Advances in Fluoropolymer Resins for Long Life Coatings

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Abstract

Fluoroethylene vinyl ether (FEVE) resins were developed to overcome some of the problems associated with the use of fluoropolymers in coatings. These resins, which yield topcoats with lifetimes exceeding 60 years, can be cured at ambient temperatures for field applications, or at elevated temperatures in the shop.

New FEVE resins have been developed to enable formulators to meet air quality regulations while still producing coatings with excellent durability. These include solid resins, which can be solubilized with VOC and HAPS exempt solvents, water emulsions, and water dispersions. In addition, new resins with silanol functionality allow the production of coatings which cure without using isocyanates.

It has also been found that FEVE water emulsions, which have excellent weatherability but average physical properties when used alone, can be used to improve the weathering of conventional resins like acrylic emulsions. The resulting fortified systems can be used for architectural trade sale paints, concrete coatings, and direct to metal coatings.

Introduction

Fluoropolymer Resins

Fluoropolymers are known for their excellent thermal, chemical, and weather resistance, along with surface properties like water and oil resistance, and optical properties. Because of these characteristics, fluoropolymers are widely used in the chemical, oil and gas, textile, paper, and plastics industries

Since their introduction in the 1930’s, fluoropolymers have been used as coatings on a variety of substrates, imparting their physical characteristics to the coatings. Examples of coatings raw materials include aqueous dispersions of polytetrafluoroethylene (PTFE), tetrafluoroethylene/hexafluoroethylene copolymers (FEP), and TFE/perfluoroalkyl vinyl ether copolymers (FEP). These materials are used primarily as non-stick and anti-corrosion coatings.

Unfortunately, use of fluoropolymers in coatings is limited due to their physical properties. Fluoropolymers have poor solubility in traditional solvents used in the coating industry. Usually, fluoropolymer resins must be heated to temperatures greater than 200^{o} C to form a coating. Finally, the low surface energy of the resins impedes acceptable adhesion to metals and other substrates.

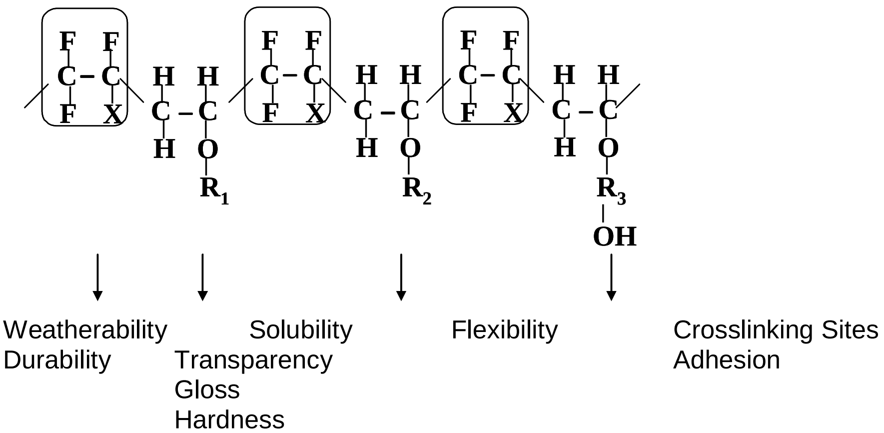
Among traditional fluoropolymers, only polyvinylidene fluoride (PVDF) is widely used in coatings. This resin is usually supplied as a dispersion in a high boiling solvent blend, and is used mainly in coil coatings, requiring exposure to a high temperature to form a coating. PVDF is employed primarily in architectural markets due to its exceptional weatherability.

Fluoroethylene Vinyl Ether Resins

A series of unique fluoropolymer resins was developed in the 1980’s in an attempt to overcome the difficulties associated with using traditional fluoropolymer resins in coatings, while still maintaining their positive properties. This class of resins, known generically as fluoroethylene vinyl ether (FEVE) resins, are solvent soluble, and can be made compatible with water. These resins are synthesized with reactive hydroxyl groups, and can be crosslinked with standard aliphatic isocyanates to make fluorourethane coatings. FEVE resins can be processed 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 fluoropolymer coatings can be used.

FEVE resins have a unique chemical structure, shown below in Figure 1. It is this structure, consisting of alternating fluoropolymer and vinyl ether segments, that imparts desirable physical properties to FEVE resins. By making changes in the polymer structure, coating properties like solubility, transparency, hardness, flexibility, pigment compatibility, adhesion, and gloss can be varied.

Figure 1: Chemical Structure of FEVE Resin



Fluorourethanes offer the same outstanding weatherability as traditional fluoropolymers, but offer a number of advantages. Fluorourethanes can be cured at either room temperature or elevated temperatures. This means they can be used as maintenance coatings, applied in the field. With the appropriate choice of additives, FEVE based coatings can be manufactured in a wide range of gloss, unlike other fluoropolymers used for coatings. Since they are solution polymers, FEVE resins have better compatibility with a wide range of pigments, enabling a broader color palette. Because fluorourethanes are crosslinked polymers, they tend to offer higher hardness and better corrosion resistance than some grades 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^{o} C.
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, fluorourethane topcoats are required to be used on all bridges in Japan.

Developments in Fluoropolymer Resins

For many years, FEVE resins have been manufactured and sold in xylene. In Japan, the resins are also sold in mineral spirits, which is considered a mild solvent there. In the U. S., however, mineral spirits is considered to be a VOC. Restrictions on the use of xylene also arise from HAPS regulations. In order to allow formulators to meet these air quality regulations, solid FEVE resins have been recently developed and widely marketed.

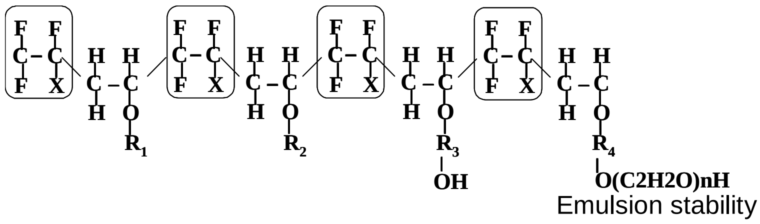
Feve Solid Resins

Solid FEVE resins are manufactured in the same manner as solvent based resins, and have the same polymer structure. Several additional steps are performed, including distillation to remove solvent, chilling the resulting resin mass, and chopping the resin into flakes. The resins can be dissolved in a range of solvents, including the VOC exempt solvents para-chlorobenzotrifluoride (PCBTF or Oxsol® 100), acetone, t-butyl acetate (TBAc), methyl acetate, and dimethyl carbonate. Non-HAPS solvents can also dissolve solid FEVE resins; these include methyl ethyl ketone (MEK), methyl amyl ketone (MAK), and a number of glycol ethers and esters.
VOC regulations vary geographically and by coating type. As usual, the strictest standards are in Southern California. Most formulators are using solid FEVE resins to meet the South Coast Air Quality Management District (SCAQMD) standard for industrial maintenance coatings, which allows a VOC level of 100 g/l. This standard can be met using one of the solvents listed above or by using blends of VOC exempt solvents with other solvents.

Feve Water Dispersions

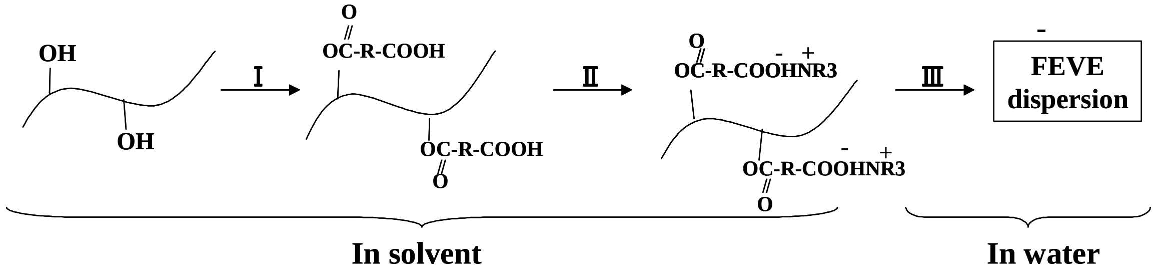
Another method of meeting air quality regulations is the use of water based coatings. Water based resins can be formulated with coalescing solvents, which aid in film formation. With proper choice of these solvents, water based formulations can meet the most stringent SCAQMD VOC standard for water based architectural paints, which is 50 g/l.
The first water-borne FEVE polymers developed were aqueous emulsions. To manufacture these resins, vinyl ether monomers substituted with polyoxyethylene (EO) units are copolymerized with a fluorinated monomer and other vinyl ethers, maintaining the conventional FEVE structure. The resulting polymers are high in molecular weight, so they can be used in either in single component coatings or in formulations crosslinked with aliphatic isocyanate dispersions. The structure of a typical FEVE water emulsion is shown in Figure 2.

Figure 2: Polymer Structure of FEVE Emulsion



Unfortunately, coating properties obtained from these FEVE emulsions are generally inferior to those obtained from solvent based FEVE resins. This is believed to be due to emulsifier from the resin system remaining 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 FEVE solvent based resins, while weatherability is usually lower. Recent work, discussed below, indicates that FEVE emulsions may best be used in combination with standard resin systems to improve weathering and potentially other properties.
FEVE water dispersions were developed to overcome the problems inherent in FEVE water emulsions. These dispersions are made through a multi-step process using solid FEVE resins as the raw material. First, FEVE solid resins are synthesized in a solvent, which is then removed by vacuum distillation. The resulting resin is chilled, and then processed into flakes. These flakes are then dissolved in a hydrophilic solvent. To make the dispersion, a portion of the hydroxyl functional vinyl ether groups are denatured with an acid anhydride to form carboxylic acid groups (I). These acid groups are neutralized with an amine (II), and the resulting polymeric carboxylic acid salt dispersed in deionized water. Finally, the solvent is evaporated, yielding an FEVE dispersion containing no solvents or emulsifiers (III). The preparation of these dispersions is shown schematically in Figure 3.

Figure 3: Manufacture of FEVE Dispersion



After synthesis of a number of dispersions, it was found that dispersion stability was influenced by several factors, including molecular weight of the polymer, particle size, and acid value. The most stable dispersions were derived from lower molecular weight, moderate particle size, moderate acid value polymers. Coatings were prepared from the FEVE water dispersion, a water emulsion FEVE resin, and a solvent-based FEVE resin. Chromate treated steel panels were coated with the coatings, which were allowed to cure for 14 days.The resulting fluorourethane coatings, along with a single component FEVE emulsion resin, were subjected to several standard tests for coatings. The results are shown below in Table 1.

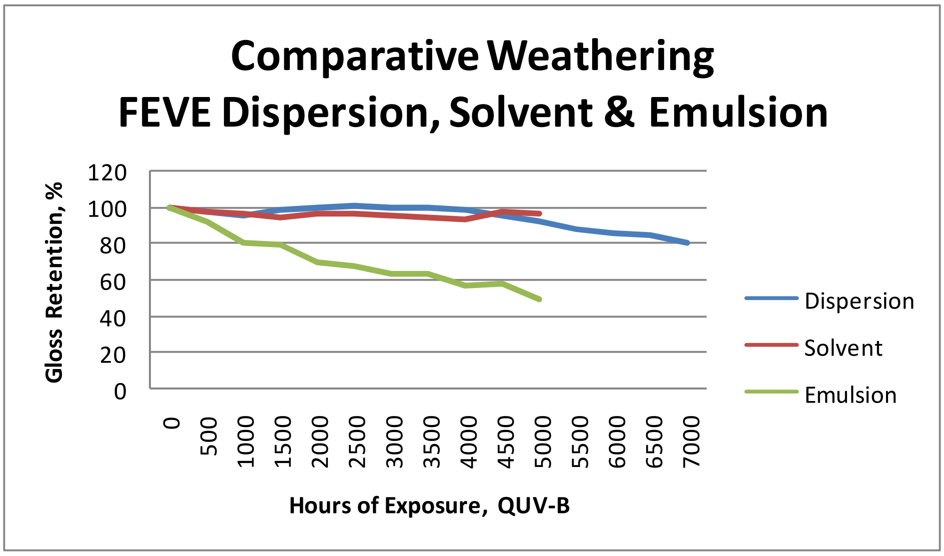
Table 1: Comparative Performance of FEVE Coatings

		FEVE Dispersion (OHV=85)	FEVE Solvent-Based (OHV=52)	FEVE Emulsion (OHV=55)	
Crosslinker (NCO/OH=1)		Water Dispersible Isocyanate	HDI Based Polyisocyanate	Water Dispersible Isocyanate	None
Gloss, 60^o	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^o 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.

Test results show that the initial gloss of the dispersion-based fluorourethane is close to that of the solvent-grade coating, and higher than that from the emulsion. Hardness and adhesion of the three crosslinked coatings are about the same, although the reacted emulsion has slightly lower impact resistance. The single component FEVE emulsion has far lower hardness and impact resistance, and poor adhesion. The emulsion alone is high enough in molecular weight to form a film using a coalescing solvent, without the isocyanate crosslinker its 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 emulsion develops blisters during the test. In this battery of tests, the FEVE dispersion offered performance equivalent to that of the solvent-based coating. This means that zero VOC fluorourethane coatings with excellent properties can be formulated using the FEVE dispersions. Fluorourethane coatings were tested in the ASTM D 53, an accelerated weathering test. Results are shown below in Figure 4.

Figure 4: QUV-B Weatherometer Testing of FEVE-Based Coatings



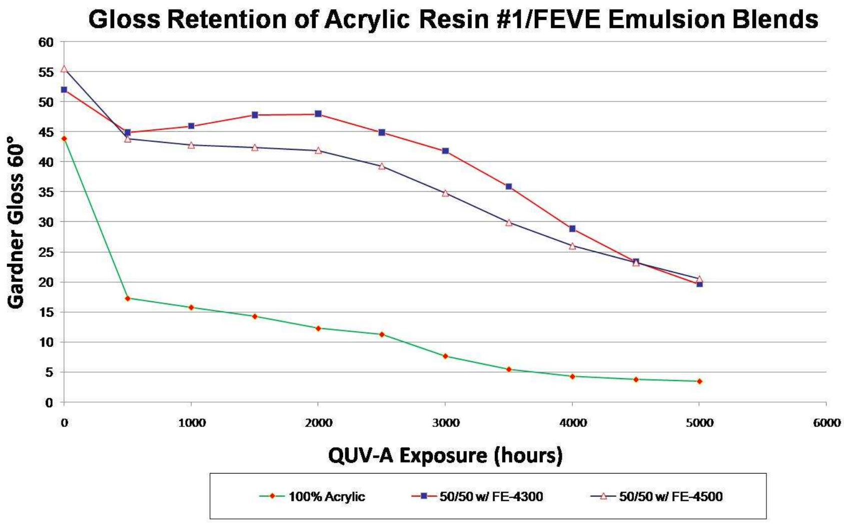
UV / Condensation Cabinet Cycle
8 hours UV at 70 deg.C and 4 hours Condensation at 50 deg.C

Accelerated weathering tests show that the dispersion-based fluorourethane weathers as well as the solvent-based coating.
Based on the test results, it should be possible to use FEVE dispersions for all applications where solvent-borne products are used today. Because FEVE dispersions can be used without coalescing solvents which may be considered VOCs, they can be used even as industrial maintenance coatings in California. In addition, the dispersions can displace solvent-based coatings in applications where solvent odor can affect occupants of a structure, such as office buildings or hospitals. Potential markets for FEVE dispersions include architectural, automotive, aerospace, and industrial maintenance coatings. The dispersions can also be formulated into coil coatings, which are used primarily on construction of new buildings. Potential applications for dispersion-based fluorourethanes include bridge coatings, water tower coatings, aircraft coatings, specialty automotive coatings, and coatings for monumental buildings.

FEVE Water Emulsions in Blended Resin Systems

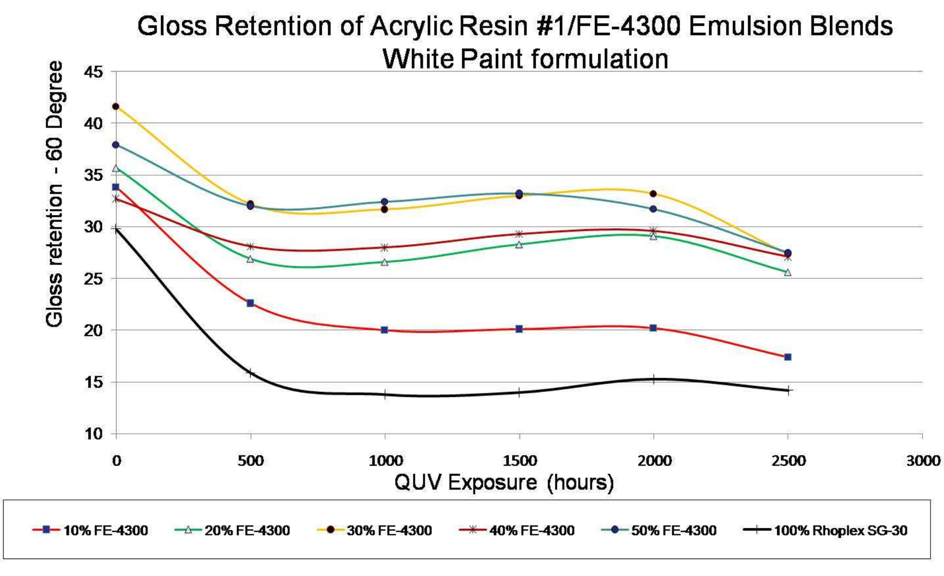
Recent work has determined that FEVE water emulsions can be used in blends with conventional resins to improve the weathering of coatings. Two FEVE emulsions, one with a hydroxyl number of 10 and a minimum film forming temperature of 35^{o} C (FE-4300) and one with OH number 13 and MFFT of 28^{o} C (FE-4500) were blended initially at 50/50 by weight with standard acrylic resins. They were then blended at lower levels to determine the minimum effective level of fluoropolymer required to yield a significant improvement in weathering. Formulated coatings were then tested for weatherability by exposure to UV-A light in a weatherometer.
Figure 5 below shows accelerated weathering test results from 50/50 blends of fluoropolymer emulsions with a commercial acrylic resin (MFFT of 17^{o} C).

Figure 5: Comparative Weathering of Acrylic Resin and FEVE Emulsion Blends



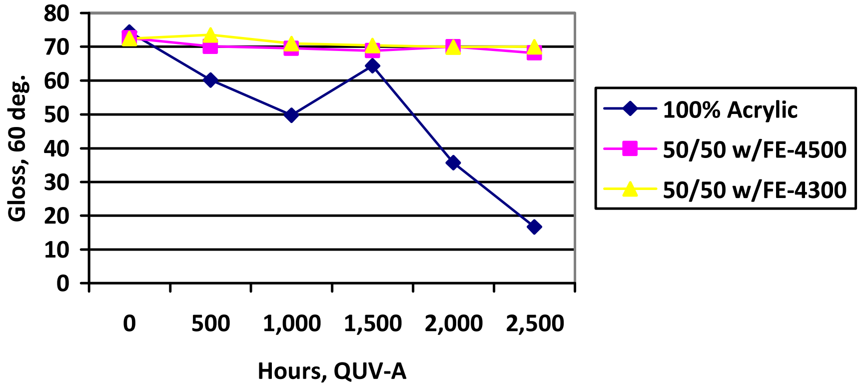
The results shown in Figure 5 reveal a substantial improvement in weathering when FEVE emulsions are blended with this acrylic resin. After it was determined that FEVE emulsions could be used to improve weathering of acrylic resins, experiments were performed to find the lowest level of fluoropolymer required to offer a significant improvement in weathering. Figure 6 below shows QUV exposure data generated in these tests.

Figure 6: Optimizing FEVE Emulsion/Acrylic Resin #1 Blends



The results shown in Figure 6 indicate that addition of FEVE resins at any level improves the weathering of the coating. However, it appears that a level of 20% offers a significant improvement in weathering, approaching that achieved even at higher concentrations of FEVE resins. Because of the relatively high cost of FEVE resins, optimizing coatings to obtain the greatest improvement in properties at the lowest levels of FEVE resin possible is important in minimizing the life cycle cost of the coating system. FEVE emulsion resins were also blended with an acrylic resin developed for direct-to-metal (DTM) coatings. Accelerated weathering testing of this resin is shown below in Figure 7.

Figure 7: FEVE Resin Blends with Acrylic Resin #2



The weathering test results show the substantial improvement in weathering of the acrylic coating on addition of the FEVE emulsion resins. In addition, the FEVE resins appear to smooth out the fluctuation in gloss retention in the acrylic coating. Work is continuing to optimize the most cost effective addition levels of FEVE resins.

FEVE blends could prove useful in several coating markets by offering the manufacturer the capability of offering products with additional exterior durability. These markets include architectural trade sale paints for both commercial and residential markets, DTM coatings for light industrial applications, and decorative coatings for concrete. The last market is of particular interest since development of and applications for decorative concrete have increased substantially over the last several years. Protection and enhancement of decorative concrete, especially in harsh environments like the Desert Southwest indicate a need for higher performing coatings.

Silanol Functional FEVE Resins

The newest product in the FEVE line is a silanol functional resin. The structure of the resin is shown below in Figure 8.

Figure 8: Silanol Functional FEVE Resins

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 F  F   H H F F  H  H
 |  |   |  |  |  |  |   |
-C-C-C-C-C-C-C-C-
 |  |   |  |  |  |  |   |
  F X  H Y F F H  O
            |             |
           Si            Z
                  |
              (OEt)3
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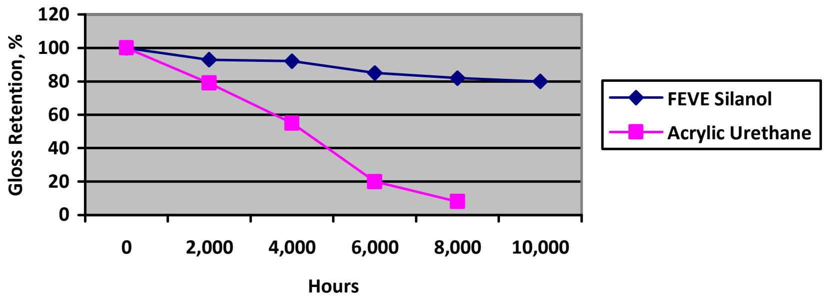
This FEVE resin does not require an isocyanate to crosslink to form a coating; rather, crosslinking occurs through the silane functionality. Isocyanates are banned in some areas in Europe due to toxicity concerns. In the U.S., isocyanates have not been banned; however, there is some concern over their toxicity profile, and some companies are moving to non-isocyanate technologies like polysiloxanes as a result. The new FEVE resin is crosslinked with organosilanes.

The silanol functional resin has the same polymer structure as other FEVE resins, and therefore offers the same durability. Figure 9 below shows the results of QUV-B accelerated weathering for a white coating made with the new resin.

Figure 9: QUV-B Accelerated Weathering of Silanol Functional FEVE Resin



Coatings made from this resin offer excellent heat stability and chemical resistance as well. With the proper choice of additives, these resins can be used to formulate anti-graffiti coatings.
The silanol resins should find application in traditional FEVE markets: architectural, aerospace, automotive, and industrial maintenance. Their use could be larger in areas where concerns over exposure to isocyanates are higher.

Conclusions

FEVE resins continue to gain market share in areas where ultra-weatherability is required. Traditional solvent-based FEVE resins are being supplemented by other types of resins that can be formulated to meet the latest environmental regulations. Fluorourethanes are gaining wide acceptance for their life cycle cost advantages in architectural, aerospace, automotive, and industrial maintenance markets. FEVE blends can be used to improve the weathering of conventional water based resin systems for similar applications.

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