

A New UV Polyurethane Dispersion for Outdoor Applications on Wood

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The changing landscape of the European outdoor joinery market presents both difficulties and opportunities for the wood finishes industry. In recent years, wooden window frames have lost market share to aluminium and even more to plastic, mainly because of appearance and the maintenance required by wooden products.¹

This is driving wood coatings manufacturers to formulate products with a longer lifetime, reducing the need for maintenance and being

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compliant with the new stringent European Union directives on chemicals and volatile organic compounds (VOCs).

In the Western European market of about 48,000 MT/year of coatings for outdoor joinery, waterborne systems have already rapidly replaced solventborne technologies. Window frames, exterior doors, shutters are mostly coated with conventional (non-radiation curable) waterborne coatings, usually based on acrylic emulsions or waterborne alkyds.

Although the performances and the ease of application of these coatings are often very good, improved productivity as well as better chemical and mechanical resistance, longer

maintenance intervals and improved weathering properties have been identified in the high-end part of the market.

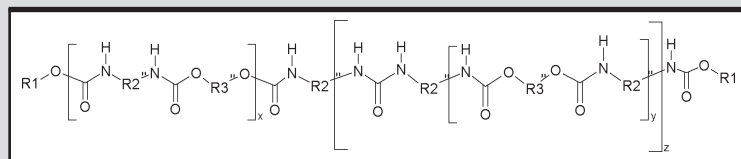
UV Polyurethane Dispersions Address High-End Market Needs

Some of the most promising developments within the waterborne polymer family involve radiation-curable polyurethane dispersions (UV-PUDs).² UV-PUDs are benefiting from a growth in the high-end coating market due to their performance and strong potential as well as energy consumption requirements. At the same time, they provide the advantages of waterborne polymers that allow easy and safe application (i.e., spray application, low-volatile organic content, and absence of irritation). So far most of their successful applications have been in indoor coatings (wooden furniture, resilient flooring, etc.).

A radiation-curable polyurethane dispersion designed especially for outdoor resistance can offer to the joinery industry the typical productivity benefits of higher cure speed such as the possibility of allowing the rapid stacking of coated items. Moreover, the coating displays a superior mechanical and chemical resistance needed to protect high-quality wooden materials from challenging use conditions. To meet these market demands, durable clearcoats are required that reduce photochemical degradation and moisture uptake. The coating must have good dimensional stability to avoid film failure (cracking) and loss of adhesion (flaking, peeling,

FIGURE 1

Model structure of an UV-PUD



blistering) arising from mechanical solicitations (scratch), thermal effects (freeze thaw) and water penetration at the coating interface.⁴

In this framework and in order to comply with these still unmet market needs, a brand new radiation-curable polyurethane dispersion has been developed and recently launched.

Chemistry Variants Obtain an Outdoor Resistant UV-PUD

UV-PUDs are at the interface between different chemistries and technologies⁴ and, hence, their unique features possess the advantages of both polyurethane polymers and radiation-curing technology.

Many variants have been used to obtain a stable colloidal dispersion of an acrylated polyurethane polymer. In most of the cases, several basic structural elements need to be present in order to obtain a balanced level of properties, at least one diisocyanate (a), at least one diol (b), at least one hydrophilic diol capable of dispersing the polymer in water and to ensure its colloidal stability (c), and at least one unsaturated alcohol and/or diol capable of binding to the polymer (d).

A model process was used for the study that was versatile enough to encompass a wide range of composition variants based on (a), (b), (c) and (d).

The modeled structure of the UV-PUD is represented in Figure 1. In all the variants, only one structural parameter was changed at a time, keeping the same stoichiometry.

An initial model polymer based on the use of 4,4'-dicyclohexylmethane diisocyanate (H12MDI) as component (a), a polyester diol made from adipic acid and neopentyl glycol as component (b), dimethylol propionic acid as component (c) and pentaerythritol triacrylate as component (d). It is referred in the text as dispersion A'.

A significant number of polymer variants have been made based on the modifications of the structural elements prone to enhance the weathering properties in the content of the known degradation pathways. The most representative of their category are shown in Table 1. The natures of the diisocyanates and the diols have been considered in this study. All the products contain the same amount of light absorber and hindered amine light stabilizer (HALS) additives, except model-dispersion A (similar to A')

TABLE 1

Characteristics of synthesized polyurethane dispersions

	Isocyanate	Diol	Solids (%)	Viscosity (mPa.s)	pH	Particles (nm)	Stability 60°C (days)
A	H12MDI	polyester 1	35.0	40	7.0	29	>10
A'	H12MDI	polyester 1	35.0	50	7.5	50	>10
B	IPDI	polyester 1	35.0	74	7.7	67	>10
C	HDI	polyester 1	35.0	2,240	7.8	75	>10
D	TMXDI	polyester 1	33.0	20	7.2	76	>10
E	H12MDI	polyester 1	35.0	48	7.6	35	>10
F	H12MDI	polycaprolactone	35.0	64	7.4	31	>10
G	H12MDI	polyester 2	35.0	48	7.1	51	>10
H	H12MDI	polyether	35.0	46	7.1	38	>10
I	H12MDI	polyacrylate	35.0	38	6.9	31	>10
J	H12MDI	polybutadiene	35.0	52	6.9	202	<10
New Dispersion K	H12MDI	polycarbonate	35.0	67	7.5	26	>10
L	H12MDI	polysiloxane	35.0	28	7.1	125	>10

TABLE 2

Formulation of polyurethane dispersions

100 parts	Polyurethane dispersion
1.5 parts	Photoinitiator
2.0 parts	Rheology modifier
1.5 parts	Matting agent
3.0 parts	Matting / scratch resistance agent
0.1 parts	Defoaming agent
0.3 parts	Wetting agent

where they are absent. All the polymers have been formulated with benzophenone-type photoinitiators except in model dispersion A" (without photoinitiator).

Application and Testing

The additives used for the formulation of water-based compositions are an essential tool for good application of the coating on wood. All the model-syntheses have been formulated with the aim to obtain a robust product for spray coating. The standard formulation is described in Table 2.

European Standard EN927 "Paints & varnishes-coatings materials and coating systems for exterior wood" inspired the tests carried out. However, although recognizing the necessity of standardized methods,⁵ these standard methods are often replaced with other methods that have proved their value in earlier comparisons of wood coatings.

The substrates used for this study are plain pinewood for the artificial weathering and beech for the chemical and mechanical resistance tests.

An impregnation primer is applied onto the wood by dipping in a commercial waterborne acrylic latex (copolymer methylmethacrylate: butylacrylate) diluted at 20% solids to obtain a 100 g/m² wet coating. The layer was physically dried at ambient temperature. An intermediate coat was then applied by dipping the sample in another commercial waterborne acrylic latex (copolymer methylmethacrylate: butylacrylate) diluted to 20% solids to obtain a 100 g/m² wet coating. The layer was physically dried at ambient temperature. The surface was sanded with a 320-grit paper.

A transparent topcoat based on formulation of the above, the A-L polyurethane dispersions was sprayed on the vertical wood pine panels at a thickness of 150 g/m² wet to obtain a

uniform and defect-free application without sagging. The physical drying started at room temperature and was completed in an oven at 40°C. The subsequent curing took place by passing the panels at 5 m/min under two 80 W/cm mercury lamps to ensure full crosslinking. In one case, an electron-beam irradiation (e.g., 50 kGy, 250 kv) was performed on a formulation containing no photoinitiator (A").

For performance testing, three coats of 75 g/m² wet of the similarly formulated A-L polyurethane dispersions were spray applied on beech wood. Physical drying started at room temperature and was completed in an oven at 40°C. The subsequent radiation curing took place by passing the panels at a speed of 5 m/min under two 80 W/cm mercury lamps. Under those conditions, a uniform and defect-free application was obtained.

The stain resistance of a coating was assessed by applying a test substance to the coating, covering it with a microscope glass and leaving it for four hours. The test substances used were a commercial glass cleaning product, 5% ammonia, 20% ethanol, butyl glycol, water, ketchup, mustard, red wine, coffee, 9% javel water, acetic acid and 2% eosine. The stains were wiped off with two rubs using a tissue saturated with isopropanol. The remaining stains were measured visually using a 0-5 scale, 0 = best. A low value (0) is expected to provide the best protection against any household product.

TABLE 3

Critical times of degradation (t_c) in hours for coated wood (beech)

	A	A'	A"	B	C	D	E	F	G	H	I	J	New Dispersion K	L	IS
t _c #1	875	875	1,500	375	500	375	625	1,125	625	625	500	NA	1,625	625	950
t _c #2	2,500	1,750	2,500	1,125	750	1,625	2,250	2,125	1,375	1,625	1,250	NA	2,875	1,125	2,350

TABLE 4

Mechanical resistance and chemical resistance after four hours (DIN 68 861) for coated wood (beech)

*best=0	Cleaning product	Ammonia 5%	Ethanol 20%	Butyl glycol	Water	Ketchup	Mustard	Red Wine	Coffee	Javel 9%	Acetic acid	Eosine 2%	Adhesion	Scratch, Erichsen	Scratch, nail	Blocking
	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	0*-5	N	0*-5	0*-5
A	0	0	0	5	0	0	0	0	0	0	0	0	1	21	0	0
New Dispersion K	0	0	0	0	0	0	0	0	0	0	0	0	0	18	0	0
IS	4	4	0	5	0	0	2	2	2	3	0	3	0	12	5	1

Adhesion was measured by crosscut and hatch and the adhesion loss was expressed in a 0-5 scale, 0 = best. A low value (0) is necessary to ensure a strong permanent bond between the coating and the substrate.

The scratch resistance was measured using the Erichsen pen tester and expressed as the minimum force (Newton) applied to the needle needed to scratch the surface. High values are indicative of a hard surface capable of efficiently protecting the wood surface.

The blocking was tested by putting the coated wood panels side by side and applying a pressure equivalent to 500 kg/m² at a temperature of 40°C during 16 hours.

Polycarbonate Backbone Provides Clear Improvement

Initially all the coated pine panels were submitted to artificial weathering using a Xenon Weather-O-Meter with the conditions described earlier.

Two types of critical times (t_c) needed to be measured: one linked to the appearance of visual defects on the wood surface and another corresponding to the complete degradation of the sample. The values recorded the means of at least

two samples and addressed the spread of results due to the naturally porous nature of the material. The results (Table 3) showed both significant trends and differences between the various polymers that would occur for the end user.

The reference product (A') performs well using the acrylic industry standard (IS) as a benchmark.

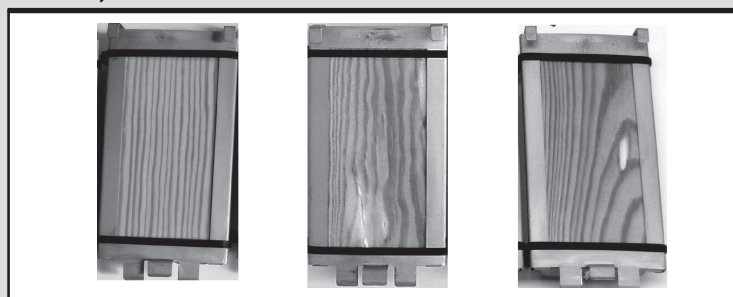
The product without the light absorber and stabilizer additives (A) seems to perform better than A'. A tentative explanation is that the hydrolytic degradation pathway is most important in a polyester-based

polyurethane, so that the additives play only a minor role in the overall degradation pathway. This assumption is confirmed by results obtained on free films.

The product without the photoinitiator (A''), cured by electron beam, showed a strong improvement of the aging behavior. This was not surprising because the photoinitiator, mandatory when UV light is used for crosslinking, stays partially unaffected in the cured film and acts as a source of radicals during the exposure of the coating to light. Perspectives are thus opened to adapt the nature and the

FIGURE 2

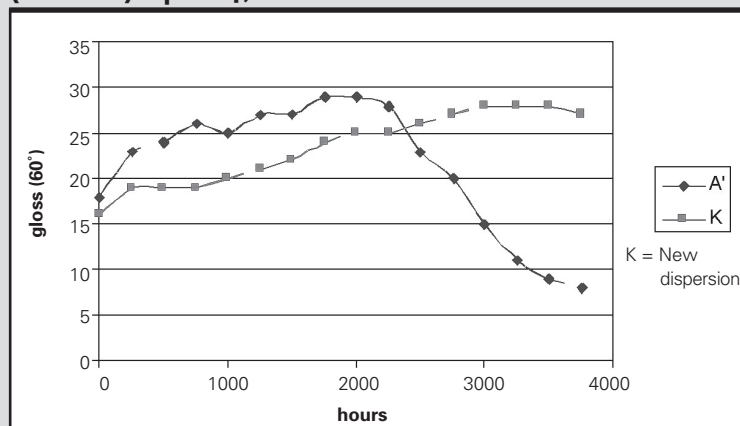
Artificial weathering (Xenon) of coated wood (pine) after 2,000 hours



From left to right: new dispersion, polyester (A) and acrylic latex (industry standard)

FIGURE 3

Artificial weathering (Xenon) of coated panels (neutral) up to 4,000 hours



level of the photoinitiator to make it the most suitable for aging. The effect of the diisocyanate (B, C, D) was not found to be critical for the aging performance. The better result was obtained with H12MDI (A').

The switch from dimethylol propionic acid to dimethylol butanoic acid (E) shows a trend for a minor improvement of the aging performance, especially on the second critical time. The use of a polycaprolactone backbone (F) shows a more obvious improvement, which is not the case for the fatty polyester backbone (G).

The polyether backbone (H) presented an overall status quo while the polyacrylate backbone (I) did not meet expectations. The polybutadiene backbone (J) was the sole modification that gave a dispersion with high-particle size and with poor colloidal stability, thus prohibiting its use in the aging test. The polycarbonate backbone provided the clearest upgrade of the aging performance, with a significant improvement of both critical degradation times. Finally, the incorporation of a silicone in the backbone (L) surprisingly depressed the aging performances.

All the results obtained used the industry standard (IS) as a benchmark. As such, it is important to note that only the new dispersion K has significantly better aging performance than the acrylic latex IS.

Taking the new dispersion K as the best candidate, the chemical and mechanical tests were performed on beech wood, using the polyester backbone (A') as the reference together with the IS. The results are disclosed in Table 4.

The two UV-PUDs are clearly better for all the stain tests and the new dispersion K is even slightly better than the polyester (A')—in particular for the severe butyl glycol stain. The radiation-cured materials are also clearly superior for scratch resistance using the nail scratch test as well as the Erichsen test. The superiority in blocking resistance is however only slight. This is probably due to the tailored-made formulation of the ready-to-use industry benchmark. The adhesion is good to excellent in every case.

As an illustration, Figure 2 shows a comparison of the new dispersion K with the polyester (A') and the IS after

2,000 hours aging with the Xenon test. Only the new dispersion K shows no degradation while the second is already quite damaged as seen by large white areas on the wood surface and the third shows the first signs of the same development.

The new dispersion K and the polyester (A') were also tested on metal panels coated with a white, super-durable polyester film. The coated plates were submitted to the Xenon test under the same conditions as the pine panels. The gloss retention was followed over time and measured every 250 hours. This evolution is presented in Figure 3.

The gloss of the two coatings was initially quite similar; they both showed an increase of the gloss up to a point where the degradation started and then the gloss decreased. For the new dispersion K, the maximum was found to be at about 3,750 hours and 2,000 hours for the polyester (A'). It is believed that the initial increase of the gloss is due to the relaxation of the coating as a consequence to the increased temperature of the test. The decrease of gloss is due to the visible coating degradation with surface defects similar to chalking and orange peel. However, this phenomenon happens later than the observed degradation of the coated wood.

Conclusions

Wood is a natural, ecological and renewable porous substrate used as building material and brings many advantages compared to plastic and aluminum. A coating is used to enhance its appearance and protect it from mechanical and chemical damage especially under challenging exterior conditions.

In this study, a novel polycarbonate based radiation-curable polyurethane dispersion has been shown to provide improved weathering resistance compared to an acrylic emulsion

industry standard. As expected by a radiation-curable resin, mechanical and chemical resistances are better than the industry standard. Moreover, the waterborne nature of the polymer presents a low viscosity that permits a robust and safe application by spray. The product is almost free of VOCs and non-irritating to skin and eyes. It is also tack-free after drying and before curing. Such a product is thus particularly recommended for use as a transparent topcoat for wooden joinery where excellent outdoor resistance is essential.

Technical innovations are still very relevant in the coating industry and can bring added value from the raw material suppliers to the consumers, via formulators and finished goods manufacturers.

Acknowledgements

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References

1. IRL Information Research, "The Western European Market for Industrial Wood Coatings," 5th edition (2004), 41.
2. M. Tielemans, P. Roose, P. De Groote and J.C. Vanovervelt, "Colloidal Stability of Surfactant-Free Curable Polyurethane Dispersions," Progress in Organic Coatings 55 (2006) 128-136.
3. M. de Meijer & al., "Mechanism of Failure in Exterior Wood Coatings" Proceedings of the International Woodcoating Congress (2002), 3d, 28-30.
4. K. Buysens, M. Tielemans and Th. Randoux, "Radiation Curable Coatings: A Variety of Technology for a Variety of Applications," Pitture e Vernici-European Coatings (2002) 19, 78, 27.

5. E.R. Miller & al., "Quality Assurance for Exterior Wood Coatings through European & British Standards," Surface Coatings Internat. Coatings J. (2006) 89, 96-99.

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