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UV Curable Powder Coating Systems: A Promising Future

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Introduction

The market. The industrial wood market is dominated by solvent borne coatings. Environmental pressure is causing a gradual shift towards water borne and UV/EB curable coatings. Table I compares current industrial wood coatings to a hypothetical powder coating system for industrial wood, demonstrating the potential advantages of the latter.

From an environmental point of view, powder coatings obviously have the best performance. Their use does not pollute the air or generate waste water (a water curtain is generally used to capture overspray). At the same time, the occupational hazards are very low.

Roughly 40% of the coatings used for industrial wood are applied by spraying. The powder coating system is the only one that attains 100% utilization of the coating during spray application, an important achievement from a cost perspective. Again, as in the case of powder coatings for the general metal market, the very same environmental and economic advantages (often referred to as the 2E's), can be assigned to powder coatings for wood. However, for full success, powder coatings for wood must incorporate a third E, the *excellence* of finish. This is a technical problem, the magnitude of which can be realized when comparing the basic differences between powder coatings for general metal application and the requirements for industrial wood as presented in Table 2.

Low temperature curing powder coating. Powder coatings have gained wide acceptance in the industrial coating market (1). The use of conventional thermal curing powder coating is almost completely limited to general metal applications. Since the introduction of powder coating, some 30 years ago, there has been a continuous striving for lower curing temperatures (2). The application of powder coating on heat-sensitive substrates, such as plastics and wood, demands cure temperatures well below 150°C and in most cases even below 100°C. Table 2 compares the main requirements for industrial wood applications with general metal applications.

The acid-epoxy chemistry that is widely used in powder coating can be catalyzed effectively at curing temperatures well below 150°C. The main problem with this chemistry is the balance between storage stability, melting, flow and cure. Because the thermally activated crosslinking reaction is governed by Arrhenius constraints, it is almost impossible to develop a system that, for example, is stable during conventional extrusion at 100°C and gives a smooth coating with full conversion at 120°C (3). One approach to solving this dilemma is the use of radiation-activated crosslinking instead of a thermally activated reaction. The proper chemistry provides a system with the desired separation between flow and cure.

Table 1. Comparison Coating Systems for Industrial Wood Spray Applications

Type of coating	Solvent content	Utilization	Air pollution	Waste water	Occupational hazard level
Cellulosic	68–75%	50%	High	Yes	High
2C systems	30–50%	50%	Medium	Yes	Medium
Unsaturated polyesters	ca. 0%	50%	Medium	Yes	Medium
UV curing acrylates	ca. 0%	50%	None	Yes	Medium
Water-borne	10–20%	50%	Low	Yes	Low
Powder	ca. 0%	100%	None	No	Low

Table 2. Main Requirements

	General Metal	Industrial wood
Curing temperature	160–220°C	< 100°C
Melting temperature	ca. 100°C	< 100°C
Glass transition temp.	min. 45°C	min. 45 °C
Melt velocity at 100°C	10^3–10^4 Pa•s	5–30 Pa•s
Flow at curing temp.	Good	Excellent

UV curable coatings. UV curing is a relatively new and fast growing coating technology that is well known in the wood coatings market. Of the wide variety of available radically-initiated polymerization systems, most are based on (meth)acrylic unsaturation (4). These systems consist of a polymer containing acrylic groups and reactive diluents as viscosity reducers. Recently, a new system was developed by DSM Desotech, based on the maleate/vinyl ether (MA/VE) technology (5). The MA/VE system consists of a resin bearing maleic or fumaric acid in the polymer chain and a vinyl ether oligomer (6). This system meets the necessary requirements for wood application, and because it is essentially a nonacrylate system, it exhibits no irritating or sensitizing properties.

UV Curable Powder Paint

The most versatile technology for powder coating, offering cure at low temperatures while maintaining basic properties like flow and powder stability, is UV curing.

A market in which UV curable powder coating may find wide applicability is the industrial wood market. The economic, as well as safety, health and environmental, aspects of powder coatings — such as the lack of solvent emission, lack of paint sludge waste, low energy consumption, high yields and a high standard of workplace hygiene — offer a very good opportunity for the use of powder paint in this market. The 100% material utilization makes powder especially suited for spraying. In applications where flat panels are painted, roll and curtain coating methods with liquid paints also attain a very high utilization efficiency, and the high line speeds of these methods cannot yet be achieved with powder paint.

A recent paper reported the stabilization of UV curable powder coating for improved outdoor durability. It was claimed that with WA and HALS compounds even outdoor applications are within reach for UV curable powder coating technology (7).

Chemistry

Materials that can be used for radiation curable powder coatings contain unsaturated double bonds. Recently a UV curable powder coating system containing (meth)acrylic unsaturations was introduced (8). The radiation curable powder coating system of DSM Resins is a nonacrylate system. It is based on the same chemistry as a commercial nonacrylate 100% reactive liquid system. The binder consists of two compounds, a resin and a coreactant. The resin is an unsaturated polyester polymer in which maleic acid or fumaric acid is incorporated, and the coreactant is a polyurethane containing vinyl ether unsaturation (9). The UV curing of the binder is based on the 1:1 copolymerization of electron-rich vinyl ether groups with electron-poor maleate or fumarate groups (10). The mechanism is shown in Figure 2. The system contains a stoichiometric balance of maleate and vinyl ether groups. MA/VE binder systems offer the advantage that the components do not, under controlled conditions, homopolymerize and that the UV curable powder paint is thermally stable. This means that the time allotted for flow can be increased as needed. This is in contrast to systems containing (meth)acrylic unsaturations because they can react under the influence of heat alone. The thermal stability of the MA/VE system ensures good flow and smooth films. However, since application takes place on substrates with a distortion temperature around 100°C, the melt viscosity of the powder must be adapted compared to conventional powder (12).

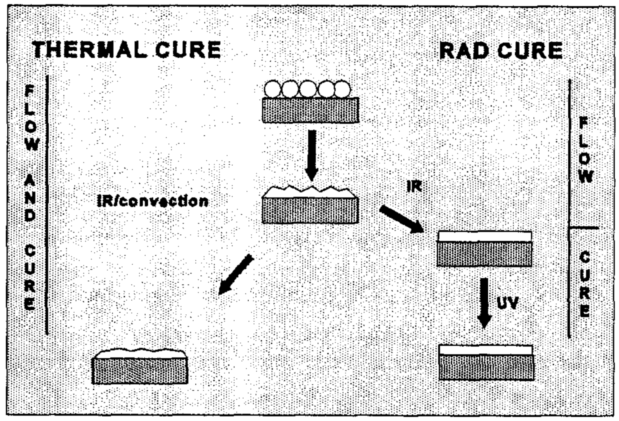

Figure 1. The separation of flow and cure in the UV curable powder system.

Paint Production

From the paint manufacturer's point of view, the UV curable powder system can be treated in a conventional way. The MA/VE binder system is solid at room temperature, which means that the UV curable powder can be produced by the existing powder paint manufacturing process. Photoinitiators, pigments and additives must be added to the binder system, and homogenizing can take place by melt extrusion. The paint can be applied electrostatically on wood.

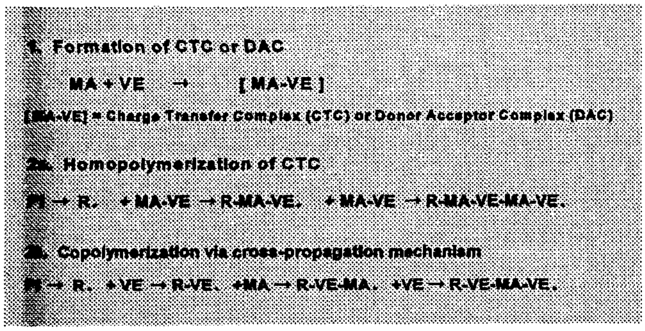

Figure 2. Mechanism of maleate/vinylether alternating polymerization (11).

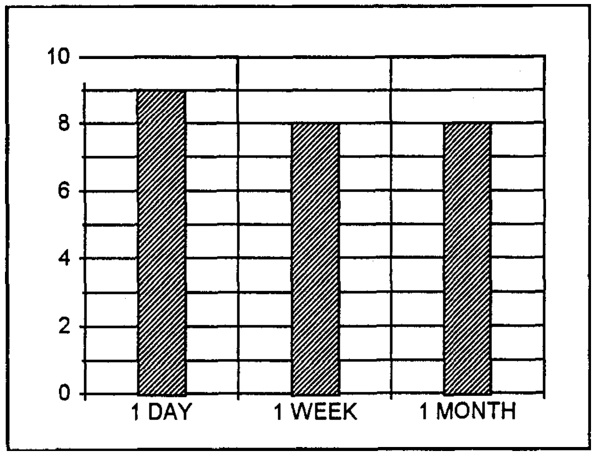

Figure 3. Physical powder stability of the prototype radcure powder paint at 35°C (10 = excellent, free-flowing powder; all values below 5 = unacceptable caking).

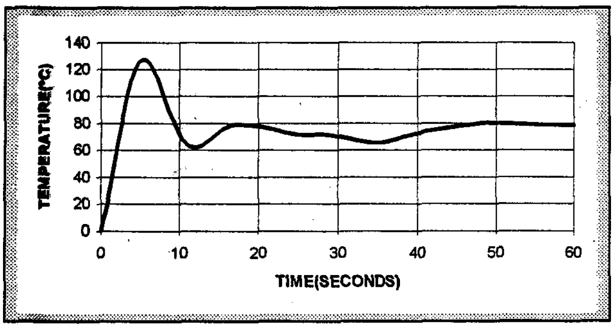

Figure 4. Temperature at the surface of an MDF panel.

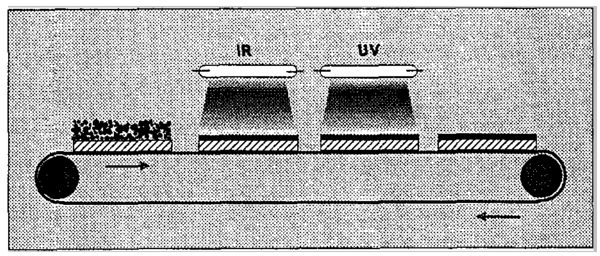

Figure 5. Combined IR/UV curing line for radcure powder paint

Figure 3 shows the physical powder paint stability (resistance to caking, etc.) of a prototype clear UV curable powder paint at 35°C. Although it is not on the same level as the best conventional powder paints, in which stability at 40°C becomes more or less the standard, the stability of the UV curable paint is sufficient to be produced and handled with existing powder coating equipment.

Chemical stability is not a concern with the MA/VE binder system. Because the system can only be triggered by UV energy, it is perfectly stable during storage.

Paint Application

Wood substrates cannot tolerate high temperatures. This means that the thermal energy used to melt the applied paint must not elevate the substrate to the same high temperatures. The combination of IR for melting and the formation of a smooth film, and UV for curing, seems to be the most efficient technology for the application of the UV curable powder paint on wood. In our laboratory a small scale IR/UV curing line is used. The heating and melting of the powder is controlled by a noncontact thermocouple which adapts the intensity of the IR lamps. This ensures a temperature control on the surface of the substrate as illustrated in Figure 4 for a 60-s melt and flow cycle.

After the melt and flow of the paint with IR, the cure is realized with mercury UV lamps. In most of the experiments a dose of 1,000 mJ/cm^2, as measured with the IL 390B Light Bug, is enough to obtain coatings with good surface properties.

Coating Performance

Clear formulations. The application of a prototype unpigmented radcure powder on medium-density fiberboard (MDF) provided well cured, smooth, clear coatings with good properties. Table 3 shows the coating performance of a prototype MA/VE-based unpigmented powder paint (Paint 2). The basic coating properties like flow, solvent resistance and hardness are very good. From a theoretical point of view, a 1:1 ratio of MA-polyester/VE coreactant should give the best results. Experiments have been performed with unpigmented formulations in which the ratio of polyester to coreactant was varied. Table 3 shows that the formulation containing an excess of polyester (Paint 1) results in a coating with less solvent resistance and flow compared to the other formulations. The paint with an excess of VE-coreactant (Paint 3) results in good flow and solvent resistances, but the pendulum hardness is inferior to the other formulations. Furthermore, the adhesion of the 1:1 formulation is superior to the others. It can be concluded from Table 3 that the best overall results are obtained with a powder paint containing the 1:1 ratio of MA/VE. It is remarkable that only a relatively small amount (1 wt% Irgacure 184) of photoinitiator is necessary to obtain coatings with a good conversion and properties.

Though the prototype UV cured powder system performs well on MDF, application on solid wood has not yet been perfected. Clear formulations on solid wood panels resulted in coatings with many blisters. This is probably caused by moisture and other volatiles that evaporate from the wood at the applied surface temperatures of 80°C during IR heating. The application of a sealer system as primer before the application of the powder paint might offer a solution for these degassing problems.

Pigmented formulations. Work has been started in our laboratories on the development of pigmented paint formulations that contain our MA/VE prototype binder. Pigmentation of UV curable coatings is still an issue with liquid systems. The state of the art at this moment is that only pigmented coatings in thin layers and/or with low pigmentation content can be cured by UV (13). Recently there have been reports on good results with a novel class of photoinitiators that are specially suitable for pigmented UV coatings, the bis-acylphosphineoxides (14). Earlier we reported good results with CGI 1800, an experimental photoinitiator from Ciba-Geigy that contains this new initiator (12). It is a 75:25 blend of Irgacure 184 (a hydroxyketone) and BAPO (the phosphineoxide) (15) and is now commercially available as Irgacure 1800.

Table 4 shows the results from paint formulations containing 2 wt% Irgacure 1800 with varying amounts (0–20 wt%) of pigment. All formulations were applied on MDF panels at a thickness of 100 μm. From these experiments it appeared that the hiding power is not acceptable below 15 wt% pigment. However, the surface properties of the coatings seem to be reasonably good, since the acetone resistance is very good in all cases. It is clear that although no distinction could be made in pencil hardness, the pendulum hardness of the coatings is very much dependent on the amount of pigment.

An interesting phenomenon is that the pendulum hardness of the pigmented coatings increases with time. This post-cure effect was reported earlier for the 100% reactive liquid MA/VE systems (6) in which the increase of hardness over time is very distinct. It is probably caused by a post-cure process in which the conversion increases over time. Indeed, IR analysis after the UV exposure confirmed that double bonds remained in the pigmented coatings, which could facilitate the subsequent increase in conversion. The fact that in the clear paint the coating hardness does not increase over time is probably due to the fact that the conversion in the clear paints is already high. This suggestion is supported by IR analysis on a cured clear coating in which no remaining double bonds could be detected directly after cure.

Table 3. UV Curable Clear Powder Paint

	Paint 1	Paint 2	Paint 3
MA/VE Ratio	1.1:0.9	1:1	0.9:1.1
Flow	±	++	++
Appearance	good	good	good
Acetone resist	±	++	++
MEK resist	±	++	++
König[1]	164	180	106
Adhesion[2]	1	0	1

All formulations contain 1 wt% Irgacure 184 and 0.66 wt% BYK 361. Extrusion: Prism 16-mm extruder, 200 rpm, 70°C. Application on MDF with a Tribo gun. Cure: 90 s IR melt, UV cure (1,000 mJ/cm², IL 390B Light Bug)

"++" represents no damage after 100 double rubs.
"±" represents surface slightly damaged.

[1] Pendulum hardness DIN 53157.
[2] Gitterschnit scale 0-5, 0 is excellent, 5 is bad, DIN 53153ISO 2409

Table 4. Effect of Pigment Content on Coating Hardness

wt% pigment:	0	5	10	15	20
Flow	++	+	+	±	±
Acetone resist	++	++	++	++	++
Pencil hardness	HB	HB	HB	HB	HB
König (sec)[1]					
— 1 day	188	111	95	81	74
— 3 weeks	183	125	109	92	90

All formulations contain 237 g polyester resin, 48 g coreactant, and 2 g BYK 361 and a varying amount of TiO_2 (Kronos 2160). The formulations contain 2 wt% Irgacure 1800, the clear formulation contains 1 wt% Irgacure 184. Extrusion: Prism 16-mm extruder, 200 rpm, 70°C. Application on MDF with a Tribo gun. Cure: 90 seconds IR melt, UV cure (1,000 mJ/cm², IL 390B Light Bug).

"++" represents no damage after 100 double rubs.
[1] Pendulum hardness DIN 53157.

Table 5. Comparison of UV Curable Powder with Solvent-Based 2-C Coating System

	Solvent-based AC/NCO[1]	Clear paint[4]	15 wt% pigment[4]	20 wt% pigment[4]
Flow	+++	++	±	±
1 hr ethanol[2]	3	0	0	0
1 hr citric acid[2]	0–0.5	0	0	0
16 h coffee[2]	0	0	0	0
16 h ink[2]	0	1	3	3
König (sec)[3]				
—1 day	106	188	81	74
—14 day	144			
—3 weeks		183	92	90

[1] URACRON CY 463 E, hydroxy acrylic cured with Tolonate HDB, 38% solids, clear formulation.
[2] Rating 0–5 according to DIN 68861; 0 is good, 5 is poor.
[3] Pendulum hardness DIN 53157
[4] See Table 4 for paint formulations

The results with the pigmented formulations show the possibility of MDF application of the MA/VE binder system in coatings containing 15–20 wt% pigment. Typical industrial wood coating properties were tested, and the performance of the prototype radcure powder binder system in clear and pigmented paints was compared to a commercial solvent-based two-component acrylic-isocyanate paint. Table 5 shows the results of the clear powder paint and the 15 and 20 wt% pigment containing paints from Table 4. It is clear that the powder coatings perform very well in comparison to the solvent based system. The alcohol resistance of the powder coatings is even better, and only in the ink resistance does the solvent-based system outperform the powder coatings.

The results from Table 5 show that the UV curable powder coating system complies to specific requirements of the industrial wood coating market.

Conclusions

The maleate/vinyl ether binder system is very versatile for application in a UV curable powder coating. The separation of flow and film formation by IR and cure by UV is the basis for the applicability of this binder system in powder paint on heat-sensitive substrates.

The results of clear paint formulations have shown that the system can be applied successfully on MDF. The balance between flow, conversion and coating hardness is very good. The performance and applicability of pigmented paint formulations on MDF are promising.

Application on solid wood has not resulted yet in coatings that fulfill the standard coating requirements. Blistering is caused by degassing problems due to the high amount of volatiles in the wood.

The application of the UV curing technology in powder coating opens new markets and can have a major impact on the continued growth of the powder coating market.

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