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FEVE FLUOROURETHANE TOPCOATS: THE FINAL STEP IN PROTECTION AGAINST CORROSION

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INTRODUCTION

Fluoroethylene vinyl ether (FEVE) resins were developed In Japan in the late 1970's 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[1].

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 ~486kJ/mol, while the energy of UV radiation at 300nm is ~399kJ/mol. The alternating pattern, shown in Figure 1, is critical for the extreme UV resistance properties. The chemically stable and UV resistant fluoroethylene unit sterically and chemical protects the neighboring vinyl ether unit[1].

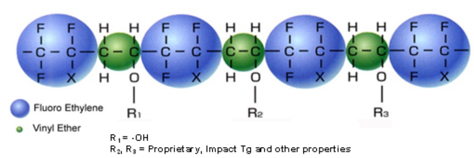

Figure 1
Alternating Structure of FEVE Resins

The vinyl ether groups make FEVE polymers useable as resins for paint. Without the vinyl ether groups, FEVE 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. The vinyl ether groups also contribute to high gloss and allow for functional groups, like hydroxyl groups, to be incorporated into the structure. Below is a table showing typical properties of FEVE resins[1].

Table 1
Typical Properties of FEVE Resins

Fluorine Content	25-30 wt%
OH Value	47-170 mg KOH/g
COOH Value	0-15 mg KOH/g
Molecular Weight	Mn = 15000-100000
Specific Gravity	1.4- 1.5
Morphology	Glassy (Tg =20-50^{o}C)
Decomposition Temp.	240-250oC
Solubility Parameter (cal'd)	8.8

The outstanding weatherability of fluorourethane coatings makes them ideally suited for exterior applications. Successful applications include water towers, aerospace, solar, and more recently, steel bridges.

HISTORY OF FLUOROURETHANE COATINGS ON BRIDGES

Fluorourethane coatings for bridge structures have been specified in parts of Asia for at least the last 20 years. The Japanese specification, JIS K 5659:1992 includes a weathering performance spec of a minimum of 80% gloss retention after 1000 hrs QUV-B. This spec interestingly also includes a requirement for fluorine content (it should be noted here that the JIS K 5659:2008 spec actually has removed the fluorine content requirement).

Figure 2
Akashi Straits Bridge, Japan

Fluorourethanes are most notable for their extreme UV resistance. Fluorourethane topcoats have been tested in both accelerated and natural weathering. The following charts show the weathering performance typical of fluorourethane coatings based on FEVE resins.

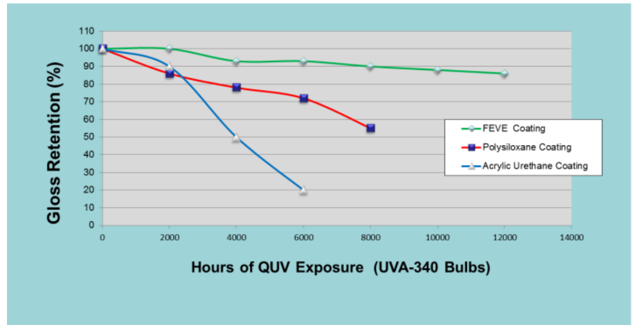

Figure 3
QUV-A Exposure

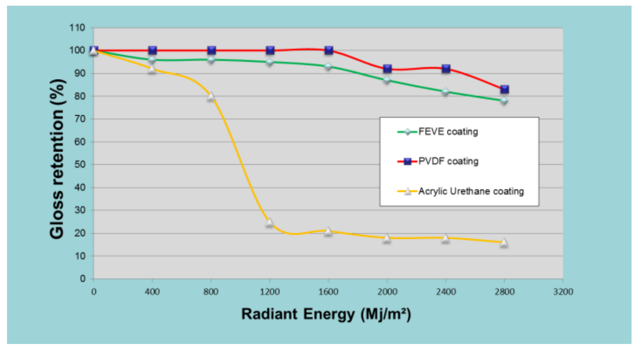

Figure 4
EMMAQUA Exposure

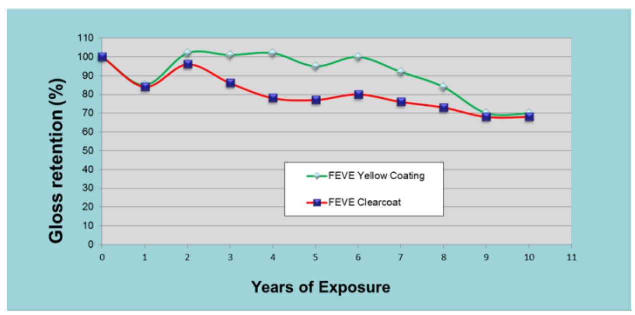

Figure 5
South Florida Exposure

Unlike the specification in Japan, the specifications used in the US tend to focus much more on corrosion resistance and less so on pure weathering resistance. National Transportation Product Evaluation Program (NTPEP, under the umbrella of

AASHTO, American Association of State Highway and Transportation Officials) includes performance specifications for both Salt Fog (ASTM B 117) and Cyclic Weathering (ASTM D 5894). Currently there are no specifications specifically for fluorourethane topcoats for steel structures.

BEYOND WEATHERABILITY: FLUOROURETHANES FOR CORROSION RESISTANCE

Fluorourethane topcoats have recently been used on bridges in certain areas of the US. Wider acceptance of the technology may come with specifications and acceptance by organizations such as AASHTO, NTPEP, and of course State Departments of Transportation (DOT).

Corrosion resistance is key to performance on steel bridge structures. Preliminary studies have been performed comparing fluorourethane topcoats against current competitive technologies in a 2-coat system (epoxy primer/topcoat). The results below show creep at the scribe after 3000 hours salt fog (ASTM B 117).

Table 2
Results of 3000 Hours Salt Fog

Formula Name	DFT (mils)	Creep (mm)	Creep Rating (ASTM D1654)
Commercial Polysiloxane White	2.07	5.9	4
Commercial Clear Polysiloxane	1.95	3.5	5
Commercial Polyurethane White	2.56	7.2	3
Fluorourethane Clear	2.12	4.8	5
Fluorourethane White	1.5	3.1	5

The results of this preliminary showed that a fluorourethane topcoat compares well with the current competitive products being used on steel structures today.

CORROSION TESTING: NTPEP

A more detailed and complex study was performed in order to determine how well a fluorourethane system performs according to the NTPEP standard corrosion tests. Twelve systems were tested for Cyclic Weathering (ASTM D 5894). All the systems utilized a commercially available organic zinc primer. Some systems contained a commercially available, epoxy primer as a mid-coat as well. Commercial polyurethane and polysiloxane topcoats were compared to a laboratory produced fluorourethane topcoat.

All coating systems were applied to smooth steel using a wire rod coating applicator. Coated panels were allowed to dry at ambient temperatures for a minimum of seven days before submission into the test cycle.

Results and Discussion

The results below are of panels tested for 5040 hours in Cyclic Weathering (ASTM D 5894). Because the test will be allowed to continue until 5000 hours, only a visual check was made. None of the panels exhibited rusting in the field but some did show blistering around the scribe. The pass/marginal/fail ratings are based on the ASTM standard rating for creepage at the scribe.

Table 4
Results of 5040hrs Cyclic Weathering

System	Max Creep (mm)	Ave Creep (mm)	% Gloss Retention
OZ/ Epoxy/PU	2	1	5.5
OZ/Epoxy/PS	6	2	34.9
OZ/Epoxy/FIU	8	3	65.3
OZ/Epoxy/mod. FIU	5	3	79.3
Epoxy/PU	16	6	9.8
Epoxy/PS	12	6	37.2
Epoxy/FIU	12	7	67.7
Epoxy/mod. FIU	8	6	58.1
OZ/PU	2	<1	16.4
OZ/PS	6	2.5	33.4
OZ/FIU	1	<1	80.7
OZ/mod. FIU	3	<1	79.7

It is clear from the results that the inorganic zinc primer systems performed much better than those with the organic zinc primer. Two types of systems also performed well with the organic zinc primers, the polysiloxane system and the modified fluorourethane systems. Two modified fluorourethane systems were tested, each having different TiO_2 pigments. Both passed over the organic zinc rich primer. Interestingly the polysiloxane system with the two coats of the topcoat actually appeared to fail over the organic zinc rich primer. It should be reiterated that the panels used were smooth steel and not blasted steel. This test might be considered a worst case scenario. The NTPEP protocol requires blasted steel panels.

ANALYTICAL CORROSION TESTING: ELECTRICAL IMPEDANCE SPECTROSCOPY

The standard lab tests ASTM B117 and ASTM D 5894 provide useful data for the lab chemist. Like many standard test methods, they tend to be time-consuming. Moreover they often are not without scrutiny to the true value and meaning of the results. For example, using scribe creep to determine the corrosion resistance of a coating has its critics. Is it a true measure of the coatings inherent corrosion resistance?

Another approach to ascertaining the corrosion resistance of a coating is an analytical technique called Electrical Impedance Spectroscopy (EIS). This technique measures the electrical resistance of a coating. Extrapolated, a lower resistance implies more potential salt intrusion. EIS testing of the systems discussed in this paper will be performed. A comparison of the results of EIS will be made against the accelerated tests already completed.

CONCLUSION

Fluorourethane coatings are the industry standard for superior weatherability. They are used widely in architectural applications where long- term aesthetics are desired. Recently, the industrial coatings market, specifically the bridge coatings market has taken notice. When it comes to bridge coatings, corrosion protection is paramount to all other performance criteria. Recent studies of ASTM B117 Salt Spray and ASTM D5894 Cyclic Weathering show that systems using a fluorourethane topcoat compare well to industry standard systems. Fluorourethane topcoats can provide a bridge with the corrosion protection it needs and the long- tern aesthetics and durability that the community values.

REFERENCES

(1) Kristen Blankenship, “Formulation Techniques Using FEVE Resins in Waterborne and High Solids Coatings,” Proceedings of the Forty-Second Annual International Symposium of Waterborne, High Solids, and Powder Coatings Symposium, p.251(2015)