# *Fluoropolymers*

## Offer High Performance Characteristics or Niche Applications

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Fluoropolymers are attractive for a broad range of applications in the paint and coatings sector. High molecular weight fluoropolymer resins serve as the basis for extremely durable, high performance coatings used for building products and other demanding applications. Low molecular weight fluoroadditives provide mar/slip and chemical resistance to paint formulations. Fluorotelomers and small chain fluorochemicals act as surfactants, improving both application properties and performance characteristics of the coatings themselves. However, environmental concerns have been raised regarding the biopersistence of the compounds perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The industry is committed to substantial reductions of PFOA/PFOS from all sources.

### THE HEAVYWEIGHTS MEAN BUSINESS

High molecular weight materials used as the binder in a paint or coating formulation account for the largest percentage of fluoropolymers sold to this market. Polyvinylidenedifluoride (PVDF) is the dominant compound, while polyfluoroethylene vinyl ether (FEVE) is the second most important fluoropolymer.

The market amount in the United States is estimated by research firm Kusumgar, Nerlfi and Growney (KNG) to be 3.5 million gallons of paint formulated with these high molecular weight fluoropolymers. The value of the market is pegged at $220 million and is growing at about ~1% per year. The largest end use application is in coil coatings.

Other types of fluoropolymers used in minor quantities include such compounds as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP), perfluoroalkoxy polymer (PFA), ethylene-chlorotrifluoroethylene copolymer (ECTFE), and ethylene-tetrafluoroethylene copolymer (ETFE). PTFE, FEP, and PFA generally provide heat, chemical, and dirt pickup resistance along with release properties. ECTFE and ETFE can increase the processability of a coating.

The market for these materials is much smaller, though—about 1 million pounds and valued at just $35 million. Demand is actually declining for these fluorinated polymers, which are used primarily in OEM applications, according to KNG.

The greatest growth for fluoropolymer resins lies in the industrial maintenance sector, where an annual rate of increase in sales of 15% has been observed. Unfortunately, the volume is very small. Total sales are just $7–8 million. Interest in fluoropolymers is growing due to the high performance characteristics of these materials, particularly their chemical and oil resistance. For these industrial applications, the high cost of the coatings can be justified.

On a geographic basis, the largest demand for fluoropolymer coatings can be found in the United States. "The U.S. has a greater number of areas within the country that experience high UV exposure, which can be effectively addressed with these coating products," notes George Pilcher, a vice president with consulting firm The ChemQuest Group. He estimates that 10–15% of OEM metal building products with factory applied coatings are painted with fluoropolymer-based products.

In Europe, end-of life issues have helped limit the demand, and only 4% of building products are coated with fluoropolymers. The high cost of PVDF coatings has kept demand at a much lower level in the Asia-Pacific region. "Pollution continues to be a problem in this part of the world. Buildings look old very quickly, and it is difficult to justify the additional cost of a high performance fluoropolymer-based coating," Pilcher adds. As a result, fluoropolymer coatings account for no more than 1% of all coated building products there.



Arkema and Solvay Solexis are the two key manufacturers of PVDF. Both companies allow only approved coating manufacturers to produce coatings based on their fluoropolymers. In fact, potential licensees of Solvay Solexis' Hylar 5000® coatings must pass a rigorous two-year qualification process.

Qualified formulations must contain a minimum of 70% PVDF based on total resin. To form a finished paint, the PVDF is blended with a compatible acrylic and dispersed into organic solvents along with pigments. They are formulated for architectural coatings as well as factory-applied coil coating and spray applications and can be applied to a broad array of metal substrates including aluminum, aluminized steel, and galvanized steel.

These fluoropolymer coatings have been shown to last more than 35 years without signs of aging. "The PVDF resin provides long-life protection against UV radiation, chemical and airborne pollution, severe weather, and environmental conditions such as salt spray or wind-borne sand," states Art Tigera, global segment manager for PVDF coatings with Solvay Solexis. He adds that large commercial buildings involve significant capital investment, and owners desire to protect that investment with the most effective coatings available.

Solvay Solexis continues to see an upward trend in demand on a global basis for architectural coating applications. Tigera estimates the global market for PVDF to be about 12,000–15,000 tonnes/year currently.

The generic description of FEVE coating polymers is that they consist of fluoro-olefin units [namely CTFE (chlorotrifluoroethylene) or TFE (tetrafluoroethylene)], along with various vinyl ether units and pendant functional groups (e.g., hydroxyl groups).

One version of FEVE is manufactured by Asahi Glass and sold under the trade name Lumiflon. It differs from PVDF in that it is soluble and can provide a higher gloss. It can also be reacted with melamines, isocyanates, and other groups to incorporate desired performance characteristics, according to Pilcher.

However, the overall lower fluorine content of FEVE systems, as well as the presence of the vinyl ether groups, make them more susceptible to UV degradation when compared with PVDF, according to Tigera.

Pilcher notes that FEVEs are most commonly used to coat aluminum composite panels, which find application in high-end architectural buildings where they provide sound-deadening properties and also make curved structures possible.

One of the biggest challenges that producers of coatings based on fluoropolymer resins face is the high cost of their products. The price of FEVE-based coatings, for example, is at least five times higher than silicone-based coatings, according to Koji Kigawa, research projects coordinator for the Daikin Institute of Advanced Chemistry and Technology (DAI-ACT).

Despite their high price, both PVDF and FEVE coatings can often be a cost-effective solution over the long term. Because they have an extremely long expected lifetime, recoating costs are minimized. "The driving force for fluoropolymers is the realization that these products can increase the life cycle of exterior coatings and subsequently increase the time between recoats. This factor makes a fluoropolymer product more 'green' than other alternatives," asserts Bob Parker, a technical service chemist with AGC Chemicals Americas. It also reduces the costs of infrastructure management by eliminating the number of recoats.

Fluorosurfactants offer a wide variety of characteristics for paints and coatings, including foam reduction, anti-blocking, leveling, and reduced cratering. Photo courtesy of DuPont.

Just like most other coatings, though, fluoropolymer-based formulations do have their limitations. While they cannot be harmed by UV light or weather, they are relatively easily scratched or otherwise damaged by physical impact.

"PVDF coatings for metal buildings originally replaced formulations based on silicone polyester polymers and were at that time a significant improvement," remarks Pilcher. "Since then, the physical limitations of PVDF have become more apparent and silicone technology more advanced. As a result, fluoropolymer coatings may begin to see increasing competition from these, particularly given the slowdown in the housing market in the U.S."

Development of improved coatings could provide opportunities, though. "We see opportunities for fluoropolymer-based coatings that are more durable from a physical perspective and for coatings with improved dirt resistance, especially in Asia, where pollution has been an issue," comments Tigera. Bob Parker notes that demand for waterborne architectural coatings is growing as well and could be potentially significant.

Daikin, in fact, is investing in the development of new water-based fluorocoatings that are VOC-free, room temperature curing varnishes. These two-component fluoropolymer dispersions exhibit the properties expected of high performance fluorocoatings, including dirt removability, excellent solvent resistance, high weatherability, and good UV transparency. In addition, with appropriate control of the coating viscosity, these coatings can be applied using various methods such as spray, coil, dip, and brush.

Other markets are opening up as well. Heat-reflective coatings for metal roofing is at present a niche application, but interest is increasing at a rapid pace and this market is expected to grow considerably. "Cool roof coatings are just another example of how 'green' fluoropolymer-based coatings truly are," Parker believes.

AGC Chemicals is developing functionality that can be crosslinked at ambient temperature, water-based one component and two-component coating systems, and fluoropolymers that can be cured by UV light. According to Parker, some of the technologies are already on the market or will be available in the near future. The company is also looking at several technologies that will make the use of fluoropolymers more environmentally friendly as well as increase the performance characteristics of these resins.

Also of note, AGC Chemicals has continued to experience overall growth in demand. "Due to an increase in interest coupled with substantial sales growth, we are anticipating some expansion of our manufacturing capabilities in the near future," says Parker.

Solvay Solexis has a technical service lab under construction in Asia and is planning to build a new plant in China that is expected to be operational in the 2011 timeframe. This investment reflects the company's expectations that the greatest growth in fluoropolymer coatings in the near term will be in Asia and the Middle East. "There is a tremendous amount of infrastructure development occurring in these areas, and we hope to capitalize on that growth," Tigera says.

The key to success with fluoropolymers, according to Tigera, will be to continuously prove to potential customers the advantage of the higher cost fluoropolymer coatings over lower cost alternatives. "We need to prove that our products truly are higher performance materials that provide a true benefit to our customers," he adds. Competition from lower-cost producers who are now entering the market must also be addressed. The quality of these products is not yet comparable, but is expected to only improve over time.

## THE LIGHTWEIGHTS HAVE INFLUENCE

Low molecular weight fluoropolymers and fluorotelomers also find use in paints and coatings as additives. Some adjust the application properties of coatings, while others modify the performance characteristics of the coating once it has been applied.

### *Fluoroadditives*

The major fluoropolymer used as an additive in paints and coating is PTFE. In the United States, about 2 million pounds of these low molecular weight polymers are sold into the paint and coatings market per year at a value of $7.5–8 million, according to KNC.

PTFE fluoroadditives provide mar/slip, abrasion, and chemical resistance, cleanability, and resistance to mold/mildew and staining in architectural paints. They are also added to various coatings to modify surface frictional (COF) characteristics, provide anti-stick behavior, and impart water repellency. Some NASCAR racing vehicles may incorporate fluoroadditive-containing coatings on wheel hubs to reduce drag, for example. Coatings containing fluoroadditives are also used to reduce shipping damage on stacked metal sheet stock—they can then serve as a processing aid during metal stamping before being stripped away.

One of the largest applications for these fluoroadditives is in printing inks, where they provide excellent gloss and anti-blocking properties while allowing the use of more quickly evaporating solvents to enable increased production efficiency.

According to Larry Campbell, marketing manager for the DuPont Zonyl* PTFE Fluoroadditives business, the largest potential for growth is in ink applications, as emerging markets such as China and India upgrade their print materials to higher quality products. Sales in mature regions such as the U.S. and Western Europe remain relatively flat.

Another potential growth area is in coatings for coil stock used on appliances. The rapidly increasing middle class population in emerging markets is becoming able to afford more consumer goods and also is demanding better quality products. Fluoroadditives will likely benefit from this situation. Demand for chemical-resistant architectural coatings may experience growth in these markets as well. Co-deposition of PTFE and metal (e.g., electroless nickel) represents another growth opportunity.

DuPont established fluoroadditives manufacturing capability in China in 2005 to meet this expected growth in demand. The company has also constructed a Chinese facility for the production of high molecular weight fluoropolymers that may be used as fluoroadditive feedstock. DuPont produces low molecular weight fluoroadditives either through direct polymerization or by degradation of high molecular weight fluoropolymers.

Solvay Solexis is also expanding their fluoroadditives manufacturing capabilities with a new facility in China in order to meet the growing global demand. The new plant complements their existing U.S. micropowder facility in Delaware. The company is vertically integrated in PTFE with a broad portfolio of both high and low molecular weight products and is committed to the fluoroadditives market, according to Tigera.

New products for the paint and coatings markets produced via both suspension and emulsion polymerization processes are being introduced by Solvay Solexis. These new fluoroadditives focus on texture and gloss improvements and offer a variety of properties to meet individual customer needs. "Solvay's patented micropowder process enables extensive product customization, allowing us to meet the most stringent requirements of our customers," Tigera adds.

With expertise in PTFE production, DuPont focuses on fluoroadditives based on PTFE, offering several grades with a wide range of characteristics. High molecular weight PTFE serves as the key feedstock, and fluoroadditives can be based on either suspension or emulsion polymerized PTFE. Some grades contain functionality (typically carboxylic acids) as end groups, while others do not. Emulsion-based grades are offered in both micropowder and aqueous dispersion form while suspension-based grades are available only in micropowder form. Besides particle size, high and low specific surface area differentiates the two types and

can be used to modify such properties as formulation viscosity.

The newest product in the Zonyl PTFE fluoroadditives portfolio from DuPont is based on 70 nm-sized particles and is available as both a micropowder and aqueous dispersion. "These products represent the smallest particle size fluoroadditives on the market," notes Campbell. Because of their small size, PTFE nano-particles can find their way into interstices where at least one observed benefit is greatly improved flex life in coated fabrics.

"Educating processors about the variation in behavior and performance of these different grades is critically important," notes Larry Campbell. For example, suspension polymerization-based grades are manufactured with a well-known particle size and particle size distribution, and neither is affected by customer processing. Fluoroadditives prepared via emulsion polymerization are sub micron primary particles with an average agglomerate size and distribution that changes/reduces when processed by the customer—the degree depending on the incorporation technique used. The effect can be significant in a paint formulation.

Fluoroadditives with reactive end groups might be of more interest for some applications, according to Campbell. "These end groups could be used to create multifunctional additives, which are receiving growing interest in the paint and coatings market today. They may also serve to anchor the additives in a certain way within the coating, allowing for targeted surface properties or perhaps for preventing migration of additives within the applied coating," he explains.

With so many alternatives, it can be difficult to ensure that customers are fully exploring the potential benefits of using fluoroadditives. In addition, despite their high price, fluoroadditives, like fluoropolymer resins, can also be very cost effective in many cases.

Campbell explains that formulators who elect to use a cheaper additive may find that it adversely affects the performance of the overall formulation. Then, those changes must be compensated through the use of additional additives, making a more complex formulation. Due to their unique chemical make-up, fluoroadditives do not typically interact with other ingredients, and therefore may often be used at an equivalent or lower cost in a less complex formulation.

Dyneon, a 3M Company, manufactures and supplies a broad range of fluoropolymer dispersions and powders used in spray, roller, curtain, and other coating processes, including PTFE, PFA, and FEP.

The company introduced a new emulsifier in 2007 for its aqueous fluoropolymer dispersions that are used in paint and coatings. According to market development manager Mike Haley, the new emulsifier technology does not rely on the use of ammonium perfluorooctanoate (APFO), a salt derived from perfluorooctanoic acid (PFOA) (see discussion in Fluorosurfactants section). "The introduction of this new technology helps our customers stay competitive in their field and further strengthens our commitment to a sustainable fluoropolymer business," he states.

### *Fluorosurfactants*

Fluorosurfactants are generally produced from fluorotelomers or short chain fluorinated compounds that often include other functionality such as phosphate groups. KNC estimates the total market for fluorosurfactants in the U.S. to be $14–15 million and 300,000–400,000 pounds. The majority of fluorosurfactants are used in solvent based coatings, although the greatest value of sales is attributed to those used in waterborne formulations.

Fluorotelomer-based or short perfluoroalkyl chain-based fluorochemicals used as surfactants in coatings provide enhanced wetting, flow, and leveling properties—characteristics that are important for proper application. According to Dr. Richard Thomas, PolyFox technical manager at OMNOVA Solutions, the superior performance is a direct consequence of the very low surface tension afforded by these materials.

Larger fluorotelomer compounds, or "smallimers," actually have the ability to be integrated into the coatings. "These low molecular weight fluoropolymers can possess a variety of functionality and are designed to affect specific performance properties of the applied coatings, such as cleanability and anti blocking," says Thomas.

A key driver for growth for these fluorosurfactants is the demand for higher performing coatings that still meet ever stricter VOC regulations. Whether a waterborne, high solids, or low-VOC solvent system, coatings producers are looking to create products with improved gloss, appearance, resistance to staining and dirt pickup; increased durability and abrasion resistance; and the ability to coat difficult substrates.

"These challenges are placing ever-increasing performance demands on typical hydrocarbon surfactants," notes Thomas. "In some cases we have had customers report an increase in coating defects like orange peel and pinholes. The low surface tension and superior flow and leveling characteristics of fluorosurfactants seem to be particularly effective at reducing these defects."

"Removing solvent creates numerous formulation challenges," agrees Thomas H. Samples, global business manager for the DuPont Surface Protection Solutions business. "It is much more difficult to find a direct substitution for additives when switching to a waterborne formulation, and it can take a combination of several non-fluorinated ingredients to achieve the same level of performance. A single fluorosurfactant, however, can often provide the same or better results."

As with other fluoroadditives and high molecular weight fluoropolymers, even though the prices of fluorosurfactants are higher than their hydrocarbon-based counterparts, they can be more cost efficient overall and also "greener" because less material can be used.

"The challenge, of course, is to get customers to choose a fluorosurfactant first and test it with a base formula rather than replacing a hydrocarbon surfactant in a complicated coating that contains several different additives," Samples remarks. "The best way for customers to realize the true benefits is to take this approach." DuPont will often take a customer formula and redesign it with a fluorosurfactant by starting with the base components. In most cases a more cost-effective solution that provides the same performance can be found.

Fluorosurfactants are also highly efficient, which contributes to their cost effectiveness. Fluorotelomers are incorporated into paint formulations at a level of 50–200 ppm. Hydrocarbon-based additives, on the other hand, are used at a level of 1–2%. "As a result, much less surfactant is required while at the same time eliminating the need for the use of multiple additives," stresses Samples. "The coating is thus green from the VOC perspective and from the perspective of reduced resource consumption."

While the switch to low VOCs has been a positive trend, fluorosurfactant producers have also been contending with environmental concerns associated with the compounds perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). PFOA and PFOS have demonstrated biopersistent potential and have been detected in a variety of media worldwide, including various flora, fauna, and water.

The source of these compounds is still being investigated, but it may include some of the traditional fluorosurfactants used historically. Production of fluoropolymer resins and additives has also been identified as a possible source of emissions, and manufacturers of these products are addressing the issue.

"The world community is now sensitized to the presence and possible consequences of materials such as PFOA, PFOS, and their degradation products in the environment. As a result of this recent publicity, coatings users and formulators are now very aware of many of these issues," Thomas states. "They like the properties afforded to coatings by fluorosurfactants but do not want to have any adverse environmental impact associated with their use."

In January 2006, the U.S. EPA announced its 2010/15 PFOA Stewardship Program. All eight invited companies, including DuPont, 3M, AGC Chemicals, Daikin, and Solvay Solexis, have committed to reduce by 95% all sources of PFOA both from facility emissions and their products by 2010 and to eliminating all sources of PFOA from emissions and products by no later than 2015.

Most producers of fluorotelomers, including those not directly involved in this program, have responded to this situation by developing new products that provide the desired characteristics but avoid any of the environmental concerns associated with PFOA/PFOS.

It is important to note that fluorotelomer products are not made with, nor do they use, PFOA in the manufacturing process. However, PFOA is an unintended reaction byproduct that is present at trace levels in some of these products.

OMNOVA Solutions, for example, has developed a family of short chain fluorosurfactants ($<C_6$) and low molecular weight reactive fluoropolymers under the PolyFox™ trade name that are not capable of producing PFOA/PFOS or substances that can degrade to these problematic chemicals. The company will also be introducing a line of improved anionic fluorosurfactants that have been developed in response to the EPA's Design for the Environment (DfE) program. Customers should be able to receive EPA DfE recognition for their products containing this innovation.

In addition, OMNOVA has introduced products that can be used to modify polymers such as polyesters, acrylates, and polyurethanes. "We consider this chemistry to be a 'hybrid' between fluorosurfactant and fluoropolymer and providing attributes of both," explains Thomas.

DuPont's Capstone™ repellents and surfactants are designed to deliver maximum performance with a minimal environmental footprint.

For the electronics industry, which Thomas believes will be a key source of growth in the future, OMNOVA has launched a line of electronic grade fluorosurfactants/fluorochemicals for use specifically in semiconductor coatings manufacturing. The company also continues to invest in production capabilities in order to meet the growing demand for its full range of products.

DuPont has also had an active program to address the PFOA issue. The transition has been a two-step process, which began with the introduction in 2006 of LX Platform products, which were made via a manufacturing process that removed greater than 97% of trace levels of PFOA, its homologues, and direct precursors from fluorotelomer products. That program was completed in 2007, when at the end of the year the company began introducing its new Capstone™ short chain fluorotelomers that cannot break down in the environment to PFOA.

Capstone FS50 and FS51 are the newest products in the line and were launched at the end of March 2008. DuPont plans to have several new products for paint and coatings applications on the market by the end of the year, and will be expanding the entire Capstone portfolio over the next 18 months. To that end, the company has recently tripled the capacity for its Capstone products.

"This significant investment demonstrates our commitment to the market and makes clear our intention to be able to provide products for the long term and to be able to meet the needs of our customers in the future," Samples states. In particular, DuPont is expecting to see increased demand for fluorotelomers and small-imers used in industrial coatings and ink jet printing inks. Architectural paints in emerging markets such as China, India, and Central/Eastern Europe, where high levels of construction are occurring, will also serve as a source of growth.

In the process of developing these new fluorotelomers, scientists at DuPont have found ways to create multifunctional fluorocompounds that could be of great interest, according to Samples. "During the conversion process, we have begun to explore a tremendous amount of technology that will allow us to incorporate multifunctionality into small polymers," he explains. "We believe this technology will enable us to develop products that take on the role of both polymers and surfactants in a single ingredient.

"In the future, interest in multifunctional additives that make it possible for formulators to do more with less will provide a huge opportunity for these new fluorochemicals. We expect demand for these types of products to account for a large part of our future growth," Samples continues.

Opportunities for "greener" fluorosurfactants in general that do not biopersist but still provide the same or enhanced benefits as older PFOA/PFOS or telomer-based surfactants are anticipated to be significant.

"Customers are demanding more sustainable raw materials so that they can produce 'greener,' more sustainable end use products without sacrificing performance. Fluorosurfactants, which are used at extremely low levels, are very effective at modifying the coating surface. Newer, multifunctional products could potentially have even more dramatic effects on key coating characteristics and the performance of other additives as well," Thomas asserts. "The true potential of these fluorochemicals and related products will be determined by the demands of the paint and coatings industry and must come from a collaborative effort between fluorosurfactant/fluorochemical suppliers and the coatings manufacturers."

## FACING THE FUTURE

Undoubtedly, the high cost of fluoropolymers—whether high molecular weight resins, low molecular weight additives, or short chain surfactants—will prevent the use of these interesting compounds from commanding a large share of the overall paint and coatings market. However, their unique properties will continue to make them attractive in formulations designed for high performance applications.

The growing interest in "greener" coatings and the regulatory drive toward lower VOC products may create additional opportunities for growth, as will the increasing demand for higher quality products in emerging economies. Manufacturers of fluoropolymers are also addressing concerns about PFOA/PFOS and creating further growth potential through the development of more environmentally friendly products. In the process they may also uncover new technologies that enable wider application of fluorochemicals in paint and coatings. CT