The Uses of Polyvinylidene Fluoride based resins in Chemical Handling Systems

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Abstract

Polyvinylidene fluoride (PVDF) based polymer resins have been used for corrosive and chemically aggressive fluid containment since 1964. In the 1980's copolymers of vinylidene fluoride and hexafluoropropylene (HFP) were introduced that complimented the very rigid PVDF product line with a more flexible version of PVDF. Recently, other new technologies have been introduced for PVDF where it has been functionalized which allows it to be bonded to lower cost structural polymers during processing. Additionally, recent development of special grades of PVDF allow for finely woven and non-woven chemical filtration products and the creation of reliable conductive versions. Due to special properties not found in other plastics or metals, PVDF is used extensively in the following industries: chlor-alkali containment, bromine, acid production & distribution, mining, metal preparation, petrochemical, pharmaceutical, food & beverage, semiconductor, pulp & paper, waste water treatment, and power generation. This paper will outline the use of PVDF, reactive PVDF and/or PVDF based copolymers in specific chemicals and the special corrosive conditions that can be associated with them. It will also feature visual examples of PVDF-based components and how they are used in chemical applications.

Keywords: corrosion, PVDF, copolymer, HFP, fluoropolymer.

Introduction

Polyvinylidene Fluoride is a polymer that combines unique qualities of mechanical strength at ambient and elevated temperatures, abrasion resistance, chemical stability, flame retardancy, purity in natural form, and resistance to outdoor weathering conditions that have led to this product and its copolymers to being one of the top 3 fluoropolymers sold in the world based on volume. The major uses of this polymer in applications related to corrosion resistance are as fluid handling components such as rigid pipe & fittings, flexible pipe on long reels, microporous membranes, automotive fuel lines, dump tower packing, flexible tubing & fittings, pumps, electrical wiring insulation or sleeving, and long life decorative paint finishes for aluminum extrusions and architectural components. For each of these applications PVDF or PVDF copolymers have a different feature compared to alternatives that makes it the preferred material of construction. Table 1 gives physical and thermal comparison of some of the most common polymers used for chemical handling.

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Table 1 - Physical Property Comparisons of Common Polymers* Compared to PVDF

Polymer	Melting Point (°C)	Deflection Temperature (°C) @ 0,46 MPa (66 psi)	Abrasion Resistance (mg loss / 1000 cycles @ 1 Kg load)	Tensile Strength (MPa) at Break (23°C)
PVDF	170	146	5-10	53,8
PVDF Copolymer	157	70	7	41,4
PVC	140	55	12-20	48,3
PP	163	110	15-20	34,5
UHMWPE	130	65	5	38,6
PTFE	325	120	500-1000	27,6

- Data extracted from Ultrapure Water® July/August 1987 issue

* there are large ranges within a polymer family, the numbers used here are general

PVDF comes in many grade types that offer different properties. Sometimes these property differences are negligible, and other times these differences could be important enough that the service lifetime could be as little as 3 months or as great as 40 years in the same application. The intention of this paper is to aid the designer by focusing on the types of corrosive chemical services that commonly utilize PVDF to provide long life performance.

Results and Discussion

Halogens and Caustics

Halogens such as bromine, chlorine, fluorine and iodine are known to be very aggressive and corrosive to even the most expensive/exotic metal substrates. In addition, this family of chemicals can attack most other polymers that do not have the inherent stability of fluoropolymers. In the family of fluoropolymers, the small non-polar molecules that represent liquid and gaseous bromine and chlorine permeate easily through fully fluorinated polymers that are non-polar like PTFE, FEP and PFA. This permeation characteristic makes these fluoropolymers not generally preferred as a material of construction to contain chlorine and bromine, or to protect other metallic substrates from them. PVDF offers a combination of good chemical stability to halogens and a stronger polarity and higher crystallinity that limits the permeation of this family of chemicals. It is common for engineers to specify PVDF socket fused piping, PVDF copolymers (VF2/HFP) plastic lined steel piping and vessel lining, PVDF or PVDF copolymer fiberglass (FRP) wrapped piping and dual laminate tanks, PVDF pumps and nozzles, and PVDF copolymer powder coatings on metal to handle halogens [(1)]. Depending on the concentration of the halogen solution, PVDF products can handle continuous service up to 150°C (except for coatings that are limited to 110°C maximum due to expansion/contraction concerns with the substrate).

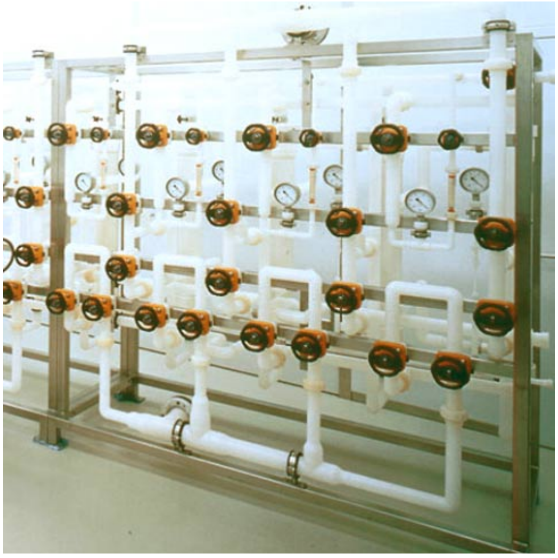


Photo 1 - Welded PVDF piping system used for handling HCl and other aggressive chemicals

Common halogen services handled by PVDF systems are: chlorine (dry and wet), brine, sodium hypochlorite solutions with low caustic content, methyl chloride, methylene chloride, ethylene dichloride, hydrochloric acid (HCl), sodium chlorate, chlorine dioxide, chlorophenols, chlorobenzene, metallic chlorides, bromine, bromine water, hydrobromic acid (HBr), bromobenzene, bromine salts, hydrofluoric acid (HF) and iodine.

Combinations of the above listed chemicals with other families of chemicals can create by-products, so if it is known that a solution will contain more than water, it is recommended that a designer contact a polymer manufacturer to see if test data is available, or to help set up a small scale test before field installation. Another issue of concern is that PVDF is very transparent to light sources. This property makes PVDF a superior material for long-term outdoor weathering performance in areas of extreme sunlight, but in corrosion applications uncovered PVDF can allow light to add energy to chlorinated chemicals breaking them down into more aggressive by-products that attack the polymer. This problem is easily remedied by covering tanks and pipe with metal, FRP, foam insulation, colored tape, or paint. Additional measures to prevent premature failure in chlorine service are to keep the sunlight away from the chemical handling system, or, pigmentation of the PVDF components (typically PVDF can be made available in red, black or blue as a standard product line) which acts as a UV absorber.

Acidic Environments

Acids create a difficult corrosion problem for engineers and designers. Based on concentration of the specific chemical, a metallic contact service may or may not have good long term chemical resistance. Metals often handle high concentration acids well, but can react poorly to low concentration acids and chemical mixtures. Polymers on the other hand, often do very well with low concentration acids and their overall resistance goes down as the acid concentration goes up. PVDF maintains excellent chemical resistance in acids even at elevated temperatures and high concentrations. The same types of chemical handling systems used in halogen containment can be used for acids. In supported systems, PVDF copolymers often have better overall chemical resistance to high concentration acids than PVDF homopolymer.

Typical mineral acids handled cost effectively by PVDF in many industries are sulfuric (up to 96% for PVDF homopolymer, and 98% for special PVDF copolymer), nitric (up to 70%), phosphoric, chromic, methane sulfonic (MSA), hydrochloric, hydrofluoric, and hydrobromic. Due to the vast difference of all of these acids, it is recommended to consult a chemical resistance guide for the temperature limitations for each chemical.

Organic acids such as acetic acid, carboxylic acid, and formic acid pose little problem for PVDF at low temperatures and low concentrations, however, at 100% concentration they can begin to swell and soften PVDF, and especially, PVDF copolymers.

In the mining and metal preparation industries, PVDF is commonly used as a welded piping system, flanged FRP lined or metal lined piping, pumps, coatings on valves and other components, and for vessel construction to maintain long life in highly corrosive acids that change in concentration (2).

Photo 2 gives an example of how PVDF components can be combined to make a full fluid handling system.

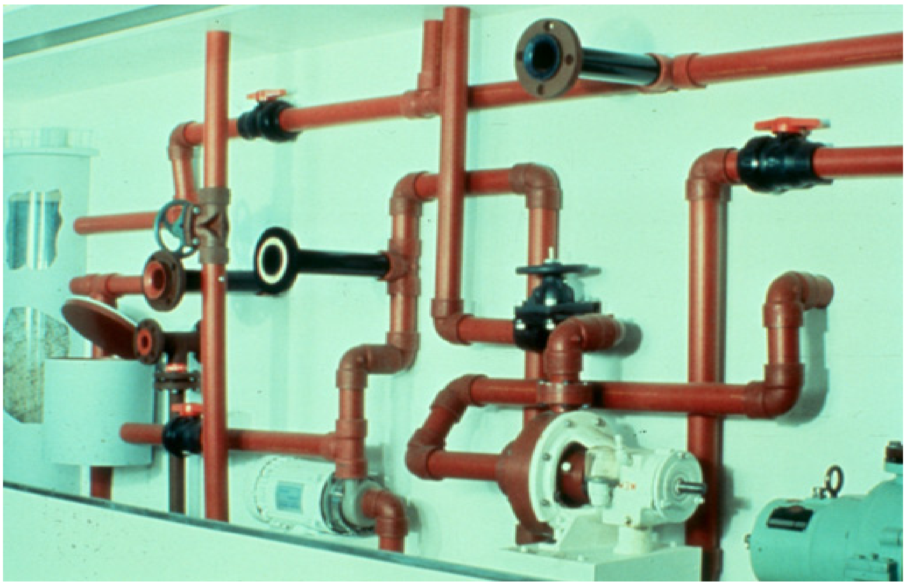


Photo 2 - Fluid Handling System Schematic Using PVDF Components for Handling Acids (Tower Packing, Holding Tank, Pipes, Lined Pipes, Valves, Pumps and Fittings)

Laboratory based chemical testing of PVDF and PVDF copolymers for various chemicals are listed in Table 2.

Table 2 - Tensile Strength at Yield in Mpa (psi) of PVDF Grades Exposed to Various Chemicals for 6 Months at Ambient Outdoor Conditions in King of Prussia, PA, USA

Chemical	PVDF Copolymer A (VF2/HFP) high HFP	PVDF Copolymer B (VF2/HFP) low HFP	PVDF Homopolymer
Typical Value Range	20,0 – 27,0 (2900 – 3900)	31,0 – 38,0 (4500 – 5500)	41,5 – 55,0 (6000 – 8000)
Mineral Acids			
Nitric Acid (71% Aq.)	21,4 (3100)	34,5 (5000)	44,1 (6400)
Hydrofluoric Acid (49% Aq.)	21,4 (3100)	35,9 (5200)	48,3 (7000)
Sulfuric Acid (96% Aq.)	21,4 (3100)	33,8 (4900)	45,5 (6600)
Hydrochloric Acid (Shielded) (37% Aq.)	22,1 (3200)	Not tested in this study	46,9 (6800)
Organic Acids			
Acetic Acid (glacial)	20,7 (3000)	31,0 (4500)	40,7 (5900)
Acetic Acid (50% Aq.)	22,8 (3300)	34,5 (5000)	45,5 (6600)
Inorganic Bases			
Sodium Hydroxide (50% Aq.)	22,8 (3300)	34,5 (5000)	46,2 (6700)
Sodium Hyprochlorite (5% Aq.)	21,4 (3100)	33,1 (4800)	44,8 (6500)
Halogens			
Liquid Bromine	21,4 (3100)	33,1 (4800)	44,8 (6500)
Iodine (10% Aq.)	22,1 (3200)	33,1 (4800)	45,5 (6600)
Solvents			
Acetone (10% Aq.)	23,4 (3400)	35,2 (5100)	44,1 (6400)
Methylene Chloride (shielded)	20,7 (3000)	29,7 (4300)	42,8 (6200)
Ethylene Glycol	23,4 (3400)	34,5 (5000)	47,6 (6900)
Distilled Water	22,1 (3200)	34,5 (5000)	46,9 (6800)

Oil & Gas Exploration

In the oil exploration industry there are challenges to recover natural resources. Many of the most fertile oil fields are in the ocean and the conditions to explore and extract the product are quite harsh compared to onshore recovery. For one thing, the initial installation can be much more expensive and the next thing is that since it is hard to make repairs, the systems themselves must be designed to be robust. With this thinking, the issue with standard metallic systems is that they tend to be very rigid and limiting in certain installations where it is necessary to move the fluid long distances. Flexible offshore composite piping systems that combine the pressure resistance of metal and the flexibility and corrosion resistance of plastic are very commonly used in off shore recovery systems. These systems can be provided on large reels onto barges and taken to the job site to be installed in a continuous system at the platform (see photos 3 and 4). When designing such a structure for 20 year and greater life, many performance factors need to be taken into account. American Petroleum Institute (API) has considered these factors in the API 17J standard for Flexible Pipelines. PVDF grades have been developed that take into consideration; 1) Mechanical & Physical Properties (density, hardness, compressive strength, abrasion resistance, flexural modulus, impact resistance, tensile strength, creep resistance and fatigue cycling); 2) Thermal Properties (thermal conductivity, thermal expansion, heat distortion temperature, softening point, heat capacity, glass transition temperature and dynamic mechanical analysis); 3) Chemical Compatibility (chemical resistance, permeation resistance, and permeability). In summary PVDF is promoted for long life in this application up to 130°C, is considered excellent for all types of oil including sour crude with H_2S and CO_2, and has high temperature blistering resistance even at high pressures. To put the use of PVDF in perspective in the Oil & Gas handling and exploration industry, it is considered by many the best material to use when Polyamide 11 cannot handle the chemical compatibility or long term temperature requirements. See Table 3 for a comparison of materials for Offshore Flexible Pipes.

Table 3 - Expected Life and Services for PVDF and PA 11 for Offshore Flexible Pipes

	PVDF (Offshore Formulation)	**PA 11**
Operating Temperature	130°C	65°C
Lifetime	20 years	20 years
Recommendation	Crude Oil Sour Gas Hot Water Corrosion Inhibitors	Crude Oil Sour Gas
Specification	API 17J	API 17J

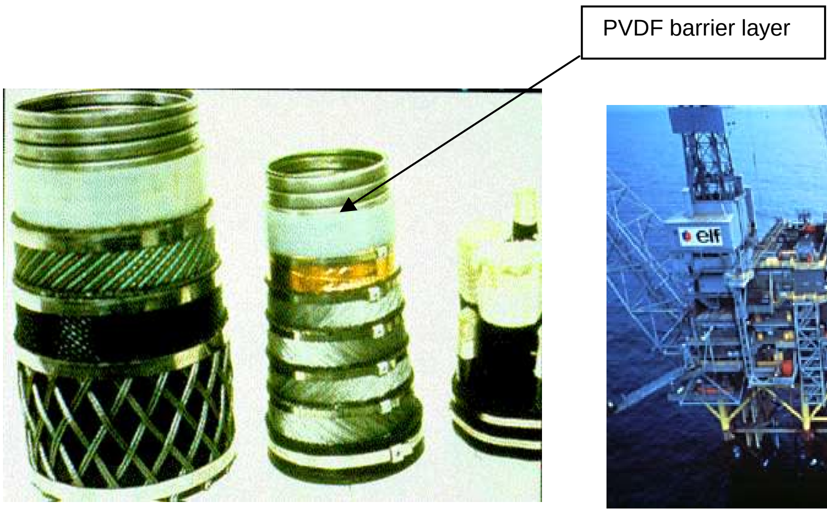


Photo 3 - Offshore Flexible Pipe Structure

Photo 4 - Oil Drilling Platform

Overall in the hydrocarbon handling industry PVDF is a premium product that gives a safety factor over other polymer choices that may be less expensive.[3] Many polymers may resist one form of aliphatic hydrocarbons, but may have severe issues in aromatic hydrocarbons.

Or, a fuel today may be a combination of aliphatics, aromatics, alcohols, biodiesels, ethers, sulfur, organics, oxidants, and a multitude of other new technologies that gain favor every 3-4 years. Should any of these combinations change after piping or tubing has already been installed, the material that originally worked in this environment could quickly fail with what would seem to be only a slight change. Polyolefins and nylons are much more limited in overall scope of chemical resistance and temperature resistance compared to PVDF.

The use of PVDF as a polymer barrier layer adhered or coextruded in a sandwich with more flexible and structural polymers that are less expensive can give outstanding results in permeation resistance, dimensional stability and heat resistance as well as being cost effective based on cost of pipe versus installation costs. Where coextrusion is used and a strong bond between the layers of polymer is desired, a functionalized PVDF is available that has been utilized to bond PVDF to other structural materials such as polyamide, polyethylene, PVC, polyurethane and ABS.

Chemical testing with hydrocarbons and fuel mixtures and various grades of PVDF and PVDF copolymer are listed in Table 2, Table 3 and Table 4.

Table 4 - PVDF Copolymer Immersion Testing in Various Biodiesel Ratios for 28 Days at Ambient Conditions. BD – Biodiesel D – Diesel

Tensile at Yield	BD – D 25/75	BD – D 50/50	BD – D 75/25	BD – D 100/0
Control Mpa (psi)	40,3 (5848)	40,3 (5848)	40,3 (5848)	40,3 (5848)
After 28 days Mpa (psi)	38,3 (5551)	38,3 (5551)	37,6 (5457)	38,7 (5614)

Table 5 - Kynar® PVDF Grade Tensile Strength Retention (%) in Various Fuels After 121 Days at 38°C

PVDF Grade/Fuel Type	PVDF Homopolymer	PVDF random copolymer	PVDF heterogeneous copolymer
ASTM Fuel C	99,6	99,4	92,0
Methanol	92,7	92,7	90,6
Ethanol	97,1	95,3	93,5
90% ASTM Fuel C/ 10% Methanol	92,6	92,6	89,9
70% ASTM Fuel C/ 30% Ethanol	95,4	94,1	90,3

Table 6 - PVDF Copolymer testing in Hydrocarbons at Elevated Temperatures for 12 weeks

Chemical	Test Temperature °C	Weight Change %	Tensile Yield Strength, Mpa (psi)
Control	23	0	23,8 (3450)
Heptane	90	0,5	25,5 (3700)
Toluene	80	0,4	22,1 (3200)

Food, Beverages, Drugs and Potable Water

PVDF and PVDF Copolymers are listed in the FDA Regulations under 177.2510 and 177.2600 respectively for repeated use for food contact. Fluoropolymers tend to have the ability to be manufactured into piping, tubing, sheets and other extrusions without the use of processing aids that can leach out as a contaminant and taste modifier. Most foods and beverages can be handled by stainless steel and/or even inexpensive plastics. However, in the entire food & beverage manufacture process and dispensing area, many things occur that make PVDF a preferred material of construction choice for this industry.

In food manufacture, metallic rusting is not desirable. Exposed to water and certain food chemistry, stainless steel can form a reddish rust which is referred to as rouging.(4) It is possible to taste this rouge in foods. If a food is very acidic, it can severely corrode metals quite quickly. Plastics will not rust or easily corrode, but many of the common plastics that have been tried for certain food applications need plasticizers or other additives to perform the required mechanical function. These plasticizers can also add to the taste of a food in a negative way. Another problem with some plastics is absorption of the food or beverage in such a way that if another food is run through the plastic it can be reintroduced to the stream. In areas where steam cleaning is needed to kill bacteria and insure safe foods, most plastics cannot stand up to continuous hot exposure without distorting. Finally, in some applications along with (or instead of) steam, bleach is used to kill bacteria in process. The chloride ions in bleach have a dramatic negative effect on common metals like stainless steel and can also ultimately cause polyolefins to become brittle.

The above problems lead to niche applications where PVDF and PVDF copolymers make sense as a cost effective contact material for food and beverages. The most common applications where piping and dispensing tubing, fittings, and nozzles are made from PVDF and PVDF copolymer are tomato based sauces, hot pepper sauces, lemon oil, lime juice, cranberry juice, milk and dairy products, beer, wine, and food preservatives. PVDF can be steam cleaned, washed with cleaning agents, and is not readily prone absorb food into the molecular matrix. For these reasons there has recently been an increased focus on composite flexible tubing with PVDF as the inner layer and a flexible elastomer as the structural material. Photos 5 and 6 show the look of piping systems and flexible tubing that can be used to handle foods at high temperatures if necessary.

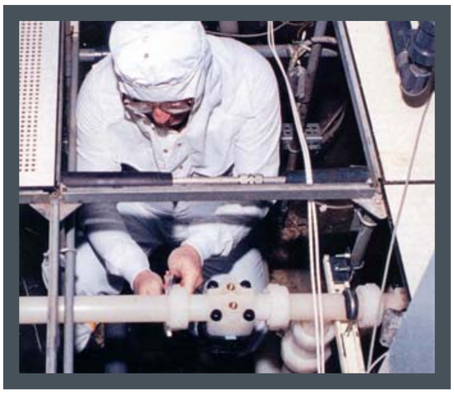


Photo 5 - Mechanically joined “Sanitary” PVDF piping system

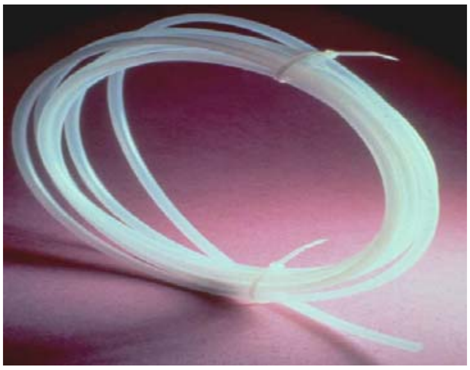


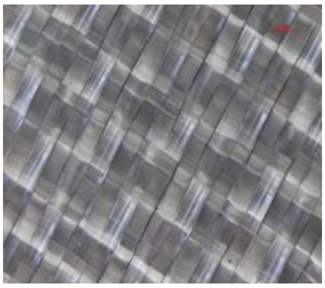
Photo 6 - Coil of PVDF Copoymer tubing meets FDA 177.2600 for repeated use

In the pharmaceutical industry similar corrosion concerns are being observed with metallic systems.[5,6] Ultrahigh purity water is being used in water for injection systems and drug manufacture. Conceptually, drug and biotech companies feel that assuring that drugs do not have varying degrees of purity is a preferred quality standard. Similar to food, but maybe more importantly to the pharmaceutical industry there is concern with particle generation, bacteria growth and regulatory compliance. The properties of PVDF that allow it to be used at high temperatures, the chemical resistance to purification agents like ozone, chlorine, bromine and peroxide, and the ability to fabricate it in such a way that there is no weld seam, make this industry one of the fastest growing users of this polymer.

The food, beverage, drug and potable water industries have a common issue. The desired final product often goes through substantial filtration to meet the intended taste and safe consumption requirements. A major portion of these filtration systems is the membrane itself where micro-porous membranes separate out undesirable components of the final consumable. As you might guess, these membranes are often parts of very big systems and users do not want to be constantly changing them before their desired lifetime. By using a material that is pure, can handle hot temperature cycles, has a chemical compatibility with almost every chemical (especially at low concentrations), has high mechanical strength, and can be put in solution by special solvent blends at the right temperature, membrane manufacturers have found what they believe is the ultimate polymer for universal application across these industries. Water systems across the world that are being developed to provide drinking water from salty water are utilizing PVDF membranes in the separation and filtration process. Photo 7 shows a “bundle” of PVDF hollow fiber membranes used for ultrafiltration systems.

Photo 7 - Hollow Fiber Membranes Made from PVDF for Water Purification

Recent technology in PVDF using a very high flow melt processing product allows the development of woven and non-woven fabrics for filtration. PVDF is an upgrade for polypropylene which is limited in temperature and resistance to cleaning fluids. Photos 8, 9 and 10 show the look of the PVDF fibers, a completed woven fabric made from PVDF, and a microscopic photo of PVDF non-woven fabrics made from fibers.



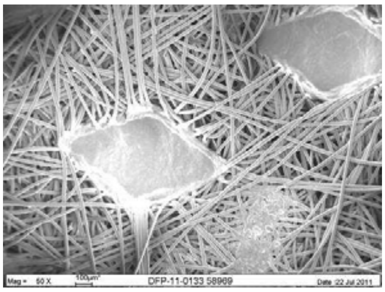


Photo 8 - PVDF Multifilament **Photo 9 - PVDF Woven Fabric** **Photo 10 - PVDF non-woven fabric**

Conclusion

PVDF-based polymer resin systems are well established as materials for many applications in the chemical processing industry. Due to their inherently broad resistance to corrosive chemicals even at elevated temperatures, these materials help reduce downtime and maintenance and serve to extend the life of equipment. In addition, PVDF-based systems serve to protect product purity in food and biotech applications. In the instances of filtration products made from PVDF, the high levels of chemical resistance and mechanical strength are combined to make long life products useful in the potable water, pharmaceutical, and food processing industries.

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