# Formulation Techniques Using FEVE Resins

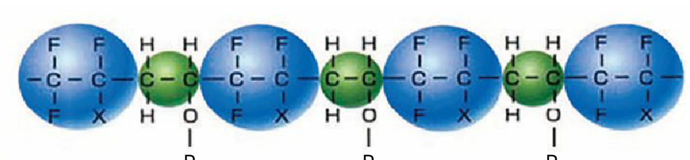
## *in Waterborne and High Solids Coatings*

Fluoroethylene vinyl ether (FEVE) resins were developed in Japan in the late 1970s and entered the commercial market in 1982. FEVE resins are amorphous A-B type copolymers with repeating units of fluoroethylene and substituted vinyl ether. Unlike pure fluoropolymers, FEVE resins are soluble in solvent due to the vinyl ether groups. Solvent solubility transforms FEVE resins from high-performance polymers into high-performance resins for coatings.

FEVE resins have characteristics of both fluoropolymers and hydrocarbons. 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 C-F bond is strong. The energy of this bond is ~486 kJ/mol,[1] while the energy of UV radiation at 300 nm is ~399 kJ/mol. The alternating pattern, shown in Figure 1, is critical for the extreme UV resistance properties.[2] The chemically stable and UV-resistant fluoroethylene unit sterically and chemically protects the neighboring vinyl ether unit.[3]

The vinyl ether groups make FEVE polymers useable as resins for paint. Without the vinyl ether groups, these resins would not be soluble in solvent. This solubility is what allows FEVE resins to be used in a wide array of coating formulations that can be applied in factory or field settings.[4] The vinyl ether groups also contribute to high gloss and allow for functional groups, like hydroxyl, to be incorporated into the structure. Table 1 shows typical properties of FEVE resins.

**FIGURE 1** » Alternating structure of FEVE resins.




$R_1$ = OH
$R_2$, $R_3$ = Proprietary; Impacts Tg and other properties

**TABLE 1** » Typical properties of FEVE resins.[3]

| | |
|---|---|
| Fluorine content | 25-30 wt% |
| OH value | 47-170 mg KOH/g |
| COOH value | 0-15 mg KOH/g |
| Molecular weight | Mn = 15,000-100,000 |
| Specific gravity | 1.4-1.5 |
| Morphology | Glassy (Tg =20-50 °C) |
| Decomposition temp. | 240-250 °C |
| Solubility parameter (calculated) | 8.8 |

### FEVE Resins in Environmentally Friendly Coatings

Years of weathering testing has shown the superior performance of coatings based on FEVE resins. This data has been discussed extensively in a previous paper;[3] Figures 2-4 present a review of the data.

The coatings industry has been shifting away from solvent-based coatings for several decades. Much of the data collected thus far has been a result of testing done with FEVE solvent-based coatings. This data is useful as a reference and an indication of the general performance properties of FEVE-based coatings, but it is no substitute for performance data of FEVE-based waterborne and high-solids coatings.

Testing of high-solids and water-based FEVE-based coatings has been ongoing in the United States for the last several years. A previous paper documented the performance of FEVE-based 1K formulations.[3] Results of more recent weathering testing of both 1K and 2K water-based FEVE resin-based coatings are shown in Figure 5.

### Formulating Water-Based Coatings with FEVE Resins

Formulating water-based coatings requires thoughtful consideration of all components. Unlike solvent-based formulations that are essentially solutions of resins and additives in solvent, water-based formulations are colloidal systems with numerous interactions. Additives

By **Kristen L. Blankenship**, Technical Service and Development Chemist; and **Robert J. Parker**, Technical Service and Development Chemist | AGC Chemicals Americas, Inc., Exton, PA

become much more critical to formulation in water-based coatings compared to solvent-based coatings where they tend to be final additions to optimize the appearance of the coating during application.

Dispersants are used in coatings primarily to provide steric and electrical repulsion between pigments to allow for proper spacing in the final film and peak hiding properties. Dispersants themselves may interact with the resins in the paint, so it is important to screen dispersants not only for performance but also compatibility.

A white coating based on an FEVE dispersion resin was tested with three different dispersants. The formulation is shown in Table 2.

The results (shown in Table 3) indicate that the hydrophobic polyelectrolyte-type dispersant did significantly reduce water absorption compared to the other two dispersants, but seemed to be slightly incompatible. This was seen in the lower initial gloss levels. Salt fog results as well as early Xenon Arc results suggest that this incompatibility may reduce overall weathering performance.

Dispersants are important additives for pigmented coatings, but all water-based coatings may require the use of a coalescing aid to improve flow and leveling, and help in film formation depending on the Tg of the resins. FEVE resins all have Tgs at or above room temperature and so often will require a coalescing aid if they are used as the sole binder. Table 4 lists coalescing agents used to aid in film formation of a higher-Tg (Tg = 56 °C) FEVE emulsion.

Often, water-based coatings may rely on one resin for performance. This, however, is not a rule. Successful formulators tailor coatings for optimal performance at the lowest raw material cost. FEVE resins are oftentimes the higher-cost binder, but the benefits of long-term weatherability and chemical resistance can be realized in blended formulations.

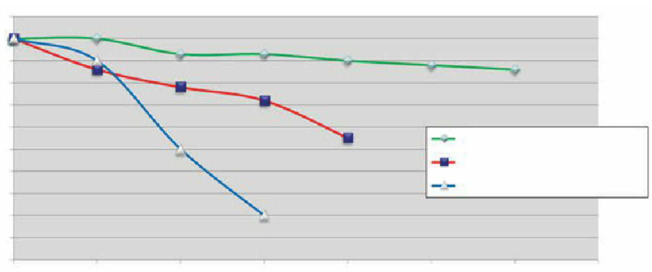
One market that requires high performance at a competitive price point is the cool roof coatings market. Currently, soft or low-Tg acrylics tend to be used for these formulations because they provide flexibility, have good adhesion to various substrates, and tend to be "breathable" or vapor permeable. Unfortunately, the low glass transition temperatures of these acrylics tend to allow for dirt pick up and high water absorption. Studies blending

**TABLE 2** » Water-based white formulation based on FEVE dispersion resin.

| Part A | |
|---|---|
| FEVE dispersion | 72.4 |
| Surfynol 465 (1) | 1.7 |
| BYK 1785 (2) | 0.3 |
| Optiflo H3300 VF (2) (44%) | 1.4 |
| White dispersion | 22.6 |
| $NaNO_2$ (15%) | 1.6 |
| **Part B** | |
| Bayhydur 302 (3) | 11.2 |

| White Dispersion | |
|---|---|
| DI water | 16.3-21.9 |
| Dispersant | 6.8-12.3 |
| BYK 024 (2) | 1 |
| DF75 (1) | 1 |
| TiPure R960 (4) | 68.8 |
| Optiflo H3300 VF (2) | 0.6 |

(1) Air Products; (2) BYK Additives; (3) Bayer; (4) Dupont



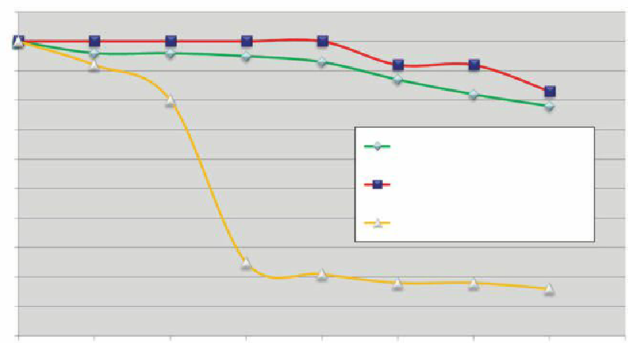


**FIGURE 4** » South Florida exposure of a FEVE-based coating.

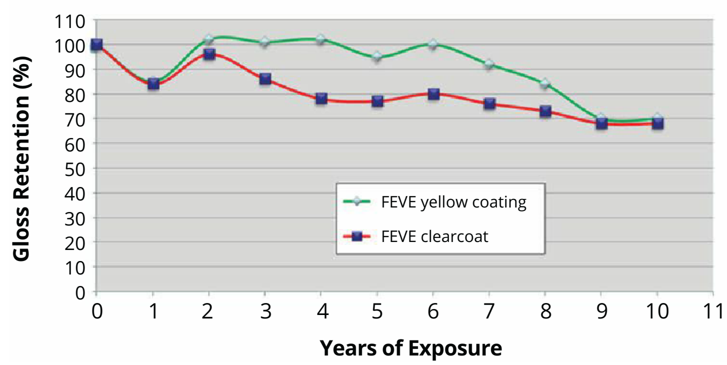



**FIGURE 5** » Xenon arc exposure of water-based FEVE coatings.

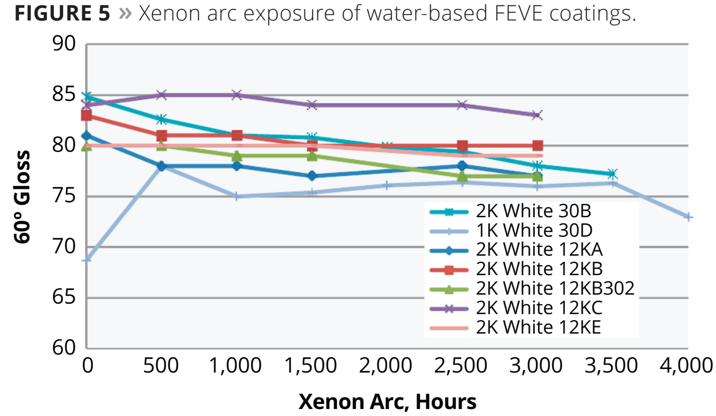


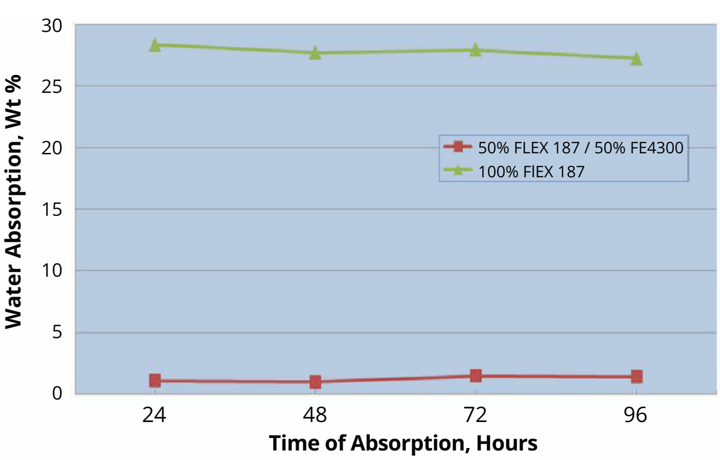
**TABLE 3** » Results of dispersant study.

| ID | Dispersant Type | Initial Gloss (60°) | Xenon Arc (% Gloss Retention at 3,000 h) | Salt Fog, B117 (>8 rating) | Water Absorption, % at 96 h | Vapor Perms |
|---|---|---|---|---|---|---|
| B | Solution copolymer, amine and acid groups, pH=7.4 | 80 | 97 | 1,200 h | 12.1 | 12.2 |
| D | Solution hydrophobic polyelectrolyte, pH=8.8 | 53 | 79 | <700 h | 4.2 | 10.8 |
| E | Solution copolymer, acid groups, pH=6.7 | 80 | 99 | <1,200 h | 7.9 | 13 |

**TABLE 4** » MFFT of high-Tg FEVE resin with various coalescing aids.

| Coalescing Solvent | Water Solubility (%) | Coalescent Amount on Resin Solids (%) | Temperature of Film Formation (°C) |
|---|---|---|---|
| Ethylene glycol monobutyl ether | Infinite | 10 | 27 |
| Ethylene glycol monobutyl ether acetate | 1.1 | 10 | 12 |
| Diethylene glycol monobutyl ether acetate | 6.5 | 7 | 3 |
| Propylene glycol monophenyl ether | 1 | 10 | 23 |
| Propylene glycol monomethyl ether acetate | 19 | 10 | 42 |
| Dipropylene glycol monopropyl ether | 19 | 10 | 16 |
| Dipropylene glycol monobutyl ether | 5 | 10 | 14 |
| Dipropylene glycol dimethyl ether | 53 | 10 | 20 |
| Tripropylene glycol monobutyl ether | 3 | 10 | 18 |
| Texanol | 0.9 | 10 | 24 |

**FIGURE 6** » Water absorption testing.




an FEVE emulsion resin with two acrylics used in roof coatings were performed.

Solar Reflective Index is the key criterion for a roof coating to be considered a cool roof coating. Different standards are used to define a cool roof coating, but one example is Ashrae Standard 90.1. It defines a cool roof for non-residential buildings as having a minimum solar reflectance of 0.70, a minimum thermal emittance of 0.75, or a minimum Solar Reflective Index of 82. Table 5 shows results of SRI testing according to ASTM E1980.

It is clear that blending FEVE resins with acrylic resins does not significantly impact the solar reflective properties of the coating.

Mildew resistance testing (Test 800.2) and algal resistance testing (Test 850.2) have also been performed. AMME™ mildewcide supplied by Thor was used in the formulations at the supplier-recommended levels. The dry films of these coatings have shown zero growth in these tests.

Cool roof coatings need to be breathable but resistant to water absorption. Blending an FEVE emulsion resin with acrylic does significantly reduce water absorption while maintaining breathability. Figure 6 shows this dramatic reduction in water absorption.

Finally, blending with FEVE resins significantly improves the weathering of the cool roof coating, as shown in Table 6.

## Formulating High-Solids Coatings with FEVE Resins

FEVE resins range in solids from 40-70 wt%. The higher-solids resins can be formulated into high-solids coatings. High-solids coatings typically are solvent-based coatings that have lower VOC content due to their high solids content in combination with the use of exempt solvents. High-solids coatings are still favored over water-based coatings in many industrial maintenance applications. These applications tend to want a solids level of 80% and higher by weight.

In order to achieve a higher solids level, inorganic fillers may be used. Table 7 shows the results of some preliminary testing of FEVE resins with various inorganic fillers.

**TABLE 5** » SRI testing results.

| Acrylic Emulsion (Wt %) | | LUMIFLON FE4300 Emulsion (Wt %) | Solar Reflectance (%) | Thermal Emittance | SRI |
|---|---|---|---|---|---|
| Flex 187 (Arkema) | Rhoplex EC-1791 (Dow Chemical) | | | | |
| 100 | | 0 | 83.9 | 0.87 | 105 |
| 50 | | 50 | 83.9 | 0.86 | 105 |
| | 100 | 0 | 84.3 | 0.87 | 106 |
| | 50 | 50 | 84.9 | 0.88 | 107 |

**TABLE 6** » QUV-A weathering of FEVE/acrylic blend water-based cool roof coating.

| Acrylic Emulsion (Flex 187, Wt%) | FE4300 Emulsion (Wt%) | 60 Gloss % Retention | |
|---|---|---|---|
| | | 2,000 h | 10,000 h |
| 100 | 0 | 7.8 | 5.2 |
| 50 | 50 | 53.0 | 41.0 |

**TABLE 7** » QUV-A weathering of high-solids FEVE coating with various inorganic fillers.

| ID | Filler | Type | P:B | 60° Gloss | $H_2O$ Abs. (%) | Vapor Perms |
|---|---|---|---|---|---|---|
| 61 | Minex 7 (Unimin) | Nepheline syenite | 0.5 | 9.0 | 0 | 7.5 |
| 61A | Duramite (Imerys) | Calcium carbonate | 0.5 | 9.0 | 0 | 4.6 |
| 61B | MP1250 (Specialty Minerals) | Talc | 0.5 | 4.0 | 0 | 5.9 |
| 61C | WG325 (Imerys) | Mica | 0.5 | 1.4 | 0.7 | 13.1 |
| 61D | W210 (3M) | Ceramic microspheres | 0.5 | 7.0 | 2.8 | 8.9 |
| 61E | Atomite (Imerys) | Calcium carbonate | 0.5 | 25.5 | 1.2 | 4.8 |
| 61G | Aerosil R-972 (Evonik) | Fumed silica | 0.07 | 51.7 | ---- | ---- |
| 61H | None | ---- | 0 | 82.5 | 2.2 | 2.5 |

**FIGURE 7** » QUV-A weathering of high-solids FEVE coating with polyester polyol.

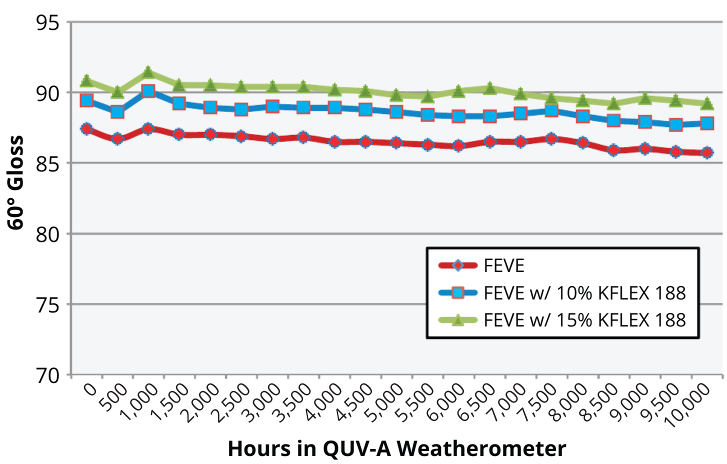



**TABLE 8** » Chemical resistance of FEVE resins.

| Chemical | Exposure Time (h) | Clear 2K Formulations with FEVE | |
|---|---|---|---|
| | | High Solids | Water-Based |
| 50% Sulfuric acid | 1 | No change | No Change |
| 10% Hydrochloric acid | 1 | No change | No change |
| 25% Sodium hydroxide | 1 | No change | No change |
| Heptane | 2 | No change | No change |
| Methanol | 1 | No change | No change |
| Vegetable oil | 2 | No change | No change |
| Motor oil | 2 | No change | No change |
| MEK | 2 | No change | No change |
| Toluene | 2 | No change | No change |
| Xylene | 2 | No change | No change |
| 10% Acetic acid | 2 | No change | Slight whitening during exposure, full recovery |
| Ethanol | 2 | No change | No change |
| Red wine | 2 | No change | No change |
| Ketchup | 2 | No change | No change |
| Mustard | 2 | No change | No change |
| Crayon | 2 | No change | No change |
| Pencil | 2 | Slight stain | No change |
| Coffee | 2 | No change | No change |

Research into another method of increasing solids while lowering VOC and cost in many cases has been done using polyester polyols. Formulations with a high-solids FEVE solvent-based resin and KFLEX 188 (King Industries) polyester polyol were made. The addition of the polyester polyol improved flexibility and gloss without significantly reducing performance in accelerated weathering (Figure 7).

## FEVE Resins for Chemical Resistance

FEVE resins are known for long-term weatherability in outdoor exposure. The strength and inertness of the C-F bond is also strong against chemical attack. Immersion testing and spot testing have been performed. Table 8 shows the results of spot testing of various acids, bases, solvents and food products.

## Summary

FEVE resins are fluoropolymer resins that have an alternating copolymer structure between a fluoroethylene unit and a vinyl ether unit. The vinyl ether unit affords solubility in solvents. Research has shown the superior resistance to UV degradation that FEVE resins possess. As the coating industry continues to shift towards environmentally friendly coating solutions, new testing of FEVE resins in waterborne and high-solids coating applications is being performed. Results show that FEVE resins provide water-based and high-solids coatings excellent resistance to UV degradation. FEVE resins can be used in water-based architectural coatings (VOC <50 g/L) and high-solids, low-VOC coatings for industrial maintenance applications. Research in the United States is ongoing as the coatings industry continues to push the standard for energy efficient and green coating solutions. ■

## References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