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Resin and Cross-linker Chemistry for Powder Coatings

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Abstract:

Resins and cross-linkers are combined to form the binders used in today's thermosetting powder coatings.

The various chemistries used in modern powder coatings will be the topic of this paper.

All powder coatings are based upon resin systems that contribute to the ultimate performance capabilities of each powder coating.

Answers to the following questions will be provided.

What kinds of chemistries are available?

What kinds of cross-linkers are available?

Synthesis of polyesters will be covered.

Introduction:

At first glance, powder coating resins do not seem to be very complex[1]. This is especially true if one compares the number of constituents in a powder coating formulation with a conventional liquid paint formulation. Although solvent is essentially environmentally unacceptable, it is a great help in adjusting the many properties of a liquid coating.

Most of the properties associated with a powder coating are determined by the binder.

This paper will help explain the various binder chemistries associated with today's powder coatings.

The coatings user now not only has the option of various finishes from powder, water borne, high solids, exempt and compliance solvent borne systems, but also has many choices within the range of powder coatings. There are several types of thermosetting resin systems:

Polyester/TGIC

Polyester/Urethane

Hybrid (Polyester/Epoxy)

Polyester/Hydroxyalkyl Amide, HAA

Epoxy

Acrylic, (Acrylic/Diacid, Acrylic/Urethane)

Glycourils

UV chemistries

Thermosetting powder coatings have shown steady growth for the past 25 years. During the last few years, polyesters and hybrids have been growing faster than epoxies. Polyesters are displacing epoxies to take a dominant position in the market. There are a number of reasons for this change:

A. Large variety of polyesters available.
B. Lower cost general purpose polyester systems.
C. Better exterior durability while maintaining cost advantage.
D. Epoxy resins have been increasing in price faster than the competitive systems.

Because there are increased numbers of resins and curing agents available, the number of options is increasing for powder coatings formulators.

Polyesters and how they are synthesized

Polyester Resins as Binders for Powder Coatings

Most polyester resins used for the thin film decorative powder coating market today are thermosetting polyesters. Thermosetting polyesters can be defined as typically having functional groups such as hydroxyl, OH or carboxyl, COOH functionality. Hydroxyl functional polyesters react with curatives such as polymeric blocked isocyanates to form a film that melts, flows, and chemically reacts only once. Thermoplastic polyesters are not designed to chemically react during the application process when the coating is subjected to heat causing the coating to melt and flow. The final physical properties of thermoplastic resins are determined by their structural components and molecular weight of the resin; where as, the final physical properties of thermosetting resins are determined by the combination of the thermosetting resin and the curative chosen. Thermosetting resins can be formulated to achieve higher flows and thinner films than thermoplastic resins. Thermosetting resins usually have high flows at lower bake temperatures than their thermoplastic counter parts.

The most widely used reactants are **neopentyl glycol** and **terephthalic acid**. Numerous other difunctional acids and glycols are used to impart particular properties to the coating, such as increased detergent resistance or improved flexibility. These polyesters can be designed to possess two or more hydroxyl groups per molecule, (hydroxyl functional) or two or more carboxyl groups per molecule (carboxyl functional or acid functional).

The ancestor of virtually all North American polyesters is Amoco PC-600.

Amoco PC-600 [2]

Amoco (Flint Hills Resources) is a supplier of raw materials for the coatings, fiber and packaging industry**.** They have developed starting point polyester formulations to promote their products for use in powder coatings. One of the very first starting point formulations was a polyester for powder coatings designated PC-600. This product was developed in 1970.

Amoco PC-600 was formulated with NPG (neopentyl glycol) and TPA (terephthalic acid).

Amoco PC-600 was formulated to a 1.1 to 1.0 molar ratio of NPG to TPA.

Amoco PC-600, Poly Calc data:

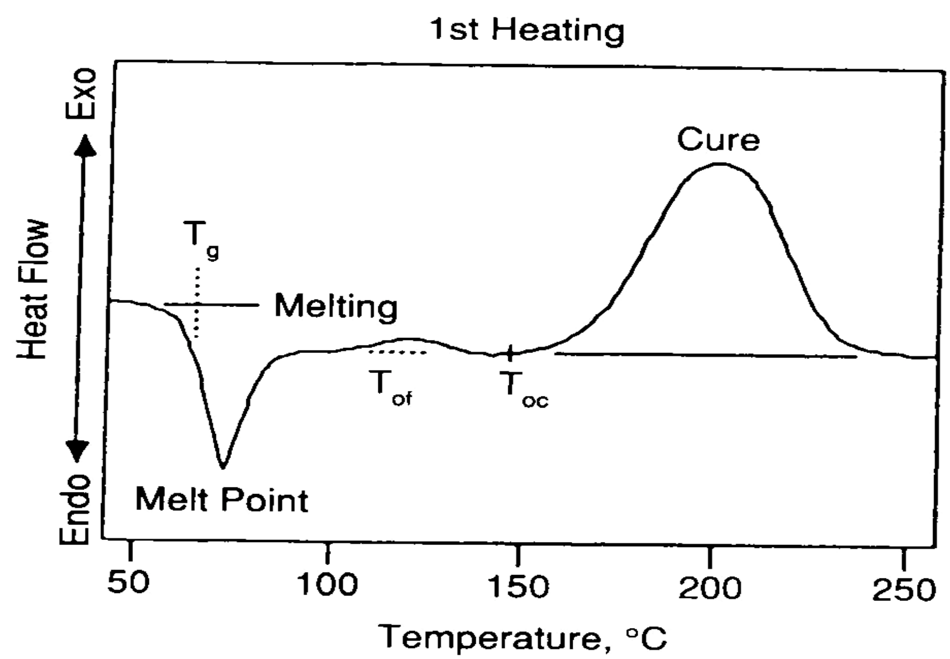
Acid value	=	9.5
OH value	=	55.2
Mn	=	1734.0
OH EQ Wt	=	1016.0

This product could be cured with melamine curing agents like Cymel 300 and/or Monsanto X-745. Typical powder coatings would require 10% by weight Cymel 300. This much of a semi-liquid curing agent leads to package stability problems like caking/sintering.

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.

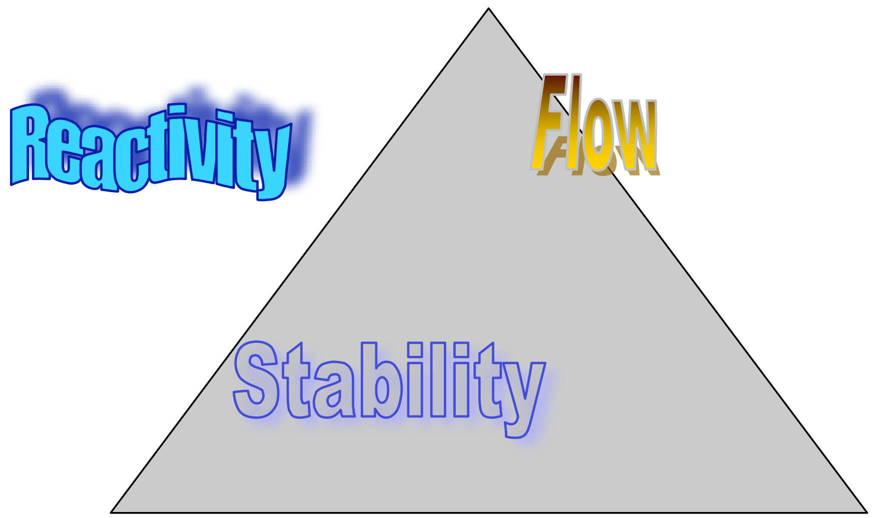
Glass transition temperature can be defined as:
Temperature range at which an <u>amorphous</u> material changes from a glassy to a rubbery state [3]

Typical DSC Thermogram for an Epoxy Resin-Based Powder Coating†



Both the Tg and melt viscosity of the polyester are greatly influenced by the choice of monomers. 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.

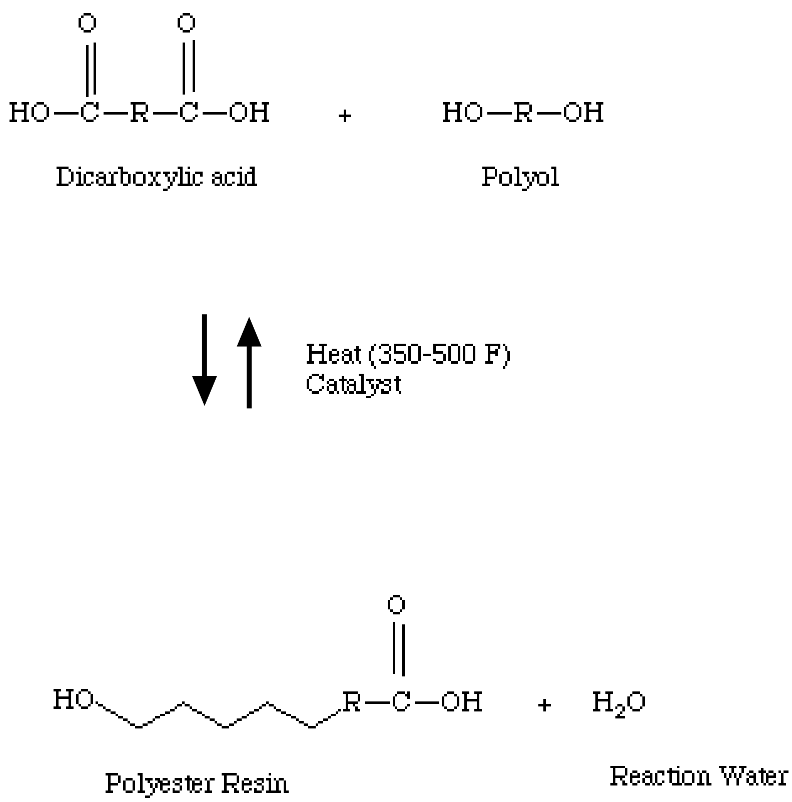
The Magic Triangle



It is difficult to achieve all three at the same time [3]

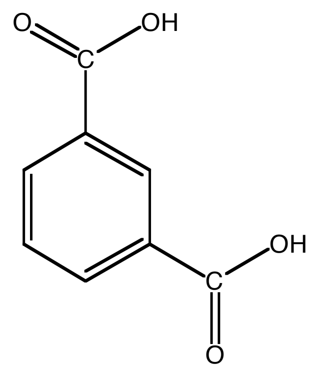
Compatibility of resins is determined by how closely all three can be matched.

Polyester Chemistry

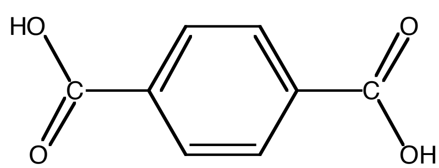


Reactants used in formulating thermosetting polyester powder resins:

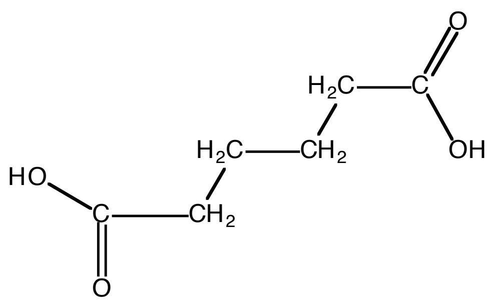
Isophthalic Acid can be used for formulating “super-durable” polyesters as well as modifying standard durability polyesters.



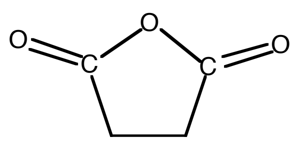
Terephthalic Acid is used for formulating standard durability polyesters



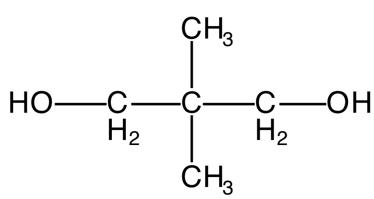
Adipic Acid is used as a modifying reactant to increase flexibility



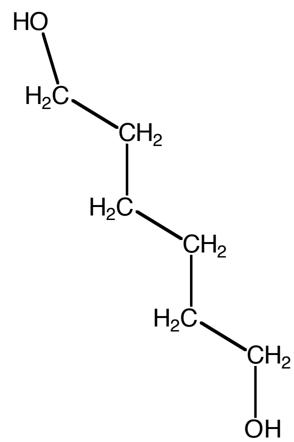
Succinic Anhydride is used to help improve flexibility



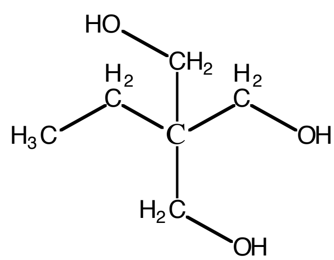
Neopentyl Glycol is a basic building block glycol for polyester powder resins



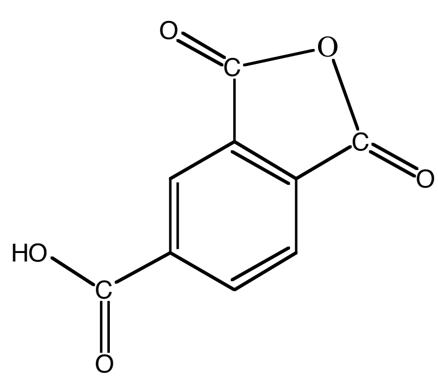
1,6 Hexane diol is used to help improve flexibility



Trimethylol propane is used to increase branching/functionality of the polyester



Trimellitic anhydride is used to increase branching/functionality of the polyester

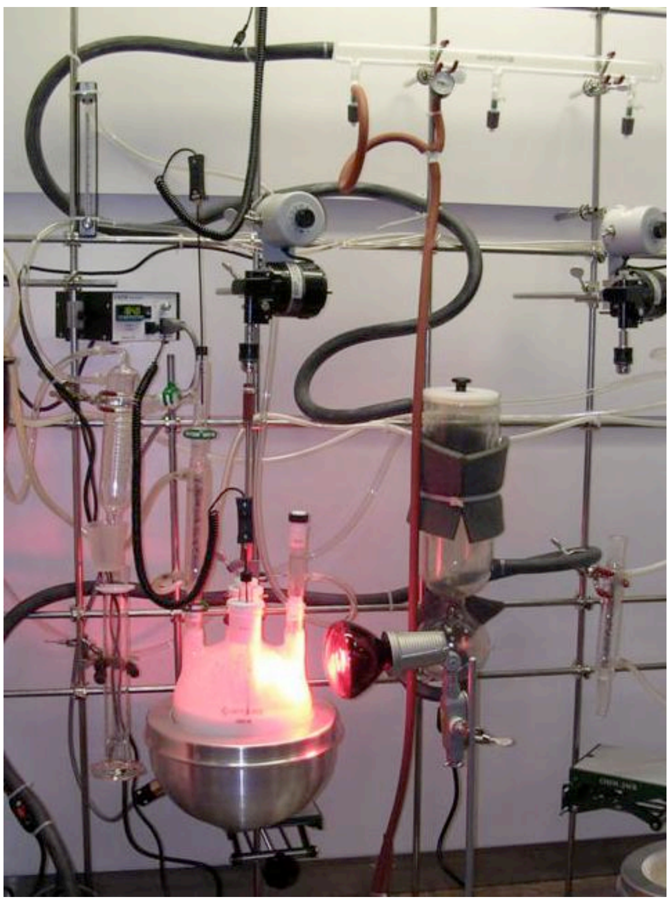


Polyester Synthesis Apparatus:

The laboratory apparatus pictured below can be used to synthesize polyester resins for powder coatings.

What is pictured is a 5 liter round bottom flask, Talboy stirrer, stainless steel stirring shaft and paddle.

Packed column, steam-jacketed, Friedricks condenser, graduated cylinder for receiving reaction water, nitrogen inlet, nitrogen flow meter, temperature controller, 5-liter heating mantle and an IR lamp.



The resulting lab resin is discharged in molten form. It is then cooled and crushed to prepare it for use in a typical thermosetting polyester powder coating formulation.

A typical thermosetting polyester powder coating will contain: polyester resin with carboxyl or hydroxyl functionality, a curative for the chosen resin, flow control additive, degassing additive, pigments, fillers and other potential additives.

Polyester Resin:

Polyester resins are generally cooled and flaked to allow easy weighing, premixing, compounding etc.

Polyesters for powder coatings are comprised of dicarboxylic acids and diols . Through the use of computer modeling software [17], like Polycalc V ™, much time and effort designing polyesters for powder coatings can be saved.

They can be modified for appearance and performance properties with tri functional carboxylic acids/anhydrides and tri functional polyols. The basic approach has been replacement of some of the dicarboxylic acid, terephthalic acid or isophthalic acid with flexibilizing reactants such as adipic acid or 1,6 hexane diol, for example.

The challenge with any formulation is to balance the properties so that when flexibility is increased, other resin parameters such as glass transition temperature Tg, do not decrease too much.

The typical Tg range of standard thermosetting polyesters for powder coatings is 50-65 degrees C.

Resins with lower Tg’s can contribute to sintering ,clumping of the powder coating.

Polyester powder resins that have been modified for increased flexibility may have slightly lower Tg's, typically in the range of 50-60 C.

Another reactant , such as Succinic anhydride for example, has been used to improve flow and flexibility of thermosetting hydroxyl polyesters. This concept is covered in a US patent. [4]

Linear polyesters have been shown to have better flexibility and flow than some of the more highly branched products. Increased branching can help increase toughness of the powder coating resulting in improved impact resistance, especially when molecular weight of the resin is increased.

The down side is that flow may be decreased. We have to always consider balancing of the conflicting performance parameters.

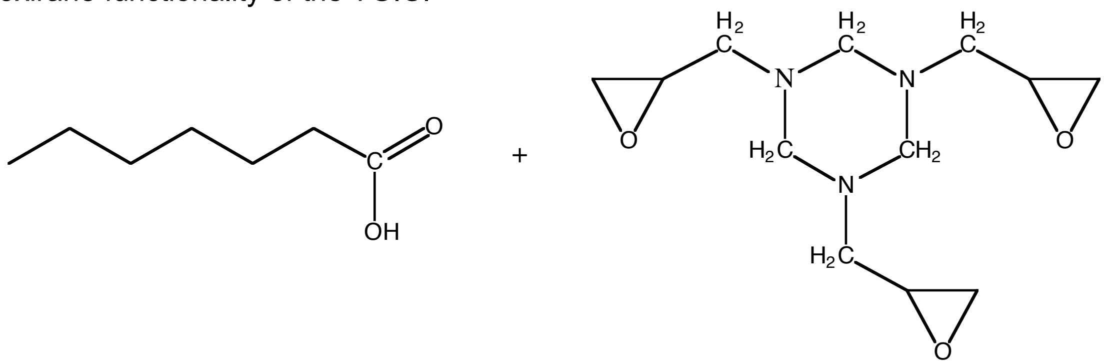
Range of Polyesters With Crosslinker Options

- **polyester**
  - **hydroxyl**
    - hydroxyl value
      - 25-30
      - 35-40
      - 45-50
      - 55-60
      - 60-70
      - 100-110
      - 280-300
    - **Curing agents**
      - aliphatic polymeric blocked isocyanates
      - aromatic polymer blocked isocyanates
      - uretdione isocyanates (self-blocked)
      - glycourils (Powderlink 1174)
      - acids and anhydrides
  - **carboxyl**
    - Acid value
      - 25-30
      - 35-40
      - 45-50
      - 55-60
      - 65-70
      - 75-80
      - 85-100
      - 120-140
      - 150-200
    - **Curing agents**
      - epoxy resins (hybrid pwd coatings)
      - oxirane terminated (TGIC
        GMA acrylics
        PT-910
      - hydroxyl terminated resins
      - hydroxyalkylamide (Primid)

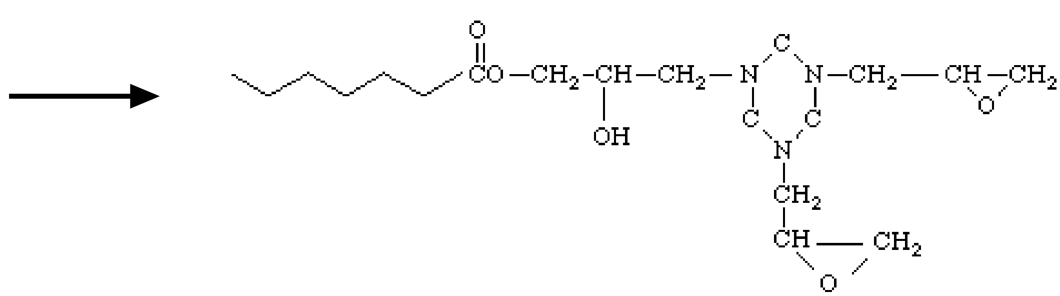
Polyester/TGIC powder coatings

Carboxyl polyesters cured with TGIC

Most conventional TGIC cured polyesters are somewhat 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.

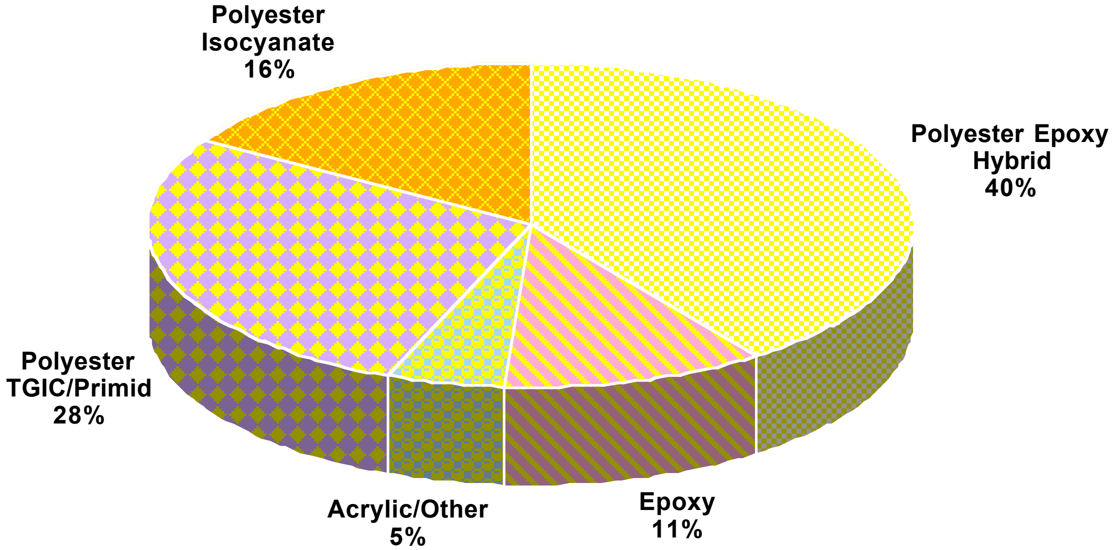


Polyester Resin TGIC (Triglycidyl isocyanurate)



Polyester/TGIC powder coatings is one of the fastest growing segments of the North American market.

North American Powder Coatings Market 2004 [5]



Why? Decreasing cost of the cross-linker, (curative) TGIC, triglycidylisocyanurate, has helped this segment to dominate the North American market.

TGIC cured polyesters provide robust powder coatings. In this case, robust means:

• Not film thickness critical (thick or thin films both have good properties.)

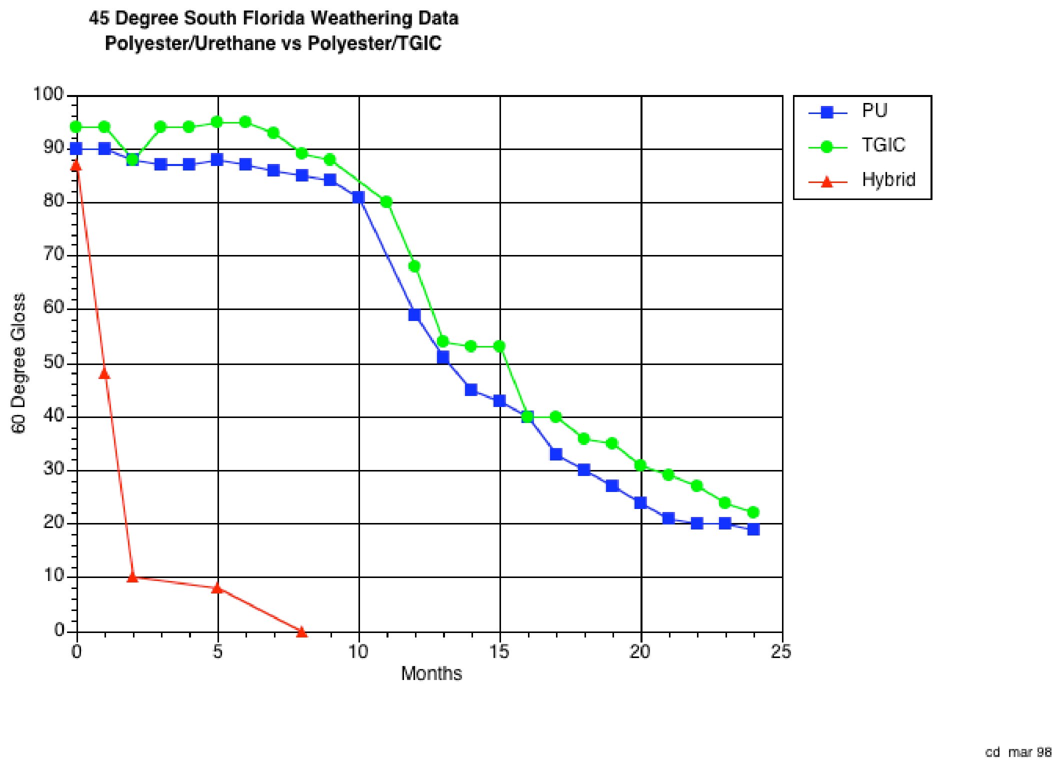
• Exterior durable

• Corrosion resistance

• Color stability, resistance to over bake conditions

Epoxies are continuing to lose market share since their peak in the early 1970's of nearly 90 % share. They are being replaced by Hybrids where ever possible. Today, Epoxy powder coatings are used for more functional/chemical resistant applications and fewer decorative applications. The primary factor is cost.

South Florida Weathering Comparison [6]



The above graph shows that PU powder coatings and TGIC powder coatings weather quite similarly. Hybrid powder coatings weather severely after 3 months in South Florida.

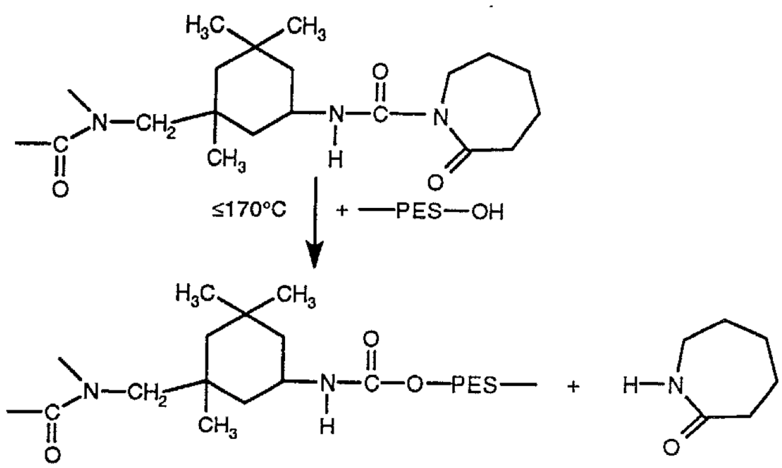
Polyester/urethane powder coatings

Hydroxyl functional polyester cured with a polymeric blocked isocyanate

The North American market has been dominated by this urethane chemistry for over 20 years. Most recently, due to lower costs of competitive chemistries such as TGIC, urethane systems have lost market share.

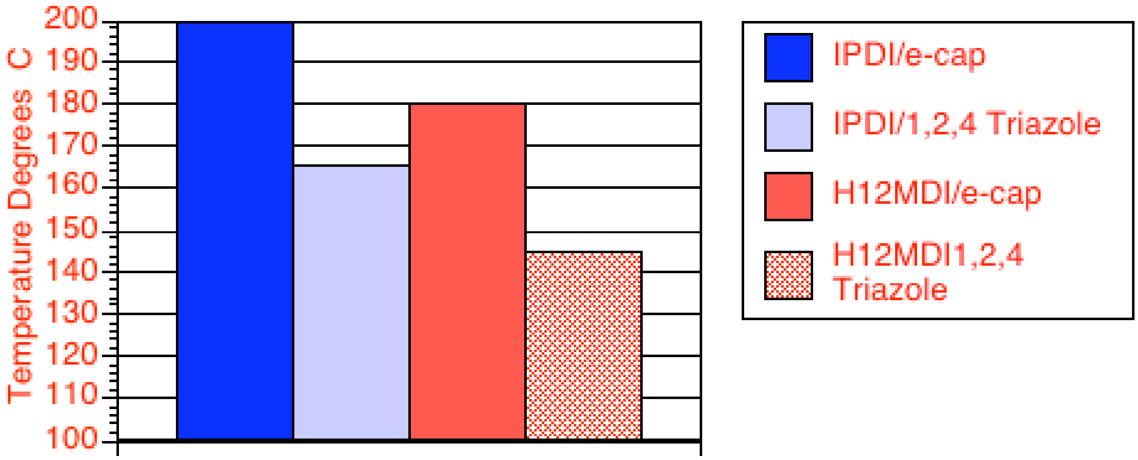
Polyester-urethanes provide advantages to the powder coatings formulator. Polyester-urethanes can be described as achieving the ideal attributes of a thermosetting coating; namely to be a highly reactive system during cure conditions and to be virtually unreactive during manufacture, storage and application.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

Polymeric blocked isocyanate curative reacting with a hydroxyl polyester, PES-OH.

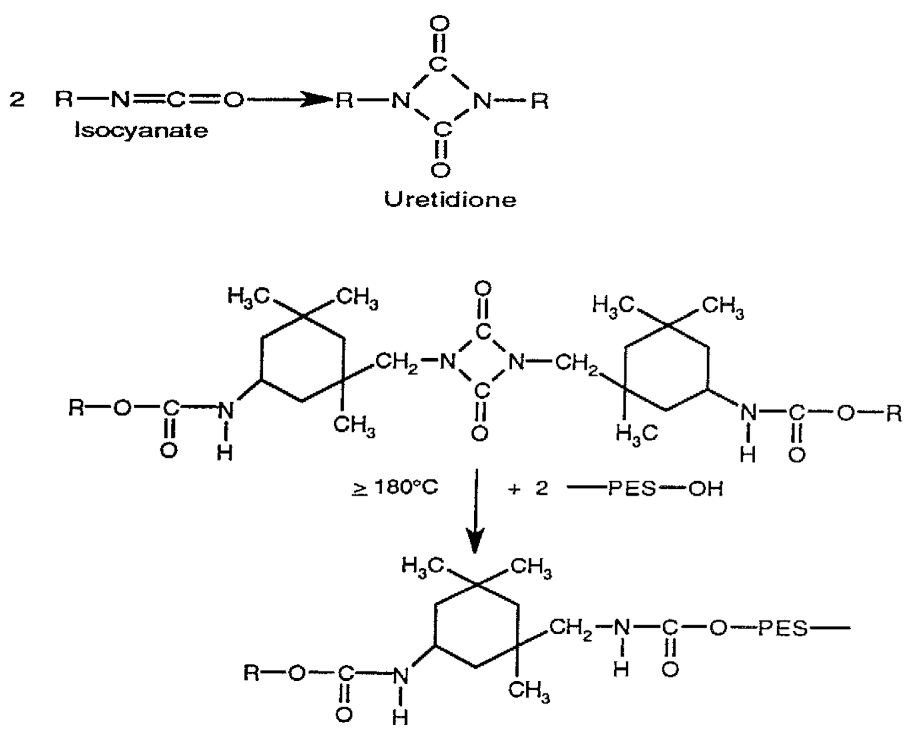


During the curing reaction, the blocking agent, such as E-caprolactam
Evolves

De-blocking temperature of IPDI and H12 MDI polymeric blocked isocyanates. Blocking agents used were e-caprolactam and 1,2,4 Triazole.[7]



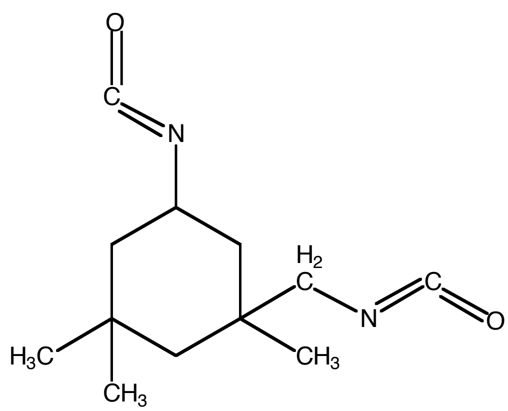
Uretdione cured polyesters are used where blocking agents may pose a problem. Thicker films can be applied when using uretdione curing agents (cross –linkers).



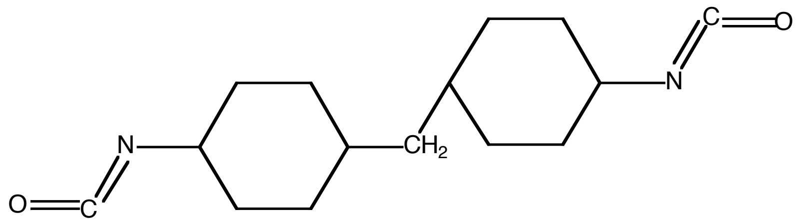
Common diisocyantes used in powder coatings:

Isocyanates like IPDI can be reacted with polyols like trimethylol propane and blocked with e-Caprolactam or specialty low temperature blocking agents like 2,4 triazole to form polymeric blocked isocyanates.

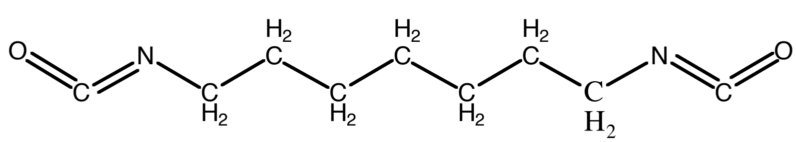
IPDI (isophrone diisocyanate)



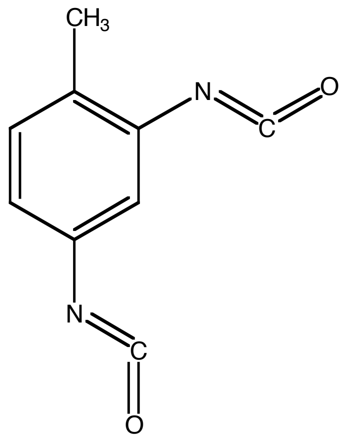
H12MDI (Desmodur W)



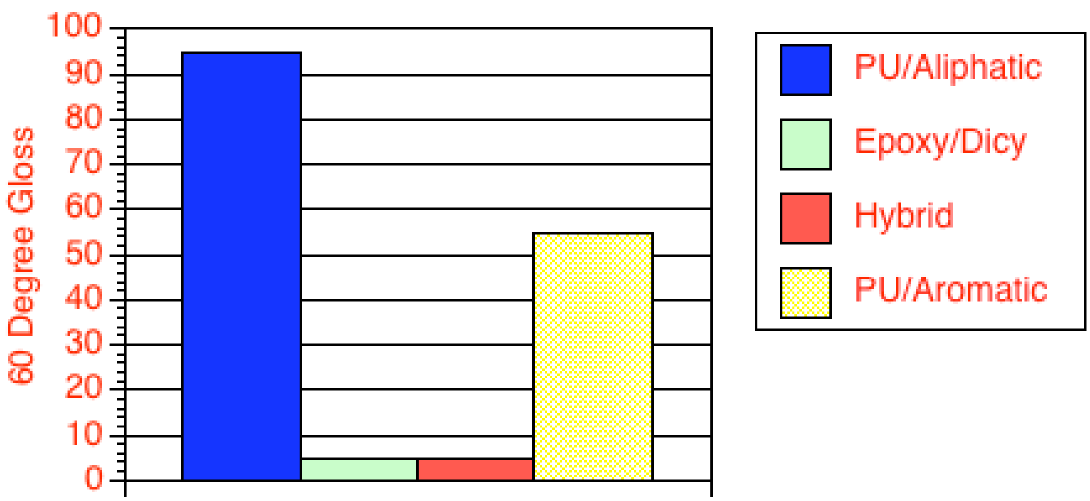
HDI (hexamethylene diisocyanate)



TDI (toluene diisocyanate) is used to make low cost cross-linkers that can be used as alternatives to Hybrid systems, because thay have weathering characteristics between aliphatic isocyanate cured systems and Hybrid powder coatings.



12 Month 45 degree South Florida exposure [8]



The graph pictured above shows polymeric blocked aliphatic isocyanate cured polyester-urethanes retain 60 degree gloss better than their polymeric aromatic blocked isocyanate counterparts.

May be polymeric aromatic blocked isocyanate cured polyester-urethanes should be considered for some general purpose exterior applications, since they retain almost 60 percent of their original gloss after one year South Florida exposure.

Hybrid powder coatings and a dicy-cured epoxy retain very little gloss after one year South Florida exposure.

Advantages of Polyester/Urethanes

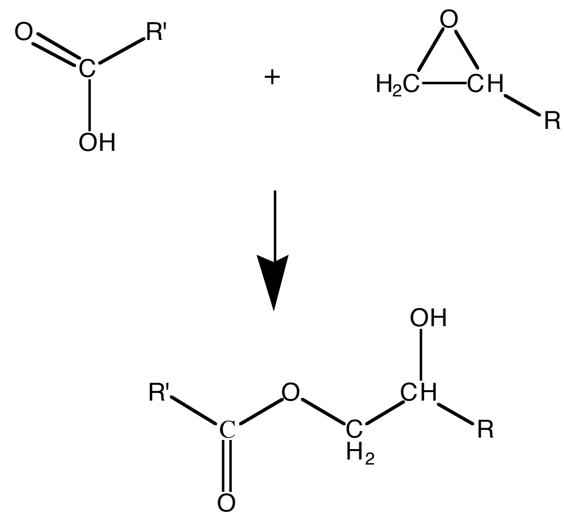
Polyester/urethanes provide advantages to the powder coatings formulator. Polyester/urethanes can be described as achieving the **ideal attributes** of a thermosetting coating; namely to be a **highly reactive** system during cure conditions and to be **virtually unreactive during manufacture, storage 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. Today's world also seeks products which have a low order of toxicity. Polyester/urethane powder coatings meet this challenge. 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.[9]

Some countries in Europe associated powder polyester urethanes with some not so safe liquid two component polyurethanes which can have substantial levels of monomeric isocyanate present.

This is not the case with the blocked polymeric isocyanate curing agents used in polyurethane powder coatings. Risks of exposure to monomeric isocyantes is minimal when using polyurethane powder coatings. The only possibility for exposure to isocyanate monomer occurs when polyurethane powder coatings are burned or otherwise thermally decomposed. Good oven exhaust will prevent exposure in this case.

Polyester/Epoxy (hybrids)

Reaction of an acid functional polyester with an epoxy



The reaction yields a hydroxy ester

The epoxy could be a bisphenol A epoxy

Hybrids now have the largest share of the North American Powder Coatings Market.

Hybrids are blends of carboxyl polyesters and Bis phenol A Epoxies.

The following ratios are being used:

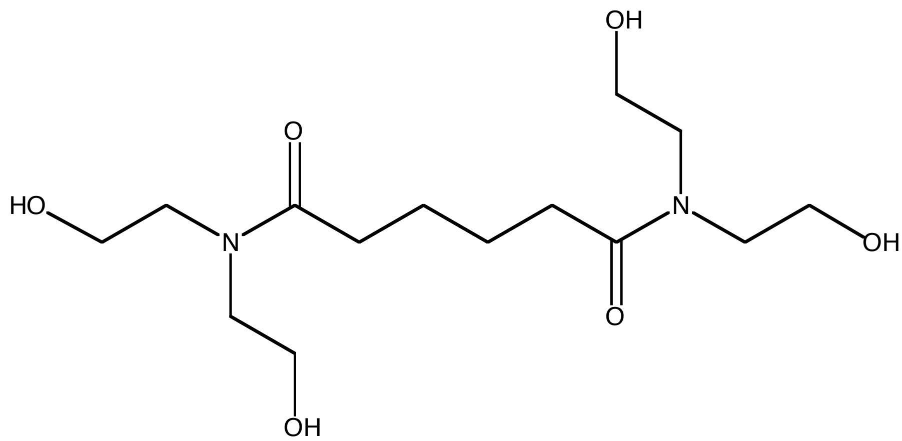
50:50 PE/Epoxy

60:40

70:30

As the amount of carboxyl polyester is increased, chemical resistance is reduced, hardness is reduced and binder cost is reduced.

Polyester hydroxyalkyl amide, HAA powder coatings are typically cured with the hydroxyalkylamide, like the one below. [10]



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

Resin [6]	Acid Value	ICI viscosity @ 200 C
A	30-35	7000-8000 cps
B	30-35	5800-6800 cps
C	32-38	3300-4800 cps
D	32-38	3000-3800 cps

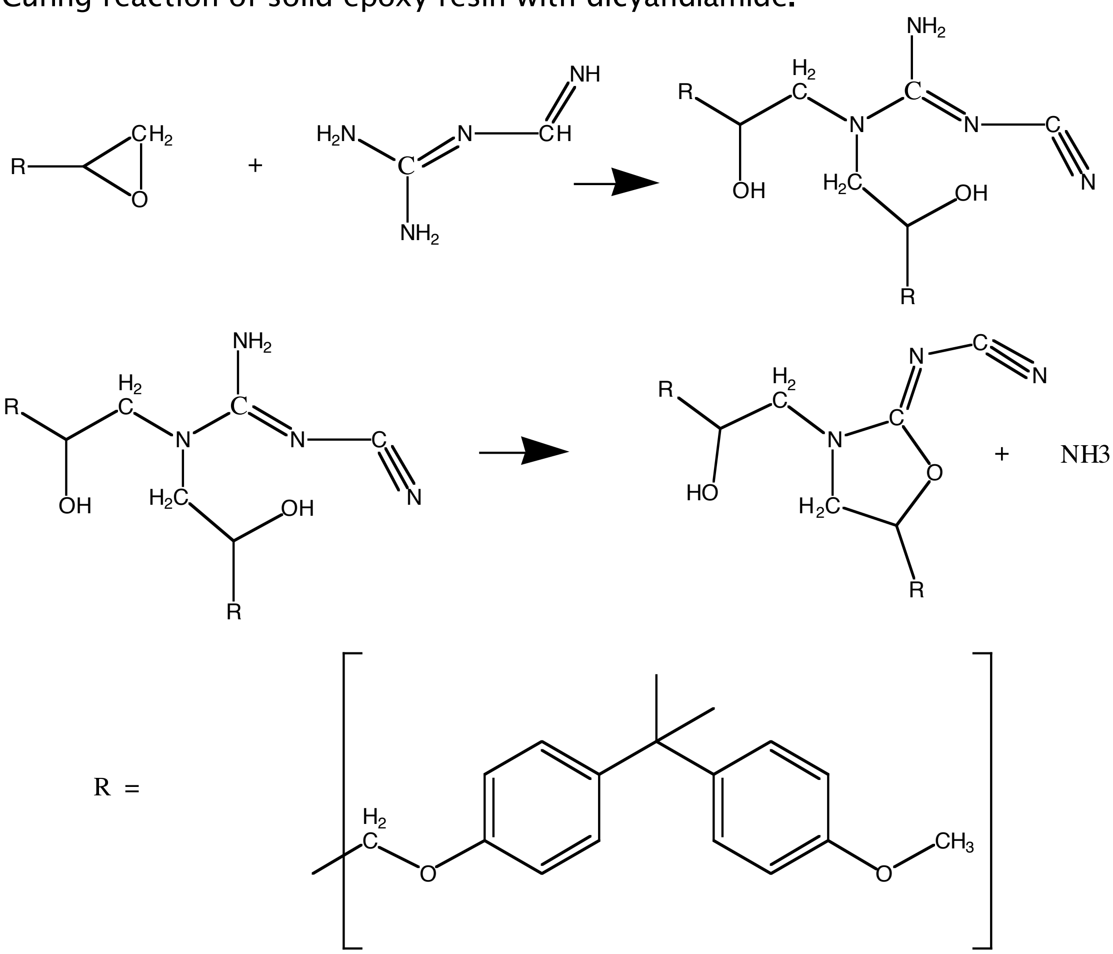
Increased speed of cure is attained as the molecular weight of the polyester component is increased. The highest viscosity polyester described above corresponds to the highest molecular weight polyester in this series of products. Cure can be achieved in as little as 1-2 minutes at 220-240 C. (coil line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

Hydroxyalkylamides liberate water during cure with carboxyl polyesters. Specific additives have been identified to permit thick films without pin holing. A white paper has been written by The Powder Coatings Institute describing the health and safety aspects of hydroxyalkylamide crosslinkers. [13]

In summary, on the basis of its toxicology and environmental profile, HAA cross-linker can be used safely and with very low associated risk for adverse effects on health or the environment when good industrial hygiene practices are followed.

Epoxy powder Coatings

Curing reaction of solid epoxy resin with dicyandiamide.



This cross-linking reaction liberates NH_3 (ammonia)….

Note: Phenolic epoxy technology is currently being used for mostly functional applications and will not be covered in this paper.

Acrylics

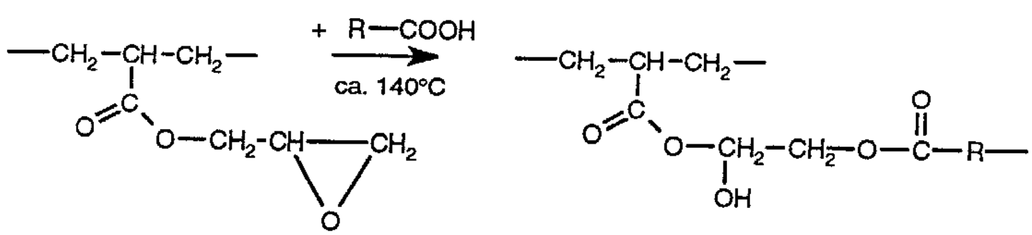
Epoxy, glycidyl, functional acrylics with acid functional crosslinkers

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

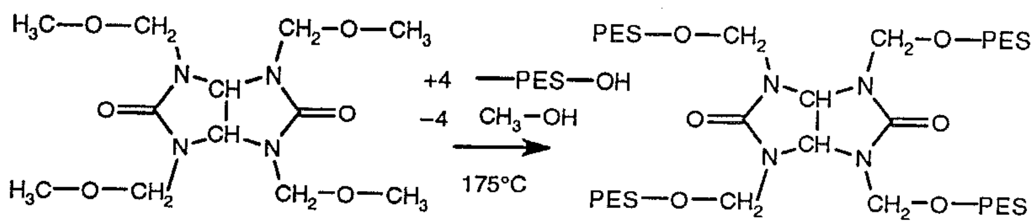
Epoxy functional acrylics are typically cured with long chain dibasic acids such as dodecanedioic acid, DDA, azelaic acid, and other long chain acids. The brittle GMA acrylics require the flexibility of the long chain diacid portion in order to achieve acceptable film properties and performance. The 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.
Since this is an **addition reaction, no reaction by-products are released.**

Glycoluril Crosslinkers for Powder Coatings 11

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.



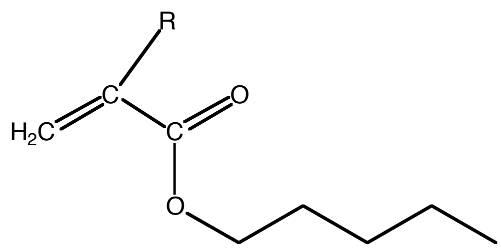
Methanol is released during the curing cycle of powder coatings formulated with glycoluril crosslinkers.

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.

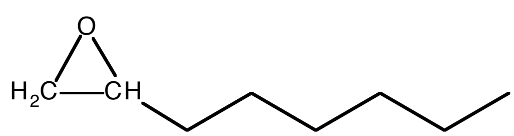
UV Chemistries [16]

When powder coatings and UV technology are combined, improved film formation, and improved adhesion at lower cure temperatures can be obtained.

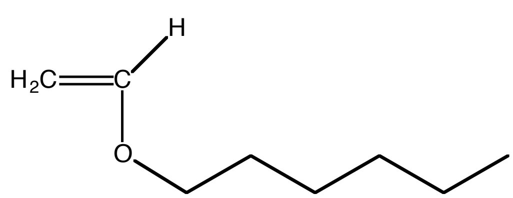
Acrylates



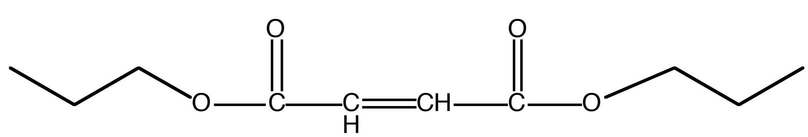
Epoxies



Vinyl ethers



Maleates



UV-curing Reaction

The UV free radical curing reaction in a simplified form can be represented as follows:

Initiation

$$R{-}R \xrightarrow{hv} 2R\bullet$$

Propagation

$$R\bullet + M \longrightarrow R{-}M\bullet$$

$$R{-}M\bullet + nM \longrightarrow R{-}M\ (n+1)\bullet$$

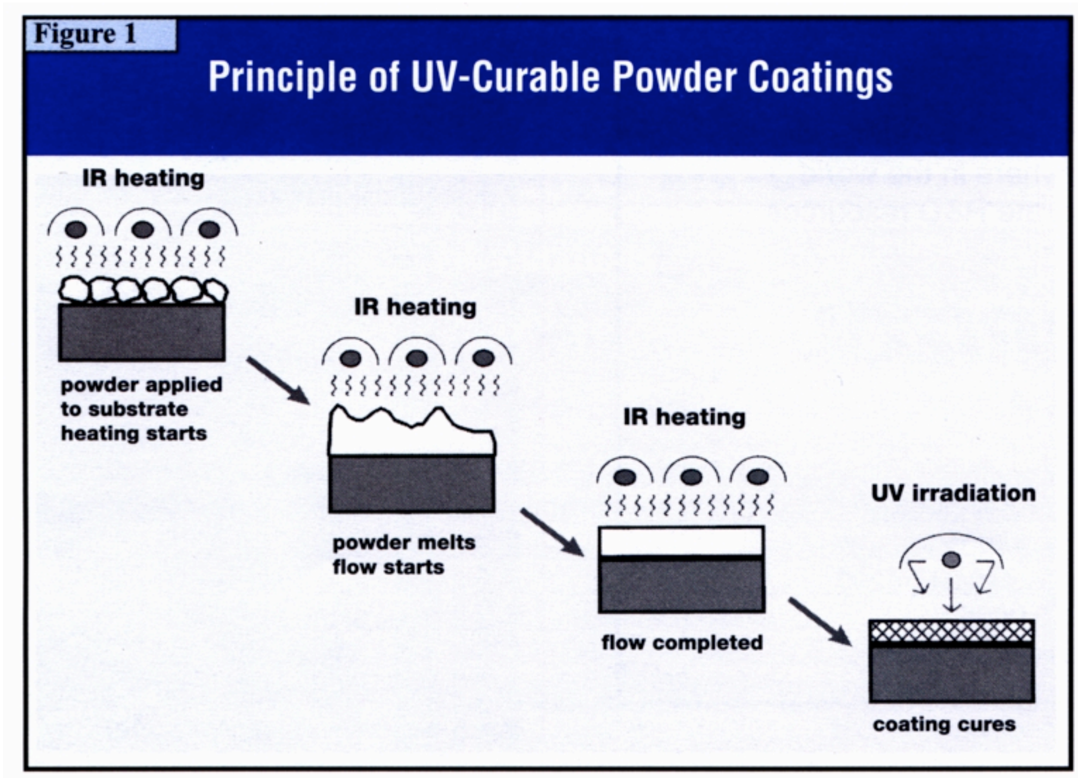
Termination

$$2R{-}M\bullet \longrightarrow R{-}M{-}M{-}R$$

$$R{-}M\bullet + R{-}M{-}M\bullet \longrightarrow R{-}M + R{-}M{=}M$$

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.



[14]

Major resin suppliers to the powder coating industry have started to market polymers for UV cure. These polymers utilize free radical cross-linking mechanisms initiated by UV light.

Some suppliers are investigating ionic cure mechanisms.

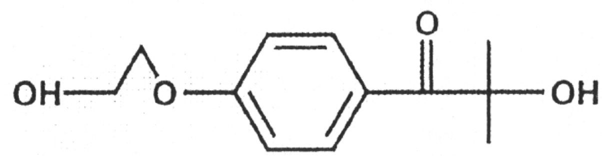
The most obvious problem with UV cure powder is how can UV be used to cure titanium dioxide (white) powder coatings? Specialty chemical suppliers have developed a class of visible light photo-initiators to help cure pigmented UV cured systems.[12] When combined with selected co-initiators and other typical UV initiators, a new photo-initiator significantly enhances the UV cure of highly pigmented TiO2 coatings.

Other Specialty Chemical Suppliers, have introduced photo-initiator systems that are blended to achieve surface cure and through cure.[15]

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.

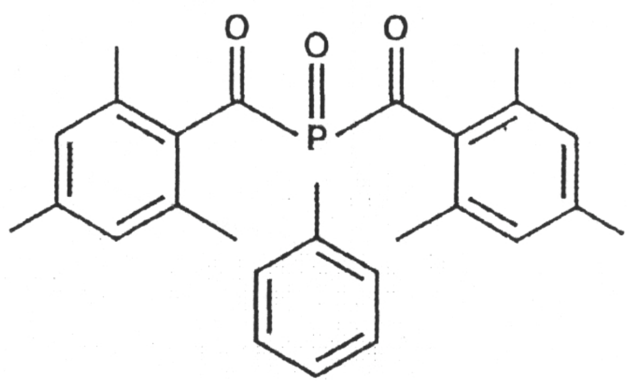
Some photo-initiator combinations are helping achieve cure in pigmented systems.[14]

Alpha-hydroxyketon type photo-initiator (AKH) provides: Surface Cure



Blends 50:50 to 30:70

Bisacylphosphine-oxide type photo-initiator (BAPO) provides: In-depth Cure



Review:

The answers to the following questions have been discussed.

What kinds of chemistries are available?

Polyester/TGIC

Polyester/Urethane

Hybrid (Polyester/Epoxy)

Polyester/Hydroxyalkyl Amide, HAA

Epoxy

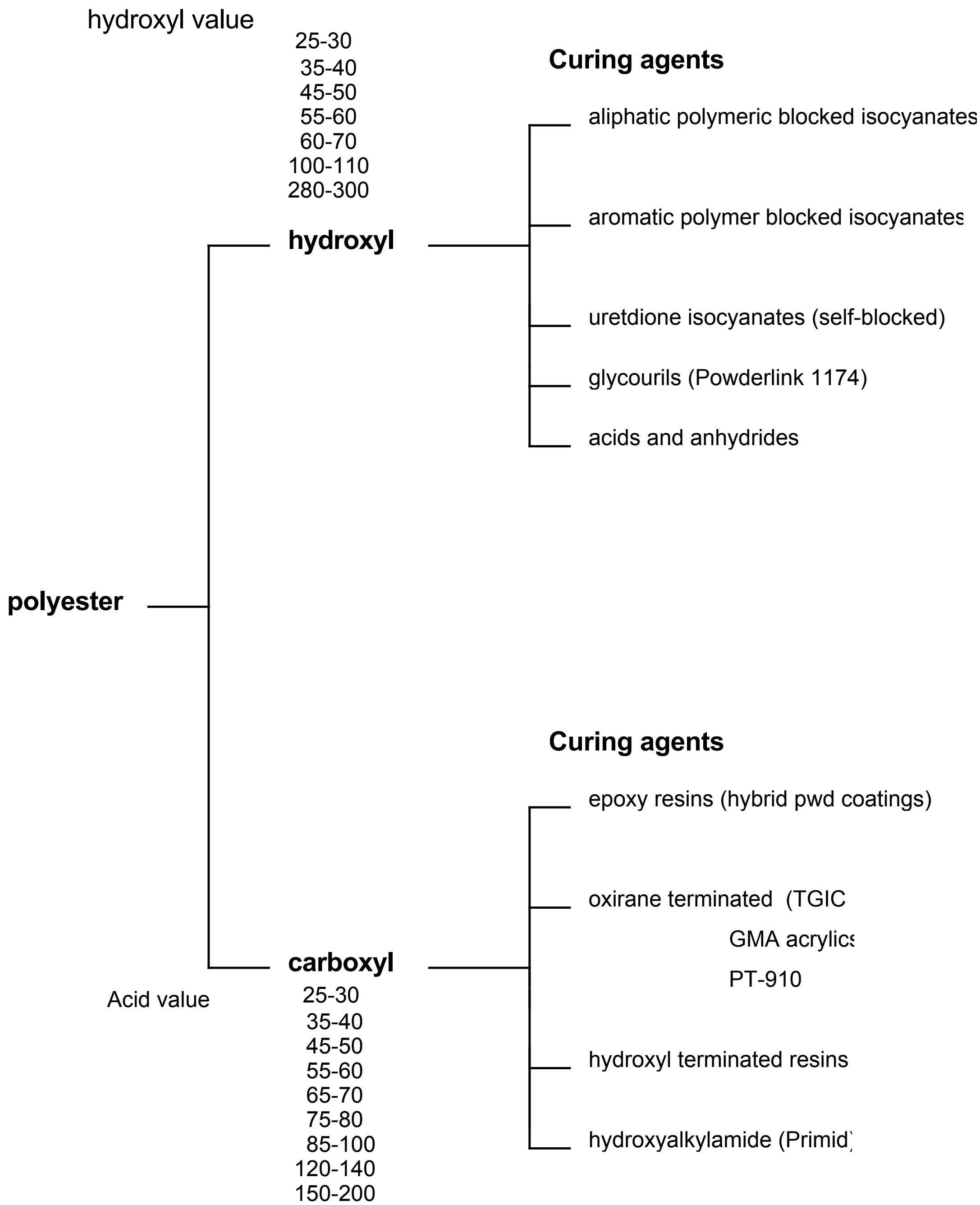
Acrylic, (Acrylic/Diacid, Acrylic/Urethane)

Glycourils

UV chemistries

What kinds of cross-linkers are available?

Range of Polyesters With Crosslinker Options



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