

“FEVE FLUOROPOLYMER TECHNOLOGY FOR HIGH-PERFORMANCE, LONG-LIFE COATINGS ON STEEL AND CONCRETE BRIDGES”

Bob Parker, AGC Chemicals Americas, 610-423-4328, rparker@agcchem.com

Winn Darden, AGC Chemicals Americas, wdarden@agcchem.com

Takasi Takayanagi, AGC Chemicals, Tokyo, Japan, takasi-takayanagi@agc.co.jp

Sho Masuda, AGC Chemicals, Chiba, Japan, sho-masuda@agc.co.jp

Isao Kimura, AGC Chemicals, Chiba, Japan, isao-kimura@agc.co.jp

ABSTRACT

Applications for coatings made with FEVE resins have traditionally been used in architectural markets, where gloss and color retention are the properties of interest. However, FEVE coatings also offer excellent corrosion resistance, which makes them ideal candidates for bridge coatings. This paper will discuss the chemistry of FEVE resins and present a variety of exposure data (both laboratory and real-life). It will also present results of corrosion testing.

INTRODUCTION

Fluoropolymers have been used for many years to manufacture coatings and linings. They offer a number of desirable physical properties, including weatherability, corrosion resistance, and chemical resistance. These properties arise from the nature of the chemical bond formed by fluorine with carbon.

Unfortunately, the use of most fluoropolymers has been limited to applications where heat can be applied to soften, solubilize, or melt the products to form coatings and linings. Examples of fluoropolymers of this type are poly(tetrafluoroethylene) (PTFE), polyvinyl fluoride (PVF), ethylene tetrafluoroethylene (ETFE) and polyvinylidene fluoride (PVDF). Of these, PVDF has found the widest applicability in coatings. To improve adhesion and handling, PVDF is usually blended with an acrylic resin and then dispersed in a solvent. PVDF coatings are formed by melting and fusing the solvent-based blend at temperatures of about 300 °C. These coatings are the most widely used of fluoropolymer coatings, mainly in architectural applications. PVDF coatings offer excellent weatherability, with a coating life of 30 years. Components coated with PVDF can be shop and field fabricated, and have good chemical resistance.

PVDF coatings do have several drawbacks. First, the products must be melted or solubilized at high temperatures to form a barrier coating. This means that PVDF coatings are not amenable to field application since they generally don't cure at ambient temperatures. Coil coating is the most common method of applying PVDF coatings. The gloss range of PVDF coatings is limited to the 20-40 range at 60 °, due to the difference in refractive indices and chemical compatibility of the fluoropolymer resin and the acrylic resin.

In the early 1980's, a new type of fluoropolymer resin was introduced. These resins were copolymers of a fluoroethylene monomer (FE) and a vinyl ether monomer (VE). These resins were developed to overcome the handling disadvantages of traditional fluoropolymer resins. The chemical structure of the FEVE polymer is shown below.

THERMOSET FEVE FLUOROPOLYMER RESINS

Characteristics of FEVE Resins

Unlike traditional fluoropolymer resins, FEVE resins can be cured at either ambient or elevated temperatures. As shown below in Figure 1, the chemical structure of FEVE resins consists of regularly alternating units of fluoroethylene ($\text{C}_2\text{F}_3\text{X}$) and vinyl ether ($\text{C}_2\text{H}_3\text{OR}$) entities.

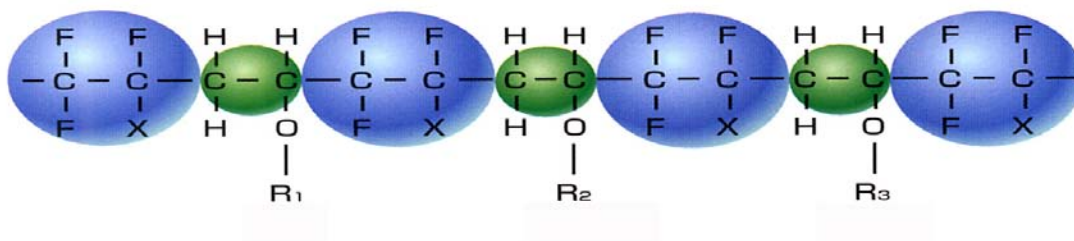


Figure 1: Chemical Structure of FEVE Polymer

The kinetics of the polymerization reaction are such that the regularly alternating units of FE and VE make up the bulk of the polymer. The very stable fluorinated segment's influence is extended over the vinyl ether segment of the molecule. The resulting polymer has outstanding weatherability and corrosion resistance when incorporated into a thermoset coating formulation.

By their nature, traditional fluoropolymers are not very soluble materials, nor are they reactive with other materials. By including the vinyl ether segment, the nature of the entire FEVE polymer can be substantially increased by changing the nature of the alkyl groups (the "R" groups in Figure 1). The inclusion of cycloalkyl groups, for example, can increase the solubility of the entire polymer so that a true solution is formed, characterized by its clarity. Incorporating hydroxyl (-OH) groups allows the polymer to be crosslinked using isocyanates for ambient cure coatings and melamines and isocyanates for elevated temperature cure. Changing the amount of crosslinking, molecular weight, and the nature of the "R" groups on the vinyl ether can modify properties, such as flexibility, hardness, and chemical resistance of the resulting coating. Unlike most fluoropolymer resins, FEVE polymers are thermoset and solvent soluble, with outstanding pigment compatibility. They can be formulated to yield field-applied coatings, substantially broadening the types of applications where fluoropolymer properties are useful. Because they are solution polymers, FEVE resins yield coatings with a range of gloss, from low (<10 at 60°), to high (88 at 60°). The resins allow the use of a wider range of pigments and colors, and it is possible to produce bright, vivid colors that may be difficult to achieve with standard fluoropolymer resins. Because of their higher cost, FEVE resins are used to formulate topcoats, and are used at the least thickness possible.

FEVE resins are available in three types: solvent-borne, usually in xylene, water-based emulsions and one dispersion, and solid resins. Solid FEVE resins can be dissolved in combinations of solvents, including exempt solvents like t-butyl acetate, acetone, and parachlorobenzotrifluoride to make low VOC coatings that meet the new California standard of 100 g/l for industrial maintenance coatings.

Standard aliphatic isocyanates can be used to crosslink FEVE resins to formulate ambient cure coatings. It has been determined that even in the finished coating, the fluorinated segment adequately protects urethane and urea linkages, which form during the crosslinking reaction, as well as vinyl ether segments, from degradation by UV light¹.

Applications for FEVE Based Coatings

Because of their outstanding weatherability, the major application for FEVE based coatings is in the architectural market. They are especially useful in applications where long-term durability is desirable, for example, on metal surfaces of tall buildings, which can't be repainted easily. Other applications in this

market include those in which bright, vivid colors are of considerable value, for example, in construction of gas stations. There is a growing market in metal composite panels, which are coated with FEVE resins and used in corporate identity programs, for example, for car dealers and fast food franchises.

However, the fastest growing market segment for FEVE based coatings is industrial maintenance coatings. This segment includes coatings for structures like water towers, bridges, and offshore facilities such as oil rigs. These types of structures are difficult to coat due to limited access and the high cost of downtime during painting operations. Aesthetics are becoming more important for bridges and water towers as government organizations seek to improve the image of their communities. Finally, all of these types of structures require exceptional corrosion control due to the critical nature of the services provided by each. Corrosion control is especially important when such structures are in a marine environment, due to the harsh conditions found there. FEVE based coatings are able to meet all of these requirements.

PERFORMANCE OF FEVE RESIN BASED COATINGS

Weatherability of FEVE Coatings

FEVE based coatings offer exceptional weatherability in both accelerated weathering tests and real time exposure tests. Figure 2 shows test results of an FEVE-based coating compared to a polysiloxane coating and an acrylic urethane coating. These test panels were exposed for 15,000 hours in a QUV Weatherometer.

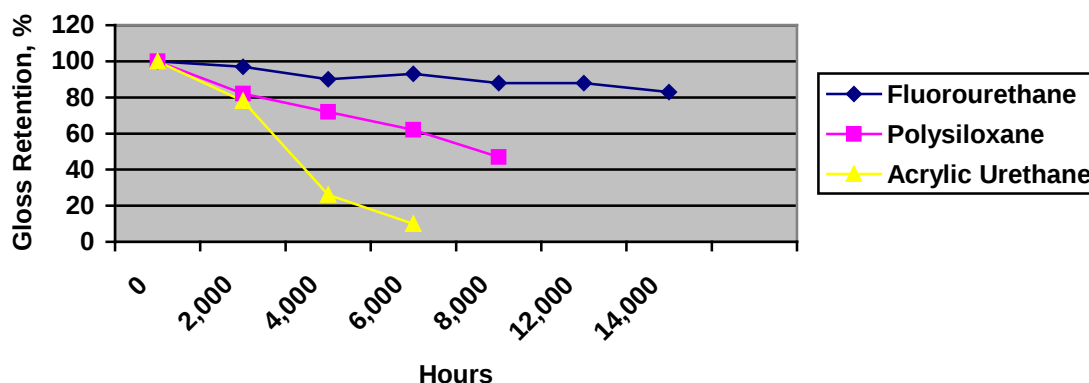
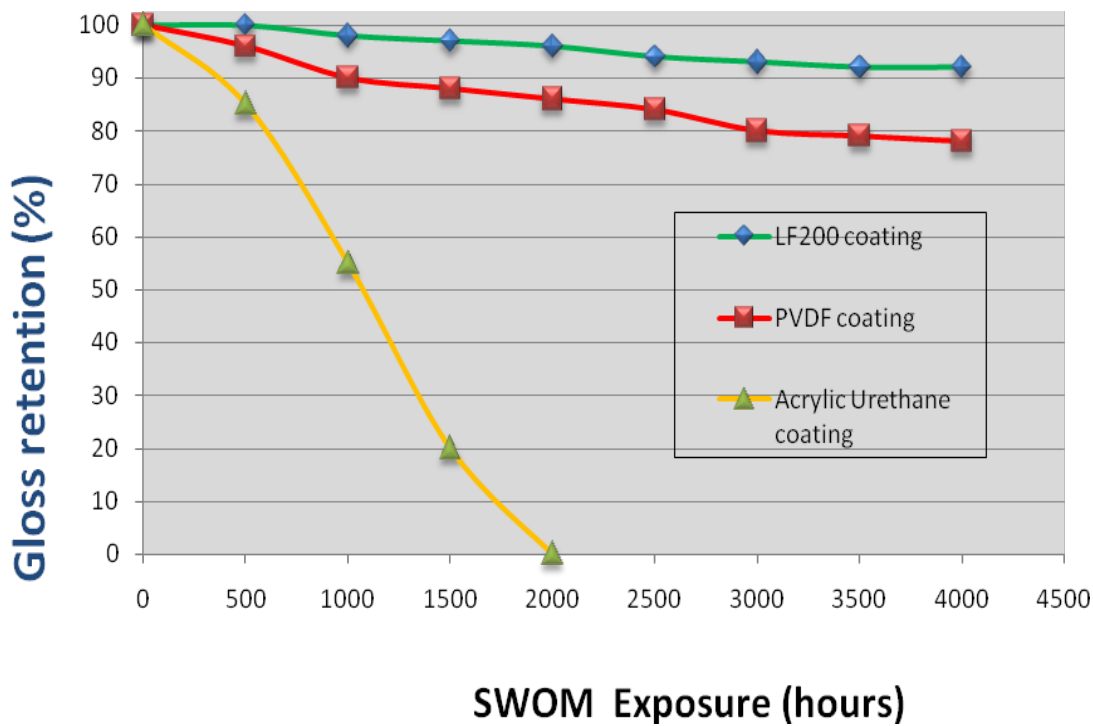


Figure 2: Weathering of FEVE Coatings
QUV-A Test (ASTM D4587)

Another accelerated weathering test is the Sunshine Carbon Arc Weatherometer (SWOM) Test. In this test, a carbon arc is used to generate radiation to which coated panels are exposed. The range of wavelengths used in this test is lower than that found in natural sunlight. The test involves cycling of exposure temperatures, humidity, and water spray to approximate natural conditions. Figure 3 below shows test results for a fluorourethane, an acrylic urethane, and PVDF for 4,000 hours of testing. It is said that 1,000 hours in the SWOM test is equivalent to 5 years of real time exposure. A direct correlation has not been validated, however, both FEVE based coatings and PVDF coatings are known to offer excellent gloss retention after 20 years. The acrylic urethane coating failed after only 2,250 hours in this test.



Black Panel Temperature: 60-65 °C
 Relative Humidity: 60%
 Water Spray Cycle: 12 minutes/hour

Figure 3: Comparative SWOM Testing of Fluorourethane, Acrylic Urethane, and PVDF

A third accelerated method is the Equatorial Mount with Mirrors for Acceleration with Water (EMMAQUA) test. This test concentrates sunlight via 10 reflective mirrors onto the coating sample, which exposes the panel to the entire spectrum of radiation found in natural light. Coatings are also sprayed with deionized water on a preset schedule to simulate natural exposure to rain. Results are reported as energy exposure per unit area rather than in time exposed. The standard units of measurement are megaJoules per square meter. 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. Compared in the EMMAQUA test, the FEVE based coating and the PVDF coating far outperform the acrylic urethane coating. Figure 4 shows the results.

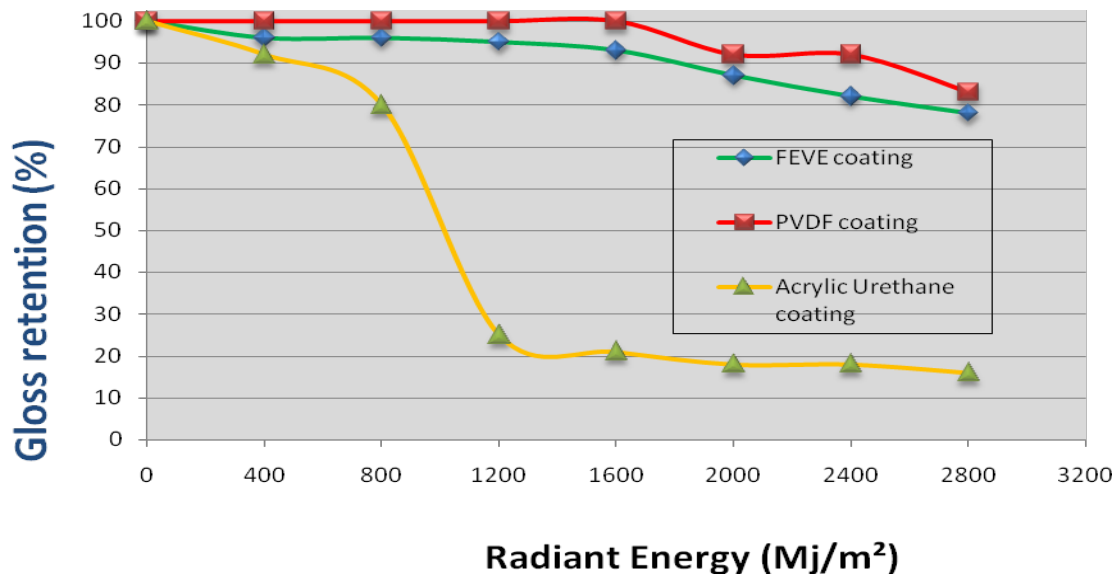
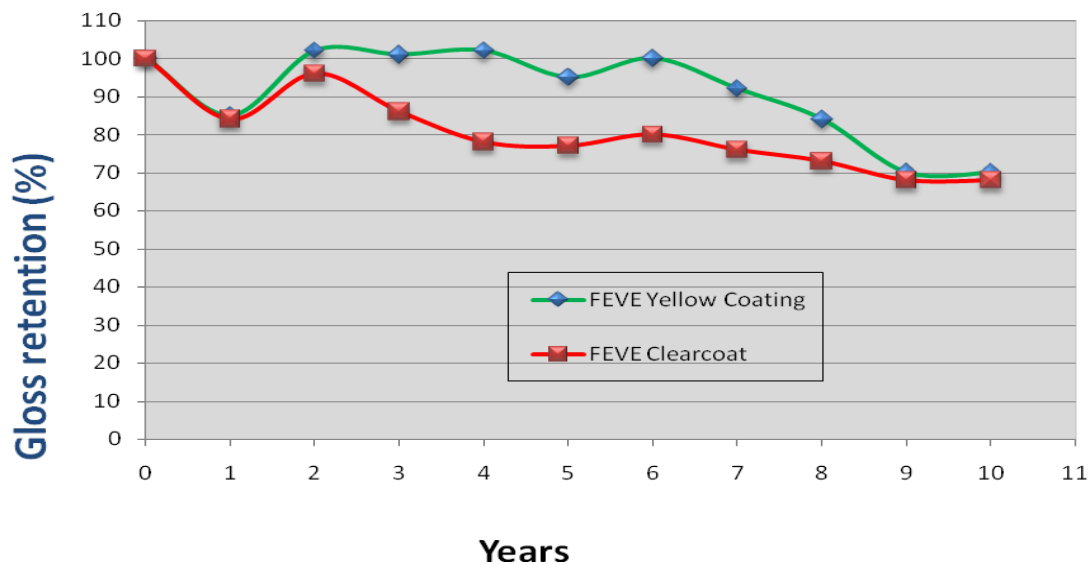


Figure 4: EMMAQUA Testing of FEVE Coating, PVDF, and Acrylic Urethane

FEVE based coatings offer exceptional weatherability in both accelerated weathering tests and real time exposure tests. Figure 5 shows test results for 10 years of South Florida weathering. Results show that FEVE based fluorourethanes have a gloss retention of over 70% after this time.



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

Figure 5: South Florida Weathering of FEVE Based Fluorourethane Coating

Ultimately, accelerated weathering only approximates exposure in the real world. FEVE coatings have been in service for many years. Results indicate excellent results over time. Figure 6 below shows a progression of photographs taken over a period of 17 years on the Towika Bridge in Japan.. Gloss retention is seen to be outstanding to date.

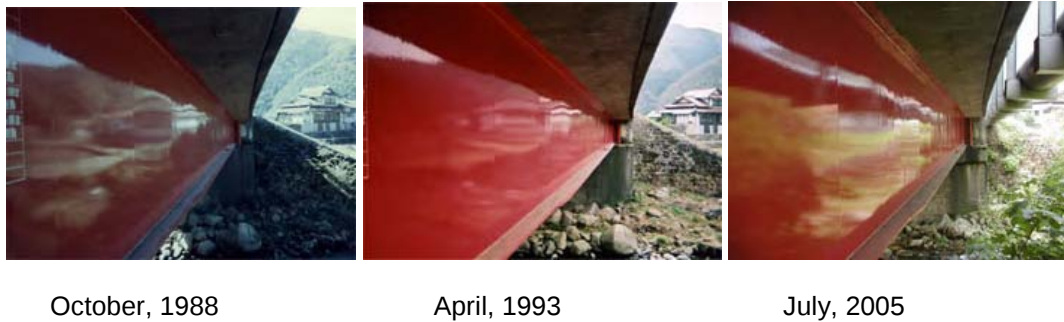


Figure 6: Weathering of Tokiwa Bridge, Hiroshima, Japan

Corrosion Resistance of FEVE Based Coatings

The main reason for using protective coatings on structures like bridges and oil rigs is to prevent corrosion of the asset. Typically, coating systems in marine environments, which are more severe than other environments, consist of a zinc rich primer, epoxy middle coat, and a topcoat that offers good UV stability. Examples of topcoats include urethanes and siloxanes. The same chemical characteristics of FEVE resins that impart outstanding weatherability also make the resins suitable for prevention of corrosion of metal structures.

Because coatings based on FEVE resins are more stable to degradation by UV radiation, surface removal of the decomposition products by rain, wind, and other factors is far less than urethanes and other coatings. This means that FEVE coatings maintain their thickness for far longer periods of time than other coatings.

The Ministry of Land, Transportation, and Infrastructure in Japan built a marine test station 250 meters offshore in Suruga Bay, the deepest bay in Japan. FEVE based fluorourethane coatings were tested alongside standard polyurethane coatings over a period of 15 years on this structure. The coatings were periodically evaluated during this time. The fluorourethane coating system consisted of an inorganic zinc primer (75 μm , 3 mils), two epoxy middle coats (120 μm and 30 μm , total 150 μm , 6 mils), and a fluorourethane topcoat (25 μm , 1 mil).

During the first seven years of the test, the fluorourethane topcoat showed no change in thickness. For the next eight years, the FEVE topcoat showed an average change of 0.38 μm (0.015 mils) per year. After 15 years, the FEVE topcoat had an average remaining thickness of about 22 μm (0.88 mils). At the average rate of coating loss, the theoretical life of the fluorourethane topcoat is over 60 years. In contrast, the polyurethane topcoat tested lost an average of 2 μm (.079 mils) per year beginning in the second year. The urethane was completely removed from the test coupon after about 12 years. While this is acceptable for some applications, the FEVE topcoat offers the potential to last 60 years.

At the end of the exposure period, the coupon with the FEVE fluorourethane coating was cut in cross section and analyzed by scanning electron microscope (SEM), and by Energy Dispersive X-Ray Microanalysis (EDX). SEM is a visual examination on a micro scale of the coating, while EDX is used for elemental analysis. The SEM scan of the fluorourethane coating system is shown below in Figure 7.

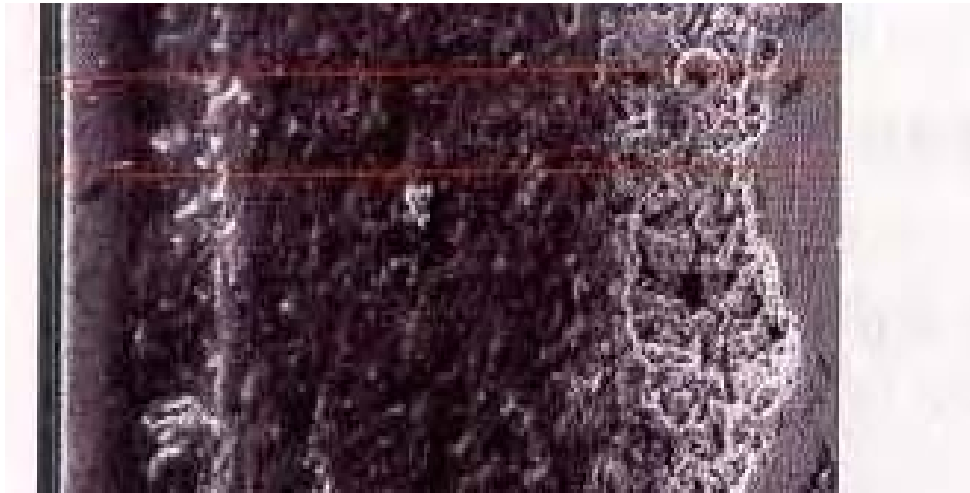


Figure 7: SEM of Fluorourethane Coating System

The FEVE topcoat is on the left side of the micrograph. The epoxy midcoat and zinc rich primer can be seen to its right, while the steel panel substrate can be seen at the right. The topcoat shows no obvious cracking or deterioration.

The EDX scan of the same coating system shows a considerable amount of chloride ion, a corrosion initiator, on the surface of the coating system. However, there is no chloride present at either the surface of the metal or in the coating system, indicating that the FEVE fluorourethane topcoat has prevented migration of chloride ion.

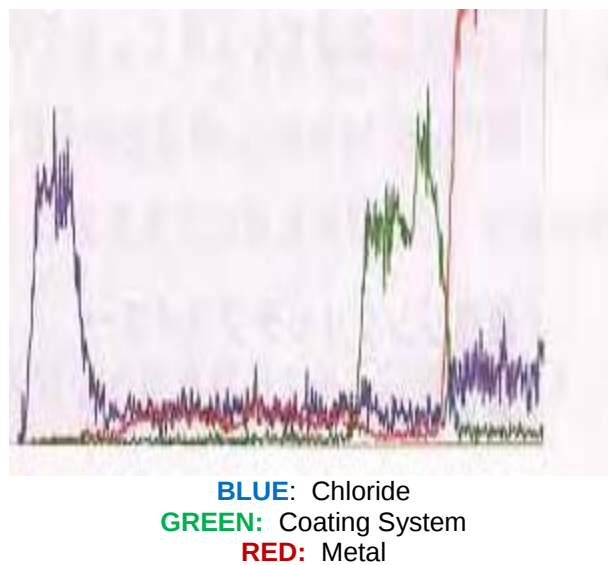


Figure 8: EDX Scan of Fluorourethane Coating System

Finally, an SEM was run on the zinc rich primer, shown below in Figure 9. The initial scan is shown on the right; the scan taken after 15 years is shown on the left. The zinc primer retains its characteristic globular shape even after 15 years. This indicates that no chloride has penetrated to the primer layer.

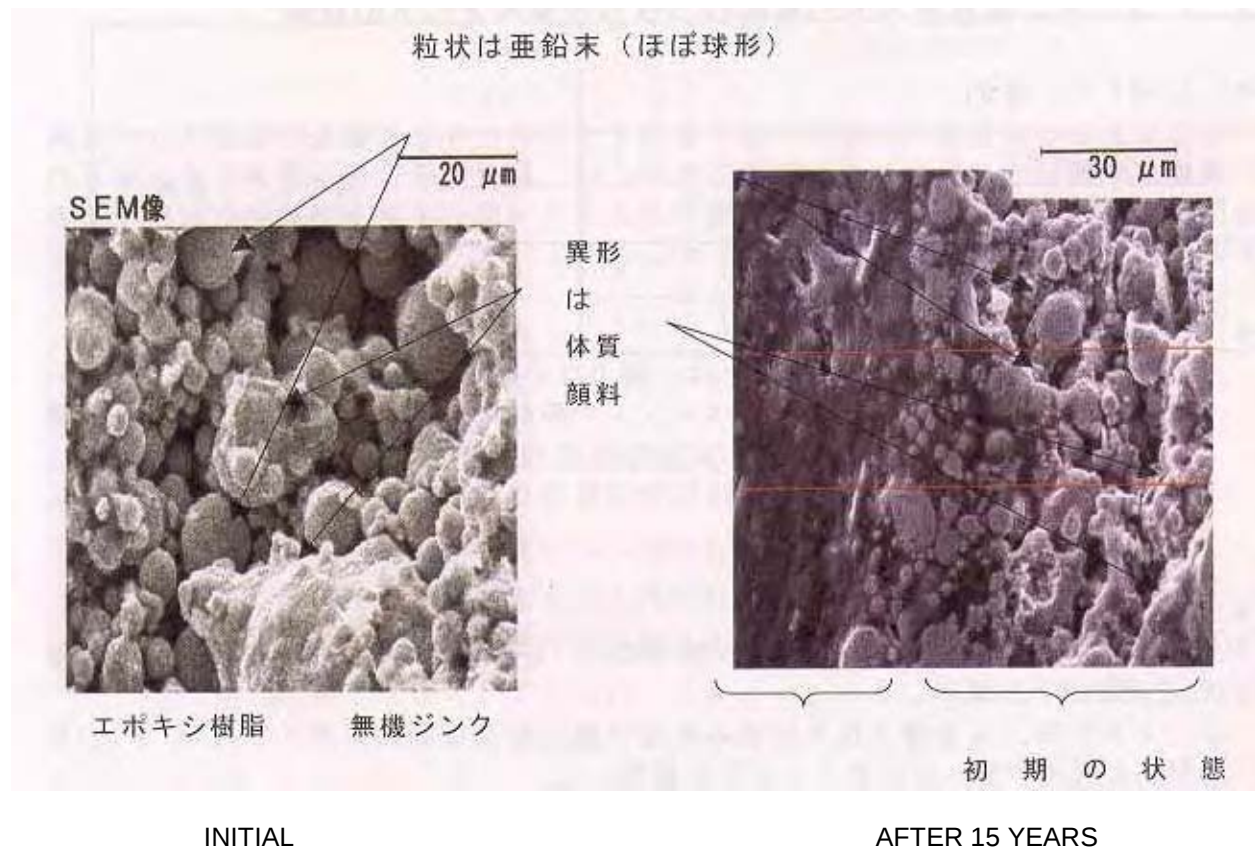


Figure 9: SEM Scan of Zinc Rich Primer

A 3-coat fluorourethane system, as well as three competitive systems, were tested by electrochemical impedance spectroscopy. In this test, the coatings were first weathered for 1,000 hours in the SWOM test described earlier. Then, the unscribed coated panels were subjected to 500 and 1,000 hours of exposure in the ASTM B-117 salt spray test. EIS involves sending an alternating current between electrodes, where the main electrode is in a 3% salt water solution, and the counter electrode on the metal substrate. The change in impedance at a constant measurement frequency of 1 kHz is then measured. The smaller the change in impedance during the test, the better the corrosion protection given by the coating system. The test results are shown below in Figure 10.

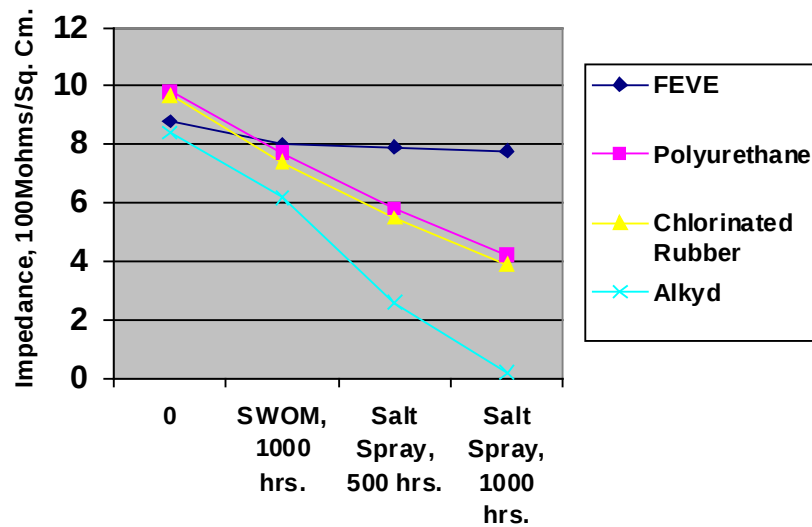


Figure 10: Electrochemical Impedance Spectroscopy Test Results

LIFE CYCLE COST ADVANTAGES OF FEVE BASED COATINGS

FEVE based coatings tend to be much more expensive than standard polyurethane and even polysiloxane coatings. However, the longevity of these coatings can mean that they offer substantial life cycle cost advantages over alternative technologies. In Japan, the Ministry of Land, Transportation, and Infrastructure now require the use of fluoropolymer topcoats on all bridges, whether new construction or rehabilitation of older structures. Expectations for topcoat life range from 30 years up to 60 years. Based on project costs in Japan, it is estimated that the initial cost disadvantage of a coating system using an FEVE topcoat is only about 5-10% compared to a standard polyurethane system. The cost disadvantage is much lower than expected because the cost of the primer and midcoats are the same regardless of which topcoat is used, and because the applied cost of a coating is constituted primarily by labor.

Based on the work done on the testing platform discussed earlier, a 1 mil urethane topcoat disappears after 12 years. This means that a much thicker topcoat is required, or that more frequent repainting will be required. If the urethane is recoated after 12 years, the FEVE based coating has a lifetime cost advantage of about 30%. Even if the urethane is presumed to last for 18 years, the FEVE coating still offers a life cycle cost advantage of about 20%.

There are a number of other costs that are not taken into account in the life cycle cost analysis above. Facility downtime can be required during coating operations, which can lead to increased product costs and loss of revenue. Loss of revenue is particularly important when coating bridges, electrical equipment, aircraft, and even gas stations. FEVE coatings also maintain the image of quality that many companies want, since they resist fading and color change.

CONCLUSIONS

FEVE based fluoropolymer coatings have now been in service for more than 20 years. Over that time, they have gained acceptance as an alternative to other coating systems to reduce life cycle coating costs, improve asset utilization, and eliminate the need for multiple painting cycles. FEVE coatings offer outstanding weatherability, and also exceptional corrosion resistance, especially important when used in topcoats for bridges in both inland and marine environments.

REFERENCES

1. M. Nagai, T. Matsumoto, H. Tanabe, DaiNippon Toyo Co., "Weatherability of Fluoropolymer Topcoat," Presented at NACE 2006, San Diego, CA.
2. T. Bahway, Keeler & Long, "Advanced Fluorocarbon Coatings for Maintenance and Architectural Applications," Presented at SSPC 1997, San Diego, CA.
3. S. Munekata, Asahi Glass Co., Ltd., Progress in Organic Coatings, "Fluoropolymers as Coating Materials," 16 (1988), pp. 113-134
4. T. Takayanagi, Asahi Glass Co., Ltd., "An Excellent Weather-Resistant Maintenance Coating System with an FEVE Fluoropolymer as a Topcoat," Asahi Glass Co. Research Report, 1988.
5. A. Asakawa, Asahi Glass Co., Ltd., "Performance of Durable Fluoropolymer Coatings," Presented at 7th Annual Nurnburg Congress, European Coatings Show, April 2003, Nurnburg, Germany.
6. Tohpe Paint Co. Product Catalog.