

Polyvinylidene Fluoride-Based Coatings Technology

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This article discusses the technology of organic coatings based on polyvinylidene fluoride (PVDF) resins. Metal structures that have been finished with PVDF-based coatings typically retain their original color and gloss for long periods of time in most outdoor environments, sometimes up to 40 years. Extreme ultraviolet (UV) light, humidity, smog, acid rain, industrial gases, and other airborne hazards have little effect on the metal structures coated with these finishes, provided formulators develop their coatings from high-quality pigments and additives.

This article covers:

- Fluoropolymer background
- General properties of PVDF
- Polymerization of PVDF
- Polyvinylidene fluoride resin types
- Coating formulation of PVDF
- Application of PVDF-based coatings
- Coating properties of PVDF
- Typical end uses of PVDF-based coatings
- Opportunities for improvement
- Health and safety considerations of PVDF

Fluoropolymer Background

Fluoropolymers are a unique family in the large choice of organic materials available to the coatings industry. Fluoropolymers are most often present in applications where exceptionally high performance is needed. There have been a number of fluorine-base polymers available over the years. Several of them have found their way into specialty applications other than coatings. These include chemical process handling systems, containers, computer wire insulation, electrical wire jacketing and components, piezo- and pyroelectric applications, monofilaments, membranes, and microporous filters.

Among these uses, coatings are accepted as one of the most important because they benefit most from the versatile, advantageous properties of fluoropolymers. Consequently, the technology for coatings has been extensively developed. The advances in formulation, application, processing, substrate preparation, and

new polymer synthesis have resulted in optimal performance and economy.

The three fluoropolymers most commonly used for coatings are polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). While PVF, PVDF, and PTFE all possess similar properties, their individual performance characteristics can be better understood by considering the molecular structure of each material. The carbon-fluorine bond of all three fluoropolymers is the key to their thermal, chemical, and UV resistance properties. The number of fluorine atoms present has a direct bearing on the performance properties of each type of fluoropolymer. The unique combination of properties of fluoropolymers is attributed to two intrinsic characteristics of fluorine atoms: their extremely high electronegativity and small atomic radius. The atomic structure of fluorine gives rise to some of the strongest chemical bonds known. As seen in Fig. 1, the carbon-fluorine bond strength is 116 kcal/mol.

The chemical structures of PVF, PTFE, and PVDF are shown in Fig. 2. Polyvinyl fluoride contains only one fluorine atom (Fig. 2a). Because its fusion and decomposition temperatures are so close, PVF can decompose during the baking

process when used as a coating. Consequently, the baking temperature range of PVF is very small and requires close control, making it difficult to use as a practical organic coating.

Polytetrafluoroethylene has four fluorine atoms (Fig. 2b). It has no crystalline melting point per se, has a high sintering point, and consequently forms a relatively porous surface when used as a coating. The sintering point is well above the temperature that typical coating substrates can withstand before losing their mechanical properties. In addition, PTFE has no known commonly-used solvents that could be used to prepare a practical formulation.

The structure of PVDF (Fig. 2c) contains alternating carbon-fluorine and carbon-hydrogen bonds. This structure provides a polarity that enables the formulation of practical coatings that resist environmental degradation, dirt retention, oxidation, photochemical deterioration, fading, chalking, cracking, and airborne pollutants. Thus, PVDF has a balance of properties that makes it particularly suitable for use in coatings, especially for outdoor and architectural uses.

General Properties of Polyvinylidene Fluoride

Polyvinylidene fluoride is a high-molecular-weight, semicrystalline polymer that has many unique properties, including:

- Exceptional weathering resistance
- Resistance to UV light
- High thermal and chemical resistance
- Resistance to nuclear radiation
- High mechanical strength and toughness
- High purity
- Good moisture and fungus resistance
- High electrical resistivity
- Low surface energy and low coefficient of friction to provide a maintenance-free, dirt-resistant, nonstaining coating surface
- Low refractive index

Table 1 lists the chemical and physical properties of PVDF (Ref 1).

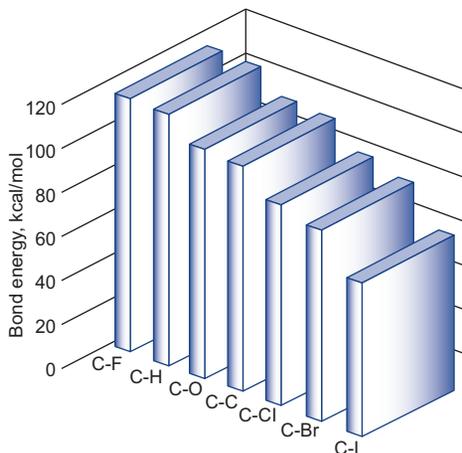


Fig. 1 Carbon bond energies

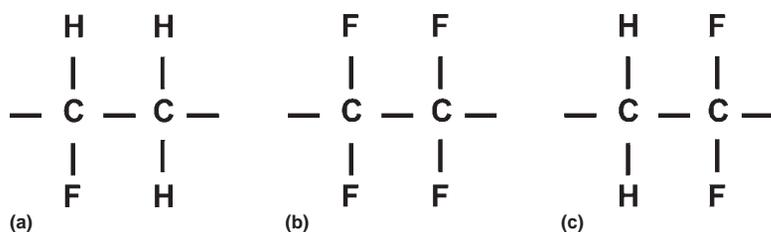


Fig. 2 (a) Polyvinyl fluoride (PVF). (b) Polytetrafluoroethylene (PTFE). (c) Polyvinylidene fluoride (PVDF)

Table 1 Properties of polyvinylidene fluoride

Property	Value or description
Clarity	Transparent to translucent
Melting point, crystalline, °C (°F)	155–192 (310–380)
Specific gravity	1.75–1.80
Refractive index	1.42
Mold shrinkage, average, %	2–3
Color possibilities	Unlimited
Machining qualities	Excellent
Flammability	Self-extinguishing, nondripping
Tensile strength, MPa (ksi)	
At 25 °C (77 °F)	42–58.5 (6.1–8.5)
At 100 °C (212 °F)	34.5 (5.0)
Elongation, %	
At 25 °C	50–300
At 100 °C	200–500
Yield point, MPa (ksi)	
At 25 °C	38–52 (5.5–7.5)
At 100 °C	17 (2.5)
Creep, at 13.79 MPa (2 ksi) and 25 °C for 10,000 h, %	2–4
Compressive strength, at 25 °C, MPa (ksi)	55–90 (8.0–13)
Modulus of elasticity, at 25 °C, GPa (ksi)	
In tension	1.0–2.3 (145–334)
In flexure	1.1–2.5 (160–363)
In compression	1.0–2.3 (145–334)
Izod impact, at 25 °C, J/m (ft · lbf/in.)	
Notched	75–235 (1.4–4.4)
Unnotched	700–2300 (13.1–43.0)
Durometer hardness, Shore, D scale	77–80
Heat-distortion temperature, °C (°F)	
At 0.455 MPa (0.066 ksi)	140–168 (285–335)
At 1.82 MPa (0.26 ksi)	80–128 (175–260)
Abrasion resistance, Tabor CS-17, 0.5 kg load, Mg/1000 cycles	17.6
Coefficient of sliding friction to steel	0.14–0.17
Thermal coefficient of linear expansion, per °C	$0.7\text{--}1.5 \times 10^{-4}$
Thermal conductivity, at 25–160 °C (75–320 °F), W/(m · K)	0.17–0.19
Specific heat, J/(kg · K)(a)	1255–1425
Thermal degradation temperature, °C (°F)	390 (735)
Low-temperature embrittlement, °C (°F)	–60 (–75)
Water absorption, %	0.04
Moisture vapor permeability, for 1 mm (0.04 in.) thickness, g/(24 h)(m ²)	2.5×10^{-2}
Radiation resistance(⁶⁰ Co), MGy(b)(c)	10–12

(a) To convert J to cal, divide by 4.184. (b) Retains tensile strength of approx. 85% of its original value. (c) To convert Gy to rad, multiply by 100.

Crystallinity can vary from approximately 35 to 70%, depending on the method of preparation and thermomechanical history. The degree of crystallinity is important because it affects toughness and mechanical strength. The characteristics of PVDF depend on molecular weight, molecular weight distribution, extent of irregularities along the polymer chain (including main-chain defect structures and side groups), and crystalline form.

Polymerization of Polyvinylidene Fluoride

Polyvinylidene fluoride is the addition polymer of 1,1-difluoroethene, $\text{CH}_2=\text{CF}_2$, commonly

known as vinylidene fluoride (abbreviated VDF or VF_2). It is produced by suspension or emulsion polymerization, but most frequently by emulsion polymerization. Vinylidene fluoride is polymerized readily by free-radical initiators to form a high-molecular-weight, partially crystallized polymer that contains 59.4 wt% F and 3 wt% H. The spatially symmetrical disposition of the hydrogen and fluorine atoms along the polymer chain gives rise to a unique polarity that affects solubility, dielectric properties, and crystal morphology. The dielectric constant is unusually high.

In addition to the PVDF homopolymer, many copolymers of vinylidene fluoride have been prepared. Among the numerous co-monomers,

hexafluoropropylene ($\text{CF}_3\text{CF}=\text{CF}_2$) has assumed an important commercial role. High-performance fluoroelastomers based on vinylidene fluoride copolymers with approximately 15 to 40 mol% hexafluoropropylene (HFP) have been produced. Also, a tough, flexible copolymer of PVDF and tetrafluoroethylene (TFE) has been produced, as well as a terpolymer of PVDF, TFE, and HFP. These copolymers and terpolymers are used in the manufacture of organic coatings with lower bake temperatures than the PVDF homopolymer.

Polyvinylidene fluoride used for coatings is most commonly produced by emulsion polymerization. Traditionally, the use of fluorosurfactants such as perfluorooctanoic acid (PFOA) has been considered to be necessary for the PVDF emulsion polymerization process. Recently, however, health concerns have arisen because various studies have shown PFOA and similar long-chain fluorosurfactant species can bioaccumulate in the blood of humans. As a result, responsible PVDF manufacturers have made a concerted effort to eliminate the use of PFOA and similar fluorosurfactants from their processes. One manufacturer, Arkema, even manufactures a PVDF coating grade that is completely free of fluorosurfactants.

Polyvinylidene Fluoride Resin Types

Polyvinylidene fluoride homopolymer has been commercially available since the 1960s. Coatings based on PVDF homopolymer are regarded as being synonymous with architectural coatings having outstanding long-term durability in even the most severe environments. Two prominent U.S. manufacturers of PVDF resins for use in coatings are Arkema and Solvay Solexis. Polyvinylidene fluoride homopolymer resins are amenable to solvent-based, waterborne, and powder coating formulations. Polyvinylidene fluoride homopolymer is also available in an aqueous latex form for coating specialty items such as fabrics or filtration elements to improve their weatherability and chemical resistance.

Polyvinylidene fluoride Copolymers. Coatings grades based on copolymers of PVDF with TFE and/or HFP are also available for applications requiring lower bake temperature, enhanced coating flexibility, or other specialized properties. Specifically, PVDF-TFE copolymers have been designed for use in solution- and dispersion-based coatings. They have increased flexibility and impact resistance, especially at sub-zero temperatures. Coatings based on PVDF-TFE copolymers are easily custom formulated and can be applied to a broad range of substrates.

Terpolymers of PVDF-TFE-HFP have also been specifically designed for use in solution- and dispersion-based coatings. Like the PVDF-TFE copolymers, they have greater flexibility and impact resistance than PVDF homopolymers. However, the PVDF-TFE-HFP terpolymers have a lower melting point and broader formulation capability than PVDF-TFE copolymers,

rendering them particularly suitable for use on heat-sensitive substrates such as plastics and wood.

Recent Development. There is a new innovative platform of PVDF-based waterborne latex dispersions, which are used by paint formulators to make premium weatherable water-based coatings. Coatings formulated with these latex products can provide the durability and performance of traditional PVDF-based resin coatings, but with volatile organic compound (VOC) levels below 100 g/L (0.83 lb/gal). These products can be formulated into air-dry or low-temperature-bake coatings, making them suitable for use on heat-sensitive materials such as plastics, wood, and textiles, in addition to substrates such as metals and concrete.

Coating Formulation of Polyvinylidene Fluoride

Polyvinylidene fluoride-based coatings can be formulated as solvent solution or dispersion coatings, waterborne coatings, or powder coatings. However, most PVDF resins are used as dispersion coatings in organic solvents.

The primary components of PVDF-based coatings are:

- Polyvinylidene fluoride resin
- Acrylic modifier
- Pigments
- Organic solvents
- Other additives

The PVDF resin is the primary binder component that provides the key properties of the coating. Suppliers of PVDF resin do not manufacture coatings themselves; instead, they sell the various homopolymer and copolymer grades worldwide under licensing agreements. A license is granted only to quality coating companies, and only after a rigorous testing program is completed that encompasses both outdoor exposure testing and extensive laboratory testing. The license grants the licensee the right to identify their products as formulated from PVDF resins, and rights to the respective trademarks of the various resin suppliers. For example, Arkema requires that a PVDF licensee formulation must meet the following criteria in order to identify the product as a KYNAR 500-based coating: (a) at least 70 wt% of the total resin content must be PVDF; (b) at least 40 wt% of the total solids must be PVDF.

Acrylic Modifier. The acrylic modifier is usually a thermoplastic acrylic based on methylmethacrylate. The primary purpose of the acrylic is to improve pigment dispersion and increase adhesion to the substrate. The acrylic also improves the phase stability of the final coating. The inertness of PVDF, while a benefit in terms of exterior durability and chemical resistance, is a detriment when producing a coating formulation: it makes pigment dispersion difficult and inhibits interactions with the substrate to achieve

good adhesion. Consequently, acrylic modifiers are used to improve pigment dispersion and coating adhesion.

The acrylic used can also be a thermosetting type. Several worldwide coating manufacturers that use PVDF resins produce their own proprietary acrylics for use with PVDF-based coatings. These proprietary acrylics provide unique properties to the coating, such as higher hardness or gloss.

Pigments are added to PVDF-based coatings for three main reasons: coating aesthetics, color stability, and UV light opacity. The effects of the pigments on coating aesthetics (e.g., metallic appearance) and color are obvious. However, the primary functional role of pigments is to provide UV opacity. As stated previously, PVDF-based coatings are completely resistant to degradation by UV light because the PVDF resin does not absorb UV radiation. However, PVDF-based coatings are transparent to UV light. Thus, UV light can pass through a PVDF-based coating and attack underlying layers such as primers if the UV energy is not absorbed or reflected. This transmission of UV light can result in coating delamination because of destruction of the underlying layer(s).

A critical consideration in the selection of pigments for PVDF-based coatings is that the pigments must have the same long-term (20 to 40 years) atmospheric durability as PVDF resins. The following pigments are usually used to achieve this long-term durability:

- Calcined metal oxides and mixed metal oxides
- Rutile titanium dioxide (exterior grades)
- Mica pearlescent (exterior grades)
- Aluminum flake (coated grades)

The calcined inorganic pigments are manufactured at very high processing temperatures (up to 1315 °C, or 2400 °F) that stabilize the metal oxide. The calcining process imparts excellent chemical and thermal stability to the pigment, thereby providing excellent exterior durability, bleed resistance, and color retention to the coating in even the most severe environments.

Exterior-grade rutile titanium dioxide is the most commonly used white pigment because of its nonchalking characteristics and long-term exterior durability.

Exterior-grade mica pearlescent and light-interference pigments are used to produce special effects such as a metallic appearance, or the appearance of different colors when viewed from different angles. These pigments function by allowing multiple light reflection from different depths throughout the coating. High-quality infrared-reflecting pigments are also suitable for use in PVDF-based coatings to reduce heat absorption on architectural surfaces such as roofs.

The following types of pigments are not recommended for use with PVDF-based coatings because they do not match the long-term exterior durability of the PVDF resin:

- Organic pigments
- Fluorescent pigments
- Phosphorescent pigments
- Anatase titanium dioxide
- Extender pigments (clays, talcs)
- Cadmium pigments

Solvents. The primary functions of the solvents used with PVDF-based coatings are:

- To provide the carrier medium for solid components (i.e., disperse PVDF resin, pigments, and other solid additives)
- To modify the coating rheology to match the desired application method
- To dissolve PVDF resin and promote alloying with the acrylic modifier during the baking cycle (i.e., coalescence aid)

There are three general classes of solvents associated with PVDF resins:

- *Active solvents*, which dissolve the PVDF resin at room temperature: polar solvents, amides, phosphates, lower ketones
- *Latent solvents*, which dissolve PVDF resin at elevated temperature but not at room temperature: higher ketones, esters, glycol ethers, glycol ether esters
- *Nonsolvents*, which do not dissolve PVDF resin at any temperature: hydrocarbons, alcohols, chlorinated solvents

Latent solvents are the most common solvents used for PVDF resins. They produce dispersion coatings, allowing the solids content of the coating to be in the range of 40 to 50 wt%. In these dispersion coatings, the PVDF resin is suspended as a fine powder. The resin is carried as a stable fluid dispersion that is unaffected at room temperature. When heat is applied during the baking cycle, the PVDF resin solubilizes in the solvent and coalesces to form a uniform film as the solvent evaporates.

Active solvents can be used to produce solution coatings. However, the solids content of solution coatings is generally limited to approximately half that of a dispersion coating because of the high viscosity that results from dissolution of the PVDF resin. The lower solids and associated higher amount of solvent raises the VOC level of the coating.

Nonsolvents are used in PVDF-based formulations to act as diluents.

Other Additives. Several other additives are often added to PVDF-based formulations in small quantities to impart various properties without affecting long-term weathering resistance. Examples of these additives include:

- Anti-settling agents
- Defoamers and antifoams
- Dispersion and emulsifying agents
- Preservatives and fungicides
- Surfactants
- Flattening agents
- Drying agents
- Anti-skinning agents

- Rheology modifiers
- Ultraviolet absorbers

Typical PVDF Component Quantities. The following is an example of the typical components of a PVDF-based formulation:

Component	wt%
PVDF resin	20–25
Minimum 70% of total resin content	
Minimum 40% of total solids content	
Acrylic resin	8–11
Pigments	12–16
Solvents	50–60
Other additives	Typically <5

Application of Polyvinylidene Fluoride-Based Coatings

Application Techniques. Polyvinylidene fluoride-based coatings can be applied by coil coating, spray coating, or electrostatic powder coating. Coil coating and spray coating are the predominant methods used. Powder coating is used to only a limited degree. Typical application conditions are given in Table 2.

Primers. Polyvinylidene fluoride-based coatings are usually used with a thin organic primer. The primers are used to improve adhesion to the substrate and increase resistance to underfilm corrosion and delamination. Typical primers include solvent-based epoxy, solvent-based acrylic, and waterborne acrylic. These primers are sometimes enhanced with a small amount of PVDF to increase primer-topcoat adhesion. The primers are almost always doped with passivating pigments (e.g., chromium and nonchromium types) to protect exposed metal substrates at cut edges and at microcracks and voids in the coating.

Substrates. Polyvinylidene fluoride-based coatings are suitable for application to all common metallic substrates. These include aluminum, galvanized steel, carbon steel sheet coated with aluminum-zinc alloy, and 5Al-95Zn. The required surface preparation is similar to that used for application of any other organic coating. That is, the metal surface must be cleaned to remove dirt, oils, oxides, and other surface contaminants. The cleaned surface must then be pretreated with a thin inorganic conversion coating to maximize coating performance. For example, the preferred pretreatment for aluminum surfaces is chromium chromate. For zinc surfaces, zinc phosphate or complex cobalt oxide pretreatments are preferred.

The use of nonchromium and dried-in-place pretreatments is increasing. However, it is recommended that thorough testing be conducted with these types of pretreatments to assess the suitability of the pretreatment with the specific type of paint system and substrate being used. Proper cleaning and pretreatment is a critical step to ensure excellent long-term adhesion and corrosion resistance, as with any paint system.

Film Formation and Crystallinity of PVDF-Based Coatings. Polyvinylidene fluoride homopolymer resin is most commonly used in dispersion coatings. The PVDF powder resins are present as dispersed particles in a latent organic solvent. No dissolution or swelling of the PVDF particles occurs at room temperature because of the use of latent solvents. During the bake cycle, partial swelling and dissolution of the PVDF particles occurs at $\sim 80^\circ\text{C}$ (175°F). As the temperature is increased further, the partially dissolved PVDF particles begin to fuse during solvent evaporation. Further increases in temperature (up to $\sim 220^\circ\text{C}$, or 430 to 480°F) cause complete evaporation of solvent and fusing of the PVDF resin particles into a smooth, continuous film.

Because PVDF homopolymer is a thermoplastic, semicrystalline polymer, the properties of coatings based on PVDF are affected by their degree of crystallinity and crystal size. If PVDF-based coatings are quenched after baking, such as when the coating is applied on a coil coating line, the crystallinity is suppressed to the degree that the crystallites are very small. However, this state of suppressed crystallinity is metastable, and the crystallites will become larger when aged at elevated temperatures and/or for extended lengths of time. The larger crystallites can contribute to microcracking of the coating when the material is fabricated, such as roll forming coil-coated sheet. If PVDF-based coatings are air cooled after baking, such as coatings sprayed onto extrusions or architectural curtain walls, then large crystallites are prevalent. The thermal history (i.e., bake temperature, particularly extended time at elevated temperature) of coatings based on PVDF also affects crystal size. The levels of crystallinity and crystal size have an effect on final coating properties such as flexibility, hardness, impact resistance, gloss, adhesion, clarity of clear coats, and overall appearance. Thus, it is important to control the degree of crystallinity and crystal size of coatings based on semicrystalline polymers such as PVDF by carefully controlling the thermal history of the coating and the cooling rate after baking.

Coating Properties of Polyvinylidene Fluoride

The most significant property of PVDF-based coatings is their outstanding exterior durability. The exceptional weatherability is a result of the strength of the carbon-fluorine bond (116 kcal/mol), which is one of the strongest chemical bonds known. The bond strength provides a chemically inert coating with complete resistance to UV light degradation. Ultraviolet radiation is one of the major causes of deterioration of coatings exposed to the atmosphere.

In addition to exterior durability, PVDF resins also possess several intrinsic properties that are ideally suited to produce coatings with desirable properties. These are summarized in Table 3 and discussed in detail in the following sections.

Exterior Durability. There is only one method that can accurately evaluate the exterior durability of coatings: actual outdoor exposure. Accelerated weathering methods with equipment such as Xenon Weather-Ometers (Atlas Material Testing Solutions) and QUV fluorescent cabinets (Q-Lab Corporation) are useful for screening materials under controlled conditions but are not a substitute for actual outdoor weathering. Xenon and QUV arc tests are regularly conducted to screen variables and detect extreme anomalies in a coating formulation. However, outdoor exposure data is used to determine the true properties of a coating.

Thousands of samples of PVDF-based coatings and other architectural coatings have been on outdoor exposure at sites such as Miami, Fla., and Phoenix, Ariz. These samples comprise materials coated on commercial coil coating lines and spray lines, along with samples prepared in the laboratory. Miami and Phoenix represent extreme environmental conditions of UV radiation, heat, and humidity. Some of the samples have been exposed for more than 40 years. These samples consistently demonstrate that PVDF-based coatings have excellent color and gloss retention, low chalking, and the ability to maintain overall coating integrity.

Some outdoor exposures were initiated several years ago to provide a direct comparison of PVDF-based coatings to other commonly used architectural coatings. Figures 3 and 4 give gloss retention and color-change data of PVDF-based coatings in comparison to these other coatings. In Fig. 3, the non-PVDF coatings were removed from exposure after 16 years because they were badly deteriorated.

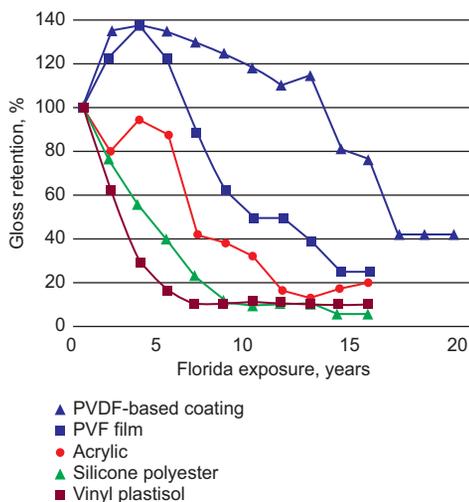
As a testament to the excellent properties of coatings with high PVDF content, their performance has been used as the basis for the American Architectural Manufacturers Association (AAMA) 2605 voluntary specification for “Superior Performing Organic Coatings” (Ref 2). The purpose of this specification is to “assist the architect, owner and contractor to specify and obtain factory-applied organic coatings, which will provide and maintain a *superior* level of performance in terms of film integrity, exterior

Table 2 Application conditions of typical polyvinylidene fluoride-based coatings

Conditions	Coil coating	Spray coating	Powder coating
Metal temperature, $^\circ\text{C}$ ($^\circ\text{F}$)	232–249 (450–480)	221–249 (430–480)	221–249 (430–480)
Baking time	30–60 s	10–20 min	10–20 min
Primer thickness, μm (mils)	5–8 (0.2–0.3)	5–10 (0.2–0.4)	5–10 (0.2–0.4)
Topcoat thickness, μm (mils)	20–25 (0.8–1.0)	25–30 (1.0–1.2)	28–51 (1.5–2.0)

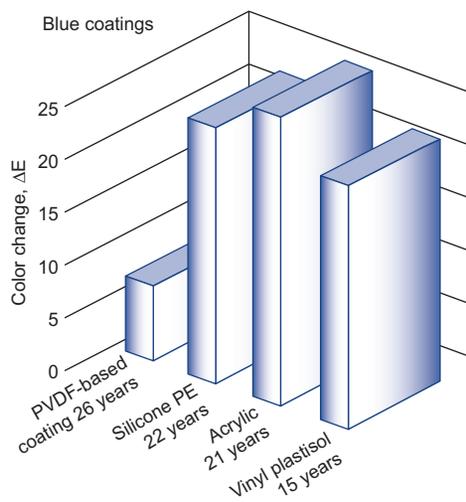
Table 3 Properties of polyvinylidene fluoride-based coatings

Desirable properties of a coating	Intrinsic properties of PVDF-based coatings
Exterior durability	Resistant to ultraviolet degradation Long-term color and gloss retention High chalk resistance
Resistant to atmospheric pollutants, gaseous and liquid corrosives	Excellent chemical resistance—acids and liquid alkalis Not attacked by ozone
Low maintenance, including low dirt pickup, nonstaining surface	Hydrophobic surface Low surface energy Low coefficient of friction
Low mildew and bacterial staining	Good moisture resistance Non-nutrient for fungal growth
Resistance to mechanical damage	Good impact resistance in tension or compression mode
Good corrosion resistance	Excellent chemical resistance Low permeability to oxygen, moisture, and corrosive ions High electrical resistivity
Good formability after coating	Good adhesion Good mechanical properties, flexibility, adhesion

**Fig. 3** Gloss retention during Florida exposure. PVDF, polyvinylidene fluoride; PVF, polyvinyl fluoride

weatherability and general appearance over a period of many years.” Other high-performing coatings that are commonly used for outdoor applications, such as silicone polyester, polyester, acrylic, urethane, and PVC have very good outdoor weathering characteristics but do not meet the stringent AAMA 2605 specification. To meet the AAMA 2605 specification, the coating must satisfy the following criteria:

- South Florida outdoor weathering (Ref 3) for 10 years exposure:
 - a. Color retention must have a ΔE color-change value of 5 units or less (Ref 4).
 - b. Chalk resistance must have a chalking rating of 8 or higher (Ref 5).
 - c. Gloss retention must be at least 50% (Ref 6).
 - d. Erosion resistance after weathering: coating must not lose more than 10% in thickness.
- Accelerated testing for 4000 h:
 - a. Cyclic corrosion testing (Ref 7) must have #8 or greater blisters rating and #7 or greater rating at scribes (Ref 8).
 - b. Humidity testing (Ref 9) must have less than size #8 blisters (Ref 10).

**Fig. 4** Color change during Florida exposure. PVDF, polyvinylidene fluoride; PE, polyester

Resistance to Atmospheric Corrosives.

Polyvinylidene fluoride-based coatings resist attack by most acids and liquid alkalis. This feature is the key to the excellent resistance PVDF-based coatings have to atmospheric pollution (e.g., acid rain) and other gaseous, liquid, and solid corrosives that can come in contact with a structure. Resistance to both strong and weak acids is particularly good. Resistance to weak alkalis is very good, but certain strong alkalis can attack PVDF surfaces. Polyvinylidene fluoride resins have been extensively tested for resistance to hundreds of chemicals. Table 4 highlights some of the chemicals that are relevant to architectural uses.

Low Maintenance. Polyvinylidene fluoride-based coatings require little maintenance because of their resistance to dirt pickup, chemical staining, and mildew/bacterial staining. The PVDF resin resists dirt pickup because of its hydrophobic nature, having a low surface energy (~ 23 dyne/cm) and low coefficient of friction (sliding friction to steel ~ 0.15 to 0.17).

Resistance to chemical staining is due to its excellent chemical inertness. The ability to resist mildew and bacterial staining is due to

Table 4 Polyvinylidene fluoride resin chemical resistance

Chemical	Concentration	Maximum use temperature	
		$^{\circ}\text{C}$	$^{\circ}\text{F}$
Acetic acid	10% in water	107	225
Ammonium hydroxide	Concentrated	107	225
Bleaching agents	...	135	275
Brine	...	140	285
Carbon dioxide	...	140	285
Carbonic acid	...	135	275
Citric acid	...	135	275
Cresol	...	65	150
Diesel fuels	...	140	285
Fatty acids	...	140	285
Ferric chloride	...	140	285
Ferric hydroxide	...	121	250
Ferric sulfate	...	140	285
Formic acid	...	121	250
Natural gas	...	140	285
Unleaded gasoline	...	140	285
Hydrochloric acid	Concentrated	140	285
Hydrofluoric acid	40% in water	121	250
Hydrogen sulfide	...	135	275
Nitric acid	10% in water	79	175
Nitrogen dioxide	...	77	170
Ozone	...	107	225
Sodium chlorite	...	121	250
Sodium hydroxide	10% in water	38	100
Sulfur dioxide	...	79	175
Sulfuric acid	60% in water	121	250
Tar	...	121	250
Urea	...	121	250
Vinyl chloride	...	93	200
Salt water	...	140	285
Sewage water	...	121	250

Source: Ref 11

PVDF being a non-nutrient for fungal growth. It will not support fungal growth when tested according to Ref 12. Also, PVDF resin has good moisture resistance, with a water absorption value of 0.05% maximum per Ref 13. Most organic coatings used for outdoor environments have water absorption values of approximately 0.1 to 3.0 wt% (Ref 14).

Resistance to mechanical damage and wear is attributable to the good abrasion resistance (Table 5) and impact resistance of PVDF-based coatings. The impact resistance of PVDF-based coatings is so good that usually the metal substrate can be ruptured on impact with no cracking or loss of adhesion of the coating.

Corrosion Resistance. Polyvinylidene fluoride-based coatings are recognized as having excellent corrosion resistance when exposed to even the most severe environments. They are frequently chosen for use in severe environments over other coatings and construction materials that cannot withstand such conditions over the long term.

Polyvinylidene fluoride-based coatings are chemically inert. In addition, they possess several other intrinsic properties that contribute to their excellent corrosion resistance, such as:

- Low permeation rate of oxygen, moisture, and corrosive ions
- High electrical resistivity (2×10^{14} ohm-cm)
- Good mechanical properties, flexibility, and adhesion to the substrate

The importance of these characteristics can be seen by considering the mechanisms of paint blistering and corrosion of painted metal substrates.

Electrochemical Considerations. Corrosion of a metallic substrate in the presence of an aqueous electrolyte is an electrochemical process. In such environments, local anode and cathode cells are established on a microscopic scale. In these cells, corrosion is accelerated at the anode and slowed at the cathode. These processes are exacerbated by the presence of oxygen, moisture, and corrosive ions.

Paint Blistering. All paint films are semipermeable membranes. Water-soluble impurities commonly exist at the coating-substrate interface (e.g., salt residues from pretreatment processes, hard water salts, etc.). These impurities can lead to osmotic blistering. That is, water permeates through the paint film to achieve equilibrium with the impurities (i.e., osmosis). The water pressure that builds at the coating-substrate interface exceeds the necessary force to deform the film and breaks the interfacial bonds leading to blistering. Osmotic pressure in blisters can be as high as 25 to 30 atmospheres.

The area under a paint blister is a likely location for an electrochemical corrosion cell to exist. Permeation of moisture and oxygen through the paint can accelerate the corrosion process and lead to the generation of voluminous corrosion products under the paint. These corrosion products can eventually rupture the coating and exude unsightly residues onto the painted surface.

The oxygen and moisture permeation rate of the coating is a key determinant in the formation of osmotic blistering. The low permeability rates of water vapor, oxygen, and other gases for the PVDF resin are given in Table 6.

The low electrical conductivity of the PVDF resin is also important because of the electrochemical nature of corrosion. An electrically insulating paint film helps to reduce current flow in the coating system.

The mechanical properties, flexibility, and adhesion of the paint film are also important to preserve coating integrity when parts are formed and help to prevent paint blistering. The data in Table 7 demonstrates the excellent flexibility, coating adhesion, and impact resistance of PVDF-based coatings.

Accelerated Tests. Polyvinylidene fluoride-based coatings with a minimum of 70 wt% PVDF resin routinely exhibit excellent performance in severe accelerated tests designated by various technical associations. Typical performance in some of these tests is given in Table 8.

Table 5 Sand abrasion resistance

Abrasion coefficient(a)	PVDF-based coating	Silicone polyester	Baked enamel	Urethane	Plastisol
Sand, liters	59	23	32	44	32

(a) Liters of sand per mil of coating to wear a 4 mm (0.16 in.) diameter hole in the coating per Ref 15. PVDF, polyvinylidene fluoride

Typical End Uses of Polyvinylidene Fluoride-Based Coatings

Polyvinylidene fluoride-based coatings are usually used in architectural applications that require excellent long-term exterior durability with little maintenance. Architectural coatings are designed to provide protection and to keep wind and weather outside. The best coatings protect for decades and keep their color and finish just as long. Polyvinylidene fluoride is one of the toughest resins available to coatings formulators. It resists many chemical hazards and retains color and gloss for decades. Therefore, these coatings are ideal for structures such as high-rise office buildings, apartment buildings, businesses, airport air traffic control towers, and sports stadiums. Typical components include metal siding and roofing, storefronts, curtain walls, skylight frames, and other miscellaneous trim and extrusions. The uses are as varied as the architectural designs themselves. Components can be either postformed from pre-coated coil stock or spray coated after fabrication.

The structures shown in Fig. 5 to 7 are examples of the versatility and typical applications of PVDF-based coatings.

Opportunities for Improvement

Although PVDF-based coatings have outstanding overall properties, there are two opportunities for improvement, as with all organic coatings:

Harder Coatings. Polyvinylidene fluoride coatings are generally slightly softer than several

other organic coatings. This higher softness can result in scuffing and marring during fabrication, handling, and use of painted components. Harder coatings are also more resistant to graffiti.

Wider Range of Gloss. Coatings based on PVDF have a limited gloss range, approximately 15 to 30 gloss units measured at 60° incident light. A higher gloss range is desired in many applications, perhaps as high as 80 in some cases; this approaches automotive-like finishes. Lower gloss (approximately 10) is desired for a few applications such as airport control towers to limit glare.

There appears to be some ability to address both these opportunities by means of the new waterborne PVDF technology. For instance, one coating company is now offering a coating system based on a low-temperature-bake, cross-linked topcoat, which is capable of achieving 3H-pencil hardness. This coating complies with AAMA 2605-13 (Ref 2).

Health and Safety Considerations of Polyvinylidene Fluoride

Polyvinylidene fluoride is inert and is not hazardous under typical processing and use conditions. It contains no dangerous components and is not harmful. Based on toxicity studies (including acute oral, systemic, subchronic, subacute contact, implantation, and tissue culture tests), PVDF is nontoxic (Ref 19). However, mechanical

Table 7 Flexibility and adhesion of polyvinylidene fluoride-based coatings

Test	Value
Elongation	
24 °C (75 °F)	50–300%
99 °C (210 °F)	200–500%
T-bend—no cracking or adhesion loss(a)	IT
Cross-hatch adhesion—reverse impact(b)	No adhesion loss
Boiling water cross-hatch—reverse impact(c)	No adhesion loss

(a) NCCA II-19 method (Ref 16). (b) NCCA II-16 method (Ref 17): 0.635 mm (0.025 in.) aluminum panel, 58 cm-kg (50 in.-lb). (c) AAMA 2605 method (Ref 2): 0.635 mm aluminum panel, 58 cm-kg (50 in.-lb)

Table 6 Permeability of polyvinylidene fluoride resin to common gases

Gas	Permeability, mg/mil/100 in. ² /24 h
Water vapor	100
Oxygen	3.1
Carbon dioxide	1.7
Nitrogen	0.7
Hydrogen	55
Chlorine	0.3

Table 8 Accelerated test results of polyvinylidene fluoride-based coatings

Test	Conditions	Method	Results
Humidity	4000 h	AAMA 2605(a)	No blisters
	38 °C (100 °F)	ASTM D2247(b)	
Salt spray	100% relative humidity		No scribe delamination
	4000 h	AAMA 2605(a)	
Muriatic acid Mortar	5% NaCl	ASTM B117(c)	No blistering or change in appearance
	15 min spot test	AAMA 2605(a)	
Nitric acid	Wet mortar	AAMA 2605(a)	No adhesion loss or change in appearance
	100% relative humidity		
Detergent	24 h		No color change
	38 °C (100 °F)	AAMA 2605(a)	
Detergent	Contact with 70% nitric acid	AAMA 2605(a)	No adhesion loss, blistering, change in appearance
	30 min	ASTM D2244(d)	
Detergent	3% detergent solution	AAMA 2605(a)	No adhesion loss, blistering, change in appearance
	38 °C (100 °F)	ASTM D2244(d)	
	72 h		

(a) Ref 2. (b) Ref 9. (c) Ref 18. (d) Ref 4



Fig. 5 Rio Five, Las Vegas, Nevada, USA



Fig. 6 Toys-R-US, Norman, Oklahoma, USA

malfunction or human error may lead to thermal decomposition at elevated temperatures, with evolution of toxic hydrogen fluoride. The thermal decomposition temperature of PVDF is over 375 °C (705 °F) (Ref 20), well above its normal bake temperature of ~200 to 250 °C (390 to 480 °F). In the extremely unlikely event of thermal decomposition, precautions must be taken to prevent inhalation of or other physical contact with hydrogen fluoride, a slow-acting poison whose symptoms of contact are not immediately apparent. Victims should get immediate professional medical attention in case of suspected exposure.

Summary

Polyvinylidene fluoride-based coatings are typically used in outdoor applications that require exceptionally high performance and excellent long-term exterior durability with little maintenance. The most significant property of PVDF-based coatings is their outstanding exterior durability. The exceptional weatherability is a result of the strength of the carbon-fluorine bond (116 kcal/mol), which is one of the strongest chemical bonds known. The bond strength provides a chemically inert coating with complete

resistance to UV light degradation. Ultraviolet radiation is one of the major causes of deterioration of a coating exposed in the atmosphere.

Metal structures that have been finished with PVDF-based coatings typically retain their original color and gloss for long periods of time in most outdoor environments, sometimes up to 40 years. Extreme UV light, humidity, smog, acid rain, industrial gases, and other airborne hazards have little effect on the metal structures coated with these finishes, provided formulators develop their coatings from high-quality pigments and additives.

Solvent-based, waterborne, and powder-coating-bakeable formulations are available for use on metal substrates. Low-temperature-bake and air-dry formulations have recently been developed for use on heat-sensitive substrates such as plastics and wood. Polyvinylidene fluoride is also available in an aqueous latex to coat specialty items such as fabrics or filtration devices.

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