"FEVE based coating systems: Protecting Steel Bridges for over 30 years"

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Abstract. Fluoro Ethylene Vinyl Ether (FEVE) resins were commercialized by AGC in 1982 under the brandname Lumiflon as the first soluble fluorinated resins for coating formulations. FEVE resins are renowned for their extremely high durability due to the high C-F bond energy. Therefore, they do not degrade under the influence of UV radiation from the sun. Coatings based on FEVE resins show outdoor durability performance of over 30 years. This paper discusses the basic chemistry behind the extreme durability of Lumiflon based coating systems. Two case studies of actual steel bridge applications will be shown. The Daiichi- Mukaiyama bridge, which was newly constructed and coated in 1987, and the Tokiwa bridge, which was recoated with a Lumiflon based system in 1986. Through these examples, this paper demonstrates that FEVE based coated systems provide the best possible protection of steel bridges.

1. Introduction
Fluoroethylene vinyl ether (FEVE) resins were developed in Japan in the late 1970’s and were first commercialized in 1982. FEVE resins are amorphous A-B type copolymers with repeating units of fluoroethylene and substituted vinyl ether (see Figure 1). Unlike pure fluropolymers, FEVE resins are soluble in solvents due to the vinyl ether groups. Solvent solubility transforms FEVE resins from high performance polymers into high performance resins for coatings. [1]

![Figure 1. Alternating Structure of FEVE Resins](image-url)
FEVE resins have characteristics of both fluoropolymers and hydrocarbons. The fluoroethylene groups are the strength of the FEVE resin. These groups are responsible for the polymer’s high resistance to UV degradation. The C-F bond is very strong (see Table 1). The energy of this bond is higher than the energy of UV radiation at 290nm which is ~411KJ/mol. The alternating pattern, shown in figure 1, is critical for the extreme UV resistance properties. The chemically stable and UV resistant fluoroethylene units sterically and chemically protect the neighbouring vinyl ether units. [1]

Table 1. Bond energy of Fluoro-Chemicals and Commodity Chemicals [2]

| Resin               | C-C Chain | C-F | C-F C-H | KJ/mol |
|---------------------|-----------|-----|---------|--------|
| Fluoro Compound     | CF3-CF3   | F-CF2-CH3 | 414     | 523    |
| Fluoro Compound     | CF3-CH3   | CF3CH2-H | 424     | 447    |
| Commodity Chemical  | CH3-CH3   | CH3CH2-H | 379     | 411    |

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 on-site settings. A wide range of curing temperatures can be employed ranging from Room Temperature to 230 °C. 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 2. Typical Properties of FEVE Resins

| Property               | Value              |
|------------------------|--------------------|
| Fluorine Content       | 20-30 wt%          |
| OH Value               | 47-170 mg KOH/g    |
| COOH Value             | 0-15 mg KOH/g      |
| Molecular Weight       | M_n = 15000-100000 |
| Specific Gravity       | 1.4 – 1.5          |
| Morphology             | Glassy (T_g = 20-50°C) |
| Solubility Parameter (cal’d) | 8.8          |

2. Durability

As explained above FEVE resins are renowned for their extremely high durability due to the high C-F bond energy. Therefore, they do not degrade under the influence of UV radiation from the sun. Fluorourethane topcoats have been tested in both accelerated and natural weathering. The following figures show the weathering performance typical of fluorourethane coatings based on FEVE resins. Figure 2 shows a comparison of a FEVE coating to polysiloxane and acrylic urethane based coatings in QUV accelerated weathering. The FEVE coating clearly outperforms the other resins which are renowned on their own in the industry for their good weatherability. Furthermore Figure 3 shows South Florida exposure of a clear and a yellow FEVE coating. This data clearly shows the excellent performance of the FEVE based coating technology achieving a gloss retention of around 70% after 10 years of exposure.
Besides excellent gloss and color retention FEVE topcoats also offer a great benefit in terms of general protection of underlying substrates. Due to the high UV resistance and lack of degradation of the resin the coating itself will stay intact much longer than for example an acrylic urethane based topcoat. Figures 4 and 5 show film consumption for the fluoro-polymer coating and polyurethane coating in cross section after 15 year of exposure. A portion of the coating was covered with tape and thus was not exposed to sunlight. Under the tape the film was not damaged. The film thickness of each topcoat after 15 years outdoor exposure could be compared to the original film thickness under the tape. After 15 years, the fluoro-polymer topcoat has lost about 1.1μm total (less than 0.1 μm/year), while the polyurethane topcoat has lost 22-28μm (about 2μm/year).

Figure 2. QUV Exposure of an FEVE Based Coating

Figure 3. South Florida Exposure of an FEVE Based Coating
In Figure 6, two sections of the coating are analysed by Imaging IR (IRT7000\textsuperscript{[3]}). That measurement can detect amide (II) absorbance and quantify it in comparison to the C-H band or C-F band. A chemical map is generated, which shows the distribution of the amide bond through the cross-section. The color gradient of this map directly relates to the concentration of isocyanates. In the case of the Fluoro-polymer, comparing the cross-section which has been light-sealed (map A) and the cross-section which has been exposed (map B) shows that the decomposition of isocyanates is very limited. Indeed, the same intensity in the gradient can be observed with the red color present through the depth of both cross-sections. In the case of the Polyurethane, the protected cross-section (maps C) and the exposed cross-section (map D) show large differences. In the map of the exposed cross-section, the yellow color indicates that the isocyanate concentration is much lower in comparison to that of the protected cross-section in red. UV light has induced the degradation of the isocyanate in the polyurethane coating, even at a 20\textmu m depth from the surface.
Due to their high durability, FEVE based coatings are highly suitable for use in the protection of steel bridges. In Europe, only Italy has an optional fluorinated coating specification (ANAS IT.CDTG.05.18). Most other European countries specify coatings towards ISO 12944-5 which focuses on corrosion protection but does not mention gloss or color retention. The recently released ISO 12944-9 includes a category for protective systems offering a durability of 25 years or longer. FEVE resins are mentioned as a possible technology to achieve this. In contrast the Japanese Road Authorities allow bridges only to be coated with topcoats based on fluorinated resins due to their extremely long lifetimes. Maintenance cycles and resulting bridge closures, which generate an enormous economic cost, are therefore minimized. Nowadays over 80% of all bridges in Japan are coated with these coating systems. AGC has tracked the performance of Lumiflon based bridge coatings in Japan for over 30 years. These coatings still perform admirably after such long time without ever being re-coated. The expected lifetime of these coating systems is now estimated to be 60 years or more, far surpassing polyurethane and polysiloxane technologies that are commonly used throughout Europe.

3. Case Studies
In this section two case studies will be shown to demonstrate the excellent performance of Lumiflon based bridge coatings. The first example is the Daichi-Mukaiyama bridge, which was newly constructed and coated in 1987. The second example will show the Tokiwa bridge which was repainted with a Lumiflon in 1986. Both bridges were never recoated and have been monitored from the start of the application until now. Both show excellent color and gloss retention and overall performance.
3.1. Daiichi-Mukaiyama bridge

The Daiichi-Mukaiyama bridge was newly build in 1987 (see figure 7). The primer and middle coats were shop applied and the topcoat system, based on a *Lumiflon* resin system, was applied on site. Color and gloss measurements were taken initially and after 22 and 30 years. Furthermore the coating was inspected for chalking and other degradation signs. As is demonstrated in Table 3 and Figure 7 the paint system performed admirably after 30 years of service life. A gloss retention of over 70% was measured after wiping the coating free of dust and dirt. Also, no rust peeling or cracking was observed. Color measurements could not be compared due to a change in colorimetric techniques throughout the years. However the red color still appears as bright as when it was applied 30 years ago.

![Figure 7. Daiichi-Mukaiyama bridge](image)

![Figure 8. Daiichi-Mukaiyama bridge inspection after 30 years](image)

### Table 3. Gloss Retention.

|         | Initial | 22 years | 30 years |
|---------|---------|----------|----------|
| **Non wiped** | Measured value | 52.4 | 46.5 | 28.3 |
|         | Retention | - | 88.7% | 54% |
| **Wiped** | Measured value | 52.4 | 49.9 | 38.7 |
|         | Retention | - | 92.5% | 7.8% |

### Table 4. Appearance Observation after 30 years.

| Part Investigated | Rust | Peeling | Crack |
|-------------------|------|---------|-------|
| **Upstream Side** |      |         |       |
| Brace             | 0    | 0       | 0     |
| Cross Girder      | 0    | 0       | 0     |
| Arch Rib          | 0    | 0       | 0     |
| **Downstream Side** |     |         |       |
| Brace             | 0    | 0       | 0     |
| Cross Girder      | 0    | 0       | 0     |
| Arch Rib          | 0    | 0       | 0     |
3.2. Tokiwa bridge

The Tokiwa bridge was repainted in 1986 (see Figure 9). The original paint system was a chlorinated rubber coating applied in 1977. For the repainting the surface was prepared according to an ISO st3 level (3rd B grade). The performance of the coating was then followed for 30 years. As can be seen in table 5 and fig.10 the gloss and color retention are exemplary. At some locations some rust was found (see Table 6). However it should be noted that at the time of application no zinc rich primers were used. Also this particular bridge is located in the north of Japan and is therefore regularly exposed to road salt due to icy winter conditions. Overall the performance of the coating during its 30 year lifespan has been formidable.

![Figure 9. Tokiwa Bridge](image)

![Figure 10. Tokiwa bridge inspection](image)

| Year     | Gloss Retention (Non-wiped) | Gloss Retention (Wiped) |
|----------|------------------------------|-------------------------|
| Initial  | Measured value 75.2          | Measured value 75.2     |
|          | Retention 88%                | Retention 103.2         |
| 2 years  | 66.2                         | 77.6                    |
| 22 years | 52.7                         | 73.2                    |
| 30 years | 70.1                         | 97.3                    |

Table 5. Gloss Retention.


Table 6. Appearance Observation after 30 years.

|                | Main Girder | Rust | Peeling | Crack |
|----------------|-------------|------|---------|-------|
| **Upstream Side** |             |      |         |       |
| Upper flange / lower side | 0 | 0 | 0 |
| Web Plate | 0 | 0 | 0 |
| Lower flange / upper side | 1 | 1 | 0 |
| Lower flange / lower side | 1 | 1 | 0 |
| Joint Part | 0 | 0 | 0 |
| **Downstream Side** |             |      |         |       |
| Upper flange / lower side | 0 | 0 | 0 |
| Web Plate | 0 | 0 | 0 |
| Lower flange / upper side | 2 | 1 | 0 |
| Lower flange / lower side | 2 | 1 | 0 |
| Joint Part | 0 | 0 | 0 |

4. Conclusion
FEVE based resins are extremely durable in outdoor conditions due to the high strength of the C-F bond. These resins find applications in coating systems where long lifetimes, color and gloss retention and corrosion protection are required. Hence they are extremely suitable for the formulation of bridge coatings. Both the accelerated weathering data and the actual outdoor performance of coatings based on Lumiflon resins systems show unmatched performance with respect to color and gloss retention but also in regards to protection of the underlying substrate against the elements.

References
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