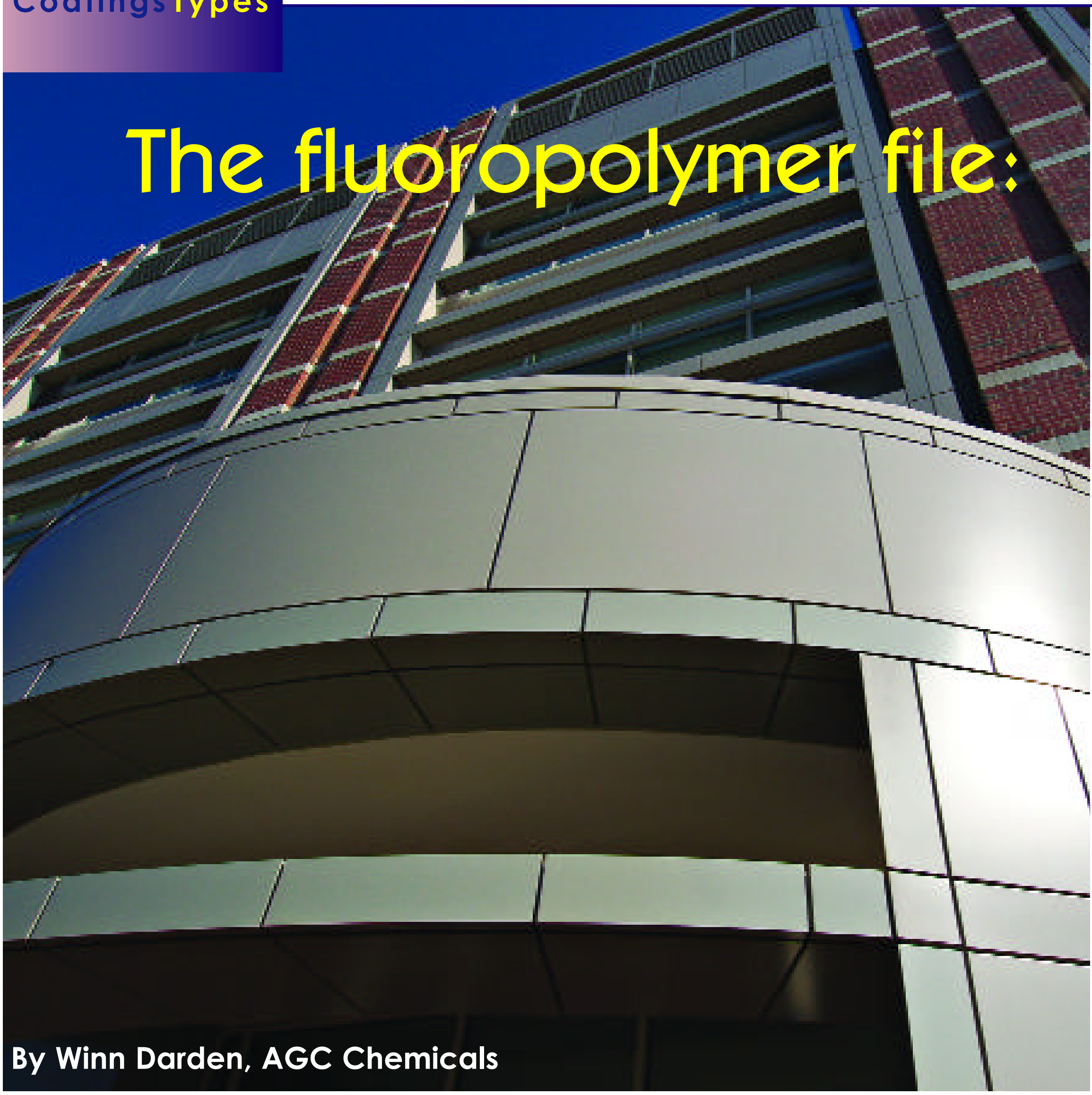


# The fluoropolymer file:

By Winn Darden, AGC Chemicals

Fluoropolymers have been used in coatings for more than 40 years due to their physical properties, including low surface energy, excellent weatherability, and outstanding corrosion, abrasion, temperature, and chemical resistance. Because most fluoropolymers are high-molecular-weight thermoplastics, their use has been limited to applications where heat can be used to soften or melt them to form coatings and linings.

Thermoset fluoropolymer resins that offer similar physical properties are now available, and these can be used to formulate coatings that cure at either ambient or elevated temperatures. The formulation of these resins has led to the development of field-applied coatings, substantially increasing the versatility of fluoropolymer resins.

This article will discuss the various types of fluoropolymer resins and their properties. The focus will be on fluoroethylene-vinyl ether (FEVE) thermoset resins, which can be formulated into coatings with a wide range of gloss, a high degree of pigment compatibility, service lifetimes exceeding 30 years, and improved adhesion to a range of substrates. A review of applications will also be included.

# Style with staying power

## Chemical bonding holds key to technology's reputation for seemingly ageless aesthetics

***(Facing page): At the College of Engineering, North Carolina State University the exteriors are coil coated with Coraflon®, a PPG coating containing the Lumiflon® resin.***
***(Below): A Nissan auto dealershipin VA is also coated with Coraflon. Both photos courtesy of Mitsubishi Chemical Functional Products, Inc.***


### Physical properties of fluoropolymers

The physical properties of fluoropolymers are the result of the high bond and ionization energies of the carbon-fluorine chemical bond, which delivers stability to UV light and chemical and solvent resistance. The physical properties are also derived from the low-bond polarization energy of fluoropolymers, which imparts resistance to diffusion of corrosion initiators and low surface energy.

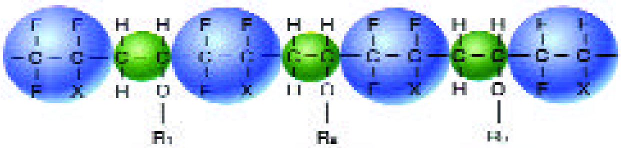
Examples of fluoropolymers used in coating and lining applications include polytetrafluoroethylene (PTFE, or TEFLON®); tetrafluoroethylene-hexafluoropropylene copolymer (FEP); tetrafluoroethylene-ethylene copolymer (ETFE); poly[vinylidene fluoride] (PVDF), and polyvinyl fluoride (PVF). Due to high softening temperatures, poor or limited solubility in organic solvents, and an inability to achieve thin-film application without pinhole formation, only the PVF and PVDF types of these materials are commonly used in coatings. These polymers can be dispersed in organic solvents, becoming soluble at high temperatures (latent solvents), and can form thin films without pinholes.

### Fluoropolymers used in coatings

PVF is usually incorporated in a film-forming coating by melt casting the polymer in a latent solvent. Unfortunately, the melting point of PVF is very close to its decomposition temperature, which requires the use of additives that limit its usefulness as a coating. PVDF possesses a greater difference between its melt and decomposition temperatures, but by itself may form pinholes during application and suffer from poor adhesion.

To improve melt-flow properties and adhesion, PVDF is blended with acrylic resins, usually at a 70/30 ratio. This blend is dispersed

***Akashi Straits Bridge in Kobe, Japan, is coated with paint supplied by Dai Nippon Toryo Paint (DNT). Photo courtesy of AGC Chemicals***




Fluoroethylene Segment (Blue): Weatherability, durability, chemical resistance
Vinyl Ether Segments: (Green):
R1=Clarity, gloss, hardness
R2=Flexibility
R3=Crosslinkng site (-OH). solubility

***Figure 1: Chemical Structure of FEVE Polymer***

in a latent solvent and is sold under the trade names KYNAR® or HYLAR®. To form a coating, this polymer blend is heated to temperatures in excess of 250 C. PVDF goes into solution at these temperatures, forming a pinhole-free coating with good adhesion.

PVDF coatings set the standard for performance of fluoropolymer coatings for a wide range of applications. Coatings based on PVDF exhibit durability that exceeds 20 years, color and gloss retention over the life of the coating, good chemical resistance, and the flexibility required to fabricate precoated construction components.

Coatings based on PVDF, however, are characterized by certain limitations that affect their use. First, the products are usually applied to the substrate at elevated temperatures. PVDF coatings can be field applied; however, they are generally not used on large structures like bridges. This usually limits their applications to construction components that can be precoated in a factory or shop setting.

Second, due to the limited chemical compatibility between PVDF and the acrylic resin, the gloss range for PVDF coatings is usually restricted to the 20–40 range (viewed at 60°). Pigment and color compatibility can also be limited.

## Thermoset fluoropolymer resins

Thermoset FEVE copolymer resins were developed as an alternative to thermoplastic fluoropolymer resins, in an attempt to overcome the limiting factors of conventional resins. FEVE resins are synthesized via free-radical polymerization of a fluoroethylene (FE) monomer and a vinyl ether (VE). Fig. 1 shows the structure of the polymer, which consists of regularly alternating units of the monomers.

This alternating structure is crucial to the weatherability of the resin. The fluorinated segments protect the vinyl ether segments from degradation by UV light, chemicals, and other contaminants.

The vinyl ether segments provide characteristics not available in most fluoropolymers. The segments can be altered to make the resin soluble in organic solvents by changing the nature of the "R" groups shown in Fig. 1. This results in a true solution polymer, characterized by its clarity. By incorporating hydroxyl groups (-OH) in the vinyl ether, resins can be crosslinked using common aliphatic isocyanates at room temperature. Carboxylic acid groups (-COOH) can be included to improve the pigment compatibility of the polymer. By changing the number of the molecular weight of the polymer and the number and type of the groups mentioned above, properties of the resulting coating, such as flexibility, hardness, and chemical resistance, can be modified.

Unlike other fluoropolymer coatings, coatings made with FEVE resins are thermosetting—curable at room temperature or at elevated temperature—exhibit excellent compatibility with a wide range of inorganic and organic pigments, and offer a wide range of gloss, up to 87 at 60°. Because FEVE resins are solution polymers, coatings made with the resins can be produced in bright, vivid colors unavailable with traditional fluoropolymers. Care must be taken, however, to ensure that the life of the pigments match that of the FEVE resin. FEVE-based coatings also can be field applied, making them suitable for recoating projects.

To make ambient-cure coatings, FEVE resins are crosslinked with standard aliphatic isocyanates, such as isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), and hydrogenated methylene diphenyl diisocyanate (HMDI). The reactivity and handling characteristics of FEVE-based coatings are said to be similar to those of acrylic urethanes. FEVE resins can also be formulated into single-component coatings for high-temperature cure. Typically, blocked isocyanates and melamines are used as crosslinkers.

Because they exhibit characteristics of fluoropolymers as well as urethanes, FEVE-based coatings offer excellent adhesion to substrates ranging from aluminum and steel to fiberglass, and they bond well to primers and undercoats such as epoxies and polyurethanes. FEVE coatings can be recoated as well, and can also be used to repair and refinish other fluoropolymer coatings. As with any other type of coating, surface preparation is the key to successful adhesion.

## Types of FEVE resins

There are three types of FEVE resins currently available on the market: solvent-borne, solid resins, and water-borne.

*The Allied Material Building in Singapore, coated with a Lumiflon-based product*
*Photo courtesy of Mitsubishi Chemical Functional Products, Inc.*

### Solvent-based FEVE resins

For ambient-cure coatings based on FEVE resins, xylene is the solvent currently used. Xylene is commonly used in coatings due to its physical properties and because of its low cost. The solids content of FEVE resins in xylene ranges from 40–67%. Unfortunately, xylene is considered to be a volatile organic compound (VOC), and is also is regulated as a hazardous air pollutant (HAP). This means that, in many cases, coatings with xylene content cannot be used.

For heat-cured coatings, FEVE resins are typically dissolved in a cyclohexanone/aromatic 150 solvent blend, which is commonly used in the coil coating industry.

### Solid FEVE resins

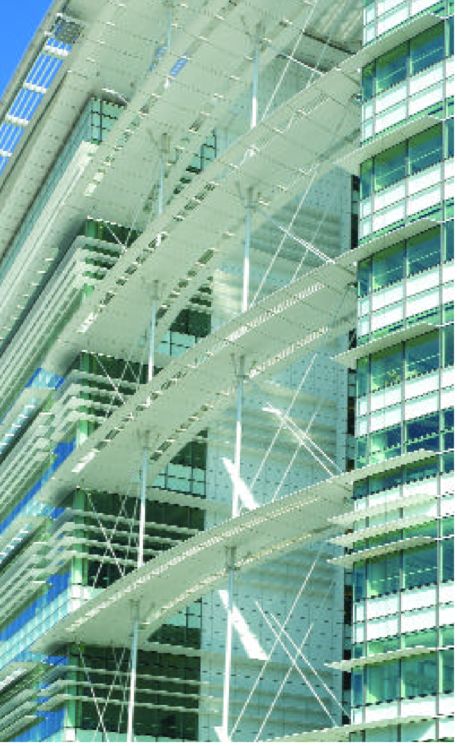
Over the last several years, VOC and HAP regulations have become more stringent, particularly in areas where current air pollution standards are not being met, such as southern California. In response, solid FEVE resins have been developed as an alternative to solvent-borne coatings. These solid resins can be used to make low-VOC and HAP-free coatings. Typical solvents for solid FEVE resins include methyl ethyl ketone (MEK), methyl amyl ketone (MAK), methyl isoamyl ketone (MIAK), ethyl 3-ethoxypropionate (EEP), t-butyl acetate, acetone, and parachlorobenzotrifluoride (Oxsol 100). The latter three solvents are considered VOC exempt. Most likely, blends of solvents will be required to make low-VOC and HAPS-free coatings and to retain the required handling characteristics such as evaporation rates.

### Water-based FEVE resins

FEVE resins also can be emulsified with surfactants to make water-based fluoropolymer resins. These products can be polymerized with water-dispersible isocyanates to form fluorourethane coatings with excellent weathering properties. Coalescing agents such as Texanol® ester alcohol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) must be used to reduce the film-forming temperature and achieve ambient-cure coatings. Single-component FEVE emulsions also can be used to formulate coatings.

## Performance of coatings based on FEVE resins

Coatings made with FEVE resins offer superior weatherability and corrosion resistance. Each of these characteristics is



*National Library Board in Singapore, coated with Lumiflon-based product. Photo courtesy of Mitsubishi Chemical Functional Products, Inc.*

*Rainbow Bridge, Tokyo, Japan, coated with Nippon Paint Photo courtesy of AGC Chemicals*

discussed below.

- Weathering properties. The outstanding weatherability of FEVE-based coatings is attributable to the high bond energy of the carbon-fluorine bond. This means that it is difficult to generate free radicals in FEVE resins, the method by which degradation of coatings by UV light is propagated. Fig. 2 shows gloss retention of a fluorourethane after 10 years of weathering in south Florida. South Florida is typically used for accelerated weathering tests due to the intense sunlight year-round.
- Corrosion resistance. Fluorourethanes made with FEVE resins can perform effectively in the presence of corrosion initiators such as chloride ions, water, and oxygen, even after years of exposure to the elements. Several factors contribute to this capability. First, the small van der Waals radius of the fluorine atom makes FEVE coatings "tight." Second, the degradation rate of FEVE-based coatings is extremely low, typically ranging from 0.014–0.018 mils per year. This means that even at a coating thickness of 1 mil, there is a substantial amount of coating remaining even after 20 or more years, and the coating continues to resist contaminants. FEVE topcoats have been applied in thicker coats to give expected lifetimes of more than 60 years to a coating system.

## An impressive application record

Coatings based on FEVE resins have been applied to structures in a range of markets for more than 20 years. The major market for FEVE-based coatings has been concentrated in the architectural segment, where the retention of coating appearance and color is paramount. Not only do these coatings retain the original appearance for extended periods, but subsequent repainting can be postponed, in some cases for periods exceeding 30 years. Warranties of 15 and even 20 years are not uncommon.

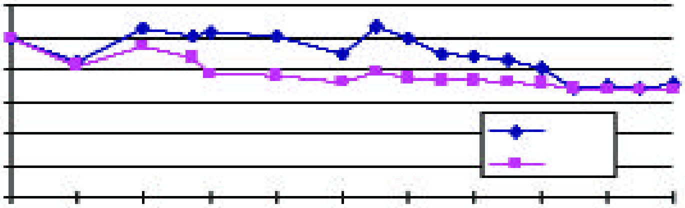


*Fig. 2: South Florida Weathering of FEVE Based Coating*

Aluminum composite panels finished with FEVE-based coatings are used in gas stations, commercial and industrial buildings, and in metal buildings and roofing. Most of these applications involve the use of coil-coated panels that are fabricated in the field.

Air-dry fluorourethane coatings are also finding widespread application in field-applied architectural uses, including the recoating of surfaces where PVDF-based coatings were originally applied. FEVE resins enable field-applied coatings to match the performance of shop- or coil-applied fluoropolymer coatings.

The use of FEVE-based coatings on the metalwork of monumental buildings is also on the upswing, as is the use of these coatings as industrial maintenance or heavy-duty coatings for water towers and other structures.

Interestingly, coatings based on FEVE resins are commonly used for bridge coatings in Japan and Asia. The Japanese Ministry of Land, Infrastructure, and Transport now requires the use of fluorourethane topcoats for all bridges. The ministry is counting on an estimated coating life of more 30 years and, in some cases, as many as 60 years. Such applications are receiving more consideration in the U.S. and Europe as well.

FEVE-based coatings are also used in the aerospace industry, primarily for military applications. The Air Force has initiated an "Advanced Performance Coating" program where FEVE-based coatings serve as the standard of performance. In this program, the fluorourethane topcoat, compared to conventional topcoats, is estimated to give a 5- to 15-fold improvement in color stability, and a five-fold increase in gloss retention. The resins are currently being evaluated for use in commercial aviation applications.

FEVE-based coatings find some limited use in the automotive industry; however, they are generally too expensive for large-scale applications in this market. They are used for specialty applications where quality issues are particularly important.

### Lifecycle cost factor

Not surprisingly, FEVE-based paints are expensive when compared to other technologies. It is important, however, to consider lifecycle costs when determining whether the use of a FEVE-based coating should be considered. In a three-coat system (primer, intermediate coat, and topcoat), the only difference in application costs between a system incorporating a FEVE-based coating and a standard urethane coating is the cost of the topcoat. All other costs, including application, remain the same. If the cost of a FEVE coating is assumed to be 10 times the cost of a urethane, the initial cost disadvantage of the FEVE coating system is about 12%. Experience in Japan and in the U. S. places the actual cost disadvantage at 6–12%.

Due to the outstanding weatherability of FEVE-based coatings, however, recoating is not required for at least 20 years. If it is assumed that a polyurethane coating will need to be replaced after 10 years, the FEVE coating can claim a lifecycle cost advantage of about 31%. Many urethanes that give adequate corrosion protection for 10 years will often begin fading prior to the end of the anticipated service life of the coating.

*A water tower at Miramar Beach, FL. Fluoropolymer coating manufactured by Tnemec. Photo courtesy of Tnemec*

A number of other costs can be mitigated by using coatings based on FEVE resins. One such cost is tied to downtime for recoating, in the case of commercial aircraft, electrical equipment, and gas stations, for example. In these cases, a coating that retains appearance characteristics also helps to maintain the image of quality, an important consideration in perception-driven commercial markets.

In the case of bridges, costs associated with maintenance repainting, such as traffic congestion and lost service time, can be substantial, not to mention the reduction in future maintenance costs made possible by a longer-lasting coating. This, in turn, can free up funding for other projects. A side benefit is the potential for reduced liabilities associated with overspray claims due to the decreased frequency of repainting.

### The fluoropolymer factor: Performance under pressure

Fluoropolymer coatings represent a high-performance technology for architectural coatings applications. The technology has compiled an impressive track record of long-term color and gloss retention in challenging service environments, particularly those where UV exposure is a major factor. Coatings based on FEVE resins represent an important facet of the fluoropolymer-coatings marketplace, thanks to a combination of performance attributes and application flexibility.

Performance data on fluoropolymer coatings based on FEVE resins indicate that these coatings can deliver substantial lifecycle cost savings. New solid resins and water-based resins offer the opportunity to formulate low-VOC and HAP-free coatings to meet emerging regulatory requirements.

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