DEVELOPMENTS IN LOW TEMPERATURE CURE POWDER COATINGS

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ABSTRACT

A novel approach to low temperature cure carboxyl terminated polyesters is realized by this research effort. 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 properties are described. This technology pushes conventional polyester powder resin raw material capabilities to the apparent limit of performance for low temperature cure. It is believed that the described technology can be used as a possible alternative to crystalline polyesters and UV cured powder coatings.

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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). Typical approaches to low temperature cure carboxyl polyesters have been centered around 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.

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 this research effort. These properties are often in conflict and present challenges to the polymer chemist. 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).

Powder coatings based on this technology can give faster cure at elevated temperatures. This results in optimum coatings performance properties and permits faster line speeds.

Normal cure versus low temperature cure [3]

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. 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:

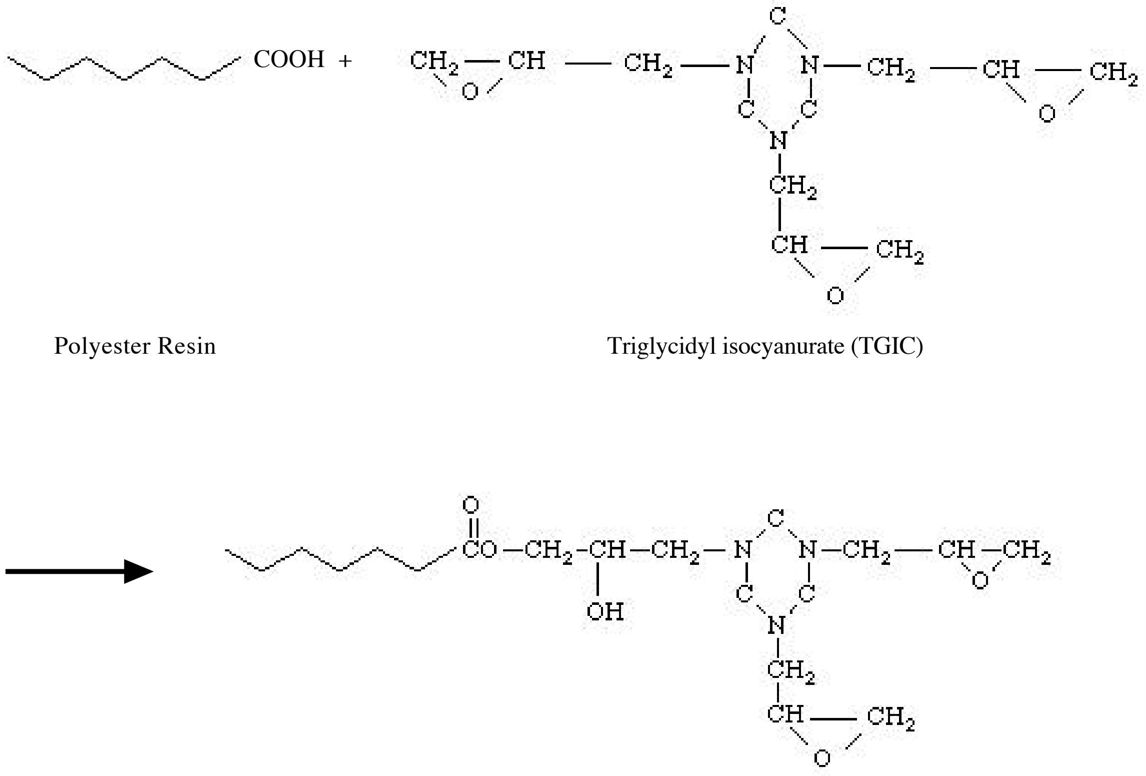
- Extremely high levels of catalyst in some low temperature curing powder coatings may cause powder package stability problems due to premature curing of the powder coating even at room temperature. (This instability could be measured by a change in gel time, a decrease in gel plate flow, GPF, and increased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

Conventional Technology

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.



Polyester Resin

Triglycidyl isocyanurate (TGIC)

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”[4].

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:

- Replacing 25-40 mole percent terephthalic acid with isophthalic acid.
- Formulating a 100% isophthalic acid based polyester.

Low Temperature Cure Polyesters

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.

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. To achieve low temperature cure,the required catalyst concentration is about 0.3-0.5 weight percent of the polyester.

Formulation of a polyester for low temperature cure involves: (see Table 1)

- **Optimizing** melt viscosity. Low melt viscosity promotes better flow. Glycols evaluated included neopentyl glycol, cyclohexane dimethanol, 1,6 hexanediol, 1,4 BD, 2-butyl-2-ethyl-1,3-propanediol and trimethylolpropane.

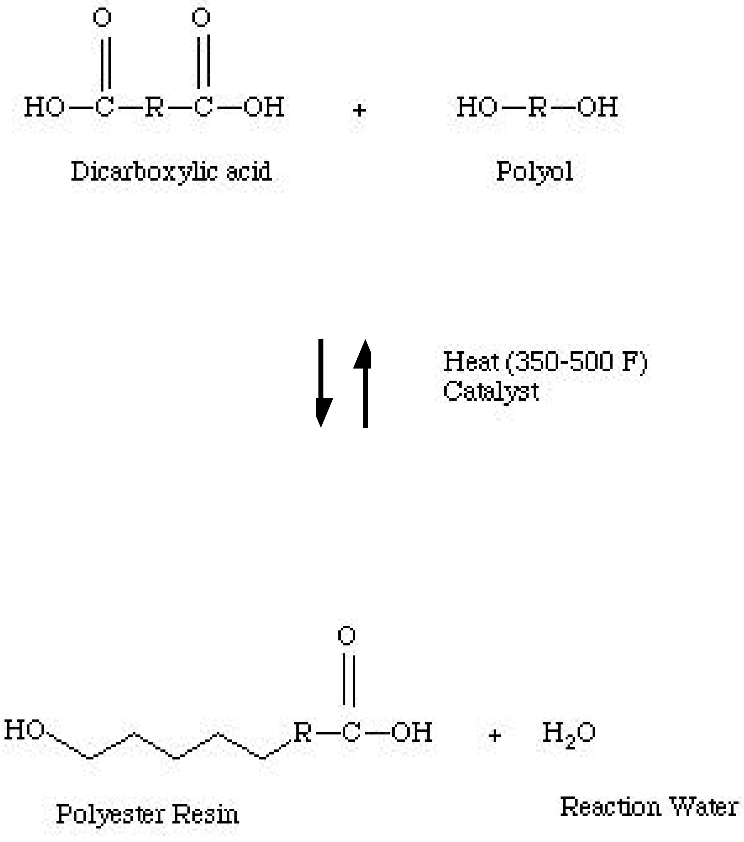
- **Maintaining/improving** flexibility. Use of modifying glycols/acids is necessary. Glycols and acids evaluated included 1,6 hexanediol, 1,4 butanediol, adipic acid, succinic anhydride, azelaic acid and glutaric acid.

- **Maintaining** package stability. Balance composition and molecular weight to maintain Tg, glass transition temperature.

- **Selecting** an appropriate catalyst. Latency is important; therefore phosphonium halides were evaluated.

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.[4] 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.[5] This product is then reacted with the appropriate amount of diacid, like adipic acid or fumaric acid 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.



Experimental:

Table 1

Composition of the Polyesters (grams)

	1	2A	2B	2C	2D	2E	2F	2G	2H	2I	2J
NPG	707		719	819	805						707
CHDM	6	894	6	5	6	913	293	903	878	875	6
1,6 HD	142										142
BEPD		105				108	109	106	103	103	
1,4 BD			110								
TMP					14						
TPA	703		711	715	692						700
IPA	466	993	473	476	461	1006	1038	995	968	1085	466
FC4100	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
FA	179		182			173					179
AA		208		185	223						
SA							150				
GA								195			
1,4 CHDA									250		
AZA										137	
PHC	8	8	8	8	8	8	8	8	8	8	

Key:

	Polyols
NPG	neopentyl glycol
CHDM	cyclohexane dimethanol
1,6 HD	1,6 hexanediol
BEPD	2-butyl-2-ethyl-1,3-propanediol
1,4 BD	1,4 butanediol
TMP	trimethylolpropane

	Other
FC 4100	Esterification catalyst,ATO Chem
PHC	phosphonium halide catalyst

Carboxylic Acids/anhydrides	
TPA	terephthalic acid
IPA	isophthalic acid
FA	fumaric acid
AA	adipic acid
SA	succinic anhydride
GA	glutaric acid
CHDA	1,4 cyclohexanedicarboxylic acid
AZ	azelaic acid

Resin Characteristics:

Table 2

Characteristics

	1	2A	2B	2C	2D	2E	2F	2G	2H	2I	2J
AV	39.8	35.6	35.9	34.2	35.7	32.4	30.4	38.2	33.9	32.4	35.1
ICI vis.	18.6	26.4	21.4	12.4	13.8	81.0	30.0	29.0	52.0	54.0	13.6
Tg	49.2	45.5	53.4	44.5	41.2	52.3	51.8	57.4	63.8	47.7	49.2

Acid number, AV, (mg KOH/g)

ICI cone and plate viscosity at 200 C, (poise)

Tg, glass transition temperature ,(C), (DSC)

Ideal resin characteristics:

Low ICI cone and plate melt viscosity

Tg,glass transition temperature, of 45- 50 C

Resin numbers 1, 2B and 2J come close to this target. Remember, an ideal polyester for low temperature cure would have a low melt viscosity and still have a softening point,Tg, of 45-50 C and high reactivity.

Onium catalysts, like triphenyl ethyl phosphonium bromide,TEP, help increase the reactivity of carboxyl groups,(acid groups) on the polyester with epoxy groups on the curative,TGIC,triglycidyl isocyanurate.

Specific end-groups like fumaric acid and adipic acid help increase the reactivity of the polyester with the curative. See formulations 1, 2B and 2J. This effect can be explained by the fact that the resulting polyesters have very low melt viscosities thus allowing these polyesters to be more mobile during the cure process. This would lead us to believe that the increased low temperature reactivity of Resin 1 is due to physical characteristics of the resin and the use of catalyst.

Differences in cure response between fumaric modified polyesters and adipic modified polyesters suggest that the acidity of the modifying acid may have some effect on the overall low temperature reactivity of the polyester.

Preparation of powder coatings:

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

Powder Coating Formulation Table 3

		wt.	phr	wt %
Premix (grams)	carboxyl polyester	883.9	100.0	88.39
(high Intensity)	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
polyester/TGIC 93/7		1000.0		100.00

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)

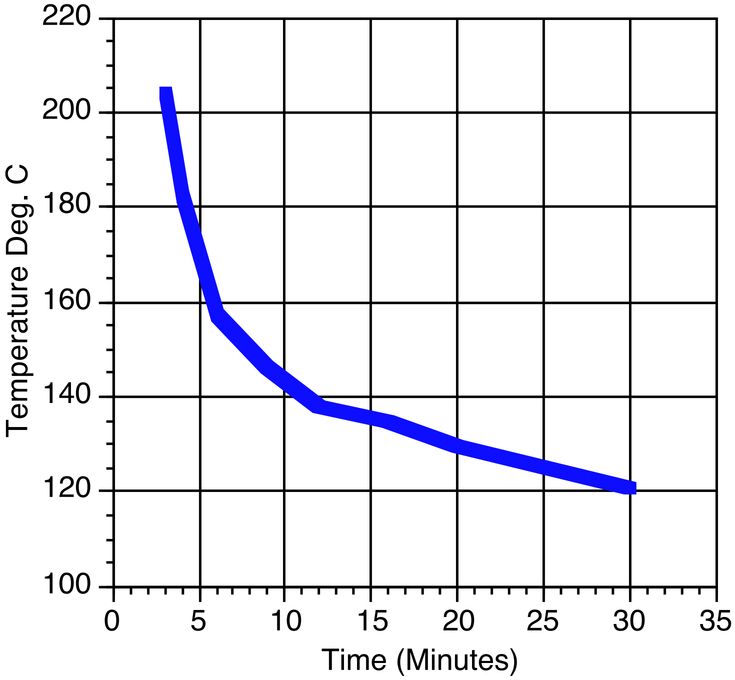
Evaluate (Test performance properties)

Table 4
Powder Coating Properties:

	1	2A	2B	2C	2D	2E	2F	2G	2H	2I	2J
Gloss 60 deg.	94	93	93	92	92	41	92	92	91	93	89
Gloss 20 deg.	73	73	65	75	62	8	73	76	52	64	60
Impact F	160	160	160	160	160	160	160	80	50	100	120
Impact R	160	160	160	160	160	160	80	<20	10	40	120
Adhesion	E	E	E	E	E	E	E	E	E	E	E
Pencil hard.	2H	2H	3H	2H	F	2H	2H	2H	2H	H	2H
MEK Rubs (50 dbl rubs)	5	2-3	5	4	4	5	5	5	3	3	3
Flexibility (1/8” Mandrel)	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
Flow (PCI std.)	7	2	2	7	2	4	4	4	1	2	5
Pwd Storage stability @ 40 C	pass	pass	pass	pass	pass	fail	pass	pass	pass	pass	pass

Low Temperature Polyester/TGIC Powder Coating Cure Curve:

A powder coating was made from **Resin Number 1** from **Table 1** utilizing the **Powder Coating Formulation** from **Table 3.**



Good low temperature cure capability was achieved. Review of the **Powder Coatings Performance** data from **Table 4, Powder Coating 1** shows that gloss,impact resistance, adhesion, pencil hardness, MEK resistance, flexibility, flow and powder storage stability are all close to optimum.

Results, Conclusions and Recommendations:

Melt viscosity increases as the terephthalic acid,TPA, content of the polyester is increased.

Increased CHDM, cyclohexane dimethanol, content raised the melt viscosity but did not increase the Tg.

Adipic acid,AA, or fumaric acid,FA, terminated polyesters have better low temperature reactivity than other carboxylic acids.

Additional research needs to be planned to define what mechanism is responsible for the better low temperature reactivity of fumaric acid and adipic acid.

Resin 1 has good low temperature cure capabilities while maintaining a balance of other properties.

Additional experimentation needs to be made to see if further optimization of Resin 1 can be achieved. The goal is to increase the Tg, maintain reactivity and other performance properties without increasing viscosity.

If improved powder storage stability (anti-sintering) is needed, Resin 1 from Table 1 can be blended with higher Tg polyesters such as Albester 505[6].

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