Pigmented UV-Curable Powder Coatings: Possibilities for A Bright White Future

by Emmanouil Spyrou and Andreas Wenning, Degussa AG;
and Corey L. King, Degussa Corporation

Abstract

Pigmented, UV-curable powder coatings were formulated using novel crystalline and amorphous resins containing urethane acrylate groups known for their outstanding weatherability. The amorphous and crystalline resins were mixed at several weight ratios to provide a range of physical properties in white, UV cured powder coatings. These properties were examined using several percentages of titanium dioxide, multiple radiation sources, and on steel and MDF substrates. The resulting coatings have excellent adhesion and mechanical properties.

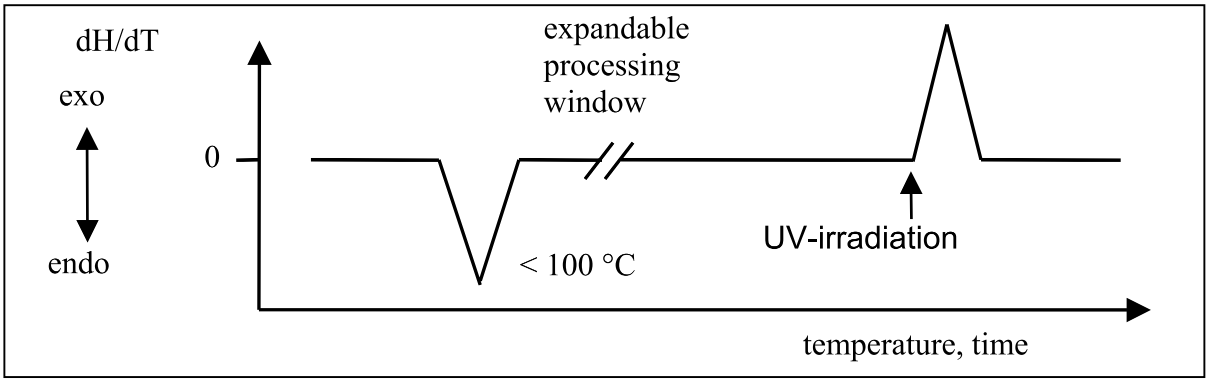
Introduction

Conventional thermosetting powder coatings have become a well-established technology for many interior and exterior applications, including metal office furniture, lawn and garden furniture, appliances, pipe coatings, and automotive and off-road coatings. Powder coatings are known particular for their outstanding balance between their chemical and mechanical durability and no solvent emission. In addition, powder coatings have the benefits of recycling overspray, and obtaining medium to high film thicknesses in one application. Unfortunately, conventional thermoset powder coatings are limited to metals and other substrates that can withstand the 150-200°C cure temperatures.

There are several heat-sensitive substrates like thermoplastics, hardwood, engineered wood, paper and pre-assembled parts that could be coated with powder if the cure temperatures of thermoset powder coatings were reduced. It is unlikely to reduce cure temperatures of current technologies below 120°C, which is required to maintain the integrity of engineered wood and plastics.

Using UV curing technology, the curing process can be separated from the melting process (see Figure 1), such that the substrate only needs to be exposed to enough thermal energy to provide melt and flow of the powder. The coating may then be cured using UV radiation while the coating is still in the molten phase, and the substrate only sees temperatures of 80-120°C, and for a significantly shorter period of time than thermally-cured powder coatings.

Figure 1. Melting and curing process of UV-curable powder coatings (DSC)



UV-curable powder coatings will play an important role in the future of the powder coatings industry, as more substrates are possible to gain the benefits that the metal and aluminum markets have achieved with traditional powder coatings. The industries that can be benefited include pre-coated particleboard and MDF, headlight lenses, pneumatic door closers, blank and coil coatings. [1]

UV powder coatings have been commercially available for several years. The binders used for these coatings differ chemically from the system introduced here, and range from cationically polymerized epoxies to radically or dual-cured vinylethers and (meth)acrylated polyesters.

Solid epoxy resins based on bisphenol-A are cured cationically. Upon irradiation, the photoinitiator generates a strong acid that results in cationic polymerization of the epoxy groups [2]. This ring-opening polymerization exhibits low shrinkage, no inhibition by oxygen and can be post-cured thermally. However, this curing mechanism has disadvantages of slower propagation rate and inhibition of the curing reaction by water and basic pigments.

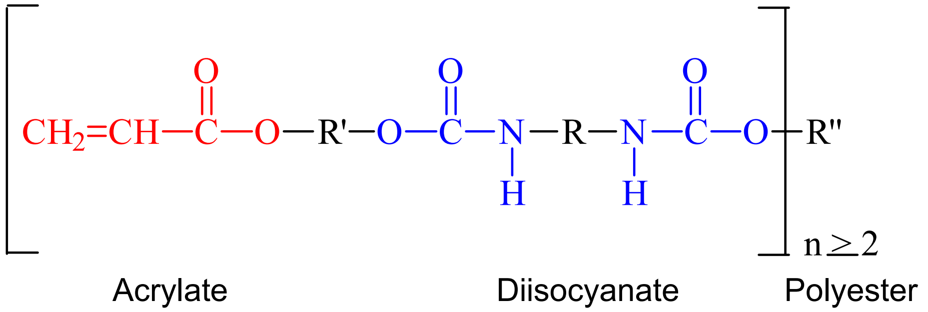
Unsaturated polyesters combined with urethane acrylics or urethane vinylethers as hardeners have been designed recently [3,4]. These UV-curable coatings are cured by free radical polymerization. Acrylated and/or methacrylated polyesters as special amorphous or semi-crystalline binders are developed for the coating of metal, wood or pvc substrates [5]. The films exhibit excellent surface properties like chemical and scratch resistance. By using binder mixtures of amorphous and semi-crystalline resins, the flexibility of the cured films can be increased. However, the hardness of these coatings is not very high.

New binders are needed which give flexible, yet hard and durable films. Urethane acrylates are a new class of binders for UV-curable powders, and require further understanding to better formulate these coatings and optimize hardness, UV-durability, and mechanical and chemical properties. These binders have previously been studied in clearcoat systems [6], which are beneficial to metal and hardwood applications. However, many formulations are pigmented and the pigments and dyes obstruct the transmission of UV radiation. White coatings pigmented with titanium dioxide are the most prominent [7], and are principally targeted to coat engineered wood in applications such as kitchen cabinets and furniture. This study examines use of combinations of crystalline and amorphous urethane acrylates in white powder coatings, to determine the effects of formulation and curing protocols on coating properties.

Procedure

Resins

Three novel urethane-acrylate resins were used in this study, two amorphous (RA1 and RA2) and one crystalline (RC). The three resins have a general structure as shown in Figure 2, and polymer characteristics shown in Table 1. The resins were produced using hydroxyl-functional amorphous and crystalline polyesters, respectively, which were then reacted with diisocyanates, and further functionalized with hydroxyl-functional acrylates.



$$\left[\mathrm{CH_2{=}CH-\overset{O}{\overset{\|}{C}}-O-R'-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O}\right]_{n\geq 2}\mathrm{-R''}$$

Figure 2. Structure of the urethane acrylate resins RA1, RA2 and RC.

Table 1. Characteristics of urethane acrylate resins RA and RC. [8]

	RA1	RA2	RC
Tg (°C)	45	50	-
Tm (°C)	-	-	77
Melt viscosity (Pa*s), 120°C	160	250-350	1.3
Unsaturation (mol/kg)	0.78	0.71	0.68

Coating Formulation

Clearcoat formulations containing RA1 or RA2 as the sole binder have a very high hardness but low flexibility. Upon addition of RC, the melt viscosity decreases and allows for flexibility, impact resistance, and smoothness [6]. White powder coatings were prepared with RA1:RC weight ratios of 100:0, 90:10, 85:10, and 80:20. Based on total percent of the formulation, there was 1.0% degassing agent and 1.0% flow and leveling aid. Two levels of pigmentation were used, 15% titanium dioxide and 20% titanium dioxide, with two types of photoinitiator to optimize surface and through cure. The photoinitiators used were an α-hydroxyketone type and a BAPO type, at 1.0% and 2.0%, respectively. In addition, a highly pigmented coating with an 85:15 ratio of RA2:RC was prepared with 30% titanium dioxide to test the limits of UV curing with a high pigment level and a resin system that had high viscosity.

Powder Processing

Each powder was prepared by weighing the components together and premixing them. The premix was then added by hopper to a twin screw, Werner & Pfleiderer extruder. The extruder had zone temperatures of 70°C for both zones, a screw speed of 250 rpm, and a torque of 30% for all of the coatings processed. The extrudate was then ground in a mill and sieved to less than 100µm.

Powder Application and Cure

The powders were applied using corona guns to cold-rolled steel and MDF (medium density fibreboard) panels. Thickness of the steel coated panels ranged from 50-80µm, while the MDF panels were coated with 160-250µm. The panels were then passed along a conveyor belt through individually controlled IR and UV zones. The IR temperature was held at 118-120°C, and the belt speed was varied between 0.2 and 0.4 m/min. The IR energy absorbed was 9.0 and 4.5 W/cm^2, respectively. The panels were then subjected to UV radiation by passing directly to the UV belt speed which had a speed of 3.0 m/min. Mercury and gallium additive lamps were used, by themselves and in combination. An irradiant energy density of 4.75

J/cm^2 was held constant with each formulation, with the energy density being measured in the VUV and UVA regions.

Powder Testing

MDF coated panels were tested for yellowness index, crosshatch adhesion, PCI smoothness, and Konig hardness. Crosshatch adhesion values ranged from 0-5, with 0 indicating no removal, and 5 indicating complete removal, and PCI smoothness values range from 1-10, with 10 indicating no orange peel. Steel coated panels were tested using the same tests as MDF, plus direct impact resistance and Erichsen cupping. Impact resistance values had a maximum of 160 in-lb, and cupping values were limited to a distortion of 10 mm.

Results and Discussion

Effect of Binder Composition on Coating Properties

Seven formulations with two levels of titanium dioxide and four ratios of RA1 and RC were prepared to study the effect of binder composition on the coating properties. These coatings were cured on steel using mercury lamps and an IR belt speed of 0.2m/min, and the coating properties are listed in Table 2. The seven formulations were then applied to MDF, and cured using mercury lamps and an IR belt speed of 0.4m/min. Table 3 lists the properties of the coatings cured on MDF.

Table 2. Effect of coating composition (%RC with RA1) on coating properties on steel

% RC of total resin	Yellowness index	Impact (in-lb.)	Crosshatch adhesion	PCI smoothness	Cupping (mm)	Konig hardness (s)
15% TiO_2						
0%	0.8	30	3-5	9	0.5	223
10%	4.2	30	0	10	10	209
15%	1.9	90	0-1	10	10	196
20%	3.8	150	2-3	10	10	171
20% TiO_2						
10%	2.6	40	2	9	10	209
15%	3.9	50	0-2	10	10	187
20%	3.2	150	0	9	10	180

Table 3. Effect of coating composition (%RC with RA1) on coating properties on MDF

% RC of total resin	Yellowness index	Crosshatch adhesion	PCI smoothness	Konig hardness (s)
15% TiO_2				
0%	5.9	0	7	148
10%	7.1	5	8	171
15%	6.7	0	8	139
20%	6.0	5	8	110
20% TiO_2				
10%	5.9	0-1	8	148
15%	6.6	2-4	9	-
20%	6.7	0-5	8	115

Coating properties on steel were observed to change dramatically when the percentage of crystalline resin was increased. The impact resistances of the 0% and 10% RC coatings were 30 in-lb, while the 20% RC coating had an impact resistance of 150 in-lb, regardless of pigmentation level. In addition, the adhesion improved with RC addition. The increases in mechanical properties, adhesion and smoothness are primarily due to the decrease in melt viscosity of the coating upon addition of the crystalline resin. This also has a positive effect on crosshatch adhesion, which is likely due to better coalescence of the powder particles. Unfortunately, the coating hardness decreased with RC addition. Very few differences were observed between the respective 15% and 20% TiO_2 coatings, which indicates that no difficulty in curing was observed upon increase of the titanium dioxide content.

Similar effects of RC and titanium dioxide levels on coatings properties were mirrored in the MDF coatings. As the RC concentration was increased, the smoothness increased and the hardness decreased. The effect of adhesion was less defined, which may be due to inability of the coating to adequately wet the surface of the MDF, due to either high viscosity or water on the panel surface. Despite this, some of the coatings exhibited perfect adhesion to the MDF.

Effect of IR intensity, Irradiation Type and Pigmentation Level

The type of irradiation and pigmentation directly affects amount of cure in the UV powder coating. Titanium dioxide, while it obscures the transmission of UV radiation from the photoinitiator, does offer scattering and reflection of the radiation such that curing can be sufficient in the presence of TiO_2 [7]. Sufficiency does not imply full development of the UV coating properties, thus this study looked at the effect of lamp combinations of mercury, gallium additive, and mercury and gallium additive combinations, while altering the weight percentage of TiO_2 in the coating. The IR belt speed was also changed, to ensure that complete fusion of the powder particles was obtained. Table 4 lists the coating properties of two UV powder coatings with 80:20 ratios of RA1:RC cured using these process variables.

Table 4. UV coating properties on steel with varied IR belt speed, lamp type, and TiO_2 level

	IR belt speed = 0.2 m/min			IR belt speed = 0.4 m/min		
	Ga	Hg	Ga/Hg	Ga	Hg	Ga/Hg
Impact resistance (in-lb.)						
15% TiO_2	120	150	60	60	80	20
20% TiO_2	150	150	160	130	150	160
Yellowness index						
15% TiO_2	1.9	3.8	3.1	1.3	3.7	4.1
20% TiO_2	1.4	3.2	0.7	1.4	3.2	0.9
Crosshatch adhesion						
15% TiO_2	0	2.5	0	3	3	3.5
20% TiO_2	0	0	0	5	5	5
Konig hardness (sec)						
15% TiO_2	172	171	174	169	176	162
20% TiO_2	180	180	182	164	173	169
PCI smoothness						
15% TiO_2	10	10	10	7-8	10	10
20% TiO_2	9-10	9-10	9-10	8-9	8-9	7

All three variables studied in this test, IR belt speed, type of lamp, and concentration of TiO2, affected the final properties of these coatings. Changes in the process variables - lamp type and IR belt speed - affected both 15% and 20% TiO_2 coatings similarly. The lamp type affected the performance of the UV powder coatings, but to a much lesser degree than the IR belt speed. The mercury and gallium additive lamps provided better impact resistance than the combination of the two lamps, with the mercury lamp providing the highest impact resistance in the 15% and 20% TiO_2 coatings. The gallium additive lamp provided the least amount of yellowing in the final coating.

Decreasing the belt speed allowed for an increased amount of heat energy to be absorbed by the coating. The additional energy allowed for better coalescence, which imparted high impact resistances, better adhesion, higher hardness, and better flow. This data indicates that the sintering of the powder particles is critically important to the final performance of the UV powder coating. If the particles do not fully coalesce, then the UV radiation will crosslink the polymer resins inside the loosely bonded powder particles, and full properties will never be obtained. Thus, it is necessary to preheat the coating sufficiently to ensure excellent mechanical properties and better adhesion.

Effect of Surface Temperature on Performance of Highly-Pigmented Coatings

To follow through with the previous results, a UV powder coating containing 30% TiO_2, and a higher viscosity amorphous resin (RA2) was prepared with an 85:15 ratio of RA2:RC. The powder was applied to steel and cured using a mercury lamp, with an IR preheat that exposed the powder to surface temperatures of 127°C and 136°C. The results of this test are shown in Table 5.

Table 5. Surface temperature effect on properties of a 30% TiO2 coating with RA2:RC (85:15)

Surface Temperature (°C)	Thickness (μm)	Impact (in-lb.)	Crosshatch adhesion	PCI smoothness	Cupping (mm)	Konig hardness (s)
127	49-61	<10	5	8	2.5	178
136	56-75	70	3-4	8	>10	183

The higher surface temperature allowed for better coalescence of the powder particles, and thus, higher hardness, better adhesion, and significantly better impact resistance and cupping. Furthermore, these results show that a pigmented UV powder coating containing a very high amount of titanium dioxide can be formulated to achieve high hardness, good smoothness, and excellent mechanical properties.

Conclusions

Urethane acrylates based on amorphous and crystalline resins can be used to formulate UV powder coatings that have good hardness, full adhesion, and excellent mechanical properties. This work has shown that the coating composition, lamp type, IR belt speed, and percentage of titanium dioxide all affect coating properties. The IR belt speed and coating composition affect the coating properties the most, with the best properties present with 15-20% crystalline resin, and sufficient IR exposure to allow particle coalescence. These coatings can be used to coat both steel and MDF with similar protective properties. Using this knowledge, a coating was formulated with high titanium dioxide content and cured to provide good smoothness, high hardness, and excellent mechanical properties.

References

1. P. Mills, ”The market potential for UV powder coatings”, *RadTech Report*, July/August 1999, p. 31.
2. M. Reisinger, ”UV-curable powder coatings for temperature sensitive substrates“, RadTech Europe 99, Berlin, p. 628; Patent EP 0 667 381.
3. D. Fink, G. Brindöpke, “UV curing powder coatings for heat sensitive substrates“, *European Coatings Journal*, 9 (1995), p. 606; Patent EP 0702 040.
4. F.M. Witte, “Radiation curable powder coatings“, *European Coatings Journal*, 3 (1996), p. 115; Patent EP 0 636 669; Patent WO 99/14254.
5. D. Hammerton, K. Buysens, Y. Souris, “New UV powder systems for metal, wood and pvc“, RadTech North America 2002, Indianapolis, p. 592; Patent EP 0 739 922; Patent EP 0 934 359.
6. A. Wenning, “Tailor-made UV-curable Powder Clear Coatings for Metal Applications, PCI Powder Coating 2002, Indianapolis.
7. R. Jahn, T. Jung, “Relationship between pigment properties and UV-curing efficiency”, *Prog. Org. Coat.*, 43 (2001), p. 50.
8. Degussa Corporation, Technical Data Sheets, VESTAGON EP-UV 100, VESTAGON EP-UV 300, and VESTAGON EP-UV 500, 2003.