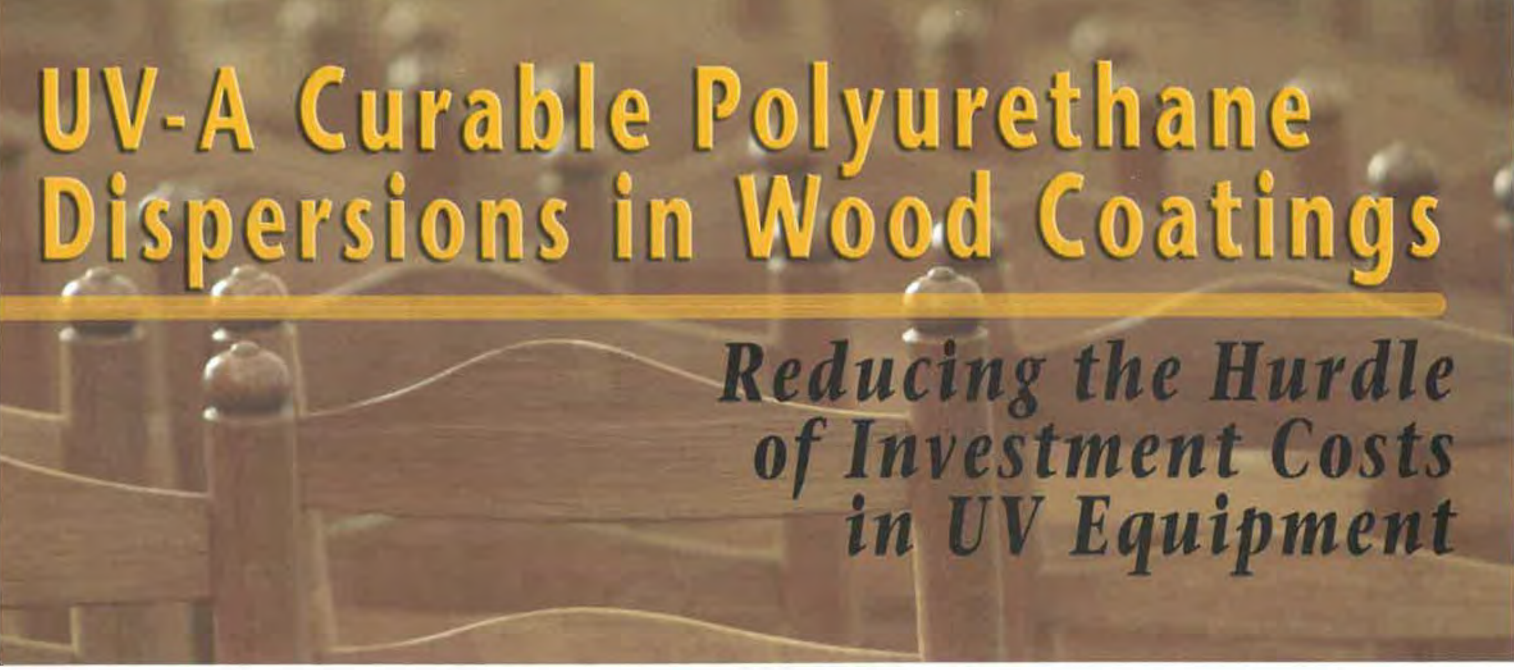

UV-A Curable Polyurethane Dispersions in Wood Coatings

Reducing the Hurdle of Investment Costs in UV Equipment

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

When complex substrates must be coated there is always the concern of uncured surfaces in shadow areas. Typically, more expensive UV equipment that optimizes a homogeneous radiation exposure is necessary, which requires higher capital investment. This has been seen for years as the largest hurdle for the industrial coater.

A new waterborne coatings system based on UV-PUDs can be cured with low energy UV-A lights, without sacrifice of performance properties for wood coatings applications. These types of lamps are significantly cheaper in their investment costs as well as in their maintenance. In this article, coatings performances are discussed with special respect to low intensity UV-A lamps, UV-curing PUDs, and the effect of adding self-crosslinking dispersions. The effects of adding water-dispersible polyisocyanates and carbodiimide crosslinkers to such coatings are also be presented.

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: 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 spe-

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cific 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.

By far, the major benefit of UV coatings is improved productivity. UV curing is fast, with line speeds up to 1,000 ft/min. This allows coated products to be packaged immediately after curing and ready for shipment. The quick cure also minimizes substrate heating, which is ideal for curing heat sensitive substrates. Additionally, UV coatings are environmentally friendly—most systems are typically solvent-free so emissions (VOC/VHAPS) and flammability are not a concern.

The high investment costs of UV equipment were seen for years as the biggest hurdle for the industrial coater entering into UV-curing technology. This can be a major roadblock that keeps suppliers from switching from conventional coatings to UV coatings. Particularly, smaller manufacturers may not have the capital to invest in a new UV line.

Recent developments in the automotive refinish market have addressed the cost issue of UV-curing equipment. New low intensity lamps are available from numerous suppliers that can effectively cure properly formulated UV coatings. The major benefits are lower cost and improved worker safety.

In 2001, the concept of using a UV-A lamp (conventional UV lamp that has a filter that blocks UV-B and UV-C) to cure a primer system for the automotive refinish market was introduced. Ultraviolet radiation is more energetic than visible light, consisting of radiation less than 400 nm. Traditional lamps for radiation cure emit UV-A, UV-B, and UV-C light, of which UV-A radiation (315 nm to 400 nm) is the lowest in energy. UV-C overexposure is associated with corneal burns and severe sunburns. UV-B is linked to DNA damage, which can lead to cataracts and skin cancer. UV-A radiation is present in the sun's rays, tanning booths, and phototherapy devices. *Figure* 1 shows spectral data from a UV-A lamp where filters are used to block the higher energy ultraviolet light.[1]

Overexposure to UV-A radiation can be harmful, but there is much less risk associated with UV-A radiation versus shorter wavelength UV light. However, the lower energy and shifted spectral output of UV-A lamps introduce limitations to the coating's formulator. Oxygen inhibition of the coating's surface and pigmentation preventing through-cure are two concerns. Since the concept was introduced, paint suppliers to the refinish market have worked to formulate materials tailored to UV-A light sources. One recent introduction involves the use of a proprietary pulsing light source instead of a continuous source of UV-A energy. This pulsed light source is purported to be effective in minimizing oxygen inhibition by generating a large number of active polymerization sites.

RADIATION-CURING DISPERSIONS

Conventional UV coatings consist of liquid oligomers, monomers, photoinitiators, and various additives. UV coatings may or may not require solvent to reduce viscosity to improve appearance characteristics. Typically, reactive diluents are used to lower viscosity and eliminate the need for a solvent flash-off step before UV curing. However, these reactive diluents are very low molecular weight resins that have safety concerns, especially for spray applications.

A broad variety of products have been commercialized in the wood coatings market. The most promising technology of these systems is the 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 toolbox available for the design of each segment allows for 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-suited method is to introduce double bonds along the polyurethane chain, rather than to attach acrylic units to only the end of the chain or to mix polyurethanes with acrylic monomers or oligomers.[2-4]

Figure 1—UV-A lamp spectral output with blue filters (wavelength in nm).

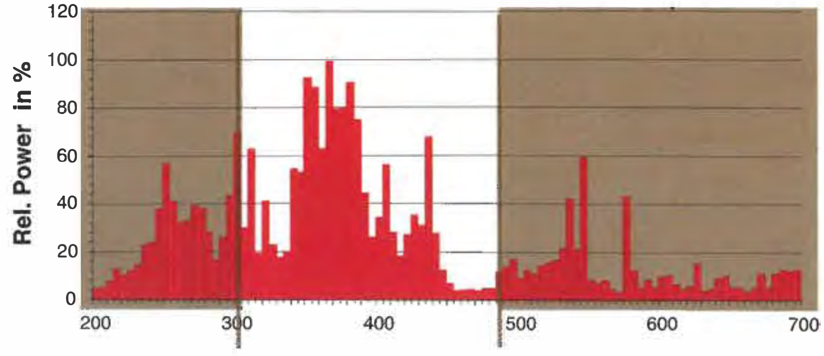


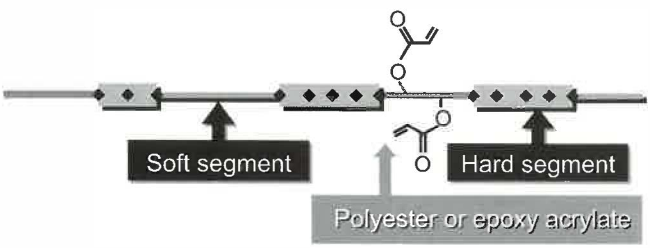
Table 1—Hardness Properties at Various Cure Conditions

System	Flash/Bake	Lamp Type	Cure Time Distance	Dosage (UV-A) J/cm^2	Pendulum Hardness (sec)			Block Resistance
					Initial	1 week	2 weeks	
A	7 min @ 100°F/ 10 min @ 150°F	No UV	N/A	N/A	23	34	34	pass
A	7 min @ 100°F	H+S Autoshot UV-A 400	6 min 10 in.	18	98	106	115	pass
A	7 min @ 100°F	Panacol 450 Fe UV	8 min 10 in.	7.7	92	113	118	pass

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 PUD 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 systems consisting of an unsaturated acrylate and a reactive thinner—a very striking advantage. This 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.

Figure 2—Building blocks of UV-curing polyurethane dispersions.



We developed a specialized "acetone-process" to manufacture PUDs without the presence of cosolvents like N-methyl pyrolidone (NMP) in the final product. This acetone-process is also used in the manufacture of radiation-curing dispersions. The acetone used for polymer synthesis is stripped off afterwards, resulting in raw materials with no solvent content. The benefit is a solvent-free dispersion with a highly reproducible molecular structure.

LOW-INTENSITY UV-A CURED WATERBORNE COATINGS

The speed of cure for conventional high intensity UV-cured coatings is ideal for high throughput lines. However, some applications may not require a three-second cure and six minutes may be suitable. New developments in the automotive refinish market have broken new ground for UV technology. These inexpensive low intensity lamps that emit only in the UV-A region can significantly increase the throughput of cars in a body shop and improve worker safety.

Recent developments using similar UV light technology from the auto refinish market were evaluated for wood coatings applications. New wood formulations were developed that cure in four to eight minutes us-

Table 2—Chemical Resistance Properties at Various Cure Conditions

System	Bake	Lamp Type	Cure Time Distance	Dosage UV-A) J/cm^2	Acetone[a]		Ethanol/Water 1/1[a]		Muphy's Oil Soap[a]	
					Covered	Uncov.	Covered	Uncov.	Covered	Uncov.
A	7 min @ 100°F 10 min @ 150°F	No UV	N/A	N/A	bl, soft[b]	bl, soft	soft	NE	soft, dull	dull
A	7 min @ 100°F	H+S Autoshot UV-A 400	6 min 10 in.	18	NE	NE	NE	NE	soft, dull	NE
A	7 min @ 100°F	Panacol 450 Fe UV	8 min 10 in.	7.7	NE	NE	NE	NE	soft, dull	NE

(a) 16-hr chemical exposure.
(b) Rating system: NE—no effect; bl—blistered; soft—softened; dull—downglossed.

Table 3—Hardness and Chemical Resistance with Addition of Carbodiimide Crosslinker (System B)

		Pendulum Hardness (sec)		Acetone[a]		Ethanol/Water 1/1[a]		Murphy's Oil Soap[a]	
System	Lamp Type	Initial	7 days	Covered	Uncov.	Covered	Uncov.	Covered	Uncov.
B	No UV	36	44	sl. soft[b]	NE	sl. soft	NE	NE	NE
B	Hotshot UV 400	87	118	sl. soft	NE	NE	NE	NE	NE

(a) 16-hr chemical exposure.
(b) Rating system: NE—no effect; sl. soft—slight softening when scraped with wood applicator stick.

ing UV-A lamps, and pass standard industry testing, e.g., KCMA, office furniture, etc.

Initial developmental formulations consisted of a UV-curable polyurethane dispersion combined with a fatty acid modified polyurethane dispersion. The addition of the self-crosslinking PUD was found to provide the following benefits:

- improved physical drying
- improved cure/properties in shadow areas
- reduced white pore effect over open pore woods
- positive synergistic effect

Extensive testing was performed to select a photoinitiator that has peak absorption rates in the UV-A spectral output range (315 nm–400 nm). A photoiniator based on BAPO (bis-acyl phosphine oxide) with an absorption peak in the UV-A range of 370 nm was found to provide excellent surface/throughcure properties. The optimal level determined was 1.5% photoinitator based on resins (as supplied). The complete formulation consisted of a waterborne UV-curable PUD, self-crosslinking waterborne PUD, photoinitiator, flow additive, defoamer, and polyurethane thickener.

A formulation (System A) was prepared and applied to glass panels to test film hardness. *Table* 1 shows the curing parameters and Konig pendulum hardness of the coatings (curing parameters: no UV exposure, with UV-A light exposure, exposure time, and distance). The non-UV exposed films physically dry after the flash/bake cycle, but have significantly lower hardness properties compared to films exposed to UV-A light. Two different UV-A lamps were tested and both provided excellent initial hardness development. Standard block resistance testing for wood coatings was performed to evaluate drying properties.

The same formulation (System A) was spray-applied over sealed wood substrates and tested for chemical resistance. Testing consisted of a 16-hr exposure (covered and uncovered) to acetone, ethanol/water (1/1) and Murphy's Oil Soap® spray. As seen in *Table* 2, the chemical resistance is excellent for both UV-A exposed films; however, some softening/dulling was observed for the *covered* Murphy's Oil Soap spray exposure. The non-UV exposed films showed significant failures for all reagents tested.

These results demonstrate that coatings based on UV-curable polyurethane dispersions can be cured with low energy UV-A lights, without sacrifice of performance properties for wood coatings applications. The non-UV exposed areas have excellent adhesion properties and physical drying properties, but may not have the desired chemical resistance for certain working surfaces.

Further testing was performed to increase the chemical resistance properties and hardness of non-UV exposed areas. The objective is to improve properties for 3D objects that may have shadow areas unexposed to UV light.

This can be achieved by reacting the carboxyl group present in the PUD with: (a) carbodiimides, (b) epoxy functional groups, and (c) polyaziridines.

A constraint for these systems is that the addition of crosslinkers will introduce pot-life issues to the coatings application (typically four to six hours).

A revised formulation (System B) consisted of a UV-curable PUD, a self-crosslinking PUD, and a carbodiimide crosslinker. The combination of these materials produces three curing mechanisms, as follows: free radical cure by UV radiation, oxidative cure by fatty acid modification, and carboxyl crosslinking with a carbodiimide crosslinker.

Table 3 shows the hardness and chemical resistance data of System B. The addition of the carbodiimide crosslinker increased hardness slightly and greatly improved the chemical resistance of non-UV exposed areas. Specifically, Murphy's Oil Soap spray had no effect on non-UV or UV-exposed films. Scraping the films with an applicator stick revealed the slight softening reported for acetone and ethanol/water. The films were visually unchanged if undisturbed. Reduced acetone resistance is reported for the UV-A exposed film (System B) compared to previous testing for System A.

ADDING WATER-DISPERSIBLE POLYISOCYANATES

The addition of water-dispersible polyisocyanates (PIC) can significantly increase the property level of UV-curable waterborne coatings. The water-dispersible

Table 4—Hardness with Addition of Water-Dispersible Polyisocyanates

System	Prebake	UV-A Radiation Time/Distance	Initial Pendulum Hardness	Pendulum Hardness After 7 Days	Pendulum Hardness After 14 Days
A—no PIC	7 min at 100°F	No UV	23 sec	34 sec	34 sec
A—no PIC	7 min at 100°F	6 min 10 in.	98 sec	106 sec	115 sec
A—with PIC	7 min at 100°F	No UV	64 sec	123 sec	119 sec
A—with PIC	7 min at 100°F	6 min 10 in.	63 sec	137 sec	140 sec

polyisocyanate reacts with the amino groups and/or moisture to form a crosslinked network. Now the curing mechanisms include free radical cure by UV radiation and crosslinking using NCO groups. The curing mechanism provided by the NCO groups improves the coatings performance in shadow areas that are not exposed to UV radiation.

System A is blended with a water-dispersible polyisocyanate (isocyanate-terminated hydrophilic polyether modified HDI trimer) at a 90/10 blend ratio. Formulations with and without polyisocyanate were applied to glass panels to test film hardness. *Table* 4 shows the influence of adding water-dispersible polyisocyanates to films exposed to UV-A radiation and to non-UV exposed films.

The additional curing mechanism provided by the NCO groups improved the overall hardness of films. The films with polyisocyanate had lower initial hardness but developed excellent hardness due to post-cure. Additionally, the chemical resistance improved significantly for non-UV exposed areas containing polyisocyanate.

SUMMARY

UV-curable PUDs are very high molecular weight polymers that require much less radical crosslinking to obtain desired properties. High performance coatings are possible by curing with low-intensity UV-A lamps that are significantly lower in cost than traditional high intensity UV ovens.

The addition of self-crosslinking PUDs shows a positive synergistic effect with UV-curable PUDs when cured with low intensity UV-A lamps. The addition of crosslinkers such as carbodiimides and water-dispersible polyisocyanates improved performance in shadow areas that are not exposed to UV radiation. The addition of crosslinkers to the formulation will introduce pot-life issues for the coatings system.

By using creative chemistries in combination with lower cost curing equipment, it is possible to reduce the hurdle of investment costs for UV technology.

ACKNOLWEDGMENTS

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