FLUOROPOLYMER COATINGS FOR PLASTICS

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Introduction

Fluoropolymers have been used in coatings for many years. These products have many desirable properties, including outstanding weatherability, excellent chemical resistance, good thermal stability, and stain, oil, and water resistance. Because of these characteristics, fluoropolymers have been widely used for coatings and linings in the chemical, oil and gas, textile, paper, and plastics industries. Examples of fluoropolymers used as coatings include polytetrafluoroethylene (PTFE), tetrafluoroethylene/hexafluoroethylene copolymers (FEP), and TFE/perfluoroalkyl vinyl ether copolymers (PFA). These products are mainly used as non-stick and anti-corrosion coatings.

Perhaps the best known fluoropolymer resin used for coatings is polyvinylidene fluoride (PVDF). This resin is supplied as a dispersion in a high boiling solvent, usually blended with an acrylic resin at a 70/30 fluoropolymer/acrylic ratio. PVDF is typically applied as a coil coating, requiring processing at high temperatures in a plant setting to successfully form a protective coating. PVDF has been used successfully in architectural coatings for over 40 years, and demonstrates the excellent weatherability achievable with fluoropolymers.

Unfortunately, the use of fluoropolymers in coatings is limited by their properties. The same surface characteristics that contribute to stain resistance also limit adhesion of fluoropolymers to substrates. In general, fluoropolymers are not soluble in solvents commonly used in the coatings industry. In order to form a coating or lining, fluoropolymers often must be heated to temperatures in excess of 200^{o} C, which severely limits their potential use in the field. High processing temperatures also limit the use of fluoropolymers on plastics.

In order to address the shortcomings of fluoropolymers in coatings, unique fluoropolymers known generically as fluoroethylene vinyl ether (FEVE) copolymers were developed in the early 1980's. These resins are discussed below.

Fluoroethylene Vinyl Ether (FEVE) Resins

FEVE resins were developed to address the shortcomings of traditional fluoropolymer resins. FEVE resins are manufactured by copolymerization of a fluoroethylene monomer with a vinyl ether monomer. The structure of these materials is shown below in Figure 1.

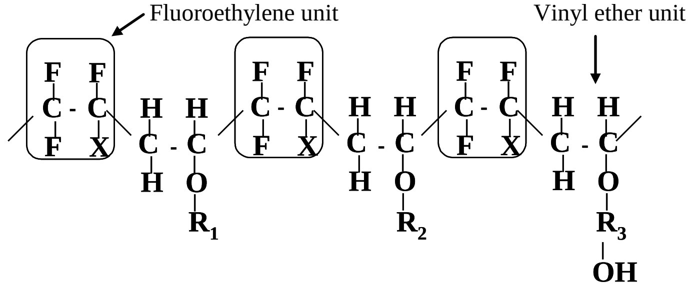


Figure 1: Chemical Structure of FEVE Copolymers

The unique structure of FEVE resins imparts to coatings made from them the same excellent weatherability characteristic of fluoropolymers. Their durability is derived from the fluoroethylene portion of the polymer. The nature of the vinyl ether groups can be changed to influence other physical properties. Gloss, flexibility, hardness, adhesion, pigment compatibility, and transparency can be modified by changing vinyl ether monomers. Hydroxy-functional groups allow the FEVE resin to be crosslinked using industry standard aliphatic isocyanates to form fluorourethanes. This crosslinking reaction can be run at elevated temperatures or at ambient temperatures.

Coatings made with FEVE resins offer several advantages over other fluoropolymer resin-based coatings. FEVE resins can be used to formulate coatings that cure at room temperature. This means they can be used in field applied maintenance coatings, unlike traditional fluoropolymers which must be applied at elevated temperatures. They can also be used as coatings for temperature sensitive substrates like plastics. FEVE resins can be formulated to yield coatings with a wide range of gloss, from flat finishes to high gloss. Because they are solution polymers, FEVE resins have better compatibility with a wide range of pigments, increasing color options for designers. Fluorourethanes have better hardness and corrosion resistance than some other fluoropolymers, with improved mar and scratch resistance. FEVE coatings offer flexibility to -40^{o} C and below.

Weathering of Fluorourethane Coatings Based on FEVE Resins

FEVE-based fluorourethane coatings are primarily used for their outstanding weatherability. Accelerated and outdoor testing of FEVE resin-based fluorourethanes demonstrates their excellent weatherability compared to more conventional coatings.

Figure 2 below shows test results of QUV-A weathering (ASTM D-4587) for an acrylic urethane, a polysiloxane, and a fluorourethane coating. In this test, the coatings are exposed to UV light of one wavelength. Results show that the fluorourethane outperforms even the siloxane, which is considered to be a weatherable coating in the industry.

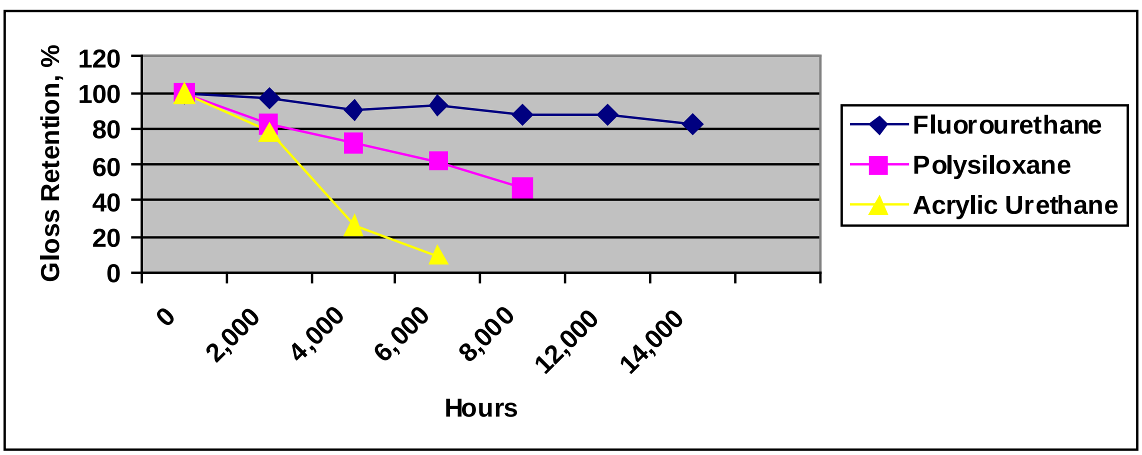


Figure 2: Comparative Weathering of Fluorourethane in the QUV-A Test

Another accelerated weathering test is the Equatorial Mount with Mirrors for Acceleration with Water Test (EMMAQUA). This test concentrates sunlight onto the coating sample via reflective mirrors, exposing the panels to the entire spectrum of radiation found in natural light. Test panels are sprayed with deionized water on a preset schedule to simulate exposure to moisture. Results are reported as energy exposure per unit area. Because the EMMAQUA test uses the full range of radiation found in natural light, it is gaining acceptance as an accelerated test that approximates real life exposure.

Results shown below in Figure 3 show that the PVDF coating and the FEVE resin based coating far outperform the urethane coating. The results indicate that both fluoropolymers are equal in performance.

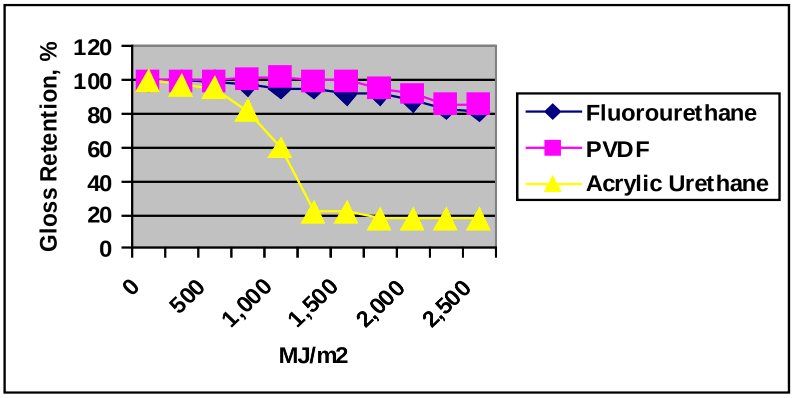
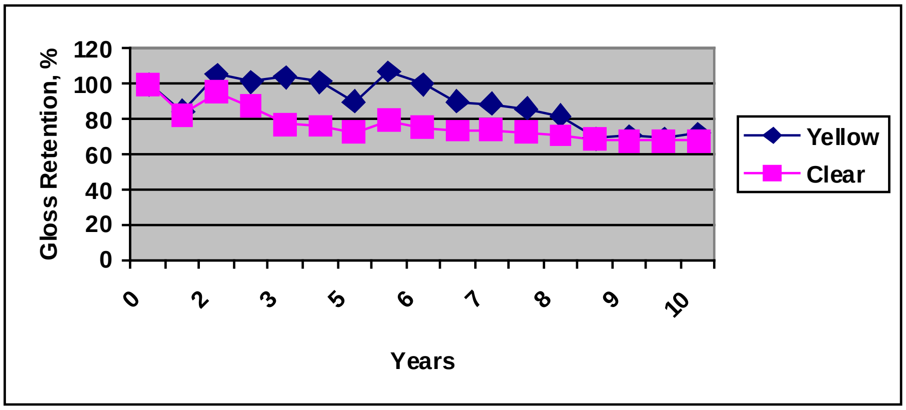


Figure 3: Accelerated Weathering, EMMAQUA Test

Weathering in the real world is the best test of coating durability. Because of severe conditions of sunlight, rain, humidity, and airborne salt found there, south Florida is often used as the location for real time weathering of coatings. Test results shown in Figure 4 below indicate that fluorourethane coatings retain 70% of their initial gloss even after 10 years of south Florida exposure.



Location: Miami, FL
Exposure: Direct, 30 Deg. South, Open Back

Figure 4: South Florida Weathering of FEVE-Based Fluorourethane Coatings

Based on results from accelerated and actual weathering tests, and from actual coating applications over a period of 25 years, several regional transportation authorities and engineering groups based in Japan estimate the life of FEVE-based fluorourethane topcoats to be a minimum of 30 years, to as long as 100 years. Since 2006, fluorourethanes are required to be used as topcoats on all bridges in Japan.

Highly durable coatings made from FEVE resins offer the capability of matching more closely the life of the asset being protected with the life of the coating. For example, a bridge may be built with an expected life of 100 years. Using an FEVE resin can reduce or even eliminate the need for frequent repainting of the bridge, substantially reducing life cycle costs of protecting the bridge from corrosion and preserving its appearance.

Types of FEVE Resins

FEVE resins are manufactured, and still sold today in, xylene. There are several exceptions: a coil coating grade of resin is sold in a blend of high boiling solvents more suitable to that coating process, and an aerospace grade of resin is blended with EEP (ethyl 3-ethoxypropionate). Today, the use of solvents is being more closely regulated. Current and future air pollution regulations could limit the use of xylene. Several new forms of FEVE resins have been developed to enable coating manufacturers to meet these regulations, the two best known being VOC (volatile organic compounds) and HAPS (hazardous air pollutants) regulations.

Solid FEVE resins enable the formulation of solvent-based coatings that meet VOC regulations around the U. S. These coatings are manufactured by evaporating the xylene used as the polymerization medium, chilling the resulting viscous resin, then chopping the cool resin into flakes. While there are federal VOC regulations, many states have implemented more stringent regulations, mainly in response to non-attainment of pollution regulations. California is perhaps the best known entity with stricter regulations. The South Coast Air Quality Management District (SCAQMD) has VOC regulations that in some cases are more difficult to meet than the statewide California standards. Solid FEVE resins can be dissolved in VOC exempt solvents such as t-butyl acetate and Oxsol® 100 (parachlorobenzotrifluoride). In these cases, VOC-free coatings can be formulated. Solid resins can be dissolved in blends of these solvents with ketones and esters to make low VOC coatings. These solid resins offer the same weatherability as solvent-based FEVE grades.

FEVE water emulsions were also developed to enable formulators to meet VOC regulations. These products are manufactured in an emulsion polymerization process. The chemical structure of these resins is similar to that of the solvent-based resins with two exceptions. First, emulsifiers are used to improve compatibility of the FEVE polymer with water, and second, some of the hydroxyl groups in the FEVE polymer are modified with ethylene oxide (EO) groups to improve compatibility with the emulsifier. Unfortunately, these modifications have a negative effect on the performance of coatings made with the FEVE water emulsions. The weatherability of crosslinked coating is not as good as that of coatings made with the solvent-based resins. Figure 5 below shows comparative weathering on Okinawa of fluorourethanes made with a solvent grade resin and one from the FEVE water emulsion, and a standard polyurethane coating. While the water emulsion far outperforms the polyurethane, it does not weather as well as the solvent-based FEVE coating.

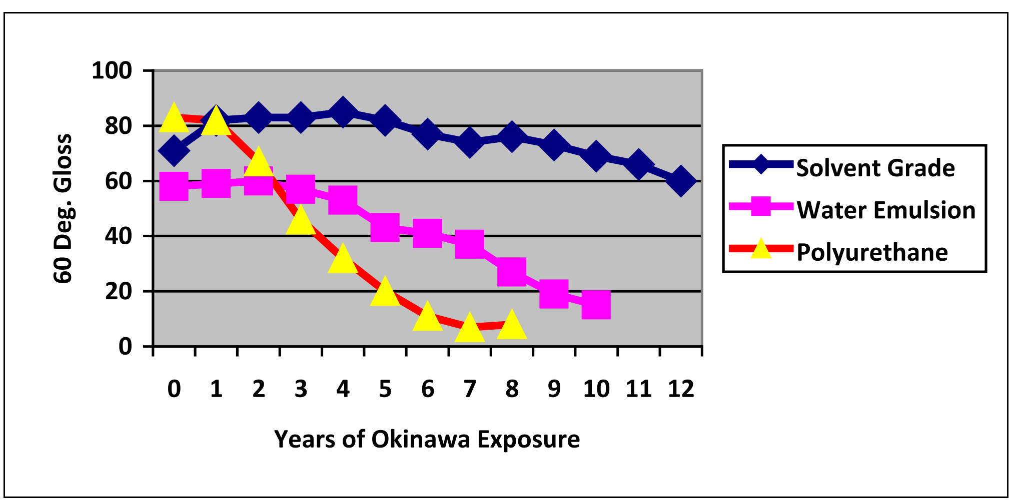


Figure 5: Comparative Weathering of FEVE Water Emulsion and Solvent Grade Resin

Coatings made with FEVE water emulsions can also be sensitive to water. This is evidenced by the formation of blisters in the water-based fluorourethane in tests where coated panels are immersed in warm water. The presence of EO groups in the backbone of the FEVE resin is the likely cause.

In an effort to improve the performance of water-based fluorourethanes, a new class of FEVE coatings has been developed. The new water-based resins are dispersions, rather than emulsions. Because these materials require less modification of the basic FEVE polymer structure, their performance is closer to that obtained with coatings made with solvent-based FEVE resins. Substantial improvements in water resistance and weathering are achieved when these dispersions are crosslinked with aliphatic isocyanates. Figure 6 below shows results of an accelerated weathering test involving a water dispersion resin, a water emulsion resin, and a solvent-based FEVE resin. It should be noted that the weatherability of the fluorourethane from the dispersion is equal to that obtained with the solvent-based FEVE resin.

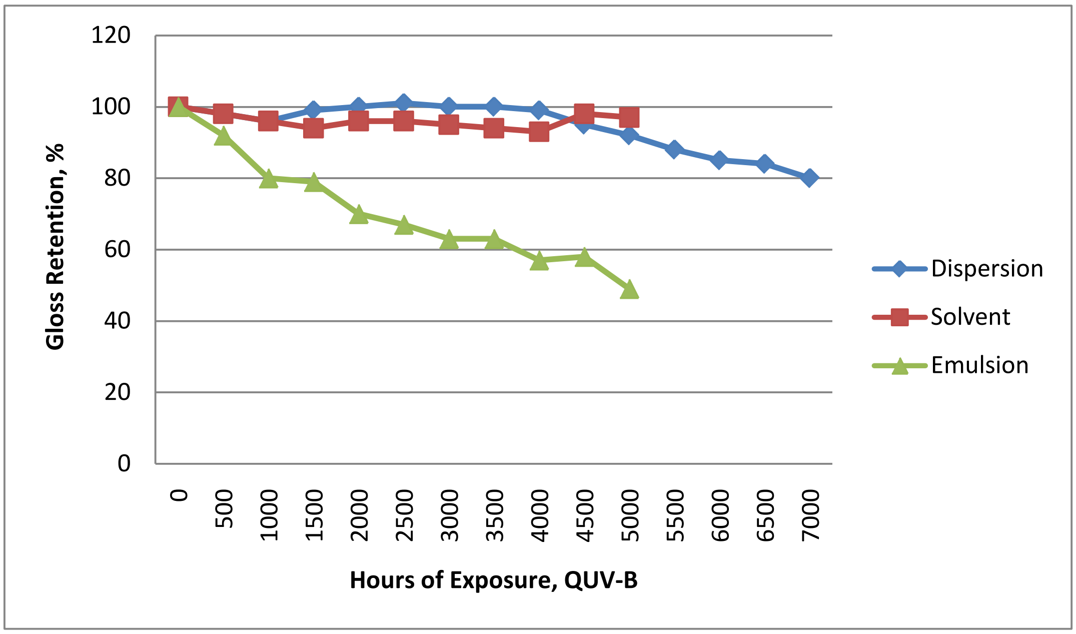


Figure 6: Accelerated Weathering Test Results of FEVE Dispersion, Emulsion, and Solvent Grades

Weathering of FEVE Blends With Acrylic Resins

The fluorourethanes on which data was presented in Figures 2-6 above were made using the appropriate FEVE resin as the sole reactant. When maximum weatherability is required, the FEVE resin should be used as 100% of the resin component. However, FEVE resins can also be used as blends with standard acrylic or polyester polyols to improve the weatherability of these urethane systems. This can provide a method to improve weathering, and potentially other properties (mar resistance, for example) without incurring the cost of a fully fluorinated coating. Many markets, for example, automotive, do not require weathering exceeding 20 years. However, in some of these markets, an improvement in long-term appearance can add value to the coated product. In addition, increasing the longevity of a coating can impart properties such as corrosion resistance and barrier properties for longer periods of time.

Figure 7 below shows accelerated weathering results from a single component coating composed of blends of an FEVE water emulsion and an acrylic latex resin. Even at a concentration of 25%, the FEVE blend offers a substantial improvement in weathering, with 67% gloss retention compared with gloss retention of 25% for the pure acrylic resin at the end of the test.

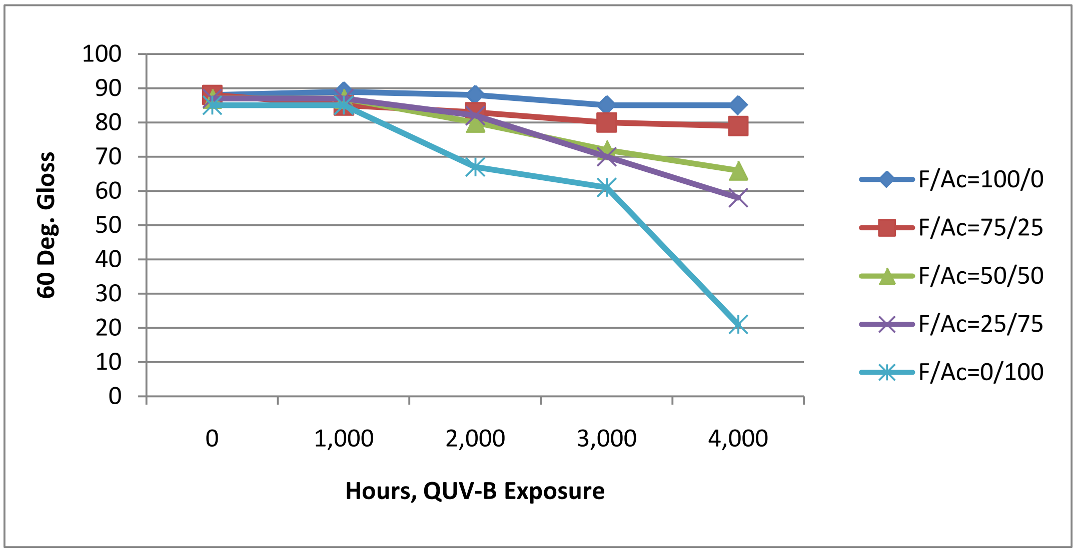


Figure 7: Accelerated Weathering of FEVE Resin Blends With Acrylic Resin

Markets for FEVE Based Coatings

Coatings made with FEVE resins are used primarily in markets where their extreme durability is most useful. The largest market for fluorourethane coatings is architectural. This includes coil coatings based on FEVE resins, used primarily for aluminum composite panels for new construction. Examples include gas station canopies and multi-story office buildings with metal components. Air dry coatings made with FEVE resins are often used in architectural maintenance painting. Typical examples include monumental buildings and sports stadiums. In some cases, the fluorourethane coating is used to recoat a building originally coated with PVDF using coil coatings. FEVE powder coating resins are used on aluminum extrusions, replacing solvent-based coatings. The extrusions are used for windows, banisters, flagpoles, and other architectural items.

FEVE coatings are also used in industrial maintenance coatings. In the U. S., the largest use is for water towers. In Japan, the coatings are used in other IM applications, including bridges and storage tanks. There are some small applications for FEVE resins in automotive coatings, but the resins are considered to be too costly for widespread use in this market.

Fluorourethanes are also used in both commercial and military aerospace coatings. In both case, FEVE resins are used in blends with other resins to improve the weathering of the coating without overwhelming increases in cost. In this case, the application does not require over 30 years of color and gloss retention; 5-7 years are considered to be adequate. For commercial aircraft, extending the repainting cycle allows them to reduce lost revenue. This cost savings more than offsets the increase in the cost of the topcoat. In addition, the FEVE blends keep colors vivid and bright for the expected life of the coating.

In all of these cases, the use of FEVE resins substantially reduces life cycle costs associated with repainting assets like buildings, bridges, and aircraft. These costs include not only labor, paint, and staging costs directly associated with repainting, but other costs as well, including revenue loss, the cost of traffic mitigation, and costs associated with increased delays for commuters and freight. In addition, due to the long life of FEVE coatings, their use can substantially reduce environmental impacts, including solvent emissions and CO_2 emissions from equipment and other sources. Long experience in

Japan has shown that the use of FEVE resin based coatings can reduce life cycle costs by 15-60%, depending on the competitive coating, even without including other costs and advantages.

FEVE Based Coatings for Plastics

FEVE fluorourethane coatings have been used on plastic for many years. In most cases, they have found application in the same market areas where FEVE coatings are successfully used on metal, for example, in architectural applications. The use of these coatings on plastics is not as common as their use on metal, probably because fewer plastics are used in construction applications where extremely high weatherability is required.

Adhesion of Fluorourethane Coatings to Plastic Substrates

FEVE based coatings have good adhesion to a range of plastic substrates. In some cases, a primer or surface treatment may be required to ensure adequate adhesion. This is particularly true in the case of plastics with low surface energy or with little polarity. Adhesion to some plastics for fluorourethanes compared to that obtained with an acrylic urethane coating is shown below in Table 1. Adhesion of the fluorourethane matches that of the acrylic urethane on all substrates.

Table 1: Adhesion of Fluorourethane Coatings to Plastics

Substrate	Surface Treatment	Fluorourethane Adhesion, %	Acrylic Urethane Adhesion, %
Unsaturated Polyester (FRP)	Degreased	100	100
Epoxy	Degreased	100	100
Polyurethane	Degreased	100	100
Acrylic	Degreased	100	100
Nylon 6	Degreased	100	100
Rigid PVC	Degreased	50	50
	Urethane Primer	100	100
Polypropylene	Corona Discharge	100	100
Polycarbonate	Degreased	100	100

Protection of Plastic Substrates by Fluorourethane Coating

The ability of FEVE coatings to protect plastic substrates was tested. Samples of several plastics were coated with a fluorourethane clear coat containing a benzophenone/triazine UVA stabilizer package. Since the FEVE coating is transparent to some wavelengths of damaging UV radiation contained in sunlight, the UVA package is required to ensure that degradation of the substrate does not occur. Uncoated samples were also prepared. Physical properties of the plastics were tested before and after accelerated weathering exposure of the samples in the dew cycle Weatherometer test (ASTM D-3361). This test involves subjecting samples to alternating periods of light and darkness, and with periodic exposure to moisture. Changes in the physical properties, in this case, tensile strength and elongation, were noted. Test results are shown in Table 2 below. Results indicate that the samples coated with the FEVE topcoat retain their physical properties even after exposure in this accelerated weathering test, while uncoated samples showed various degrees of degradation. In particular, uncoated Nylon 6 and polypropylene samples showed extreme loss of physical properties in the accelerated weathering test.

Table 2: Changes in Physical Properties of Coated and Uncoated Plastic Panels

Plastic Substrate	FEVE Coating Used?	Hours of Irradiation in Dew Cycle Weatherometer			
		200	400	200	400
		Tensile Strength Retention, %		Elongation Retention, %	
Polycarbonate	No	71%	62%	63%	55%
	Yes	118%	106%	123%	121%
Nylon 6	No	38%	44%	13%	3%
	Yes	97%	86%	89%	90%
Polypropylene	No	14%	12%	19%	9%
	Yes	103%	105%	102%	95%

FEVE Coatings on FRP
FRP structures are used in architectural applications such as stadium seating and skylights. While FRP has excellent strength/weight properties, and can admit natural light, it tends to yellow, crack, and haze over time. In the worst cases, resin encapsulating glass fibers can be destroyed over time by exposure to UV light. Accelerated degradation can then occur as moisture wicks into the structure via the fibers. FEVE coatings can be used on FRP to eliminate degradation of the polyester and prevent damage to the structure by UV light.

Coating thickness turns out to be an important aspect of successful coating of FRP with fluorourethanes. The UVA stabilizers do not appear to be effective at a film thickness of less than 25 µm. Apparently, thinner films do not provide sufficient path length for filtering all UV light. In addition, bleed-out of the UVA stabilizers can occur at thin film thicknesses. Finally, the use of thicker coatings ensures complete coverage of irregular features on the FRP surface. Table 3 below shows the effect of fluorourethane film thickness on adhesion to FRP after accelerated weathering. While the thinner film performs well for a short period of time, long term adhesion is poor. This is likely due to degradation of the FRP by UV light, followed by delamination of the FEVE coating.

Table 3: FEVE Coating Adhesion to FRP at Variable Coating Thickness

Exposure Time, QUV-B	2,000 Hours		5,000 Hours	
	Appearance	Adhesion, %	Appearance	Adhesion, %
FEVE Coating, 25 µm	Excellent	100%	Excellent	100%
FEVE Coating, 13 µm	Fair (slight yellowing of FRP)	100%	Poor (yellowing of FRP)	0%

Transmittance of UV light through a fluorourethane coating with UVA stabilizers was measured. Results are shown below in Figure 8. Transmission of higher wavelength light (>380 nm) has no significant impact on the weathering of the FRP under the coating. However, at lower wavelengths (<360 nm), there can be a significant impact on degradation of the FRP. Notice that the transmittance of damaging UV light through the coating at thicknesses >25 µm approaches zero. Thus, degradation of FRP by UV radiation can be minimized using an adequate coating thickness.

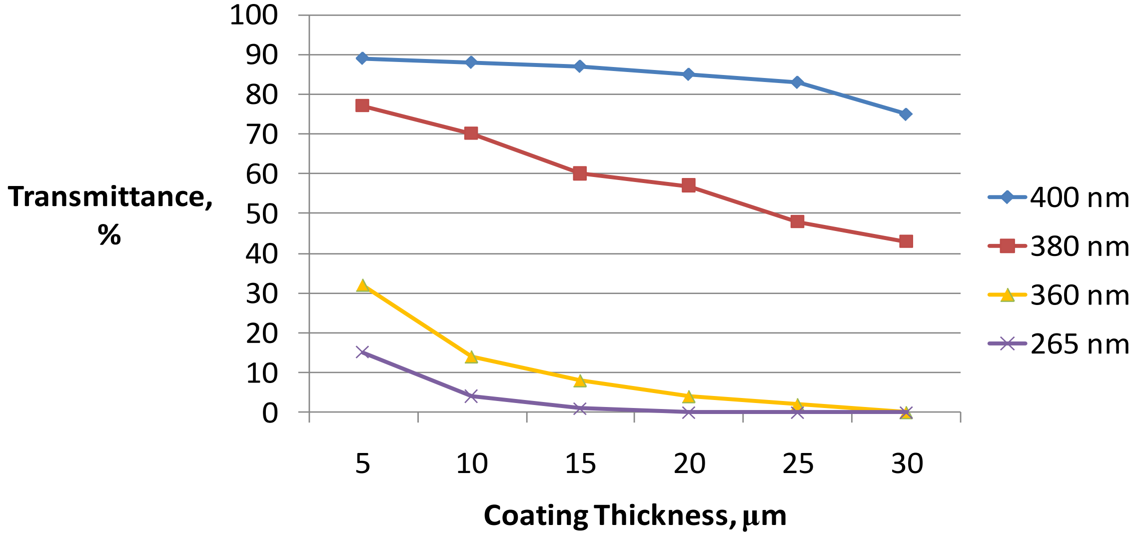


Figure 8: Transmittance of UV Light Through Fluorourethane Coating

Long-term actual weathering tests yield the best data on coating performance. Fluorourethane coated FRP was tested in outdoor weathering on Okinawa, a subtropical island located at about the same latitude as Jacksonville, FL. In this case, the performance of the FEVE coating was compared to that of polyvinyl fluoride (PVF) film on FRP, as well as to that of uncoated FRP. Results are shown below in Figure 9. The FEVE coating retains more than 60% of its initial gloss in the test.

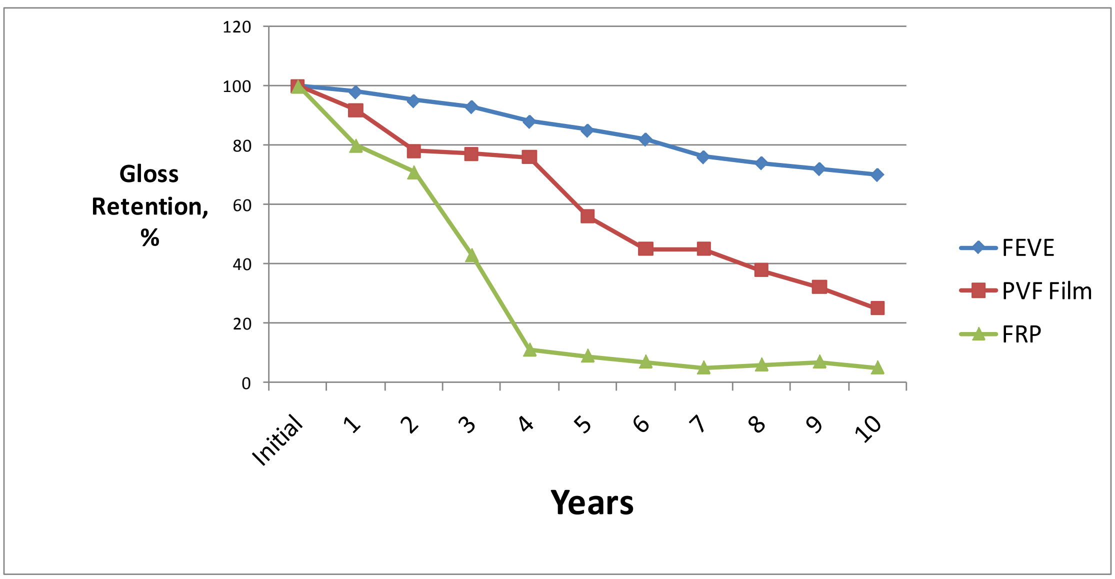


Figure 9: Okinawa Weathering Test of FEVE Coating, PVF Film, and FRP

Fluorourethane Topcoats for FRP

In 1987, FRP stadium seating at a track and field facility in Tokyo, Japan was clear coated with a fluorourethane topcoat. Photographs of the benches and seats taken in 2007 are shown in Figure 10 below. The FRP seating retains its initial color even after 20 years. The high gloss of the FEVE topcoat can clearly be seen in the photographs.

Figure 10: Fluorourethane Topcoat on FRP Stadium Seating After 20 Years

Applications for FEVE Resin Based Coatings on Plastics

FEVE resin based coatings can be used wherever superior exterior durability is required. The architectural market is a good fit for these types of coatings. In many cases, long term weatherability is critical for components and structures favored in this market. Examples of applications include coatings for skylights, wall and curtain wall systems, awnings and canopies, and stadium seating and components. FEVE coatings can also be used to coat synthetic shingles for houses and light commercial construction. These shingles can be made from recycled plastics, and can be manufactured to reproduce the appearance of tile, slate, and other common roofing materials.

Other applications are also possible. These include coatings for highway signs, and for exterior graphics. In addition, coatings for automotive plastics could be made with FEVE resins. In the last case, blends of FEVE resins with standard resins would likely be used, since exterior durability of 20 years or more is not required.

As composite materials are used more often, opportunities for coating them increase as well. FEVE resins are being used in coatings for the new Boeing 787 aircraft. This plane differs from earlier models in its extensive use of composites, which are even being used in the fuselage. In addition to offering exterior durability, additional performance requirements are demanded, including conductivity. Newer FEVE resins with extremely high hydroxyl numbers are used in this application to ensure excellent chemical resistance for fluids like Skydrol and jet fuel.

CONCLUSIONS

FEVE resins have been in use for over 25 years in a wide range of applications including coatings for architectural, aerospace, industrial maintenance, and automotive markets. They have been used on plastics to provide protection from the elements, primarily from degradation by UV light. FEVE resins can be used in blends with standard resins to improve weather resistance in applications where 20 years or more of exterior durability is not required; for example, in aircraft coatings. Care must be taken to ensure that FEVE coatings are used at adequate thickness, usually >25 µm. This allows for complete coverage of irregular plastic surfaces, and also provides the best protection from UV light in clear coats with UVA stabilizers.

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