Fluoroethylene Vinyl Ether Resins for High-Performance Coatings

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THIS ARTICLE DISCUSSES THE TECHNOLOGY of organic coatings based on fluoroethylene vinyl ether (FEVE) resins. These resins entered the commercial market in 1982 and have been used in coatings for architectural, industrial maintenance, aerospace, and marine markets. Many bridges in Japan are coated with an FEVE polyurethane-based topcoat, including the Akashi Strait Bridge (Fig. 1).

The FEVE-polyurethane topcoats are also used in architectural applications.

In the United States, one example of an industrial maintenance application of an FEVE-based topcoat is the Rosemont Water Tower in Rosemont, IL, near Chicago (Fig. 2).

These structures need to function and maintain their aesthetic appeal for a long time. The FEVE-based coatings offer this protection.

The demand for longer-life coatings was the driving force behind the development of FEVE resins. The original fluoropolymer resins were known for their superior properties, such as weatherability and chemical resistance, but they possessed limited application capabilities due to their high melting point, high melt viscosity, and insolubility in organic solvents. Several different types of fluoropolymer resins were studied before the FEVE resins were chosen as the most viable candidate. Some of the important criteria were solvent solubility, hydroxyl (–OH) functionality, reasonable glass transition temperature (T_g) properties, and an adequate presence of fluorine in the polymer backbone that would offer protection to the weaker bonds in the polymer.

The FEVE resin family consists of several different products that can be used in a wide variety of coating systems. There are solvent-based solution resins, 100%-solid flake resins, water-based emulsions, and a water-based dispersion. A more detailed explanation of each of these products is given later in this article. Also, formulation guidelines are covered as well as application techniques and performance characteristics. Finally, a short segment on health and safety is presented.

The Chemistry of FEVE Resins

The FEVE resins were developed in the late 1970s in Japan. These resins are amorphous copolymers consisting of a combination of fluoroethylene and substituted vinyl ether chemistry in a regular repeating, alternating pattern. The FEVE polymers are not pure fluoropolymers; they have characteristics of both fluoropolymers and hydrocarbons. Pure fluoropolymers exhibit excellent durability but require specific application conditions. They are not soluble in solvents and therefore cannot be used in liquid coatings. The incorporation of the vinyl ether monomer in the FEVE polymer transforms it from a traditional pure fluoropolymer to a copolymer that is soluble in solvents. The alternating pattern (Fig. 3) is critical for the extreme ultraviolet (UV)-resistance properties it possesses.

Fig. 1 Fluoroethylene vinyl ether polyurethane-based topcoat used on the Akashi Strait Bridge in Japan. Photo property of Asahi Glass Co. Ltd.

Fig. 2 Fluoroethylene vinyl ether-based topcoat used on the Rosemont Water Tower near the Chicago O'Hare International Airport. Courtesy of Tnemec Company, Inc.

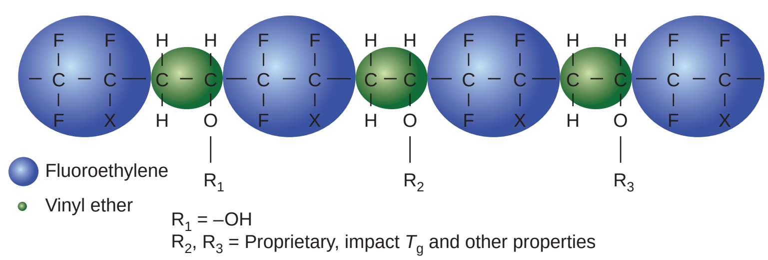

Fig. 3 Alternating structure of fluoroethylene vinyl ether resins. "X" is proprietary. T_g, glass transition temperature

Alternating Structure of FEVE Resins

The solubility afforded by the vinyl ether monomer is what allows FEVE resins to be used in a wide array of coating formulations that can be applied in the factory as baked coatings or in field settings where the coating is air-dried. Another unique characteristic of FEVE polymers compared to pure fluoropolymers is their ability to achieve high gloss. The vinyl ether monomers not only provide solubility into solvents, but they also increase the refractive index of the polymer, which increases gloss.

Coatings for factory and field application can be made with these soluble FEVE resins. Hydroxyl functionality is incorporated into many FEVE resins, allowing them to be cross linked via polyisocyanates or amino resins. Low-hydroxyl-functional FEVE resins are available for one-component (i.e., 1K) coatings. Physical properties such as flexibility and chemical resistance are tailored by the R groups. Cycloaliphatic R groups provide increased chemical resistance, while softer, lower-T_g linear aliphatic groups provide flexibility. Acid-functional R groups improve pigment wetting. Hydroxyl-functional R groups allow for cross linking of FEVE resins with cross linkers such as melamine formaldehyde and polyisocyanate. The FEVE resins are available as solution resins, solids resins for powder coatings, and waterborne resins.

The fluoroethylene groups are the strength of the FEVE resin. These groups are what make this class of polymers so resistant to UV degradation. The carbon-fluorine bond is strong. The energy of this bond is ~486 kJ/mol (Ref 1), while the energy of UV radiation at 300 nm is ~399 kJ/mol. Often, total fluorine content is used as a predictor of UV resistance, but this is not the case with FEVE resins. The alternating structure is of key importance. The chemically stable and UV-resistant fluoroethylene unit sterically and chemically protects the neighboring vinyl ether unit (Ref 2). Typical properties of FEVE resins are shown in Table 1.

In addition to the FEVE chemistry, which this article addresses specifically, there is another type of fluorinated copolymer resin: fluoroethylene vinyl ester. Instead of a vinyl ether monomer, a vinyl ester monomer is used to copolymerize with the fluoroethylene monomer. Debate regarding which performs better is ongoing. For the purposes of this article, discussion is limited to FEVE technology.

FEVE Resin Types

The first iteration of the FEVE polymer was synthesized as a solution polymer in organic solvent. The molecular weight varied significantly, from as low as 2,000 to upward of 80,000 (number average M_w = 4000–150,000). The solution-grade resin was studied extensively. It was used in two-component (i.e., 2K) formulations with melamine-formaldehyde resins in bake systems and polyisocyanates in ambient cure systems. A low –OH-functional solution resin was also synthesized for use in 1K air-dry systems.

As market demand increased, a method to tailor the solvent in which the resin was supplied was developed. Depending on the application, the solution resin precursors were further processed to be diluted in different solvents. A step in this processing was the removal of the original carrier solvent. This yielded a solid, flakelike resin. This form was later marketed for use in powder coating applications. The flakelike resins had a T_g slightly above room temperature and therefore remained solid in storage. For use in powder coating applications, the flakes were typically pulverized into fine particles. The powder coating resins were formulated with blocked polyisocyanates and used in bake applications. The bake temperature depended on the unblocking temperature of the polyisocyanate and usually was approximately 195 °C (380 °F).

As the "green" movement gained traction globally, another use was found for the flake-grade FEVE resins. Laboratory studies were done to test the solubility of the various flake-grade resins in the major volatile organic compound (VOC)-exempt solvents. It was discovered that FEVE flake grades were soluble in all but one of the five major VOC-exempt solvents. The FEVE resins are soluble in acetone, Oxsol 100 (Makhteshim Agan Industries), t-butyl acetate, and dimethyl carbonate. They are not soluble in propylene carbonate. This ability to be used in VOC-exempt solvents, coupled with the use of FEVE flake grades for powder, elevated FEVE technology to the front of the green-coatings movement.

In the early 1990s, another step into the forefront of the environmental coatings movement was made when the first FEVE waterborne emulsion was manufactured. Now formulators had three options for environmentally friendly coatings: powder, low-VOC solution resins, and waterborne emulsions for water-based coatings. Part of the synthesis of waterborne emulsions enlisted the use of surfactants. These water-sensitive surfactants remained in the subsequent formulated coating film. It was found that the performance of the emulsions was not quite at the level of the solution or flake-grade resins. It was theorized that if the surfactant could be removed from the film, the performance of the waterborne emulsion could all but match that of the original solution-type FEVE resins.

In the early 2000s, this concept was studied and developed into a viable resin product. In 2012, a water-based FEVE resin dispersion was presented to the market. The emulsion grades are produced using emulsion polymerization, but the dispersion grade was made quite differently. The precursor used was a flake resin dissolved in a polar solvent. A small portion of the hydroxyl groups are then modified to acid groups and then stabilized by amine. At this point, the polymer was dispersed into water. The final dispersion included no surfactants to compromise its water resistance. Instead of surfactant, stability in water was achieved by the neutralized acid groups. This new dispersion retained its low molecular weight (M_n = 7000) and exhibited excellent film formation. The performance of this dispersion-grade FEVE resin surpassed that of the emulsion FEVE resins and did approach the performance of the solution resins.

Methods of Formulation for FEVE Resins

This section is divided into three separate segments: solvent-based coating formulations, water-based coating formulations, and powder coating formulations. The first two segments discuss both one-component and two-component systems, because both of these systems are possible with FEVE resins. The powder coating segment is limited to one-component baking systems.

Solvent-Based Coating Formulations

The first generation of FEVE resins were solutions of polymers that were cured by the hydroxyl-isocyanate reaction. Because this reaction can occur at ambient temperatures, these systems were either two-component in nature or the isocyanate component had its functional group chemically blocked to stabilize the coating until its application. The basic formulation for these FEVE resins consisted of three ingredients—FEVE resin, isocyanate resin, and tin catalyst—with solvent addition to adjust the viscosity. Because most formulations must have the necessary robustness to conquer application issues, additives played a big part in making these coatings a success. The following are some of the important considerations that are helpful when formulating these types of FEVE-based coatings.

Choice of Isocyanate. Most FEVE-based coatings are used on exterior structures, so it is necessary to use aliphatic isocyanates as the cross linker for the hydroxyl groups of the FEVE resin. Beyond this recommendation, the

Table 1 Typical properties of fluoroethylene vinyl ether resins

Fluorine content	25–30 wt%
OH value	47–170 mg KOH/g
COOH value	0–15 mg KOH/g
Molecular weight	M_n = 2,000–80,000
Specific gravity	1.4–1.5
Morphology	Glassy (T_g = 20–50 °C, or 70–120 °F)(a)
Decomposition temperature	240–250 °C (460–480 °F)
Solubility parameter (calculated)	8.8

(a) T_g, glass transition temperature

choice of isocyanate depends on the desired properties for the coating. Performance properties such as flexibility, speed of cure, and viscosity vary with each different isocyanate resin.

Catalyst Choice. Historically, dibutyltin dilaurate has been the workhorse catalyst for the two-component systems since the beginning of the FEVE technology. It is suggested that the catalyst level be kept at a much lower level than the standard 0.005% (based on resin solids) used in traditional two-component acrylic or polyester polyurethanes. The suggested range of catalyst levels is 0.0002 to 0.001% (based on resin solids). The reason for the lower amount is because the hydroxyl (OH) groups are strictly primary in nature, causing a faster reaction rate with the isocyanate groups.

Solvent Choices. There are a wide variety of solvents that are compatible with the FEVE resins. As with a wide variety of organic resins for coatings, the FEVE resins show varying degrees of viscosity decrease, depending on the polarity of the solvent. The lower-molecular-weight resin is used to manufacture coatings with lower VOC content (Tables 2, 3).

Pigment Choices. There are no restrictions when pigments must be chosen for an FEVE formulation. Because a majority of the coatings that use FEVE resins are expected to possess substantial weatherability characteristics, it is recommended that any organic pigment chosen have a high degree of lightfastness. The protection from UV degradation offered by the presence of the FEVE resin extends primarily to the resin itself. Because it is transparent to UV light, it cannot protect opaque organic pigments from absorbing UV light and suffering the consequences of chemical structure alteration, which will result in a color change. It is recommended that UV absorbers and hindered amine light stabilizers be added to these types of pigmented formulations for additional protection from color change. Mixed metal oxide pigments offer improved UV resistance compared to organic pigments, so they should be used whenever possible. Extender pigments also can be used in FEVE resin-based formulations for the adjustment of the gloss level of the coating. Talc, nepheline syenite, calcium carbonate, barium sulfate, and fumed and precipitated silicas have been used in these formulations for gloss adjustment and for reduction in VOC content.

Additive Choices. Several types of additives have been used in FEVE resin-based coatings. In pigmented coatings, the use of a pigment dispersant is highly recommended when dispersing dry pigments into the FEVE resin itself. The wetting ability of a typical FEVE resin is limited due to the presence of fluorine atoms in the structure. Also, flow and leveling aids are sometimes used, depending on the application method and the desired appearance. Depending on the physical properties desired in the coating, the additive choices will vary.

Compatibility with Other Resins. The degree of compatibility possessed by all of the FEVE resins is quite high. This information has been discovered by extensive blending performed in the generation of a wide variety of formulation types. Both acrylic and polyester polyols of varying molecular weights have been blended with the FEVE resins and tested for compatibility by observing the clarity of the mixture. This level of compatibility is important when specific properties of the coating must be improved by the use of non-FEVE resins in the formulation. The reason for adding non-FEVE polyols to an FEVE formulation is to improve specific physical properties, such as flexibility and abrasion resistance. Also, the final cost of the formulation can be decreased by the addition of these polyols.

Water-Based Coating Formulations

This section is divided into two parts: formulating with FEVE emulsion resins and formulating with FEVE dispersion resins. The physical properties of the FEVE emulsion and the FEVE dispersion resins were presented in a previous section. This discussion covers the appropriate methods for creating successful coatings when these FEVE resins are in the formulation.

The FEVE emulsions have similar behaviors when compared to many acrylic or vinyl acrylic emulsions. They need assistance from coalescing solvents to form good films. They associate with associative thickeners for viscosity adjustment of the coating. They can accommodate the pH range that is popular for most water-based systems. In summary, they can be treated similarly to the standard emulsions used in coatings today (2015). However, they are not shear stable, so they cannot be used as a grinding medium for the dispersion of pigments.

Choice of Coalescing Solvent. The standard coalescing solvents have been tested with the FEVE emulsions to measure their effectiveness in facilitating film formation. Table 4 provides a list of solvents that can be used for this purpose.

Choice of Isocyanate Cross Linker. One of the FEVE emulsions has sufficient hydroxyl functionality to permit additional cross linking with water-dispersible isocyanates. There are a wide variety of these types of isocyanates from which to choose for the final formulation. It is important to mention that catalysts are not necessary to initiate the hydroxyl-isocyanate reaction in these types of coatings.

Choice of Pigments. As with the solvent-borne FEVE resin-based systems, there are no limitations when choosing the appropriate

Table 2 Percent solids and viscosity of fluoroethylene vinyl ether high-molecular-weight resin in various solvents

Solvent	Solids, wt%	Brookfield viscosity, cP
Xylene	49.5	630
t-butyl acetate	50.2	869
Acetone	50	250
Oxsol 100(a)	48.6	6632
Methyl acetate	51.8	333
Dimethyl carbonate	50	825
Methyl ethyl ketone	50.8	263
Methyl n-amyl ketone	50.5	470
Methyl isoamyl ketone	52.2	648
Ethyl 3-ethoxypropionate	50.7	1941
Propylene glycol monomethyl ether acetate	50.9	1573
Methyl propyl ketone	49.7	244
Methyl isobutyl ketone	52.9	545
n-butyl acetate	49.9	496
Propyl Cellosolve(b)	47.5	1939

(a) Makhteshim Agan Industries. (b) Dow Chemical Company

Table 3 Percent solids and viscosity of fluoroethylene vinyl ether low-molecular-weight resin in various solvents

Solvent	Solids, wt%	Brookfield viscosity, cP
Xylene	50.1	202
t-butyl acetate	42.9	110
Acetone	50	22.5
Oxsol 100	50.5	1748
Methyl acetate	59.9	157
Dimethyl carbonate	50	70
Methyl ethyl ketone	52.0	44
Methyl n-amyl ketone	63.3	579
Methyl isoamyl ketone	50.0	83
Ethyl 3-ethoxypropionate	48.6	160
Propylene glycol monomethyl ether acetate	49.5	192
Methyl propyl ketone	49.2	38
Methyl isobutyl ketone	51.0	67
n-butyl acetate	49.9	96
Propyl Cellosolve	51.1	452

Table 4 Coalescing solvents for fluoroethylene vinyl ether emulsion (T_g = 56 °C, or 133 °F)

Coalescing solvents	Water solubility, %	Coalescent amount on resin solids, %	Temperature of film formation	
			°C	°F
Ethylene glycol monobutyl ether	Infinite	10	27	81
Ethylene glycol monobutyl ether acetate	1.1	10	12	54
Diethylene glycol monobutyl ether acetate	6.5	7	3	37
Propylene glycol monophenyl ether	1	10	23	73
Propylene glycol monomethyl ether acetate	19	10	42	108
Dipropylene glycol monopropyl ether	19	10	16	61
Dipropylene glycol monobutyl ether	5	10	14	57
Dipropylene glycol dimethyl ether	53	10	20	68
Tripropylene glycol monobutyl ether	3	10	18	64
Texanol(a)	0.9	10	24	75

T_g, glass transition temperature. (a) Eastman Chemical Company pigment(s) for these coatings. Also, the same cautions apply when choosing organic pigments, due to the inability of the FEVE resin to absorb UV radiation from sunlight.

Choice of Additives. Water-based formulations require a number of different additive types to overcome the limitations of this type of coating technology. This fact is also true for FEVE emulsion-based finishes. The standard commercial additives available in the market for properties such as pigment stabilization, surface tension reduction, and foam control work equally well in FEVE emulsion-based systems. Associative thickeners are effective for viscosity control; however, the degree of association with FEVE emulsions is somewhat less than with typical acrylic and vinyl acrylic emulsions. Oftentimes, higher levels are needed in FEVE emulsion-based coatings.

Compatibility with Other Water-Based Emulsions. Table 5 shows acrylic emulsions that have been found to be compatible with the FEVE emulsions.

The second-generation water-based FEVE resin was created to improve the water resistance of this class of resins. The approach used for this product took into account the need to eliminate the presence of surfactants as the stabilizing mechanism in an aqueous medium. The stabilization comes from the presence of neutralized carboxyl groups that allow the creation of a stable dispersion. Some of the formulating differences are the higher importance of a cross-linking resin and the lower importance of a coalescing solvent for proper film formation. This is due again to the lower molecular weight of the FEVE dispersion.

Table 5 Acrylic emulsions compatible with fluoroethylene vinyl ether emulsions

Trade name	Manufacturer
UCAR Flex 187	Arkema
UCAR Latex 625	Arkema
UCAR Latex 629	Arkema
Acronal Optive 110	BASF
Acronal Optive 130	BASF
Acronal Optive 230	BASF
Acronal Optive 350	BASF
Acronal NX 3250M	BASF
Joncryl 1522	BASF
Joncryl 1982	BASF
Joncryl 1984	BASF
Joncryl 1987	BASF
Avanse MV-100	Dow Corp.
Avanse ST-410	Dow Corp.
Maincote HG-86	Dow Corp.
Rhoplex SG-10M	Dow Corp.
Rhoplex SG-30	Dow Corp.
Rhoplex EC-1791	Dow Corp.
Rhoplex HG-706	Dow Corp.
Rhoplex VSR-50	Dow Corp.
EPS 2293	Engineered Polymer Systems
Carboset CR-761	Lubrizol
Carboset CR-795	Lubrizol
Aquamac 440	Momentive
Setalux 37-6770	Nuplex Resins
Viscopol 7788	Nuplex Resins
Viscopol 9898	Nuplex Resins
Pliotec CR30	Omnova Solutions
Texicryl 13-031	Scott-Bader
Texicryl 13-034	Scott-Bader
Texicryl 17-0376	Scott-Bader
Texicryl AD 8077	Scott-Bader

There are also similarities with the FEVE emulsions when creating these water-based formulations. Generally speaking, the same additives used for the FEVE emulsion formulations can be used for the FEVE dispersion formulation.

Powder Coating Formulations

The FEVE powder coating resin has the appropriate properties for fabricating a powder coating: high T_g and significant hydroxyl functionality for cross linking with isocyanates. There are some formulation guidelines that will help to achieve successful performance with this type of powder coating.

Choice of Isocyanate Cross Linker. Blocked isocyanates and melamines can be used as cross-linking resins for the FEVE powder resin. These hardeners are typical for all powder coating formulations, and the choices are as varied as with the standard powder resins. Some choices for blocked isocyanates are listed in Table 6.

Choice of Catalyst. Several catalysts have been used in FEVE-based powder coatings. Dibutyltin dilaurate, stannous octoate, and bismuth octoate have been used successfully. Catalyst levels depend on which isocyanate is used in the formulation.

Choice of Pigments. The same guidelines given for the liquid FEVE coatings also apply for the FEVE powder coatings.

Choice of Additives. Benzoin, a popular degassing agent in standard powder coatings, is also used in FEVE powder coatings. Flow additives are also employed to minimize the degree of the "orange-peel effect" on the surface of the coating.

FEVE Coating Properties

The performance properties of FEVE resins that have drawn the most attention from the coatings marketplace are their superior weatherability, their significant degree of chemical resistance, and their thermal resistance (compared to the rest of the organic resin family).

Table 6 Some commercially available blocked isocyanates

Blocked isocyanate	Manufacturer	Isocyanate type(a)
Crelan Ui	Bayer Material Sciences	IPDI
Vestagon B-1065	Evonik	IPDI
Vestagon B-1530	Evonik	IPDI
Crelan VPLS 2256	Bayer Material Sciences	IPDI
Crelan VPLS 2181/1	Bayer Material Sciences	IPDI/HMDI
Crelan VPLS 2122	Bayer Material Sciences	HMDI
Crelan NW5	Bayer Material Sciences	HMDI

(a) IPDI, isophorone diisocyanate; HMDI, hexamethylene diisocyanate

Figures 4 to 7 (which indicate gloss-retention properties after UV radiation exposure) give some indication as to the level of weatherability attainable when FEVE resins are the principal binder in a coating formulation.

The solvent- and chemical-resistance properties of the FEVE resin family can be seen in Tables 7 and 8, respectively.

The FEVE having a higher cross-link density shows improvement in performance with two of the reagents. When chemical resistance is an important property desired for an FEVE-based coating, the use of the FEVE resin with the highest cross-link density is suggested.

Resistance to water vapor permeation is also a key property of the FEVE resin products. This attribute is important for improving corrosion-resistance properties of these coatings. Table 9 presents data from ASTM E 96, "Standard Test Methods for Water Vapor Transmission of Materials."

In addition to these properties, FEVE resin-based coatings exhibit physical properties (flexibility, hardness, abrasion resistance, etc.) that are comparable to standard 2K polyurethane coatings. Such properties can be changed, depending on which FEVE resin is used, which isocyanate is picked as the cross linker, and if a non-FEVE modifying resin is included in the formulation.

Table 10 shows typical properties of coatings based on FEVE resins cross linked at ambient conditions with an aliphatic polyisocyanate, and cross linked at elevated temperature with a melamine cross linker.

Performance of FEVE Resins

As mentioned in a previous section, the greatest performance attribute of the FEVE resin family is their ultraweatherability. The ability to endure the harsh effect of the sun's UV radiation with minimal loss of gloss and color is the reason for their use. Both major types of fluororesins for thin-film coatings—FEVE and polyvinylidene fluoride—offer superior protection against degradation from sun and humidity.

The carbon-fluorine bonds are higher in energy than the sun's UV wavelengths. In addition, the FEVE polymer transmits >80% of UV radiation at wavelengths above 250 nm, and >90% at wavelengths above 300 nm. Generally, the total fluorine content in the polymer is used as a predictor of UV resistance, but the structure of FEVE resins allows for them to perform at fluorine levels of 20 to 30%. The chemically stable fluoroethylene unit also protects the usually weak vinyl ether both sterically and chemically from attack from acids and bases (Ref 2).

The FEVE fluorourethane coatings have been used to protect bridges and other large structures in Japan for over 30 years. Several case studies have been reviewed, and it has been observed that FEVE-based topcoats also protect the underlying coatings from corrosion. This gloss retention results in brilliant color retention and a fresh appearance.

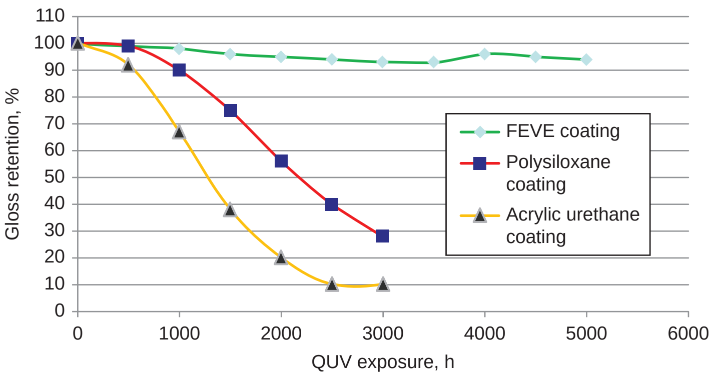

Fig. 4 Exposure of test panels in QUV (Q-Lab Corporation) weatherometer (using UVB-313 light source). FEVE, fluoroethylene vinyl ether

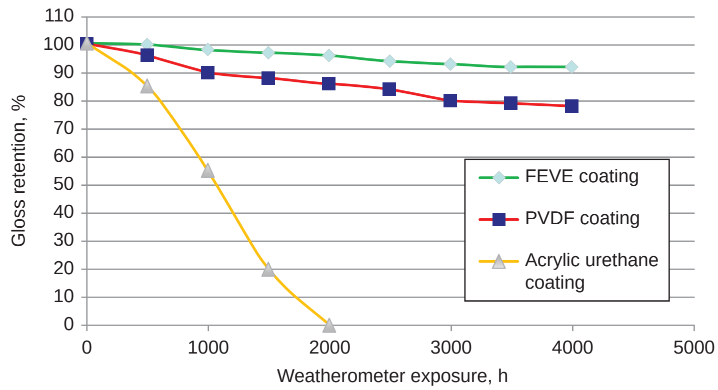

Fig. 5 Exposure of test panels in sunshine carbon arc weatherometer. FEVE, fluoroethylene vinyl ether; PVDF, polyvinylidene fluoride

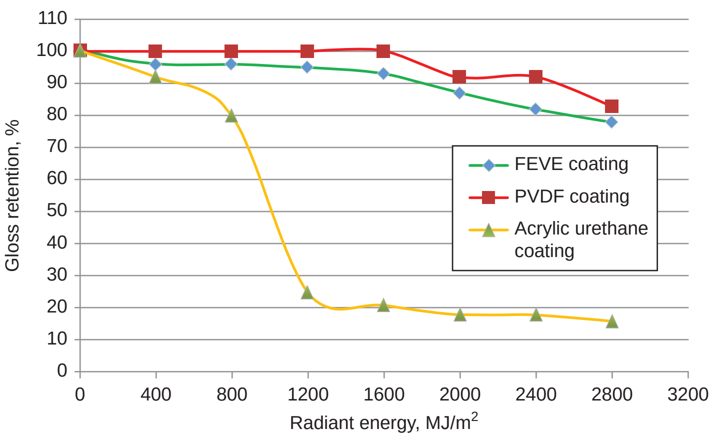

Fig. 6 Exterior exposure of test panels (EMMAQUA exposure site, Arizona). FEVE, fluoroethylene vinyl ether; PVDF, polyvinylidene fluoride; EMMAQUA (DSET Laboratories, Inc.), equatorial mount with mirrors for acceleration with water

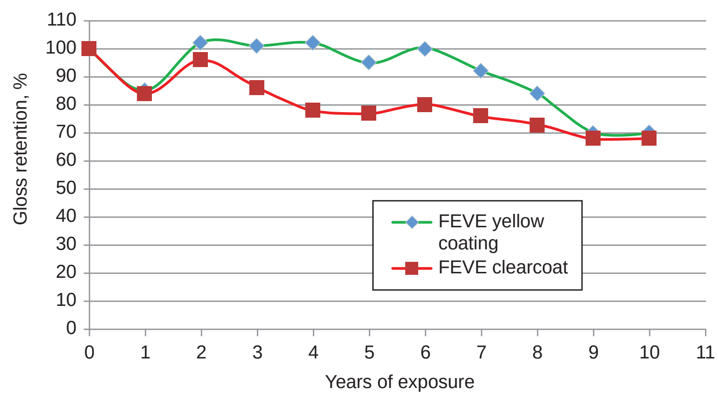

Fig. 7 Exterior exposure of test panels (South Florida exposure site). FEVE, fluoroethylene vinyl ether

Table 7 Solvent-resistance properties of fluoroethylene vinyl ether (FEVE) resins

Solvent exposure	FEVE resin with medium cross-link density, days to failure	FEVE resin with high cross-link density, days to failure
Aqueous formaldehyde	>30	>30
Benzene	>30	>30
Xylene	10	>30
Acetone	20	20
Isopropanol	20	20

Note: Failure is defined as one of the following changes in the dry film: the appearance of blisters, gloss reduction, or total paint film degradation.

Table 8 Chemical-resistance properties of fluoroethylene vinyl ether (FEVE) resins

Chemical exposure (acid or base)	FEVE resin with medium cross-link density, days to failure	FEVE resin with high cross-link density, days to failure
10% HCl (hydrochloric acid)	>30	>30
10% H_2SO_4 (sulfuric acid)	>30	>30
5% CH_3COOH (acetic acid)	17	>30
1% H_2SO_3 (sulfur dioxide)	3	3
10% NaOH (sodium hydroxide)	>30	>30
12% NaOCl (sodium hypochlorite)	>30	>30

Note: Failure is defined as one of the following changes in the dry film: the appearance of blisters, gloss reduction, or total paint film degradation.

Studies have been performed that measure the actual erosion of FEVE-based coatings over time. Results of one study are shown in Fig. 8. The results show little to no erosion over a 15 year exposure period for the FEVE-based coating. This performance is superior to the performance of the best traditional polyurethane system, which shows measurable erosion over this same period.

The FEVE resins are a prime candidate for exterior applications. Recently, however, FEVE resins have been studied for use in interior applications where resistance to staining and harsh chemicals is needed. The strength of the carbon-fluorine bond provides the performance for these requirements. The FEVE-based coatings are being used in interior hospital settings. The interior of hospitals, specifically patient-care and treatment areas, is exposed to iodine as well as harsh cleaning agents. The FEVE resins have been formulated into coatings that meet the resistance requirements of these materials. Also, some hospital areas use UV radiation for testing and sterilizing, and FEVE resins aid in protection against this as well.

In addition to the intense radiation from sunlight, exterior environments can be high in salt

Table 9 Moisture permeation-resistance properties of fluoroethylene vinyl ether (FEVE) resins

Resin type	Cured with hardener	Film thickness µm	Film thickness mil	Total moisture permeation, g of water vapor per cm^2/h
FEVE polyol(a)	No	20	0.79	1.09×10^{-3}
Acrylic polyol	No	20	0.79	4.5×10^{-3}
FEVE polyol(a)	Yes	21	0.83	0.45×10^{-3}
Acrylic polyol	Yes	14	0.55	1.55×10^{-3}

(a) Medium-cross-link-density resin

and moisture. Warm, coastal areas, such as many parts of Florida and Okinawa, provide conditions that are severe to important building materials such as steel and concrete. The FEVE-based topcoats have shown good performance in real-world applications. Recent lab studies have shown that FEVE-based coatings appear to offer superior barrier protection against corrosive environmental salt and moisture as compared to conventional urethanes.

Physical degradation from elements such as sand and dirt is a real factor in the performance of many exterior coatings. The abrasion resistance of FEVE coatings is limited. More work is required in this area of study. Because FEVE resins are not pure fluoropolymers, they do not exhibit superhydrophobicity or very low surface energy. Theoretically, it is unclear if the fluorine content of FEVE resins provides an advantage against abrasion.

Applications of FEVE-Based Coatings

The FEVE-based coatings are used to aesthetically improve exterior structures and to protect various substrates from degradation. In structural steel protection, FEVE-based coatings serve as the topcoat in a three-coat system that uses a zinc-rich primer and an epoxy intermediate coat preceding it. The advent of two-coat systems has generated interest in using FEVE-based coatings for these applications. However, there has been minimal use of this type of two-coat system to date.

These coatings have been used on many steel structures: commercial buildings, sport stadiums, water storage tanks, bridges, rail cars, offshore drilling platforms, and other assorted applications. Application techniques have included spray, brush, and rolling methods. These types of coatings can be applied at ambient temperatures with standard commercial spray equipment. The typical pot lives of these coatings are long enough to eliminate the need for dual-component spray equipment.

The following are application guidelines (from Tnemec's technical data sheet for HydroFlon Series 701) for a standard two-component, solvent-based, isocyanate-cross-linked FEVE-based coating.

Table 11 lists the recommended coverage rates.

The average times to apply the coating after mixing (pot life) are:

- 5 h at 10 °C (50 °F)
- 2 h at 21 °C (70 °F)
- 1 h at 32 °C (90 °F)

The surface temperature during application should be a minimum of 4 °C (40 °F) and a maximum of 49 °C (120 °F). The surface should be dry and at least 3 °C (5 °F) above the dewpoint. The cure times necessary to resist direct contact with moisture at the surface temperature are:

- 4 °C (40 °F): 44 h
- 10 °C (50 °F): 21.5 h
- 16 °C (60 °F): 11 h
- 21 °C (70 °F): 7 h
- 27 °C (80 °F): 5 h
- 32 °C (90 °F): 3.5 h
- 38 °C (100 °F): 2 h

If the coating is exposed to moisture before the preceding cure parameters are met, a dull and/or spotty appearance may develop. The times listed will vary, depending on air movement, film thickness, and humidity levels.

Table 10 Typical properties of fluoroethylene vinyl ether coatings cross linked with different cross linkers at different temperatures

Clear formulation, 25 µm (1.0 mil) dry film thickness	Room-temperature formula	Baking formula
Cross linker	Hexamethylene diisocyanate trimer	Butylated melamine
Cure conditions	Ambient, 7 days	210 °C (410 °F) × 5 min
Physical properties		
Contact angle of water	85°	78°
Static friction coefficient	0.45	0.33
Water absorption, %	0.71	0.22
Water permeability, $g/cm^2 \cdot s \cdot mm\ Hg$	6.2×10^{-4}	4.3×10^{-4}
Oxygen permeability, $cm^2 \cdot s \cdot mm\ Hg$	0.92×10^{-10}	0.85×10^{-10}
Mechanical properties		
Tensile strength, kg/mm^2	2.8	3.0
Elongation, %	5	4
Tear strength, kg/mm	1.8	4.0
Flexural fatigue, times	200	60
Thermal properties		
Glass transition temperature, °C (°F)	35 (95)	63 (145)
Decomposition temperature, °C (°F)	...	214 (417)
Dimensional change, %		
After 120 °C (250 °F) × 600 h	−1.7	−4.3
After −20 °C (−4 °F) × 24 h	0.0	−0.1
Electrical properties		
Volume resistivity, Ω · cm	1.4	1.3

Source: Ref 2

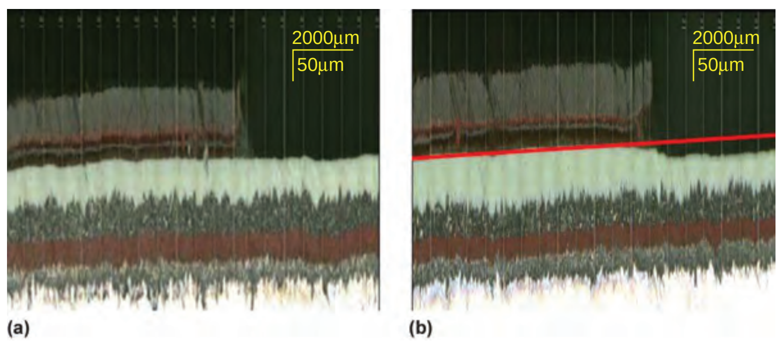

Fig. 8 Micrographs comparing the erosion of (a) fluoroethylene vinyl ether white coating (0 to 1.1 µm, or 0.04 mil, of erosion) and (b) polyurethane white coating (22 to 28 µm, or 0.87 to 1.1 mil, of erosion) after 15 years of exposure. Micrographs property of Asahi Glass Co. Ltd.

Table 11 Recommended coverage rates for a standard two-component, solvent-based, isocyanate-cross-linked fluoroethylene vinyl ether-based coating

Recommended coverage rates(a)	Dry µm	Dry mils	Wet µm	Wet mils
Suggested	63	2.5	100	4.0
Minimum	50	2.0	75	3.0
Maximum	75	3.0	125	5.0

(a) Application of coating below minimum or above maximum recommended dry film thicknesses may adversely affect coating performance.

Surface-preparation requirements include the following:

- *For exterior exposures:* SSPC-SP 6, "Commercial Blast Cleaning"
- *For all surfaces:* Must be clean, dry, and free of oil, grease, and other contaminants

Table 12 provides the curing times for the coating.

One-component solvent-based cross-linked FEVE-based coatings are also achievable if the coating is exposed to high temperatures during the application. In this case, the cross-linking resins are either blocked isocyanates or amino resins. The blocked isocyanates become unblocked and reactive when the coating is exposed to heat (in the beginning of the baking schedule). These coatings are restricted to factory applications and have gained popularity as coil coatings.

There are one-component solvent-based FEVE coating formulations that contain an FEVE resin that does not have the necessary level of hydroxyl functionality for meaningful cross linking. These resins have been synthesized for use in coatings that are applied for the repair of building components damaged at the construction site. However, these resins are not limited for use in only one coatings market. They can be blended into any solvent-based, one-component coating for the improvement of specific properties that FEVE resins have the capacity to improve. Application techniques for these types of coatings are identical to those used for two-component FEVE-based coatings.

The FEVE-based powder coatings follow a different path in their application technique. Electrostatic spray application is the sole method for transferring FEVE-based powder coatings to their destination. Standard electrostatic spray equipment and electrostatic fluidized-bed equipment work well with these coatings. Both corona and tribo spray guns can be used. The cure temperature range of these coatings is 190 to 220 °C (375 to 425 °F). The average baking time is 15 min. Both steel and aluminum substrates have been coated successfully with FEVE-based powder coatings. Pretreatment of the aluminum is necessary to achieve the level of adhesion needed for this application.

Table 12 Curing times for a standard two-component, solvent-based, isocyanate-cross-linked fluoroethylene vinyl ether-based coating

Temperature				
°C	°F	Dry to touch	Dry to handle	Minimum recoat(a)
32	90	10 min	4 h	5–8 h
21	70	30 min	6–8 h	10–12 h
10	50	1 h	12–15 h	16–24 h

(a) Maximum recoat: 30 days. Curing time varies with surface temperature, air movement, humidity, and film thickness.

Water-Based Coatings

This section is divided into two parts: application guidelines for one-component, water-based FEVE resin-containing coatings, and also two-component, water-based FEVE resin-containing coatings. The important difference between these two types of coatings is the limitation of time available for applying the two-component coatings after the two parts are mixed, which is not applicable to the one-component coatings. The presence of a limited time for application (called pot life) is identical to the solvent-based FEVE resin-containing coatings. However, the increase in viscosity observed as the end of the pot life of the solvent-based coatings approaches does not occur with the two-component, water-based FEVE-containing coatings. The pot life of these products must be predetermined and stated by the formulators of the coatings. The presence of water and the morphology of the water-based FEVE resin particles prevent a noticeable physical change in the coating. If these coatings exceed the pot life designated for them, their performance will not reach its potential.

Application techniques for the two-component, water-based FEVE resin-containing coating are identical to those used for their solvent-based counterparts. However, the presence of water in the formulations increases the importance of the relative humidity of the environment during application of the coating. Attempting application when high-humidity conditions are present is not recommended, because the evaporation rate of the water will decrease, and the ability of the coating to dry without flowing down the substrate will decrease.

The application guidelines for one-component, water-based FEVE-containing coatings mimic those of typical water-based finishes used for light industrial applications. The guidelines are as follows:

- *Recommended dry film thickness per coat:* 50 to 75 μm (2 to 3 mils)
- *Wet film to achieve dry film thickness:* 125 to 190 μm (5 to 7.5 mils)

Drying times at 21 °C (70 °F) and 50% relative humidity are:

- *Dry-to-touch:* ½ to 2 h
- *Time to recoat:* 4 h

Specifications for specific substrates include the following:

- *Ferrous metal:* Surface must be primed before application; solvent- or water-based primers can be used
- *Galvanized/aluminum:* Surface must be primed before application; solvent- or water-based primers can be used
- *Exterior smooth block (concrete block):* Water-based primer recommended
- *Exterior porous block:* Water-based block filler recommended

Additional application guidelines include the following:

- Stir material prior to application.
- Equipment must be clean prior to start. Flush airless lines with clean water.
- Apply by brush, roller, or spray. A good-quality synthetic brush makes application easier. Select a roller cover suited for the texture of the surface to be coated. Airless tip sizes of 0.015 to 0.017 are recommended.
- Apply the product in full, even coats and maintain a wet edge. Allow the product to dry between coats.
- Do not thin.
- Protect product from freezing prior to and during application.
- Minimum surface and air temperature required for application is 10 °C (50 °F) and at least 3 °C (5 °F) above the dewpoint. Curing is affected by temperature, humidity, and air movement. The minima must be maintained for at least 8 h to achieve proper film formation.
- Application at elevated temperatures, wind conditions, and/or low humidity may require special application procedures to achieve proper film formation.

Concerns When Formulating and Using FEVE Coatings

The following are concerns when formulating and using FEVE coatings:

- The FEVE resins are known for their resistance to degradation from UV radiation. However, they cannot absorb UV radiation. They allow UV radiation to pass through them quite easily. Therefore, any clearcoat FEVE resin-based coatings that are applied over a colored basecoat or a substrate susceptible to degradation from UV radiation must have additives that absorb this radiation. The most common additives are the commercial UV absorbers and hindered amine light stabilizers (HALS) available for the coatings industry.
- The FEVE resins do not directly protect the pigments that are present in coatings of color. Because FEVE resin-based coatings retain their gloss longer than conventional two-component acrylic or polyester-urethane coatings, they reflect more UV radiation than coatings that degrade at a faster rate. However, these pigments still need some protection from UV radiation. Therefore, the presence of UV absorbers and HALS helps improve the color-retention properties of the coating.
- The adhesion properties of water-based FEVE emulsion resins are compromised. They should be used only in blends with acrylic emulsions for adhesion enhancement.
- The reactivity of solvent-based FEVE resin polyols is faster than the conventional acrylic

and polyester polyols due to the presence of only primary hydroxyl groups on the resins. It is important to reduce catalyst levels in formulations that contain these types of resins. Also, some of the UV absorbers and HALS promote the polymerization reaction between isocyanate groups and hydroxyl groups and decrease the length of the pot life. Depending on the expectations of the appropriate pot life in a given application, careful screening of these types of additives may be necessary.

Health and Safety

The FEVE resins are fluorinated. This causes alarm to many in areas of environmental safety. The key to FEVE resins is that they are polymeric. They have a relatively high molecular weight when compared to many other fluorinated materials used in coatings, such as surface additives. Also, FEVE resins can be used in 2K cross-linkable coating systems. This means the effective molecular weight increases even more. Generally speaking, FEVE resins will not leech into groundwater. Also, because of their fluorination they are insoluble in water. (When reacted and dried, even the waterborne emulsions are not soluble in water.)

Testing has confirmed that the manufacturing process of FEVE resins does not produce any C8 (perfluorooctanoic acid) or even C6 (perfluorohexanoic acid) compounds. These compounds have been shown to be a risk to the environment due to their biopersistence. The FEVE resin chemistry could be considered C2 chemistry, because the fluorinated monomer used in synthesis has a two-carbon chain.

Only the solvent-based resins may have issues with being hazardous. This is because they contain solvents, such as xylene (which is considered hazardous by the Occupational Safety and Health Administration). Organic solvent emissions are also regulated. Many solvents contribute to the overall volatile organic compound of a coating. Regulations vary by country, so consulting the material safety data sheet for each product is essential.

Summary

The FEVE resin technology is unique to the coatings industry. The combination of fluorine chemistry and vinyl ether chemistry allows the creation of a resin that fits well into standard coatings formulations while incorporating properties that can only be reached by the use of fluorine chemistry. By using this technology, FEVE resin-based coatings can offer performance properties that extend the life of exterior organic coatings and exterior structures. The presence of these coatings in the marketplace—for bridges, commercial buildings, sports stadiums, water tanks, and a multitude of steel structures—gives the customer a coating choice that will increase the lifetime of the coating system and reduce the number of recoats necessary to ensure protection of these structures.

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