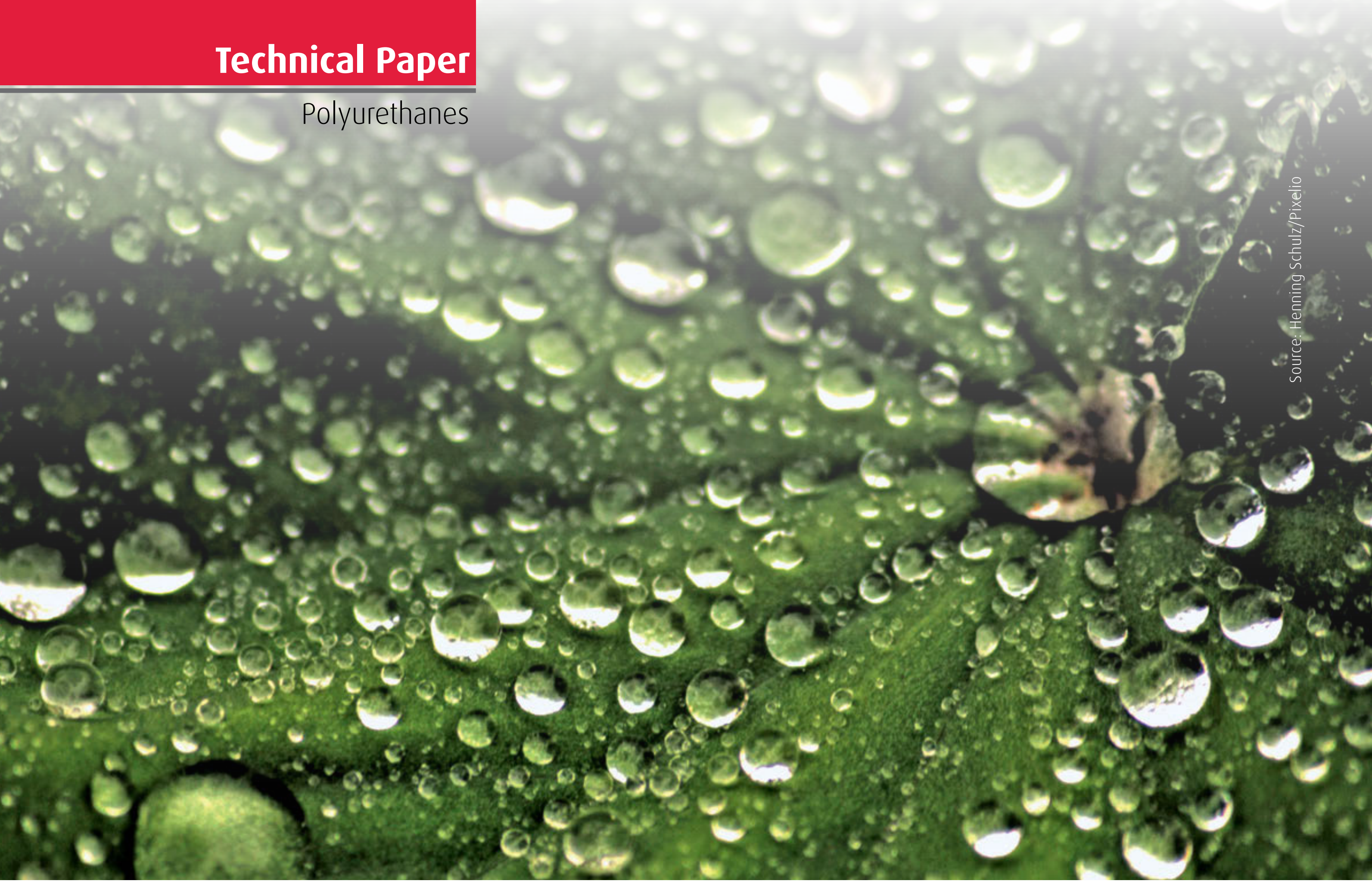

High performance in the frame

Waterborne finishes for PU pultrusion window profiles need no primer

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This paper was presented at the European Coatings Congress, 18-19 March 2013 Nuremberg, Germany

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Reinforced plastic composites known as pultrusions are becoming popular for window profiles. Polyurethane pultrusions offer enhanced performance but priming and/or pretreatment is usually required before topcoating to obtain adhesion. A highly weatherable 2K crosslinking PVDF-acrylic hybrid coating now offers the highest levels of durability without priming.

Depending on the region of the world, a wide variety of materials may be used for exterior window and door profiles. In North America, wood and more recently vinyl have tended to predominate in the residential window profile segment (which is mainly single-family homes).

For the commercial window profile segment, and particularly for larger buildings, aluminium is often the material of choice for window profiles. Pultrusion technology offers another option for both residential and commercial applications.

Pultrusions are thermoset composite materials which typically combine glass fibres with a resin system, such as unsaturated polyester or polyurethane. While the market share of pultrusion is still relatively small, it is growing rapidly at the expense of other substrate options.

Commercial windows are a market segment that is particularly attractive for polyurethane pultrusions. Here polyurethane technology offers physical properties that are almost equivalent to aluminium, with significantly better insulation properties.

Polyurethane is the only composite binder that can match the strength of aluminium for large commercial window applications. The polyurethane resins contain biobased feedstocks and are styrene-free, offering benefits to both producers and consumers.

Standards applicable to window profiles

A variety of standards are used in different parts of the world to specify window and door profile materials. In North America, the AAMA voluntary standards [1] are commonly used by architect-engineers and other designers to specify building components, including window profiles.
There are a number of AAMA standards which are devoted specifically either to thermoset composite materials themselves, or to coatings/finishes on thermoset composites. For finishes on pultrusions or other composites, three different standards embody a "good, better, best" hierarchy of performance: AAMA 623, 624 and 625.
In this hierarchy, a key differentiator is an increasingly high standard of weathering performance (gloss and colour retention, and chalking and erosion resistance). The standard of weathering performance for finishes on premium buildings has traditionally been set by the corresponding 'Superior' AAMA standard for aluminium, AAMA 2605, with its requirement of 10-year South Florida gloss and colour retention.
While the AAMA 625 standard for finishes on composites generally follows the AAMA 2605 requirements for coating performance, it does allow for Fresnel solar concentrator (ASTM-G90) accelerated weathering testing to be used as an alternative to ten years of Florida testing.

Plastic composites have limited coating options

There are several limitations at present to the growth of polyurethane pultrusion technology for windows and doors. To meet the standards for exterior window profiles, some kind of coating or cladding of the pultrusion is almost always necessary, due to the limited weatherability of the pultrusion resins, as well as the need for uniform surface quality.
For polyurethane pultrusions, because of the Tg of the polyurethane, high temperature stoving options such as powder coatings have not been a viable option. For low temperature stoving liquid coatings, some additional steps are usually required to assure good adhesion to the substrate. These steps might include a surface flame or plasma pre-treatment, and/or the use of a primer coat. All these procedures add cost and additional work.

Results at a glance

››› Reinforced plastic composites known as pultrusions are taking a growing share of the market for window profiles. New polyurethane pultrusion technology offers improved processing, physical and thermal properties.

››› However, the PU profiles require a surface coating to provide UV resistance. This normally involves pretreatment and/or priming, which increases costs.

››› Highly weatherable 2K urethane topcoat formulations have been developed, based on hydroxy-functional PVDF-acrylic hybrid emulsion polymers crosslinked with water-dispersible polyisocyanates.

››› These coatings adhere strongly to pultruded substrates without a primer coat. The formulations were optimised to provide early hardness and solvent resistance, as well as the mechanical and chemical resistance properties required for window profiles.

Waterborne PVDF-acrylic hybrids require no stoving

For premium finishes on aluminium window profiles, poly(vinylidene fluoride) (PVDF) based coatings [2] have been used for many years to meet the requirements of the AAMA 2605 'Superior' standard. These coatings, where the polymer binder is typically a blend of 70-80 wt % PVDF resin with 20-30 wt % of a miscible acrylic resin, usually require high temperature stoving (230-250 °C).
In the past few years, new water-based hybrid resin technology has become commercially available, combining PVDF copolymers and acrylic resins in similar proportions [3]. This technology allows durable PVDF-based coatings to be applied under field and low temperature stoving OEM conditions, without high levels of volatile organic compounds (VOCs).
Several such waterbased hybrid products are now commercially available. As with standard solvent PVDF finishes, most of these binders are designed for use as thermoplastic systems, with the final properties of the coating being built up through polymer entanglement.
More recently, a new hydroxy-functional product in this class has been introduced, which can be combined with commercially available water-dispersible polyisocyanate crosslinkers to make 2-component (2K) formulations [4]. In such systems, contributions to certain key properties such as early hardness, solvent resistance and adhesion can come both from the entangled polymer network and from crosslinking reactions and the networks that they form.

New system performs well in weathering studies

Because of their track record on aluminium window profiles, 70 % PVDF stoved finishes provide a very useful weathering benchmark for window profile coatings based on new resin technologies. Thermoplastic PVDF hybrid waterborne coatings have already demonstrated weathering performance comparable to the stoved PVDF finishes (at the same 70 % PVDF level), with more than ten years Florida gloss and colour retention [5].
To meet the most demanding weatherability requirements, it is necessary that the binder PVDF level should be as high as possible (in the 70 % range), and it is also very important to attend to all the other details of the formulation including pigment choice, pigment volume concentration and the quality of the dispersion of the pigment in the paint film [6].
Since the crosslinkable PVDF hybrid technology is relatively recent, accelerated weathering comparisons

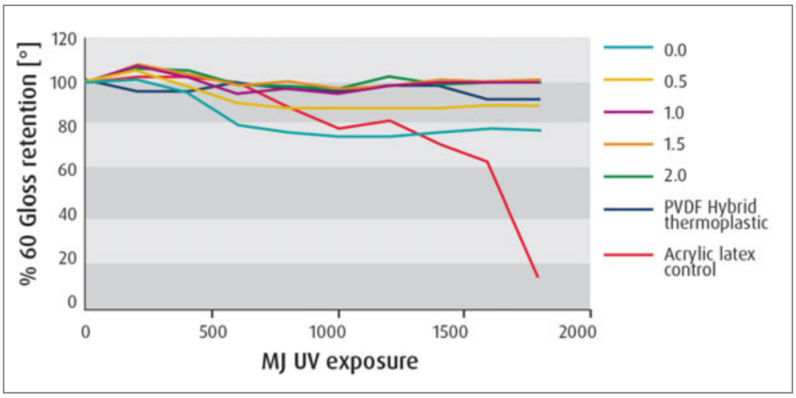

Figure 1: Per cent gloss retention of semi-gloss PVDF hybrid 2K coatings as a function of polyisocyanate crosslinker level (index = ratio of isocyanate to hydroxy equivalents), as a function of UV exposure dose in a Fresnel solar concentrator

against other PVDF-based coatings can be used to obtain a good estimate of weatherability. *Figure 1* shows some results to date for Fresnel solar concentrator (ASTM-G90) accelerated weathering tests of paint formulations with the new 2K PVDF hybrid binder.

The samples have surpassed the AAMA 624-10 milestone of 1450 MJ UV and are easily on track to meet the much more demanding AAMA 625-10 requirement of a minimum of 50 % gloss retention after 2900 MJ UV exposure. Colour retention is likewise excellent (*Figure 2*), with typical colour changes measured to date for tinted coatings in the range ΔE < 1 (the AAMA 625-10 standard is ΔE < 5 after 2900 MJ UV exposure).

Compared to non-fluorinated finishes that are commonly used for window profile topcoats, such as 2K solvent acrylic urethanes, or 2K waterborne acrylic-urethane hybrids, the weatherability of PVDF hybrid coatings is vastly superior. As one example, *Figure 3* shows the colour fade of some 2K coatings (commercial solvent acrylic urethane, and waterborne PVDF hybrid), after 1000 hours UVB fluorescent cabinet testing.

The UVB radiation accelerates the degradation of the binders, similar to what happens over several years of south-facing Florida exposure. A grey colour was chosen so that it is easy to assess, through colour fade, when the coatings have reached the chalking stage (i.e. when photooxidation has caused a complete loss of binder integrity near the top surface).

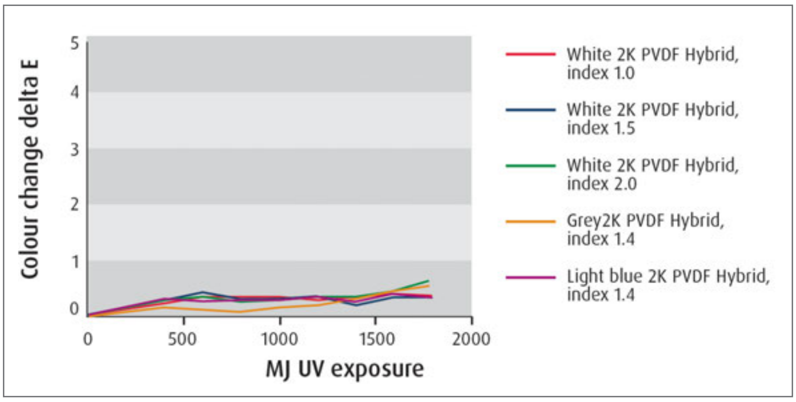

Figure 2: Colour retention of semi-gloss PVDF hybrid 2K coatings as a function of UV exposure dose in a Fresnel solar concentrator

Other key performance properties outlined

In addition to standards for ultimate coating properties, such as those in the AAMA or the European Qualicoat standards, most profile manufacturers also have some additional requirements for coating systems, related to the realities of the manufacturing process. The most common of these are some kind of requirement for early block and print resistance after a particular stoving schedule, and the need for some level of early solvent resistance, since cleaning solvents are used in the window assembly process.

In this context, one advantage of using aqueous dispersions and water-dispersible polyisocyanates, rather than conventional solvent 2K urethane systems, is that it is often possible to decouple certain 'early properties' that are important for general industrial finishes, e.g. drying speed and early hot print resistance, from longer-term properties such as chemical resistance which depend on the crosslink density. Because of the high molecular weight of waterborne dispersion binders, reasonably good early mechanical properties can be obtained as soon as the coating film is physically dry, before the isocyanate crosslinking reactions are complete [7]. Arkema lab studies have found that early physical properties of the PVDF hybrid system are generally comparable to those of commercial acrylic dispersions using the same 2K crosslinking approach.

Formulating to maximise chemical resistance

Extensive studies have also been made of the ability of different PVDF hybrid formulations, both 1K and 2K, to meet common mechanical and chemical resistance requirements for window profile coatings. While the results are to some extent formulation- and substrate-dependent, some generalisations are possible.

Assuming the topcoat adhesion is good (to the substrate, or to an appropriate primer), it is usually easy to pass almost all of the AAMA chemical tests (window cleaner, detergent, hydrochloric acid, nitric acid, mortar) with any of the commercial PVDF hybrid grades.

The introduction of the 2K crosslinking technology brings distinct advantages in terms of improved solvent resistance (e.g. isopropanol, MEK), pencil hardness, and direct adhesion to a variety of substrates. *Figure 4* shows some data for the evolution of the solvent resistance as a function of crosslinking index (the index is defined as the stoichiometric ratio of charged isocyanate to hydroxy equivalents).

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. *Figure 5* shows some representative data for pencil hardness.

Direct adhesion on PU pultrusions studied

The AAMA standards test adhesion in several ways. Crosshatch adhesion is tested both wet and dry, and after

a 2-hour boiling water test. The adhesion is also tested in a humidity cabinet for 4000 hours, and the window cleaner and detergent chemical tests also have an adhesion component. Obviously, for such tests, if a primer is not used, the exact details of substrate preparation and coating application play a significant role.
Tests by a number of paint companies indicate that 2K PVDF hybrid formulations easily achieve excellent adhesion directly to unsaturated polyester pultrusions. However, the newer polyurethane-based pultrusions, with their high fibre content, are known to be much more challenging in terms of achieving direct binder adhesion. Accordingly, Arkema and Bayer MaterialScience have conducted a series of joint studies to look at ways to improve direct adhesion.
The polyurethane pultrusion resin formulation consists of two components. The A component is a polymeric MDI isocyanate. The polyol or B component is a blend of polyols, catalysts, and internal release agent to allow for processing through the pultrusion die.
The internal release agent is a required part of the formulation. Several types can be used and typically are composed of fatty group compounds. In earlier studies at Bayer MaterialSciences, changes in the level and type of internal release agent did not affect the ability to achieve paint adhesion on the polyurethane pultruded parts.
In earlier Arkema studies, a prototype version of the 2K PVDF hybrid binder showed some promising results in terms of achieving direct adhesion to polyurethane pultrusions [8]. Key factors for good adhesion identified in that study included the use of a particular polyisocyanate crosslinker, and the use of a specific internal release agent in the pultrusion formulation.
More recently, this adhesion question was re-examined with the newly available commercial version of the 2K binder. For the standard commercial pultrusion substrate, the new version of the binder provided good adhesion simi-

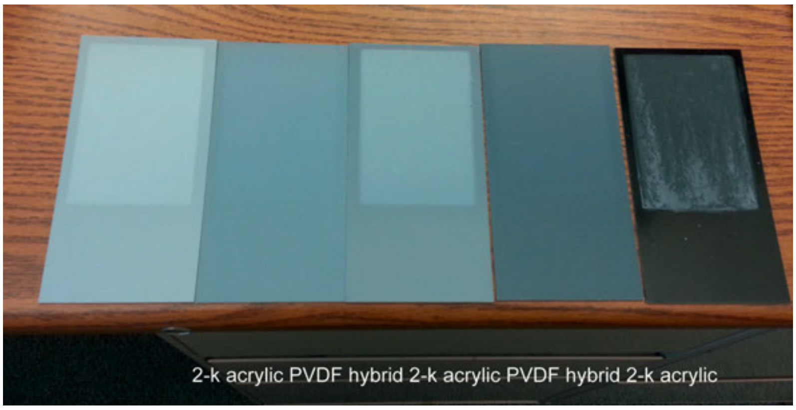

Figure 3: Comparison of semi-gloss PVDF hybrid 2K coatings and a commercial solvent 2K acrylic topcoat for window profiles, after 1000 hours UVB fluorescent cabinet exposure

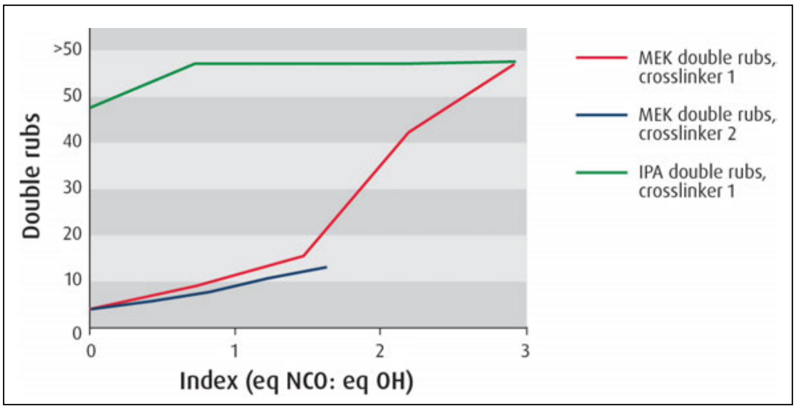

Figure 4: Solvent resistance of PVDF hybrid 2K coatings as a function of the index (eq NCO: eq OH), for two commercial polyisocyanate crosslinkers, after a typical low temperature stoving schedule.

lar to the previous version of the binder, as long as similar stoving schedules and crosslinker loading levels were used. Lower crosslinker levels gave inferior direct adhesion (it should be noted that the level giving good adhesion with the new binder works out to an isocyanate:OH equivalent ratio, or index, of about 3, a rather high value).
There is no adhesion advantage in stoving at temperatures above 100 °C; if anything, samples stoved at 120 °C have somewhat worse adhesion than samples stoved at 70-100 °C. The use of a silica flatting agent appears to bring some advantages in terms of direct adhesion.

Polyol choice in pultrusion may be critical

These results led to a new joint study, looking at pultrusion formulation factors. In order to achieve the required physical properties of the polyurethane, and good processing during the pultrusion process, the B component is a complex blend of several different polyols, where the molecular weight, functionality, hydrophobicity, and compatibility of each of the components can be varied.
Several experiments examined the effect of these variables on paint adhesion. Three different test coating formulations, each based upon the latest version of the 2K PVDF binder, were applied directly to the pultrusion test samples. These three formulations had differing gloss levels and were formulated at indices of from about 1.0 to 2.0. Two formulations were prepared in-house at Arkema, while the third formulation was supplied by a coatings company. The coated specimens were given a short force-stoving at 60-100 °C, depending on the formulation; then after an additional two weeks of bench aging, the specimens were tested for wet, dry and boiling water adhesion according to AAMA 625-10.
The results indicate that the composition of the polyol blend can have a significant effect on paint adhesion, but the factors controlling paint adhesion are not straightforward. Certain components of the polyol blend can result in pultruded parts that have excellent adhesion without any pre-treatment, and that pass all the relevant AAMA 625 specifications.

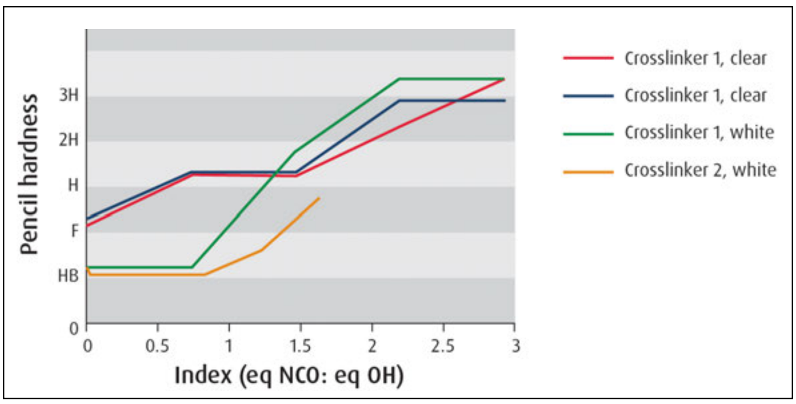

Figure 5: "Berol" pencil hardness of PVDF hybrid 2K coatings on chromated aluminium, as a function of the index (eq NCO: eq OH), for two commercial polyisocyanate crosslinkers, after a typical low temperature stoving schedule

PVDF coating is also suitable for other substrates

New hydroxy-functional PVDF hybrid emulsion polymer technology now offers, for the first time, the possibility of low temperature stoving finishes which can meet all the requirements of AAMA 625 finishes for window profiles based on polyurethane pultrusions.
These 2-component, very low VOC paint systems can also be used on any of the other common architectural window profile substrates, including primed aluminium, polyester glass fibre composites and vinyl, to meet the highest performance standards of the window profile industry, both in terms of exterior weatherability and physical properties.

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