Title: Effect of Fluoropolymer Architecture on the Exterior Weathering of Coatings

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ABSTRACT:

Fluoropolymers of several different types (poly(vinylidene fluoride), alternating copolymers, perfluorinated ether polyols) are commercially available as coatings resins. While all these resins share certain chemical properties (e.g. hydrophobicity), the performance in the area of weathering depends crucially on details of the molecular structure. A number of recent studies have examined the mechanisms by which different fluorinated coatings weather, and have highlighted some ways in which the molecular structure affords photochemical protection that is not possible with conventional polyester or polyurethane coatings. The most weatherable fluoropolymer systems not only meet the most stringent worldwide industry specifications for high performance architectural and protective topcoats, but have demonstrated over thirty years chalk and fade resistance in south-facing Florida exposures.

High performance fluoropolymer resins for coatings applications have been commercially available for nearly forty years[1]. While it is sometimes convenient to consider fluoropolymers as a class, the differences between fluoropolymers are often more important than the similarities. It is in fact the unique molecular structure of each resin which leads to the special properties that render it useful.

Considering features common to fluoropolymers (at least, carbon-based fluoropolymers), the strength of the C-F chemical bond undoubtedly contributes to the excellent chemical and electrochemical resistance of many fluoropolymers. Fluoropolymers are often also associated with hydrophobicity and low surface energy. In fact the lowest surface energy fluoropolymers achieve this property through a high concentration of trifluoromethyl (CF_3) groups at the surface[2]. Fluorinated acrylics—copolymers of normal acrylic monomers with monomers possessing perfluorinated side chains—are an example of this class of fluoropolymer. These particular materials can be highly oleophobic and stain resistant, and therefore useful as fabric treatments and anti-graffiti coatings.

Those fluoropolymers designed for use in exterior topcoats require specialized chemical and UV resistance properties. As with other coating properties, the performance in the area of weathering depends crucially on details of the resin molecular structure. Those details turn out to vary significantly among the different kinds of fluoropolymers proposed for use in highly weatherable coatings.

A number of recent studies have examined the mechanisms by which different fluorinated coatings weather, and have highlighted some ways in which the molecular structure affords photochemical protection that is not possible with conventional polyester or polyurethane coatings. This paper will examine the effect of molecular architecture on exterior weatherability for four different types of fluoropolymer. A number of literature mechanistic studies of these materials will be reviewed, which are illustrative of degradation routes in commercial exterior coatings. Then, we present some new data from our laboratory, which illustrates particularly the kind of protective effects that can be obtained from thermoplastic PVDF coatings, leading to excellent color retention in South Florida exposure tests.

Important mechanisms of degradation of fluorinated coatings in the outdoors.

Among the mechanisms for coating degradation that have been identified as relevant for fluoropolymer coatings, are resin main chain or side chain oxidation, photooxidation of non-fluorinated crosslinks or adjuvant resins, hydrolytic or other non-photochemical attacks on crosslinks or the resin main chains, and effects associated with specific pigment grades.

    A. Resin main chain oxidation—example of FEVE resins.

Many conventional polyester or polyurethane type coatings are built up using diol or polyol type segments as an integral part of the molecular structure. For purely aliphatic systems, which are normally preferable when outdoor weatherability is sought, coating

network degradation can often begin at sites in the immediate vicinity of the linking groups formed from the original diol hydroxy group (ether, ester or urethane). In particular, hydrogens in the alpha position relative to the diol oxygen are highly susceptible to abstraction from any free radical species which may be in the coating[3] (Figure 1). These kinds of hydrogen abstraction events can lead to the formation of hydroperoxides on the polymer backbone, which in turn lead to chain scission as well as the generation of new radical species that can start the degradation process in other locations.
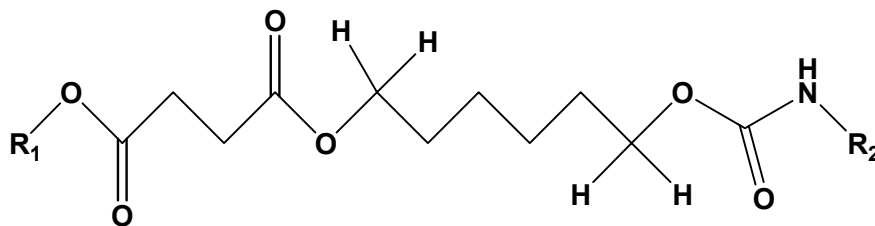

Figure 1. Generalized structure of an aliphatic polyester-urethane. The diol hydrogens in the alpha position relative to the ester and urethane oxygens are shown.

In so-called "FEVE" (fluorinated ethylene vinyl ether) resins, fluorinated monomers and vinyl ethers are copolymerized in an alternating fashion[4]. (Figure 2) By using vinyl monomers containing pendant functional groups, e.g. hydroxyl groups, functional FEVE resins can be made and used with conventional crosslinkers like polyisocyanates and melamines, in 2-component crosslinked formulations. It has been reported in a series of studies by Gardette and co-workers[5] that the hydrogen abstraction rate at the vinyl ether alpha position is greatly reduced relative to the rate for non-fluorinated polymers. This reduction is attributed to the electron withdrawing effects of the fluorines.
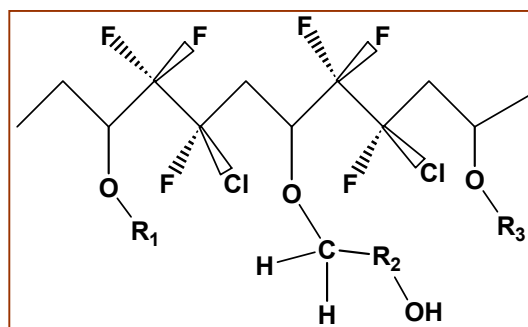
Figure 2. Schematic structure of FEVE resin made with chlorotrifluoroethylene as the fluorinated monomer.

This protective effect is limited to those atoms immediately adjacent to the fluorine. Urethane and ether linkages generated through crosslinking reactions are still subject to the same degradation processes as non-fluorinated thermoset coatings and would presumably need to be protected by other mechanisms, e.g. by using additives such as hindered amine light stabilizers (HALS).

B. Resin side chain oxidation—example of fluorinated acrylates.

In a few instances, the electronegativity of fluorine may actually destabilize neighboring C-H bonds, with respect to their susceptibility to hydrogen abstraction. Such an effect has been reported for some acrylic copolymers, made from monomers possessing fluorinated side chains[6]. The rate of hydroperoxide formation during irradiation, attributed to hydrogen abstraction at the side chain alpha position, was found to be greater when fluorinated side chains were present (fluorines in the alpha or beta position with respect to the hydrogen), compared to the case of a butyl group side chain (Figure 3). As with other kinds of acrylics, the decomposition of the hydroperoxides formed along the side chains can eventually lead to other kinds of more dramatic degradation (chain scission, polymer "unzipping", or crosslinking).

Figure 3. Fluorinated methacrylate monomers with side chains reported to have lower stability than butyl side chains (Reference 6).
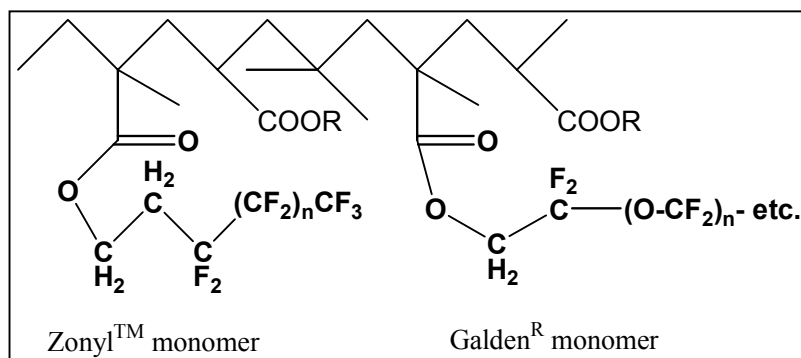

C. Photooxidation of non-fluorinated crosslinks—example of perfluorinated polyethers

Another class of fluorinated resins which has become available in recent years, is based on perfluoroether oligomer ("ZDOL") diols:

$$HO-CH_2CF_2-O-(CF_2CF_2)_x-O-(CF_2)_y-O-CF_2CH_2-OH$$
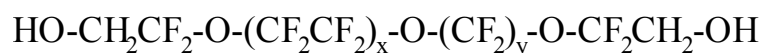
Coatings made with these materials reportedly have very low surface energies, but the weatherability has been reported to be poor[7]. This might be due in part to photochemical attack on unprotected secondary hydrogens at the alpha position relative to the non-fluorinated diol chain ends, as described in the previous section. However, Luda et al. have postulated a different degradation mechanism to explain the poor weatherability of this class of resins[8]. They identify the non-fluorinated crosslinker region of the coating network as the locus of photodegradation effects. For instance, when IPDI trimer is used as the crosslinking agent, hydrogen abstraction at the position alpha to the urethane nitrogen is identified as the system's weak point (Figure 4):

Figure 4: Hydrogens adjacent to nitrogen which are main attack points for IPDI-crosslinked perfluoroether urethane coatings, according to reference 8.
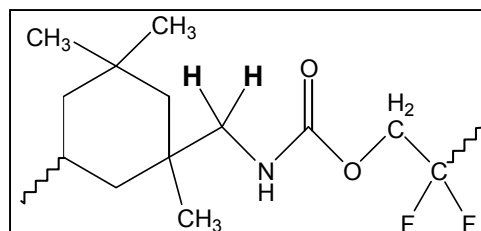
Regardless of the relative contribution of the two degradation mechanisms (i.e. hydrogen abstraction occurring at the aliphatic or fluorinated side of the crosslink), the use of HALS was found to significantly improve the weatherability of the ZDOL-based coating, as measured by the retention of film mechanical properties in accelerated tests.

The same mechanism identified by Luda et al. should in principle be operative in other classes of fluorinated polyols, crosslinked with non-fluorinated isocyanates or melamines, e.g. FEVE resins. In these systems as well, the use of HALS should theoretically improve the system weatherability.

D. Photooxidation of non-fluorinated adjuvant resins—example of PVDF coatings

The beneficial protective effect of the fluorine bond is most dramatically visible, however, in poly(vinylidene fluoride) (PVDF) resins. The structure of PVDF consists of alternating $-CF_2-$ and $-CH_2-$ units:
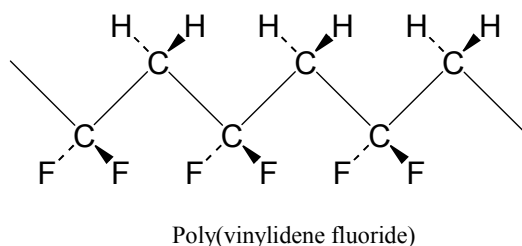

Poly(vinylidene fluoride)

Figure 5. Structure of PVDF, or poly(vinylidene fluoride).

In the PVDF structure, every C-H bond is adjacent to four C-F bonds. The net result is a resin that is completely photochemically inert[9], as well as electrochemically extremely stable. At the same time, the alternating structure gives the PVDF chain units a strong dipolar character. This confers excellent compatibility of the resin with a variety of other polymers such as poly(methyl methacrylate) (pMMA). It also means that low molecular weight ketones and esters can be used as active or latent solvents for the resin, so that it can be used easily in liquid coating formulations.

In fact PVDF coatings have been available commercially since the mid-1960s[10]. Typical commercial formulations contain 70-80 % by weight PVDF in the coating binder, with the remainder of the binder being some sort of compatible acrylic such as pMMA. The acrylic resin is added because of the inertness of the PVDF molecule, in order to improve the pigment wetting and coating adhesion. Thus it functions as an "adjuvant" or helper resin. While the PVDF fluoropolymer is highly resistant to any kind of outdoor degradation, the acrylic component might be expected to be more susceptible to eventual photochemical attack. However, premium PVDF coatings contain no more than 30 weight percent acrylic on binder, limiting the impact of any degradation if it does occur.

The photooxidation of acrylic resins, including the acrylic resins in commercial PVDF coatings can be monitored in several different ways, but each of them has some limitations. The method that has been perhaps most widely used is to look directly for

photooxidation products, such as carboxylic acid groups, in the infrared or Raman spectrum[11]. This method has the advantage of directly providing chemical information about the sample— and in some cases, more specifically, about the exposed surface of the sample. However, it can only be used to identify those chemical species that remain in the coating, and which have characteristic isolated vibrational bands.

Since low molecular weight degradation products may volatilize, a complementary method is simply to monitor the mass loss of the coating due to the exposure[12]. While it does not provide chemical information, the weight loss method can be valuable especially in cases where little chemical change in the coating is apparent, for instance when the rate of coating erosion is at least as fast as the rate of chemical degradation. In one study in our laboratory of several weathered PVDF coatings, this was apparently the situation— only small changes were observed in the infrared spectra of a series of white coatings aged 10-15 years, yet they had suffered a substantial loss of gloss[12]. Unfortunately, the mass loss method could not be used in this particular case, because accurate initial weights for the samples were not available. This illustrates another disadvantage of the weight loss method: the experimenter must have the foresight to record initial weights, and to assure that samples do not suffer physical damage or accretions, which could affect the mass, during the entire duration of the test. Because of these limitations, mass loss measurements are best suited for laboratory accelerated tests, rather than outdoor tests that could last for years.

A recent innovative method, used to study acrylics, is to use chromatography techniques to directly measure the evolution of the molecular weight distribution during exposure[13]. Both unzipping and crosslinking reactions have been reported for different acrylics, depending on the composition. While one is able to measure in this way only the distribution of the soluble fraction, the relative size of the soluble and insoluble fractions can in principle also be measured either by using peak heights, or through direct gravimetric methods.

    E. Hydrolytic or other non-photochemical attacks on resins or crosslinks.

Besides photochemical oxidation processes involving, for instance, hydrogen abstraction, other chemical processes can occur which degrade fluoropolymers and particularly crosslinked networks. Such processes could include the hydrolysis of ether linkages formed from melamine crosslinking, or urethane linkages from isocyanate crosslinking. For a non-fluorinated polyester-melamine crosslinked system, the relative rates of photochemical and non-photochemical degradation have recently been quantitatively measured by Van Landringham et al.[14], and the effect of purely hydrolytic effects was shown to be substantial.

Accelerants of hydrolysis and other non-photochemical processes can include low pH from the environment (acid rain), residual catalysts in the coating, and heat—such as might be generated when a dark colored paint sits directly in the sun on a warm day. Since many of the crosslinked coatings are based on low molecular weight resins, and depend crucially on crosslinks to achieve coating performance, the loss of crosslink

density could have dramatic effects on coating properties. Of course, the degradation effects can also be retarded at least for a time, by having a high enough crosslink density to help exclude water and other agents from the bulk of the binder.

While many kinds of crosslinks can be acid sensitive, most fluoropolymers themselves used in coatings are inherently acid resistant. PVDF, for instance, is so acid resistant that the neat resin is used for CPI (chemical processing industry) applications involving strong mineral acids. PVDF is only attacked chemically under extremely strong basic conditions, which would not be expected in exterior coating environments.

In contrast to crosslinked coatings, thermoplastic coatings based on semi-crystalline resins-- such as commercial PVDF coatings-- should generally be highly resistant to the effects of hydrolytic degradation processes. Not only are the resins themselves inherently resistant to the loss of properties through hydrolysis, but the advantageous properties of the coating are enhanced through the crystalline associations of the component fluoropolymer[15]. As with thermoset crosslinks, the PVDF crystalline structures have excellent barrier properties, keeping water, oxygen and other destructive agents away from both the coating bulk and the substrate layers underneath the coating. At the same time, being non-covalent in nature, the crystalline structures have some limited ability to reform themselves, so that the loss of network structure is much less of a possibility.

F. Pigment effects—example of PVDF coatings

For highly weatherable paints, it is essential that high performance pigments are used. These pigments should not only have exceptional inherent color stability throughout the coating application, curing, and weathering processes, but additionally should not promote any breakdown of the coating binder. For PVDF coatings, certain inorganic pigments and particularly mixed metal oxides have been used as pigments of choice for many years. For some formulations, masstone PVDF paints made with mixed metal oxide pigments have gone over thirty years with minimal color change (Figure 6).
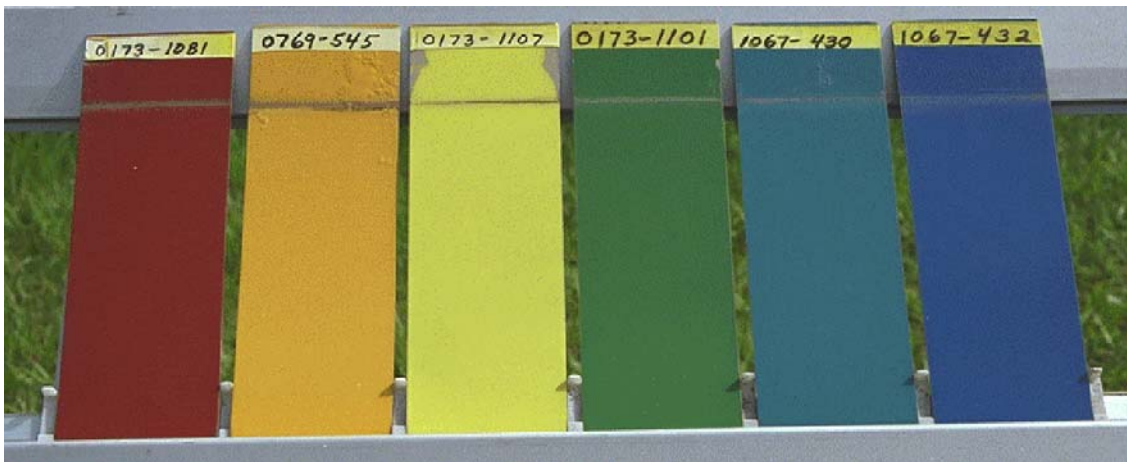

Figure 6. Some KYNAR 500® panels on exposure in Florida, circa 1998. The number at left is the month and year the exposure first went out; the other number is a serial number. The top section is covered with a flap, and the bottom section is exposed to the elements at 45 degrees south.

To make light colored paints, rutile titanium dioxide is widely used because of its great hiding power, chemical stability, and cost effectiveness. However, for the most weatherable paints, grade selection is critical since TiO_2 crystals, like many other inorganic materials, are inherently photochemically active[16]. In these materials, highly reactive radical species such as OH radicals can be generated photolytically at the pigment particle surface, when the absorption of light inside the pigment particle forms electron-hole pairs. Those electron-hole pairs which avoid recombination can migrate to the particle surface, and then react there with species such as adsorbed water. To reduce the tendency to generate surface radicals, various inorganic treatments are applied to the surface of the pigment particles.

For coating binders with low outdoor weatherability, the addition of rutile TiO_2 almost always increases the weatherability of the coating, since the effect of UV absorption by the pigment generally outweighs the photocatalytic effects. However, the more inherently weatherable the binder, the more important it is to carefully choose the grade of TiO_2 used in the coating[17]. Figure 7 shows SEM micrographs of the surface of a white PVDF coating, made with a newer "universal grade" of TiO_2 said to have good weatherability, after two and five years Florida exposure. At the two year mark (left), some pitting of the coating around pigment particles can be observed. This kind of pitting was not observed for a control coating made with the standard recommended most weatherable grade. For the universal grade, this pitting was subsequently observed to lead to premature gloss loss in the coating, with a completely degraded coating surface after five years Florida exposure (right).
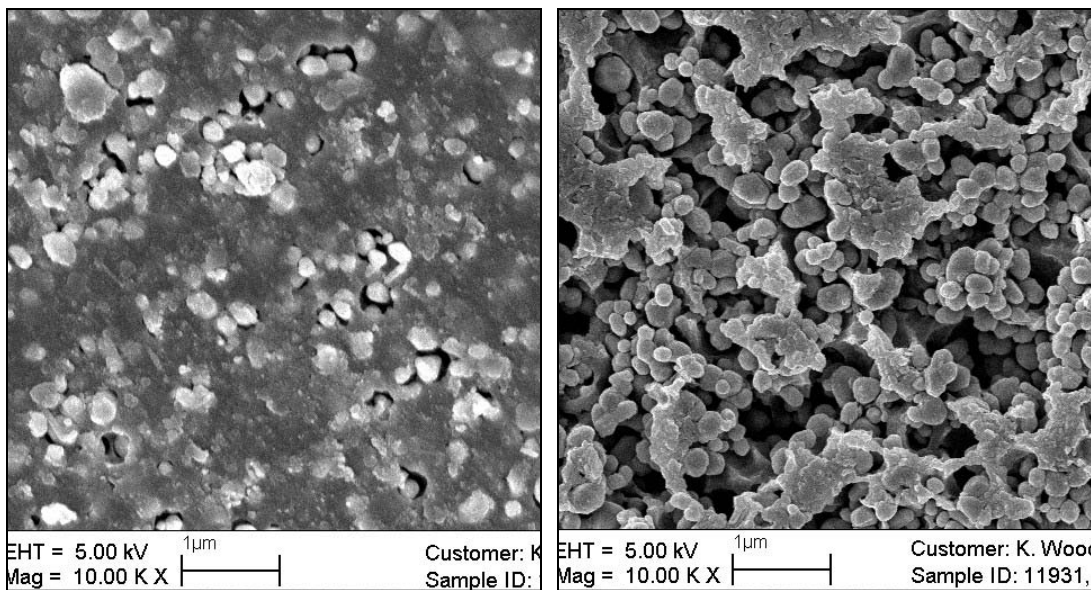

Figure 7. SEM micrographs of white PVDF coatings made with a "universal grade" TiO_2 pigment, after 24 and 57 months south Florida exposure.

It should also be noted that for these two coatings, a ranking of the coating weatherability in QUV-B accelerated testing gave results which were opposite from the Florida

performance (Figure 8). The universal grade pigment had almost 100% gloss retention after 10,000 hours (15 months) QUV-B exposure, while some gloss was evident for the case of the highly weatherable grade. In this case, the accelerated testing method gives a "false positive" result—i.e., it suggests, falsely, that the coating made with the universal grade pigment will be highly weatherable in the outdoors. The mechanistic reason for this reversal in the accelerated test is still under investigation. It could potentially be related to differences in the relative light intensity between the QUV-B bulbs and the solar spectrum, particularly in the spectral region near 400 nm where the TiO_2 band gap lies. Another possibility may be moisture effects—since in the QUV-B testing protocol used, the light and condensation humidity cycles are anti-correlated.
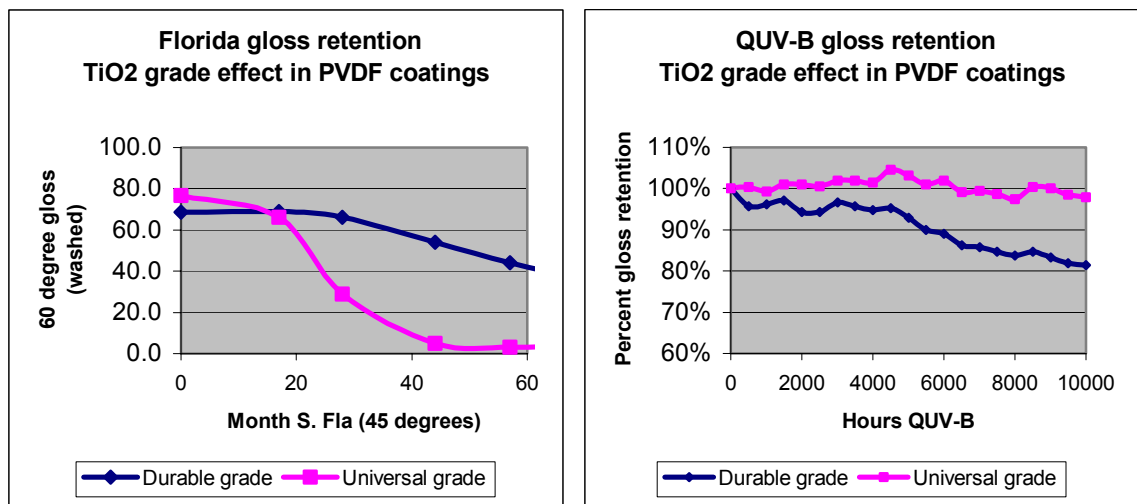

Figure 8. Comparison of Florida gloss retention and QUV-B retention, for two different grades of TiO2.

Protective effects in PVDF coatings

As was mentioned previously, the crystalline structures in PVDF coatings are in a state of dynamic equilibrium. They have some limited ability to rearrange and reform themselves over time, due to the relatively low glass transition temperature (T_g) of the amorphous phase (pure PVDF has a T_g of about –40 ºC; since it is typically used with high T_g acrylics, the blend T_g is often around room temperature). This means that local stresses generated in the film can be relieved, and coating integrity maintained, much more easily than in a thermoset system where crosslinks enforce a degree of network rigidity. We believe that the ability of PVDF coatings to protect not only substrate materials, but also other components of the coating itself, can be attributed largely to the barrier properties generated by these labile crystalline structures.

One example of this protective effect can be noted in a series of panels, now fifteen years old, comparing PVDF coatings with color-matched polyester powder coatings. As might be expected, the non-fluorinated polyester coatings showed serious color fade and chalking, after just a few years Florida exposure (Figure 9).
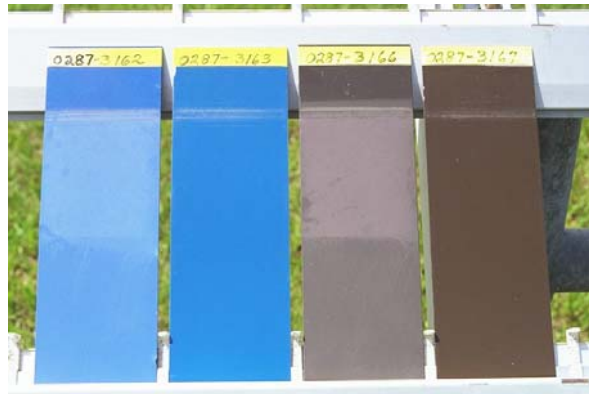
Figure 9. Color-matched polyester (left) and PVDF (right) panels after 12 years Florida exposure. Top strip: covered portion showing original color; middle: unwashed portion of panel showing dramatic chalking and color fade of polyesters; bottom: washed portion.

The protective effect of the PVDF coatings is clearly seen in the same series, when comparing masstone paints of the same formulation, with and without an additional PVDF clearcoat. The degree of color fade in the PVDF color coat is reduced even more by having the PVDF topcoat over it—typical color change values are only about delta E =1—i.e. barely perceptible to the eye—after fifteen years (Figure 10).
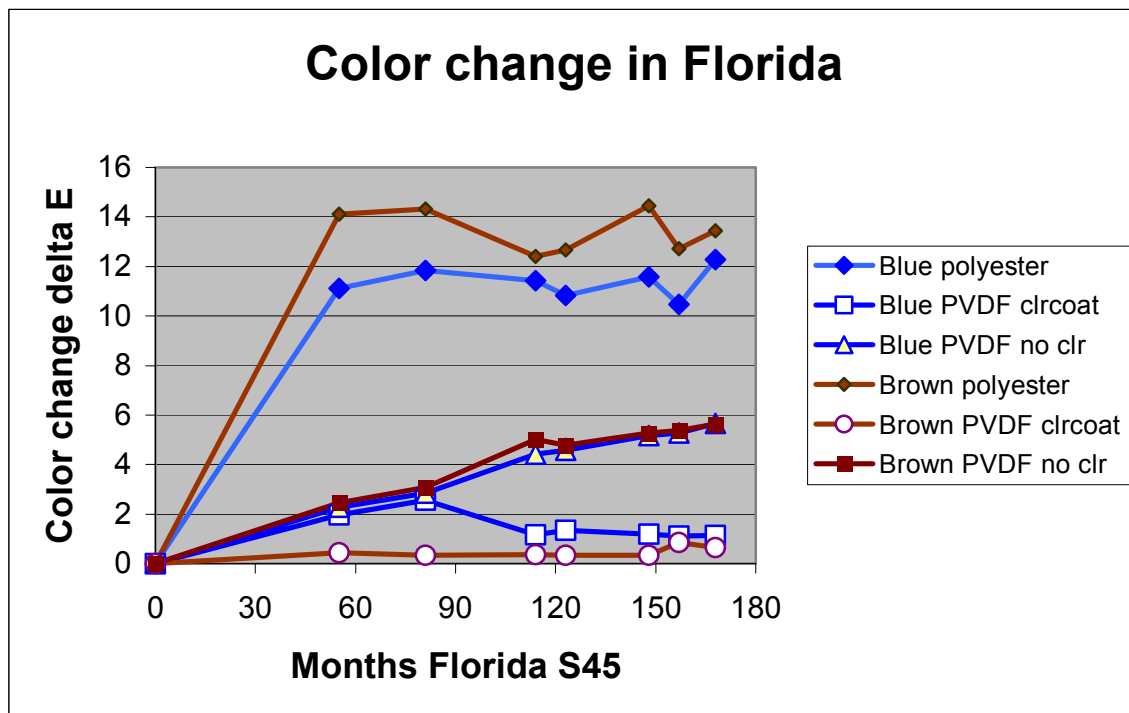

Figure 10. Color change of PVDF masstone coatings, with and without a PVDF clearcoat, in Florida. Results for color-matched polyester powder coatings are shown for comparison purposes.

Another study, which followed coating erosion during 15 year Arizona exposure by directly measuring the coating thickness, shows evidence for PVDF's ability to protect the acrylic component within the coating itself. Photodegradation of the acrylic inside

the coating, with eventual volatilization, would be expected to lead to loss of coating thickness over time[18]. However, within the level of experimental uncertainty, a series of PVDF coatings showed <u>no</u> loss of film thickness during this extended period (see Table).

Conclusions

A number of highly fluorinated polymers are inherently highly weatherable, and in particular are resistant to hydrogen abstraction which leads to direct photooxidation of the fluoropolymer structure. However, in most commercial coating systems, non-fluorinated resin components are also present, being introduced either as crosslinkers or adjuvant resins. These non-fluorinated binder components can degrade according to mechanisms identified in non-fluorinated coating systems (polyester or acrylic based). It therefore remains important in all these systems to reduce the access to the bulk of water, molecular oxygen, and other destructive species. In crosslinked systems, some limited degree of protection for these less weatherable components may be provided by high crosslink density, until the integrity of the crosslinked network begins to be compromised.

By contrast, thermoplastic fluoropolymer systems such as PVDF coatings benefit from the semi-crystalline structure of the PVDF resin. This structure provides mechanical strength and barrier properties similar to conventional crosslinked coatings, but also has some ability to rejuvenate itself, so that the effects of any gradual damage to other coating components do not lead to catastrophic coating failure. As a result, protection is provided both for other components of the PVDF coating, and for the coating substrate. The most weatherable fluoropolymer systems not only meet the most stringent worldwide industry specifications for high performance architectural and protective topcoats, but have demonstrated over thirty years chalk and fade resistance in south-facing Florida exposures.

[1] R.A. Iezzi, Fluoropolymer Coatings for Architectural Applications, Modern Fluoropolymers (Wiley, 1997), p. 14.

[2] T. Shimizu, Fluorinated Acrylic Ester Polymers, Modern Fluoropolymers (Wiley, 1997), p. 513.

[3] J.-L. Gardette, B. Hailhot, F. Posada, A. Rivaton, and C. Wilhelm, Macromol. Symp. 143 (1999) 95-109.

[4] T. Takakura, CTFE/Vinyl Ether Copolymers, Modern Fluoropolymers (Wiley, 1997), p. 557.

[5] J.-L. Philippart, F. Posada and J.-L. Gardette, Polymer Degradation and Stability 53 (1996) 33-37; F. Posada and J.-L. Gardette, Polymer Degradation and Stability 70 (2000) 17-29.

[6] N.S. Allen, C.J. Regan, W.A.E. Dunk, R. McIntyre and B. Johnson, Polymer Degradation and Stability, 58 (1997) 149-157. It should be noted however that the rate of hydrogen abstraction from 2-ethyl hexyl side chains (having a tertiary hydrogen) is even greater; cf.O. Chiantore, M. Lazzari, M. Aglietto, V. Castelvetro, and F. Ciardelli, Polymer Degradation and Stability 67 (2000) 461-467.

[7] T. Temchtcko, "New Developments in Perfluoropolyester Resins Technology", Proceedings of 26th International Conference in Organic Coatings, July 2000, Athens, Greece (Institute of Materials Science, New Paltz, New York USA), 357-372.

[8] M.P.Luda, G. Camino, E. Laurenti, S. Novelli, T. Temtchenko and S. Turri, Polymer Degradation and Stability 73 (2001) 387-392.

[9] J.-L. Philippart, N. Siampiringue, A. Strassel and J. Lemaire, Makromol. Chem.. 190 (1989) 413-418.

[10] The Pennsalt Corporation introduced the coatings grade KYNAR 500® PVDF resin in 1965.

[11] See, for instance, J.L. Gerlock, C.A.Smith, V.A. Cooper, T.G. Dusbiber and W.H. Weber, Poly. Degr. Stab. 62 (1998) 225-234; G. Ellis, M. Claybourn and S.E. Richards, Spectrochimcia Acta 46A(2) (1990) 227-241.

[12] K.A. Wood, C. Cypcar and L. Hedhli, J. Fluorine Chem. 104 (2000) 63-71.

[13] O. Chiantore and M. Lazzari, Polymer 42 (2001) 17-27.

[14] M.R. VanLandringham, N. Tinh, W.E. Byrd, and J.W. Martin, Journal of Coatings Technology 73(923) (2001) 43-50.

[15] S.R. Gaboury and K.A. Wood, "Tailoring Coating Properties Through Control of PVDF Copolymer Phase Behavior", Paper 17, Fluorine in Coatings IV Conference Proceedings (Paint Research Association, Teddington UK 2000).

[16] M.P. Diebold, Surface Coatings International 1995 (6) 250-256; 1995 (7) 294-299.

[17] M.P. Diebold, "Unconventional Effects of TiO2 on Paint Durability", Proceedings of 5th Nurnberg Congress 371-389 (Paint Research Association, Teddington, UK).

[18] N.S. Allen, C.J. Regan, W.A.E.Dunk, E. McIntyre and B. Johnson, Polymer Degradationa and Stability 58 (1997) 149-157.

Table: Comparison of coating thickness for KYNAR 500® coatings exposed in Arizona for 15 years:

Panel ID	Coating average thickness, in microns	
	Initial thickness	Final thickness
Control panel: no exposure	22.1 ± 1.5	20.3 ± 0.5
1997A	18.8 ± 1.8	18.5 ± 1.3
1998A	20.6 ± 1.0	20.3 ± 1.3
1999A	21.1 ± 1.5	20.1 ± 1.0
2002A	19.3 ± 1.0	18.3 ± 0.8
2003A	21.1 ± 2.0	19.0 ± 1.0
2004A	19.0 ± 1.3	18.0 ± 0.5