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Imidazole Based Curing Agents for Low Temperature Powder Coatings

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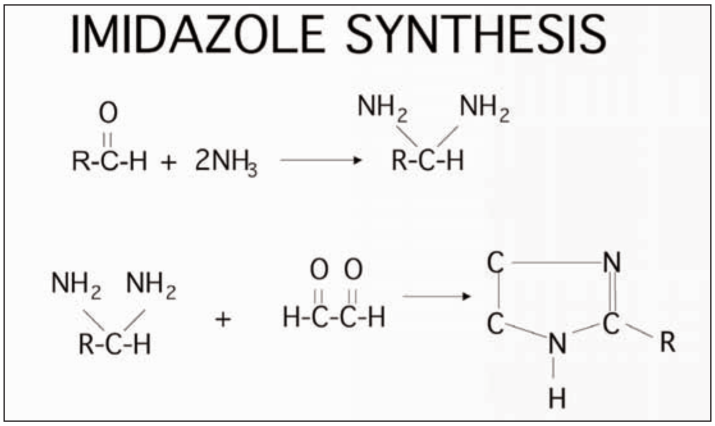
Abstract

One of the current trends and desires is powder coatings with lower and lower curing temperatures for heat sensitive substrates. A class of curing agents and catalysts that can meet the needs for these lower temperature curing powder coatings are the substituted imidazoles and their adducts. Substituted imidazoles have long been used as curing agents for epoxy resins and as catalysts for the reaction of different functional groups such as acid, phenolic and amidic with epoxy resins. The specific chemical and physical properties of imidazoles can be changed by varying the substituent on the imidazole ring and/or the material used to adduct the imidazole. The properties of a number of imidazoles and their adducts including the properties of formulated powder coatings will be presented and compared.

As the powder coating market continues to mature and capture an increasing amount of the high bake metal coatings market, powder coatings suppliers have begun to look for new opportunities. High on the current list of new opportunities are those that require a coating that can be cured at lower-than-normal cure temperatures. Examples of such heat sensitive substrates are wood, certain plastics and pre-assembled metal components like shock absorbers.

Figure 1



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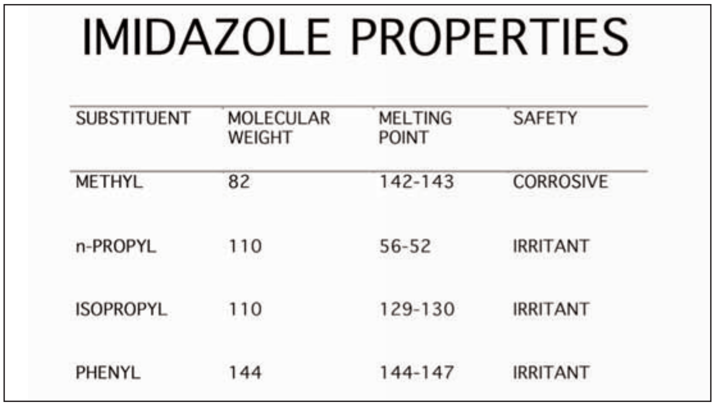
There are two predominant approaches to meeting the requirements for low temperature curing. UV curing has been the subject of extensive research and development for this market and has positioned itself as a more glamorous, high-tech solution. The other approach involves the modification of current thermoset technologies to lower cure temperatures through the use of catalysts and lower viscosity resins. Among the catalysts that are being evaluated for these low temperature applications are the substituted imidazoles. Imidazoles have long been used as catalysts and curing agents for liquid and solid epoxy resins and there are a number of reasons for their popular use.

Imidazoles as a class have competitive economics compared to other type of curing agents. They are produced from aldehydes, ammonia and glyoxyl, with a relatively simply manufacturing process (Figure 1). A large number of commercially available aldehydes make it possible to produce a wide number of imidazoles for use as curing agents. Which specific aldehyde is used for the synthesis determines the substituent in the 2 position on the imidazole ring. If acetaldehyde is used in the preparation, then the side group is methyl; if isobutyraldehyde is used then the side group will be isopropyl. The side group on the imidazole ring has a major influence on a number of properties of the imidazole and its use as a curing agent. The differences effected by the change of the side group are the primary subject of this paper.

The curing mechanism between epoxy resins and imidazoles is very complex, since the imidazole can react directly with the epoxy group and also catalyze the homopolymerization of the epoxy resin. Therefore, the determination of the amount of imidazole to use in a formulation is generally determined empirically rather than on stoichiometric calculations. This complex reaction profile can be an advantage because it lessens the need to have a precise ratio of curing agent to base resin. On the other hand, large changes in the ratio can have a major influence on coating properties such as curing speed.

Table 1



IMIDAZOLE PROPERTIES

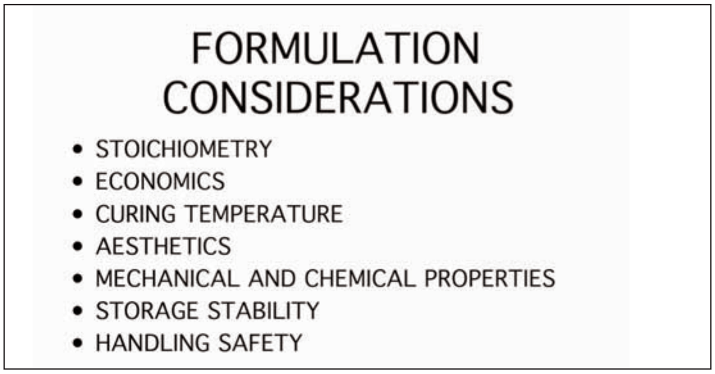
SUBSTITUENT	MOLECULAR WEIGHT	MELTING POINT	SAFETY
METHYL	82	142-143	CORROSIVE
n-PROPYL	110	56-52	IRRITANT
ISOPROPYL	110	129-130	IRRITANT
PHENYL	144	144-147	IRRITANT

For the purpose of this study, four different substituted imidazoles were investigated that are listed in Table 1.

The four imidazoles selected for this study have a very useful range of properties. Although, the reaction between imidazole and epoxy does not follow strict stoichiometic rules, it is evident that the amount of imidazole necessary to achieve a certain degree of cure or crosslink density will be proportional to its molecular weight. Thus, the range in molecular weights of the four imidazoles is from 82 to 144. Additionally, two materials were included that have the same molecular weight, but different side groups and much different physical properties.

As with molecular weight, there is also an interesting range of melting points. The methyl and phenyl imidazoles have very similar melting points, but substanial molecular weight differences. The two propyl imidazoles have equal equivalent weight, but widely different melting points. The melting point of the imidazoles has a big influence on the compounding properties, cure kinetics and product package stability. Also to be noted is a significant difference in the toxicological properties between 2-methyl imidazole and the others. The corrosive properties of 2-methyl imidazole requires additional personal protective equipment during the manufacture of powder coatings

Table 2



FORMULATION CONSIDERATIONS

- STOICHIOMETRY
- ECONOMICS
- CURING TEMPERATURE
- AESTHETICS
- MECHANICAL AND CHEMICAL PROPERTIES
- STORAGE STABILITY
- HANDLING SAFETY

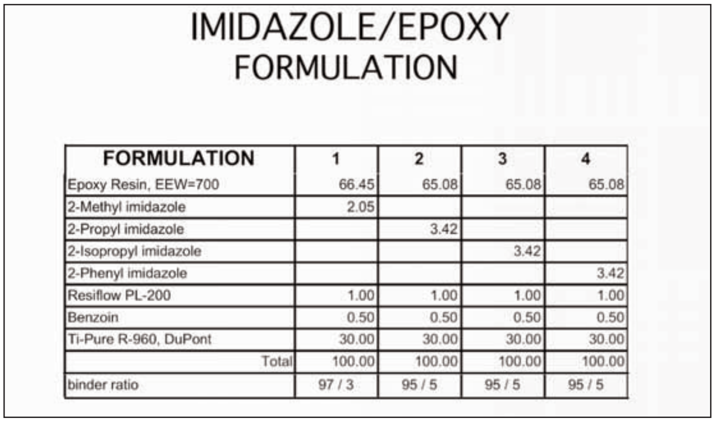
When formulating low temperature cure powder coatings with imidazoles, the formulator must take into consideration a

number of factors; the more important of which are listed in Table 2. The relative importance of these properties will help to determine which imidazole and concentration will provide the desired properties for the targeted application.

As mentioned earlier, the epoxy imidazole reaction does not follow strict stoichiometric combining ratios. For this reason, there is a range of concentrations of imidazole that can be used to produce coatings with acceptable performance properties. In general, increasing the amount of imidazole will decrease the cure time and temperature necessary to achieve full cure. Economics are related to the individual cost of the different curing agents and the amount necessary to achieve the desired cure profile. The oven capability, the temperature sensitivity of the substrate and the cure capability of the curing agent will dictate the cure temperature. Aesthetics considerations, especially as related to imidazole curing agents, include flow and leveling, orange peel, and yellowing. Almost every coating application has certain requirements for mechanical (hardness, flexibility, mar resistance) and chemical resistance (solvent, stain and corrosion resistance) properties. Storage stability issues involve both the imidazole curing agent and the final powder coating. The melting point of the curing agent should be high enough to avoid sintering in the package, a melting point above 1,000°C will usually assure package stability. The other concern is the chemical package stability of the powder coating; very fast, low temperature curing powder coatings have shorter shelf lives than those with higher cure temperatures. With these systems it is very important to physically measure the package stability at different storage conditions and determine their practical shelf life. The toxicological properties of the different imidazoles will not be as much of a consideration in the compounded powder coating as with the imidazole raw material itself; the differences among the imidazoles will be most important in handling of the raw material in the powder coating manufacturing plant.

The first comparison of the different imidazoles was in powder coatings in which the imidazole is the sole curing agent. In this type of formulation, the imidazole plays the dual role of crosslinker and catalyst for epoxy homopolymerization. The formulations

Table 3



IMIDAZOLE/EPOXY FORMULATION

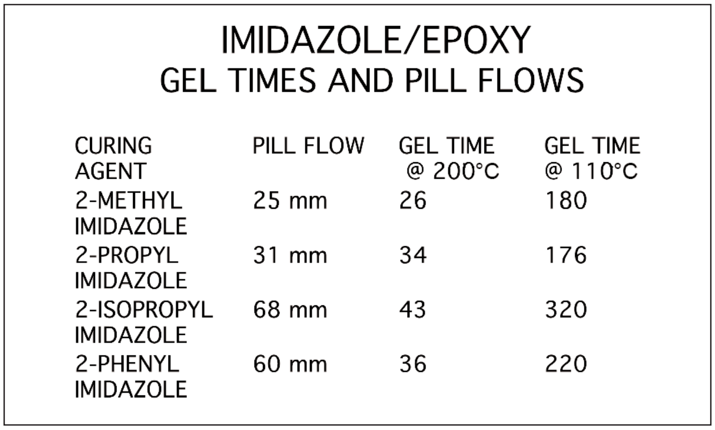
FORMULATION	1	2	3	4
Epoxy Resin, EEW=700	66.45	65.08	65.08	65.08
2-Methyl imidazole	2.05			
2-Propyl imidazole		3.42		
2-Isopropyl imidazole			3.42	
2-Phenyl imidazole				3.42
Resiflow PL-200	1.00	1.00	1.00	1.00
Benzoin	0.50	0.50	0.50	0.50
Ti-Pure R-960, DuPont	30.00	30.00	30.00	30.00
Total	100.00	100.00	100.00	100.00
binder ratio	97 / 3	95 / 5	95 / 5	95 / 5

are given in Table 3. In this series of formulations, the ratio of the imidazole to epoxy resin was kept constant on a weight-to-weight basis of 5.26 phr of epoxy resin for all but the 2-methyl imidazole. At the 5.26 phr of epoxy resin, the 2-methyl imidazole was too reactive to be processed, so the concentration was reduced to 3.1 phr.

The other ingredients of the formulations are standard i.e. a flow control agent, benzoin as a degassing agent and TiO_2 to provide color and hiding. The powder coatings were prepared in a normal manner. The ingredients were premixed in a food processor and extruded through a single screw extruder with Zone 1 and Zone 2 both set at 93°C. The extruded flake was ground in a Strand Mill and sieved through a 170-mesh screen prior to spraying.

The pill flows and gel times at two different temperatures are listed in Table 4. There are a number of interesting observations in this data. The methyl imidazole as expected has the shortest pill flow and gel time at 2,000°C. However, note that at 1,100°C, the gel time is actually longer that that of the propyl imidazole. This could be the result of a much higher melting point. It is interesting that, although the propyl imidazole and the isopropyl imidazole have the same molecular weight and very similar molecular structures there is a significant difference in their gel times and pill flows. The orange peel and yellowing results are listed in Table 5 below. The four imidazoles fall into two groups: the methyl and propyl imidazoles have extreme yellowing and poor flow and leveling. The isopropyl and phenyl imidazoles on the other hand have only slight yellowing and rather good flow and leveling. Of course, the latter two also have the longer gel times and pill flows. Note also that the 2-propyl imidazole has a high degree of yellowing even at the lower bake temperatures.

Table 4

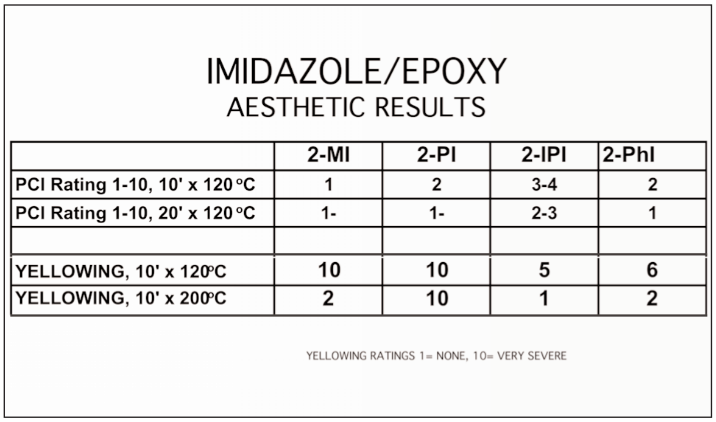


IMIDAZOLE/EPOXY

GEL TIMES AND PILL FLOWS

CURING AGENT	PILL FLOW	GEL TIME @ 200°C	GEL TIME @ 110°C
2-METHYL IMIDAZOLE	25 mm	26	180
2-PROPYL IMIDAZOLE	31 mm	34	176
2-ISOPROPYL IMIDAZOLE	68 mm	43	320
2-PHENYL IMIDAZOLE	60 mm	36	220

Table 5



IMIDAZOLE/EPOXY

AESTHETIC RESULTS

	2-MI	2-PI	2-IPI	2-PhI
PCI Rating 1-10, 10' x 120 °C	1	2	3-4	2
PCI Rating 1-10, 20' x 120 °C	1-	1-	2-3	1
YELLOWING, 10' x 120°C	10	10	5	6
YELLOWING, 10' x 200°C	2	10	1	2

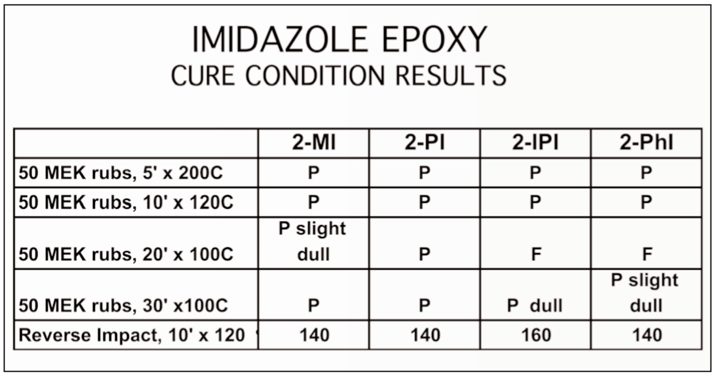
YELLOWING RATINGS 1= NONE, 10= VERY SEVERE

In these formulations the 2-isopropyl imidazole has the best color and smoothness of the four curing agents.

The cured film properties of the various formulations are shown the next table. All of the formulations were well cured at 2,000°C for 5 min. Based on MEK resistance and reverse impact they are also well cured at 1,200°C for 10 min. One should also note that the 2-isopropyl imidazole has slightly better impact resistance at this latter cure schedule.

Reducing the cure temperature reduced to 1,000°C, reduces the MEK resistance of the films of the powder coatings prepared with 2-isopropyl and 2-phenyl imidazoles.

Table 6



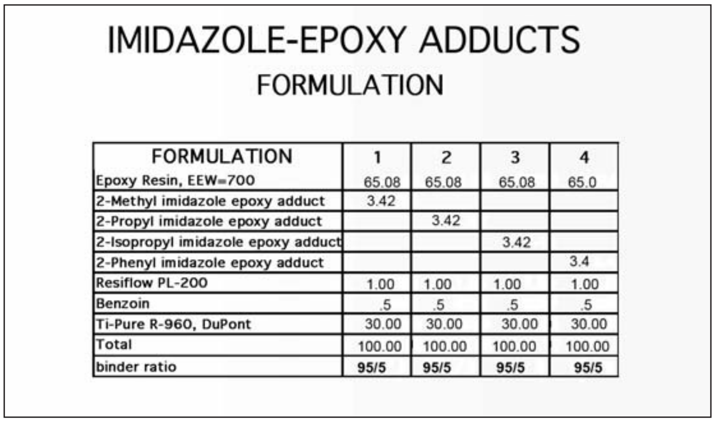
IMIDAZOLE EPOXY

CURE CONDITION RESULTS

	2-MI	2-PI	2-IPI	2-PhI
50 MEK rubs, 5' x 200C	P	P	P	P
50 MEK rubs, 10' x 120C	P	P	P	P
50 MEK rubs, 20' x 100C	P slight dull	P	F	F
50 MEK rubs, 30' x100C	P	P	P dull	P slight dull
Reverse Impact, 10' x 120	140	140	160	140

The next formulations studied were those in which the curing agents for the epoxy resin are the adducts of the imidazoles with bisphenol A diglycidyl ether. These adducts are commonly used as curing agents because of their better handling and formulation properties. The particular imidazole epoxy curing agents used in this study were prepared by reacting two moles of imidazole with one mole of bisphenol A diglycidyl ether. By necessity these adducts will contain some free imidazole and some extended molecules. Techniques

Table 7

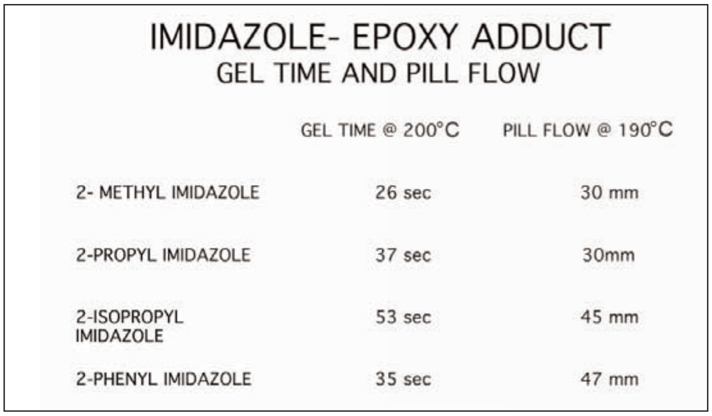


IMIDAZOLE-EPOXY ADDUCTS

FORMULATION

FORMULATION	1	2	3	4
Epoxy Resin, EEW=700	65.08	65.08	65.08	65.0
2-Methyl imidazole epoxy adduct	3.42			
2-Propyl imidazole epoxy adduct		3.42		
2-Isopropyl imidazole epoxy adduct			3.42	
2-Phenyl imidazole epoxy adduct				3.4
Resiflow PL-200	1.00	1.00	1.00	1.00
Benzoin	.5	.5	.5	.5
Ti-Pure R-960, DuPont	30.00	30.00	30.00	30.00
Total	100.00	100.00	100.00	100.00
binder ratio	95/5	95/5	95/5	95/5

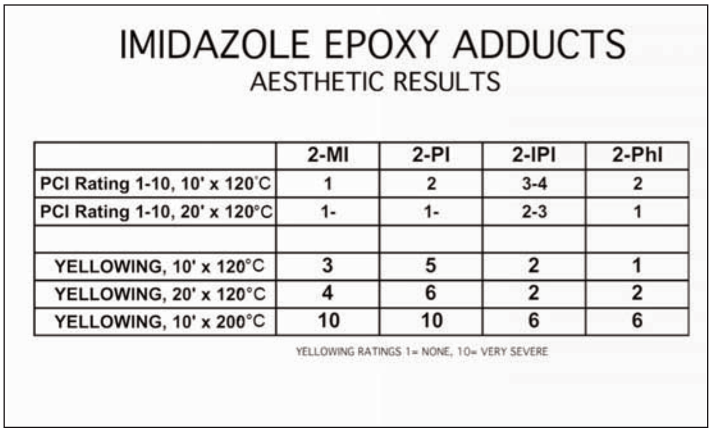
Table 8



IMIDAZOLE- EPOXY ADDUCT
GEL TIME AND PILL FLOW

	GEL TIME @ 200°C	PILL FLOW @ 190°C
2- METHYL IMIDAZOLE	26 sec	30 mm
2-PROPYL IMIDAZOLE	37 sec	30mm
2-ISOPROPYL IMIDAZOLE	53 sec	45 mm
2-PHENYL IMIDAZOLE	35 sec	47 mm

Table 9

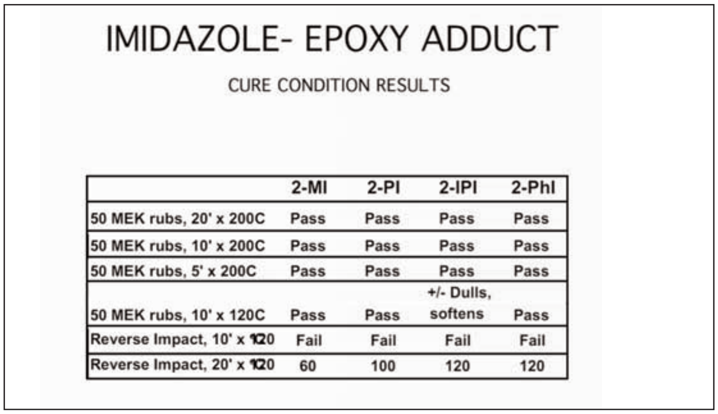


IMIDAZOLE EPOXY ADDUCTS
AESTHETIC RESULTS

	2-MI	2-PI	2-IPI	2-PhI
PCI Rating 1-10, 10' x 120°C	1	2	3-4	2
PCI Rating 1-10, 20' x 120°C	1-	1-	2-3	1
YELLOWING, 10' x 120°C	3	5	2	1
YELLOWING, 20' x 120°C	4	6	2	2
YELLOWING, 10' x 200°C	10	10	6	6

YELLOWING RATINGS 1= NONE, 10= VERY SEVERE

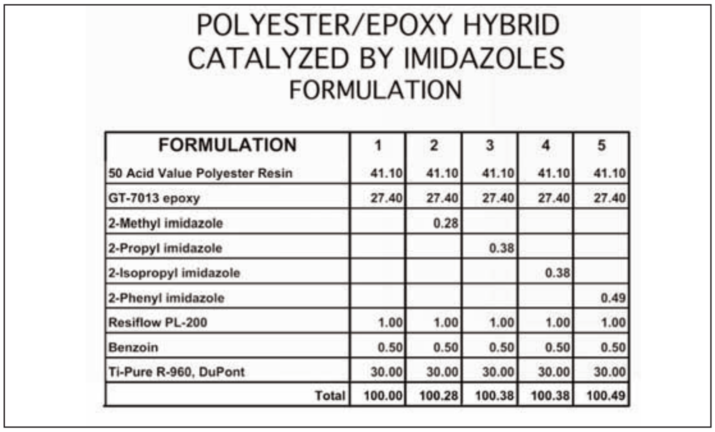
Table 10



IMIDAZOLE- EPOXY ADDUCT
CURE CONDITION RESULTS

	2-MI	2-PI	2-IPI	2-PhI
50 MEK rubs, 20' x 200C	Pass	Pass	Pass	Pass
50 MEK rubs, 10' x 200C	Pass	Pass	Pass	Pass
50 MEK rubs, 5' x 200C	Pass	Pass	Pass	Pass
50 MEK rubs, 10' x 120C	Pass	Pass	+/- Dulls, softens	Pass
Reverse Impact, 10' x 120	Fail	Fail	Fail	Fail
Reverse Impact, 20' x 120	60	100	120	120

Table 11



POLYESTER/EPOXY HYBRID
CATALYZED BY IMIDAZOLES
FORMULATION

FORMULATION	1	2	3	4	5
50 Acid Value Polyester Resin	41.10	41.10	41.10	41.10	41.10
GT-7013 epoxy	27.40	27.40	27.40	27.40	27.40
2-Methyl imidazole		0.28			
2-Propyl imidazole			0.38		
2-Isopropyl imidazole				0.38	
2-Phenyl imidazole					0.49
Resiflow PL-200	1.00	1.00	1.00	1.00	1.00
Benzoin	0.50	0.50	0.50	0.50	0.50
Ti-Pure R-960, DuPont	30.00	30.00	30.00	30.00	30.00
Total	100.00	100.28	100.38	100.38	100.49

were used to minimize the amount of both of these.

The different imidazole epoxy adducts were formulated at the same weight percent concentration. The formulations are show in Table 7. The adducts were formulated at 5.25 phr of imidazole to epoxy resin. The flow control agent, benzoin and pigment are the same as in the previous formulations.

The Gel Time and Pill Flow for these formulations are show in Table 8 below. As with the free imidazoles, the 2-methyl imidazole adduct has the shortest gel time and pill flow. The 2-isopropyl and phenyl adducts have the longest gel times and pill flows. The gel times for these formulations are not much different than those for the pure imidazoles, which would indicate they could be cured at the same conditions.

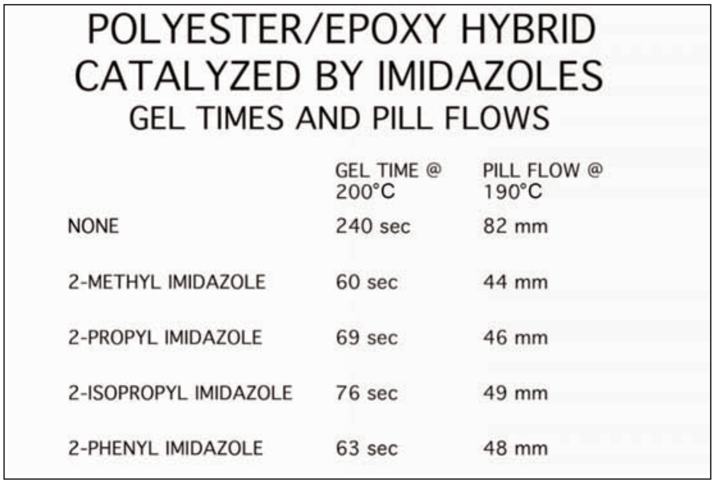
The color and smoothness properties achieved with the imidazole epoxy adducts are also very similar to those of the pure imidazoles as shown in the next table. The 2-isopropyl imidazole adduct is clearly the best in terms of the aesthetic properties of the four adducts. The poor PCI orange peel rating at the 1,200°C bake is due more to the poor flow of the formulation at this low temperature than to cure kinetics. The high color ratings at the 2,000°C bake emphasize that these curing agents should not be used for high temperature applications if color is important.

The cure properties of the powder coatings formulated with the epoxy imidazole adducts are presented Table 10. As the table shows, these formulations also have low temperature cure capability. The MEK resistance and the reverse impact both indicate a reasonable degree of cure for all of the adducts at 1,200°C. The slightly higher impact properties combined with the better non-yellowing properties of the 2-isopropyl and 2-phenyl imidazole adducts make them the clear choice for powder coatings based on these adducts as the curing agent.

Besides being useful as a curing agent, imidazoles are also quite useful as catalysts for the reaction of a number of functional groups with epoxy resins. Since the reaction of carboxyl function polyesters with an epoxy group, ie polyester/epoxy hybrids and polyester/TGIC, is the bases of well over fifty percent of powder coatings used, the catalytic effect of the different imidazoles on these systems was of interest.

The formulations used to determine the effect of the imidazoles on a polyester/hybrid powder coating are listed in the table below. Since this series of formulations involve the use of imidazoles as catalysts rather than as a curing agent, a formulation that contains no imidazole is included as a control. As with the previous formulations, these formulas are quite simple, containing only a flow control agent, benzoin and TiO_2 in addition to the binder resins. Note also that the amount of the individual imidazole that is incorporated into the coating is proportional to its respective molecular weight rather than being added at equal weights. These formula-

Table 12

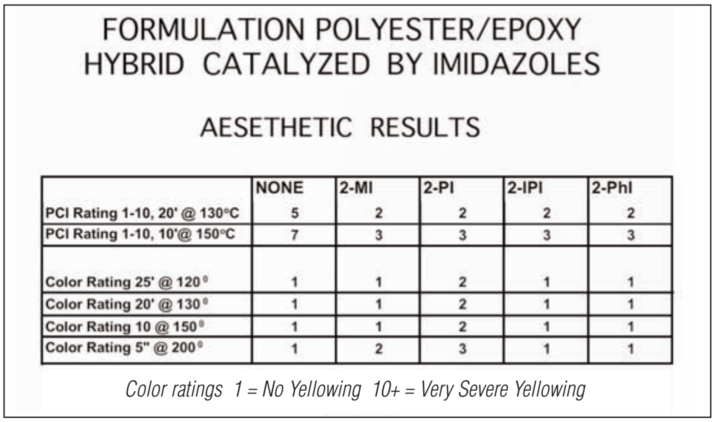


POLYESTER/EPOXY HYBRID CATALYZED BY IMIDAZOLES

GEL TIMES AND PILL FLOWS

	GEL TIME @ 200°C	PILL FLOW @ 190°C
NONE	240 sec	82 mm
2-METHYL IMIDAZOLE	60 sec	44 mm
2-PROPYL IMIDAZOLE	69 sec	46 mm
2-ISOPROPYL IMIDAZOLE	76 sec	49 mm
2-PHENYL IMIDAZOLE	63 sec	48 mm

Table 13



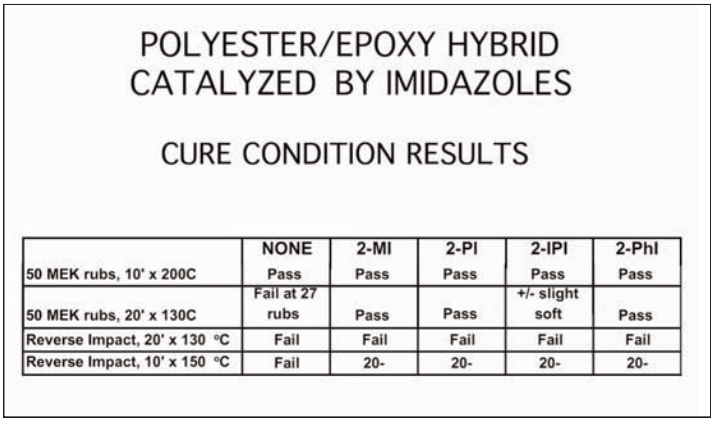
FORMULATION POLYESTER/EPOXY HYBRID CATALYZED BY IMIDAZOLES

AESETHETIC RESULTS

	NONE	2-MI	2-PI	2-IPI	2-PhI
PCI Rating 1-10, 20' @ 130°C	5	2	2	2	2
PCI Rating 1-10, 10'@ 150°C	7	3	3	3	3
Color Rating 25' @ 120°	1	1	2	1	1
Color Rating 20' @ 130°	1	1	2	1	1
Color Rating 10 @ 150°	1	1	2	1	1
Color Rating 5" @ 200°	1	2	3	1	1

Color ratings 1 = No Yellowing 10+ = Very Severe Yellowing

Table 14



POLYESTER/EPOXY HYBRID CATALYZED BY IMIDAZOLES

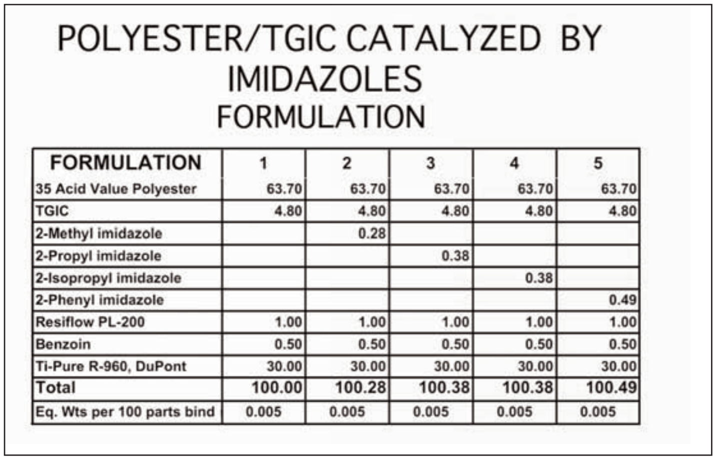
CURE CONDITION RESULTS

	NONE	2-MI	2-PI	2-IPI	2-PhI
50 MEK rubs, 10' x 200C	Pass	Pass	Pass	Pass	Pass
50 MEK rubs, 20' x 130C	Fail at 27 rubs	Pass	Pass	+/- slight soft	Pass
Reverse Impact, 20' x 130 °C	Fail	Fail	Fail	Fail	Fail
Reverse Impact, 10' x 150 °C	Fail	20-	20-	20-	20-

tions were extruded at 1,060°C in zone 1 and 1,130°C in zone 2.

As expected, the gel times and pill flows confirm that the imidazoles are indeed acting effectively as catalysts. The 2-methyl, 2-propyl and 2-phenyl have similar gel times so a decision as to which to use would be based on other factors rather that the amount of cure acceleration. In fact, the catalytic effect of the 2-isopropyl imidazole is similar enough to group it with the others in terms of catalytic activity.

Table 15



POLYESTER/TGIC CATALYZED BY IMIDAZOLES

FORMULATION

FORMULATION	1	2	3	4	5
35 Acid Value Polyester	63.70	63.70	63.70	63.70	63.70
TGIC	4.80	4.80	4.80	4.80	4.80
2-Methyl imidazole		0.28			
2-Propyl imidazole			0.38		
2-Isopropyl imidazole				0.38	
2-Phenyl imidazole					0.49
Resiflow PL-200	1.00	1.00	1.00	1.00	1.00
Benzoin	0.50	0.50	0.50	0.50	0.50
Ti-Pure R-960, DuPont	30.00	30.00	30.00	30.00	30.00
Total	100.00	100.28	100.38	100.38	100.49
Eq. Wts per 100 parts bind	0.005	0.005	0.005	0.005	0.005

Catalyzing the hybrid formulation in this series while decreasing the cure temperature also decreases the flow and leveling as is shown in Table 13. The results also show that similar to the decrease in gel times and pill flows, there is little differentiation among the different imidazoles with respect of flow and leveling. On the other hand, there is some differentiation with respect to the degree of yellowing. The 2-isopropyl and the 2-phenyl imidazoles have a clear advantage in yellowing resistance.

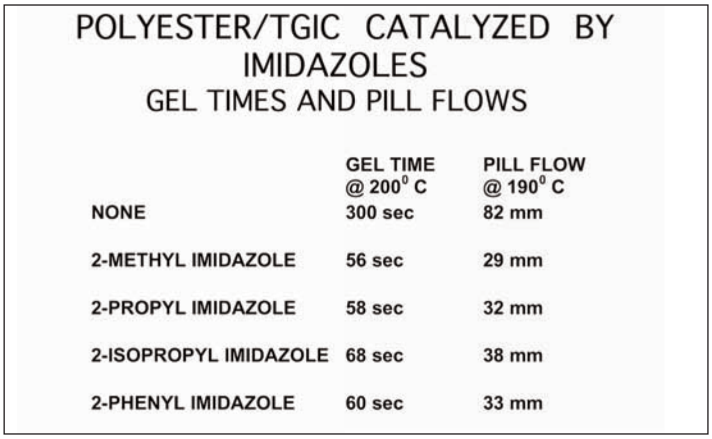
The cure data in the table below suggest that even with imidazole catalysis, cure temperatures in excess of 1,500°C are necessary for complete cure as determined by reverse impact. However, if the only requirement is for good solvent resistance, then a cure temperature as low as 1,300°C is possible.

Finally the catalytic effect on TGIC/polyester powder coatings was investigated. The formulations for this study are shown in Table 15. As with the polyester/epoxy hybrid study, the amount of imidazole catalyst in each formulation was determined by its molecular weight, 0.005 molecular weight phr of binder. The same additives and pigment as in the previous series were used.

Examination of the gel time and pill flow data reveals similar results as those with the polyester hybrid formulations; there is not much differentiation among the four different imidazoles in either the gel time or pill flow data, the 2-methyl imidazole having slightly shorter values and the 2-isopropyl imidazole slightly higher values.

The orange peel and yellowing below are also very consistent with that obtained in the polyester hybrid system. However, it is interesting to note that the yellowing at 2,000°C is more pronounced in these TGIC powder coatings than in the polyester/epoxy coating. This result is a bit surprising, as one would speculate that the formulations containing epoxy resin would be more prone to yellowing than those based on TGIC. As with the hybrids, catalyzing these powder coatings also causes sever orange peel. Comparison of the PCI ratings for the uncatalyzed formula cured at 1,300°C and 1,500°C reveals that the lower temperature alone is partially responsible for the reduced flow and leveling.

Table 16



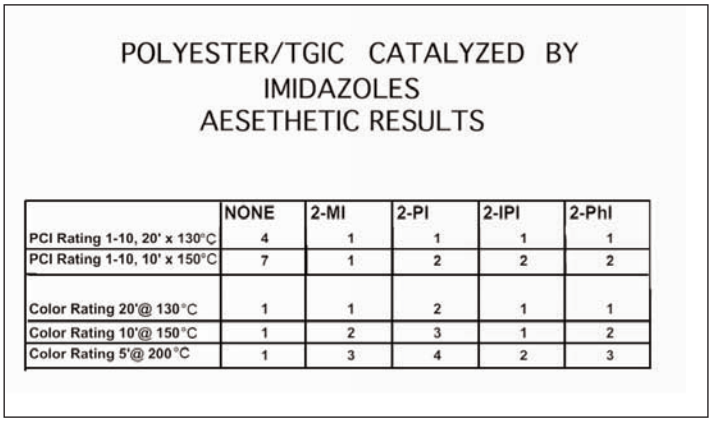
POLYESTER/TGIC CATALYZED BY IMIDAZOLES

GEL TIMES AND PILL FLOWS

	GEL TIME @ 200^0 C	PILL FLOW @ 190^0 C
NONE	300 sec	82 mm
2-METHYL IMIDAZOLE	56 sec	29 mm
2-PROPYL IMIDAZOLE	58 sec	32 mm
2-ISOPROPYL IMIDAZOLE	68 sec	38 mm
2-PHENYL IMIDAZOLE	60 sec	33 mm

The cured film properties especially the reverse impact properties indicate that with these catalysts full cure at temperatures as low as 1,500 are possible. TGIC powder coating are used mostly for outdoor applications that require high UV durability and appearance after years of exposure. For this reason on the 2-isopropyl or the 2 phenyl imidazole should be used as a catalyst for these applications. The other imidazoles are too yellow after cure to be acceptable.

Table 17



POLYESTER/TGIC CATALYZED BY IMIDAZOLES

AESETHETIC RESULTS

	NONE	2-MI	2-PI	2-IPI	2-PhI
PCI Rating 1-10, 20' x 130°C	4	1	1	1	1
PCI Rating 1-10, 10' x 150°C	7	1	2	2	2
Color Rating 20'@ 130°C	1	1	2	1	1
Color Rating 10'@ 150°C	1	2	3	1	2
Color Rating 5'@ 200°C	1	3	4	2	3

A number of conclusions can be drawn from this work. Most importantly is that the substituent on the imidazole ring has a major influence on both the physical and performance properties of the imidazole. When used as a curing agent, either as the pure imidazole or adducted with an epoxy resins the differences in performance of imidazoles with different substituents is very pronounced. When used as a catalyst for carboxy/epoxy curing reactions, the difference in catalytic activity is very similar for the four different imidazoles investigated. As a curing agent 2-methyl imidazole is the fastest reacting of the four imidazoles studied. However, this fast reactivity can have a negative influence on the flow and leveling as well as the yellowing tendencies of the powder coating. The 2-propyl imidazole was the worst performer in terms of oven yellowing and its activity was only moderate as compared to the 2-methyl imidazole. The 2-isopropyl, while the least active of the imidazoles, provides the best flow and leveling and the least oven yellowing. And, the 2-isopropyl imidazole or its adduct with epoxy resin can be used to formulate epoxy powder coating that will cure at temperatures as low as 1,200°C.

Dr. Green received his BA degree in from Southern Illinois University in 1962 and his Doctorate in Organic Chemistry from the University of Arizona in 1966. Following college he spent 16 years with Celanese in a number of technical and technical management positions related to the coatings and resin industries. After Celanese he joined Reichhold Chemicals Coatings Resin Division where he become Vice-President of Technology. Following Reichhold he joined Ferro where he served as Technical Director of their Powder Coatings Division. During the last nine years he has been the Technical Director of Estron Chemical, a major supplier of additives and other raw materials for the powder coating market.

This paper was originally presented at Powder Coating 2004, Formulators Technical Conference, September 2004, Charlotte Convention Center. It is reprinted with permission of PCI.

One Shot Low Gloss Weatherable Powder Coatings

KATHERINE RATLIFF and THOMAS FAECKE, Bayer Material Science LLC.

Abstract

Low gloss powder coatings have always been of interest to consumers because of a variety of reasons like toughness, durability and aesthetics. But the manufacture of weatherable low gloss coatings with tight gloss control has been a major challenge. There are different cure chemistries and methods to achieve the low gloss, the important ones being the blending of powder coatings of different reactivity or by using a combination of resins with different functionality. There are limitations to these approaches namely the 'difficulty to dial in the desired gloss' and consistency. So the concept of "one-shot low gloss system" is the ultimate formulator's dream.

Our research and development efforts were focussed to solve this issue, which resulted in a novel urethane crosslinker with dual functional groups. This crosslinker has numerous advantages over any other low-gloss powder technology available in the market and can be formulated to desired gloss levels with consistent gloss control. The details of the crosslinker development, formulation details, hurdles and lessons learnt, and coatings properties will be presented.

Introduction

One of the "greenest" coating technologies available on the market today comes in a rainbow of colors and finishes. Powder coating technology has been growing by leaps and bounds over the last decade.[1] The eco-friendly technology has low VOC emissions, is 100 percent solids, and has the ability to be recycled and resprayed.[2] The advantages of powder coating become clearer every year, in part to the costs of regulatory compliance continuing to increase for metal finishers.

Spanning the market from washing machines to high-end automobiles, powder coatings are formulated for high gloss, superior impact resistance, outdoor exposure stability, or specialty decorative finishes. Semi gloss and matte finishes are a growing trend. "Even with its maintenance drawbacks, a flat finish is still the most desired finish…A flat finish doesn't reflect glare and is easy on the eyes…."[3]

There are several ways to produce matte powder coating finishes. The oldest approach is the dry blend method, in which two formulations of the same color are produced separately using binders of extremely different functionalities. The coatings are then dry blended together in a ball mill. The process is not favored by the industry, because the process is more expensive as the two powder coatings must be produced separately and then combined. In addition to signs of demixing in overspray recycling, the method can achieve only a semi gloss appearance with values around 30 at a 60° reflectance angle. Both the manufacture and application of a matte powder coating are easier and less expensive if all the raw materials are mixed and extruded together. Therefore, a one shot approach based on two polymer systems of differing reactivity was developed. This difference in reactivity causes defects in film formation during curing, because of a phase separation in the powder paint. This results in a rough surface structure due to the extremely different reactivities of the resins. The method produces a matte finish but it shows different gloss levels depending on the viewing angle (flop). In addition, the repeatability of gloss levels can be rather cumbersome.[4]

There are epoxy and epoxy polyester matte powders in production, but due to poor weatherability, they are limited to indoor applications.

Weather stable coatings, which yield matte films, are an important field of application. Because of their outstanding weather stability, excellent flow, and surface properties, polyurethane powder coatings are among the systems used, for example, in the coating of wall cladding elements, garage doors, door and window profiles and car accessories.[5]

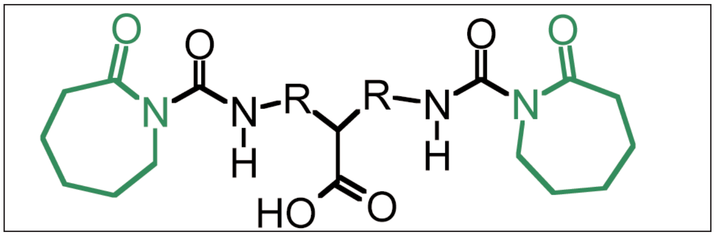
One Shot Low Gloss Bifunctional Crosslinker

In this paper we want to discuss a new approach to produce matte powder coatings. We propose to use a new bifunctional urethane crosslinker, that achieves a one shot, low gloss, weatherable powder coating. A sketch of the structure of this crosslinker is given in Figure 1.

Developed to produce matte finishes with a gloss of < 5 at a 60° reflectance angle, the two functionalities in the molecule – an isocyanate and a carboxyl group – permitting two curing reactions. The carboxyl group reacts with an epoxy or a hydroxyalkylamide to form, during the bake of the material, a high functional polyurethane crosslinker as sketched in Figure 2 using TGIC as an epoxide.

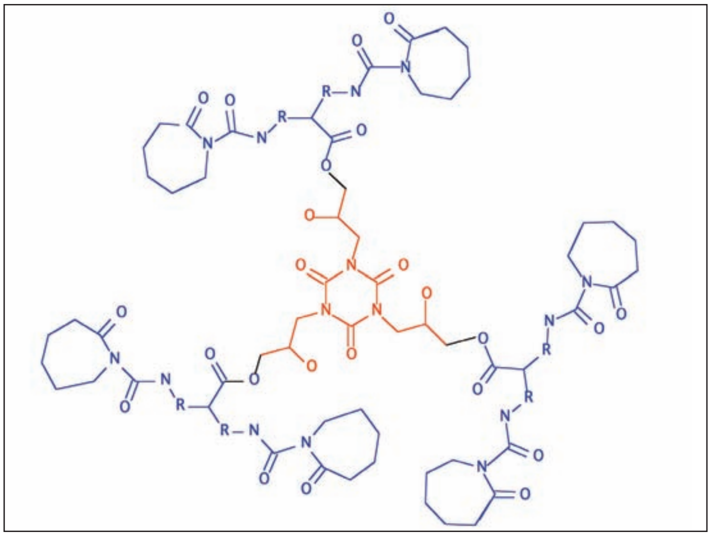
During further cure, the blocked isocyanate is activated by the

Figure 1



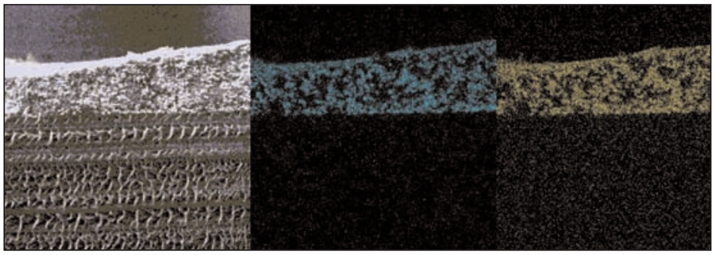
Generic structure of a bifunctional Polyurethane Crosslinker being useful in weatherable powder coatings

Figure 2



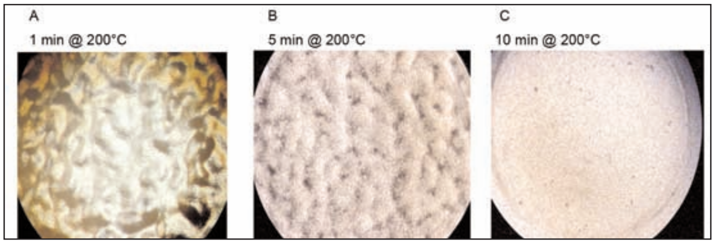
Intermediate formed when TGIC is used as part of the formulation. Extremely high crosslinkers functionalities can be achieved.

Figure 3



Scanning Electron Microscope picture (450x) of a microtomed matte powder coating baked for 10 min @ 200°C based on bifunctional crosslinker. A: SEM Picture at 450 magnification. The EDX mode is used for element mapping (B: Barium-mapping and C: Sulfur-mapping for Barium Sulfate). A uniform barytes distribution is visible.

Figure 4a-4c



Microscope pictures at 50 times magnification show the initial flow out of the paint. The orange peel disappears over the full bake cycle, while the microscopic roughness appears after 1-2 min.

deblocking reaction. The hydroxyl groups of polyester react with the isocyanate groups. Due to the high functionality, the gelling of the system happens at a time when only a small amount of urethanes are already formed. Further reaction occurs, but due to the inability of the system to flow, more crosslinking leads to an internal stress buildup causing a shrinking effect. This dual functionality crosslinker produces a dead matte finish of uniform roughness and good mechanics. The uniform roughness showing no flop effect is also a major benefit of this approach.

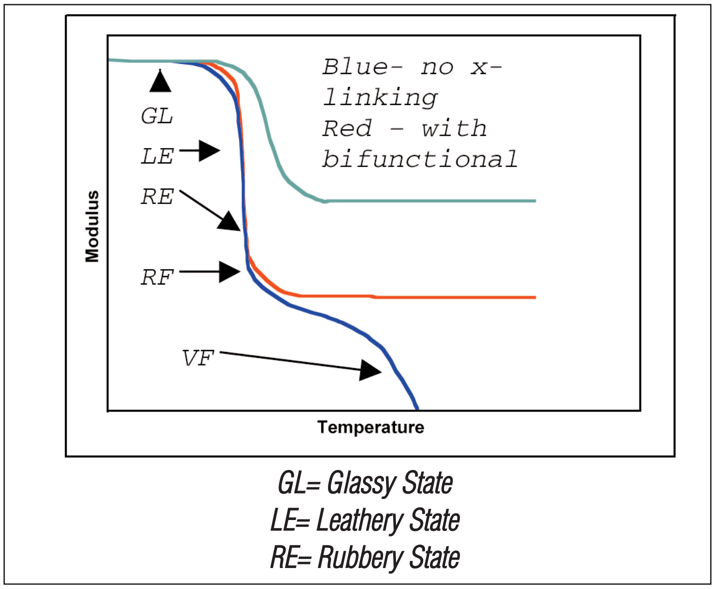
Scanning electron microscope pictures of a microtomed matte coating show a uniform distribution of the barytes filler (Barium Sulfate) in the film. This is in contrast to the common use of matting agents in liquid paints, where the matting agent flows to the surface of the paint. Although it is known that fillers can be used in powder coatings for matting purpose, real low gloss numbers are not possible to achieve.

When the surface structure of the coating is observed during stoving using a microscope, an orange peel mid gloss structure seen in Figure 4A develops in the first minute of stoving at 200°C as the resin just starts to flow out and begins leveling. In the beginning, the microroughness of the surface is slight and therefore the gloss of the coating is relatively high at a measurement of 38 at a 60° reflectance angle.

Later, (see Figure 4C) the rather smooth surface forms a microstructure that is responsible for the matte performance of the paint. So what is the reason for the formation of this microstructure? Our current model is based on a shrinking phenomenon, which can be explained best with a polymer phase diagram as given in Figure 5.

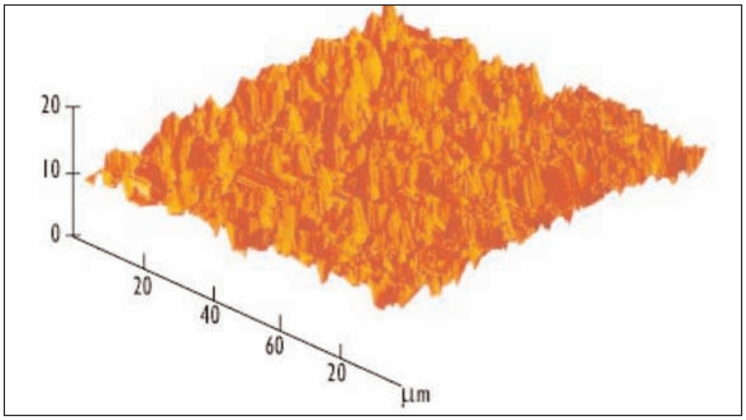
In the beginning of the stoving, the formulated powder coating paint behaves like an amorphous resin (shown in blue). Exceeding the glass transition temperature, the system goes in a rubbery state. A further increase in the temperature leads to a viscous flow,

Figure 5



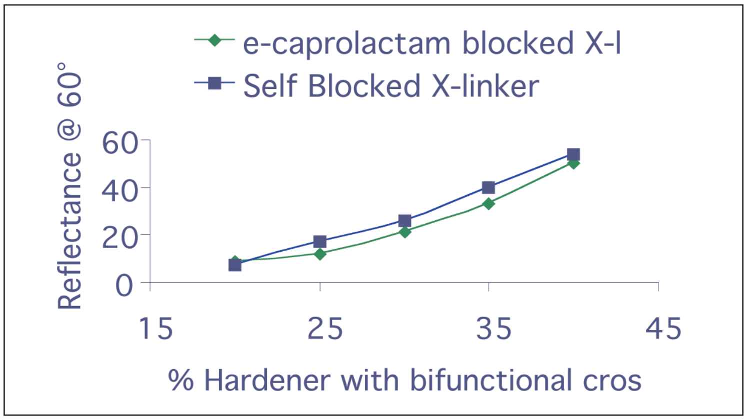
Polymer Phase Diagram: blue: non crosslinked polymer – After passing the glass transition temperature the material goes into the rubbery state. With increased temperature a viscous flow can be observed. Red: a slightly crosslinked polymer is not capable to flow anymore. Green: a highly crosslinked polymer lacks any flow.

Figure 6



SEM picture showing the Microstructure of a surface of a bifunctional crosslinker based paint. The alpine like morphology rationalizes the observation of a flop free matte appearance. [4]

Figure 7



Dialing in of the gloss level by the use of additional polyurethane crosslinkers

this is responsible for the rather smooth film formation. In the next step, the high functional crosslinker is formed, that leads then to a gelling of the system, without consuming all isocyanate groups and alcohol groups available. At the gelpoint, the system behaves like a slight crosslinked rubber – like the red curve in Figure 5. No flow is possible in a gel and additional crosslinks formed lead to an internal stress induced by the reduced free volume. The material starts to shrink without flow. Due to the filler/pigment particles in the system, the shrinking around these solids lead to the microstructure that becomes visible.

As seen in Figure 6, after stoving for 15 minutes, the surface structure of a dull matte powder coating containing bifunctional crosslinker resembles an alpine landscape when viewed at an appropriate resolution.4

Methods to Adjust the Gloss

The importance of having a true matte coating is only surpassed by having the ability to increase that coating to a specific number for different application preferences.

When using the bifunctional aliphatic isocyanate, research has shown the degree of matting is influenced very little by the process conditions during the production and application of the powder. There are three significant ways to dial up the desired gloss of the coating; the use of an additional crosslinker, modifying the pigment to binder ratio, and changing the particle size of the filler or filler type.

Combination with Another PU-Crosslinker. The preferred method for tweaking the gloss of a matte coating based on the bifunctional aliphatic isocyanate is to incorporate an additional crosslinker. Using a traditional blocked isocyanate crosslinker decreases the overall intermediate functionality and thereby delays the gel point. As a consequence, less internal stress is formed because less crosslinker contributes to a shrinkage. It is also beneficial to use this approach because overall flow improves here, too. Let's have a look at common curing conditions (15 min at 200°C), two isocyanate crosslinkers are combined with a 30 OH # polyester/bifunctional crosslinker/TGIC formulation as shown in Figure 7.

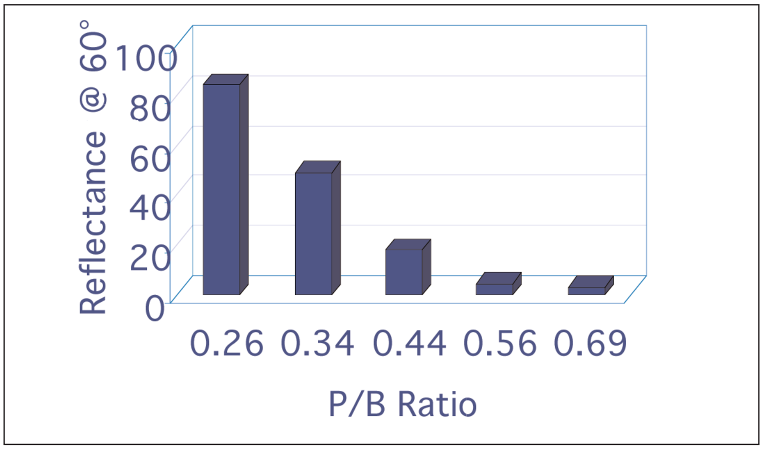
The gloss level can be changed easily by substituting the bifunctional crosslinker with a well-known blocked isocyanate. E-Caprolactam blocked isocyanates and self-blocked (uretdione) type crosslinkers can be used here. The higher the substitution levels, the higher the gloss.

A substitution of 30 percent by a traditional blocked isocyanate crosslinker can increase the gloss nearly linearly to 20-30 at a 60° angle of reflectance. Even higher mid gloss levels can be achieved. This allows the formulator to simply choose a required reflectance performance from this range and find the corresponding amount of secondary crosslinker.

Pigment to Binder Ratios. Another effective, cost efficient method of tuning the gloss is the adjustment of the pigment to binder ratio. The bifunctional crosslinker needs a minimum pigment or filler load to produce dead matte coatings. From this a strong dependence of the gloss level can be seen: In Figure 8, the gloss levels of a black formulation with the bifunctional aliphatic crosslinker and a hydroxyl functional resin is shown in different p/b ratios. The gloss decreases from 80 to <5 at a 60° reflectance angle as the pigment to binder ratio increases from 0.26 to 0.69. Depending on the formula, dead matte performance can be obtained already when a typical p/b ratio of ~30-35 percent is used. In the black formulation discussed in Figure 8 a dead matte performance is obtained using higher filler loads (>50 percent). This leads to another important factor: the type of filler/pigment or extender.

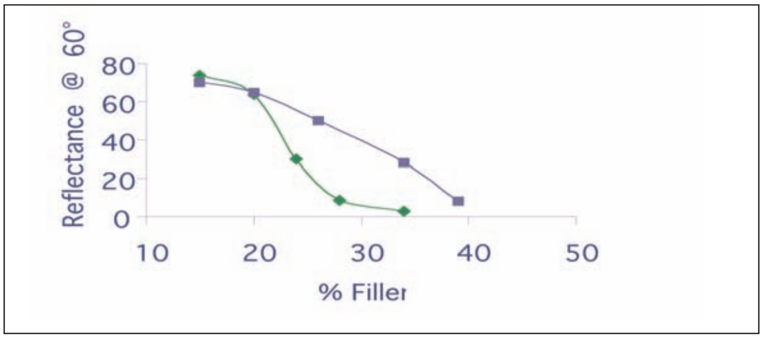
Type of Pigment or Filler. The third expedient method of altering the gloss of the matte system involves changing the particle size of the filler. Barium sulfate or Baryte comes in a variety of particle sizes. In a black matte formulation with the bifunctional aliphatic isocyanate with a pigment to binder ratio of 0.34, a filler with an average particle size of 40 microns produces a coating with a gloss of 27 at a 60° reflectance angle. The same coating, formulated with a filler having an average particle size of <1 micron, generates a coating with

Figure 8



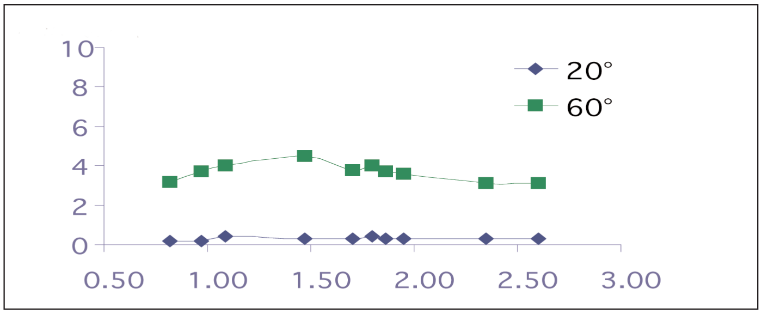
Dependence of the gloss level by changes of the pigment to binder (p/b) ratio

Figure 9



Effect of particle size and pigment to binder ratio on the gloss in a black formulation: A higher p/b ratio decreases the gloss of the paint. Diamonds: 0.7 micrometer Barium Sulfate filler; Squares: 40 micrometer sized Barium Sulfate filler. Smaller particle sizes decrease the gloss at lower filler levels..

Figure 10



The film thickness has no effect on the gloss level: The reflectance at 20 and 60 degree viewing angle is plotted as a function of film thickness.

a gloss of<5 at a 60° reflectance angle. Figure 9 shows how the use of a smaller particle size filler reduces the gloss of a black matte coating formulated with a bifunctional aliphatic isocyanate much more rapidly than the same coating formulated with a larger particle size.

The ability to use different particle sized fillers also produces matte finishes with varying smoothness. With these three tools, additional crosslinkers, pigment to binder ratio, and particle size and type of the filler, the bifunctional PU crosslinker for matte coatings provides a method for formulating a coating with a gloss ranging from 70 to <5 at a 60° reflectance angle.

Robustness of Formulation

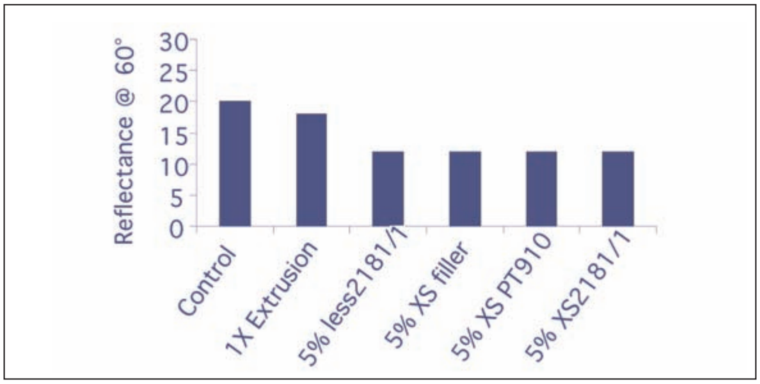
Formulating with the bifunctional aliphatic crosslinker also provides a great degree of robustness through the processing, application, and curing of the coating.

In Figure 10, the independence of film thickness is plotted versus the gloss. Changing the film thickness by 2 mils alters the gloss by < 1.5 at a 60° reflectance angle.

In addition to the independence of film build, a matte coating formulated with the bifunctional aliphatic isocyanate exhibits a processing robustness that covers extrusions conditions and the over or under indexing of formulation components. Figure 11 illustrates the variety of conditions a black semi matte coating can withstand without substantial gloss alteration.

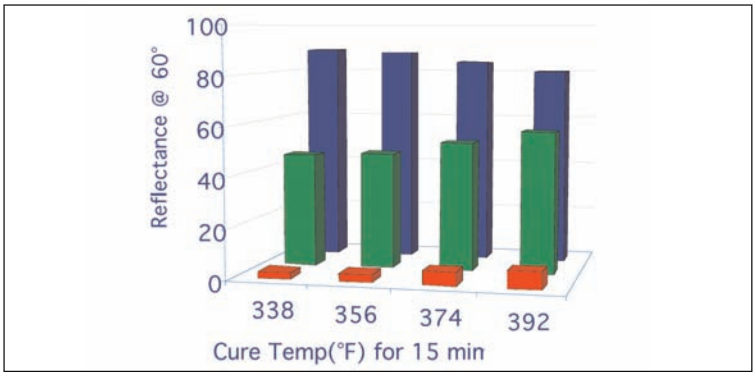
An additional advantage in the robustness of the bifunctional aliphatic isocyanate is the stability of gloss levels throughout different bake conditions. 15 min @ 392°F is the standard recommended bake

Figure 11



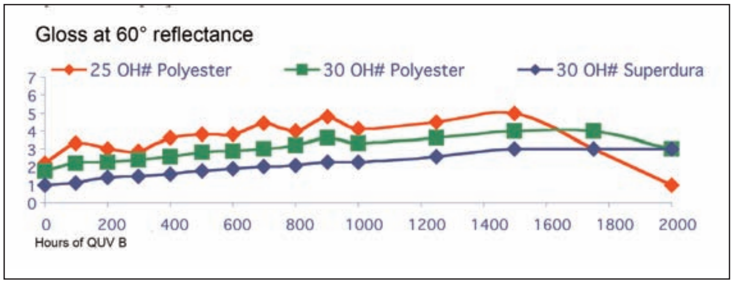
Alterations in processing and charging conditions. Control: Double Extrusion. Changes in extrusion conditions, crosslinker, filler and epoxide over- and undercharges are given.

Figure 12



Only slight changes in gloss are found, when the bake conditions are varied. Red graph is a dead matte system. Green graph is a matte system, and blue graph is a semi gloss system.

Figure 13



Accelerated Weathering data (QUV-B) on three different dead matte formulas using a 25 OH# and a 30 OH# weatherable polyester and a 30 OH# superdurable polyester.

cycle suitable to obtain decent mechanics. At underbake conditions the curing performance is not at its optimum, although the obtained gloss level is fairly independent from this change. Figure 12 shows the gloss levels in a dead matte, matte, and a semi-gloss system exhibiting only slight variations. This has special benefits, when the applicator cannot assure constant surface temperatures.

Accelerated Weathering Data

As well as processing and application robustness, a coating formulated with the bifunctional aliphatic isocyanate withstands simulated weathering tests with minimal surface degradation. In Figure 13, three black systems formulated with a 25 OHN polyester, a 30 OHN polyester, and a superdurable polyester have been exposed to 2000 hours of QUV-B 313 nm 140C accelerated weathering. While the 25 OHN and 30 OHN polyesters both show very good performance, it is the combination of the bifunctional crosslinker and the superdurable polyester that exceeds at 2,000 hours of exposure.

Summary

A bifunctional aliphatic isocyanate is especially useful for one shot matte coatings. The gloss range can be adjusted by different means, e.g., using of additional crosslinkers, filler and pigment loads and particle sizes. All gloss ranges from dead matte to medium and semi gloss ranges can be dialed in.It is proposed that the mechanism of low gloss development is based on a shrinkage phenomenon. This can be explained by assuming that the system gels in a crosslinked rubbery state where flow is not possible anymore. At this time, additional crosslinking induces stress that leads to a uniform shrinkage. Pigments and fillers are necessary for dead matte films.

Formulations employing a bifunctional aliphatic isocyanate exhibit an excellent robustness throughout the processing, application, and curing process. And finally, as the market demands, this unique crosslinker produces a dead matte, matte, or semi-gloss coating with excellent resistance to weathering.

Acknowledgements

Farhad Cama and the Materials Analytical Department of Bayer Material Science LLC for the SEM and EDX data of Crelan 2181/1.

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Peter Thometzek and Michael Grahl of Bayer Material Science AG for robustness tests and weathering data of Crelan 2181/1.

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Katherine Ratliff is a graduate of the University of South Alabama in Mobile, Alabama. After obtaining her Bachelor of Science in chemistry in 2000, Katherine worked for Ruco Polymers in Georgia developing and synthesizing polyesters for powder coatings. In July 2001, she took a position with Bayer Material Science LLC researching new and novel polyesters and crosslinkers for powder coatings. After two years in research, and a year in radiation curable coatings, Katherine is now a senior research specialist in the powder coatings business development group. She can be reached at katherine.ratliff@bayermaterialscience.com. Thomas Faecke can be reached at thomas.faecke@bayermaterialscience.com.

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U.S. Patents

Powder coating of cooh acrylic resin, polyepoxide and low t catalyst

U.S. Patent 6,797,385
Issued: September 28, 2004
Inventors: Hart, Stephen C. et al.
Assigned to: **H.B. Fuller Licensing & Financing Inc.**

A powder coating composition for heat sensitive substrates which cures at a temperature of about 300°F. or below for about 30 minutes or less comprise a) from about 10 percent to 90 percent by weight of carboxylic acid-functional resin(s), from about 10 percent to 90 percent by weight, of polyepoxy resin(s); a catalyst in an amount sufficient to cure the composition at a temperature of about 300°F. or below for about 30 min or less, and optionally, a flexiblizing agent.

Powder coating compositions

U.S. Patent 6,797,749
Issued: September 28, 2004
Inventors: Cordiner, Andrew George
Assigned to: **International Coatings Limited**

The invention provides a powder coating composition in which powder particles are an agglomerate of individual particulate components fused or bonded together into composite particles. Maximizing the amount of larger sized uncolored component(s) gives cost advantages, and the invention allows a rapid and flexible manufacture of a range of colored powder coating compositions.

Powder coating composition incorporating a wax in post-blended form

U.S. Patent 6,800,334
Issued: October 5, 2004
Inventors: Care, Martyn P. *et al.*
Assigned to: **International Coatings Ltd.**

A powder coating composition incorporating a wax in post-blended form, the composition incorporating the wax and the same composition without the wax being separated, preferably widely separated, in a turboelectric reference series indicative of the extent to which powder coating compositions may be distinguishable from one another when electrically charged. The powder coating composition incorporating a wax in post-blended form is especially suitable for coating articles having recessed portions. A quantitative basis is given for determining separation in the turboelectric reference series, and preferred minimum separation criteria are given. The effects obtainable using post-blended wax may be enhanced by the use, as further post-blended additives, of a combination of aluminum oxide and aluminum hydroxide.

Solid, radiation-curing powder coating binders and a process for preparing the same

U.S. Patent 6,809,126
Issued: October 26, 2004
Inventors: Facke, Thomas, et al.
Assigned to: **Bayer Aktiengesellschaft**

The present invention relates to powder coating binders containing polyurethanes having (meth) acryloyl groups which are applied onto a substrate, fused with heat and cured by electromagnetic radiation and to a process for preparing the same.

Process for preparing an aqueous powder coating dispersion

U.S. Patent 6,812,269
Issued: November 2, 2004
Inventors: Koenraadt, Martinus, et al.
Assigned to: **Akzo Nobel N.V.**

A process for preparing an aqueous powder coating dispersion comprising components A and B, wherein component A is a binder resin or a mixture of binder resins and component B is a crosslinker or a mixture of crosslinkers wherein the process comprises the steps of: a) dispersing a composition comprising component A by the addition of aqueous medium in a phase inversion emulsification process, b) adding component B simultaneously with or after the addition of the aqueous medium, and c) optionally mixing the obtained composition to obtain a dispersion comprising components A and B The process enables the preparation of stable powder coating slurries with particles in the range from 50 to 800 nm.

Fluidization additives to fine powders

U.S. Patent 6,833,185
Issued: December 21, 2004
Inventors: Zhe, Jesse, et al.
Assigned to: **The University of Western Ontario**

The present invention provides powder fluidization additives for increasing flowability of fine powders. The powder fluidization additives have both a smaller size than the fine powder and a mean apparent particle density less than the mean apparent particle density of the fine powder. The particles of the additive act to separate the fine powder particles and reduce interparticle forces allowing the flowability of the fine powder to be increased.

Polymerization, compatibilized blending, and particle size control of powder coatings in a supercritical fluid

U.S. Patent 6,849,678
Issued: February 1, 2005
Inventors: Lee,Sungyu , et al.
Assigned to: **The University of Akron**

The current process for producing powder coatings can be replaced with a process utilizing supercritical fluids including polymer polymerization, compatibilized blending of powder coating ingredients, and particle size control and classification of the powder coating. Traditionally, powder coating resins are polymerized in solvent based system. Next, the resin is blended with additives in twin screw extruder at high temperatures. The material is then ground and separated by particle size to form the finished powder coating. This invention replaces the previous process by performing all operations in a supercritical fluid, preferably, carbon dioxide. Polymerization is conducted at any pressure above critical pressure and temperature above critical temperature up to 190°C. Solubility of the polymer in the supercritical fluid allows for control and narrow distribution of the molecular weight and a polydispersity of about 2 or less. Compatibilized blending is effected by a chemical or a physical technique to encapsulate the powder coating additives in the polymer. Particle size control is effected by stepwise controlled depressurization of the mixing chamber or through controlled depressurization of the material into one or more chambers.

Bifunctional polhyaddition compounds as crosslinkers for polyurethane powder coatings

U.S. Patent 6,849,705
Issued: February 1, 2005
Inventor: Wenning, Andreas
Assigned to: **Degussa AG**

A polyaddition compound having uretdione and carboxyl groups and having a melting range of between 40 and 200 degrees C., a free NCO group content of from 0 percent to 5 percent by weight and an NCO functionality of at least 1.5 and a number-average molar mass of between 1000 and 10,000, may be prepared by reacting at least one polyisocyanate containing uretdione groups, at least one hydroxycarboxylic or mercaptocarboxylic acid, and one or more of at least one monofunctional compound having a functional group which is reactive toward an isocynate, at least one aliphatic and/or cycloalphatic and/or cycloalphatic polyamine. Polyurethane plastics, especially polyurethane powder coating materials may be prepared from the polyaddition compound of the present invention.

Low gloss free radical powder coatings

U.S. Patent 6,852,765
Issued: February 8, 2005
Inventors: Decker, Owen Hugh et al.
Assigned to: **E.I. duPont de Nemours & Co.**

The present invention is directed to a powder coating composition that produces a low gloss coating upon cure. The powder coating composition includes one or more crosslinkable base polymer, a crosslinkable acrylic polymer and one or more free radical initiators. By adding spheroidal particles to the powder coating composition further reduction in gloss can be obtained while improving smoothness. These compositions are well suited to produce coatings on metallic substrates, such as automotive bodies and non-metallic substrates, such as constituted wood substrates, used for desk or table tops.

Radiation curable powder coating compositions and their use

U.S. Patent 6,861,465
Issued: March 1, 2005
Inventors: Wenning, Andreas, et al.
Assigned to: **Degussa AG**

A radiation curable powder coating composition that contains a) a binder having at least one amorphous urethane acrylate having a glass transition temperature of at lest 35°C. and a melting point of from 50 to 120°C., and b) an auxiliary, can be crosslinked by radiation to produce a lightfast and weather-stable film.

Powder coating composition

U.S. Patent 6,861,467
Issued: March 1, 2005
Inventor: Nakano, Hiroshi
Assigned to: **Okitsumo Inc.**

A powder coating composition contains a binder component of either a silicone resin or a mixture of a silicone resin and at least one selected from the group consisting of an epoxy resin, a phenolic resin, an acrylic resin, a polyester resin and a fluororesin, and a reinforcing pigment of a least one of a mica and whisker, wherein the content of the silicone resin in the binder component is at least 60 percent by weight. Such a composition can be free from the occurrence of paint film cracks and peeling under heat at high temperature of 300°C. or higher and can have good heat resistant adhesion. Therefore, the present invention provides a powder coating composition which is excellent in heat resistant adhesion at a high temperature of 300°C.

Smooth, flexible powder coatings

U.S. Patent 6,861,475
Issued: March 2, 3005
Inventors: Ilenda, Casmir Stanislaus, et al.
Assigned to: **Rohm & Haas**

The present invention, a powder composition for making power coatings, comprises one or more than one curable polymer or resin and an agglomerate of a core shell polymer. The powders in accordance with the present invention provide a cured powder coating that is flexible, smooth, and which may be applied in a thickness of only from 0.3 to 8 mils. In a preferred embodiment of making a powder in accordance with the present invention, the agglomerate is cryoground to form a reduced agglomerate prior to adding it into a powder as a post blend or a powder forming mixture as a preblend. The preferred core shell polymer for use in accordance with the present invention comprises an acrylic impact modifier having a poly (methyl methacrylate) shell and a poly (butyl acrylate) core. Further, the preferred curable polymer or resin powder is an epoxy resin, wherein the powder composition is a low temperature curing one component powder composition which cures at from 107 to 149°C.

POWDER R&D

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