Faster finishing

Benefits of waterborne UV curable resins on flexible substrates

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The chemistry and curing requirements of waterborne UV PUD coatings are outlined. Isocyanate-cured waterborne PUDs are widely used as leather coatings. Two such coatings were modified by inclusion of UV-curable PUDs. The UV coatings showed very good performance, with the advantage that final properties are attained very rapidly after curing.

Waterborne (WB) UV PUD curable finishes are a viable alternative to solventbased coatings due to their excellent scratch and chemical resistance, in wood furniture and cabinetry markets in particular. Since this success has expanded over the years, it was of interest to investigate the use of these materials in other markets, specifically as coatings for flexible substrates. Target markets would include genuine leather for automotive and furniture markets and imitation leathers such as polyvinyl chloride (PVC).

Waterborne UV PUD coatings possess many inherent advantages, including excellent blocking resistance. This allows the coated substrate or part to be stacked, packaged and shipped right off the production line. The cross-
link density of the coating is immediate once exposed to the UV radiation. For this reason WB UV coatings impart excellent chemical and stain resistance immediately after curing while conventional 2K systems require time to develop these properties.

The viscosities of WB UV PUD coatings can easily be adjusted with traditional rheology modifiers and water as a diluent. Their high initial molecular weight and moderate degree of crosslinking provides excellent adhesion due to the low amount of cure-related shrinkage, unlike traditional 100 % solids UV systems. The gloss of these WB UV PUD coatings can be controlled from high sheen to extremely matte using traditional silica and organic matting agents. Easy equipment clean-up using water ultimately leads to lower operating costs. These outstanding performance features coupled with immediate, low energy, UV curing can provide economical productivity advantages.

**Chemistry of UV curing outlined**

The chemistry of UV curing is a photochemical process whereby ultraviolet radiation in the presence of a photoinitiator is used to crosslink the coating [1]. The process is most commonly achieved through a free-radical mechanism using a photoinitiator. The UV radiation splits the photoinitiator into free radicals which react with the double bonds of the UV resin. This produces more free radicals and the process continues until termination is achieved due to a high level of crosslinking.

With the use of multifunctional resins, a three-dimensional cured network can be created and the crosslink density can be controlled to meet the needs of a variety of coatings applications. This reaction process occurs once water has been removed from the coating.

The development of WB UV resin technology has advanced in recent years. Resin suppliers have a growing ability to tailor the resin for specific performance needs [2]. There are three basic variables used in the industry that influence the final properties of the resin: UV acrylate selection, incorporation process of the UV acrylate and modification [3-5]. Since there is an almost endless amount of choices and combinations resulting from these variables, a wide range of WB UV resins is available with drastic differences in coating properties and performance.

**UV PUDs have some unique advantages**

UV PUDs are a versatile class of products offering high-end performance. They can be polyether, polyester and/or polycarbonate based. They offer the advantage of polyurethanes such as flexibility and toughness and show the highest growth rate in waterborne UV technology due to their unique performance. Many different design and processing parameters are available for the final resin composition [6]. Because emulsification allows very high molecular weight materials to be provided in a low-viscosity form, the UV PUDs can have a high molecular weight and functionality, leading to higher coatings performance [7]. Besides the choice of resin for the WB UV coating, other factors can make an impact on performance, including formulation ingredients such as defoamers, surfactant package, waxes, matting agents, pigments, rheology modifiers and choice of photoinitiator. Apart from the photoinitiator, these components function in the same manner as when used in a typical acrylic emulsion or PUD.

**Results at a glance**

» The chemistry and curing requirements of UV PUD coatings are outlined.

» Isocyanate-cured waterborne polyurethane dispersions (PUDs) are widely used as leather coatings. Two such coatings were modified by incorporating a UV curable PUD system and omitting the isocyanate.

» Test results showed that the performance of the UV cured leather coatings was equal to or better than that of the thermally crosslinked PUDs in terms of resistance to chemicals, rub and flexing tests.

» The UV coatings had the considerable advantages of attaining their final properties a very short time after curing, and eliminating isocyanates with their toxicity issues and pot-life limitations.

![Figure 1: Flexibility test comparison of conventional and UV curable PUDs on natural and synthetic leather](image1)

![Figure 2: Appearance of natural and synthetic leathers after Bally flexibility test](image2)
Why photoinitiator selection is critical

The most critical part of formulation with WB UV curable coatings is the selection of the photoinitiator(s) and this decision should be made wisely. With the increased popularity of WB UV coatings, many of the manufacturers of photoinitiators used in traditional 100 % solids UV systems are now producing versions that are stable in water. The choice of the type of photoinitiator is determined by various factors such as coating type, additive package and the light source. When deciding on the choice of photoinitiator(s) the first step is to consider whether the coating is clear or pigmented. For a clear coating the predominant choice is a blend of alpha-hydroxy ketone and benzophenone. If the WB UV coating system is to be pigmented, an additional photoinitiator such as bis or mono-acyl phosphine oxide is added to this blend. The absorbance of the photoinitiator(s) should be aligned with the spectral output of the light source for maximum cure potential. Optimal loading levels vary depending on the type of WB UV system being used and must be experimentally determined. An excessive amount of photoinitiator can hinder the cure potential as its excess UV absorption can prevent the UV radiation from penetrating the coating.

The extent of UV exposure influences the degree of cure for the coating which in turn affects the performance capabilities. The extent of cure can be impacted by several variables during the curing process: line speed, reflector placement, irradiance and spectral distribution or wavelength. For most WB UV curable coatings, energy alone is not an adequate measure of the level of exposure. Therefore, all variables must be specified for a consistent degree of cure and performance.

Photoinitiator and pigment affect lamp selection

Another factor affecting the degree of cure is the choice of the curing lamp, which is not dependent on the choice of the WB UV resin system, but is determined by the photoinitiator and the opacity of the coating. Lamps with shorter wavelengths, such as mercury lamps, are used for clear coatings and for surface cure of pigmented coatings. Lamps which radiate at longer wavelengths, such as gallium doped lamps, are used for a through cure of pigmented coatings and with certain additives such as UV absorbers and nanoparticles. When differently doped lamps are combined, the lamp emitting the longest wavelengths should be used first to ensure that the coating receives a full through cure before the shorter wavelength lamp which delivers the surface cure.

One condition for a complete cure is to ensure that the photoinitiators used within the system have the ability to absorb the UV radiation from the doped lamp source. Since pigments have the ability to reflect, scatter, and absorb UV radiation, a reduction in the rate of polymerisation can occur in pigmented UV coatings. This can ultimately undermine the crosslink density, chemical/water resistance, gloss, adhesion and flexibility of the coating. All pigments possess their own characteristic UV absorption profile and care must be taken to choose photoinitiators that absorb in a different wavelength range from the pigments.
Formulation and application of experimental coatings

The objective of this study was to demonstrate performance differences between a conventional 2K system consisting of both an ‘NMP containing’ (NMP = N-methyl pyrrolidone solvent) and a ‘solvent-free’ PUD crosslinked with an isocyanate, versus the same PUDs with the incorporation of a WB UV PUD. The performance criteria is based on the systems being flexible but also possessing adequate block resistance, water and chemical resistance, degree of cure and abrasion resistance. Table 1 represents a traditional formulation for a matte topcoat for leather. Table 2 outlines the formulations used in this study.

The coatings were applied using a No. 22 wire bound rod to both full grain genuine leather coated with a standard PUD basecoat and to a cloth-backed PVC. The substrate was dried for five minutes at 120 °C in a convection oven, delivering a dry film thickness of some 35 micrometres. The UV PUD films were first exposed to a gallium doped lamp then followed by an exposure to an undoped mercury lamp on a conveyor traveling at 13 ft/min (4 m/min).

Good flexibility and blocking performance

The flexibility of the coatings was tested using a Bally Flexometer with the requirement of 100,000 cycles at room temperature with no cracking being visible at 10 X magnification. Figures 1 and 2 employ a grading system defined as follows: 1 = Worst; 5 = Best, with > 4 as passing. All formulations were found to pass after testing the substrates over a 24 hour period. No difference was found between the standard and UV formulations.

The blocking performance was evaluated by two methods where coated surfaces were placed in contact with each other while exposed to heat and pressure. Specific details on the first method can be found in the automotive GM standard for resistance to blocking, which is intended for evaluating supported/unsupported plastic roll goods and finished leather under the conditions on the inside of a car on a hot day [8]. All formulations met the requirements of this blocking test, showing no damage to the coated surfaces.

The second method evaluated blocking under more severe conditions by applying 2 kg/in² (0.31 kg/cm²) pressure to a coated substrate for 24 hours at 110 °C, followed by cooling to room temperature and separation. The blocking performance of the WB UV curable systems when separated was far superior to the conventional 2K coating. As can be seen in Figure 3, there was severe damage and delamination to the 2K systems when the face-to-face samples were separated after the exposure. During the leather finishing process the surface is first basecoated, force dried and then a topcoat is applied and again force dried. Since a conventional 2K system needs time to develop its curing, the finished leather is sent through a drying tower (‘air off tunnel’) so the leather can be stacked face to face off the back of the coating machine. This additional drying or development time lengthens the production run. The instantaneous cure of the UV PUD films significantly minimises any potential for surface defects due to incomplete cure and improves production efficiency by eliminating this additional drying step.

Good resistance properties are achieved rapidly

Water and abrasion resistance were evaluated using a Veslic Abrader which rubs the coating against a wool cloth and scores the surface in a defined manner. The gloss of the coatings was measured with a gloss meter following the ISO 2812-1 standard.

Table 1: Formulation of a typical isocyanate-curable PUD

<table>
<thead>
<tr>
<th>Component</th>
<th>Total weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>23.00</td>
</tr>
<tr>
<td>Alberdingk USA Polyurethane</td>
<td>70.30</td>
</tr>
<tr>
<td>Defoamer</td>
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</tr>
<tr>
<td>Fumed silica matting agent</td>
<td>6.00</td>
</tr>
<tr>
<td>Flow aid</td>
<td>0.20</td>
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<tr>
<td>Anti-settling agent</td>
<td>0.40</td>
</tr>
<tr>
<td>Total percent</td>
<td>100.00</td>
</tr>
<tr>
<td>Solids</td>
<td>30.0 ± 10 %</td>
</tr>
<tr>
<td>Viscosity</td>
<td>300 - 700 cP</td>
</tr>
<tr>
<td>pH</td>
<td>8.0 - 9.0</td>
</tr>
<tr>
<td>Gloss (60 °)</td>
<td>0.7 - 1.0</td>
</tr>
</tbody>
</table>

Table 2: Formulations of isocyanate-curable and UV PUDs used in testing

<table>
<thead>
<tr>
<th></th>
<th>Control A</th>
<th>UV sample A</th>
<th>Control B</th>
<th>UV sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane A matte – containing NMP</td>
<td>-</td>
<td>84.00</td>
<td>-</td>
<td>84.00</td>
</tr>
<tr>
<td>Polyurethane B matte – solvent-free</td>
<td>-</td>
<td>-</td>
<td>84.00</td>
<td>58.40</td>
</tr>
<tr>
<td>UV curable polyurethane resin</td>
<td>-</td>
<td>30.00</td>
<td>-</td>
<td>30.00</td>
</tr>
<tr>
<td>Silicone emulsion</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Long wavelength photoinitiator</td>
<td>-</td>
<td>0.30</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>Short wavelength photoinitiator</td>
<td>-</td>
<td>0.30</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>Block pigment dispersion</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Isocyanate crosslinker</td>
<td>5.00</td>
<td>-</td>
<td>5.00</td>
<td>-</td>
</tr>
<tr>
<td>Total percent</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

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pad saturated with water for 500 cycles with a 500 g weight. The results for the coated leather substrates are presented in Figure 4. The leather substrate based on the 2K systems needed a dwell time of 24 hours to meet the passing criterion (≥ 4), while the WB UV systems received a passing grade one hour after exposure to the UV radiation.

The results for coated PVC are shown in Figure 5. The 2K NMP system performed poorly independently of dwell time, while the UV finish was found to pass only after 24 hours. It is likely that a tie coat is needed to improve performance. The performance of both the 2K and UV solvent-free PUDs was much better, giving pass results after the dwell period.

The General Motors test method GMW14897 was used to evaluate various chemical resistances. This standard specifies a passing grade showing no film degradation after five firm finger press rubs using a cloth saturated with at least 92 % concentrated ethanol. The remaining chemicals are required to withstand ten firm finger press rubs with minimal transfer of colour to the cloth. Resistance to IPA (90 %) was also evaluated using an AATCC crockmeter for ten cycles. Figure 6 compares results for the NMP-containing finishes versus the solvent-free. It is clear that the WB UV systems have higher resistances overall compared to the 2K systems, especially for IPA. As expected, an additional dwell time is needed for the conventional finishes to meet the chemical resistance requirements.

UV PUDs offer a high-quality finishing system

An innovative UV PUD has been developed with excellent flexibility, abrasion and chemical resistance for flexible substrates, including leather and PVC. The results from this study clearly show that when properly formulated and cured, a high end coating is produced that meets the requirements for the automotive interior market. Removal of isocyanate from conventional 2K systems is highly beneficial and reduces the overall formulation cost. Strong consideration can be given to an initial capital investment in adding UV curing equipment at the end of a traditional production coating line. By eliminating this component from the coating system, infinite pot life can also be achieved along with lower toxicity and no need for any VOC-containing components.

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REFERENCES


Want to learn more about waterborne UV curable polyurethane dispersions?

Tune in for the free web-based presentation by Mark P. Gilbert on 28 October 2014, 15.00 CET at www.european-coatings.com/live
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