A novel acrylic/polyester system for powder coatings

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Introduction

In the past decade there have been many significant changes in the coatings industry. The control of VOCs, workers' safety and waste disposal are placing continuing pressure for change on the coatings industry. The powder coating industry has enjoyed a substantial growth rate in this period.

This expanding market has created demands for specialised powder products with better durability and new cross-linking mechanisms.

Summaries

A novel acrylic/polyester system for powder coatings

An acrylic/polyester system has been introduced for powder coatings as an alternative system to TGIC.

In a typical polyester/blocked-isocyanate system or polyester/TGIC system, a higher terephthalic acid (TPA) content polyester resin shows good mechnical properties, but the exterior durability is not good enough. On the other hand, a polyester based on isophthalic acid (IPA) shows excellent exterior durability, but the high IPA content adversely affects the mechanical properties.

Both excellent exterior durability and good mechanical properties were given by this acrylic/polyester system, especially by the combination of the acrylic resin (having glycidyl-epoxy groups and OH groups), bi-functional polyester (having OH groups and COOH groups) and blocked isocyanate.

Ein neue Acryl-Polyestersystem für Pulverlacke.

Ein Acryl-Polyestersystem für Pulverlacke wurde gefuhrt als Alternative zu TGIC ein. Bei einem konventionllen Polyester-verkapptisocyanatesystem order einem Polyestre-TGIC system zeigt gute Mechanischeigenschaften, aber Aussendauerhaftikeit ist nicht genügend. Auf der anderen Seite gibt ein auf Isophthalsäure basierte Polyesterharz ausgezeichnete Eigenschaften Aussendauerhaftigkeit, aber der HochIPAgehalt beeinträchtigt d die mechanischen Eigenshaften. Ausgezeichnete Aussendauerhaftigkeit und gute mechanischen Eigenschaften wurden von diesem Acryl-Polyestersystem erreicht, vor allem durch die Verbindung des Polyesterharzes (mit Glycidyl-Epoxid- und Hydroxylgruppen, des zweifunktionellen Polyesterharzes (mit Hydroxyl- und Carbonsäuregruppen) und der Verkapptisocyanate.

Un nouveau système acrylique-polyester pour revêtements en poudre.

Un système acrylique-polyester a été introduit en revêtements en poudre comme un alternatif à l'isocyanate de triglycidyle (TGIC). Dans un conventionnel système polyester-isocyanate bloqué ou polyester-TGIC, une résine de polyester ayant une teneur plus élevée en l'acide téréphtallique témoigne de bonnes caractéristiques mécaniques, mais la durabilité à l'extérieur n'est pas suffisante. D'autre part une résine de polyester basée sur l'acide isophtallique offre d'excellente durabilité à l'extérieur, tandis que la teneur élevée en l'acide isophtallique altère les caractéristiques mécaniques. D'excellente durabilité à l'exterieur et a la fois de bonnes caractéristiques mécaniques sont rendues par ce système acrylique-polyester, surtout en raison de la combinaison de la résine acrylique (ayant de groupements glycidyle-époxidiques et hydroxyliques) et de la résine de polyester bifonctionnelle (ayant de groupements hydroxyliques et carboxyliques) et l'isocyanate bloque.

For decorative thermoset powder coatings, there are three main resin types used, epoxy, polyester and acrylic. Among these, the use of polyester resin is growing more rapidly than the others due to its attractive cost/performance relationship.

Usually, the polyester resins are cured with epoxy, TGIC (triglycidyl isocyanurate) or blocked isocyanate, depending on whether the polyester resin contains carboxyl or hydroxyl groups. Their main advantages and disadvantages are shown in Table 1.

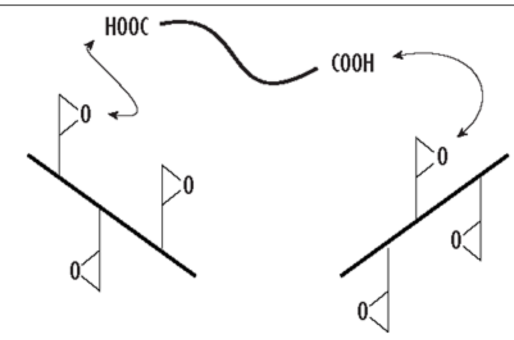
Table 1: Conventional thermosetting powder coatings

Resin	Hardener	Advantages	Disadvantages
Epoxy	Dicyandiamide	Corrosion resistance	Exterior durability
	Anhydride	Volatile free	Yellowing
COOH polyester	TGIC	Volatile free	Toxicity
	Primid	Mechanical property	Bubbling
OH polyester	Blocked NCO	Smooth appearance	Volatiles
	Aminoplast	Mechanical property	Storage stability
OH acrylic	Blocked NCO	Exterior durability	Impact resistance
GMA-acrylic	Dibasic acid	Exterior durability	Mechanical properties

Acrylic/polyester hybrid systems

A new type of crosslinking mechanism has been developed, based on a polyester and a glycidyl methacrylate (GMA) acrylic that offers novel powder coatings with improved durability, stable matt finish, smooth appearance, and high mechanical film properties. The usual resin properties for these acrylic/polyester systems are shown in Table 2. The original curing mechanism utilises the glycidyl group of an acrylic resin combined with the carboxyl group of the polyester as shown in Figure 1A. This is addition reaction with no volatiles, very similar to TGIC or epoxy/polyester hybrid types with the advantages of lower toxicity and good exterior durability.[1]

Figure 1A. Curing reaction model of the acrylic/polyester hybrid curing system.



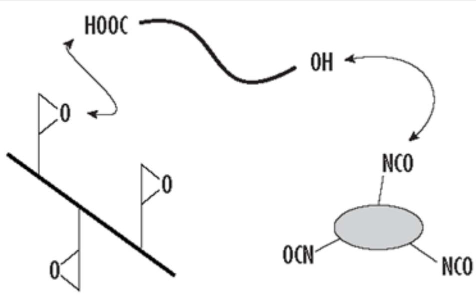
COOH polyester/GMA-acrylic hardener
<Acrylic cure polyester system>

Table 2: Typical resin specifications for polyester/acrylic hybrids

	Polyesters		Acrylic hardeners		
Resin	M-8400	A-239-X	A-229-30-A	A-244-A	A-249-A
Softening point (°C, R&B)	115–119	108–112	106–112	108–114	118–122
Hydroxyl value (mgKOH/g)	–	19–25	–	(53)	–
Acid value (mgKOH/g)	23–25	13–15		–	–
Epoxy equivalent weight	–	–	505–545	570–630	450–510
Tg (°C)	65	63	66	74	63

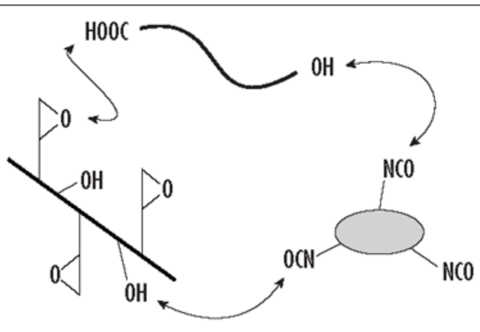
The second system is based on a bi-functional polyester with hydroxyl and carboxyl groups. The carboxyl group reacts with the oxirane group in the acrylic as before, but the NCO cures the hydroxyl group in the blocked isocyanate hardener as shown in Figure 1B. In this system, by using the high styrene content of the GMA-acrylic hardener, a stable matt finish can be produced. The powder coating formulation for a matt finish system with good flow and mechanical properties is given in Tables 3 and 4. By blending two GMA-acrylic hardeners which have different styrene contents, it is easy to obtain full matt to full gloss films.[2]

Figure 1B



Bifunctional (COOH and OH) polyester/
GMA-acrylic hardener
<Multi-cure acrylic/polyester system>

Figure 1C



Bifunctional (COOH and OH) polyester/
Bifunctional (glycidyl and OH) acrylic hardener/
blocked polyisocyanate
<Multi-crosslink acrylic/polyester system>

The third system is shown in Figure 1C. It is also based on a bi-functional polyester having both OH and COOH groups. The GMA-acrylic hardener has both oxirane and hydroxyl groups, as before. The oxirane group reacts with the COOH group of polyesters but now the hydroxyl group in the acrylic hardener also reacts with the blocked isocyanate. This system has excellent mechanical properties and stain resistance suitable for blank coatings.[3]

TPA/IPA ratio in the polyester

Recently, there has been a strong demand for polyester powder coatings which have better exterior durability. There have been many attempts to meet this need.[4–10]

However, in spite of these efforts, there are no powder coatings which have both excellent durability and good mechanical properties. Normally a TPA (terephthalic acid) is used mainly in polyester powder coatings as the dibasic acid, due to the high Tg of its polyester and reasonable price. Although a high TPA content polyester resin shows good mechanical properties, the exterior durability is not good enough to meet the needs of the market.

On the other hand, it is well known that a polyester based on isophthalic acid (IPA) shows excellent exterior durability, while a high IPA content affects the mechanical properties. In a conventional acrylic/polyester system (Figure 1B), the relationship between the TPA/IPA ratio of

Table 3.

Matt Finish Formulation

Material	Notes	Amount
Polyester A-239 X		64.5
Acrylic hardener A-249-A		24
Blocked Isocyanate	(1)	12
Dicarboxylic acid	(2)	1.5
Catalyst	(3)	0.2
Catalyst	(4)	0.2
Flow additives	(5)	0.5
Benzoin		0.5
Titanium dioxide	(6)	43

Notes:
(1) B-1530 (15% NCO), Huls America, Inc
(2) Dodecanedioic acid, Du Pont Nylon, Inc
(3) C17 Zimadazole catalyst, Air Products and Chemicals Inc
(4) DBTDL
(5) Modaflow 2000, Solutia, Inc
(6) R-960, Du Pont Mineral Pigments Inc

Table 4: Matt finish film properties

	Notes	
Baking schedule (min/°C)		10/200
Film thickness (mils)		2.5-3.0
Gloss 60°/20°		10/2
'b' Value		0.7
Flow rating (PCI)	(1)	7-8
Pencil hardness		H
Gardner impact (F/R)		160/160
Mar resistance		Good
Crosshatch adhesion		100%
Solvent cure (PCI #8 B)	(2)	Full cure
Inclined Plate flow (PCI #7)	(3)	38min
Gel time (PCI #6)	(4)	30-40sec

Notes:
(1) PCI Powder Smoothness Standards, 1-10 rating, 10 = best
(2) 10/90 blend of MEK/xylene, rub test
(3) 180°C 65°angle
(4) 200°C hot-plate method

Figure 2. TPA/IPA ratio against weather durability and Erichsen value
(○) Exterior durability, (●) Erichsen value.
Exterior durability is shown as the time during which gloss retention fell below 60%.

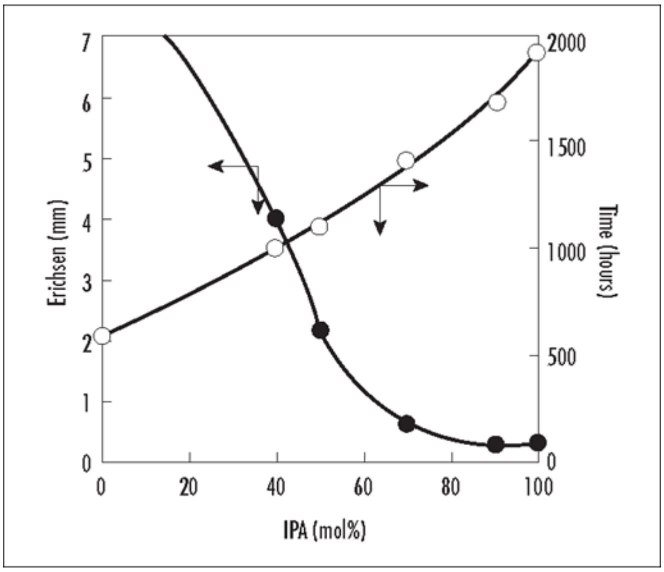
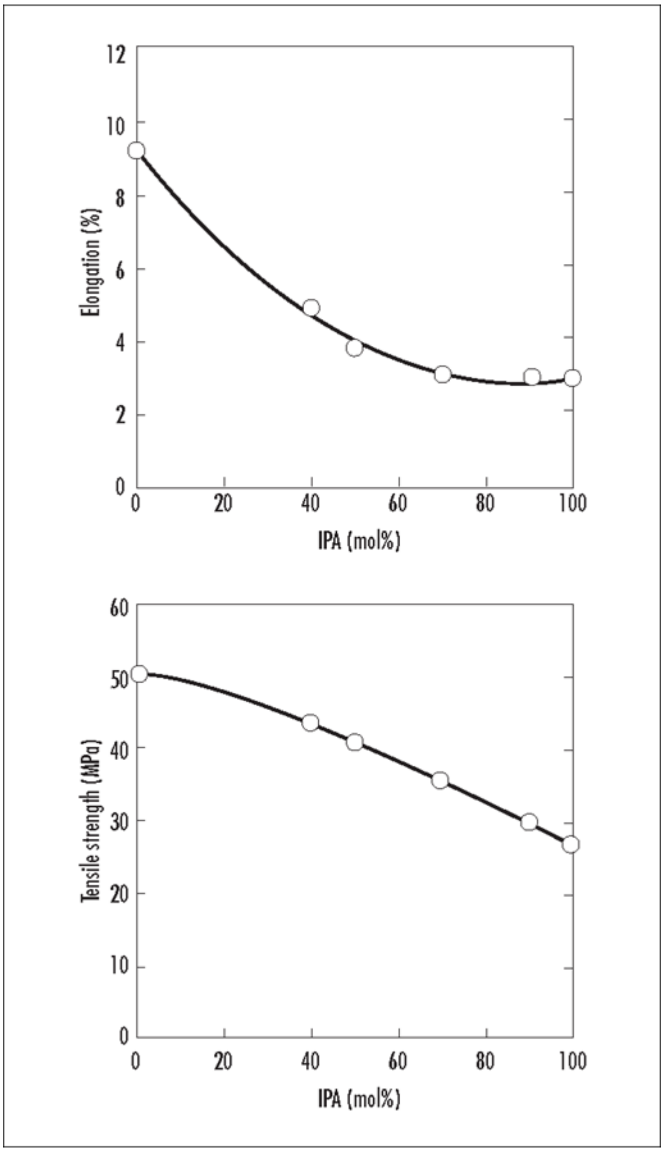


Figure 3. The effect of the TPA/IPA ratio of the polyester resin on film elongation and tensile strength.



the polyester resin and durability and flexibility is shown in Figure 2. By increasing the IPA content of the polyester resin, the durability can be improved. However, the mechanical properties become worse. Figure 3 shows the relationship of the TPA/IPA ratio in polyester resin and film elongation and tensile strength. It is clear that the high IPA content polyester resin is hard and brittle.[1]

Bi-functional acrylic hardener

In this study, some bi-functional (carboxyl and hydroxyl) polyesters having different TPA/IPA ratios were prepared. These polyesters were cured with some bi-functional (glycidyl and hydroxyl) acrylic hardeners and blocked isocyanate similar to the third acrylic/polyester system (Figure 1C). In these polyesters the acid value and the hydroxyl value were fixed at 15 and 22, respectively. The typical properties of polyester and acrylic hardeners are shown in Table 5. The test formulations of powder coatings are shown in Table 6. In these powder formulations, OH (polyesterOH+acrylicOH): NCO and COOH: glycidyl ratios are 1:1 stoichiometrically. Pigment by weight concentration is 30%. Raw materials were dry blended using a Henschel mixer and extruded through a Buss-Kneader PR-46 at 90°C. After extrusion, samples of the powder were pulverized and classified by a 200-mesh screen. They were applied to a zinc phosphatised 0.8mm thick steel panel and cured at 180°C for 20 minutes. Exterior durability was evaluated by gloss retention after Sunshine Weather Meter* exposure (*Made by Suga Testing Instruments Co Japan). The mechanical properties of the film were determined by Erichsen value and impact resistance. (Du-Pont type, 500g, and 1/2 inch impact rod) Figure 5 shows the relationship between the functionality in the acrylic hardener and the mechanical properties of the film. This bi-functional acrylic hardener combined with an IPA type polyester showed a better balance of durability and mechanical properties than a conventional acrylic/polyester system as shown in Figure 5.

Table 5: Properties of typical polyesters and hardeners.

	Polyester	Blocked isocyanate	GMA-acrylic hardener
Hydroxyl value (mg KOH/g)	22	–	50
Acid value (mg KOH/g)	15	–	–
NCO content (Total %)	–	15	–
Epoxy equivalent weight	–	–	380
Melting point (°C)	–	88	–
Softening point (°C, B&R)	115	–	98
Molecular weight (Mn)	3500	–	2000

Table 6: Test formulation of powder coatings.

Substance	Note	Amount
Polyester	(1)	81
GMA-acrylic hardener	(2)	8
Blocked isocyanate	(3)	11
Catalyst	(4)	0.2
Flow additive		1
Benzoin		0.5
Titanium dioxide		43

(1) AV = 15 (mg KOH/g), OHV = 22 (mg KOH/g).
(2) Epoxy equivalent weight = 380, OHV = 50 (mg KOH/g).
(3) Isocyanate content = 15 (total %).
(4) Tin compounds.

Figure 4. The effect of the OHV of the acrylic hardener on mechanical properties of the film.
The epoxy equivalent weight of the acrylic hardener is fixed at 380.

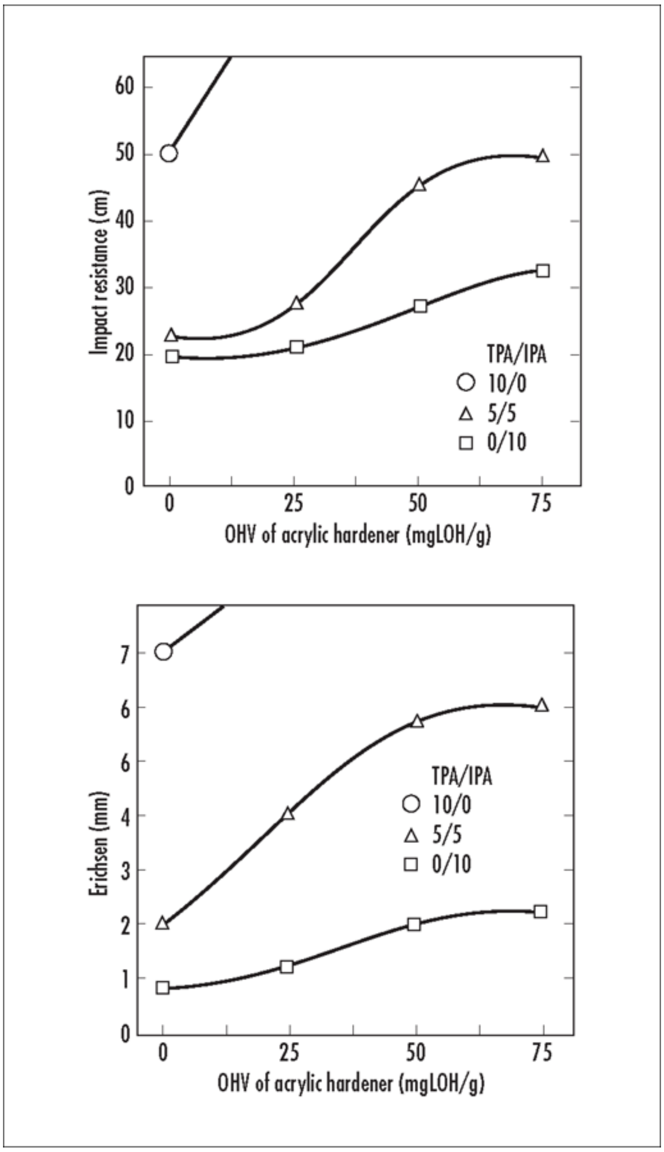
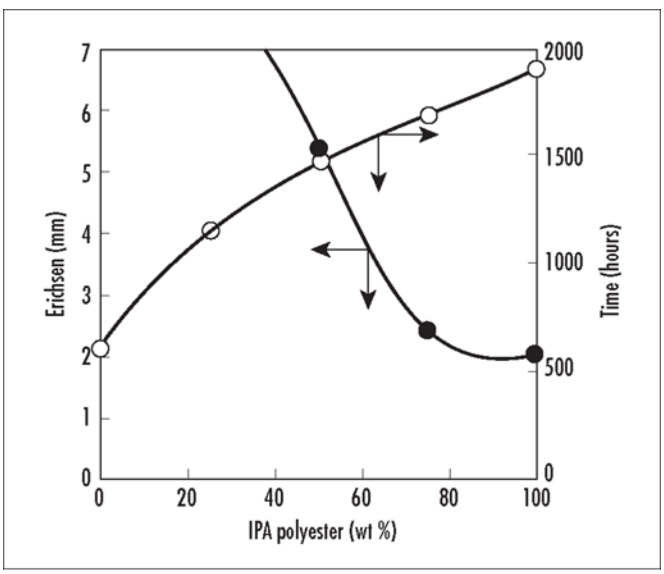


Figure 5. TPA/IPA ratio against weather durability and Erichsen value
(○) Weather durability, (●) Erichsen value.
Weather durability is shown as the time at which gloss retention fell below 60%.



Conclusions

Powder coatings which have both excellent exterior durability and good mechanical properties are given by the acrylic/polyester curing system. The advanced acrylic/polyester system was composed of a bi-functional polyester having a high IPA content cured with a blocked isocyanate and a bi-functional acrylic hardener. This hybrid system is capable of meeting a wide range of application demands for high durability coatings.

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