

Development of UV-A Curable Coatings for Military Aircraft Topcoats

By C. Todd Williams,
Mike Dvorchak and
Chuck Gambino

UV-A curable coatings are investigated as an alternative to traditional two-component polyurethane aerospace topcoats due to their rapid cure rates, low volatile organic compounds, low volatile hazardous air pollutants and high-performance properties. The development of a formulation that approaches military specifications for aircraft topcoats will be described in this paper, and this paper will also review the results of recent field trials of a UV-A curable stencil coating after 600 service hours on a C-130 aircraft.

Background

Developments in UV-A light sources and photoinitiators have allowed for significant progress of site-applied markets such as automotive refinish¹ and flooring. Footprint limitations are still an issue in the automotive refinish markets and are expected to be the bottleneck in the application of UV-A curable coatings onto large surfaces.

Recently, there has been a government initiative to develop UV-curable aerospace coatings in an effort to decrease the return-to-service time while still maintaining high-performance properties.² Conventional coatings in this market are based upon two-component polyurethanes that require 72 hours to fully develop their physical properties. The development of UV-curable aerospace coatings would significantly decrease refurbishing time.

The physical properties of aerospace topcoats for military applications are currently defined by military specification 85285 (MIL-PRF-85285), and the critical properties in this specification are outlined in Table 1. Coatings that qualify to these standards are based on high-performance industrial resins that yield a good balance of physical properties, including chemical resistance, flexibility, adhesion and weathering. Since the cost of the coating is only a fraction of the overall painting cost, high-quality raw materials are used in aerospace

FIGURE 1

Curing of stencil coating on C-130



TABLE 1

Salient properties of camouflage coatings that conform to MIL-PRF-85285 and properties of stencil coating

| Property | MIL-PRF-85285 Specification | Stencil Coating |
|--------------------------------|--|-----------------------|
| Flexibility – GE Impact Test | 40% | 2% |
| Chemical Resistance | Jet fuel, hydraulic fluid, or oil – softening no more than 2 pencils | Pass |
| Crosshatch / Wet tape Adhesion | >4A | Pass |
| Gloss | 85° ≤ 9 60° < 5 | 85° = 39 |
| Accelerated Weathering | ΔE < 1 after 500 hours | ΔE = 0.9 at 500 hours |

coatings to make these coatings some of the highest performance systems found in the market.²

UV-curable coating formulations were developed at Bayer MaterialScience—Deft and evaluated by the U.S. Air Force’s Coatings Technology Integration Office in 2007.³ These coatings displayed promising physical properties with room for improvement in the areas of flexibility and gloss (Table 1). This formulation was used as stencil coatings on a C-130 and F-16, and has been periodically evaluated for color change and gloss retention. After 600 flying hours (14 months), the stencil coatings on the C-130 had ΔE values comparable to the conventional polyurethane fluoropolymer (Table 2).

UV-curable coatings based on oligomeric chemistry are typically hard and chemically resistant, which imparts deficiencies in flexibility. Furthermore, gloss reduction can also be challenging with this type of chemistry due to the lack of shrinkage of the polymer upon solvent evaporation. The stencil coating was reformulated to address the aforementioned performance issues and approach military aerospace specifications.

Coating Formulations and Results

Coatings were applied at two dry mills film thickness and UV cured for eight minutes at eight inches standoff distance using an H&S Autoshot 400W light, unless otherwise specified. All coatings were evaluated

on freshly primed, Alodine-treated 2024-T3 aluminum panels (Figure 2) with the exception of flexibility that was tested on 2024-T0 aluminum panels. Evaluations were performed immediately after curing using the guidelines provided in MIL-PRF-85285.

Typically, UV-curable coatings lack flexibility and give superior chemical resistance due to their high crosslink density. Aerospace coatings require a compromise of both chemical resistance and flexibility while maintaining hardness. These properties are primarily dictated by the filler concentrations and the resin(s) functionality/glass transition temperature. Three urethane acrylate resins and a reactive diluent were evaluated for their flexibility in the

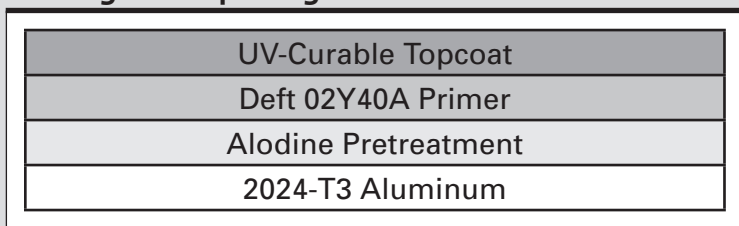
TABLE 2

Weathering properties of coatings on C-130

| Coating | ΔE 7 months | ΔE 14 months | Δ 60° Gloss 7 months | Δ 60° Gloss 14 months |
|------------------------|-------------|--------------|----------------------|-----------------------|
| Black UV Stencil | 1.56 | 0.87 | (-5.2) | (-4.8) |
| 2K Gray Fluorourethane | 0.57 | 1.23 | (-0.13) | 0.00 |

FIGURE 2

Coating stackups diagram



stencil formulation by preparing the formulation using only one resin. The results are shown in Table 3. The data shows an inversely proportional relationship between average acrylate functionality and flexibility as expected. Both the monofunctional reactive diluent and difunctional resin show improved flexibility, although

at the expense of hardness. This data indicates that a mixture of hard and soft resins along with reactive diluents is required to get the balance of flexibility, hardness and chemical resistance required to meet MIL-PRF-85285.

Low gloss in UV coatings is typically accomplished by adding micron-sized

silica or crosslinked polymer particles to form a rough surface that scatters light. The formulation of very low gloss coatings that meet MIL-PRF-85285 standards requires a large concentration of flatteners, which is detrimental to the coating's flexibility. Alternative strategies were explored to maintain a balance of physical and aesthetic properties. Table 4 shows the effect of curing conditions on gloss for the same formulation. Higher gloss values are obtained when the electrode-less full spectrum focused UV light is used compared to when UV-A lights are used to cure the coatings.

OEM style electrode-less UV lamps have higher irradiance and are focused lights as compared to the flood style UV-A lights that emit lower irradiance light (See Figure 3). The focused

TABLE 3

Stencil coating properties made with different resins

| Resin / Reactive Diluent | GE Flexibility (%) | MEK Double Rubs | Average Acrylate Functionality | Pencil Hardness |
|--------------------------|--------------------|-----------------|--------------------------------|-----------------|
| Resin 1 (20% HDDA) | <2 | >100 | 3.8 | 2H |
| Resin 2 | 20 | >100 | 3.2 | HB |
| Resin 3 | 60 | >100 | 2 | 4B |
| Soft Reactive Diluent | 60 | 39 | 1 | <6B |

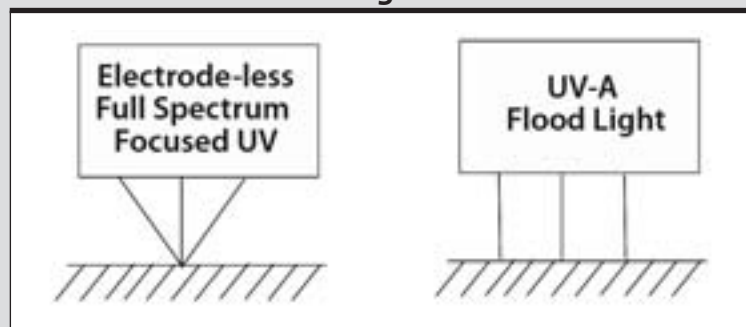
TABLE 4

Effect of curing conditions on gloss

| Curing Conditions | 60° Gloss | 85° Gloss |
|---------------------------------------|-----------|-----------|
| Electrode-less Full Spectrum UV Light | 47 | 81 |
| H&S UV-A Metal Halide Light | 3 | 26 |
| Quantum UV-A Fluorescent Light | 4 | 27 |
| H&S UV-A Light + 10% Reactive Diluent | 3 | 3 |

FIGURE 3

Focused versus flood UV lights



light and higher intensities allow the coatings to cure more uniformly since oxygen inhibition is overcome at a much faster rate because the consumption of oxygen is faster than oxygen diffusion. On the other hand, the lower irradiance UV-A light cures the coating from the bottom up since the surface has a high oxygen concentration that inhibits the free-radical reaction. Eventually, the photoinitiators reduce the oxygen concentration to a level that allows polymerization to occur at the surface.⁴ This explanation is further supported by the observation that lower gloss values are obtained when a higher monomer concentration is present in the formulation. An increased concentration of acrylate

groups produces increased inhibition of polymerization at the surface, causing the cure of the surface to occur well after the bottom layers have polymerized.

Gloss reduction using full spectrum lights can be obtained by curing with a 172 nm excimer lamp followed by a mercury arc lamp.^{5,6} Reduced penetration by the 172 nm lamp limits the crosslinking to near the surface, producing wrinkled structures. Through-cure is obtained with the mercury arc lamps, yielding a matte finish. The oxygen inhibition method of reducing gloss works in a similar manner (curing the bottom layers first and then the surface) which also produces a wrinkling effect.

Improved accelerated weathering has been a focus of the military over the past decade and these properties are typically ameliorated via the introduction of UV-A absorbers and hindered amine light stabilizers (HALS). Unfortunately, these additives can interfere with the absorbance of UV-A light by the photoinitiators resulting in partially crosslinked coatings. UV-A curable formulations can permit a low level of HALS additives; however, they are especially sensitive to the presence of UV-A absorbers. Raw material selection is especially critical to obtain good weathering properties since the traditional weathering additives can not be used at the recommended level (See Table 5).

Conclusions

Overall, the performance of UV-A curable coatings has been shown to rival that of conventional polyurethane coatings. Formulations that yield a balance of chemical resistance, flexibility and hardness were obtained using a combination of hard and soft urethane oligomers and reactive diluents. Gloss reduction of these coatings was achieved by a combination of flatteners and oxygen inhibition, leading to flexible, low-gloss

TABLE 5

Critical properties of UV topcoat – preliminary evaluations

| Test | MIL-PRF-85285 Specification | BMS UV Topcoat |
|------------------------------|--|------------------------|
| GE Impact Test | 40% | 40% |
| Chemical Resistance | Jet fuel, hydraulic fluid, or oil—no softening | Softened with jet fuel |
| Crosshatch/Wet Tape Adhesion | >4A | Pass |
| Gloss | 85° ≤ 9 60° < 5 | 85° = 10 |
| Accelerated Weathering | ΔE < 1 after 2,000 hours | ΔE = 0.6 at 500 hours |

formulations. Weathering of UV-A aerospace systems is another critical property that can be chiefly controlled by raw material selection. The stencil coating reformulation efforts have resulted in significant progress toward formulating a UV-A coating that meets MIL-PRF-85285 and these coatings are currently being evaluated for their performance against the full specification. ▀

Acknowledgements

Bayer MaterialScience would like to acknowledge Concurrent Technologies Corporation and Environmental Security Technology

Certification Program for partially funding this research.

References

1. Dvorchak, M. J.; et al., *Radtech Report* November 2003
2. Johnson, J. A.; et al., *Radtech Report* July 2006, 21-25.
3. Dvorchak, M. J.; et al., UV/EB West Conference Presentation "UV-A Curable Aircraft Markings/Stencils" February 2009
4. Wicks, Z. W.; et al., in *Organic Coatings: Science and Technology*, 3rd ed., Wiley, New York, 2007, pp. 580-581.
5. Ananthachar, S., et al., U.S. patent 7,338,986 (2008)
6. Bauer, F., et al., *Prog. Org. Coat.*, 2009, 64, 474.

—C. Todd Williams is senior associate scientist, Coatings, Adhesives and Specialities; Mike Dvorchak is strategic technology manager for UV Cure Oligomers & UV PUDs Government Programs; and Chuck Gambino is R&D specialist with Bayer MaterialScience in Pittsburgh, Pa.

UV inks and coatings for food packaging

GENOPOL* Polymeric Photoinitiators

RAHN is the European market leader with its GENOPOL* range of polymeric photoinitiators for low migration inks and coatings.

Key benefits

- **Low odor**
- **Low extractibles**
- **Low migration**
- **Known toxicology**

Formulating with the GENOPOL* range can provide products that comply with stringent food packaging regulations.

RAHN has recently prepared a comprehensive Product Flash covering this range of materials that offers valuable information on the product line, the legislative background and formulating guidance. This information can be requested from any of our main offices or your local RAHN-sales contact.

RAHN AG
Zürich, Switzerland
Tel: +41 (0)44 315 42 00
EnergyCuring@rahn-group.com
www.rahn-group.com

RAHN GmbH
Frankfurt am Main
Germany
Tel: 0900 1 816 015

RAHN USA Corp.
Aurora, Illinois
USA
Tel: +1 630 851 42 20

RAHN | EnergyCuring
Your partner for excellence