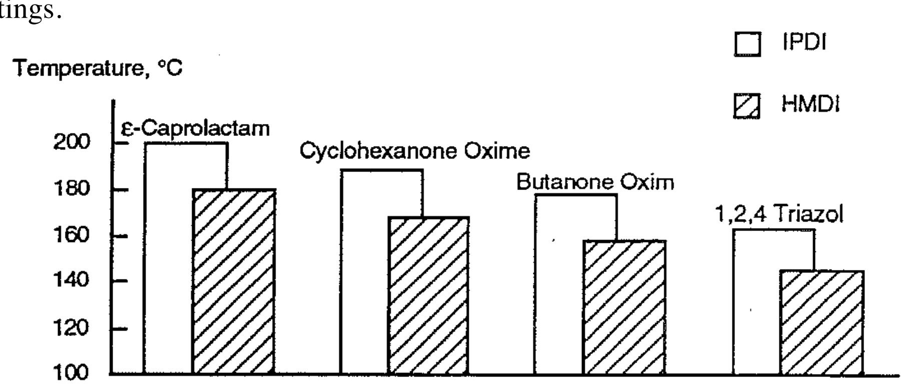


Desmodur ®W (H_{12}MDI) based curing agents can be expected to reduce the deblocking temperature of powder coatings by at least 10 degrees C.

Catalysts like DBTDL, dibutyltin dilaurate, and Zn AcAc, zinc acetyl acetonate, can be expected to further reduce the deblocking temperature by 10-20 degrees C.

Other tin catalysts like stannous octoate can be expected to increase the speed of cure. (reduce the cure time) [6]

Other blocking agents can be used to further reduce the temperature needed to cure powder coatings.



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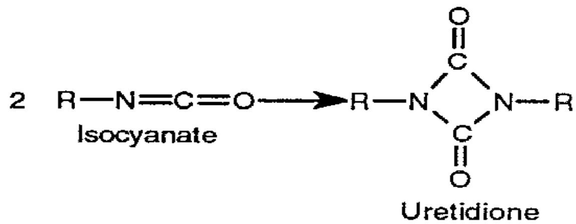
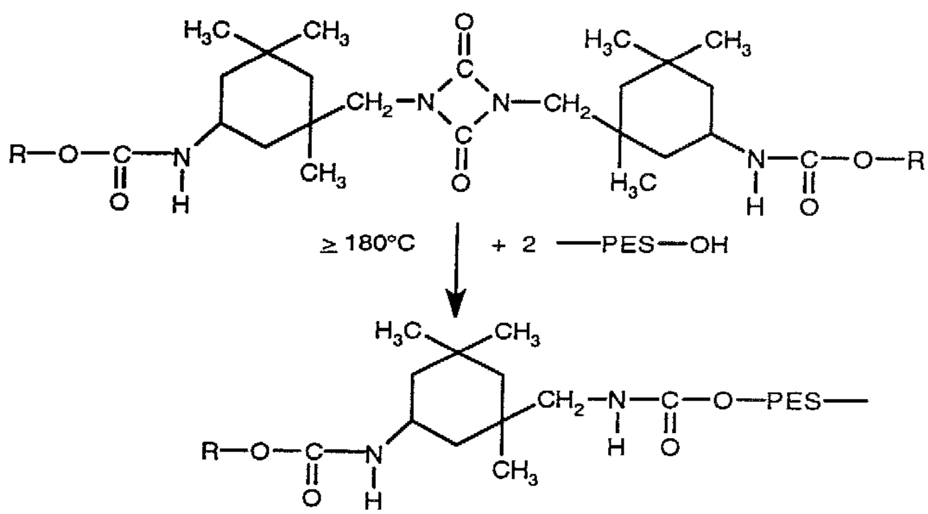
A curing agent formulated with IPDI and blocked with 1,2,4 triazole has been recently made in commercial quantities.[7,8] Alcure® 4470 is a crosslinker blocked with 1,2,4 triazole capable of curing at 140 C.

A developmental curing agent formulated with Desmodur ® W, H_{12}MDI, has been sampled to the powder coatings industry.[8]

Uretdione crosslinkers for powder coatings [5]

Uretdione curing agents are "self-blocked" via the formation of the uretdione ring structure. The NCO groups are made available to cure with hydroxyl polyesters when the uretdione ring opening temperature is reached during the cure process. (These products are typically slower reacting and require slightly higher cure conditions than their ε-caprolactam counter parts. Uretdione crosslinkers are ε-caprolactam free and are considered non-emissive. Alcure® 4147 is one of the uretdione crosslinkers being distributed in the USA.





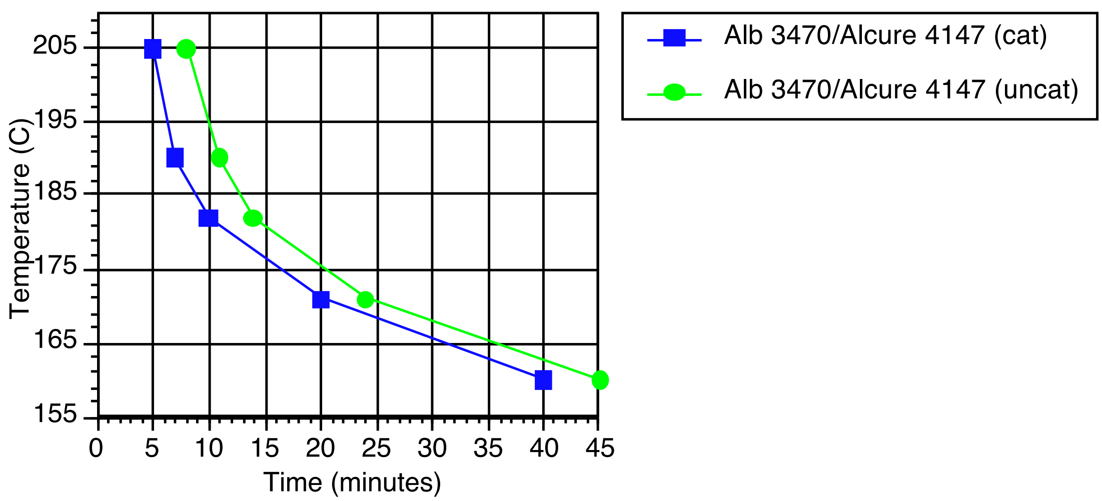
The use of pre-catalyzed polyester resins and resins with increased functionality has improved the cure response for uretdione curing agents for powder coatings. [8]

note: Alcure is a registered trade mark of McWhorter Technologies

Cure Curve for Hydroxyl polyester (Albester 3470)/Uretdione (Alcure® 4147)[8]

Cure curves like the one below are subject to the interpretation about when a powder coating can be considered cured. Typically a powder coatings performance characteristic such as impact resistance is used to determine the degree of cure. Then the question arises, how much impact resistance is enough to be considered cured?

The cure curve below was plotted using 320/320 in-lbs F/R impact resistance as an indicator of cure. It can be expected that if a lower impact resistance target was used, the curves would shift to the left and show even more speed and lower temperature cure.



New polyesters, like Albester® 3470, with hydroxyl values in the range of 55-60 have been formulated to be particularly reactive with uretdione crosslinkers like Alcure® 4147 and Alcure® 4470 for example.[8]

The above system has been formulated to cure at 160 C (320 F) with a high level of impact resistance.

Preparation of powder coatings:

Hydroxyl polyesters synthesized were evaluated by the typical melt/mix method in a white powder coating:

Powder Coating Formulation

Premix (grams)
(high Intensity)

	(uncatalyzed) wt.	(catalyzed) wt.	phr	wt % (catalyzed)
Albester 3470	756.0	756.0	100.0	50.40
Alcure 4147	226.5	226.5	30.0	15.10
Flow agent	15.0	15.0	2.0	1.00
De-gassing additive	7.5	7.5	1.0	0.50
Actiron® DBT (70% active DBTDL)	……..	10.0	1.3	0.67
Titanium dioxide	495.0	485.0	64.2	32.33
	1500.0	1500.0		100.00

OH polyester/urethane CA 77/23

Extrude (Werner and Pfleiderer ZSK-30)
Grind
Sieve (Through,T- 140 mesh,105 micron)
Spray (Electrostatic,Onada gun set at 40 kv)
Bake (15 minutes at 182 C, 360 F)
Film Thickness (1.7-2.4mils , 42.5-60 microns)
Evaluate (Test performance properties)

Powder Coating Properties:

Gloss 60 deg.	93
Gloss 20 deg.	67
Impact F	160
Impact R	160
Adhesion	E
Pencil hard.	2H
MEK Rubs (50 dbl rubs)	5
Flexibility (1/8” Mandrel)	pass
Flow (PCI std.)	7
Pwd Storage stability @ 40 C	pass

Hydroxyl polyesters like Albester 3470 can be cured in 15 minutes at 182 C with uretdione crosslinkers like Alcure 4147.

note: Actiron is a registered trademark of Synthron Inc.

Preparation of powder coatings:

Hydroxyl polyesters synthesized were evaluated by the typical melt/mix method in a white powder coating:

Powder Coating Formulation

Premix (grams)
(High Intensity)

	wt.	phr	wt %
Albester 3470	994.9	100.0	54.01
Alcure 4470	184.0	18.5	9.99
Flow agent	22.1	2.2	1.20
De-gassing additive	14.7	1.5	0.80
Stannous octoate (ST-70)	18.4	1.9	1.00
Titanium dioxide	607.9	61.1	33.00
	1842.0		100.00

OH polyester/urethane CA 84/16

Extrude (Werner and Pfleiderer ZSK-30)
Grind
Sieve (Through,T- 140 mesh, 105 micron)
Spray (Electrostatic, Onada gun set at 40 kv)
Bake (15 minutes at 150 C, 302 F)
Film Thickness (1.7-2.4mils , 42.5-60 microns)
Evaluate (Test performance properties)

Powder Coating Properties:

Gloss 60 deg.	90
Impact F (in-lbs)	320
Impact R	320
Adhesion	E

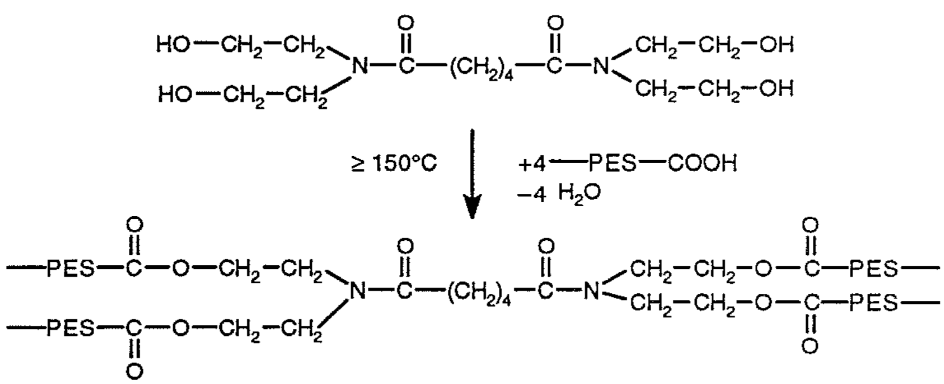
Hydroxyl polyesters like Albester 3470 can be cured in 15 minutes at 150 C with triazole blocked IPDI crosslinkers like Alcure 4470. Full impact resistance was developed at 0.8/1.0 stoichiometry NCO/OH. Since impact resistance exceeded maximum industry standards by 100%, it can be expected that the Albester 3470/Alcure 4470 system will cure at even lower temperatures and shorter times. This system is ε-caprolactam free, but is still considered to be an emissive system since the triazole blocking agent evolves during the curing process.

Hydroxyalkylamide crosslinkers [9]

Catalysts for this class of crosslinkers have not been identified.
One way to increase the reactivity of Primid®, hydroxyalkylamide, crosslinkers is to utilize higher molecular weight polyesters with the similar functionality. One supplier offers [8]:

Resin	Acid Value	ICI viscosity @ 200 C
Albester® 5080	30-35	7000-8000 cps
Albester® 5040	30-35	5800-6800 cps
Albester® 5130	32-38	3300-4800 cps
Albester® 5550	32-38	3000-3800 cps

Increased speed of cure is attained as the molecular weight of the polyester component is increased. The highest viscosity polyester described above corresponds to the highest molecular weight polyester in this series of products. Cure can be achieved in as little as 1-2 minutes at 220-240 C. (coil line temperatures) for the higher molecular weight polyesters in this series.



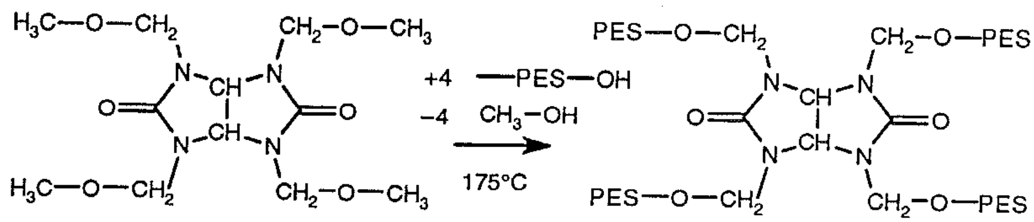
Hydroxyalkylamides liberate water during cure with carboxyl polyesters. Specific additives have been identified to permit thick films without pin holing.[9] A white paper has been written by The Powder Coatings Institute describing the health and safety aspects of hydroxyalkylamide crosslinkers.

note: Primid is a registered trade mark of the EMS Chemie Corp.

note: Albester is a registered trade mark of McWhorter Technologies

Glycoluril Crosslinkers for Powder Coatings [10]

Hydroxyl polyesters with high Tg's, glass transition temperature, are required with glycoluril crosslinkers, like Powderlink®1174, to prevent sintering or caking of the resulting powder coatings. These crosslinkers can be formulated with hydroxyl polyesters to yield high gloss powder coatings for the thin-film decorative market.



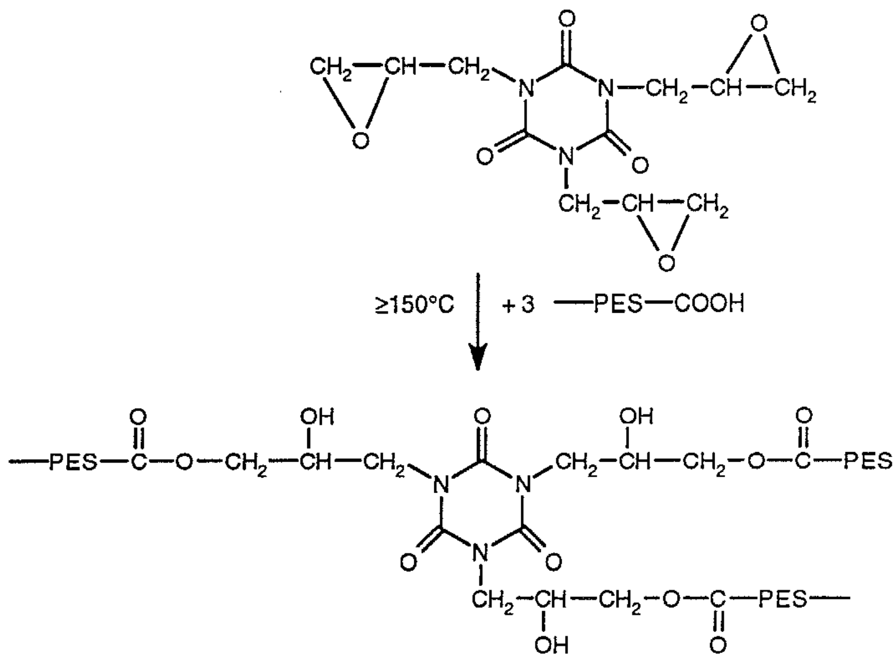
Methanol is released during the curing cycle of powder coatings formulated with glycoluril crosslinkers.

Glycoluril crosslinkers have been used with specific catalysts to create wrinkle finish powder coatings that are exterior durable. These finishes have been used in diverse applications ranging from metal furniture to lighting fixtures. Other catalysts have been identified for low temperature cure. [10]

note: Powderlink is a registered trade mark of Cytec Industries Inc.

Polyester/TGIC system Crosslinking [2, 16]

Most conventional TGIC cured polyesters are linear carboxyl polyesters. When they are baked 10-15 minutes at 160-180 C (320-360 F), these products can give excellent powder coatings. The lower temperature cure of these powder coatings is achieved by incorporating a catalyst into the polyester. The chemical reaction involved is condensation of a carboxylic group from the polyester with the oxirane functionality of the TGIC. There are no reaction by-products. This system is considered non-emissive.



These polyester/TGIC systems, when baked at temperatures lower than 150 C (300 F) , exhibit two problems:

- Powder coatings do not develop good mechanical properties as measured by impact resistance.
- Powder coatings can develop a haze commonly referred to as “blooming”[12].

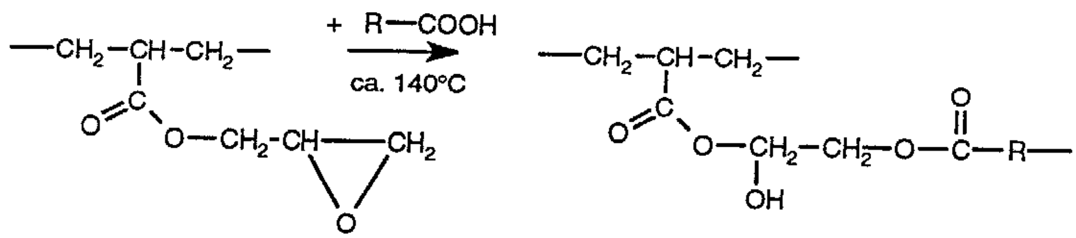
The phenomenon defined as blooming has been identified as a 22 member cyclic oligomer with a crystalline structure and a melting point of 275-280 F. Blooming can be eliminated or reduced by altering the polyester backbone.

Epoxy functional acrylics with acid functional crosslinkers

Glycidyl functional acrylics crosslinked with dibasic acids are used for speciality powder coating applications including some automotive applications.These acrylics are prepared using conventional free radical addition polymerization techniques which are well known [13] A typical composition of a glycidyl methacrylate containing powder coating resin is shown below:

Ingredient	Weight %
Butyl acrylate	11.0
Ethyl acrylate	10.0
Glycidyl methacrylate, GMA	13.0
Methyl Methacrylate	28.0
Styrene	38.0
	100.0

Epoxy functional acrylics are typically cured with long chain dibasic acids such as dodecanedioic acid, DDA, azelaic acid, and other long chain acids. The brittle GMA acrylics require the flexibility of the long chain diacid portion in order to achieve acceptable film properties and performance. The crosslinking reaction forms a beta hydroxy ester bond as shown below:



Powder coatings based on this curing system can exhibit excellent weatherability, UV resistance, hardness with acceptable flexibility. Styrene content must be kept below 15% by weight to optimize the weatherability.

Low Temperature Cure Polyesters [8]

Polyesters with hydroxyl numbers in the range of 107-125 have very good low temperature cure response when combined with conventional crosslinking agents like a polymeric blocked isocyanate based on IPDI and blocked with ε-caprolactam; Alcure® 4400, for example. Crosslinkers blocked with triazole can achieve even lower temperature cures when combined with high functionality polyesters. These polyesters have been formulated to be particularly resistant to solvents and possess good overall chemical resistance and good stain resistance properties while maintaining good exterior durability when formulated with exterior durable curing agents.

These high hydroxyl functionality polyesters also provide very good magic marker resistance.

These polyesters have been formulated for the marine industry, where 1000 hours of gasoline resistance is a basic requirement.

They have been utilized for appliance coatings where chemical/stain resistance is quite important.

Since these polyesters require additional curing agent, extremely good flow is achieved while maintaining pencil hardness in the 2H-3H range.

This attribute has been useful in some automotive applications.

Polyester characteristics for the above applications include:

Tg, glass transition temperature	51-57 C
ICI melt viscosity at 200 C	25-35 poise
Hydroxyl number	107-125

The flow of the powder coating is an important parameter, especially at lower bake temperatures. It is well known that the higher the bake temperature, the lower the melt viscosity of the powder coating and thus the better the flow and wetting of the substrate.

Low temperature cure polyester/TGIC powder coatings can result in poor flow and wetting. However, a key parameter for flow is to develop a polyester resin having a glass transition temperature,Tg, of 45-50 C with some degree of package stability, with low enough melt viscosity of the polyester resin. To get better flow, a combination of glycols and acids were used to meet these conflicting requirements.[2]

To reduce the curing temperature of carboxyl terminated polyesters cross-linked with TGIC, it is common practice to add catalyst into the molten carboxyl terminated polyester prior to discharge from the reactor. The type of catalyst as well as the concentration of the catalyst is critical to achieve low temperature cures as low as 250 F (121 C). The catalyst used is in a class of onium catalysts such as phosphonium halide compounds.[1] To achieve low temperature cure, the required catalyst concentration is about 0.3-0.5 weight percent of the polyester.

Preparation of powder coatings:

Carboxyl polyesters synthesized were evaluated by the typical melt/mix method in black powder coatings:

Powder Coating Formulation

Premix (grams)
(high Intensity)

	wt.	phr	wt %
Albester 5180	883.9	100.0	88.39
triglycidyl isocyanurate	66.5	7.5	6.65
Flow agent	14.3	1.6	1.43
De-gassing additive	6.8	0.8	0.68
Carbon Black Pigment	28.5	3.2	2.85
	1000.0		100.00

polyester/TGIC 93/7

Extrude (Werner and Pfleiderer ZSK-30)

Grind

Sieve (Through,T- 140 mesh,105 micron)

Spray (Electrostatic,Onada gun set at 40 kv)

Bake (15 minutes at 138 C, 280 F)

Film Thickness (1.7-2.4mils , 42.5-60 microns)

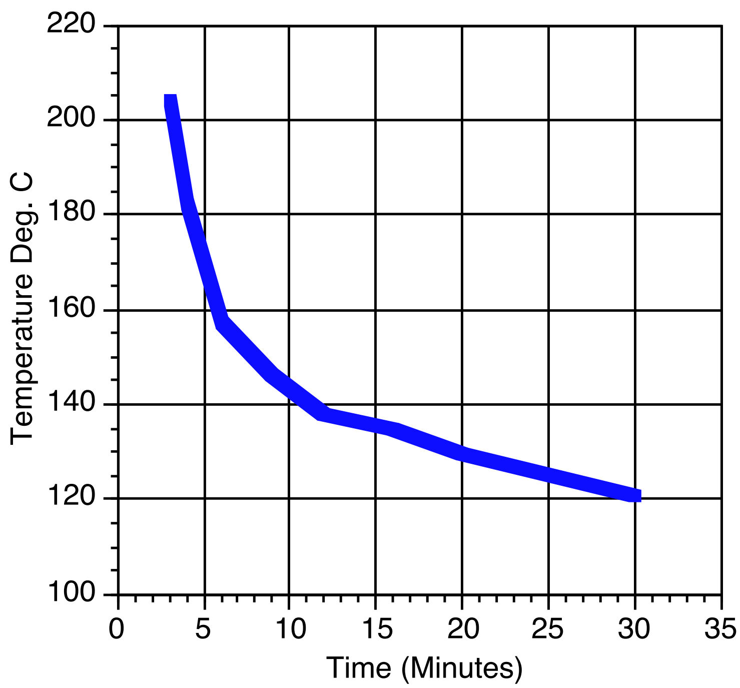
Evaluate (Test performance properties)

Powder Coating Properties:

Gloss 60 deg.	94
Gloss 20 deg.	73
Impact F	160
Impact R	160
Adhesion	E
Pencil hard.	2H
MEK Rubs (50 dbl rubs)	5
Flexibility (1/8" Mandrel)	pass
Flow (PCI std.)	7
Pwd Storage stability @ 40 C	pass

Carboxyl Polyester (Albester® 5180) /TGIC Powder Coating Cure Curve: [8]

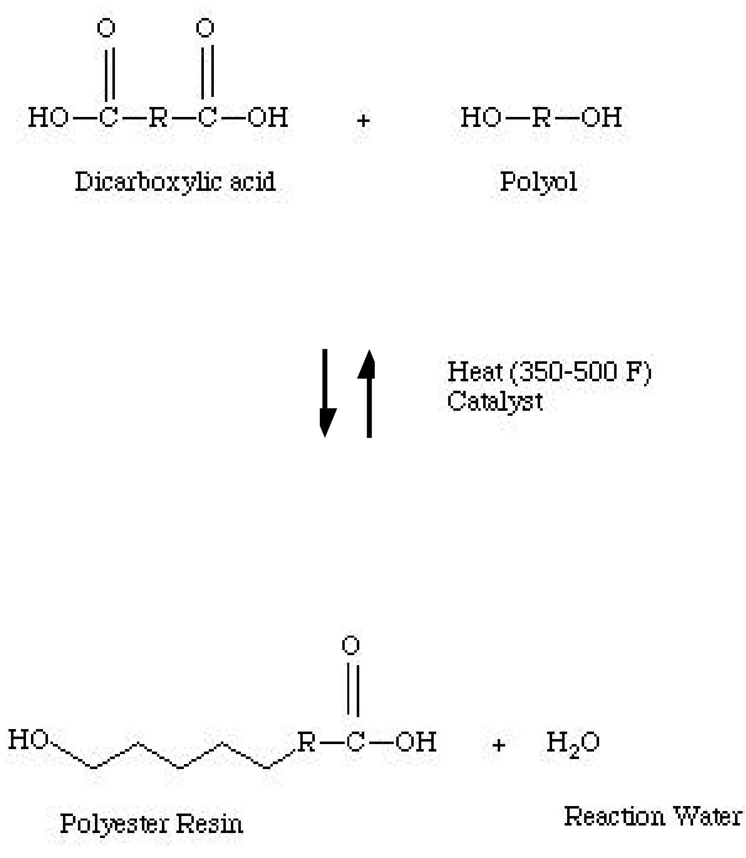
A powder coating was made from **Albester 5180**



Good low temperature cure capability was achieved.

Polyester Synthesis:

The polyesters which are useful for low temperature cure with epoxides like TGIC are thermosetting carboxyl types with a sufficiently high enough Tg, glass transition temperature, of at least 45-50 C. Both the Tg and melt viscosity of the polyester are greatly influenced by the choice of monomers. It is important that the polyester be made via a two stage process. In stage one, a hydroxyl terminated polyester is prepared and in stage two, the hydroxyl polyester is reacted with a diacid to form a carboxylated, acid functional polyester. Good mechanical properties and bloom resistance are provided by the use of a mixture of terephthalic acid and isophthalic acid. The introduction of isophthalic acid seems to prevent blooming.[12] More UV durable products are attained as the level of isophthalic acid is increased. Impact resistance must be optimized as the level of isophthalic acid is increased. The typical stage one hydroxyl polyester has a hydroxyl value of approximately 70-100.[14] This product is then reacted with the appropriate amount of diacid or anhydride, like adipic acid or TMA, trimellitic anhydride, to create the best low temperature curing carboxyl polyesters. The onium catalyst is added to the molten polyester prior to discharging the batch via a cooling/flaking belt.



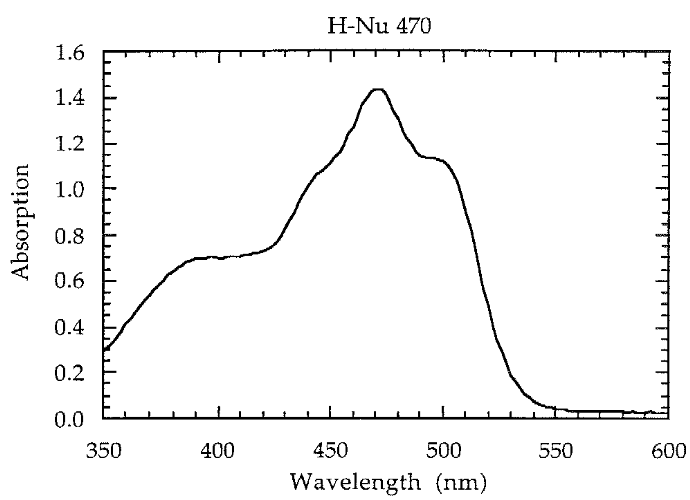
Ultraviolet cured powder coatings

The ultimate low temperature cure powder coatings may be the UV cured systems being commercialized today. To obtain good flow at such low melt temperatures, crystalline polyesters have been synthesized.These systems can melt at temperatures at or below 100 C. yielding a very smooth film. Cure can then take place in a matter of seconds upon exposure to UV light.

Major resin suppliers to the powder coating industry have started to market polymers for UV cure. These polymers utilize free radical crosslinking mechanisms initiated by UV light. Some suppliers are investigating ionic cure mechanisms.

The most obvious problem with UV cure powder is how can UV be used to cure titanium dioxide (white) powder coatings? Speciality chemical suppliers such as Spectra Group Ltd[15] have developed a class of visible light photoinitiators to help cure pigmented UV cured systems. H-NU 470 was developed to address various needs of the UV curing industry. When combined with selected coinitiators and other typical UV initiators, H NU-470 significantly enhances the UV cure of highly pigmented TiO_2 coatings.

To successfully market UV cured powder coatings, advantages of the technology must solve problems that exist with current thermally cured systems. UV cured powder coatings will be ideal candidates to coat temperature sensitive substrates, assembled components like vending machines, for example.



Since H NU-470 absorbs light in the visible range, it helps with through cure of pigmented UV coatings.

Results and Conclusions:

Low temperature curing/crosslinking can be achieved with hydroxyl polyester/urethane systems without sacrificing flow and appearance when utilizing polymeric blocked isocyanate crosslinkers.

Low temperature limits for crosslinking hydroxyl polyesters are defined by the functionality of the polyester, catalyst type and concentration of the blocking agent when blocked curing agents are used.

Low temperature cures in the range of 130-140 C have been achieved with hydroxyl functional polyesters cured with triazole blocked crosslinkers.

Hydroxyl functional polyesters provide the largest variety of products for cure with polymeric blocked isocyanate crosslinkers and uretdione crosslinkers.

Low temperature cure can be achieved with uretdione crosslinked hydroxyl polyesters.

Low temperature cures as low as 121 C have been achieved with carboxyl polyester/TGIC systems.

Hydroxyalkylmides have demonstrated cure capabilities similar to existing powder coating technology.

Hydroxyalkylamides have demonstrated the ability to increase cure speed when combined with specific carboxyl polyesters.

Glycolurils have demonstrated the ability to cure at reduced temperatures.

UV cured powder coatings have exhibited cure properties at cure temperatures of 100 C with polyesters utilizing free radical crosslinking.

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