

# UV-Curable Aerospace and Aircraft Coatings

By Nese Orbey

UV-cure coatings have been developed that meet the stringent requirements of modern high-performance platforms used in the aerospace industry. These zero-VOC, single-component, sprayable products cure within minutes, substantially reducing the time and associated costs of recoating. A dual-cure mechanism was developed to ensure thorough cure of filled coatings. Liaison with a lamp manufacturer has led to the development of affordable UV lamps specifically for UV-cure applications. Currently, the resin system developed by Foster-Miller (FMI) is undergoing qualification trials for an aerospace application.

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## Introduction

A family of UV-curable polyurethane-based coatings was developed to replace conventional products used by the aerospace industry that are constantly under scrutiny and potential phase-out due to stringent environmental regulations that govern high volatile organic compound (VOC) coatings. The coatings described here were designed to have zero VOC, toxics release inventory (TRI), and hazardous air pollutant (HAP) constituents, while still meeting or exceeding the stringent performance characteristics of aerospace coatings. The new products are single-component sprayable formulations with a long pot

life and short cure time that will substantially reduce the time between coating application and the time an aircraft can be returned to service.

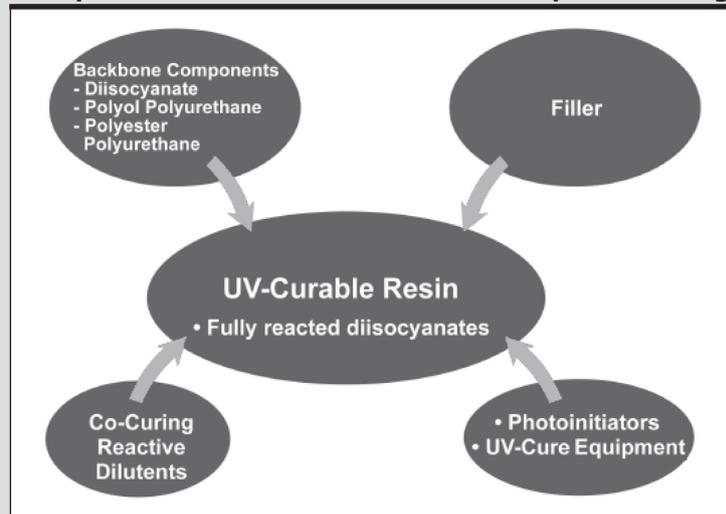
Non-volatile reactive diluents were used in place of VOC solvents to reduce the viscosity of the formulation to a sprayable consistency. During cure, these diluents react with the resin and so are incorporated into the crosslinked matrix of the finished coating. The cure is initiated by radiation with UV light that causes functional groups to attach to the ends of the resin to crosslink. The cure occurs rapidly at room temperature without evolution of vapors.

As shown in Figure 1, fillers were added to the base formulation to achieve the properties specified for various aerospace applications. Because the fillers impede the UV cure, a problem that has limited UV cure to thin or clearcoat applications, an effective cure mechanism was also developed. Another problem addressed was that industry has been slow to embrace radcure coatings, partly because of their novelty, but also because these products were often too viscous for conventional spray application. Moreover, the required UV lamps were cumbersome and expensive, and the equipment to facilitate the radiation cure was not available. However, recent advances in photoinitiator chemistry and UV lamp technology alleviate these problems.

To meet these challenges, a multifaceted program was undertaken. In addition to developing the base chemistry, FMI worked closely with a

FIGURE 1

### Components of no VOC, UV-cure aerospace coating



UV lamp supplier to ensure that affordable UV lamps would become commercially available, and also liaised with the aerospace industry to ensure that they would be receptive to evaluating products. This effort was justified in view of the value of the aerospace market—annual sales of about \$100 million in the U.S. and \$215 million globally.<sup>1</sup> The potential for supplying other important markets (automotive, furniture, etc.) also face increasing environmental restrictions along with more demanding performance requirements.

This paper describes the design of novel UV-cure formulations, the technique developed for curing pigmented coatings, and the performance of the products developed. Some background material relevant to the development of environmentally compliant coatings for the aerospace industry is discussed first.

#### Aerospace Coatings

Adhesion, durability, protection and appearance are basic requirements for most coating applications. In aerospace applications, however, coatings have to

face a particularly severe operating environment that includes exposure to aggressive fluids, temperatures ranging from -65°F to 200°F, and high speeds that impose a range of severe mechanical forces on the substrates and coatings. Protection against corrosion is an essential function of primers, while required topcoat properties include durability, weatherability, and resistance to abrasion, aggressive cleaning fluids, solvents and fuels. Low-temperature flexibility is another key performance requirement of aerospace coatings. Unique to the aerospace application is that coatings are applied over sealant filled gaps of adjoining panels. These gaps are under constant flex during flight and at low temperatures. The coating must demonstrate high elasticity to remain aesthetically and functionally operational.

Conventional polyurethane coatings generally meet these stringent performance specifications but, as stated, are under constant pressure to be discontinued because they are no longer environmentally compliant. Problems include VOCs concentrations as high as 600 g/L and the presence of

HAPs including free diisocyanates, MEK and toluene. Evaporation of these toxic substances during application and cure poses a health hazard, and containing and capturing the emissions is costly. Because toxic materials might be present in the finished coatings, depainting wastes are considered hazardous.

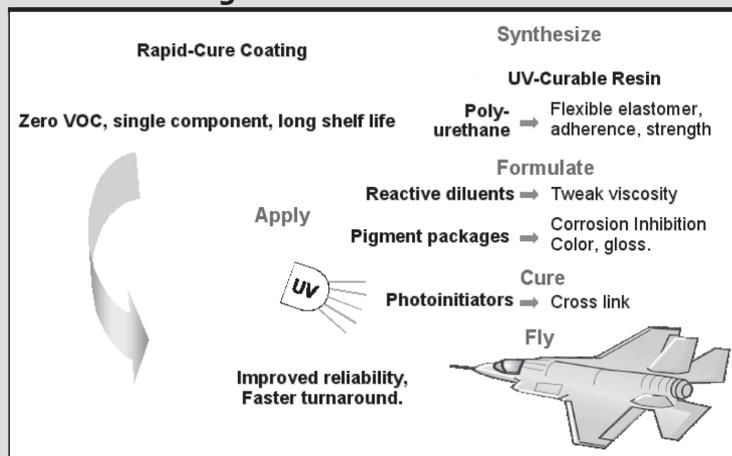
There are other problems associated with conventional coating products that, if resolved, would further facilitate the application process. These include the need to mix two-component formulations, the short pot life of the mixed coating, and the long cure time of the coating once applied. Heating to accelerate the cure is generally not an option due to the large size of the aircraft, the presence of fuel in the tanks, and energy costs.

In addition to matching the performance characteristics of conventional two-component polyurethanes, the new coatings had to be environmentally compliant—non-toxic, non-polluting, and safe when applied. As thermal and vapor-emitting cure processes were not acceptable choices, a UV-catalyzed cure was the only realistic option available. UV cure proceeds at room temperature without evolution of vapors and is complete within minutes. To foster industry acceptance of UV-cure systems, the products were single-component formulations with a long shelf and pot life, and sprayable with conventional equipment. Further, depainting would be amenable to best environmental practices (wheat-starch or plastic-media blast, laser ablation) and the stripped waste would be non-hazardous.

Steps involved in the development and application of the aerospace UV-cure coating are illustrated in Figure 2. The coating systems consist of a primer and topcoat that are applied after the substrate has been properly prepared. In the case of

## FIGURE 2

### Development and application of no-VOC, UV-cure coating



composites, substrate pretreatment is limited to scuff sanding to remove surface gloss and wiping the surface with DI water to eliminate sanding dust. Solvents are not used unless the surface has been contaminated with an organic contaminant. Consequently, composite surface preparation does not involve HAPs, VOCs or TRI chemicals and so is inherently environmentally compliant.

In the case of the more prevalent aluminum alloy substrates, the scuffing and cleaning has to be followed by degreasing, deoxidation, and formation of an oxide layer to promote adhesion of the primer. Traditionally, this final step involves application of a chromated conversion coating for corrosion inhibition and adhesion. The chromated conversion coating process is a highly regulated process due to the hexavalent chromium, and any paint stripping waste containing conversion coating residue is considered hazardous waste. Fortunately, excellent corrosion inhibition can be obtained without chromate conversion simply by ensuring good primer-substrate adhesion.<sup>2</sup> (For example, by treating the surface with compatible coupling agents that

bond with the aluminum oxide and with the primer, the coating is effectively anchored to the surface.) Environmentally compliant pretreatments for UV-curable coatings described here have been adapted from suitably modified proprietary processes.

The primer was designed to provide a bond between the topcoat and the substrate, and to protect metal substrates from corrosion. Corrosion protection was achieved in part by the exclusion of moisture and oxygen from the surface, and also by the action of corrosion inhibitors that are added to the primer. Although the use of chromate corrosion inhibitors was not an environmentally preferred option, it was anticipated that the combination of the excellent barrier properties of the resin described here and the use of commercial, non-chromate corrosion inhibition packages that are available would provide the required protection. The corrosion inhibition pigments would have to be compatible with the resin chemistry and not hinder the UV-cure process or otherwise impair coating performance. Enhancing the adhesion properties and barrier action of the primer

might afford one way of reducing the amount of corrosion-inhibiting pigment needed.

The function of the topcoat was to provide the desired appearance (color and gloss), and the ability to withstand chemical, thermal, mechanical and environmental attack. Because the new resin was expected to exhibit performance characteristics similar to its parent polyurethane, meeting the specified durability was not a concern. Meeting the desired flexibility specification, even at low temperature, was also not a concern as the flexibility/hardness of polyurethanes can be readily optimized by modifying their functionality and chain length. On the other hand, achieving the desired color and flatness required the addition of significant quantities of pigments that absorb and scatter incident UV radiation. Consequently, achieving the desired appearance of a UV-curable coating was expected to present a formidable challenge.

### Formulation Design

As indicated in Figures 1 and 2, the formulations were based on a polyurethane backbone with functional end caps and non-volatile reactive diluents were used in place of conventional VOC solvents. This 100% solids formulation undergoes in room temperature, in which all constituents in the formulation were reactive and copolymerized into an adherent, durable coating. The formulation contained photoinitiators that initiated this cure reaction when triggered by UV light, as well as other fillers that were added to achieve specific attributes. For example, a non-chromate corrosion inhibitor package was added to the primer, and pigments to obtain the desired color and gloss were added to the topcoat.

### Resin Chemistry

A family of compatible coatings that can be used as primers, topcoats or

possibly “one-coat” systems for a range of applications can be based on the resin chemistry described here by simple modifications to the formulation. The oligomer selected for the resin backbone (for example, polyol, polyester, or polyurethane, see Figure 1) as well as its chain length had a significant effect on the durability, flexibility and hardness of the coating. Increasing the functionality of the oligomer increased the crosslink density of the cured resin, increasing its tensile strength, hardness and scratch resistance as well as improving resistance to solvents, chemicals, moisture and weather. Lowering the crosslink density improved toughness, flexibility, and impact resistance, and also reduced problems such as poor adhesion that are associated with shrinkage on curing.

A polyurethane backbone was selected as its excellent performance characteristics are well established in the aerospace industry. The “terminal functionality” allowed the resin to be photochemically crosslinked through a free-radical polymerization process initiated on exposure of the wet film to UV radiation. The terminal functionality also served to reduce the viscosity of the formulation and also increased the hardness and the resistance of the coating to rain erosion and UV exposure. An important property of the functional group selected was that it stabilized the formulations during storage, preventing decomposition and premature crosslinking.

The amount and type of other ingredients in the formulation also impacted the properties and performance of the coating. Some of these are summarized in Table 1 and discussed further.

### Reactive Diluents

The end-capped oligomer was mixed with reactive diluents (monomers) to reduce the viscosity of the resin to a

sprayable consistency. During cure, the reactive diluents were incorporated into the crosslinked polymer without emission of vapors. Because they participate in the cure reaction and are an integral part of the crosslinked matrix, reactive diluents also contributed to the properties of the cured coating. Increasing the functionality or decreasing the molecular weight of the monomer typically resulted in coatings with increased hardness (higher glass transition temperature) at the expense of flexibility and impact resistance. Monomers with lower reactivity reduced the cure rate, crosslink density, and shrinkage of the coating, and improved adhesion and flexibility at the expense of reduced hardness and chemical resistance.

The amount of reactive diluent added to the formulation was limited, as addition of excess quantities compromised the performance of the coating. If adequate viscosity reduction cannot be obtained by monomer addition, other means might be considered. For example, non-reactive, non-VOC solvents such as acetone that are referred to in the aerospace NESHAP as “exempt solvents” may be suitable in some applications. Alternatively, the viscosity can be lowered by reducing the molecular weight of the oligomer backbone or by reducing the number of mobility-reducing pendant groups on the backbone. However, modifying the oligomer structure is far more useful for tailoring the performance of the resin than for viscosity reduction and is not normally used for viscosity control.

### Pigments and Additives

Pigments and additives were used to achieve or enhance specific properties and included color and gloss pigments; surface wetting, coupling and thixotropic agents; defoamers; and light stabilizers. The amount and type of filler used

depends on the type of coating and the specific application. Fillers such as silica, alumina, talc, clays and other similar materials may also be added to affect properties such as scratch and abrasion resistance, gloss/matte appearance, etc., depending upon the type of coating and the specific application. Here, we limit the discussion to pigments added for corrosion inhibition and for achieving the desired color/gloss.

### Corrosion Inhibition

As stated, protection against corrosion is one of the key requirements of aerospace primers when used on metal substrates. As chromate inhibitors are not environmentally preferred, several non-chromate corrosion inhibition packages were evaluated. In addition to providing the desired degree of protection, any inhibitors used had to be soluble in and compatible with the formulation and not adversely affect the UV cure and performance of the coating.

The inhibitor pigments evaluated were non-chromate systems that function by retarding the oxygen-reduction step of the corrosion reaction. As the formulations described here have exceptional adhesion properties, providing a durable barrier against corrosion-causing agents (moisture and oxygen), only nominal amounts of corrosion inhibition package were required. The adhesion properties of the coatings were further enhanced by the addition of silane coupling agents to the formulation as shown in Figure 3. This approach could be followed to reduce the quantity of corrosion inhibiting pigments should they adversely impact the UV-cure process.

### Color and Gloss

The design of the pigment package depends on the color and gloss requirements of the topcoat. The specified color might fall anywhere in the visual spectrum and gloss requirements range from flat to prevent visual/

TABLE 1

## Effect of formulation design on coating properties

Variable	Property	Remarks
<b>Oligomer Chemistry</b>		
Backbone type	Performance	Urethane, urea, ether, ester, epoxy. Aliphatic, aromatic.
Backbone length	Viscosity Performance	Determined by the MW of reactants used to synthesize the oligomer.
Backbone modification	Performance	Fluorinated backbones (APCs) enhance UV exposure resistance performance but are costly.
Isocyanate type	Viscosity Performance	Tetramethyl xyllylene diisocyanate (TMXDI) Trimethyl hexamethylene diisocyanate (TMDI), Isophorone diisocyanate (IPDI), uretdione. Poly-functional branched isocyanates lower viscosity and enhance hardness and fluid resistance. Aliphatic isocyanate-terminated polyester urethane pre-polymers improve resistance to rain erosion and hydraulic fluids.
Terminal functionality	Viscosity Cure rate Cross-link density Performance	The functional groups provide the UV-cure capability; the functional type affects the stability of the formulation as well as the cure process.
<b>Formulation Design</b>		
Oligomers and their blends	Viscosity Cure rate Cross-link density	Select for viscosity, clarity, gloss as well as performance properties.
Reactive diluents -type and amount	Viscosity Performance	Concentration and type. Mono, di- and tri-functional monomers.
Additives—type and amount	Application Performance	Many types available including adhesion promoters; defoamers; dispersion, wetting, thixotropic, and silane coupling agents.
Pigments and extenders—type and amount	Appearance Cure rate Performance	Typically TiO <sub>2</sub> + carbon black for 595A color. Flattening agents to reduce gloss. Pigments interfere with UV cure.
Photoinitiators and co-initiators—type and amount	Cure rate Performance	Benzyl dimethyl ketal, trimethyl-benzo-phenone. Reactive amine co-initiators. Compatibility issues. Response to specific UV wavelengths.
<b>Cure Conditions</b>		
UV irradiance and energy density	Cure rate Performance	Type and power of lamp. Rate of traverse. Adherence better with slow cure.
Coating thickness	Cure	Thick layers reduce UV penetration. Multiple thin layers require good interlayer adhesion.
Crosslink density	Performance	Determined by cure and by the MW and functionality of the oligomer and monomer. Increases hardness, thermal and chemical resistance; decreases flexibility and adhesion.
Glass transition temperature, T <sub>g</sub>	Performance	T <sub>g</sub> is a measure of the crosslink density.

IR detection of aircraft, to high gloss to minimize drag, reduce maintenance, decorate, and to identify aircraft.

In this, a pigment package to produce the color specified by Federal Color Code 595A in combination with low gloss (< 10% at 60° viewing angle) was produced. The color pigment consisted of a mixture of titanium dioxide and carbon black. At the loading levels used in this study, titanium dioxide did not significantly affect the cure process. Regular carbon black, on the other hand, adsorbed incident UV light and significantly impeded the cure. However, it was found that a grade of low-absorbance carbon marketed especially for UV-cure applications did not hamper the cure when used in combination with certain photoinitiators described here. A non-crystalline silica product was used to reduce the gloss.

## UV Cure

Proper cure is essential to achieve the target application performance of the coating. Under curing the coating can lead to reduced adhesion and insufficient physical and chemical properties. Excessive radiation can lead to photodegradation, causing discoloration and degradation of physical properties.

A complete cure does not occur even with adequate radiation if pigments in the formulation absorb (filter) the incident UV light, an effect known as pigment inhibition. Although surface layers of the coating may be adequately cured, the cure is incomplete at greater depths resulting in rapid failure of the coating due to poor adhesion and inadequate mechanical strength. In UV-cure formulations, competitive absorption of the incident UV light by pigments, fillers and other additives can lead to under curing. These effects may be particularly problematic at higher coating thickness and in formulations with high loading of absorbing additives.<sup>3</sup>

Various means of limiting the effect of pigment inhibition may be considered. For example, the coating may be applied in multiple thin layers that are cured after each application, but this is highly inefficient in terms of labor and time. A “dual-cure” mechanism in which an initial UV cure produces a tack-free finish, followed by a “dark cure,” which completes the polymerization process, is more effective.<sup>5,6</sup> In addition to the photoinitiator, dual cure requires a catalyst that promotes the conventional “thermal” polymerization reaction at near ambient temperature. Peroxides have been found to be useful catalysts in this regard and become effective at the slightly elevated temperatures attained during the UV cure. To avoid problems with residual peroxide, the catalyst should have a short half-life at temperatures approaching

the final temperature achieved during the photocure.

This work focused on attaining a complete, full-depth cure without catalyst and with the coating applied at its specified thickness. The techniques followed used a combination of photoinitiators that have been recently developed for pigment applications, together with pigments produced specifically for UV-cure coatings.

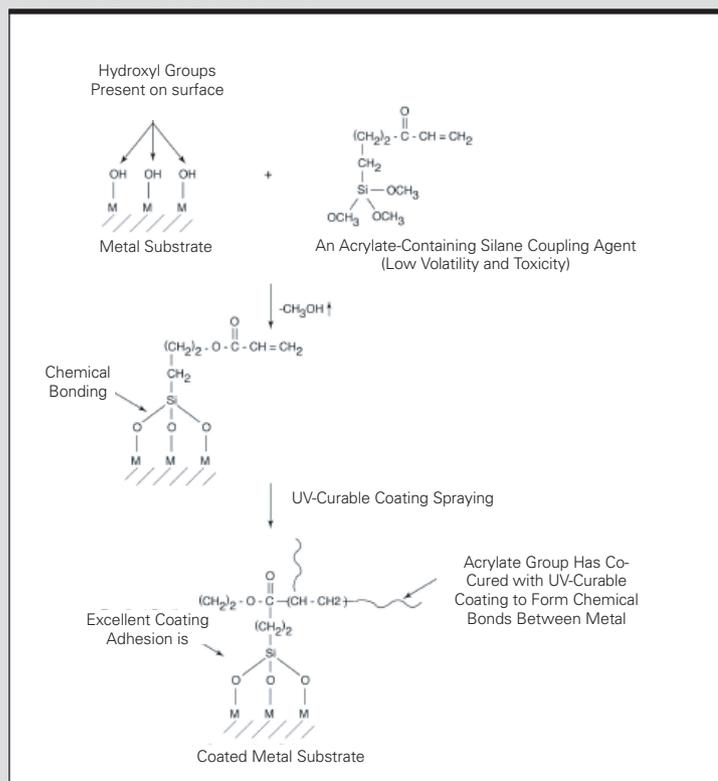
## Photoinitiators and UV Lamps

Recently, photoinitiators, which absorb over specific ranges of the spectral band, and matching UV lamps have become available.

A potential problem is that many photoinitiators are solid at room temperature and have to be dissolved before incorporating them into the

## FIGURE 3

### Use of silane coupling agents to improve bonding to metallic substrates



coating formulation. Solubilizing solid photoinitiators into the coating may require excess or additional diluents that could adversely affect the properties of the coating. Where possible, therefore, liquid photoinitiators should be selected. Other options include dissolving the photoinitiators in the reactive diluent, dissolving a solid photoinitiator in a liquid one (if used), and dissolving the photoinitiators in nontoxic, nonvolatile solvents that do not adversely affect coating properties.

### Coating Performance

The resin chemistry described here is the basis for a family of UV-cure

coatings that can be tailored to meet specifications prescribed for a wide range of applications in aerospace and other industries. To date, coatings for interior and exterior applications have been developed including primer, exterior flexibilized coating, specialty coatings, a general-purpose patch repair coating that can be expediently used for field repair with minimal surface preparation. APC-fluorinated topcoat is currently being developed.

All these coatings have been subjected to standard performance tests and shown to meet relevant ASTM and MIL-SPECs. Some results for two aerospace coatings are shown in

Tables 2 and 3. As can be seen, the coatings have passed all the performance specifications completed to date, showing not only that the base chemistry is inherently effective and dependable, but also that the pigmented coatings can be thoroughly cured.

### Discussion and Conclusions

The family of resins discussed is environmentally compliant and can be readily qualified to the stringent performance specifications of the aerospace industry. These one-component products can be tailored for primers, topcoats and repair coats for interior and exterior duty; they have long shelf-

## TABLE 2

### Properties of coating for aerospace application I

Test	Test Method	Test Condition	UV-Curable Coating Data	Pass/Fail
Hardness	ASTM D2240 Shore A		80	Pass
VOC	ASTM D5403-93	RT	1 %	Pass
Cure Shrinkage	ASTM D2240 Shore A	In Any Dimension of Volume	None	Pass
Percent Elongation at Break	ASTM D412 Die, C, 0.2 in./min	RT	36	Pass
		-65°F	7	Pass
Water Immersion		24 hr RT	No Marring or Coating Removal	Pass
Resistance to Operational Fluids		7 Days 49°C, JP-8 Oil, Coolant	No Softening, Wrinkling, Blistering, Loss of Adhesion	Pass
		7 Days 65°C, Hydraulic Fluid	No Softening, Wrinkling, Blistering, Loss of Adhesion	Pass
		7 Days, 121°F, Lubricating Oil	No Softening, Wrinkling, Blistering, Loss of Adhesion	Pass
Flexibility	ASTM D522	-65°F, 1 in. Mandrel	No Cracks Over 3/16 in. Mandrel	Pass
		RT, 1 in. Mandrel		Pass
Chemical Resistance	ASTM D5402 (using 50 double rubs)	RT	No Significant Loss of Material, Swelling, Hardness Change or Cracking	Pass
Storage Stability	GC Had Space Analysis, NMAN Method 2501	2 Year Observation, Data taken at Periodic Intervals	No Decomposition	Pass
In-Vitro Testing	Corrositex Skin Model	Ocular and Dermal Simulated Human Skin	Not Corrosive	Pass

**TABLE 3**

**Properties of coating for aerospace application II**

Test	Test Method	Test Condition	UV-Curable Coating Data	Pass/Fail
Condition in Container		RT	Homogeneous Free from Skins, Lumps an Gelled or Coarse Particles	Pass
VOC		RT	Zero VOC	Pass
Cure Time	ASTM D2240 Shore A	2 hr Hardness	Instant Cure, 84-87 Shore A	Pass
	ASTM D2240 Shore A	5 Days Hardness	Instant Cure, 84-87 Shore A	Pass
	ASTM D412 Die C, 0.2 in./min	-65°F	1650	Pass
Ultimate Tensile Strength, psi	ASTM D412 Die C, 20 in./min.	RT	450	Pass
		250°F	140	Pass
		275°F	120	Pass
		MIL-PRF-87252	430	Pass
		MIL-DTL-83133	275	Pass
		MIL-PRF-83282	390	Pass
		MIL-PRF-23699	310	Pass
		AMS 1424	350	Pass
		Heat Cycle	370	Pass
		ASTM B117 for 500 hr	430	Pass
		ASTM B117 for 2000 hr		In test
		100% Relative Humidity per ASTM DD247 at 120°F for 30 Days	480	Pass
		ASTM G85 Annex A4		In test
Percent Elongation at Break	ASTM D412 Die C, 0.2 in./min	-65°F	35	Pass
		RT	55	Pass
		250°F	13	No Spec
		275°F	9	Fail
		MIL-PRF-87252	42	Pass
		MIL-DTL-83133	27.4	Pass
		MIL-PRF-83282	41	Pass
		MIL-PRF-23699	32	Pass
		AMS 1424	51	Pass
		Heat Cycle	25	Pass
		ASTM B117 for 500 hr	52	Pass
		100% Relative Humidity per ASTM D2247 at 120°F for 30 Days	333	Pass
Chemical Resistance	ASTM D5402 (Using 50 MEK double rubs)	RT	No significant Loss of Material, Swelling, Hardness Change or Cracking	Pass

and pot-life, and can be readily applied by conventional spray or roller techniques. The formulations cure within minutes on exposure to UV radiation and neither evolve vapors nor require application of heat during cure. As the coatings can be applied using conventional spray techniques and because the rapid UV cure means substantially shorter turnaround times, it is anticipated that these products will substantially reduce the overall coating process cost.

The challenge of curing relatively thick layers of pigmented coating was successfully addressed. It was found that the dual-cure technique was effective at coating thicknesses ranging from 1-50 mils. The formulations exhibited excellent interlayer adhesion and could be applied in multiple layers up to thicknesses of 250 mils. In all cases, the coating was "frozen" in place on cure, and there was no shrinkage, void formation or settling.

The formulations described here are ideal replacements for conventional aerospace products. They form highly elastomeric coatings, retain their flexibility at temperatures down to -65°F, and exhibit excellent adhesion, hardness and resistance to operational fluids. Two important attributes of particular relevance to the aerospace industry are:

- **Inherent adhesion and barrier properties.** The formulations adhere to a large number of substrates including composites, aluminum and steel, and wood. In particular, they show excellent adhesion to primed and unprimed airframe grade aluminum. Barrier properties are outstanding, achieving excellent corrosion protection even without inhibitors.
- **Customizable flexibility and toughness.** The resin properties can be easily tailored to meet

a range of platform-specific requirements by changing the type and length of the oligomer backbone. Secondary means of customizing the properties include adjusting the crosslink density, the type and amount of reactive diluents incorporated, and the use of additives.

This chemistry is environmentally compliant in that it contains no VOCs, HAPs or TRIs. Importantly, free isocyanates are not present as the diisocyanate used for polyurethane synthesis is completely reacted. Other environmental benefits include:

- **Absence of solvents.** Reactive diluent successfully reduces the viscosity to a consistency suitable for spraying with conventional high volume/low pressure (HVLP) guns.
- **Absence of vapors.** As the reactive diluents and other components are not volatile at ambient conditions, there is little or no evaporation during application and cure. Furthermore, because the cure reaction goes to completion, solid wastes produced in service and during stripping are non-hazardous.

Foster-Miller is leading a collaboration with raw material suppliers and lamp manufacturers in the development of UV-cure coatings that meet the stringent performance requirements of the aerospace industry. They are working to insure that the industry is receptive to this viable technology.

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