Polyester-Urethanes for the World-Market

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Polyester-Urethanes for the World-Market

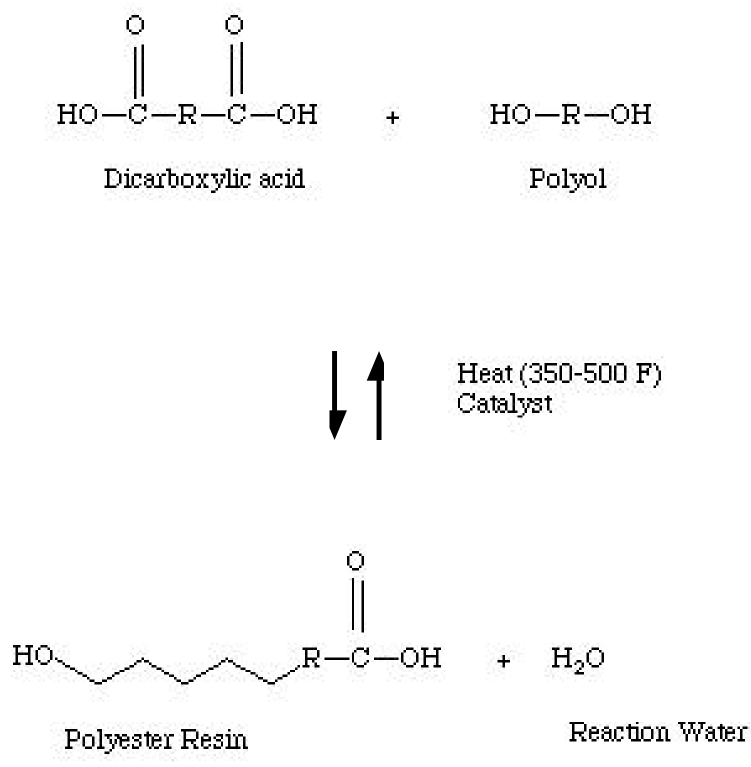
Summary:
Polyester-urethanes are particularly suited for the world market place because uretdione curing agents (blocking agent free) can be used to cure hydroxyl polyesters. These products provide a non-emissive alternative to the market place. Today's world also seeks products which have a low order of toxicity. Polyester-urethane powder coatings meet this challenge. [1]
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 ring opening reaction associated with uretdione curing agents used with hydroxyl terminated polyesters.
Polyesters for urethane cure are available in a range of products from purely decorative to highly functional. Hydroxyl values range from 25 to 300. [8]
Polyester-urethanes for specialty applications have been developed. Polyester-urethanes for low gloss applications utilize differences in reactivity of the hydroxyl resins extruded together vs dry-blended to achieve 60 degree gloss of 10 or lower. [12]
Anti-grafitti powder coatings and appliance powder coatings have been formulated with high hydroxyl functional resins.
Dye-sublimation-heat-transfer powder coatings have been formulated with hydroxyl resins with hydroxyl values around 100.
Very hard, 3-4H, pencil hardness powder coatings have been formulated with 300 hydroxyl value polyesters.
Super durable hydroxyl polyesters with 3-5 times the gloss retention of standard products have been formulated that cover the gamut of current standard durability hydroxyl polyester resins and their end-use applications. [12]

Introduction:
Eastman Chemicals is a word-wide manufacturer and supplier of Albester® resins for powder coatings and Alcure™ curing agents for powder coatings. Eastman has powder resin production facilities in the USA and in Italy. Eastman has considerable experience with the hydroxyl polyester technology alternatives. Research and development facilities for powder resins are located both in the USA and in Italy.
Today's market demands alternatives to the former standard carboxyl polyester technology that was widely used in Europe in-the-past.
Eastman manufactures not only the latest Albester® carboxyl alternative resins but also the latest Albester® hydroxyl alternative resins and Alcure™ curing agents.

Polyester-urethane powder coatings

The above words have some degree of power. They can help us envision smooth films associated with their liquid counter-parts.
"Polyesters" are associated with durability. "Urethane" conveys the feeling of having a tough, chemical resistant coating.
The ideals, mentioned above, can be achieved with the products available to powder coatings formulators today.
Hydroxyl functional polyesters are manufactured in a range of hydroxyl values from 25 to 300. This range covers the gamut of possible powder coatings ranging from purely decorative to highly functional applications.
As cost becomes more and more important to the powder industry, the push towards using lower hydroxyl containing resins increases. The goal is to use less of the costly curing agent while still maintaining good thermoset properties.

Polyester Synthesis: 2



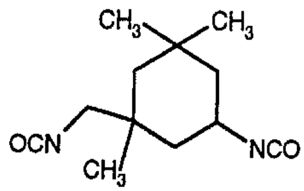
Today, hydroxyl polyesters and carboxyl polyesters are manufactured utilizing a commercial esterification process. Reactors range in size from a few tons to 30 or more tons.

Crosslinking Hydroxyl Polyesters with Polyisocyanates

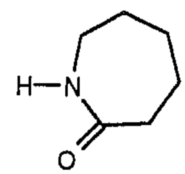
Blocking agents have been selected to present minimum risks to health and safety. The Powder Coatings Institute, PCI, has published a "white paper" covering Polyester/urethane health and safety information.[4] The conclusion is reached that polyester/urethane powder coatings are inherently safe when used properly.

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.

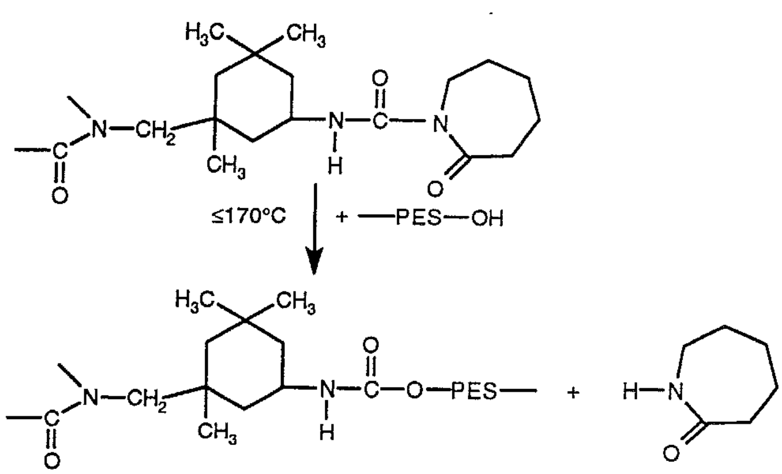
isophorone diisocyanate



e-caprolactam

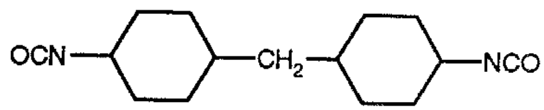


Blocked polymeric isocyanate reaction with hydroxyl polyester



Typically, IPDI is reacted with a polyol like TMP, trimethylolpropane, and blocked with a blocking agent like e-caprolactam.[3] This results in a polymeric blocked isocyanate curing agent. These products are known for their latency. Curing at temperatures below their de-blocking point is not possible. Therefore "b-staging" reaction/curing, during processing is highly unlikely. The polymeric blocked isocyanates also have the advantage of having excellent flow, since they allow time to flow beforethe blocking
agent leaves the coating.

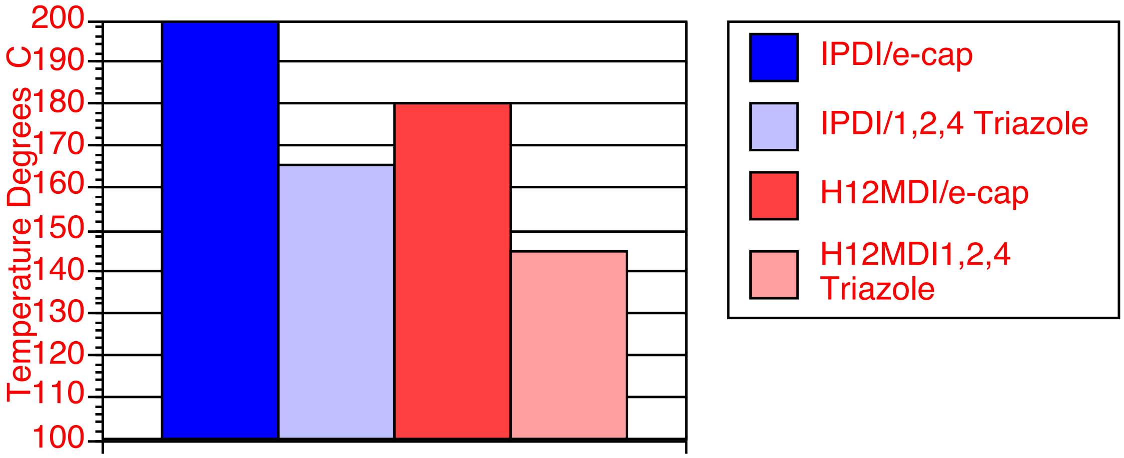
Desmodur ®W (H_{12}MDI) based curing agents can be expected to reduce the deblocking temperature of powder coatings by at least 10-20 degrees C.



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]

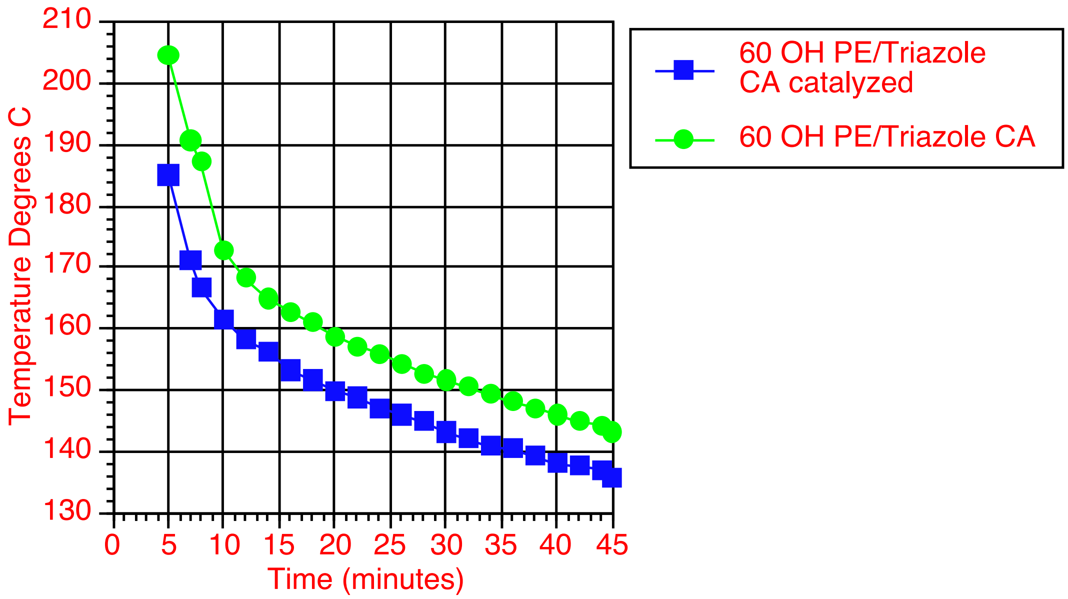
Other blocking agents can be used to further reduce the temperature needed to cure powder coatings.

De-blocking temperature of IPDI and H_{12} MDI polymeric blocked isocyanates. Blocking agents used were e-caprolactam and 1,2,4 Triazole. [10]



A proprietary 60 hydroxyl value polyester [7] can be cured in 15 minutes at 150 C with a triazole blocked IPDI crosslinker. 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 60 hydroxyl value PE/Tiazole blocked polymeric diisocyanate system will cure at even lower temperatures and shorter times. This system is e-caprolactam free, but is still considered to be an emissive system since the triazole blocking agent evolves during the curing process.

Cure curve of a 60 OH value PE cured with a Triazole blocked CA



Work continues to develop proprietary catalyst technology to push cure temperatures lower [11], while speeding the cure rate.

Powder Coating Formulation

Premix (grams)
(High Intensity)

	wt.	phr	wt %
60 OH PE	994.9	100.0	54.01
Triazole CA	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

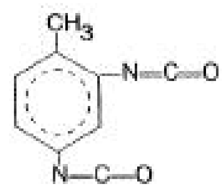
OH polyester/urethane CA 84/16

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:

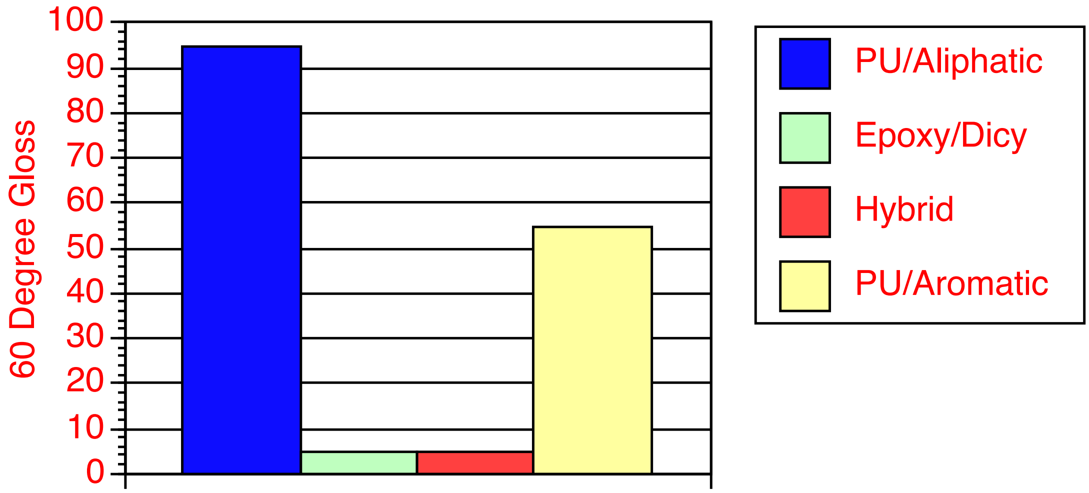
Gloss 60 deg.	90
Impact F (in-lbs)	320
Impact R	320
Adhesion	E

Aromatic polymeric blocked isocyanate curing agents, such as those manufactured with TDI, toluene diisocyanate, have not been widely used by the powder coatings industry.



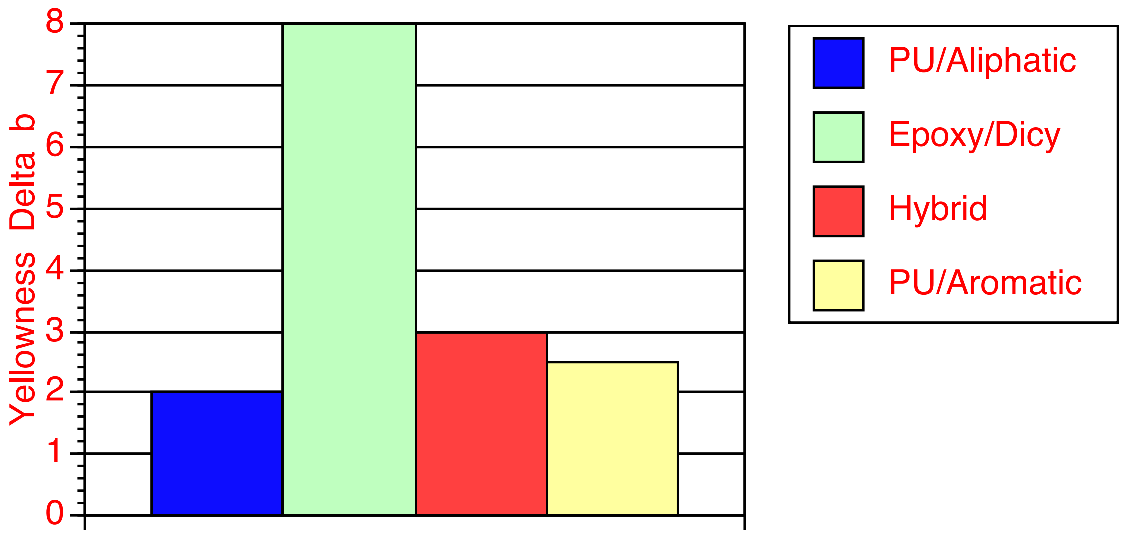
This is unfortunate, since TDI polymeric blocked isocyanate curing agents provide an interesting combination of performance properties while helping lower the cost of the curing agent component by as much as 40-50%. TDI polymeric blocked isocyanate curing agents, provide faster cure than their aliphatic counterparts and typically provide a little more chemical resistance. South Florida exposure data below, suggests that an aromatic polymeric blocked isocyanate system could be used for non-critical exterior applications. It retains over 50 % of its original gloss after one-year of exposure in South Florida. Epoxy powder coatings and Hybrid powder coatings are virtually "dead flat" after 3-4 months exposure in South Florida.

12 Month 45 degree South Florida exposure



A germicidal UV source was used to compare yellowing characteristics of typical white powder coatings. The data below indicates the TDI polymeric isocyanate cured powder coating has similar yellowing characteristics to the aliphatic polymeric isocyanate cured powder coating and the Hybrid powder coating which is 60/40 PE/Bisphenol-A epoxy.

Powder Coatings Resistance to Yellowing



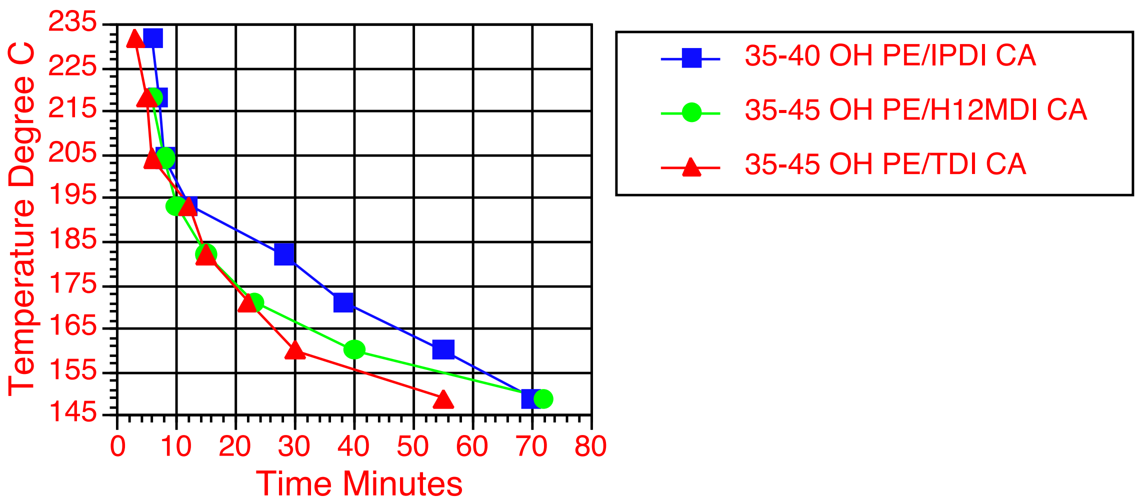
As can be seen , the epoxy powder coating yellows substantially when exposed to a strong UV light. This is one of the reasons why Bisphenol-A epoxy based powder coatings are not good candidates for exterior use when anti-yellowing is important. If we could ignore the virtually complete loss of gloss associated with the Hybrid powder coating, then it could be considered for some minor exterior applications where it could exhibit relatively good anti-yellowing characteristics.

The exciting information this data shows is: The TDI polymeric blocked isocyanate cured powder coating retains over 50% of its original gloss after one-year South Florida and has good anti-yellowing characteristics when exposed to a strong UV light source.

TDI based curing agents should be considered for use with very low hydroxyl value polyesters to help formulate more cost effective powder coatings while achieving lower weight loss from the blocking agent evolving during cure.

A typical 35-45 hydroxyl value polyester [2] can be cured with a variety of polymeric blocked isocyanates. The resulting powder coatings cure rate is in the order expected.

Cure Curves of Polyester Cured with IPDI CA, H_{12}MDI CA and TDI CA



If a typical 35-45 hydroxyl value polyester [2] is cured (160/160 in-lbs impact resistance) at times and temperatures to develop cure curves, it can be seen that the isocyanate component of the CA, curing agent, has an effect on the degree of cure at different temperatures.

- IPDI polymeric CA blocked with e-caprolactam is the slowest of this series.
- H_{12} MDI polymeric CA blocked with e-caprolactam is faster than the IPDI based system.
- TDI polymeric CA blocked with e-caprolactam is the fastest curing of this series.

Aromatic curing agents can achieve faster cures than their aliphatic counter-part.

Powder Coating Formulations

Formulation Ingredients	A wt%	B wt%	C wt%
35-45 OH PE	47.71	46.51	47.71
IPDI CA	10.50	....	....
H_{12}MDI CA		11.63	....
TDI CA	....	....	10.50
Titanium dioxide, TiO_2 [1]	40.55	40.70	40.55
Modaflow Powder [2]	0.52	0.52	0.52
benzoin [3]	0.72	0.69	0.72
	100.00	100.00	100.00

1. DuPont Pigments
2. Solutia
3. GCA Chemicals

Powder Coating formulation Parameters:

pigment/binder ratio = 0.7/1.0

polyester/curing agent ratios (PE/CA)

A.	82/18
B.	80/20
C.	82/18

Powder Coating performance Properties

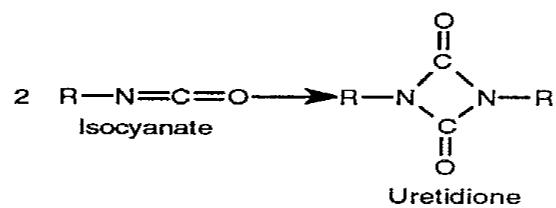
Formulation	A	B	C
substrate	B-1000	B-1000	B-1000
Bake Schedule	30’@182.2 C	15’@182.2 C	15’@182.2 C
Film Thickness (mils)	1.5-3.0	1.5-1.8	1.5-1.8
Gloss 60/20	94/85	97/62	99/77
pencil hardness	H	H	H
Impact resistance (in-lbs) F/R	160/160	160/160	160/160
Flexibility Conical mandrel (i/8”)	pass	pass	pass
Adhesion, cross-hatch %	100	100	100
PCI flow rating (10 best)	7-8	7-8	7

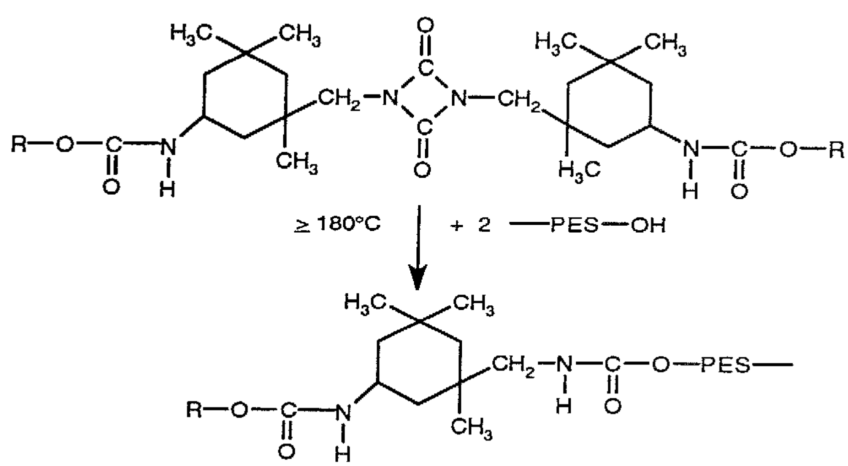
Internationally Recognized Test Methods

	Test Methods	Standards
•	Film thickness	ISO 2808; B.S. 3900D5
•	Gloss	ISO 2813; ASTM D523; DIN 67530
•	Flow (orange-peel)	
•	Color: Visual	ISO 3668
•	Colorimetry	ISO 7724
•	Adhesion (cross-cut test)	ISO 2409; ASTM D3002
•	Impact resistance	ISO 6272; ASTM D2794
•	Cylindrical mandrel bend test	ISO 1519; ASTM D1737; DIN 53152; NFT 30040
	Conical mandrel bend test	ISO 6860; ASTM D552; NFT 30078
•	Persoz pendulum hardness	ISO 1552; NFT 30016
•	König pendulum hardness	ISO 3711; DIN 53157
•	Buchholz indentation hardness	ISO 2815; DIN 53153
•	Scratch resistance	ISO 1518; ASTM 2793
•	Erichesen cupping test	ISO 1520; DIN 50102; B.S. 3900; NFT 30019
•	Pencil hardness	ASTM D3363
•	Taber abrasion resistance	ASTM D821; DIN 53774; ANF T 30015
•	Heat resistance	- - - - - - - - - -
•	Humidity resistance test	ISO 6270; DIN 50017; B.S. 3900 F2
•	Kesternich sulphur test	ISO 3231; DIN 50018; B.S. 3900 F8
•	Salt spray test	ISO 9227; DIN 50021;
	Acetic acid salt spray test	ISO 3769; B.S. 6496 C15
•	Mortar resistance	ASTM C207; B.S. 6496 C15
•	Chemical resistance	- - - - - - - - - - - -
•	Detergent resistance	- - - - - - - -- - - --

Uretdione crosslinkers for powder coatings [5]

Uretdione curing agents are "self-blocked" via the formation of the uretdione ring structure. [11]
The isocyanate, 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 e-caprolactam counter-parts.
Uretdione crosslinkers are e-caprolactam free and are considered non-emissive. Uretdione curing agents are the selection-of-choice when seeking non-emissive or an e-caprolactam free system.



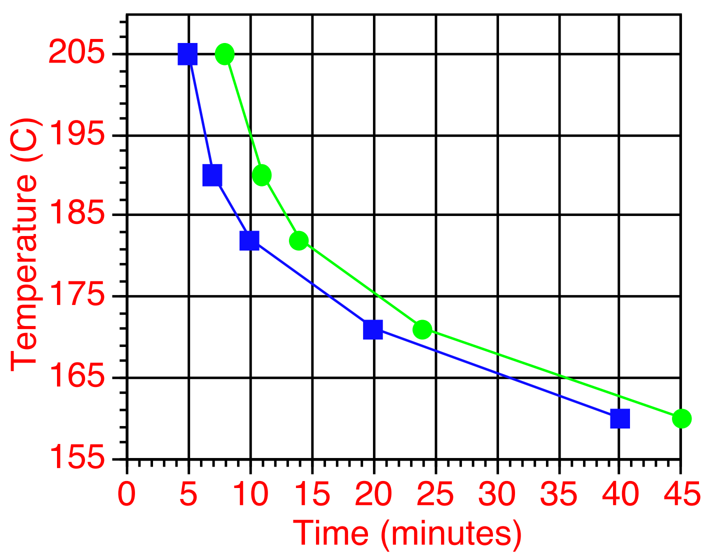


The use of pre-catalyzed polyester resins with hydroxyl values in the 35-50 range and resins with increased functionality with hydroxyl values from 60 to 100 have improved the cure response for uretdione curing agents for powder coatings.
Polyesters with hydroxyl values ranging from 100, 200 and 300 , can be formulated for anti-grafitti applications, dye-sublimation-heat-transfer applications and other demanding applications requiring superior chemical resistance and hardness.

Cure curves like the one below are subject to 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? As a formulator, I would think that 80-100 in-lbs is adequate.
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.

Cure curve of a 60 OH value PE cured with a uretdione CA [7]

Note: The square symbol represents the catalyzed [6] powder coating and the circle symbol represents the uncatalyzed powder coating.



Powder Coating Formulation

Premix (grams)
(high Intensity)

	(uncatalyzed) wt.	(catalyzed) wt.	phr	wt % (catalyzed)
60 OH PE	756.0	756.0	100.0	50.40
uretdione CA	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)

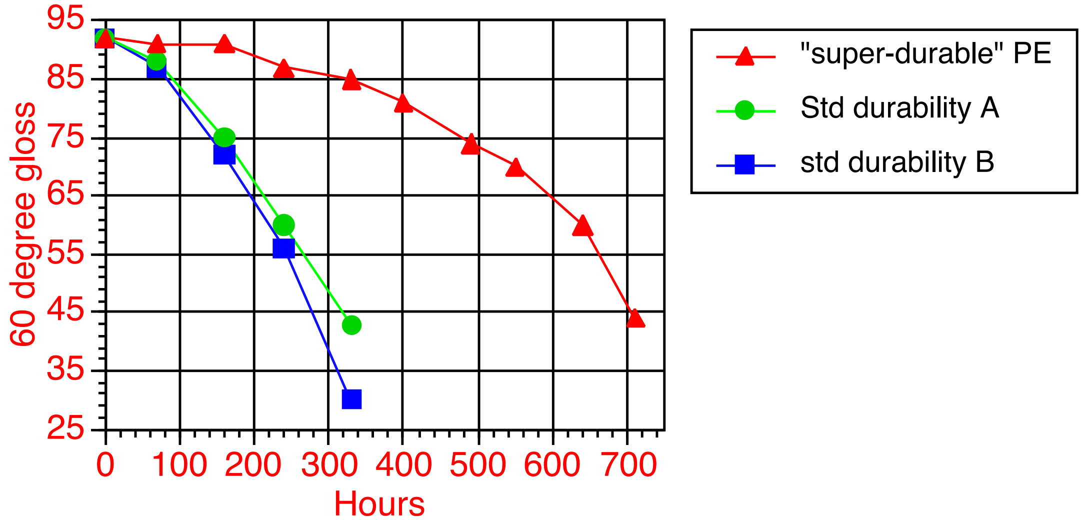
Powder Coating Properties:

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

note: Actiron is a registered trademark of Synthron Inc.

Polyesters for powder coatings with increased durability over their terephthalate counterparts have been synthesized. These products are typically synthesized with Isophthalic acid being a constituent of the formulation.
Increased durability resins with hydroxyl values ranging from 25-300 have been made. [12]

QUV B-313 "Super-Durable" 100 OH PE vs standard durability 100 OH PE



ADVANTAGES OF POLYESTER-URETHANE POWDER COATINGS

The unique characteristics of polyester-urethane powder coatings allow powder coating manufacturers to formulate thermosetting coatings that can have:

- Excellent Flow (consistent with polyurethanes 7-9 PCI flow with 35-45 OH PE's

- High Gloss (consistent with polyurethanes with 35-45 OH value resins)

- Low Gloss (chemically induced low gloss finishes, processed through-the-extruder, with 60 degree gloss less than10 with low hydroxyl polyesters and high hydroxyl polyesters designed for low gloss. [12] These coatings are especially useful for the automotive low gloss trim market.

- Thin Film Capabilities (12-25 micron coatings with excellent flow are possible)

- Re-processability (polyurethanes can be re-extruded without changing the powder coating appearance or reactivity)

- Fast Cure (catalysts can be included by the resin manufacturer in the polyester or the curing agent; they can also be added in the coatings formulation)

- Low temperature cure [12] can be achieved when curing agents are designed for low temperature capabilities and are combined with catalysts which promote low temperature cure, ie 125-135 C when combined with reactive polyesters.

- Chemical Resistance Properties (detergent resistance, solvent resistance, stain resistance, etc. can be achieved with higher functionality polyesters.

- Exterior Durability (South Florida testing has confirmed good to excellent gloss retention equal to other alternatives. New super durable versions of hydroxyl polyesters are now available that achieve three to four-fold increases in gloss retention. [12]

- Flexibility (post formability, 0T (zero T), bend capability can be achieved at 25 microns with most hydroxyl resins) 0-T capability can be achieved at higher film thickness with polyesters designed for increased flexibility.

- Hardness (hardness can range from HB-4H, with hydroxyl resins ranging from 25 OH to 300 OH .)

- Impact Resistance (160/160 inch-lbs. can be achieved with most PU systems)

- High Pigment Loadings (one to one pigment to binder ratios are possible)

- Good to Excellent Anti-Sintering (caking) Properties particularly high Tg's are achieved with polyester resins designed for better anti-sintering properties.

- Excellent Storage Stability (virtually no change in gel time or cure characteristics is observed even after years of storage.)

Conclusions:

Polyester-urethanes are one of the best options for the future of powder coatings. This is evident because they offer the most latitude for powder coatings formulators.
Hydroxyl polyesters, when combined with uretdiones or polymeric blocked isocyanates, have the ideal attributes of a thermoset system. Namely to be a **highly reactive** system during cure conditions and to be **virtually unreactive during manufacture, storage and application.**

Hydroxyl resins are available with hydroxyl values ranging from 25 to 300. This range of hydroxyl content permits formulation of purely decorative powder coatings to highly functional chemical resistant powder coatings.

When these resins are combined with the numerous curing agent options, unsurpassed formulation latitude is achieved. Of particular interest, is the value achieved by utilizing aromatic curing agents when appropriate. Aromatic curing agents can provide some exterior durability while reducing the overall costs associated with using polyester-urethanes. They can be used as alternatives to decorative Hybrid powder coatings and decorative epoxy powder coatings.

Specially formulated hydroxyl resins permit low gloss powder coatings to be manufactured in one step through-the-extruder, not post-blended.

More functional resins , with hydroxyl values in the range of 100, 200 and 300 can provide anti-grafitti powder coatings.

Super durable versions of hydroxyl functional resins are now available.
This includes resins for low gloss "through-the-extruder" processing as well as super durable resins for anti-grafitti applications.
Three to five-fold increases in durability are achieved. [12]

As powder coatings technology continues to advance, it is expected that cure temperatures will continue to decrease. The current target is to get cure at boiling water temperature. This has already been achieved with IR/UV powder coatings systems. Some people believe that it is possible to reach this target with thermoset technology.

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