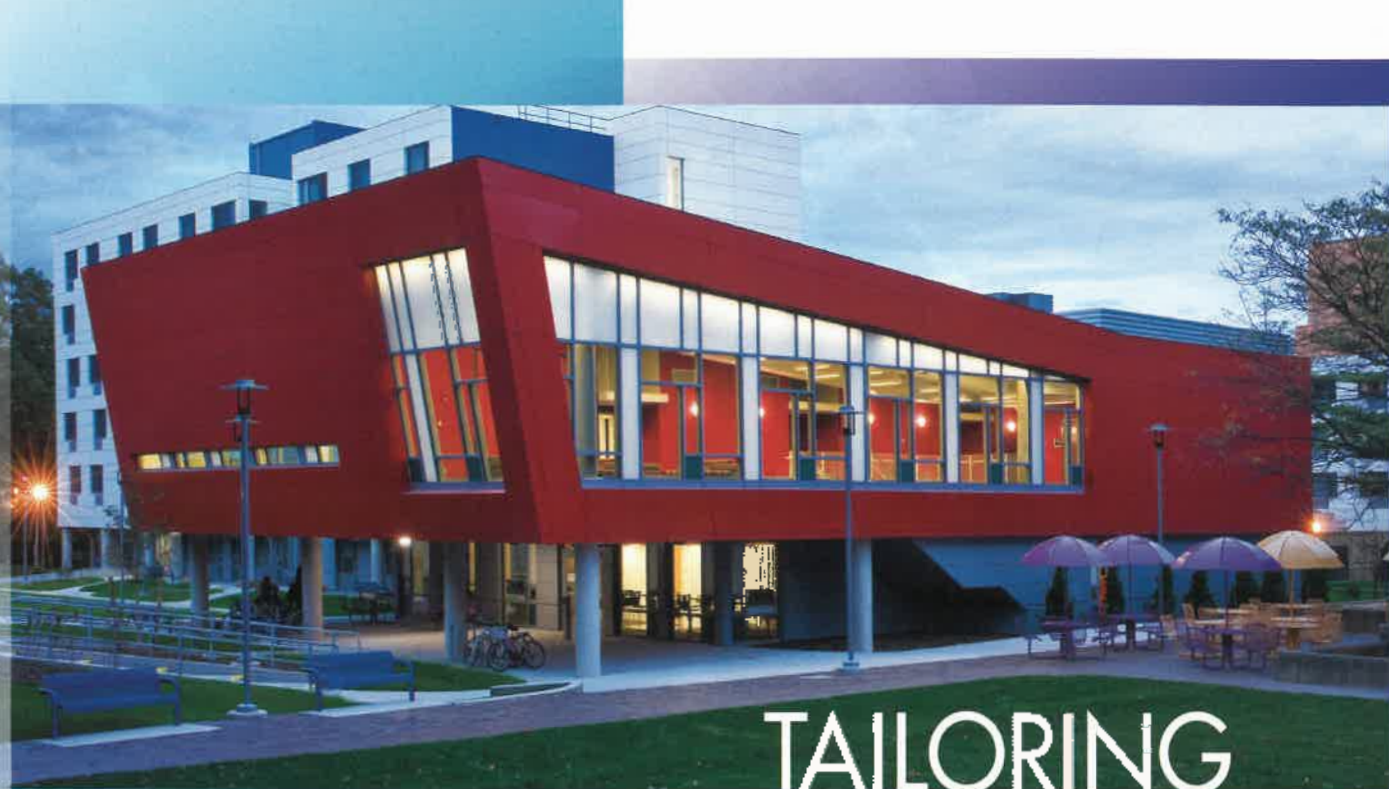




TAILORING CROSSLINK DENSITY AND INDEX IN 2K WATERBORNE PVDF COATINGS

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Hydroxy-functional PVDF (polyvinylidene fluoride)-acrylic waterborne hybrid dispersions, crosslinked with water-dispersible polyisocyanates, develop film properties through both polymer entanglements and crosslinking reactions. Since the majority component PVDF does not contain crosslinkable groups, the crosslink density which can be generated is limited. Increasing the index (isocyanate:hydroxyl equivalent ratio) above 1.0 can increase the crosslink density, through reaction of the isocyanate with ambient water to yield urea linkages. However, there are significant drawbacks to this approach (e.g., shorter formulation shelf life and slow hardness development). In this article, we describe new experiments involving blends of hydroxy-functional PVDF-acrylic hybrids with various oligomeric and polymeric polyols, which allow for independent adjustment of the crosslink density and the index to meet differing application requirements.

Presented at the 2014 American Coatings Conference, sponsored by the American Coatings Association and Vincentz Network, in Atlanta, GA, April 7-9, 2014.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF)-based topcoats¹ have been used on monumental buildings around the world for many years, to meet the needs of architects and engineers for the highest levels of decorative property durability and substrate protection. In these coatings, the polymer binder is typically a blend of 70–80 wt% PVDF resin with 20–30 wt% of a miscible acrylic resin. In most of these systems, a high-temperature bake (230–250 °C) is required for alloying of the polymer components. This requirement has historically limited the use of this technology mainly to substrates that can withstand these baking conditions (e.g., metals). In recent years, however, the baking limitation has been lifted, as new water-based hybrid resin technology has become commercially available.² This technology combines PVDF copolymers and acrylic resins in pre-alloyed form,³ in proportions similar to the baked systems. The new water-based technology allows for the application of durable PVDF-based coatings under field-applied and low-temperature bake OEM conditions, with dramatically lower levels of emitted volatile organic compounds (VOC).

Several such water-based hybrid products are now commercially available. As with standard solvent PVDF finishes, a number of these binders are designed for use as thermoplastic systems, with the final properties of the coating being built up through polymer entanglements. Coatings based on thermoplastic PVDF hybrid waterborne binders have already demonstrated weathering performance comparable to the baked PVDF finishes (at the same 70% PVDF level), with more than 10 years Florida gloss and color retention.⁴ Typical applications for these waterborne thermoplastic topcoats include restoration coatings for baked PVDF finishes on metal, finishes on commercial and residential windows and doors, coatings for residential siding, and "cool white roof" coatings.⁵

More recently, we have also introduced a new hydroxy-functional product in this class, which can be combined with crosslinkers to make thermoset or crosslinked formulations.^{6,7} These systems show enhancements in certain key properties such as early hardness, solvent resistance, and adhesion, with performance contributions coming both from the entangled polymer network, and from the network formed by crosslinking reactions.

GENERAL PRINCIPLES AND PERFORMANCE PROPERTIES OF 2K PVDF HYBRID COATINGS

For ambient temperature or low-temperature bake coatings based on waterborne OH-functional resins, water-dispersible polyisocyanate crosslinkers are often preferred. The crosslinker isocyanate groups react with the resin hydroxyl (-OH) groups to make urethane linkages, while excess isocyanate combines with ambient water in a series of reactions to make urea linkages.⁸ With this technology, while the final coating formulation is two-component (2K) and so has a finite potlife, high performance coatings are generally achievable at very low VOC levels, with reasonable dry times and cure requirements.

To achieve the expected properties in a 2K dispersion coating, it is necessary that most of the crosslinking reaction occurs after the coalescence of the dispersion particles, i.e., after the early stages of film formation are substantially complete.⁹ For this reason, because of their slower ambient reaction rate with hydroxyl groups and water, aliphatic polyisocyanates are generally used in waterborne 2K systems. Aliphatic polyisocyanates also have advantages over aromatic polyisocyanates in terms of weatherability and industrial hygiene.

Like the other PVDF-acrylic hybrid latex products, the particles of the hydroxy-functional version

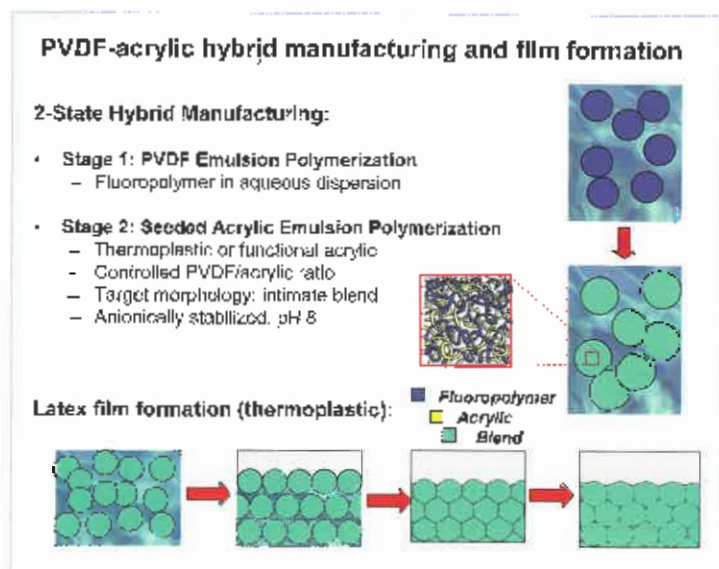


Figure 1—Schematic of the manufacturing and film formation processes for PVDF-acrylic hybrid dispersions. As shown by the color coding, the target resin morphology is a miscible alloy or "IPN" type blend structure.

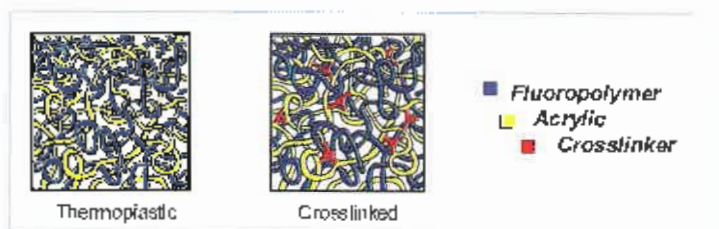


Figure 2—Schematic of expected polymer blend morphology in the final coatings film, for thermoplastic (left) and 2K urethane thermoset PVDF-acrylic hybrids. Color code: blue = PVDF resin, yellow = acrylic resin; red = polyisocyanate crosslinker.

are structured as an intimate mixture or interpenetrating network (IPN) of the two thermodynamically miscible polymers³ (Figure 1). Because the chemical inertness of the PVDF makes it difficult to functionalize, the hydroxyl functionality is on the acrylic component only. The standard model of latex film formation¹⁰ would predict that for thermoplastic systems, the latex particle morphology should be maintained during the film formation process. In the 2K systems, where crosslinking of the hydroxyl groups is occurring late in the film formation process, the expected polymer morphology in the final coating film should be a bi-continuous network of fluoropolymer and acrylic-urethane (Figure 2). In such cases, contributions to certain properties such as mechanical properties and abrasion resistance would be expected both from the PVDF fluoropolymer backbone, and from the urethane network formed by the crosslinking reaction.

The crosslinked acrylic-urethane component is designed to improve the solvent resistance of the entire PVDF resin blend binder, compared to un

Figure 3—Solvent resistance of PVDF hybrid 2K coatings, as a function of the index (eq NCO: eq OH), after a typical low-temperature bake schedule. The isopropanol resistance (required by many window manufacturers) is excellent at all crosslinker levels. However, if MEK resistance is also needed, the index must be above 2.

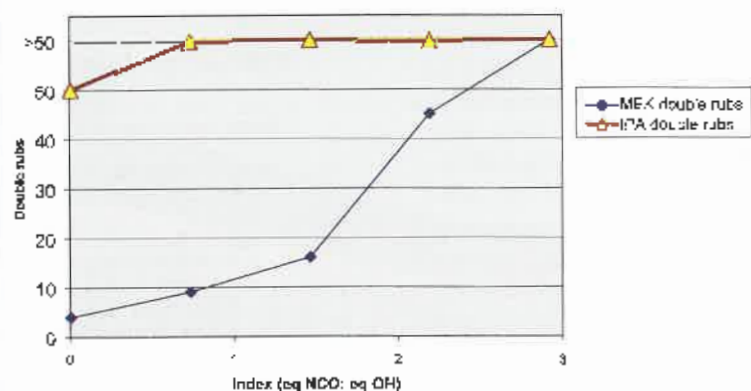


Table 1—Polyols and Diols Used in This Study

Material	Type ^a	Molecular Weight	OH Equivalent Weight on Solids or Active
"70:30" Hybrid (70 wt% PVDF/30 wt% OH-functional acrylic)	Polyol (Fn > 3)	high	3178
Acrylic latex A	Polyol (Fn > 3)	high	1300
Acrylic latex B	Polyol (Fn > 3)	high	1300
Acrylic latex C	Polyol (Fn > 3)	high	1260
Polyacrylic secondary dispersion D	Polyol (Fn > 3)	medium	587
Polyurethane diol	Diol (Fn = 2)	300s	178
Poly(propylene glycol) 400	Diol (Fn = 2)	400	200
Hydroxyalkylamide Tetra-ol 552	Polyol (Fn = 4)	300s	86

Table 2—Examples of Resin Blend Formulations

A Component	80:20 Blend with Acrylic Dispersion A	60:40 Blend with Acrylic Dispersion A	80:20 Blend with Polyacrylic Secondary Dispersion D	Blend with 10 phr HAA Tetra-ol
<i>Add in order:</i>	<i>Parts by weight:</i>			
"70:30" PVDF-acrylic hybrid dispersion (44% solids)	240	180	240	300
Acrylic latex A (44% solids)	80	120		
Polyacrylic secondary Dispersion D			64.4	
HAA Tetra-ol Primid [®] XL-552				13.2
Silica flattening paste (17% solids in water)	40	40	40	40
Pigment Grind (rutile TiO ₂ + optionally mixed metal oxide color pigment)	140	140	140	140
Polysiloxane wetting agent	0.5	0.5	0.5	0.5
Defoamer	0.5	0.5	0.5	0.5
DPMME (dipropylene glycol dimethyl ether) CAS 111109-77-4	8	8	8	8
Water	20	20	40	40
HEUR-type associative thickener	0.5	0.5	0.5	0.5
Total A Component:	509.5	509.5	533.9	542.7
B Component				
Water dispersible polyisocyanate	15.5	18.7	42	42
Index NCO:OH	1.1	1.1	2.1	1.07
wt% solids	48.8	49	50.3	50.6
vol% solids	36.2	37.4	37.2	40.2

crosslinked systems of similar blend composition—particularly resistance to active solvents for the PVDF copolymer (which, being nonfunctional, cannot chemically crosslink into the network). For instance, in some early prototype paints, it was possible to achieve two-week immersion resistance to Skydrol® hydraulic fluid with certain 50 wt% PVDF hybrid compositions. Not surprisingly, the degree of resistance to active solvents depends very much on the crosslink density that can be achieved. The density of urethane crosslinks in the final film cannot be higher than the density of hydroxyl groups in the resin. However, since isocyanates also react with water to make urea linkages, overcharging the polyisocyanate crosslinker beyond the stoichiometric ratio for urethane formation leads to even higher crosslink density.

Figure 3 demonstrates the effect of index (ratio equivalents -NCO: equivalents -OH) on solvent resistance for a typical 70% PVDF-30% acrylic hybrid coating formulation. While it is easy to meet the alcohol resistance requirement for a typical window profile application, at an index of even less than 1.0, to achieve good resistance to a more aggressive solvent, MEK, an index of at least about 2.0 was required.

One advantage of using aqueous dispersions crosslinked with water-dispersible polyisocyanates, compared to conventional solvent 2K urethane systems, is that it is often possible to decouple certain important early properties (e.g., drying speed and early hot print resistance), from ultimate properties which depend on the crosslink density (e.g., chemical resistance). In these aqueous systems, because of the high molecular weight of the polymer binder, reasonably good early mechanical properties can be obtained as soon as the coating film is physically dry, even before the isocyanate crosslinking reactions are substantially completed.¹¹

For the new PVDF hybrid aqueous systems, we have found that early properties are generally comparable to those of commercial acrylic aqueous dispersions using the same 2K crosslinking approach,¹² particularly at an index of around 1.0. However, in over-indexed systems (i.e., those with a stoichiometric excess of polyisocyanate), certain ultimate properties such as scratch resistance appear to take longer to develop¹³ than they do for the aqueous acrylic systems, at a comparable index. This may be related to the higher hydrophobicity of the PVDF-rich hybrid systems. Compared to acrylic, polyester, or PUD polyol dispersions, there will be less residual water in the dried coating film which can react with residual isocyanate, and also less mobility of uncrosslinked chain ends and other polymer segments due to reduced water plasticization.

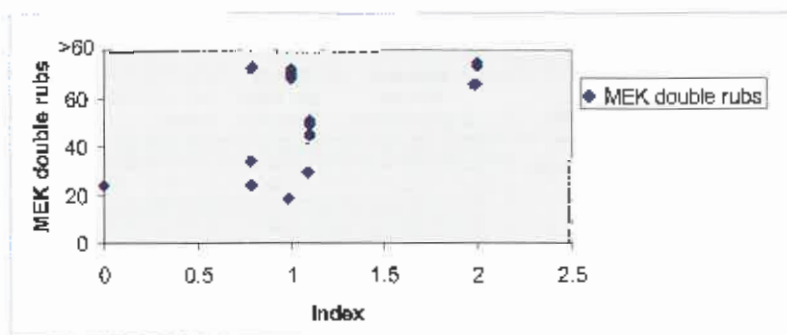


Figure 4—MEK resistance of crosslinked formulations of blends of a PVDF hybrid latex with a second, lower OH equivalent weight polyol or diol. The same commercial polyisocyanate crosslinker was used in all formulations. MEK double rub tests were stopped at about 60 double rubs, so no conclusions may be drawn about the relative performance of the coatings passing more than 60 double rubs.

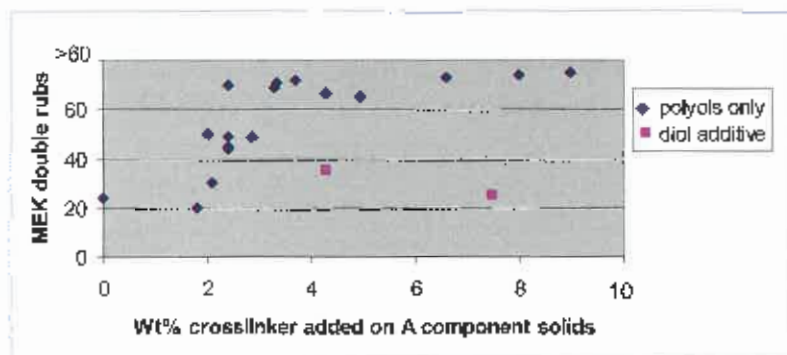


Figure 5—MEK resistance of crosslinked formulations of blends of a PVDF hybrid latex with a second, lower OH equivalent weight polyol or diol. The same commercial polyisocyanate crosslinker was used in all formulations. MEK double rub tests were stopped at about 60 double rubs, so no conclusions may be drawn about the relative performance of the coatings passing more than 60 double rubs.

USING POLYOL ADDITIVES TO DECOUPLE INDEX AND CROSSLINK DENSITY

To boost the crosslink density of 2K PVDF-acrylic hybrid coatings, while still maintaining the dry speed and early property advantages of systems with a lower index (~1.0), we began looking at blends of a specific 2K PVDF-acrylic hybrid (with a 70 PVDF:30 acrylic weight ratio) with other, lower equivalent weight hydroxy-functional materials. Both acrylic resin polyols and oligomeric diols and polyols were evaluated for their effects on properties.

In one screening experiment, a series of A-component (polyol component) blends was prepared, with the majority component (on a weight basis) being the 2K PVDF acrylic hybrid, and the minority component being either a polyol resin dispersion, or a low molecular weight polyol (added neat). Several blend materials in each category were tested, as shown in Table 1. Two-component coating formulations were then prepared from these blend formulations, using

Table 3—Solvent and consumer product resistance tests, for a series of 2K PVDF-acrylic hybrid white formulations.

Pigment Volume Concentration	With 5 phr HAA Tetra-ol?	Index	24-hr Covered Exposure Banana Boat [®] 50 SPF	10 Minutes Nail Polish Remover	10 Minutes OFF! Deep Woods [®]	MEK Double Rubs	Goof-off [™] Pro Strength Remover Double Rubs
15	No	1	Dense microblistering	Pass	Pass	28	10
15	Yes	1	No visible changes	Pass	Pass	68	35
30	No	1	Moderate microblistering	Pass	Pass	19	7
30	Yes	1	No visible changes	Pass	Pass	37	13
15	No	2	Slight microblistering	Pass	Pass	45	49
15	Yes	2	No visible changes	Pass	Pass	>100	>100
30	No	2	No visible changes	Pass	Pass	14	9
30	Yes	2	No visible changes	Pass	Pass	>100	>200

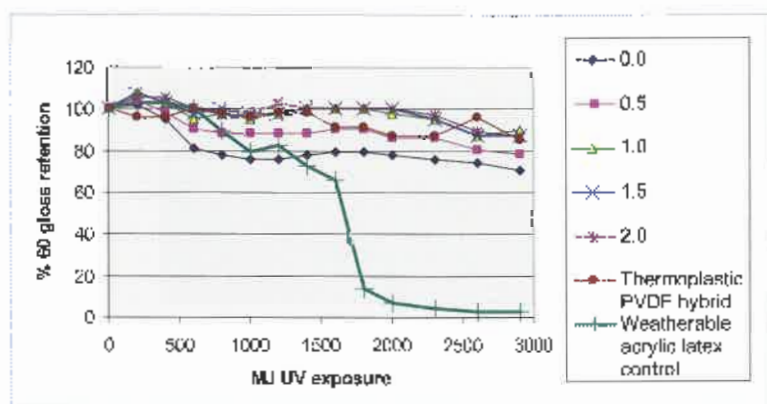


Figure 6—Gloss retention of 2K white PVDF-acrylic hybrid formulations, as a function of index vs. exposure according to ASTM G-90 solar concentrator accelerated testing with nighttime wetting. AAMA 625-10 requires a minimum of 50% gloss retention after 2900 MJ UV exposure.

the same commercial water-dispersible polyisocyanate as a B-component. Table 2 shows some representative formulations. Formulations were prepared at a variety of index levels. Typical resin blend ratios were 80:20 or 60:40 on solids (PVDF hybrid:co-resin) when the higher equivalent weight co-resins were used, or 90:10 when low molecular weight polyols were used.

The polyisocyanate crosslinker that was used in this study is believed to have a number average functionality slightly greater than 3. Since all the crosslinks in the coating should come from reactions of the polyisocyanate (either with A-component hydroxyls to form urethanes or with some other species such as water to form ureas), and since essentially all the isocyanate will eventually react over a period of weeks, the percent polyisocyanate on total binder weight can be used as a proxy measure of the ultimate crosslink density of the cured coating film.

To probe the crosslink density, after four to six weeks of bench aging, the 2K coatings were tested for MEK double rub resistance. Figures 4 and 5 show the results, plotted as a function of

index and of wt% polyisocyanate added, respectively. While there is no clear pattern to the MEK resistance data, for the various formulations at an index of about 1 (Figure 4), a clear trend is observed when the data are plotted according to crosslink density (as approximated by the % polyisocyanate crosslinker added): at crosslink densities generated by 4 wt% or more crosslinker on binder, at least 60 MEK double rubs may be reliably obtained. The two exceptions to this trend, shown as pink squares in Figure 5, happen to be the two formulations which also contained a lower functionality diol as the blend material. This is readily understandable, since diols would simply lengthen polymer chains and so would not be very effective in boosting the crosslink density of the material. Polyols with higher number average functionality are much more efficient in boosting the crosslink density.

Fully consistent with this line of argument, the screening experiment showed promising results for the hydroxyalkylamide tetra-ol as a blend additive. This material, which is sold commercially as a crosslinker for powder coatings,¹³ was originally developed as a waterborne crosslinker.¹⁴ It has a number of attributes that make it attractive in waterborne formulations: it is soluble in water, allowing for easy incorporation; it is low in toxicity; and it is aliphatic and reasonably weatherable. In clearcoat formulations, it also does not negatively impact film clarity.

Based on the encouraging results for this screening study, a second study was performed to look at resistance to a broader range of solvents, for PVDF hybrid formulations formulated with the HAA tetra-ol at a more modest 5 phr (5 parts by weight per hundred resin) level. Some results for this study are shown in Table 3. It can be seen that the addition of the tetra-ol at a 5 phr level can bring some chemical resistance improvements even at index 1, while some over-indexing (or a higher level of the tetra-ol) is required to achieve

good resistance to the most aggressive solvents. Further studies are now under way to better map out the performance that can be obtained in the intermediate formulation space—both ultimate properties and early properties.

APPLICATION PROSPECTS FOR THE 2K PVDF HYBRID TECHNOLOGY

In an earlier article,¹² we focused on the potential of the 2K PVDF technology to meet the physical property requirements of the most demanding window profile standards, such as the AAMA 625-10 Voluntary Specification for Superior Performance Organic Coatings on Fiber Reinforced Thermoset Profiles. Very recently, a series of coatings based on this technology easily passed the ASTM G90 accelerated weathering testing requirement for this standard. Figure 6 shows the effect of index on ASTM G90 gloss retention for a series of 2K PVDF hybrid coatings (without any added second polyol). While the gloss retention may be seen to be slightly better at higher index, even the index zero (no crosslinker) PVDF hybrid formulation easily passed the AAMA 625-10 requirement (>50% gloss retention after 2900 MJ UV exposure).

Based on these weathering results, 2K PVDF-acrylic hybrids are an attractive candidate for high performance topcoat formulations aimed at all common architectural window profile substrates—including primed aluminum, polyester fiberglass composites, and vinyl. Beyond this, with the option provided by polyol blend approaches for higher crosslink density, 2K PVDF hybrids would also be a candidate for applications requiring enhanced solvent resistance and hardness, such as railing and decking applications. ■

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