Exterior Wood Coatings based on New Waterborne One-Component UV-Curable Polyurethane Dispersions

Robert A. Wade, Bayer MaterialScience LLC, Pittsburgh, PA.

Michael J. Dvorchak, Bayer MaterialScience LLC, Pittsburgh, PA.

Background

Wood coatings formulators over the last several decades have continued to try and reduce VOC/VHAPs of coating systems by turning to new polymer technologies that allowed them performance yet still protecting the environment. One of the earlier introductions was a water-reducible, unsaturated polyester that was UV curable.[1] This system worked well but could not be used for exterior applications. Further developments saw the developments of polyurethane dispersions (PUDs) and the paradigm shift to products that could be produced in acetone with the unique ability to commercially distill the acetone away leaving a polymer and water. [2] The next step in these developments was the ability to cross-link the one component product PUD using UV radiation.

Pigmentation of UV cure wood coatings based on non-air-inhibited unsaturated polyesters were evaluated in the early 90's and reported in various technical papers. A low-viscosity product with no styrene and no solvent could be formulated to cure at films as thick as 11.0 mils and pigment-to-binder ratios up to 0.3. This was accomplished by using special UV equipment and proper selection of photoinitiators.[3] This paper describes new development work with unique waterborne one-component cosolvent free UV-curable polyurethane dispersions, that can be formulated to make both clear and pigmented exterior coatings.

Introduction

Radiation curable coatings have been used in the wood coatings industry for several years. Major benefits of radiation cure are the very fast curing speed and high cross-link density. High performance coatings with extremely low VOC/VHAPs, excellent abrasion as well as chemical resistance are obtained.

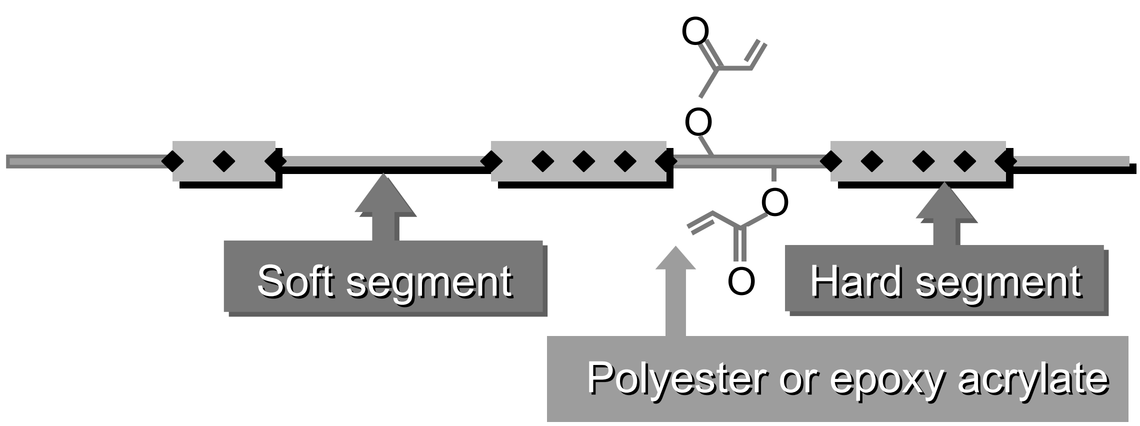
The highest volume sector for UV-cure coatings is the pre-finished wood flooring market. This is mainly because of the very high production speed and excellent abrasion resistance properties of UV-cure wood coatings. Other growth areas include interior applications such as kitchen cabinets, millwork, and furniture. Traditional UV raw materials are typically adequate to meet the coating performance requirements for these interior coatings. That is because they generally do not require high-end weathering resistance or high flexibility properties.

Coatings for exterior millwork such as window frames, exterior siding, and doors require additional performance properties such as excellent light stability, high flexibility, and freeze/thaw cycling properties. New Waterborne UV-Curing cosolvent free Polyurethane Dispersions were recently developed that provide excellent exterior weathering properties, high flexibility, and improved adhesion to difficult substrates such as wood and plastic. This paper will describe the attributes and performance properties of such systems.

Radiation-curing dispersions

A broad variety of products have been commercialized in the wood coatings market. The most promising environmentally-friendly technology of these systems is waterborne UV-curing PUDs. The chemical structure of UV-PUDs is quite similar to that of a regular PUD that consists of hard and soft segments. The broad raw material selection available for the design of each segment allows optimization of a huge variety of properties. In most cases, high performance soft segments contribute a certain flexibility, while di(poly)isocyanates and short chain diols contribute hardness and resistance. Several routes for the introduction of acrylic double bonds have been reported. In our experience, the best polymer performance can be obtained by introducing double bonds along the polyurethane chain, rather than to attach acrylic units to only the end of the chain or to physically blend polyurethanes with acrylic monomers or oligomers. The use of acrylic monomers / oligomers has additional industrial hygiene issues and stability concerns.[4-6]

Fig. I: Building blocks of UV-curing polyurethane dispersions



Coatings based on PUDs exhibit the highest growth potential in the wood market. The key property of this type of coating is its similarity to conventional PUR coatings – i.e. application methods, drying times and performance attributes.

UV-curing aqueous dispersions have a weight-average molecular weight above 200,000; which is many times higher than that of traditional 100% solids UV systems consisting of unsaturated acrylates and reactive thinners - a very striking advantage. That is why the waterborne systems need much less radical crosslinking to obtain the desired properties. These high molecular weight polymers also reduce the hazards of skin irritancy associated with traditional low molecular weight acrylic oligomers. Another breakthrough in this field is the development of cosolvent nmp-free PUDs. This helps the formulator to develop coating formulations that are near-zero VOC.

UV Curing and UV Equipment

UV radiation initiates coatings cure in the presence of photoinitiators. It can be either by free-radical or cationic mechanisms. Numerous models and types of UV curing equipment are available from many suppliers. Typically the curing systems consist of a high voltage power supply, a control panel and a curing head. Two types of lamps are typically used in UV curing i.e. regular arc lamp and microwave lamp. The spectral output of the lamps can be adjusted by doping the lamps with various trace metals. Each lamp has specific outputs measured in nanometer wavelength. The challenge of the formulator is to match the absorption of the photoinitiator to the spectral output of the lamp to cure the coatings, especially in highly-filled/pigmented systems. The desired result is a highly crosslinked film that can meet several market standards. Additionally, UV coatings are environmentally friendly – most systems are typically solvent-free so emissions (VOC/VHAPs) and flammability are not a concern.

Benefits of Waterborne UV

100% solids UV coatings are used extensively in pre-finished wood flooring because of the very high curing speed. A very important aspect is that UV wood floor coatings are applied with a roll coater, thus reducing the risk of skin irritation and atomization. Conventional UV spray coatings typically contain reactive monomers or solvents to reduce viscosity for spray. These reactive diluents are very low molecular weight resins that have safety concerns, especially for spray applications. The addition of solvents to UV resins will add VOCs to the formulated coating. Additionally, uniform very thin coatings are difficult to consistently reproduce with very high solids coatings.

Many of the issues inherent with 100% UV and solventborne UV can be overcome by using waterborne UV PUDs. Another advantage of waterborne UV is the ability of the applied coating to physically dry before UV-curing. This is a key characteristic of waterborne UV and offers the following benefits:

- Reduced dirt pick-up
- No uncured sticky overspray
- Parts can be handled before UV-cure
- Ability to spot repair before UV-cure
- Reduced hazardous waste disposal issues

One drawback of waterborne UV compared to 100% solids UV is the need to flash the water before UV-cure. This water-flash step is critical, otherwise the appearance and performance will be negatively affected. The water-flash step can be easily implemented by installing a stacking oven between the spray application zone and the UV-cure source. This additional step will increase production time to some extent, but can be engineered with minimal floor space. Production lines currently using solventborne coatings for flash/bake cycles can easily utilize existing ovens. Typical flash times required are about 10 minutes at 50°C. It is possible to reduce the water flash step to less than 5 minutes by using specialized drying equipment such as IR/Convection ovens, microwave ovens, or dry-air ovens. A combination of high circulating air speed, IR lamps and dried air can yield very short drying times. The main factors to reduce the drying times for waterborne coatings are the air velocity, humidity, and the wet film thickness.

Waterborne UV-Curable PUDs for Exterior Coatings

New UV-curable PUDs have been developed to meet the demanding property requirements for exterior coatings. These new materials are comprised of high-end aliphatic di(poly)-isocyanates and select polyols that contribute to tough elastic properties. Table I shows the typical properties of a UV-curable PUD and Table II has the physical properties of a clear formulation based on a UV-curable PUD:

Table I: Typical properties of UV-Curable PUD raw material

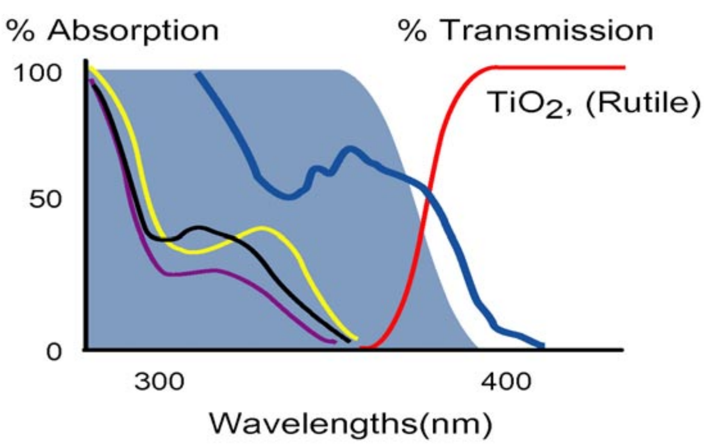
Solids %	approx. 40% supplied in water
Viscosity	< 50 sec (Ford 4 cup)
pH	7.0 – 8.0
Particle size	50 nm – 150 nm (Horiba)

Table II: Physical properties of clear formulation based on UV curable PUD:

Hardness before UV - pendulum (D4366-95)	10 sec
Hardness after UV- pendulum (D4366-95)	70 sec.
Film Clarity	Excellent
Elongation ISO 527-2	~ 80%
Tensile Strength ISO 527-2	27 N/mm2 (3900 psi)
Blocking, 0.15 Kg/cm2, 16 hr 50'C	4

Pigmented formulations are easily produced by dispersing pigments and fillers into waterborne dispersing additives and water, then mixing the pigment dispersion into the binder portion. Traditional photoinitators used for clear coatings should not be used in pigmented systems because they may activate in the same UV range that is blocked by the titanium dioxide. The absorption of titanium dioxide and various photoinitators is represented in Fig. II. As seen in Fig. II, it is very important to select a photoinitiator package that has peak absorption outside the UV wavelength of the pigment package. Gallium doped lamps e.g. ("V" lamps) are recommended for pigmented coatings because of their longer wavelength spectral output.

Fig II: Absorption curves of various photoinitiators.[3]



Formulations based on UV curable PUDs are easily modified to meet various application methods such as conventional spray, airless spray, vacuum coating, and roll-coating. Conventional waterborne additives can be used to improve surface wetting, defoaming, block resistance, and surface appearance properties. The low photoinitiator demand for UV-curable PUD's improves cost efficiency compared to traditional UV curing coatings. Standard UV absorbers and light stabilizers can be incorporated into formulations to improve exterior durability and gloss retention. Additions of acrylic emulsions are possible to improve cost performance and enhance specific property requirements. Coatings formulated with waterborne UV coatings can provide the following benefits:

- High Productivity
- Outstanding Weathering, even in clear
- One Component
- High Elasticity, even at low temperatures
- Excellent Chemical Resistance
- Tough and Scratch Resistant
- Various Application Methods
- Physical Drying Properties
- High UV-reactivity
- Fast Water Release
- Suitable for Clear and Pigmented Coatings
- Very Low VOC, Environmentally Friendly
- Reduced Emissions
- Safer to Handle

Weatherable Millwork Coatings

The term millwork is used to define a wide range of manufactured components for the construction industry. These components are used for both interior and exterior applications such as windows, doors and molding. Interior and exterior coatings can have a completely different set of property requirements based on their end-use.

For example, several high-end window manufacturers offer 10 year warranties on the durability of the finish on exterior windows. The topcoats used are generally very high performance coatings, since they require very high weathering resistance, gloss retention, and flexibility properties. Two component (2K) polyurethanes are used because of their high-performance properties.

Environmental regulations are continually changing to reduce both plant emissions and VOCs of formulated coatings. These mandates can be enforced on a Federal level, State level, or even a local level. For example, the South Coast Air Quality Management District (SCAQMD) has mandated Rule 1136 for clear and pigmented sealers, topcoats, and primers. The VOC limit will be reduced to 250 grams/liter. The following table illustrates several organization proposals:

Table III: Industrial Maintenance Coating VOC Limits for 2005.[7]

Organization	Grams/Liter
National VOC Rule	450
OTC Rule	340
DE,NJ,MD,NY,PA,VA	340
CARB SCM - STAPPA/ALAPCO	250
SCAQMD	250

Millwork manufacturers are demanding low VOC, high productivity, and high performance coatings from their paint suppliers. The options are limited but coatings based on UV curable waterborne PUD's can meet the challenge.

The Window and Door Manufacturers Association (WDMA) has implemented an Industry Specification (T.M. 12-2000) for factory applied pigmented coatings on wood and cellulosic composites for millwork. This specification includes abrasion resistance, film adhesion, chemical resistance, freeze/thaw cycling, acid resistance, mortar resistance and block resistance. In addition the coating must pass outdoor weathering exposure and accelerated weathering specifications.[8] The challenge of the formulator is to develop an excellent weathering coating that maintains toughness, flexibility, and gloss in outdoor conditions exposed to UV and thermal temperature changes.

We have developed a test method to evaluate both gloss retention and flexibility of accelerated weathered films. The test method and specifications for the accelerated weathering are as follows:

<u>QUV Accelerated Weathering Tester - ASTM G-154, cycle 1</u>

- Bulb type = UVA – 340 bulb
- Irradiance = 0.55
- Conditions = 6 hours UV @ 50°C followed by 6 hours condensation @ 60°C

Pigmented coatings were prepared, spray-applied to plastic substrates, and exposed in a QUV for 1000 hours. A duplicate of 5 panels for each system was tested. Various technologies were evaluated based on their high performance properties and low VOC attributes. Two different technologies were selected after initial screening; a one-component waterborne UV coating based on a UV-curable PUD, and two-component waterborne polyurethane based on an OH functional acrylic and a water-dispersible aliphatic polyisocyanate. Also, a control system based on a standard 2K solventborne PUR was tested. Both waterborne coatings were formulated at very low VOC, contained about 16% PVC (titanium dioxide/filler), and applied at about 30 to 40% volume solids. All the coatings contained standard light stabilizers and/or UV absorbers.

Mechanical strength and gloss were measured before exposure and after 1000 hours exposure in the QUV weathering tester. Mechanical strength was measured with an Instron tester using test method ASTM D-412 (tensile, rubber properties) at 5.0 inches per minute speed. The tensile strength (psi) and elongation % properties are reported. The coating films thickness was 1.5 – 2.5 mils (35 – 60 microns). Both 20° and 60° gloss measurements were recorded. The following table reports initial gloss and gloss after 1000 hours QUV exposure.

Table IV: Gloss readings of 1K UV-PUD, 2K Water PUR and 2K Solvent PUR

	UV-PUD	**2K Water PUR**	**2K Solvent PUR**
Initial 20° gloss	35	7	15
Initial 60° gloss	74	39	55
1000 hours QUV - 20° gloss	26	4	9
1000 hours QUV - 60° gloss	67	30	45
20° gloss retention after 1000 hrs. QUV	74%	61%	60%
60° gloss retention after 1000 hrs. QUV	90%	77%	82%

The UV-PUD gloss retention for the 20° and 60° readings were 74% and 90% respectively. The 2K Water PU gloss retention properties were slightly lower. The Delta E for yellowing was less than 1.0 for both systems. All three systems tested performed very well for gloss retention. In addition to gloss retention and light stability, exterior coatings must maintain flexibility to resist cracking and delaminating. This is especially important for outdoor exposures to UV, water, and temperature changes. The following table shows the tensile properties and elongation properties of the coating films before and after 1000 hours QUV accelerated weathering exposure:

Table V: Mechanical properties of UV-PUD, 2K Water PUR and 2K Solvent PUR

	UV-PUD	2K Water PUR	2K Solvent PUR
Initial tensile properties (psi)	1746	1918	5200
Initial elongation properties	36%	41%	8%
Tensile after 1000 hours QUV (psi)	2820	3203	6849
Elongation after 1000 hours QUV	38%	11%	1%

As seen in Table V, the tensile strength of all the coating systems increased after QUV exposure. This increased tensile result was typical based on multiple tests of several different technologies. The UV-PUD elongation % was virtually unchanged and maintained excellent flexibility properties after 1000 hours QUV accelerated weathering exposure

Accelerated weathering is one screening tool to evaluate coatings systems for exterior application. In addition to accelerated weathering it is very important to evaluate actual outdoor exposures. Outdoor weathering was conducted at 45° South in Barcelona, Spain to evaluate actual outdoor exposure. Clear coatings were prepared and applied over stained wood substrates. The UV-PUD was tested alongside commercial polyacrylate dispersion and a commercial polyurethane dispersion. The following picture in Figure III shows the actual weathering racks. Table VI reports the 60° gloss numbers up to two years outdoor exposure in Barcelona, Spain

Fig III: Weathering study in progress in Barcelona, Spain

Table VI: 60° gloss numbers of clear coatings

	Gloss 60°					
	Initial	3 Months	6 Months	9 Months	1 year	2 years
UV-PUD	90	89	89	86	83	80
Commercial PAC-Disp.	84	81	80	80	80	75
Commercial PUR-Disp.	78	73	69	67	69	65

The QUV accelerated weathering and actual outdoor weathering for the UV-PUD showed similar results. This demonstrates a very positive correlation between natural weathering and laboratory exposure techniques.

Conclusion

1. Many of the issues inherent with 100% UV can be overcome by using waterborne UV PUDs. Waterborne UV PUDs are supplied in water and comprised of very high molecular weight polymers. This significantly reduces the risk for both skin irritation and spray application hazards.

2. New Waterborne UV-Curing co-solvent free PUDs provide excellent exterior weathering properties, high flexibility, and improved adhesion to difficult substrates such as wood and plastic. Both clear and pigmented coatings are possible.

3. Formulations based on UV curable PUDs are easily modified to meet various application methods such as conventional spray, airless spray, vacuum coating, and roll-coating. Conventional waterborne additives can be used to improve surface wetting, defoaming, block resistance, and surface appearance properties.

4. Environmental regulations are continually changing to reduce both plant emissions and VOCs of formulated coatings. Coatings based on UV-Curable PUDs can meet these new stringent environmental regulations.

5. Accelerated weathering testing and outdoor exposures have demonstrated the excellent gloss retention and flexibility properties of coatings based on UV-curable PUDs.

References

1. Dvorchak, M. J. and Riberi, B. H. ‘Water-Reducible, Unsaturated Polyesters as Binders and Clear Coatings for UV-Curable Furniture Coatings’ - Journal of Coatings Technology, 64, No. 808, 43 (1992)
2. Dietrich, D. "Aqueous Emulsions, Dispersions and Solutions of Polyurethanes; Synthesis and Properties" Progress in Organic Coatings 9(1981) 281-340
3. Dvorchak, M.J. ‘UV Curing of High-Build Coatings Based on Non-Air-Inhibited Unsaturated Polyesters’ – Journal of Coatings Technology, 67 No.842, 49 (1995)
4. M. Gerlitz, R. Awad, Proc. 28th Int. Waterb., High-solids & Powder Coat. Symp., New Orleans 2001
5. W. Fischer, E. Lühmann, D. Rappen, J. Weikard, Proc. European Coatings Symp., Nürnberg 2001.
6. C. Irle, R. Roschu, M. Bayona, M. Johnson, Proc. 30th Int. Waterborne, High-solids & Powder Coatings Symp., New Orleans, 2003.
7. Kapsanis, K. Journal of Protective Coatings and Linings, Oct., 2005
8. http://www.wdma.com/i4a/pages/index., Industry specification, T.M. 12-2000
9. C. Irle, M. Bayona, B. Wade, M. Dvorchak, Proc. RadTech UV & EB Technology Expo & Conf., Charlotte 2004