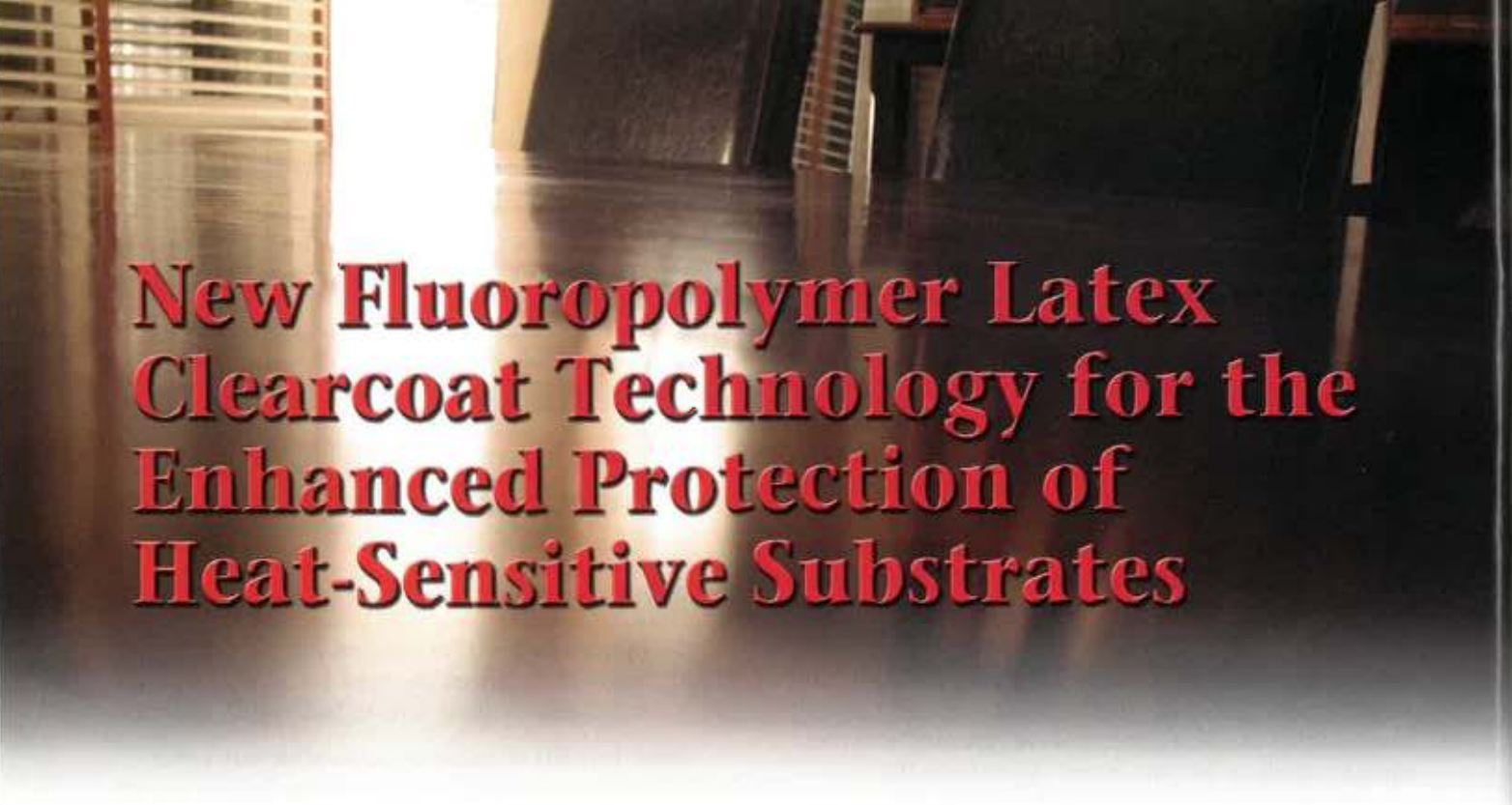

New Fluoropolymer Latex Clearcoat Technology for the Enhanced Protection of Heat-Sensitive Substrates

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Poly(vinylidene fluoride) (PVDF) clearcoats have been used for over 20 years to extend the service life of architectural coil coatings, and new waterborne PVDF technology now provides a low-VOC route to extend the same protective properties to heat-sensitive substrates of all types, including flexible PVC, basecoat paints containing organic pigments, and wood. The use of organic and inorganic UV absorbers can provide a further level of substrate protection in these systems, but for truly long-term UV protection, the chemistry of the UV absorber itself within the topcoat also needs to be considered. In particular, we will present some surprising results, comparing the performance of organic and inorganic nanoparticle UV absorbers in PVDF latex coatings.

INTRODUCTION

Clearcoats containing UV absorbers are widely used to extend the lifetime of UV-sensitive materials, such as wood and plastic substrates, as well as UV-sensitive pigments and binders in basecoats (notably in the automotive industry). There are two basic types of UV absorbers that are commercially available for clearcoats: organic and inorganic. Organic UV absorbers are typically designed for use in solution, so they have outstanding transparency in clearcoats; however, they also have two important limitations. First, the UV absorbers themselves are somewhat susceptible to photochemical attack, and so cannot be reasonably expected to provide quasi-permanent UV protection. Second, as materials in solution, the precise grade of UV absorber used must be matched correctly to the formulation's solvency properties, in order to get an appropriate amount of UV absorber into the final clearcoat film. For many water-based formulations, the choices for organic UV ab-

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sorbers are particularly limited, as dispersibility rather than solvency becomes the important factor for good performance. However, with these limitations understood, the ability of organic UV absorbers to extend the lifetime of coatings can often be quite dramatic.

Inorganic UV absorbers offer the prospect of truly long lasting UV protection; thus, they are of more interest, depending upon the weatherability of the binder. Being generally particulate in nature, however, they in turn suffer from their own set of potential drawbacks. As materials designed to work in dispersion, they must be formulated to stay in dispersion during coating storage and drying, without compromising any of the other properties of the coating. Also, being particulate in nature, they can potentially contribute some opacity to the final clearcoat, because of light scattering. The visible opacity can be minimized if the particle size can be reduced into the nano-scale (and if particle reagglomeration can be prevented). However, as the particle size becomes smaller, the colloidal stabilization process becomes more difficult. Some of the inorganic nano-materials, notably TiO_2, can also have photocatalytic surface activity, which can in turn accelerate the photodegradation of the binder.[1] Nevertheless, a variety of nanoscale inorganic UV absorbers are becoming commercially available in aqueous dispersion, in a variety of chemistries (e.g., nano-ZnO, nano-TiO_2, nano-CeO_2). In addition to these products, nanoscale transparent iron oxide grades have been available for a long time, and while they contribute some color to formulations, they are widely used in semi-transparent formulations.

In this article, we report results for evaluations of various inorganic nano-UV absorbers, with a view toward developing optimized clearcoat formulations for UV-sensitive substrates based on a new, highly weatherable, PVDF-based latex technology.

NEW PVDF-BASED LATEX TECHNOLOGY

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline fluoropolymer that is unique in its ability to be compounded with certain acrylic resins, such as poly(methyl methacrylate).[2] This property has been exploited for decades in the metal coating industry; in fact, the original PVDF grade for coatings, Kynar 500® PVDF, has been in continuous commercial production since its introduction by Pennsalt in 1965.[3] Commercial coatings based on 70–80 wt% PVDF/20–30% compatible acrylic are renowned for their excellent exterior weatherability, which is based in large part on the outstanding resistance of PVDF resins to water, to UV radiation, and to other forms of photochemical and environmental attack. When formulated with highly color stable inorganic pigments, these PVDF-based binders routinely meet the 10-year South Florida "Superior" weathering requirements for the most durable baked architectural metal finishes.[4]

While most commercial PVDF-based coatings are pigmented with inorganic pigments,[5] PVDF clearcoats are also used in specific situations; for instance, when there is a need to protect sensitive basecoat pigments, like metallic or organic pigments, or when an automotive Class A finish is required, e.g., in the case of paint film technology.[6] The use of PVDF basecoat-clearcoat constructions takes the weatherability to even higher levels, with panels showing minimal gloss and color change even after more than 20 years of Florida exposure.

In recent years, new developments in PVDF hybrid latex technology have made it possible to extend the weatherability performance of baked solventborne PVDF finishes to low-VOC, waterborne coatings. Typical waterborne systems are predominantly based on hybrid latex particles, which contain both PVDF copolymer and acrylic polymer in a 70:30 weight ratio, and where the polymers have an interpenetrating network (IPN)-type structure inside the latex particles so that a fluoropolymer continuous phase is formed during the latex film formation process.[7] The PVDF latex dispersions are anionically stabilized, and can be combined with water based pigment dispersions, and formulated with common coatings additives designed for waterborne coatings, similarly to the way acrylic latexes are formulated.[8]

Figure 1—Effect of a clearcoat on the color change of a phthalo green paint, for two different latex resin types. Coatings marked "PVDF" contained 63% PVDF, 37% acrylic. The clearcoat with UV absorber contained Tinuvin 1130, 2% solids on solids.

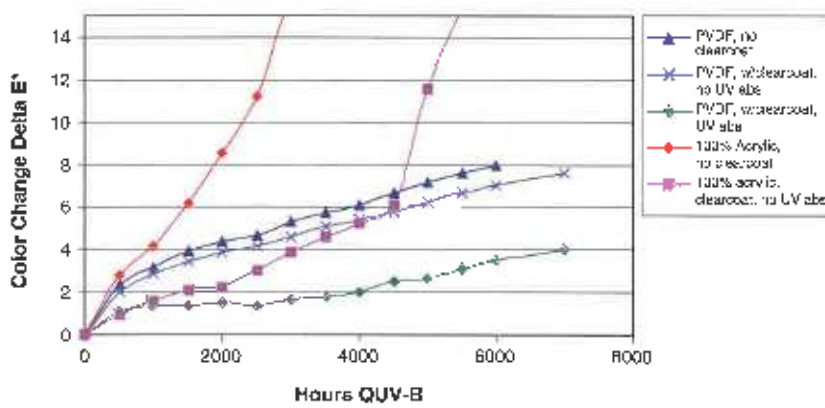


Figure 2—Phthalo green tint latex formulations with clearcoat of the same resin after QUV-B (313 nm) exposure (7000 hr for PVDF-based coatings, 5500 hr for acrylic coatings). Bottom portion is unexposed paint color. No UV absorbers were added to these formulations.

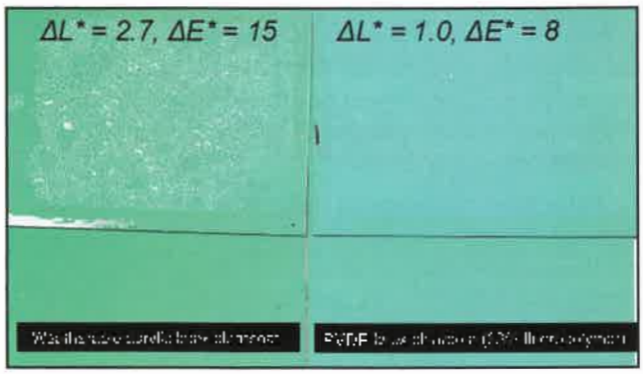
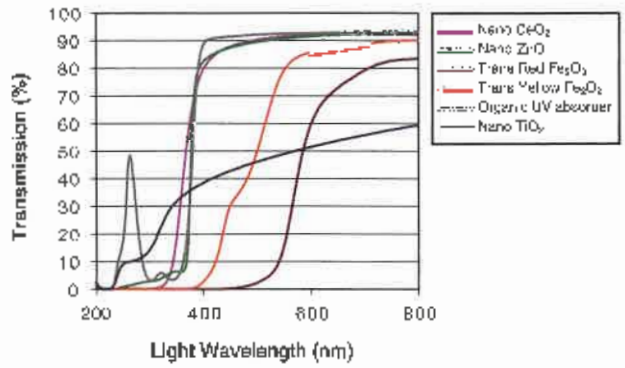


Figure 3—UV-visible transmission of free films (25 microns dry film thickness) of a waterborne PVDF-based clearcoat formulation, at 2 wt% UV absorber on solids.



CLEARCOAT PROTECTIVE EFFECTS IN THE ABSENCE OF UV ABSORBERS

For paints made using organic pigments, clearcoats can be used to provide greater color stability to the painted object. In addition to reducing the rate of UV-induced photodegradation of the pigment (through the use of UV absorbers in the clearcoat), clearcoats can also reduce the rate of color fade by two other mechanisms: by reducing or eliminating color fade due to chalking (poorly incorporated pigment particles and possibly resin fragments on the paint surface, created by binder degradation processes), and potentially also by reducing the rates of pigment and binder degradation in the color coat by providing a barrier to reactive species such as oxygen and water.[3]

Figure 1 shows one example of these protective effects, for the case of phthalo green tint paints exposed in a UV fluorescent cabinet. For a weatherable acrylic latex binder, the color shift after 5500 hours exposure ($\Delta L^* = 10.3$, $\Delta E^* = 27$) is dramatically reduced by the addition of an acrylic clearcoat with the same latex ($\Delta L^* = 2.7$, $\Delta E^* = 15$) without UV absorber. The direction of the principal color change in this case, toward the red (i.e., less green), suggests that the color change is mainly the result of bleaching of the green pigment, and that the clearcoat barrier properties are important in this instance.

A 63% PVDF latex paint with the same pigment mix shows much less color change than this, even without a clearcoat ($\Delta L^* = 1.8$, $\Delta E^* = 9$), and it can be seen from *Figure* 1 that the addition of a 63% PVDF clearcoat without a UV absorber only conferred very modest additional benefits in this case. However, further significant reductions in color fade were possible by adding a UV absorber into the PVDF clearcoat.

One potential danger of using clearcoats with conventional resin systems can be seen in *Figure* 2, which shows the visual appearance of two of the test coatings at the end of the test. The acrylic clearcoat (left) was rather effective in reducing the rate of basecoat color change, but after a certain exposure period, the clearcoat reached the point where it began to exhibit a catastrophic flaking failure. One major advantage of PVDF-based clearcoats is that the PVDF resin component is completely inert to UV-B radiation, hydrolytic

Table 1—UV Absorbers Used in this Study and Some of Their Properties

		Properties			
		% Solids	Particle Diameter (nm)	Specific Surface Area (BET) (m^2/g)	Color
Nano zinc oxide	Supplier A	50	35	30–40	Beige/cream-colored
	Supplier B	20			Beige/cream-colored
Nano cerium oxide	Supplier A	30	10–40	70–85	Beige/cream-colored
Nano titanium oxide	Supplier C	10			Transparent
Hydroxyphenyl—benzotriazole class	Supplier D	100			Yellow

Table 2—Sample Waterborne PVDF-Based Clearcoat Formulation with an Inorganic Nano-UV Absorber

Ingredients	Amount (g)	Description
Kynar Aquatec® RC-10, 206	37.90	70% fluoropolymer latex, 47% solids
Diethylene glycol monobutyl ether (DB)	2.70	Coalescent (15% of solid resin, w by w)
Acrysol RM-825	0.20	Thickener (Rohm and Haas Company)
BYK Chemie BYK-346	0.08	Wetting agent
Rohm and Haas Rhoplex SG-10M	7.50	Acrylic co-resin (20% solids on resin solids)
Nano particle dispersion	0.73	2% active ingredient on solids
Total	**49.11**	**Solid content: ~44.7%**

attack, and other common environmental degradative agents. As a result, PVDF-based clearcoats have been shown to last literally decades in the outdoors, without exhibiting any loss of mechanical integrity, or even of gloss.

STUDIES OF INORGANIC UV ABSORBERS IN A PVDF LATEX SYSTEM

The principal goal of this study was to evaluate a variety of inorganic oxide "nano" dispersions that have become available from a number of suppliers in recent years. The inorganic UV absorbers studied here were all supplied as aqueous dispersions for easy incorporation into waterborne coating formulations. *Table* 1 shows some data about these materials, as provided by the suppliers. A water dispersible organic UV absorber of the hydroxyphenyl-benzotriazole class, Tinuvin 1130, was also included in the study for comparative purposes.

Table 2 shows a representative waterborne, PVDF-based clearcoat formulation used in this study, for the case where the UV absorber is a nanoparticle dispersion. Some acrylic co resin is used in this particular formulation, giving a PVDF content of 57 wt% on total binder. The additional acrylic co-resin can be useful in modifying certain coating properties – for instance, in this case, in improving the adhesion of the coating to flexible PVC substrates. However, as the overall PVDF content of the binder is reduced, it is also to be expected that there will be a certain diminution of weatherability properties, compared to a system with 70–80% PVDF.

The various UV absorbers were incorporated into this clearcoat formulation at various levels, and the UV-visible transmission spectra of clearcoat free films was measured, in order to determine appropriate loading levels for further studies. A standard loading level of about 2 wt% (active ingredient) was used in subsequent studies as this loading level is effective in reducing the UV-B transmission in the films to less than about 10%, for nearly all of the additives. *Figure* 3 shows sample UV visible transmission curves for many of the systems, at a 2 wt% loading.

It can be seen from *Figure* 3 that there is excellent UV blocking ability of the solar UVB spectrum (between about 295 nm and 330 nm) for all of the UV absorbers, except the nano TiO_2 system. The "cut on" behavior in the UVA region of the spectrum shows considerable differences, however, with the nano ZnO showing the sharpest "cut on" of the inorganic absorbers tested.

SCREENING OF UV ABSORBERS FOR PHOTOCATALYTIC ACTIVITY

To test for photocatalytic activity for these UV absorbers, clearcoats were applied at constant thickness (approximately 25 microns) over a black 70% PVDF solvent paint, and mass loss rates were measured for the panels during exposure in a UV fluorescent cabinet (313 nm bulbs). *Figure* 4 shows the mass of the test panels as a function of time; the mass loss rate is the slope of the mass versus exposure time curve. The addition of the organic UV absorber was found to have no significant effect on the mass loss rate. Several commer-

Figure 4—Weight loss of panels coated first by black PVDF paint and then by clearcoats containing UV absorbers and their controls versus exposure time in UV fluorescent cabinet.

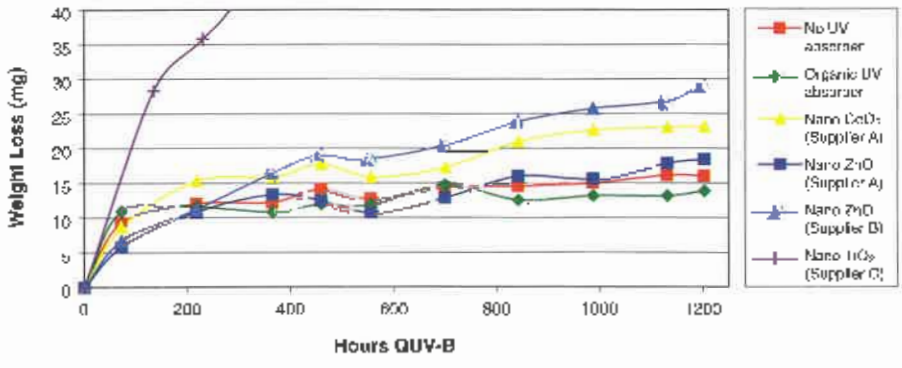
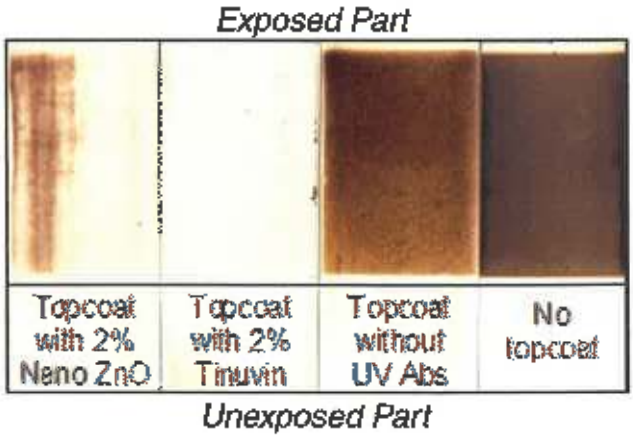


Figure 5—Aspect of off-white PVC sheets after 300 hr of exposure in UV fluorescent cabinet.



cial grades of zinc and cerium oxide had only, at most, a very small photodegradative effect (increasing the mass loss rate by no more than about 10 mg/1000 hr exposure for a 54 cm^2 exposed surface area panel). By contrast, the rutile nano-TiO_2 grade used in these studies was found to have significant photoactivity, with mass loss rates superior to 200 mg/1000 hr, at a 2% solids-on-solids level.

We have observed similar photoactivity previously in our laboratory, with other nano-TiO_2 grades. (It should be noted that TiO_2 photoactivity is most evident when highly weatherable binders such as PVDF are used.[10] When binders with poor UV resistance are used to test this property, the beneficial effect of UV absorption by the TiO_2 will tend to mask the photo-activity effect.) It is not surprising that nano-TiO_2 grades should exhibit significant photocatalytic activity. For the most weatherable pigmentary TiO_2 grades, the photocatalytic activity is suppressed by the use of substantial layers of silica, alumina, or other oxides. It would be difficult to maintain a similar thick protective layer on a TiO_2 nanoparticle, while at the same time reducing the overall particle size to nanoscale dimensions.

VISUAL METHOD FOR ASSESSING THE EFFECTIVENESS OF UV ABSORBER PACKAGES

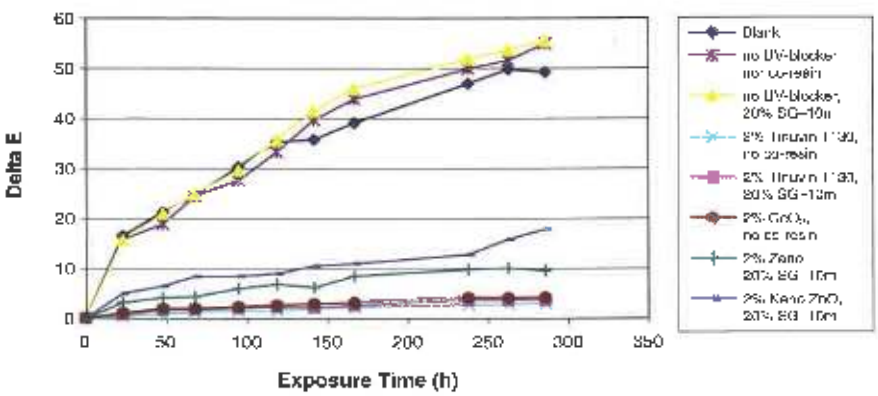
To test the protective efficiency of different UV absorber packages over a PVC substrate, a simple visual test method was devised. A series of waterborne PVDF-based clearcoat formulations, containing different UV absorber packages, were applied at constant thickness to the back side of a white PVC residential fascia strip. These were then exposed in a UV fluorescent cabinet, and the color change versus time was monitored. The UV absorbers tested were one organic and three inorganic dispersions: two nano-ZnO and one nano-CeO_2. *Figure* 5 shows some of the visual results, after 300 hr exposure.

Figure 6 shows the color change as a function of time, as measured with a colorimeter. The organic UV absorber and the nano-CeO_2 were both extremely effective in preventing color change in the PVC substrate.

The data also show that the protective effect is the same, whether or not an acrylic co-resin is used in conjunction with the 70% PVDF latex, at levels of up to 20% on total binder (corresponding to a final PVDF binder level of 57 wt%).

Based on these data, clearcoats with UV absorbers were applied to a number of commercial flexible PVC substrates, both those pigmented with TiO_2 or organic pigments, and multicolored printed substrate. The outdoor and accelerated weathering color retention of these samples is excellent. Work is now proceeding on developing optimized UV absorber packages for wood and other cellulosic substrates. These substrates are much more challenging, both because of their lower dimensional stability under conditions of varying humidity, and because of the sensitivity of wood tannins to visible light, especially in the 400–500 nm wavelength range.[11]

Figure 6—Color change of PVC sheets coated or not versus exposure time in UV fluorescent cabinet.



CONCLUSIONS

Nanoscale inorganic oxide UV absorbers, used in clear topcoats, can provide a significant degree of UV protection to photosensitive substrates. However, to benefit

from the photochemical stability of these materials, and the consequent longevity of UV protection that they can provide, it is essential that they be used in conjunction with binders having inherently high photochemical resistance, and that the inorganic oxide itself not contribute to binder degradation through surface photocatalytic activity. In this respect, nano-cerium oxide and zinc oxide grades, as well as transparent iron oxide grades, seem to be much preferable to nano-TiO_2.

When these inorganic nano oxides are used in conjunction with binders containing high levels of PVDF copolymer, the level of UV protection provided by the topcoat should essentially be retained permanently. This durability property can be used to greatly extend the color retention lifetime of basecoats or substrates containing organic pigments, as well as substrates that are inherently prone to discoloration. With recent advances in waterborne PVDF fluoropolymer technology, the same level of protection is now available both for baked finishes on metals, and for waterborne baked or air-dry coatings for heat sensitive substrates.

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