20-YEAR COLOR LIFETIMES FOR ARCHITECTURAL RESTORATION COATINGS: THEORY AND REALITY

by **Kurt Wood**,
Arkema, Inc.

Baked solventborne poly(vinylidene fluoride) (PVDF) architectural finishes on metal celebrate their 50-year anniversary in 2015. Their multi-decade service life has been validated not only through Florida weathering testing on metal panels, but also through the weathering of actual building components throughout the world. Solventborne air-dry PVDF systems for field-applied touch-up, repair, and restoration were developed in the 1980s, and have now also demonstrated more than 20 years of excellent south Florida color retention when used in conjunction with weatherable inorganic pigments. Similarly, waterborne PVDF/inorganic pigment systems developed in the 2000s have now surpassed 10 years of excellent weatherability in Florida. In this article, strategies are discussed for attaining 20-year color retention lifetimes for PVDF-based coatings incorporating other types of pigments, including flake pigments and organic pigments, in both solvent- and waterborne formulations.

Presented at the 2015 CoatingsTech Conference, sponsored by the American Coatings Association, March 9-11, in Louisville, KY.

Photos on this page courtesy of Arkema, Inc.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is universally known within the architectural community as one of the world's most weatherable coating resins.[1] The first PVDF resin grade for coatings, Kynar 500® PVDF, is celebrating its 50th anniversary this year, having been introduced commercially in 1965 by the Pennsalt Corporation[2] (known today as Arkema Inc.). Architects and specifiers have long recognized that PVDF-based coatings not only have excellent long-term color retention and chalk resistance, but also very good resistance to wind-driven sand, to chemical attack and corrosion, and to algae and fungal growth.

Commercial PVDF-based architectural topcoats, or finishes, typically contain between 70–80 wt% PVDF resin on total binder weight, with the balance of the resin being a compatible acrylic. In one common application, used for metal wall or roof applications, the formulation is based on a nonaqueous dispersion of the PVDF resin, in combination with acrylic resin, pigments, and latent solvents. This formulation is applied onto a metal substrate in a continuous coil coating process at high speeds, followed by a very short high temperature bake at 240–250°C peak metal temperature. A second common application involves spray-applied coatings on aluminum extrusions, baked at somewhat lower temperatures, which can be used for window profiles and other architectural elements. In recent years, other types of PVDF-based coatings have also been developed, including powder coatings, air-dry solution coatings, and waterborne PVDF-acrylic hybrid dispersions.[3] Many of the newer approaches allow for the application of durable PVDF-based coatings under field-applied and low temperature bake OEM conditions.[4]

The performance potential of PVDF technology is now validated by nearly 50 years of outdoor exposures, not only on test panels but on buildings around the world. In North America and many other parts of the world, the American Architectural Manufacturers Association (AAMA) voluntary standards[5] are commonly used by architect-engineers and other designers to specify building components such as window profiles. The "Superior" AAMA standard for aluminum finishes, AAMA 2605, includes requirements for gloss and color retention, and chalk resistance, after 10 years of south Florida weathering at a south-facing 45° angle.[6]

Since 10-year south Florida exposure (at south-facing 45°) is much more severe from a UV standpoint than vertical exposure at higher latitudes, 10-year Florida color changes provide a useful metric against which to assess the suitability of an architectural coating finish. However, PVDF-based finishes can provide color retention and chalk resistance for even considerably longer times than that. As one example, *Figure* 1 shows the 17-year south Florida color retention of a series of bronze-colored coil coatings based on different resin systems. While the inorganic pigments used in these coatings are quite durable, considerable color fade can be seen for the non-PVDF coatings in the series. This "chalking" is associated with the catastrophic loss of binder (i.e., resin) integrity in the topmost few microns of the coating, due to the photochemical degradation of the nonfluorinated coating binders.[7]

20-YEAR COLOR LIFETIMES? A REALITY IN AT LEAST SOME CASES

The AAMA 2605 standard, with its 10-year Florida requirement, already sets a high bar for coating weatherability. Is it possible to significantly improve upon this further, to retain the coating's decorative properties for 20 years or more? Obviously, to push the limits of durability, careful

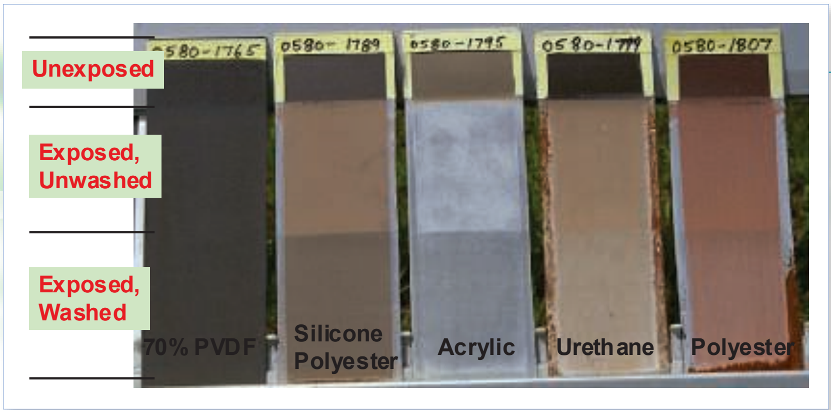

Figure 1—South Florida exposure panels for commercial bronze-colored coil coatings. Photo taken in 1997 after 17 years' exposure at south 45°. The original color may be seen at the top of the panel, where a flap kept that portion unexposed. Chalking is most apparent on the unwashed section of the panel.

attention to both the resin and pigment components of the coating is necessary.

As mentioned previously, for PVDF-based finishes, this kind of multi-decade performance is already attested to by literally dozens of buildings around the world—if not hundreds—as well as thousands of Florida test panels. *Figure* 2 shows an extreme example for a series of coatings on the Arkema test fence, all of which have been on exposure for more than 40 years. For these panels, as with many of the older PVDF architectural finishes, the color fade from pigment degradation is minimized by exclusively employing highly weatherable complex inorganic color (CICP) pigments,[1] plus the most weatherable grades of rutile TiO_2. When these highly weatherable pigments are used in combination with high enough levels of PVDF in the coating binder, color lifetimes in excess of 40 years are the norm rather than the exception. We have developed a simple weathering model to explain this behavior,[8] building on the 1970s-era "contraction model" for coating weathering developed by Colling and Dunderdale,[7] for a blend of two different resins.

Specifically, our weathering model considers the coating binder as a blend of two well-mixed resin components, one of which is much more weatherable than the other. Its general predictions are consistent with observed results for many thousands of outdoor exposure PVDF coating test panels: when CICP pigments are used, chalking and color fade are minimal as long as the relative volume fraction of PVDF in the binder is sufficient, relative to the volume of the pigment, to keep the pigment encapsulated even if all the acrylic co-resin is removed (*Figure* 3). According to this simple principle, the ultimate color lifetime should not depend on details such as the mechanism of film formation of the coating; instead, it should depend on whether a good resin blend morphology is attained. We have verified this expectation for a wide range of PVDF coating types, including the newer waterborne PVDF-acrylic hybrid products which are showing weathering behavior equivalent to baked PVDF finishes at 12–15 years Florida exposure and counting (*Figure* 4).

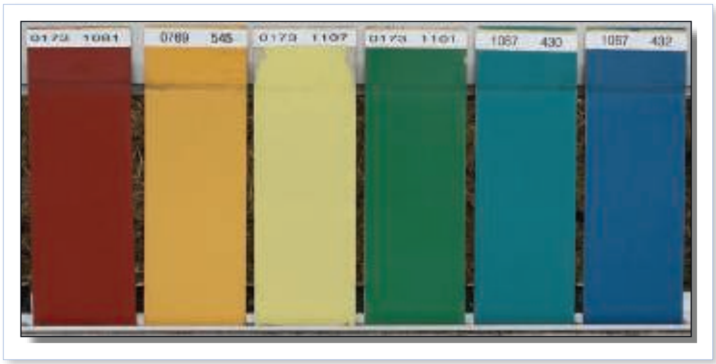

Figure 2—Early PVDF-acrylic coatings, on exposure in Florida for 40+ years. The unexposed portion of the coating is at the top. The number at the top left of each panel denotes the month and year of exposure. Typical coating thickness values are about 25 microns.

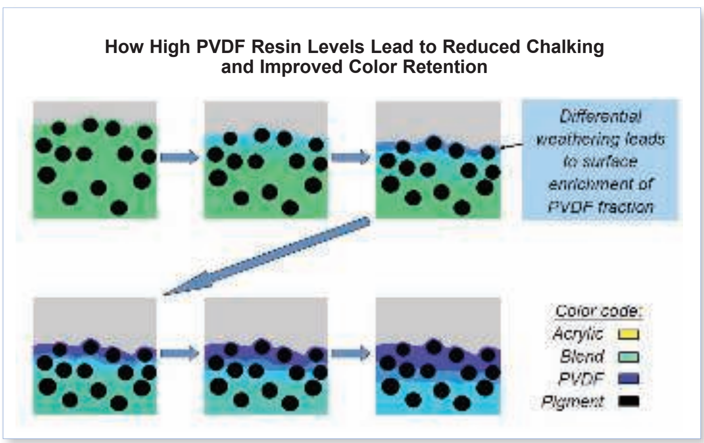

Figure 3—Schematic for compositional changes in PVDF-acrylic blends, as a result of weathering. Color change is minimal as long as the pigment remains encapsulated even after all the near-surface acrylic is gone, i.e., as long as the weathered surface of the coating remains below the critical pigment volume concentration. Likewise, long-term coating erosion is minimal (cf. as a real-life example, the panels in *Figure* 2 which have lost no more than a few microns of coating thickness over 40+ years).

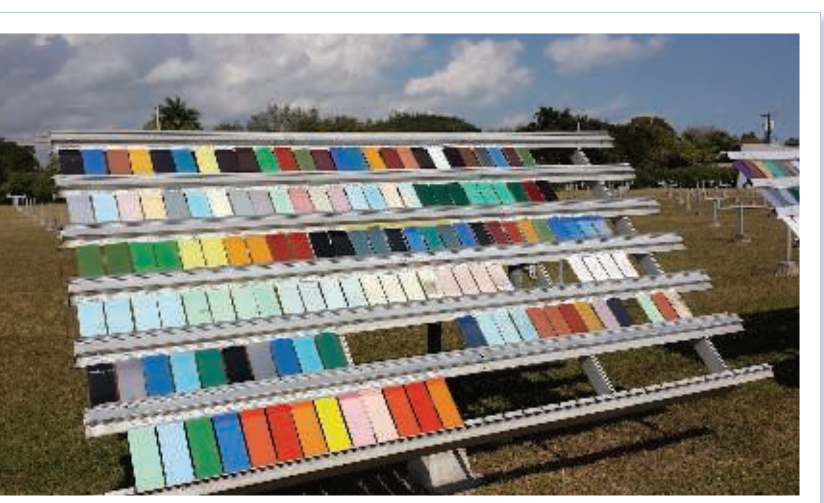

Figure 4—Arkema test fence (photo taken January 2015) showing Florida weathering series for 70% PVDF-acrylic hybrid waterborne coatings (air-dry or low temperature bake). Many of the panels on this fence have already been on exposure for over 10 years, while showing excellent color retention.

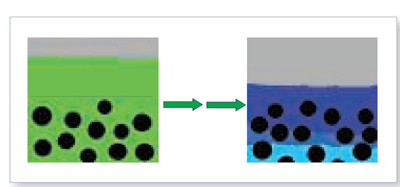

Figure 5—Schematic, using the color scheme of *Figure* 3, showing the expected evolution of the composition profile, and surface roughness, of PVDF-acrylic basecoat/clearcoat systems as a result of outdoor weathering.

CLEARCOATS TO IMPROVE COLOR AND GLOSS RETENTION

A second general class of pigments with proven success in PVDF architectural finishes is flake pigments. These are of two principal types: metallic flake pigments, usually aluminum, and mica-type effect pigments, usually based on some sort of metal oxide structure. A vast array of special color effects can be generated by these products.[9] When the most weatherable grades of these inorganic products are used, 70% PVDF coatings made with these products can also demonstrate color lifetimes in the decades—especially if a thin PVDF-rich clear topcoat is employed to compensate for the more severe effect on the flake pigments of the coating contraction during its service life. *Figure* 5 illustrates schematically what the two-resin contraction model predicts should happen during weathering, for PVDF-acrylic basecoat/clearcoat systems. Consistent with Florida test panel observations over more than 20 years, it predicts that, in addition to color retention, gloss retention should be excellent for extremely long times. *Figure 6* shows an example of representative commercial coatings with flake pigments, after 10–20 years of south Florida exposure. As with single coat systems, the model also suggests that the details of the film formation should be unimportant for the long-term weathering results. Accordingly, no significant color retention difference would be expected between traditional baked and waterborne air-dried PVDF-based coatings formulated at comparable PVDF level and pigment volume concentration.

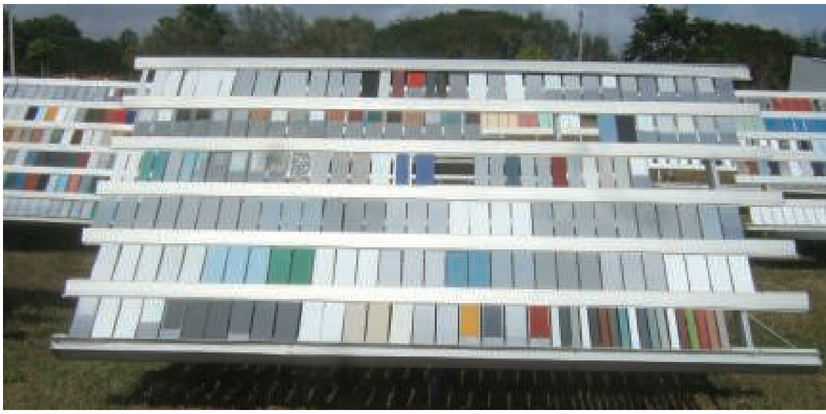

Figure 6—Commercial baked finishes, many of them 70% PVDF coatings with mica and metallic flake pigments. The panels on this fence have been on exposure in south Florida for 10–20 years.

THE CHALLENGE OF 20-YEAR COLOR LIFETIMES WITH ORGANIC PIGMENTS

While a large number of inorganic pigments are available that have demonstrated excellent color retention in PVDF-based coatings over more than 20 years of south Florida exposure, the color palette of these pigments is somewhat limited. For many of the brighter saturated colors of interest to architects and designers, the most practical way to achieve the color is by using organic pigments. While some of these organic pigments have rather good chemical stability, they are all nevertheless at least somewhat susceptible to photochemical attack. For this reason, a straightforward extension of the contraction model leads to the expectation that in PVDF-acrylic blends, the near-surface organic pigments will eventually suffer the same fate as the near-surface acrylic fraction of the binder—which would result in color fade. The color service life would then be inversely proportional to the rate of photochemical degradation of the visible fraction of the pigment material. Important factors influencing a pigment's rate of degradation, in turn, include the pigment's inherent degree of chemical and photochemical stability, and also the concentration of chemically aggressive species (e.g., photogenerated radicals) in the immediate neighborhood of the pigment molecules.

In general, according to the two-resin contraction model, we may summarize the expected effect

Table 1—Expected Effect on Color and Gloss of Various Photodegradation Processes

Weathering Process	Expected Main Effect on Color	Expected Main Effect on Gloss
Photochemical degradation of pigment	Color fade (loss of chroma); possible increase in whiteness (L*)	Little effect
Loss of binder integrity/ formation of voids near surface (chalking)	Increase in whiteness (L*), especially over unwashed portion of the panel	Significant gloss loss; gloss at later times may depend on degree of washing
Binder contraction near the surface	Minor shifts in hue resulting from increases in the local PVC, plus changes in the binder refractive index (in the case of PVDF/acrylic systems)	No clearcoat: Some gloss loss, greatest at higher PVC With clearcoat, or very low PVC: little effect on gloss

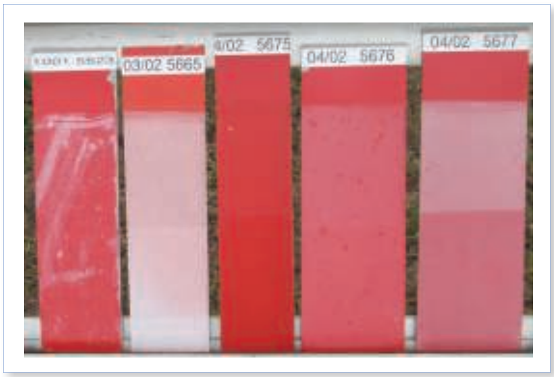

Figure 7—January 2015 photo of panels exposed in south Florida (south facing 45°) in 2001/2002, all made with DPP Red pigment at about 12 PVC. Left to right: high temperature bake 70% PVDF (with 70% PVDF clearcoat); high temperature bake 70% PVDF (no clearcoat); 70% PVDF air-dry system, solvent-type (no clearcoat); 2K FEVE urethane system, solvent-type (no clearcoat); 2K acrylic urethane system, solvent type (no clearcoat). Panel sections from top to bottom are: unexposed section under flap preserving initial color; unwashed section; washed section.

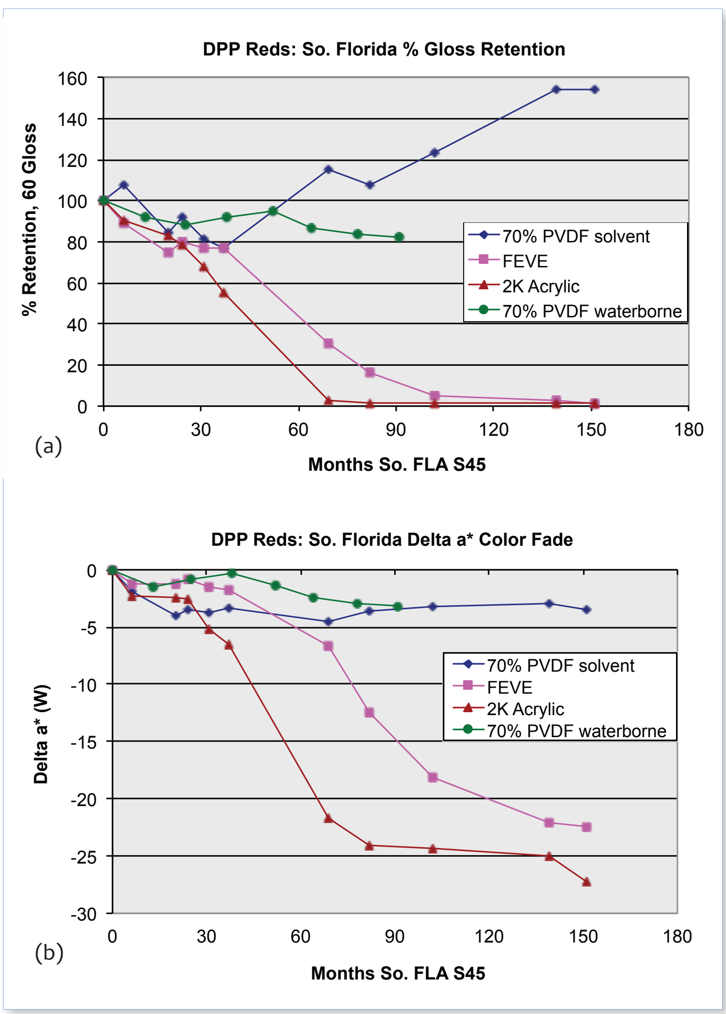

Figure 8—Florida gloss retention (a), and color fade (b) (expressed as delta a*) for air-dry coatings made with DPP Red pigment (washed portion of panel).

on color and gloss of various photodegradation processes as detailed in *Table* 1.

We have reported previously[10] on Florida and accelerated weathering studies of high temperature baked PVDF-based finishes made with seven different organic pigments, begun in 2001. The Florida color lifetimes varied significantly depending on the pigment grade (a phthalo green pigment grade performed best and a naphthol red grade performed worst). Clear topcoats were found to improve the color retention significantly. For the DPP Red (Pigment Red 254) systems, which were intermediate in color stability for the series, masstone color retention lifetimes were about four years without a clearcoat, and 10 years with a clearcoat.

Although the 2001 study on high temperature baked PVDF systems was not promising for the prospect of 20-year color retention with organic pigments, studies done during the rest of the decade on low temperature bake and air-dry PVDF-based coatings, both solvent- and waterborne versions, reveal a dramatically improved color retention performance when there is *not* a high temperature bake. *Figure* 7 shows a comparison of baked and air-dry 70% PVDF systems with the DPP Red pigment, plus two control systems, after about 13 years' south Florida exposure. It can be seen that the air-dry PVDF system (panel 5675, center) shows excellent color retention after almost 13 years—even without a clearcoat. Numerical values for the gloss retention and color fade for the *Figure* 7 air-dry coatings (the latter expressed as the change in the red component of the color, delta a*), plus a more recent waterborne air-dry PVDF-based coating, are shown in *Figure* 8.

To gain a better mechanistic understanding of the underlying weathering processes occurring in these systems, it is useful to consider the information available in the color data, specifically the evolution of the L*, a*, and b* components of the color.[11] For instance, as may be easily seen in the rightmost test panel in *Figure* 7 (panel 5677), a 2K acrylic coating, the color of the unwashed portion of the panel is much lighter (higher L* value) than the color of the washed portion. Some of the whitening has been removed by washing, indicating a surface layer with poor binder integrity (i.e., chalking). The additional whitening in the unwashed portion may be attributed to voids in the coating binder causing increased light scattering, associated with the chalking. By contrast, the other panels in *Figure* 7, which are all fluoropolymer-based and which are not chalking, show more similar colors between the washed and unwashed sections of the panel (the darker color for the unwashed part of the second panel from the left suggests surface dirt).

Table 2—Expected Effect on Color and Gloss of Various Weathering Processes for DPP Red Masstone Coatings

Weathering Process	Expected Main Effect on CIELab* Color	Expected Main Effect on Gloss
Photochemical degradation of pigment	Color fade (loss of chroma; a*, b* both decrease; possible increase in L*)	Little effect
Loss of binder integrity/ formation of voids near surface (chalking)	Increase in whiteness (L*), especially over unwashed portion of the panel	Significant gloss loss; gloss at later times may depend on the degree of washing
Binder contraction near the surface (leading to increase in local PVC, plus a lowering of the binder refractive index in the case of PVDF/acrylic systems)	Blue shift in the color (decrease in b*)	Some gloss loss, greatest at higher PVC

In terms of the specific changes in color and gloss expected for different weathering processes, for the case of these DPP Red masstone coatings (where initial color coordinates were measured to be about L* = 35, a* = 64, b* = 54, i.e., on the yellow side of red), the expectations are shown in *Table* 2.

Figure 9a and b shows the relative component color changes for the air-dry coatings of *Figures* 7 and 8, for the washed section of the panels exposed in Florida. For the non-PVDF systems, it can be seen that after an initial induction period, there are proportional changes in L*, a* and b*, in directions that are consistent with color fade from pigment degradation. The end of the induction period corresponds approximately with the time at which significant gloss loss begins for the two systems (about 2.5–3 years for the acrylic, and five years for the FEVE).

The PVDF-based systems, on the other hand, show a rather different behavior. During the first couple of years of exposure, there is a blue shift (negative delta b*) of several color units, attributable to a small amount of binder contraction near the surface. Since then, the color has remained almost unchanged up to the present—for the past 10 years, in the case of the solvent version put on exposure in 2002. In the absence of markers showing some kind of developing degradation in the system, it is difficult to predict the color service life of these panels. Certainly they are on track to last at least 20 years, but they could well last even longer than that. More work will be needed to be able to accurately predict the color service-life of these very long-lived systems.

Thirteen-year Florida data with the solvent PVDF air-dry systems using organic pigments is only available for the DPP Red pigment, and a blend of green and yellow organic pigments. However, a more extensive series of organic pigments was evaluated in 2006–2008 in waterborne PVDF-acrylic hybrid formulations. The DPP Red formulation shows gloss and color retention similar to that of the solvent air-dry PVDF-based system from 2002 (both systems containing at 70% PVDF resin on total resin weight). *Figure* 9 shows some comparisons for gloss and delta a* color fade. After seven to eight years, similar excellent color retention is being shown in

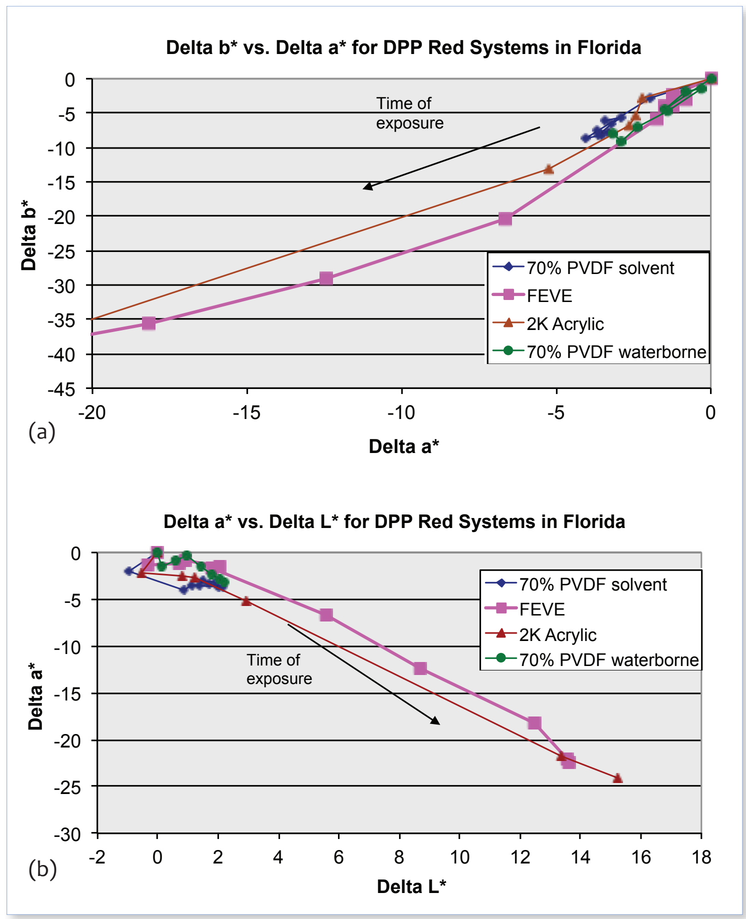

Figure 9—Relative changes in the washed panel color coordinates during the course of Florida weathering, for air-dry coatings with DPP Red pigment.

waterborne masstone formulations for many other organic pigments, including phthalo blue and green, carbazole violet (pigment violet 23), and quinacridone violet (pigment violet 19).

The superior color retention of organic pigments in air-dry PVDF-based coatings, relative to high temperature baked PVDF-based coatings, is striking. We hypothesize that for the latter case, the high temperature bake conditions, combined with the latent solvents used in these formulations, are compromising in some way the photochemical stability of the pigment particles.[12] If this is the case, the relative color stability of the different pigments evaluated in the original 2001 study may be more reflective of the pigment stability under the baking conditions, rather than the inherent photochemical stability of the pigment.

CHALLENGES FOR THE FUTURE

With color lifetimes measured in decades across the full inorganic pigment color spectrum, as well as color lifetimes of at least 10–20 years for a good number of bright organic pigments, air-dry or low temperature bake PVDF-based coatings (both solvent- and waterborne) are excellent candidates for use in architectural restoration and repair. Likewise, for OEM finishes, PVDF-based formulations with these same pigments can be adapted for nearly any substrate. Nevertheless, in some color spaces, notably pastel colors ("tints") like pink or lavender made with organic pigments, color lifetimes are still significantly shorter than 10 years, even with air-dry PVDF-based binders. Among the strategies that might extend the color lifetime for these shades are:

- Use of a clearcoat, possibly with UV absorber;
- Use of inorganic pigments which develop their color through an interference mechanism, rather than through absorption;
- Use of higher levels of PVDF in the binder than 70 wt%;
- If the technology exists, use of TiO_2 grades with even lower levels of residual photocatalytic activity than is available with the standard highly weatherable rutile grades that are in common use today.

Besides these formulation approaches, further progress in fundamental studies is also needed to be able to predict multi-decade color lifetimes in relatively short times. It may be of little practical value to know whether a very durable system, such as the classic PVDF coatings with CICP pigments, will have a color lifetime of 40 years, 100 years, or 1000 years, but for the more exotic colors, the ability to differentiate between 5-year, 10-year, and 20-year systems would be very useful from a warranty perspective. We are beginning to examine whether one might be able to use the evolution of the CIELab* color components to assess how close the "chemical balance" of different accelerated weathering methods is to Florida weathering. This kind of inquiry is similar in spirit to the approach taken by the Gerlock group at Ford for automotive clearcoat systems.[13] CT

References

1. Hatcher, H. and Tocher, A., "The Role of High Performance Inorganic Pigments in Surface Coatings," *Paint Coat Ind.* (March 2002).
2. Humphrey, S. and Drujon, X., *Polymeric Materials Encyclopedia,* CRC Press, Inc., Vol. 11, 8591, 1996; Iezzi, R.A., "Fluoropolymer Coatings for Architectural Applications," in *Modern Fluoropolymers*, Wiley, 1997.
3. Gupta, R. and Wood, K., "Novel Fluoropolymer-based Emulsion Technology: Striving for 'Green' Coatings," *Paint Coat. Ind.*, pp. 70-80 (July 2007); also published in the *Proc. Waterborne and Higher Solids Symp., Advances in Intelligent Coating Design*, February 2007, New Orleans, LA. See also www.kynaraquatec.com.
4. Wood, K., "Optimizing Waterborne 2-k Topcoat Formulations for Exterior Architectural Profiles on Multiple Substrates," presentation at the AMI Profiles 2014 Conf., Philadelphia, PA, June 24-25, 2014.
5. American Architectural Manufacturers Association, www.aamanet.org.
6. Petersheim, J., Weidner, C., and Wood, K., "Water-based Fluoropolymer Coatings Meet Stringent Weathering Properties," *Proc. 2011 CoatingsTech Conf., "The New Face of Innovation,"* March 14-16, 2011, Rosemont, IL.
7. Colling, J.H. and Dunderdale, J., "The Durability of Paint Films Containing Titanium Dioxide—Contraction, Erosion, and Clear Layers Theories," *Prog. Org. Coat., 9,* 47-84 (1981).
8. Wood, K.A., "How Can We Effectively Use Accelerated Methods to Predict the Decorative Properties of PVDF-based Coatings? A Practical Approach," *Prog. Org. Coat., 77*, 2140-2146 (2014).
9. Pfaff, G. et al., *Special Effect Pigments: Technical Basics and Applications, 2nd Revised Ed.*, Vincentz Network, Hamburg, 2008.
10. Wood, K.A. and Gaboury, S.R., "Service Life Prediction of Colour Retention for PVDF Architectural Coatings with Organic Pigments," *Surf. Coat. Internat. Part B: Coatings Trans., 89,* B3, 231-235 (September 2006).
11. In the CIELAB 1976 system, L* is a measure of whiteness, while a* measures color in the red-green direction, and b* measures color in the yellow-blue direction.
12. Hao, Z. and Iqbal, A., "Some Aspects of Organic Pigments," *Chem. Soc. Rev.*, *26*, 203-213 (1997), DOI: 10.1039/CS9972600203.
13. Gerlock, J.L., Peters, C.A., Kucherov, A.V., Misovoski, T., Seubert, C.M., Carter, R.O., and Nichols, M.E., "Testing Accelerated Weathering Tests for Appropriate Weathering Chemistry: Ozone Filtered Xenon Arc," *J. Coat. Technol., 75,* No. 936, 35-45 (2003).

AUTHOR

Kurt Wood, Kynar® PVDF R&D, Arkema, Inc., King of Prussia, PA 19406; kurt.wood@arkema.com.