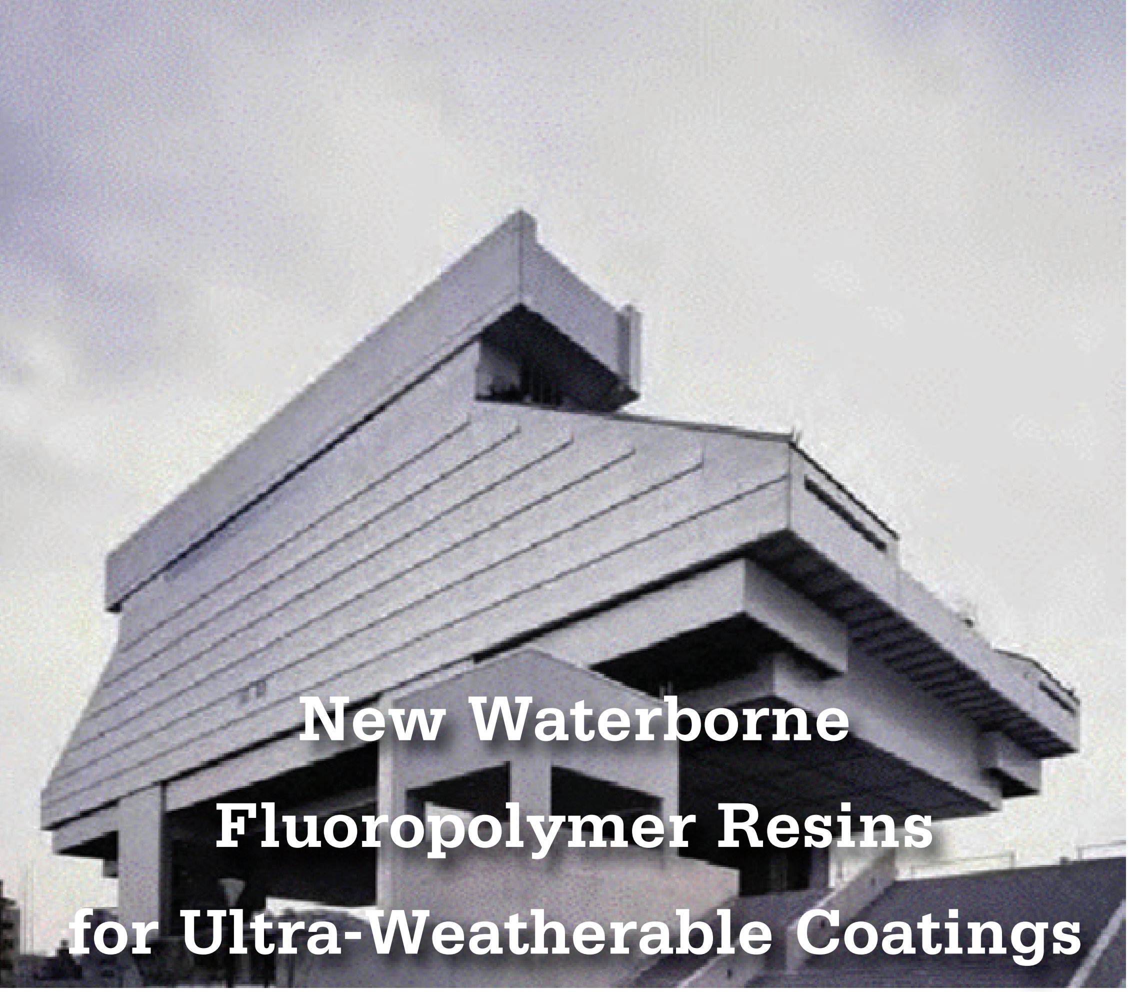

New Waterborne Fluoropolymer Resins for Ultra-Weatherable Coatings

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Editor's Note: This article is based on a paper the authors presented at PACE 2009, the joint conference of SSPC: The Society for Protective Coatings and the Painting and Decorating Contractors of America, held February 15–18, 2009, in New Orleans, LA.

Above: Tokyo Edo Museum, with FEVE coating
Photos courtesy of the authors

Fluoropolymers, introduced in the 1930s, are known for their excellent thermal, chemical, and weather resistance, along with surface properties like water and oil resistance, and optical properties. Because of their properties, fluoropolymers have been used in coatings on a variety of substrates. For example, fluoropolymers for coatings include aqueous dispersions of polytetrafluoroethylene (PTFE), tetrafluoroethylene/hexafluoroethylene copolymers (FEP), and TFE/perfluoroalkyl vinyl ether copolymers (PFA). These materials are used primarily in non-stick and anticorrosion coatings.

Unfortunately, the use of fluoropolymers in coatings is limited due to their physical properties. Fluoropolymers have poor solubility in traditional solvents used in the coatings industry. Usually, fluoropolymer resins must be heated to temperatures greater than 200 C (392 F) to form a film. In addition, the low surface energy of the resins impedes acceptable adhesion to metals and other substrates, a property needed in primers and direct-to-metal coatings, for instance. Hence, fluoropolymers are not typically used as primers.

Among traditional fluoropolymers, only polyvinylidene fluoride (PVDF) is widely used in coatings. This resin is usually supplied as a dispersion in a high boiling solvent blend, and is used mainly in coil coatings, where it is processed at high temperatures. PVDF is employed primarily in architectural markets due to its exceptional weatherability.

A fluoropolymer resin was developed in the 1980s in an attempt to overcome the difficulties found in using traditional fluoropolymer resins in coatings, while still maintaining their advantages. These resins, known generically as fluoroethylene vinyl ether (FEVE) resins, are solvent soluble, and can be made compatible with water. This article describes solvent-borne as well as two types of waterborne FEVE resins—emulsions, which have been around for some time, and new dispersions—and the potential for uses of the new FEVE dispersion resins in coatings for field application where high weathering properties are needed.

FEVE Resins in Solvent-Borne Coatings

FEVE resins can be synthesized with reactive hydroxyl groups and can be cross-linked with standard aliphatic isocyanates to make fluorourethane coatings. FEVE resins can be used at high temperatures to make coil coatings, or at room temperature for field-applied coatings. This versatility in use substantially broadens the types of applications where FEVE-based fluorourethane coatings can be used.

Fluorourethanes have the same outstanding weatherability as traditional fluoropolymers but offer other advantages, as well. Fluorourethanes can be cured at either room temperature or elevated temperatures, so they can be used as maintenance coatings, applied in the field. Using appropriate additives, FEVE-based coatings can be manufactured in a wide range of gloss, unlike other fluoropolymers used for coatings. As solution polymers, FEVE resins have better compatibility with a wide range of pigments, enabling a broader color palette. And because fluorourethanes are cross-linked polymers, they tend to offer higher hardness and better corrosion resistance than some types of fluoropolymers commonly used in coatings. Yet, fluorourethanes retain enough flexibility and toughness for use as topcoats for military aircraft, where flexibility and adhesion are required at -40 C (-40 F) as well as at higher temperatures.

FEVE-based fluorourethane topcoats can be formulated and applied to yield a coating life exceeding 50 years. Based on work done by several Japanese transportation authorities, engineering organizations, and private parties, these topcoats are required to be used on all bridges in Japan, with an expected life of 100 years in some cases.

FEVE Emulsion Polymers for Coatings

The first waterborne FEVE polymers were aqueous emulsions, manufactured via emulsion polymerization. The resins were developed to enable coating manufacturers to meet VOC and HAPS regulations, which restrict the amount and type of solvents used to formulate coatings.

Institute for Global Environmental Strategies, with FEVE coating

Vinyl ether monomers substituted with polyoxyethylene (EO) units were copolymerized with the fluorinated monomer and other vinyl ethers to obtain stable emulsions and to maintain the structure of the FEVE copolymer. The resulting polymers are high in molecular weight, so they can be used in single-component coatings, or they can be cross-linked with aliphatic isocyanate dispersions. The emulsions have found use in blends with other waterborne resins to improve the weatherability of conventional coatings.

Unfortunately, coating properties obtained from these FEVE emulsions are generally inferior to those obtained from solvent-borne FEVE resins. This inferiority is believed to be due to residual emulsifier from the resin system in the cured FEVE coating, the presence of the EO units in the polymer, and the high molecular weight of the resins. In general, water sensitivity of FEVE emulsions is higher than that of solvent-borne FEVE resins, while weatherability is usually lower.

The shortcomings in performance of the FEVE water emulsions have limited their usefulness as low VOC and low HAPS coatings in the U.S. While solid FEVE resins provide a way to meet such regulations, the resins still require the use of solvents to produce coatings. There thus appears to be a need for a waterborne FEVE resin that offers the same performance as that of solvent-borne FEVE resins. FEVE water dispersion resins, as demonstrated below, yield properties in cross-linked coatings approaching those obtained with solvent-grade FEVE resins.

FEVE Water Dispersion Resins

Preparation of Resins

FEVE water dispersions are derived from FEVE solid resins of varying molecular weight, acid numbers, and hydroxyl numbers. To be useful as a coating raw material, a resin must first be stable enough in storage to impart a reasonable shelf life to the formulated coating. It was found that dispersion stability was influenced by several factors, including molecular weight, particle size, and acid value. The most stable products were derived from lower molecular weight, moderate particle size, moderate acid value polymers.

A FEVE water dispersion with properties shown in Table 1 (p. 34) was prepared and then formulated to make a fluorourethane topcoat.

Preparation of Fluorourethane Coatings for Testing

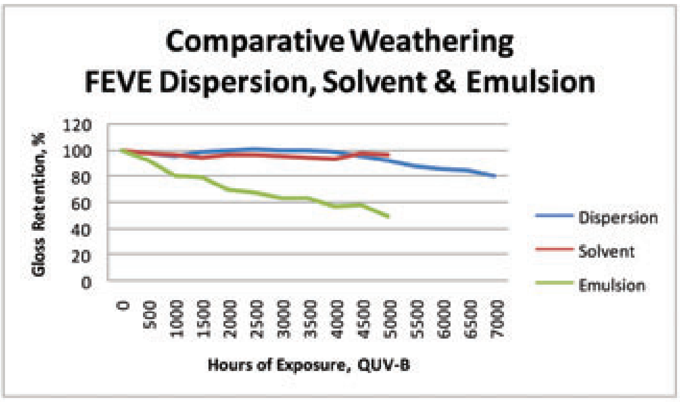
Coatings were prepared from the selected FEVE water dispersion, a two-part water emulsion FEVE resin, and a solvent-borne FEVE resin. Then, all three types of coatings were applied to chromate-treated steel panels, cured for 14 days, and subjected to a variety of tests.

Comparative Test Results for Physical Properties

The resulting fluorourethane coatings, along with an unreacted FEVE emulsion resin, were subjected to several standard

Table 1: Properties of FEVE Water Dispersion

Property	Value
Appearance	Milky White Liquid
Solids, Wt. %	40% ±2%
pH	7–9
Particle Diameter, nm	50–300
Minimum Film Forming Temperature, °C	27
Acid Value, mg KOH/g-polymer	15
Hydroxyl Value, mg KOH/g-polymer	85
Hydroxyl Equivalent Weight (HEW)	660



UV/Condensation Cabinet Cycle
8 hours UV at 70 C (158 F) and 4 hours Condensation at 50 C (122 F)

Fig. 1: QUV-B weathering testing of FEVE-based coatings

tests for the coatings' physical properties.

Of the results shown in Table 2, several are noteworthy. First, the gloss of the dispersion-based fluorourethane is close to that of the solvent-grade coating, and higher than that of the cross-linked emulsion coating. Hardness, impact resistance, and adhesion of the three coatings are about the same, although the cross-linked emulsion has slightly lower impact resistance. The FEVE emulsion that is not cross-linked has far lower hardness and impact resistance, and poor adhesion compared to the other three cross-linked coatings. While the emulsion is high enough in molecular weight to form a film using a coalescent, without the isocyanate cross-linker, film properties are poor.

The biggest difference in performance is in the water resistance of the three fluorourethane coatings. The water dispersion and solvent-grade fluorourethanes show excellent water resistance, while the cross-linked emulsion develops blisters during the test. In this battery of tests, the FEVE dispersion offered performance equivalent to that of the solvent-borne coating. This means that zero VOC fluorourethane coatings with excellent properties can be formulated using the FEVE dispersions.

Comparative Weathering

Fluorourethane coatings were tested in the ASTM D 53 accelerated weathering test. Accelerated weathering tests show that the dispersion-based fluorourethane weathers as well as the solvent-borne coating (Fig. 1).

SEM Comparison:
FEVE Dispersion and Emulsion

Scanning electron micrography (SEM) showed that the dispersion formed a uniform, dense film with no surface defects after cross-linking. Thus, water resistance in the dispersion was improved; water could not penetrate the film. In contrast, the cross-linked emulsion had surface defects thought to adversely affect physical properties such as gloss and water resistance. Also, the surface of the emulsion film was irregular, and the coalesced portions of the film could be seen. These imperfections could reduce the performance of the emulsion film.

Application Characteristics of FEVE Dispersions

FEVE dispersions are formulated as two-component systems using water-dispersible isocyanates as cross-linkers. They are combined with pigments and additives for control of flow, gloss, foaming, and other application and physical properties. These systems can be applied with air or airless spray equipment, by

Table 2: Comparative Performance of Various FEVE Coatings

Property	Test	FEVE Dispersion (OHV=85)	FEVE Solvent-Based (OHV=52)	EVE Emulsion (OHV=55)	
Cross-linker (NCO/OH=1)	N/A	Water-dispersible isocyanate	HDI-Based polyisocyanate	Water-dispersible isocyanate	None
Gloss, 60°	ISO 2813	88	90	78	78
Pendulum Hardness	ASTM D 4366	79	80	75	19
DuPont Impact	ASTM D 2794 (D=0.5")	>1.0 m	>1.0 m	1.0 m	0.3 m
Cross-Cut Adhesion*	ASTM D 3359	5B	5B	5B	0B
Water Resistance ISO 2812 40 C, 24 hrs	Adhesion, ASTM D 3359	4B	5B	3B	0B
	Blistering, ASTM D 714	No Blistering	No Blistering	<8, Medium	2, Dense

**Cross-cut adhesion test performed after soaking in hot water for 24 hours.*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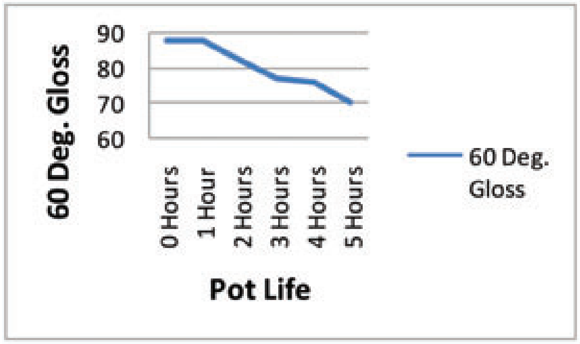

Fig. 2: Charge in 60° gloss versus pot life

roller, or by brush, depending on the environment at the job site.

As with other waterborne coatings, one of the difficulties in using FEVE dispersions is determination of the useful pot life of the blended coating system. Unlike solvent-borne coatings, the blended FEVE dispersion does not increase substantially in viscosity as the end of its pot life approaches. Other measures are used to determine the pot life, namely, a decrease in gloss during application, and a decline in physical properties of the finished coating after a certain pot life is achieved.

The FEVE dispersion was blended with a water-dispersible isocyanate at a NCO/OH ratio of 1.0. Coatings were then applied at one-hour intervals over the estimated pot life of the system. The gloss of the resulting coatings was examined. In addition, the solvent resistance of the cured coatings was examined.

Figure 2 shows the results of the gloss test for different pot lives. After 5 hours, the gloss of the cured coating measurably changed. After 6 hours, the cured coating showed extensive cracking, indicating that the pot life was exceeded. Solvent resistance of the cured coatings began to degrade at 4 hours' pot life. These results indicate that the expected pot life of the FEVE dispersion at 25 C (77 F) is a maximum of 4 hours. For use in the field, on-site testing should be performed, probably using gloss measurements, to ensure that the useful pot life is not exceeded.

Markets for FEVE Dispersions

It is possible to use FEVE dispersions for all applications where solvent-borne products are used today. Because FEVE dispersions can be used without coalescents, which may be considered VOCs, they can be used as industrial maintenance (IM) coatings for structures such as bridges, process plants, and water towers, even in California, where the current VOC limit for IM is 100 g/L. In addition, the dispersions can replace solvent-borne coatings in applications where the smell of solvents can affect occupants of a structure, such as office buildings. Other potential markets for FEVE dispersions include architectural, automotive, and aerospace.

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