# FEVE FLUOROPOLYMER EMULSIONS FOR PERFORMANCE IMPROVEMENT IN ARCHITECTURAL COATINGS

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## ABSTRACT

Fluoro-olefin vinyl ether (FEVE) copolymer resins have been used in high performance exterior coatings since 1982. They offer superior weatherability, excellent color fade resistance, and curing capabilities at ambient temperature. Due to increasing environmental regulation of solvents, traditional solvent based resins have been supplemented by the development of water based FEVE emulsions. These emulsions have been part of the FEVE family of resins for the last 8 years. These resins also possess a high degree of exterior durability and the ability to be formulated into air-dry coatings. The FEVE emulsions are currently part of an evaluation of different architectural coating formulations. They have been included as part of the binder system of exterior semi-gloss house paints and also DTM Industrial Maintenance coatings to access their influence on gloss retention, weatherability, and fade resistance. The degree of performance of these coatings has been measured by the exposure of panels coated with the test formulations in a QUV Weatherometer and on an exterior test fence. The results-to-date have indicated marked improvement in performance of the FEVE emulsion-containing coatings as compared to coatings that use only conventional acrylic emulsions as the binder in their formulations.

## Introduction

Fluoropolymers are distinguished particularly by their high thermal, chemical and weather resistance, excellent surface properties (especially oil and water repellency) and optical properties (low refractive index). Accordingly, fluoropolymers are indispensable materials in a wide variety of industries.

Since fluoropolymers came on the market in 1930s, they have been applied as coating materials in order to achieve those characteristics mentioned above on the surfaces of various substrates. Typical examples include coatings made from aqueous dispersions polytetrafluoroethylene(PTFE), tetrafluoroethylene/hexafluoroethylene copolymers (FEP), and tetrafluoroethylene/perfluoroalkyl vinyl ether copolymers (PFA) for non-stick and anti-corrosion applications. However, those fluoropolymers are not necessarily suitable for use as coating materials due to their poor solubility in conventional organic solvents, the requirement of baking temperatures greater than 200°C and weak adhesion to substrates [1].

Among the well-known fluoropolymers, only polyvinylidene fluoride (PVdF) has been used for coatings as an organic dispersion, mainly for architectural applications due to its outstanding weatherability [2].

A unique solvent soluble fluoroolefinvinyl ether copolymer (abbreviated as FEVE copolymer, with the trade name "LUMIFLON") was developed in 1982 by Asahi Glass. This copolymer consists of alternating sequences of fluoroolefin and several specific vinyl ether units (Fig.1), and is completely amorphous. This alternating sequence is responsible for extremely high weather resistance of the resultant paint finishes. Combinations of several kinds of vinyl ether comonomers provide the polymer with other useful physical properties, such as solubility in organic solvents, pigment compatibility , crosslinking sites and impart good adhesion, hardness and flexibility to the coating. The major reason for the use of FEVE copolymers as raw materials for coatings is their excellent weather resistance. The hydroxyl group in the FEVE polymer functions as the crosslinking site with blocked isocyanates or melamine resins for heat cured coatings, and with aliphatic polyisocyanates for on-site coatings [3].

The water-borne FEVE emulsions are prepared by emulsion polymerization. Vinyl ether monomers with polyoxyethylene (EO) unit are used as intramolecular emulsifiers to obtain stable emulsions and to maintain the alternating FEVE polymer sequence. The resulting emulsions have high molecular weight and toughness, so they can be used in one component systems. The resins can also be used in two component coatings by introducing more hydroxy functional vinyl ether monomer. However, we will only be formulating with the emulsions that have been synthesized for 1 component coatings.

## Experimental

**Physical Properties and Compatibility of the FEVE Emulsions.** The physical properties of the 2 FEVE emulsions that have been incorporated into the architectural coating formulations are shown in Table 1. Before these emulsions were placed into any complex coating formulations, they were blended with 8 different acrylic emulsions. A coalescing solvent (Texanol) was also added to these blends at levels from 7.5% to 15% (on resin solids).The blends were placed in a 140°F. oven for 2 weeks, then observed for cleanliness. 3 mil drawdowns also were cast and compared to the 3 mil drawdowns that were cast before the oven exposure. All of the blends showed good compatibility of the acrylics and the FEVE emulsions.

**Testing White Architectural House Paints.** A Standard White House Paint Formulation was created for performance testing of the FEVE emulsions. The formulation had the physical properties shown in Table 2. Test formulations were made with both 100% acrylic emulsion as the resin component and 50%/50% blends using the FEVE emulsions. Four commercial acrylic emulsions from two different manufacturers were part of the study.

For each acrylic emulsion, three formulations were made:

100% acrylic emulsion as the resin component
50% acrylic emulsion & 50% FE-4300 as the resin component
50% acrylic emulsion & 50% FE-4500 as the resin component

Test panels were made with these formulations and placed in the QUV Weatherometer for exposure. QUV "A" bulbs were utilized in the Weatherometer. The light/condensation cycle of was 8 hours light exposure at 60°C. and 4 hours condensation at 50°C.

Figures 2 through 5 show the exposure time of each panel when a 60° gloss decrease of 60-70% was reached. The panel for each coating that utilized 100% acrylic emulsion as the resin component was compared to the coatings that had the FEVE emulsions mixed in with the acrylic emulsions in each of the 4 graphs labeled Figure 2 through Figure 5.

**Testing Red Architectural House Paints.** A second house paint formulation was created for testing of the FEVE emulsions. This time, the formulation was a semi-gloss house paint with a dark red color. The formulation had the physical properties shown in Table 3. In this part of the project, only one acrylic emulsion and one FEVE emulsion were used in the coating formulations. Six formulations were made, each with a different ratio of the 2 emulsions:

| | BINDER SYSTEM |
|---|---|
| Formulation #1: | 100% Acrylic Emulsion |
| Formulation #2: | 50% Acrylic Emulsion + 50% FE-4500 emulsion |
| Formulation #3: | 40% Acrylic Emulsion + 60% FE-4500 emulsion |
| Formulation #4: | 30% Acrylic Emulsion + 70% FE-4500 emulsion |
| Formulation #5: | 20% Acrylic Emulsion + 80% FE-4500 emulsion |
| Formulation #6: | 10% Acrylic Emulsion + 90% FE-4500 emulsion |

Panels were coated with each of these formulations and placed the the QUV Weatherometer. QUV "A" bulbs were utilized in the Weatherometer. The light/condensation cycle of was 8 hours light exposure at 60°C. and 4 hours condensation at 50°C.

Figures 6 &7 compare the loss of gloss of Formulation #1 (which had 100% acrylic emulsion as the binder system) with the other five formulations that had different levels of the FE-4500 FEVE emulsion as part of the binder system.

**Testing White Direct-To-Metal Industrial Coatings.** A third formulation was incorporated into this project – a DTM (Direct-To-Metal) Industrial Maintenance Coating Formulation. These coatings are meant strictly for metal substrates.The acrylic emulsions that are typically used in these types of formulations possess different properties than those used in exterior house paint formulations.

Three commercial acrylic emulsions marketed for this type of coating were utilized in these DTM formulations. We will call them Acrylic Emulsion #5, #6, and #7. Stability testing was done by blending these acrylic emulsions with the FEVE emulsions to guarantee success in these new formulations. The oven stability test was the same as the test performed with the acrylic emulsions from the White House Paint Formulations. There was no indication that these blends were unstable, so the formulations were made.

The physical properties of this formulation are listed in Table 4. Test formulations were made with both 100% acrylic emulsion as the resin component and 50%/50% blends using the FEVE emulsions. Three commercial acrylic emulsions from two different manufacturers were part of the study.

For each acrylic emulsion, two formulations were made:

1) 100% acrylic emulsion as the resin component
2) 50% acrylic emulsion & 50% FE-4300 as the resin component

Panels were coated with each of these formulations and placed the the QUV Weatherometer. QUV "A" bulbs were utilized in the Weatherometer. The light/condensation cycle of was 8 hours light exposure at 60°C. and 4 hours condensation at 50°C.

Figures 8, 9, & 10 compare the loss of gloss of Formulation #1 (which had 100% acrylic emulsion as the binder system) with the other formulation that had 50% acrylic emulsion & 50% FE-4300 FEVE emulsion as part of the binder system.

**Testing Black Direct-To-Metal Industrial Coatings.** A fourth formulation was incorporated into this project – a Black DTM (Direct-To-Metal) Industrial Maintenance Coating Formulation. This formulation is identical to the White DTM Formulation except for the color. Some of the physical properties of the fourth formulation differ from the third formulation due to the color change.

Two of the three commercial acrylic emulsions tested in the White DTM Formulation were utilized in these Black DTM formulations - Acrylic Emulsion #5 and #6. The physical properties of this formulation are listed in Table 5. Test formulations were made with both 100% acrylic emulsion as the resin component and 50%/50% blends using both of the FEVE emulsions. The two commercial acrylic emulsions were from the same resin manufacturer.

For each acrylic emulsion, three formulations were made:

1) 100% acrylic emulsion as the resin component
2) 50% acrylic emulsion & 50% FE-4300 as the resin component
3) 50% acrylic emulsion & 50% FE-4500 as the resin component

Panels were coated with each of these formulations and placed the the QUV Weatherometer. QUV "A" bulbs were utilized in the Weatherometer. The light/condensation cycle of was 8 hours light exposure at 60°C. and 4 hours condensation at 50°C.

Figures 11 and 12 compare the loss of gloss of Formulation #1 (which had 100% acrylic emulsion as the binder system) with the other formulations that had 50% acrylic emulsion & 50% of either the FE-4300 FEVE emulsion or the FE-4500 FEVE emulsion as part of the binder system.

## Continuation of Experiments

Some of these exposure tests are currently still in the QUV Weatherometer. They will be exposed until the data indicates the need for termination. Other architectural coating formulations, some using lower levels of the FEVE emulsions, are being evaluated for exposure testing, both in the QUV Weatherometer and on an outside test fence in Exton, PA.

Another market that is being studied is the high-gloss concrete sealer market. The formulations in this coatings market are also dominated by acrylic emulsions. These clear coatings, because they are predominantly used on horizontal exterior surfaces, have high exposure to the UV rays of the sun. Inclusion of an FEVE emulsion in these formulations as part of the binder system may increase the life of these coatings to 2 or 3 times their current lifetime.

## Conclusion

Inclusion of FEVE emulsions in architectural coating formulations can increase gloss retention and therefore prolong the aesthetic properties and the film integrity of these coatings, thereby increasing their life cycle and increasing the time between recoating exterior substrates.

*Table 1*

| Table 1: FEVE Water-Borne Emulsions | | |
|---|---|---|
| ************ | ***FE-4300*** | ***FE-4500*** |
| **Solids (Wt.)** | *50%* | *50%* |
| **pH** | *7 to 9* | *7 to 9* |
| **Specific Gravity** | *1.13* | *1.17* |
| **MFT** | *35°C.* | *28°C.* |
| **Hydroxyl Value** | *10* | *13* |

*Table 2*

| Table 2: White House Paint Formulation Properties | |
|---|---|
| **Solids (Volume)** | ***32%*** |
| **pH** | ***9.0 to 9.5*** |
| **$TiO_2$ Choice** | ***TiPure R-706*** |
| **PVC** | ***22*** |
| **Thickeners** | ***both cellulosic and associative*** |
| **60° Gloss Range** | ***50-65*** |
| **VOC** | ***1.24 #/gal. or 150 g/liter*** |

*Table 3*

| Table 3: Red House Paint Formulation Properties | |
|---|---|
| **Solids (Volume)** | ***36%*** |
| **pH** | ***9.0 to 9.5*** |
| **Pigment Choice** | ***Organic Red + Phthalo Blue (trace)*** |
| **PVC** | ***6.5*** |
| **Thickeners** | ***both cellulosic and associative*** |
| **Acrylic emulsion** | ***Acrylic Emulsion #4*** |
| **FEVE Emulsion** | ***FE-4500*** |
| **60° Gloss Range** | ***50-65*** |
| **VOC** | ***1.24 #/gal. or 150 g/liter*** |

*Table 4*

| Table 4: White DTM IM Paint Formulation Properties | |
|---|---|
| ***Solids (Volume)*** | ***38%*** |
| ***FEVE Emulsion*** | ***FE-4300*** |
| ***pH*** | ***9.0 to 9.5*** |
| ***$TiO_2$ Choice*** | ***TiPure R-706*** |
| ***PVC*** | ***18*** |
| ***Thickeners*** | ***associative-type*** |
| ***60° Gloss Range*** | ***60-80*** |
| ***VOC*** | ***1.24 #/gal. or 150 g/liter*** |

*Table 5*

| Table 5: Black DTM IM Paint Formulation Properties | |
|---|---|
| *Solids (Volume)* | *36%* |
| *FEVE Emulsions* | *FE-4300 and FE-4500* |
| *pH* | *9.0 to 9.5* |
| *Pigment Choice* | *Tint-Ayd CW5331 Masstone Black* |
| *PVC* | *2.7* |
| *Thickeners* | *associative-type* |
| *60° Gloss Range* | *70-80* |
| *VOC* | *1.24 #/gal. or 150 g/liter* |

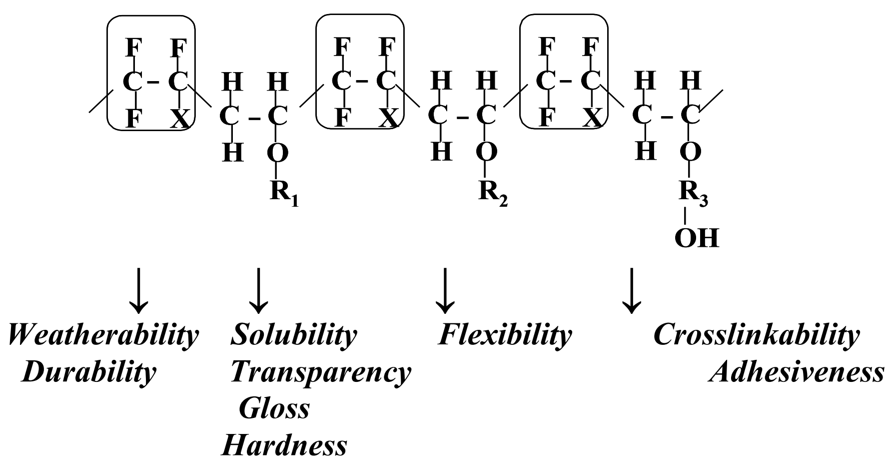


***Figure 1. Polymer structure of FEVE copolymer***

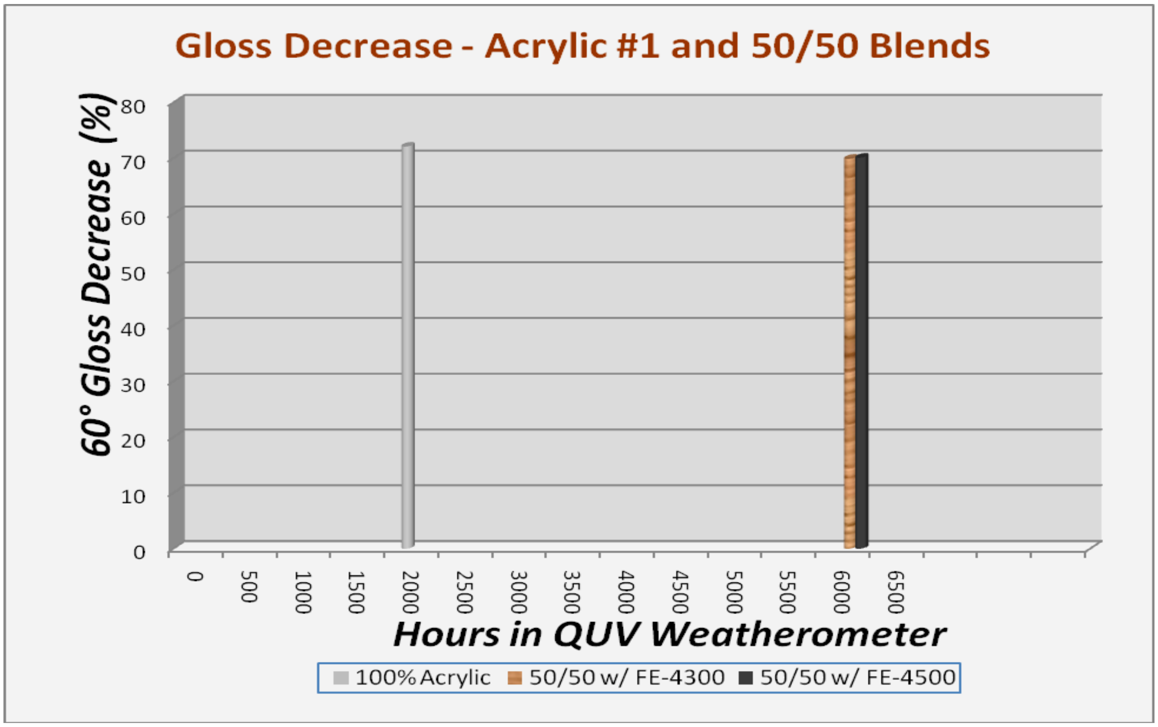


*Figure 2: QUV Results of Acrylic #1 and 50/50 Blends of LF Emulsions*

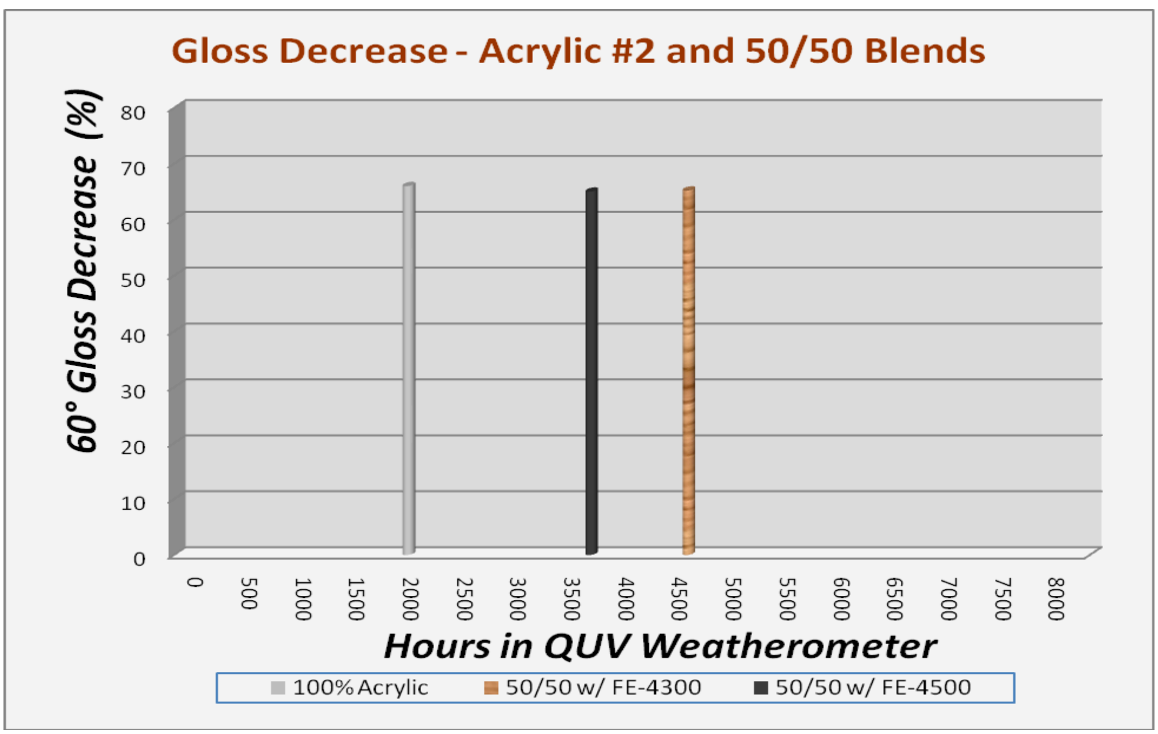


*Figure #3: QUV Results of Acrylic #2 and 50/50 Blends of LF Emulsions*

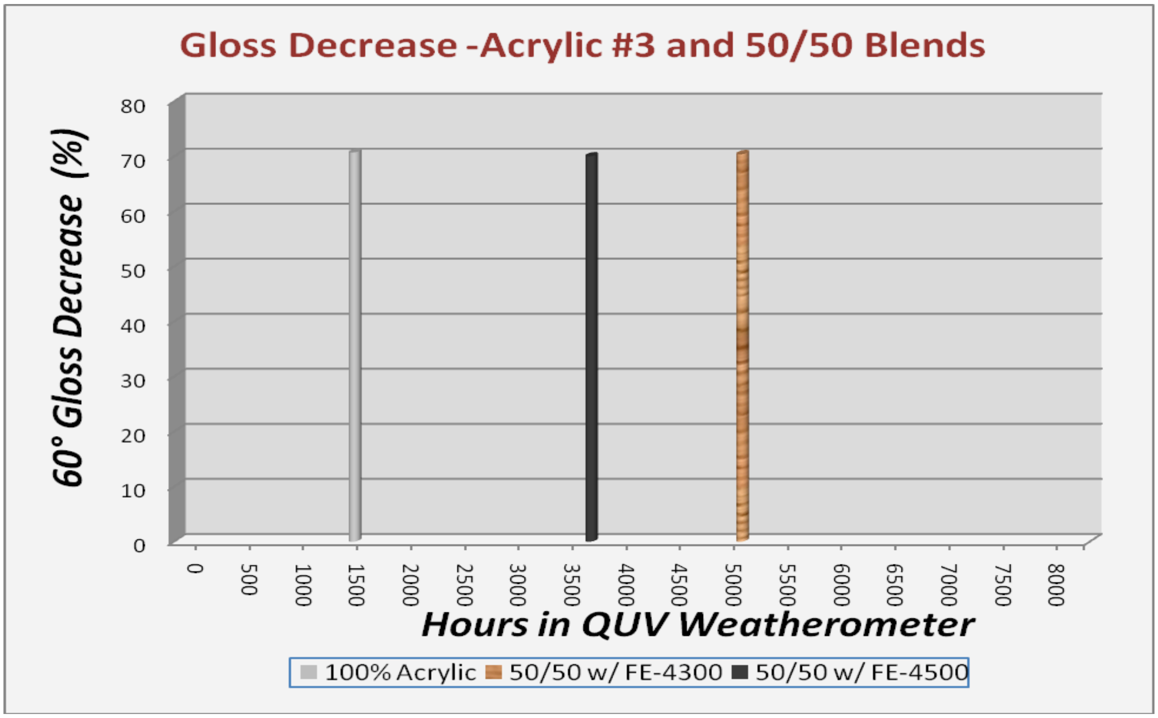


*Figure #4: QUV Results of Acrylic #3 and 50/50 Blends of LF Emulsions*

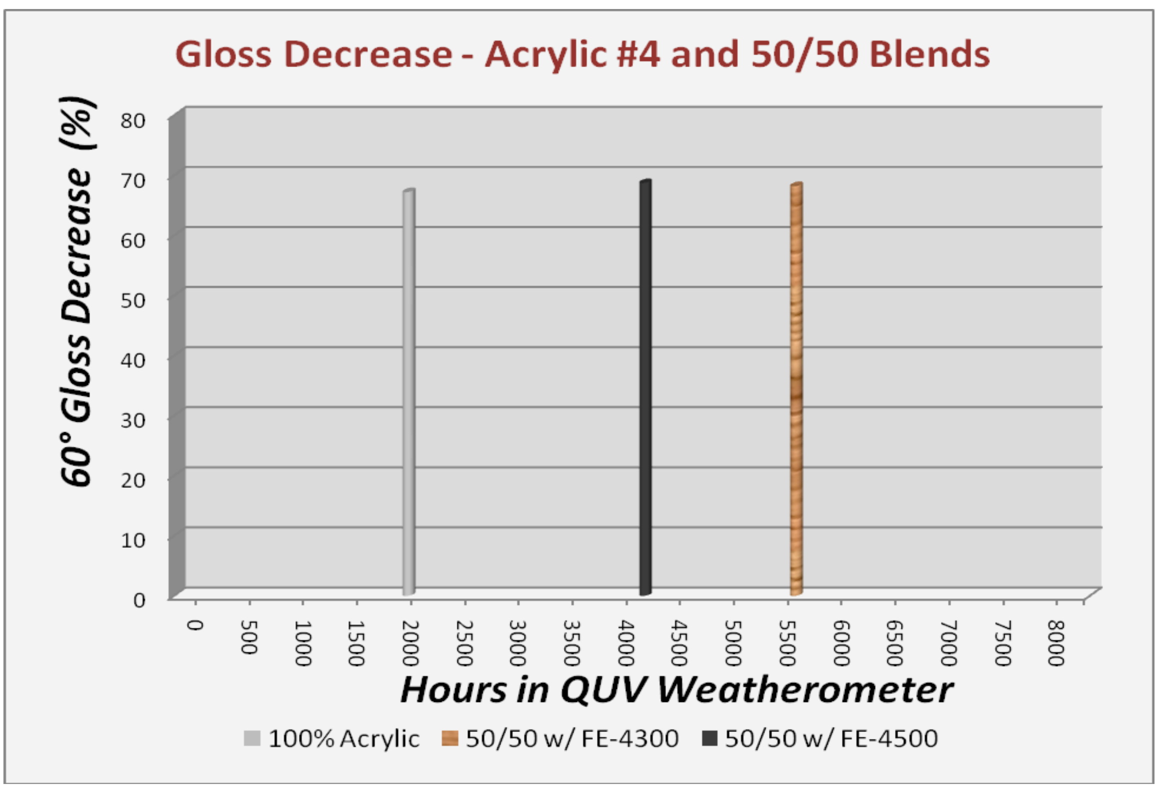


*Figure #5: QUV Results of Acrylic #4 and 50/50 Blends of LF Emulsions*

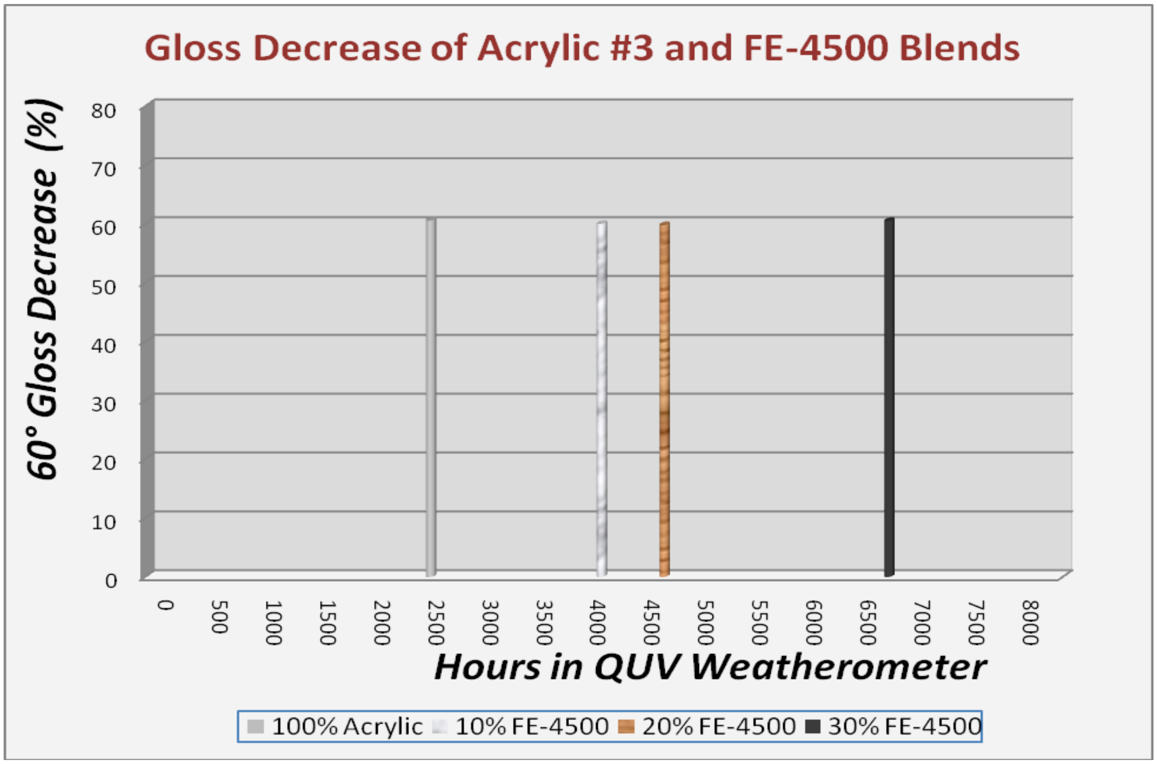


*Figure #6: QUV Results of Acrylic #3 and FE- 4500 Blends*

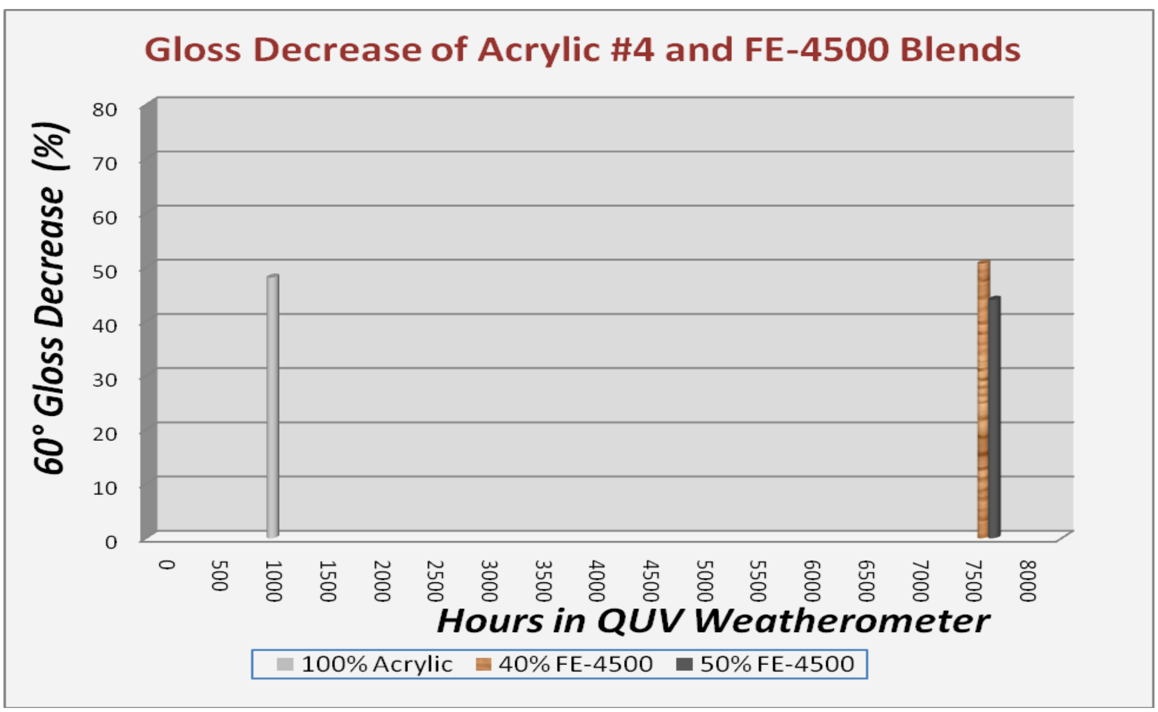


*Figure #7: QUV Results of Acrylic #3 and FE-4500 Blends*

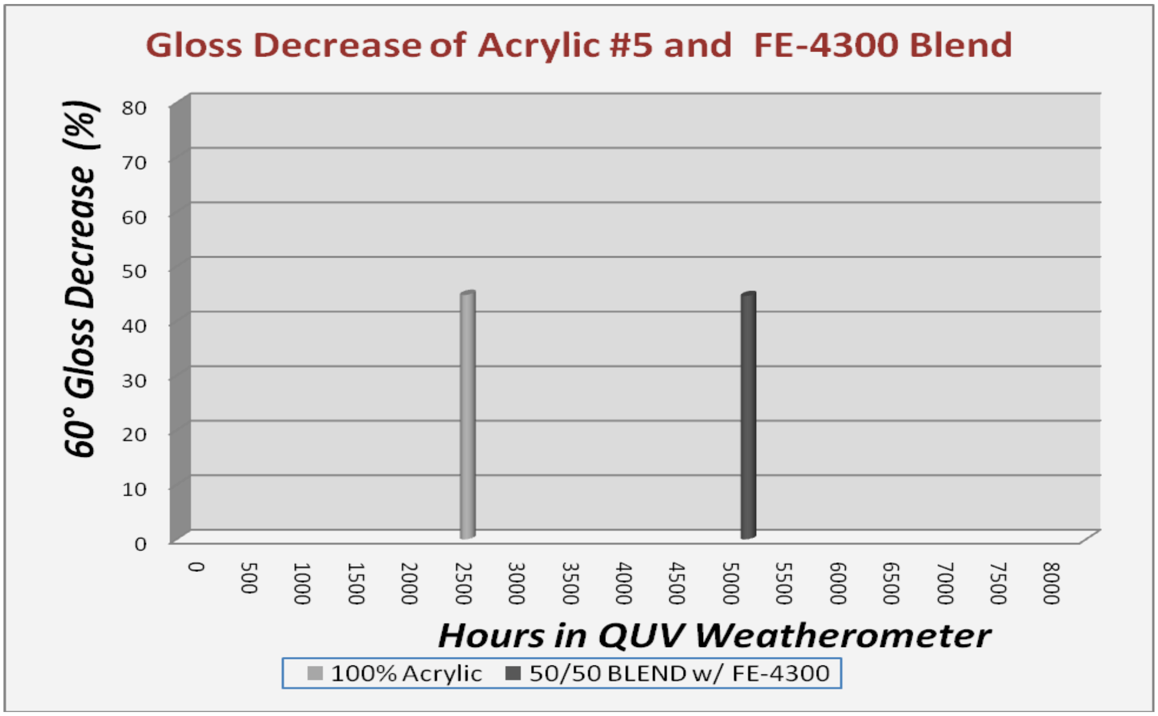


*Figure #8: QUV Results of Acrylic #5 and FE-4300 Blend*

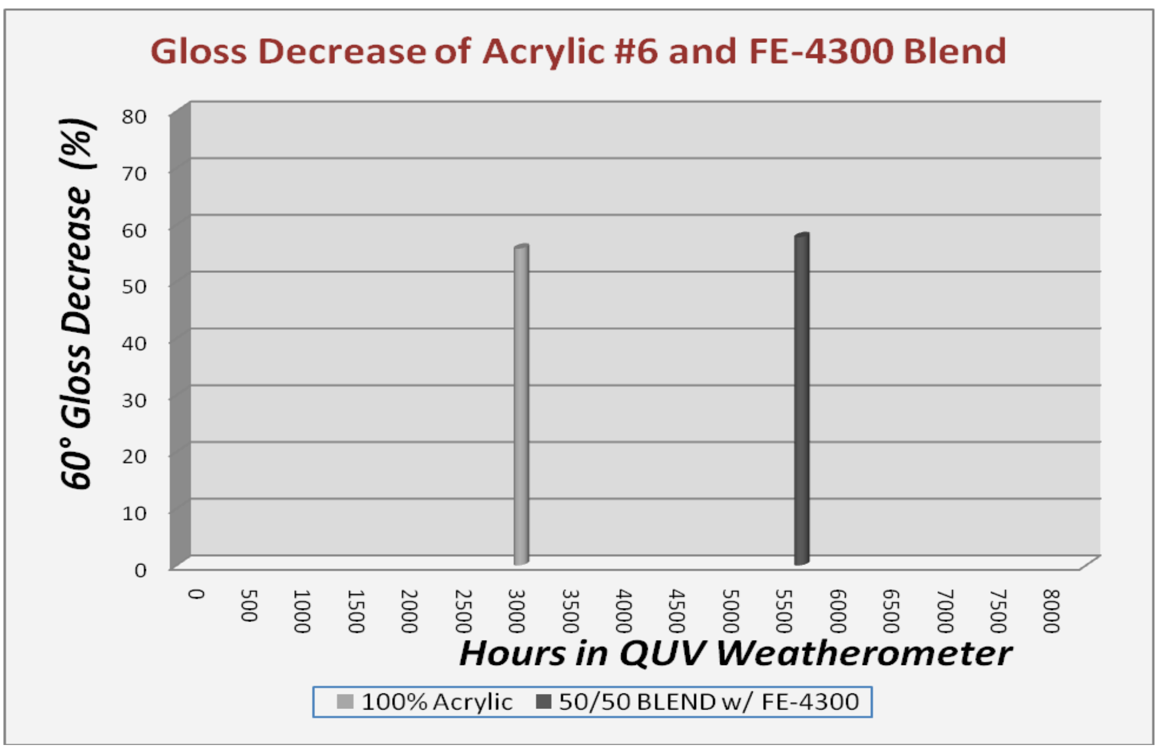


*Figure #9: QUV Results of Acrylic #6 and FE-4300 Blend*

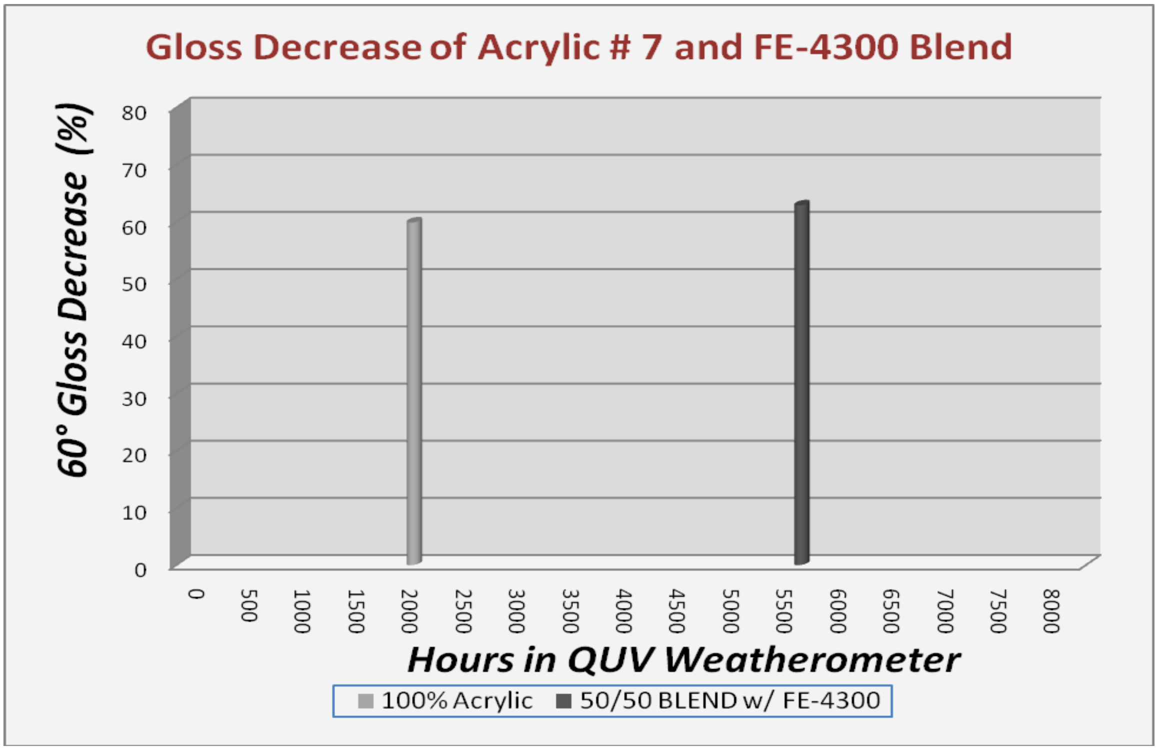


*Figure #10: QUV Results of Acrylic #7 and FE-4300 Blend*

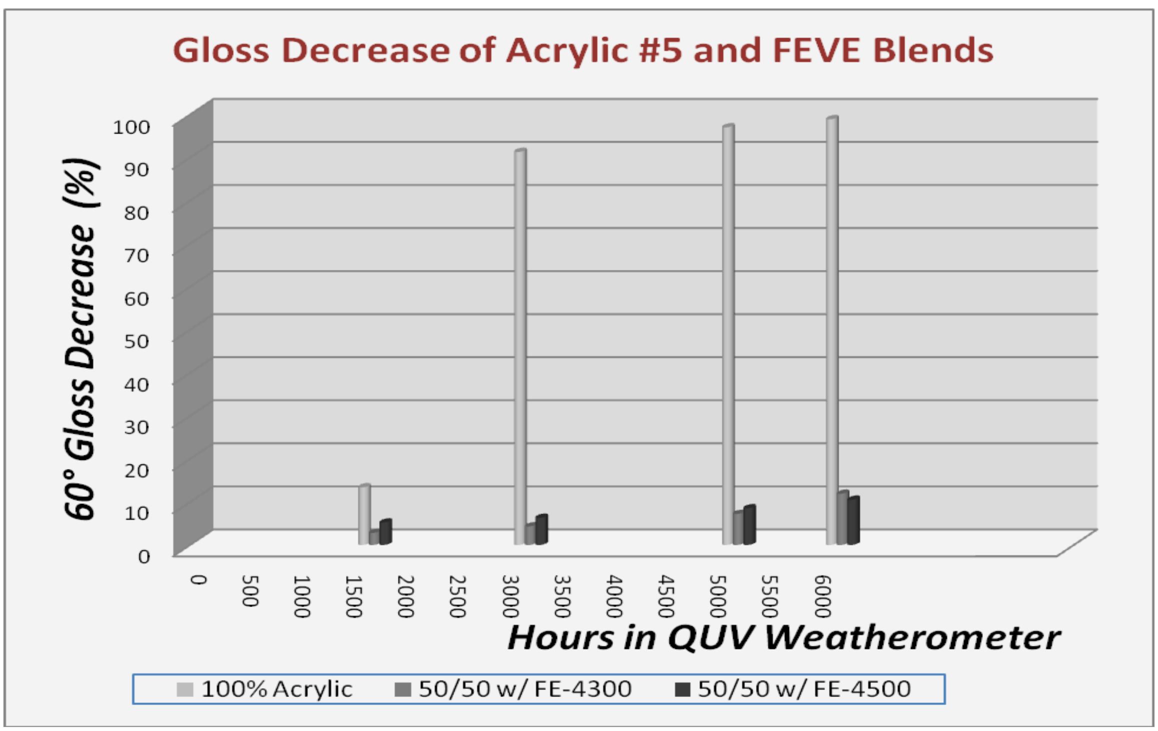


*Figure #11: QUV Results of Acrylic #5 and 50/50 Blends of LF Emulsions*

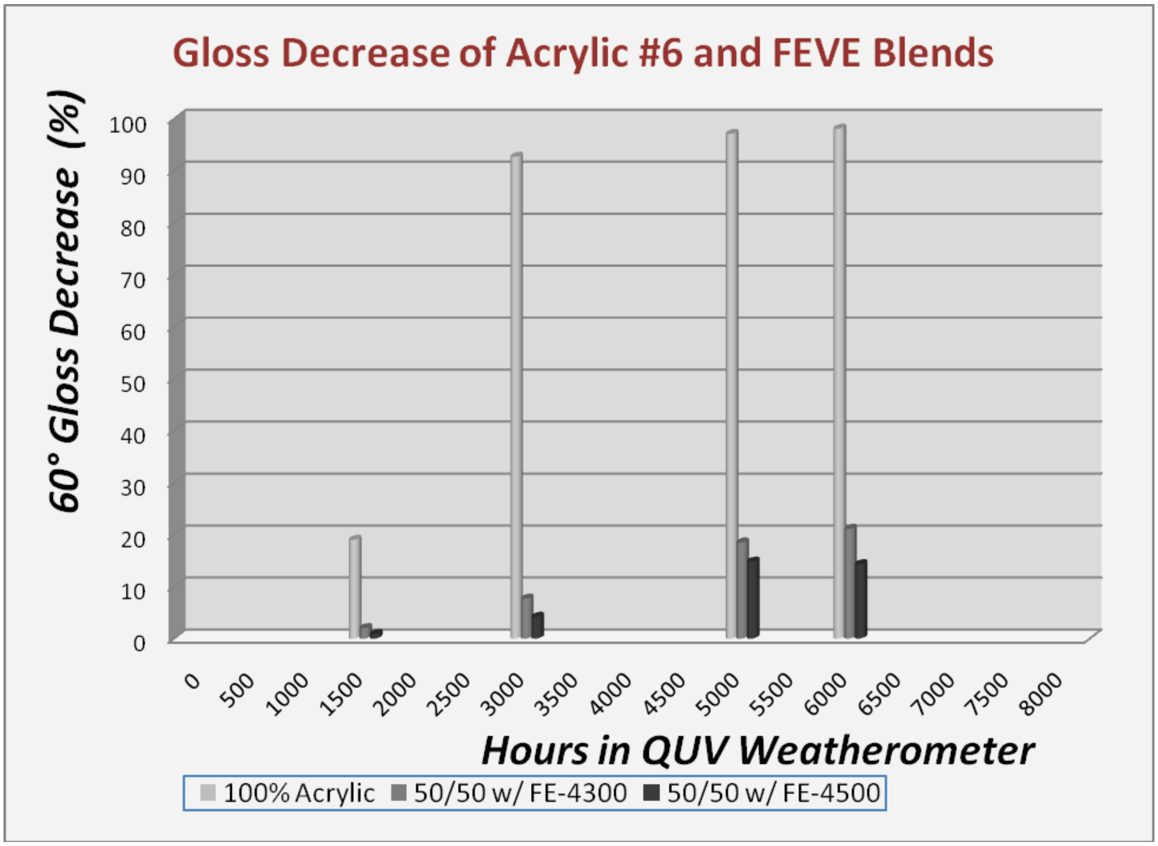


***Figure #12: QUV Results of Acrylic #6 and 50/50 Blends of LF Emulsions***

**References**

1. M. Yamabe, "Fluoropolymer Coatings," OrganofluorineCchemistry, 397 (1994).

2. S. Munekata, "Fluoropolymers as Coating Materials," Progress in Organic Coatings, 16, 113-134 (1994).

3. T. Takayanagi, M. Yamabe, "Progress of Fluoropolymers on Coating Applications Development of Mineral Spirit Soluble Polymer and Aqueous Dispersion," Progress in Organic Coatings, 40,185-190 (2000).