Flame retardant radiation curable coatings for parquet application

Since the early seventies, radiation curing technology has enjoyed an uninterrupted growth in the field of coatings, printing inks and adhesives and this trend is expected to continue into the first decade of this century. The major factors fuelling the growth of radiation-cured formulations include the outstanding performance of the coatings (gloss, durability, adhesion to substrate), very fast curing (within seconds or fractions of seconds without the need for heating), low process costs per square meter of surface, product stability on the application machines and the low space requirements of the application lines.

M. Decaux, J.P. Bleus, H. Van den Bergen, Th. Randoux. One of the most successful areas has been the wood coatings industry, also particularly the furniture and the parquet flooring sectors. The main application technique was the roll-coater and because of its flat structure wood parquet is of course perfectly designed for this kind of application. The coating usually consists of several layers in order to obtain an optimum performance in both stain and abrasion resistance. Between the different layers intermediate curing or gelling is done and depending on the circumstances and the requirements a sanding step is included. Over the years the application and curing equipment were continuously improved. This resulted for example in higher productivity (faster cure speed) and better surface properties (scratch and abrasion resistance, stain resistance). This also allowed the development of coating systems that fill the wood pores and/or splits well. For application on flat surfaces by roller coater the 100% UV products are well introduced today and a large choice of binders is now available.

Increasing environmental pressure, the recognised need to move to non-polluting alternatives but also the benefits associated with the UV technology will stimulate the penetration of more specified applications of the parquet industry.

Important: polymers with FR-properties

In a world of increasingly stringent safety regulations, it is becoming more and more important to find polymers with flame retardant (FR) properties. In the case of coatings, whether radiation curable or conventional, their flammability can contribute to fire propagation. For this reason, where a significant level of flame retardancy is required (e.g. in some wood applications) coatings with flame retardant properties have had to be developed.

Two main classes of “flame-safe” coatings

- Flame retardant coatings, coatings that delay ignition and hinder flame spread.
  - Intumescent coatings, coatings that have the properties of the first class and also protect the substrate by formation of an insulation layer during its combustion.
  - Additives such as chlorinated/brominated aromatics, antimony halides, organophosphorus compounds etc. are commonly used to impart flame retardancy. However, this approach suffers from several drawbacks:
    - low compatibility with the polymer matrix
    - negative impact on the physical and mechanical properties of the coating
    - pigmented additives reduce the UV reactivity of the resin
    - additive migration leads to a blooming of the surface and to loss of FR effect

- flame retardant clear coats are not achievable with most of FR additives
- halogen based flame retardant systems show undesirable negative side effects (corrosive fumes, toxicity, environmental issues, etc.)

In order to avoid such drawbacks, two halogen-free binders containing phosphorus flame-retardant functionalities covalently bound to the polymer backbone and an application process were specifically developed for parquet flooring application.

This system meets the requirements of the parquet coating industry in terms of wood aspect, abrasion, scratch, chemical and solvent resistance combined with flame retardant properties in the radiant flooring panel test ISO 9239-1 and ignitability test ISO 11925-2 (Euro-classification of construction materials for flooring materials).

European fire regulations

In Europe, different national regulations exist with a multitude of standards to assess the reaction to fire of construction products. Recently, a harmonized European classification system for the reaction to fire behaviour of construction products has been approved by the European commission. It consists of 7 Euroclasses: A1, A2, B, C, D, E, F for materials excluding floorings and A1FL, A2FL, BFL, C1FL, D1FL, E1FL, F2FL for flooring materials. Classes B and BFL are the highest class that can be obtained for an organic substrate (see figure 1).

From 2002, the different Members States have to accept the European Fire Standards and Euroclasses alongside the existing national systems, as far as European product standards are available. This means that from 2002, European countries have to use the radiant flooring panel test ISO 9239-1 and ignitability test ISO 11925-2 for CE-market products.

Consequences of the euroclasses system: the reaction to fire test methods are harmonised with this system. Nationally, all countries will continue to define their own safety levels and requirement concerning fire safety. The national systems have to use these harmonised standards when European product standards do exist, no national standards will be allowed after a one-year transition period.

Reaction to fire

Wood based products can be veneered or have a thin non-wooden layer (paint or other coating) and in fire situations the performances depend on the wood species, the type of panel and the possible coating. For this reason the final product has to be tested in order to know its fire performances and to assign a proper classification.

Wood without flame retardant coating

Generally wood and wood based panels without any kind of FR treatment are in the DFL or EFL (low density product) classes of reaction to fire in the new Euro-classes System. The classification depends on the wood species (density is the main characteristic) and the properties of the other wooden components that may be included (wood based panels, the wooden core for multi-layer parquet, etc.) as well as the surface finish.

Wood with flame retardant coating

The classification of the solid wood and the wood based
Panel can be improved through specific treatments and obtain higher class of reaction to fire (as Euro-classes B₁ or C₁₆). The test for obtaining the reaction to fire classification has to be made for the final product; that means that the sample has to incorporate the treatments, varnishes and coverings. The classification of the wood flooring will be obtained according to the EN ISO 9239-1 and EN ISO 11925-2 tests. Wood products where the flame retardant treatment can be requested are:
- wood based panel (vertical)
- wood flooring (horizontal)
- wooden doors
- structural wood products
- wooden houses (exterior)

In the present study only the requirements of wood flooring will be considered.

Wood panels based on MDF beech veneer (class C₁₆), coated with a UV FR multi-layer system, reach class B₁₀₁ in the new harmonised European classification of construction materials (see figure 1). This is the highest class attainable for an organic substrate.

* class obtained from orientation tests

**Products and application system**

The characteristic of the two phosphorous-based binders for adhesion primer and sealer are outlined in table 1 and starting point formulations for primer and sealer in table 2.

The amount of reactive diluent in the sealer should not exceed 20% in order to maintain a sufficient concentration in phosphorus to get the required flame-retardant performance.

The application system has a total coat weight of approximately 140 g/m² and includes:
- an adhesion primer based on a water-based phosphorus containing polyester acrylate applied at 15 g/m² wet
- a sealer based on a UV 100% phosphorus containing polyester acrylate applied in 2 or 3 coats with a total coat weight of 80 to 90 g/m². It should be applied with a heated smoothing roll-coater
- a classical abrasion resistant UV coating applied in 2 coats with a total coat weight of 30 g/m²
- a classical UV topcoat (8 g/m²)

The high thickness of the phosphorus-based sealer is necessary to get the concentration in phosphorus needed to provide the flame-retardant performance of the system (see figure 2). The multi-layer application method is the following:

**Application of the primer**
- sanding of panels with 150 - 180 sandpaper
- one layer +/- 15 g/m² of the FR primer based on WB phosphorus containing polyester acrylate, dried in the flash off (at 40°C) then in the jet dryer (at 50°C), than cured with 1 UV lamp of 80 w/cm at 15 m/min
- sanding of panels with 320 sandpaper

**Application of the sealers**
- two layers of FR sealer based on 100% liquid phosphorus containing polyester acrylate, +/- 50 g/m² of the sealer were applied and cured with one UV lamp of 80 w/cm at 15 m/min, +/- 40 g/m² of the sealer were applied and cured with one UV lamp of 80 w/cm at 15 m/min. Application is done with a heated smoothing roll-coater at 40°C
- sanding with 320 sandpaper
- two layers +/- 15 g/m² each one of abrasion resistant sealer, each layer is cured with one UV lamp of 80 w/cm 10 m/min

**Application of the topcoat**
- one layer +/- 10 g/m² of topcoat cured with 2 UV lamps of 80 W/cm at 10 m/min

**Performances and data**
The UV FR multi-layer system applied on MDF beach veneer increase the classification in the European Harmonised Euroclass system for flooring materials (radiant flooring panel test ISO 9239-1) from C₁₀₁ to B₁₀₁. It decreases the ignitability, the flame spread, the rate of heat release and the smoke density (see figure 3). The abrasion resistance of the full system (primer/sealers/topcoat) was measured according to the falling sand method (ASTM F510-93) and outlined in table 3.

**Outlook**
Over the years, radiation curing has become a successful technology in the wood coatings industry. Under environmental pressure and to take advantage of this unique curing mechanism, new chemistries, like phosphorus acrylates have been developed to meet the new requirements of the market in flame retardant application.

If these resin developments can be efficiently integrated with new developments in application and curing equipment and with new photoinitiators, pigments and additives, the future continues to look bright for radiation curing technology in the wood coatings area.

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- Jean-Pierre Bleus was born 1949. He graduated in chemistry from the Université de Liège in 1971. From 1974 to 1975 he worked at UCB Chemicals in the development of binders for pressure sensitive adhesives. From 1976 to 1993 he ws with Reliance Wood coatings, a paint company active in solvent based and radiation curable coatings. Since 1993 he is in charge of the radiation curing application pilot unit at UCB Chemicals (now Surface Specialties UCB).
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Figure 1: Euro-classification of construction material for flame retardancy. Improvement of flame retardancy properties through the use of the UV-FR system (tested with radiant flooring panel test)
Figure 2: Cross-section of the flame retardant multi-layers UV-curable system
Figure 3: Comparison of MDF beach veneer non coated, coated with standard UV coating (non flame-retardant) and with the UV FR system
### Table 1: Characteristics of the phosphorus-based FR binders

<table>
<thead>
<tr>
<th></th>
<th>Binder for FR primer</th>
<th>Binder for FR sealer</th>
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<tbody>
<tr>
<td><strong>Water soluble phosphorus containing polyester acrylate, 75% solid content</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Höppler viscosity (25°C):</strong></td>
<td>3300 mPa.s</td>
<td></td>
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<tr>
<td><strong>Molecular weight:</strong></td>
<td>3000 g/mol</td>
<td></td>
</tr>
<tr>
<td><strong>Functionality:</strong></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Phosphorus content on solid:</strong></td>
<td>5% pH=6.5-7.5</td>
<td>5%</td>
</tr>
</tbody>
</table>

| **Phosphorus containing polyester acrylate, 100% solid content** |                       |                      |
| **Höppler viscosity (60°C):** | 7100 mPa.s          |                      |
| **Molecular weight:**    | 3000 g/mol           |                      |
| **Functionality:**       | 2                    |                      |
| **Phosphorus content on solid:** | 5%                   |                      |
### Table 2: Starting point formulations for FR primer and FR sealer

<table>
<thead>
<tr>
<th></th>
<th>Formulation for FR primer</th>
<th>Formulation for FR sealer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water soluble phosphorus polyester acrylate</td>
<td>96</td>
<td>Phosphorus polyester acrylate 100% liquid</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>4</td>
<td>Photoinitiator</td>
</tr>
<tr>
<td>Brookfield viscosity (20°C)</td>
<td>3300 mPa.s</td>
<td>Aminoacrylate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difunctional reactive diluent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Talcum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crystalline SiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brookfield viscosity (40°C):</td>
</tr>
</tbody>
</table>
Table 3: Abrasion resistance of the UV FR system (ASTM F510-93)

<table>
<thead>
<tr>
<th>Weight Loss (mg)</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>1 x 1000 g on each wheel</td>
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<tr>
<td>weight loss after 500 cycles</td>
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<tr>
<td>weight loss after 1000 cycles</td>
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<tr>
<td>weight loss after 1500 cycles</td>
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<tr>
<td>weight loss after 2000 cycles</td>
<td>127</td>
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<tr>
<td>weight loss after 2500 cycles</td>
<td>170</td>
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<tr>
<td>weight loss after 3000 cycles</td>
<td>213</td>
</tr>
<tr>
<td>weight loss after 3500 cycles</td>
<td>251</td>
</tr>
<tr>
<td>weight loss after 4000 cycles</td>
<td>289</td>
</tr>
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