Rio Five, Las Vegas

Creating Coatings
for Better Buildings

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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. Fluoropolymers are the toughest resins available to coatings formulators. Known under various trade names, such as Kynar®[1] and Teflon®[2], they offer the best available coating performance. Fluoropolymer finishes resist many chemical hazards and retain color and gloss for decades.

Formulators opting for fluoropolymers will also find a variety available, with different levels of chemical resistance and processing restrictions.

Three fluoropolymer resins are commonly used in coatings. They are polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polyvinyl fluoride (PVF). Table 1 lists tradenames and formulas. The differences in performance and processing among these

[1] Kynar® is a registered trademark of Elf Atochem North America Inc.

[2] Teflon® is a registered trademark of E.I. DuPont de Nemours and Co.

materials begins with their structure. This article explains how and why fluoropolymers are used in coatings, and how to formulate the coatings that provide the best protection for buildings.

The carbon-fluorine bond is the key to the thermal, chemical and ultraviolet (UV)-resistance properties of all fluoropolymers. The number of fluorine atoms present has a direct bearing on each type of fluoropolymer's performance properties. The unique combination of properties of fluoropolymers is attributed to two intrinsic characteristics of fluorine atoms — extremely high electronegativity and small atomic radius. The atomic structure of fluorine gives rise to some of the strongest chemical bonds known (see Figure 1).

PVF contains only one fluorine atom (see Figure 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 cycle operating range is very small and requires close control.

PTFE with four fluorine atoms (see Figure 2b) has no specific crystalline melting point, and has a high sintering point; consequently, it forms a relatively porous surface. 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 (see Figure 2c) contains alternating carbon/fluorine and carbon/hydrogen bonds, which provide a polarity that enables the formulation of a practical coating that resists environmental degradation and dirt retention. This structure enables PVDF to resist 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 architectural uses.

PVDF Properties

Crystallinity can vary from about 35% to 70%, depending on the method of preparation and thermo-mechanical 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.

PVDF exhibits a complex crystalline polymorphism not observed in other synthetic polymers. There are four distinct crystal forms: alpha, beta, gamma and delta. The polymorphs are present in different proportions, depending on processing conditions during polymerization. The alpha and beta forms are predominant in industrial situations.

The alpha form prevails in coatings and normal melt processing of structural parts. It is the most common form of PVDF and the most thermodynamically stable. Therefore, it is the most readily obtained under a variety of conditions. The chain configuration of the alpha form is transgauche, placing the fluorine and hydrogen atoms alternately on each side of the chain (see Figure 3) — the

Figure 1 / Carbon Bond Energies

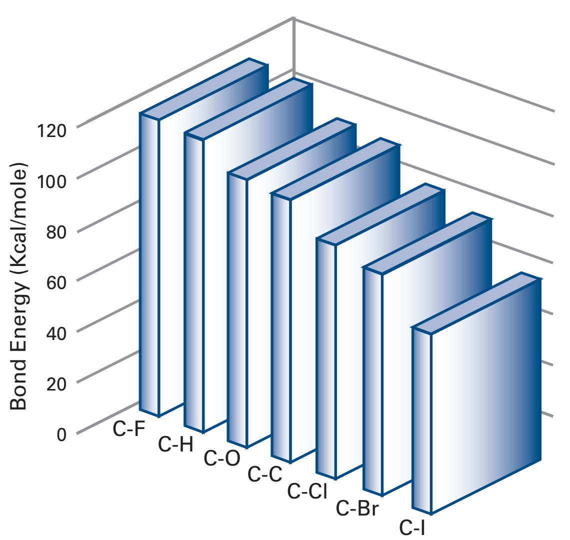

Figure 2 / PVF (A), PTFE (B) and PVDF (C)

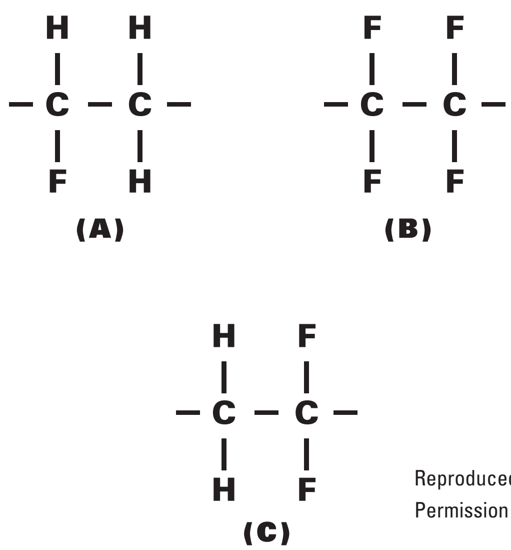

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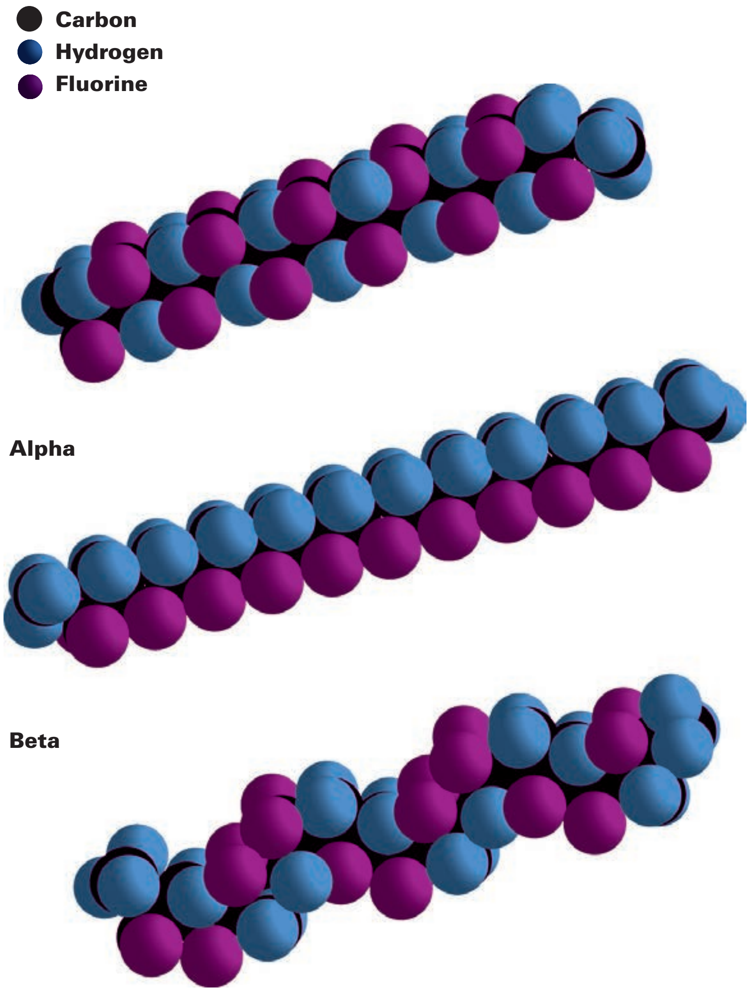
Figure 3 / PVDF Crystalline Forms



Alpha

Beta

Gamma

so-called ‘crankcase’ chain structure.

The beta form develops under mechanical deformation of melt-processed materials, usually at temperatures approaching the melting transitions. The beta form configuration consists of all the fluorine atoms on one side of the chain, and the hydrogen atoms on the other side (see Figure 3) — the ‘zigzag’ chain structure. This structure is the key to high piezo- and pyro-electric activity because the net dipole moment is very high and perpendicular to the chain direction.

The gamma form arises infrequently, and only under special circumstances (see Figure 3).

The delta form is obtained by a distortion of one of the other phases under high electric fields.

PVDF Polymerization

Polyvinylidene fluoride is the addition polymer of 1,1-difluoroethene, $H_2C{=}CF_2$, commonly known as vinylidene fluoride (abbreviated VDF or VF_2). It is produced by suspension polymerization or, 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% fluorine by weight and 3% hydrogen by weight. The spatially symmetrical disposition of the hydrogen and fluorine atoms along the polymer chain gives rise to a 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 comonomers, hexafluoropropylene ($CF_3{-}CF{=}CF_2$) has assumed an important commercial role. High-performance fluoroelastomers based on vinylidene fluoride copolymers with approximately 15% to 40% molar 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 (hexafluoropropylene).

PVDF *properties*

PVDF is a high-molecular-weight, semi-crystalline polymer that has the following unique properties.

Exceptional weathering resistance,
Resistance to ultraviolet light,
High thermal and chemical resistance,
Resistance to nuclear radiation,
Good abrasion resistance,
High mechanical strength and toughness,
High purity,
Good moisture and fungus resistance,
High electrical resistivity,
Low surface energy,
Low coefficient of friction (maintenance-free, nonstaining coating surface characteristics), and
Low refractive index.

Table 1 / Fluoropolymer Commonly Used in Coating Formulations

Trade Name	Chemical Name	Acronym	Monomer
Teflon®	polytetrafluoroethylene	PTFE	$F_2C{=}CF_2$
Kynar®	polyvinylidene fluoride	PVDF	$F_2C{=}CH_2$
*Tedlar®	polyvinyl fluoride	PVF	$H_2C{=}CHF$

* Tedlar® is a registered trademark of E.I. DuPont de Nemours and Co.

Toys-R-US, Norman, Okla.

Product Terminology

Polyvinylidene fluoride has been commercially available since 1960. Elf Atochem North America Inc. was one of the first companies to commercialize PVDF for both coatings and melt-processed applications and trademark coatings containing PVDF as Kynar®. The Kynar 500® resin is used extensively to produce architectural coatings.

Subsequent to 1965, the company developed copolymers and terpolymers based on PVDF that provide unique coating properties, particularly lower bake temperature and increased solubility (see Table 2). Despite the success of these new materials, and the fact that the weathering properties of the PVDF copolymers and terpolymers are comparable to those of Kynar 500 resin when properly formulated, the latter remains the predominantly used PVDF coating resin.

Kynar Coatings Formulation

Kynar-based coatings can be formulated as solvent solution or dispersion coatings, waterborne coatings, or powder coatings. However, most Kynar resins are formulated into dispersion coatings in organic solvents.

Kynar-based coatings are primarily composed of Kynar resin, acrylic modifier, pigments, organic solvents and other additives.

The resin is the primary binder component, which provides the key properties of the coating. Elf Atochem licenses the various homopolymer and copolymer resins worldwide. A license is granted only to quality coating companies, and only after a rigorous testing program is completed. This program encompasses both outdoor exposure testing and extensive laboratory testing. The license grants the licensee the right to identify their products formulated from Kynar resins with the Kynar trademark.

For Kynar 500 resin, a licensee formulation must meet the following criteria to identify the product as a Kynar 500-based coating.

1. At least 70% by weight of the total resin content must be Kynar 500.
2. At least 40% by weight of the total solids must be Kynar 500.

The acrylic modifier is usually a thermoplastic acrylic based on methyl methacrylate. The primary purpose of

Table 2 / Properties of Kynar-Based Coatings.

Desirable Properties of a Coating	Intrinsic Properties of Kynar-Based Coatings
Exterior Durability	Resistant to UV Degradation Long-Term Color and Gloss Retention High Chalk Resistance
Resistant to Atmospheric Pollutants, Gaseous and Liquid Corrosives	Excellent Chemical Resistance — Acids and Liquid Alkalies Not Attacked by Ozone
Low Maintenance • Low Dirt Pickup • Nonstaining Surface	Hydrophobic Surface Low Surface Energy Low Coefficient of Friction
Low Mildew and Bacterial Staining	Good Moisture Resistance Nonnutrient for Fungal Growth Resistance
Resistant to Mechanical Damage and Wear	Good Abrasion Resistance Good Impact Resistance (Tension or Compression Mode)
Good Corrosion Resistance	Excellent Chemical Resistance Low Permeability to Oxygen, Moisture and Corrosive Ions High Electrical Resistivity Good Adhesion
Good Formability After Coating	Good Mechanical Properties, Flexibility, Adhesion Under Stress

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 inert characteristics of PVDF, while a benefit in terms of exterior durability and chemical resistance, is a detriment when producing a coating formulation. The inertness of PVDF makes pigment dispersion difficult, and inhibits reaction 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 thermoset, but thermosets are much less common than thermoplastics.

Several worldwide Kynar 500 resin users produce their own proprietary acrylics for use in these coatings. These proprietary acrylics provide unique properties to the coating, such as higher hardness or gloss.

Pigments are added to Kynar 500-based coatings for coating aesthetics, color stability and UV light opacity. The pigments' affects on coating aesthetics, such as metallic appearance and color, are obvious. However, the primary functional role of pigments is to provide UV opacity. Because the PVDF resin does not absorb UV radiation, Kynar 500-based coatings are completely resistant to degradation by UV light. Because Kynar 500-based coatings are transparent to it, UV light can pass through these coatings and attack underlying layers, such as the primer, 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 or layers.

A crucial consideration in the selection of pigments for Kynar 500-based coatings is that the pigments must have the same long-term (20 to 30 years) atmospheric durability as Kynar resins. The following pigments are usually used to achieve this long-term durability.

- Calcined metal oxide and mixed metal oxides,
- Rutile titanium dioxide — exterior grade, and
- Mica pearlescent — exterior grade.

The calcined inorganic pigments are manufactured at very high processing temperatures (up to 2,400°F or 1,315°C) to stabilize the metal oxide. The calcining process provides excellent chemical and thermal stability to the pigment. This imparts 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 color shifting or a metallic appearance. These pigments function by allowing multiple light reflection from different depths throughout the coating.

Typical Kynar 500 Component Quantities

The following gives an example of the typical components of a Kynar 500-based formulation (given in percent by weight).

Kynar 500 resin (20% to 25%).
Minimum 70% of resin fraction.
Minimum 40% of total solids.

Acrylic resin (8% to 11%).
Pigments (12% to 16%).
Solvents (50% to 60%).

The following types of pigments are not recommended for use with Kynar 500-based coatings because they do not match the long-term exterior durability of the Kynar 500 resin.

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

There are three general classes of solvents associated with Kynar resins.

1. *Active solvents*, which dissolve Kynar resin at room temperature: polar solvents, amides, phosphates and lower ketones.
2. *Latent solvents*, which do not dissolve Kynar resin at room temperature, but do at elevated temperature: higher ketones, esters, glycol ethers and glycol ether esters.
3. *Nonsolvents*, which do not dissolve Kynar resin at any temperature: hydrocarbons, alcohols, chlorinated solvents.

Latent solvents are the most common solvents used for Kynar 500 resin. They produce dispersion coatings that allow the solids content of the coating to be in the range 40 to 50 wt%. In these dispersion coatings, the Kynar 500 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 resin solubilizes in the solvent and coalesces to form a uniform film as the solvent evaporates.

Active solvents can be used to produce a solution coating. However, the solids content of solution coatings is generally limited to about half that of a dispersion coating because of the high viscosity that results from dissolution of the resin.

Nonsolvents are used in Kynar 500-based formulations to act as diluents. Several other additives are often added in small quantities to impart various properties without affecting long-term weathering resistance. Examples of these additives include the following.

- Antisettling agents,
- Defoamers and antifoams,
- Dispersion and emulsifying agents,
- Preservatives and fungicides,
- Surfactants,
- Flatting agents,
- Drying agents,
- Anti-skinning agents,
- Rheology modifiers, and
- UV absorbers.

Harris Methodist Klabzuba Cancer Center, Ft. Worth, Texas

Coating Properties

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. UV radiation is one of the major causes of deterioration of a coating exposed in the atmosphere.

In addition to exterior durability, these resins also have several intrinsic properties that are ideally suited to produce coatings with desirable properties. These are summarized in Table 2 and are discussed in the following sections.

Exterior Durability

One method that can accurately evaluate the exterior durability of coatings is actual outdoor exposure. Accelerated weathering methods, such as QUV and xenon or carbon-arc weatherometers, are useful for screening materials under controlled conditions, but are not a substitute for actual outdoor weathering. QUV and carbon arc weathering 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.

About 5,000 samples of Kynar 500-based coatings and other architectural coatings are currently on exposure in Miami and Phoenix. These samples are comprised of materials coated on commercial coil-coating lines and spray lines, along with samples prepared in the laboratory. Miami and Phoenix represent extreme conditions of UV radiation, heat and humidity. These samples consistently demonstrate that PVDF-based coatings have excellent color and gloss retention, low chalking, and maintain overall coating integrity.

Also, some outdoor exposure series were initiated several years ago to provide a direct comparison of these coatings to other architectural coatings. Figure 4 and Figure 5 give gloss-retention and color-change data of Kynar 500-based coatings vs. these competitive coatings. In Figure 4, the competitive coatings were removed from exposure after 11 years, because they were badly deteriorated.

Fluorinated Ethylene Vinyl Ether

A relatively new coating for architectural use is based on a copolymer of fluoroethylene alkyl vinyl ether (FEVE). Fluoroethylene reportedly confers weathering resistance and durability to the polymer. Alkyl vinyl ether units provide solubility in various organic solvents, as well as transparency, gloss, hardness and flexibility. Coatings based on FEVE are generally two-component, thermosetting systems, which require a high degree of crosslinking to achieve final coating properties.

FEVE-based coatings are being evaluated on outdoor exposure in Florida. Results show that FEVE-based coatings have excellent gloss retention for about five years, but then the gloss decreases precipitously. The rapid decrease in weathering after five years is most likely due to degradation of the alkyl vinyl ether groups. Figure 6 shows a comparison of Kynar 500-based coatings to FEVE coatings after 13 years' exposure in Florida. The curves represent composite results of several samples of each resin.

Maintenance

PVDF-based coatings resist attack by most acids and liquid alkalis. Resistance to both strong and weak acids is particularly good. Resistance to weak alkalis is very good, but certain strong alkalis can attack Kynar 500 surfaces. This feature is the key to the excellent resistance Kynar 500-based coatings have to atmospheric pollution, such as acid rain, and other gaseous, liquid and

Figure 4 / Florida Exposure, Gloss Retention

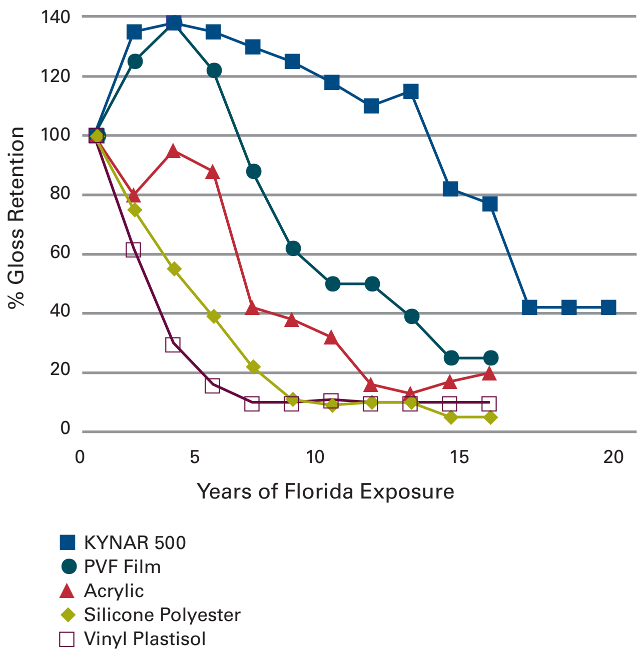
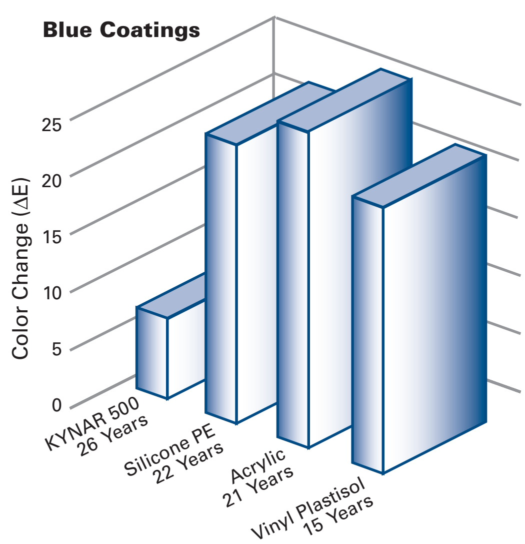


Figure 5 / Florida Exposure Data



solid corrosives, which can come in contact with a structure. Kynar 500 resins have been extensively tested for chemical resistance.

Kynar 500-based coatings require little maintenance because of their resistance to dirt pickup, chemical and mildew/bacterial staining, and mechanical damage and wear. The Kynar 500 resin resists dirt pickup because of its hydrophobicity, low surface energy (~23 dyne/cm) and low coefficient of friction (sliding friction to steel –0.15 to 0.17).

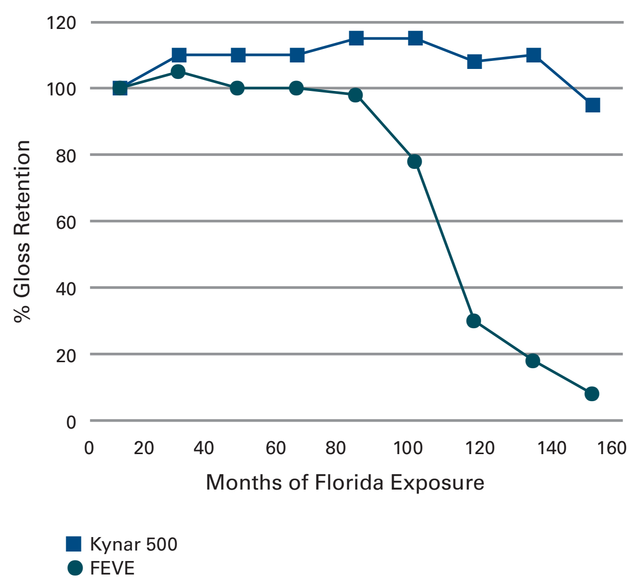
Resistance to chemical staining is due to its excellent chemical inertness. The ability to resist mildew and bacterial staining arises from the fact that the Kynar 500 resin is a nonnutrient for fungal growth. It will not support fungal growth when tested according to method 508 of the U.S. military standard 810B. Also, it has good moisture resistance with a water absorption value of 0.05% maximum per ASTM D570 method. Most organic coatings used for outdoor environments have water absorption values of about 0.1% to 3% by weight.

Resistance to mechanical damage and wear is attributable to the good abrasion resistance and impact resistance of Kynar 500-based coatings. The impact resistance is so good that usually the metal substrate can be ruptured upon impact with no cracking or loss of adhesion of the coating.

Corrosion Resistance

Kynar 500-based coatings are recognized as having excellent corrosion resistance when exposed to even the

Figure 6 / Kynar 500 vs. FEVE



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.

PVDF-based coatings are chemically inert. In addition, they have several other intrinsic properties that contribute to their excellent corrosion resistance, including the following.

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

Applications

Kynar 500-based coatings are usually used in applications where excellent long-term exterior durability is required, with little maintenance. Therefore, these coatings are ideal for structures such as high-rise office buildings, apartments, condominiums and sports stadiums. Typical components include metal siding and roofing, storefronts, curtain walls, louvers, skylights, and other miscellaneous trim and extrusions. The uses are as varied as the architectural designs themselves. Components can be either post-formed from pre-coated coil stock, or spray coated after fabrication.

Summary

After 30 years, buildings with metal components that have been finished with fluoropolymer coatings retain the color and gloss they had the day they opened. Smog, acid rain, industrial gases and other airborne hazards have little effect on the metal building components coated with these finishes. When formulators develop their coatings from quality resins and pigments, they ensure good performance and may provide coating protection that retains its color and gloss long after the buildings' designers are signing their Social Security checks.

For more information on fluoropolymer resins,
Circle Number 84.