UV-Curable Polyurethane

DISPERSIONS FOR AEROSPACE TOPCOAT APPLICATIONS

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Coating application is the rate determining step in aircraft production. Currently, aerospace coatings utilize two-component polyurethane chemistry that requires 72 hours curing time before the plane can be returned to service. UV-curable polyurethane dispersions (UV-PUDs) were evaluated as aerospace topcoats to allow for increased productivity as a result of decreased curing time. UV-PUD based coatings were formulated and evaluated for their ability to meet military topcoat specification MIL-PRF-85285D. Coatings that meet this specification require a balance of chemical and water resistance, flexibility, weatherability, and aesthetics. This article will focus on the performance of UV-PUD coating formulations with respect to these properties.

INTRODUCTION

Aerospace coatings demand a balance of chemical and water resistance, weatherability, flexibility, and aesthetics. Currently, these performance requirements can only be met using two-component aliphatic urethane coatings, which typically require 72 hours to cure before the plane can be moved outside the hangar. Because of this limitation, ultraviolet-curable coatings have been evaluated as aerospace coatings to decrease the “dry-to-fly” time, thus allowing for increased productivity during refinish and manufacturing.[1] This article will explore the formulation and physical properties of UV-curable polyurethane dispersions (UV-PUDs) as alternatives to conventional aerospace coatings.

Aerospace coatings are based on multilayer film stackups to obtain maximum protection from the extreme environments encountered by aircraft. These layers consist of a chromate conversion

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coating to prevent corrosion and enhance adhesion, an epoxy primer containing chromated pigments to provide additional corrosion protection and enhanced chemical resistance, and a polyurethane topcoat that provides weatherability and fluid resistance. Aerospace topcoats must be able to resist a wide variety of chemicals (e.g., jet fuel, motor oil, and hydraulic fluid) while maintaining flexibility to prevent cracking over a wide temperature range. Improved chemical resistance typically comes at the expense of flexibility. Weathering and water resistance are also important properties that must be considered when choosing a binder for aerospace applications.

Traditional UV-curable coatings typically lack flexibility due to high crosslink density. UV-PUDs are able to achieve the hardness–flexibility balance because, unlike traditional UV-curable oligomers, UV-PUDs require less crosslinking due to their considerable initial molecular weight. Furthermore, a high initial molecular weight imparts substantially lower oxygen inhibition, less shrinkage, and reduced health and environmental issues compared to traditional UV-curable coatings.

Since UV-PUD coatings are delivered in water their application viscosity is not an issue, overspray can be recycled, and matted coatings are easily obtained. While there are many advantages of UV-PUDs, there are also some disadvantages arising from the binder being dispersed in water. For example, water sensitivity can be an issue, although this sensitivity is dramatically reduced once the coatings have been UV cured and the tertiary amine neutralizing agent has been allowed to evaporate (*Figure* 1). Unlike latex coatings that are stabilized by surfactants that remain in the coatings, PUDs stability in water originates from a carboxylic acid neutralized with a volatile amine. The neutralizing agent's evaporation rate can be increased using an oven or forced air to dry the coatings. Elevated temperatures also facilitate higher conversions upon UV curing due to enhanced molecular mobility.[2]

UV-PUD technology was originally developed for the wood market in response to the demand for more environmentally friendly coatings, increased line speeds, and enhanced exterior durability.[3,4] This technology has gained significant market share in wood coatings (e.g., kitchen cabinetry and furniture), while expanding into new markets such as flooring.[5] Given the success of UV-PUD technology in these established markets, this research examines the suitability of these binders as aerospace topcoats that meet the military topcoat standard MIL-PRF 85285D (85285).

EXPERIMENTAL

All materials were used as received unless otherwise noted, and their manufacturers are listed in *Table* 1. Ethylene glycol was purchased from Sigma-Aldrich. Deft Inc. supplied the primer (02Y-40-B) that was used in all coating evaluations. Photoinitiators (PIs) obtained from BASF included benzophenone, alpha hydroxyl ketones (AHK), monoacylphosphine oxides (MAPO), and bisacylphosphine oxides (BAPO).

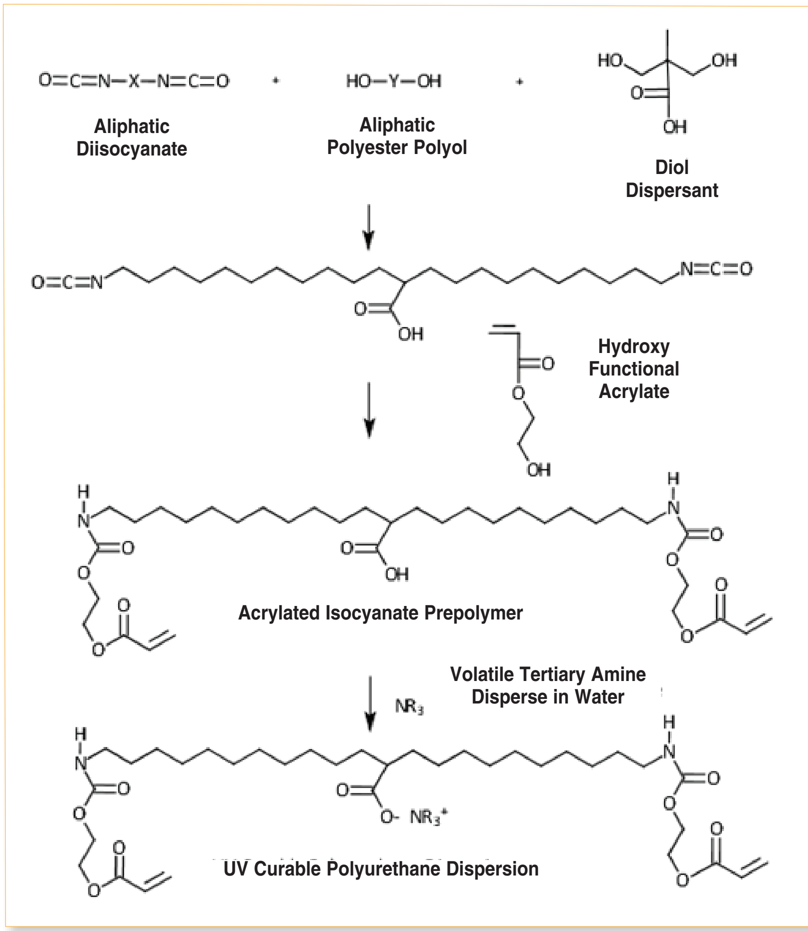

Figure 1—Typical UV-PUD synthesis.

Coatings were prepared by adding the pigment paste to the UV-PUD while stirring. Then, a solution of cosolvent, PI, and additives was added slowly to the pigmented PUD mixture. Finally, a 50% aqueous solution of thickener was added dropwise until a Stormer viscosity of 65 Kreb units was reached.

Primer components were mixed together and allowed to compatibilize for 30 minutes before application, and a minimum of three hours was allotted before topcoat application. UV-PUD coatings were then applied to freshly primed 2024-T3 aluminum panels and allowed to air dry for 20 minutes or until dry to the touch. A 1200W H&S Autoshot Cure-Tek UV-A lamp which emits UV-A light in the wavelengths between 315–400 nm was used to cure all panels. A standoff distance of eight inches was used while curing the panels for eight minutes. After curing, the panels were allowed to cool to room temperature and tested for their physical properties unless otherwise noted.

Application was according to the 85285 specification, topcoat applied between 1.5–2.0 mils over approximately one mil of epoxy primer that corresponds to MIL-PRF 23377J. All ASTM testing methods can be found in the 85285 specification.

Table 1—Generic Formulation for Aerospace Coating

Component	wt%	Company
Exterior UV-PUD binder	66.4	Bayer MaterialScience
Titanium dioxide pigment dispersion	28.6	Plasticolors
Glycol ether cosolvent	1.7	The Dow Chemical Company
Photoinitiator[a]	--	BASF
Acetylenic diol surfactant	0.5	Air Products
Polysiloxane defoamer	0.1	BYK
Modified urea thixotrope	0.5	BYK
Associative thickener	0.6	Borchers

(a) See *Table* 2.

Table 2—PI Selection vs. Color Stability and Solvent Resistance

Photoinitiator	phr	ΔE	Pass 100 MEK Double Rubs
None	0	0.1	No
AHK #1	5	1.2	No
AHK #2	5	1.1	No
Benzophenone AHK #1	2.5 2.5	1.6	**Yes**
MAPO #1	3.5	1.1	**Yes**
MAPO #1	5	2.0	**Yes**
MAPO #1 AHK #1	2 2	1.6	**Yes**
MAPO #2 AHK #1	2 2	0.7	No
MAPO #2	5	0.6	**Yes**

RESULTS AND DISCUSSION

A range of UV-PUDs was prescreened for their flexibility and chemical resistance prior to focusing on the formulation in *Table* 1. This formulation was used as a generic formulation in the coating development and the effects of various PIs, cosolvents, and pigmentation levels were evaluated to meet the 85285 specification. The goal of this project was to formulate a one-component glossy white coating that meets all physical and aesthetic properties of the aforementioned specification.

The coatings were designed to be cured with a UV-A light source due to safety concerns related to eye and skin exposure to UV-B and UV-C light that would be encountered using a full spectrum UV light. Furthermore, UV-A wavelengths provide enhanced through cure in pigmented coatings due to the polymer UV absorption competing with the PI at shorter wavelengths. PIs active in the UV-A wavelengths are a relatively new technology, and the development of MAPO and BAPO PIs have improved the through curing of pigmented films.[6] Unlike conventional UV-curable coatings where the PIs are soluble in reactive diluents, the water-based chemistry of UV-PUDs limits the PI selection due to solubility and compatibility concerns. The requirement for the PI to be active in the UV-A wavelengths further limits the selection.

Table 2 outlines a range of PIs that were evaluated for their ability to initiate crosslinking and color stability after UV-curing and heated at 100°C for 30 minutes as required by the 85285 specification. PIs active in the UV-A wavelengths contain aromatic moieties that are subject to yellowing upon heating. Antioxidant additives typically used to prevent yellowing, e.g., phosphites, were found to inhibit the free radical curing mechanism and could not be employed. *Table* 2 shows that AHK PIs have non-yellowing characteristics; however, these PIs lack

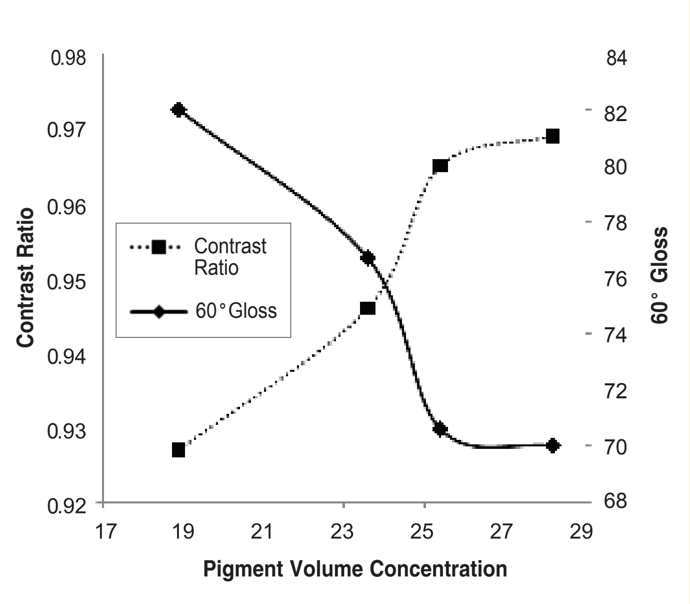

Figure 2—Effect of PVC on contrast ratio and gloss.

sufficient absorption in the UV-A wavelengths and the absorption/scattering of the titanium dioxide pigment does not allow sufficient crosslinking in the film. MAPO PIs have the ability to crosslink the coating but yellowing was unacceptable at high concentrations. A compromise of these two properties was found using five parts per hundred resin (phr) MAPO #2 that yielded acceptable yellowing and generated solvent-resistant films. A relatively newer PI technology, BAPO (not listed), was not evaluated for color stability because of its insolubility in cosolvents, and a water-dispersible BAPO displayed negative effects on gloss presumably due to incompatibility.

Once a PI package was identified, the pigment volume concentration (PVC) level was optimized to obtain sufficient contrast ratio and maximum gloss. A 60° gloss of 90 or greater and a contrast ratio of 0.95 is required to meet the 85285 specification. *Figure* 2 shows the effect of PVC on the contrast ratio and gloss, and as expected, the gloss levels decrease and contrast levels increase with increasing PVC. A contrast level of 0.95 occurs around 24 PVC, and the 60° gloss level at this PVC is only 76. This low gloss level is most likely due to physical shrinkage from water evaporation and at higher PVCs the pigment particles are more likely to protrude from the surface, reducing gloss.

Several cosolvents were evaluated in an effort to raise gloss values, and glycols were found to be the only effective additives that increased gloss. Both ethylene glycol and propylene glycol were found to increase gloss levels and it was also noted that the glycols increased the dry time. The gloss enhancements are believed to arise from an increase in mobility during the late stages of film formation, allowing flow and leveling to occur. Glycol addition is known to increase the open time or wet edge in a film by acting as a humectant and decreasing the water evaporation rate from the film.[7,8] Unfortunately, the increase in gloss levels came at the expense of initial film hardness at high glycol levels, though the hardness eventually recovers back to a pencil hardness of HB after 24 hr at ambient conditions.

Weatherability is another important aspect of an aerospace coating. Weathering additives that trap free radicals could not be used due to their absorption of UV-A wavelengths that competed with the PI and inhibited crosslinking. *Figure* 3 displays the coating's color change and gloss loss during accelerated weathering. After over 3000 hr of Xenon exposure, the color change is minimal, ΔE < 1, while the gloss slowly decreases over time. The reduction in color change after 1500 hr can be attributed to MAPO PI undergoing photobleaching. This phenomena occurs due to the degradation of MAPO chromophores upon exposure to Xenon light during accelerated weathering, causing a decrease in yellowing over time.[6]

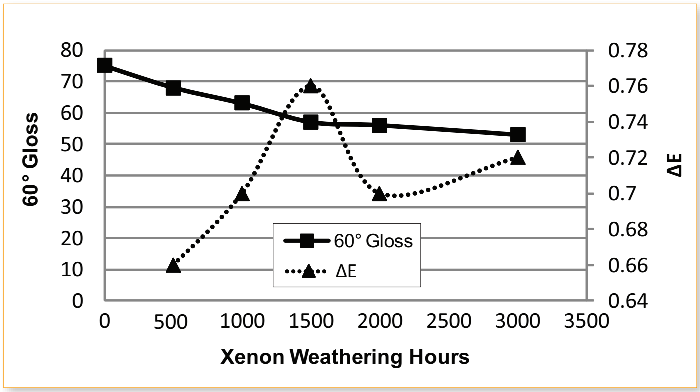

Figure 3—Change in color and gloss after accelerated weathering.

While most physical properties of UV-PUD coatings are realized immediately after UV exposure, water resistance is not maximized for some time. Initial water resistance evaluations found the coatings to be sensitive; however, it was noted that the water resistance increased substantially if the coatings were heated in an oven after UV curing (*Table* 4). The heat treatment is believed to have increased the amine neutralizer's volatility, and upon evaporation the carboxylate salt (*Figure* 1) reverts back to the carboxylic acid that is less water sensitive.[5] After 14 days at ambient conditions, water resistance increased to a level comparable to the oven-conditioned coating and passed 30 days in the Cleveland condenser (49°C and 100% humidity) as well as wet adhesion. It bears mentioning that traditional two-component polyurethane coatings also require 14 days to achieve their maximum water resistance.

Table 3—Effect of Ethylene Glycol on Gloss and Film Hardness

Ethylene Glycol (phr)	60° Gloss	Pencil Hardness
0.05	73	HB
0.1	75	HB
0.5	75	HB
1.5	81	3B
3	83	5B

Table 4—Humidity Resistance of Coatings After UV Curing

Time after UV Curing	Pass 30 Day Cleveland Condenser	Wet Adhesion
20°C/1 day	No	Fail
20°C/3 day	No	Fail
20°C/5 day	No	Fail
20°C/7 day	No	Fail
20°C/14 day	**Yes**	**Pass**
100°C/30 min	**Yes**	**Pass**

Table 5—Properties of UV-PUD Coating Compared to Military Aerospace Specification

Test	85285 Specification	UV-PUD Coating
GE impact test	≥ 60%	60%
Low temperature flexibility	Pass	Pass
Dry/wet adhesion	≥ 4A/≥ 4A	4A/4A
60° Gloss	60° ≥ 90	**80**
Xenon weathering (500 hr)	$\Delta E < 1$; 60° Gloss ≥ 80	$\Delta E = 0.7$; 60° Gloss = **75**
Initial pencil hardness	≥ 2B	HB to F
Mobil jet oil	–2 pencils	–1
Hydraulic fluid	–2 pencils	–1
JP-8 Jet fuel	–2 pencils	–2
Humidity resistance (Cleveland condenser)	30 days	Pass
Heat resistance (ΔE)	<1	**1.1**

A thorough evaluation of the coating's performance versus the 85285 specification is shown in *Table* 5. The coating exhibits a unique balance of chemical resistance, flexibility, and weathering resistance that is currently only obtainable using two-component polyurethane coatings. The major deficiency of the coating is the aesthetics, specifically the lower gloss values. The UV-PUD binder in this formulation was designed for exterior wood applications, and the correct balance of physical, aesthetic, and weathering properties are believed to be achievable using this technology. While the coating could not be qualified to 85285 specification, a touch-up specification, MIL-PRF-81352, has a lower gloss requirement—60° gloss > 80—and it is believed that this coating could be qualified to the touch-up specification.

CONCLUSIONS

A new class of binders was evaluated for their ability to meet the physical property requirements for aerospace applications to reduce the dry-to-fly time and increase productivity. UV-PUDs were found to meet the flexibility, chemical resistance, and weatherability specifications. MAPO-based PIs were found to be able to through cure the coatings with sufficient contrast ratio while maintaining color stability upon heating. UV-PUD coating's water resistance was found to increase substantially over time and was able meet the water resistance requirement after 14 days at ambient conditions. Gloss levels were found to be less than what was required by the 85285 specification and could not be raised to the level passing the specification without adversely affecting other physical properties. Based on this research, UV-PUD binders are a promising technology for the aerospace coatings market.

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