



AFFF Industry in Position to Exceed Environmental Goals

With the recent announcements by major fluorochemical manufacturers of new short-chain, C6 (six fluorinated carbons) fluorotelomer-based products, the AFFF industry is in position to exceed the goals of the EPA global stewardship program.

By Tom Cortina

FFFC

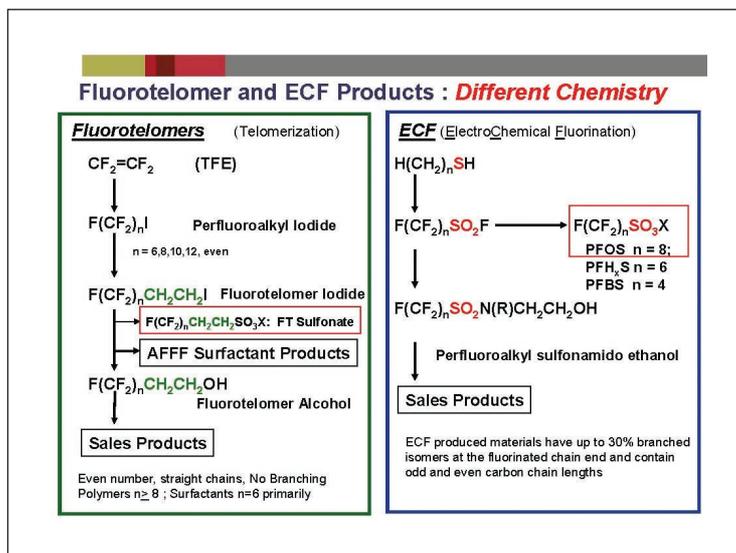
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This program has the goal to work toward the elimination of PFOA and related higher homologue chemicals from products such as AFFF and from plant emissions by 2015. This is an important set of milestones considering that since the announcement in 2000 by 3M of environmental concerns related to the use of PFOS-based products including foams, the AFFF industry has worked to address these issues in a responsible manner. Evidence of this can be seen in the smooth transition from PFOS-based to fluorotelomer-based foams, the formation of the Fire

Fighting Foam Coalition (FFFC) as a focal point for cooperation with regulatory authorities, and the industry's recent focus on the containment and treatment of foam discharges. When the PFOS issue first became public there was speculation that environmental concerns could eventually lead to a ban on the production of fluorosurfactant-based fire fighting foams. Now it appears that the foam industry will be able to exceed its environmental goals with C6 fluorotelomer-based fluorosurfactants that provide the same fire protection characteristics but with reduced environmental impacts.

Figure 1. Fluorotelomer-based and PFOS-based Chemistry



agents do not contain or degrade to PFOS, and contain 30-60% less fluorine than PFOS-based AFFF. They are not made with PFOA or PFCAs. The predominant breakdown product from the six-perfluorinated carbon (C6) based fluorotelomer surfactants is commonly referred to as the 6:2 fluorotelomer sulfonate (6:2 FtS)². They may also contain trace levels of PFOA and the C6 acid, perfluorohexanoic acid (PFHxA). The highlighted red box on the left side of Figure 1 calls out the 6:2 FtS structure (where $n = 6$). Although there have been numerous articles and conference presentations that

Fluorosurfactants are a key ingredient

Historically, most of the environmental concern related to fire fighting foams has focused on aquatic toxicity and residual foaming, which can be a concern for local waterways and sewage treatment systems, and are common problems for all foams¹. Over the past 10 years the focus has shifted to the fluorinated surfactants (fluorosurfactants) that are a key ingredient in aqueous film-forming foams (AFFF). Fluorosurfactants provide AFFF agents with the required low surface tension and positive spreading coefficient that enables film formation on top of lighter fuels. It is this film formation capability that gives AFFF its name and its effectiveness against flammable liquid fires.

3M used a unique process to manufacture the fluorinated components of the fluorosurfactants contained in its AFFF formulations. The process is called electrochemical fluorination (ECF), and fluorosurfactants produced by this process both contain and degrade into a chemical known as PFOS (perfluorooctyl sulfonate). Other competitive manufacturers use a process called telomerization to produce the chemical components of the fluorosurfactants contained in AFFF agents. Chemicals produced by this process are generally referred to as fluorotelomers.

Over the past several years there has been a substantial shift from PFOS-based AFFF agents to equally or more effective AFFF agents containing fluorotelomer-based fluorosurfactants (see Figure 1). With the withdrawal of the PFOS-based products due to their persistence, bioaccumulative and toxic properties (beginning in May 2000) and their subsequent regulation by various national governments, makers of fluorotelomer-based products began more intensive study of the toxicology and environmental fate of their products.

Environmental impacts of fluorosurfactants

A primary debate about fluorotelomer-based products centers on the perceived similarity to PFOS, the presence and/or generation of perfluorocarboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA), and the ultimate breakdown products of these surfactants.

First and foremost, fluorotelomer-based AFFF

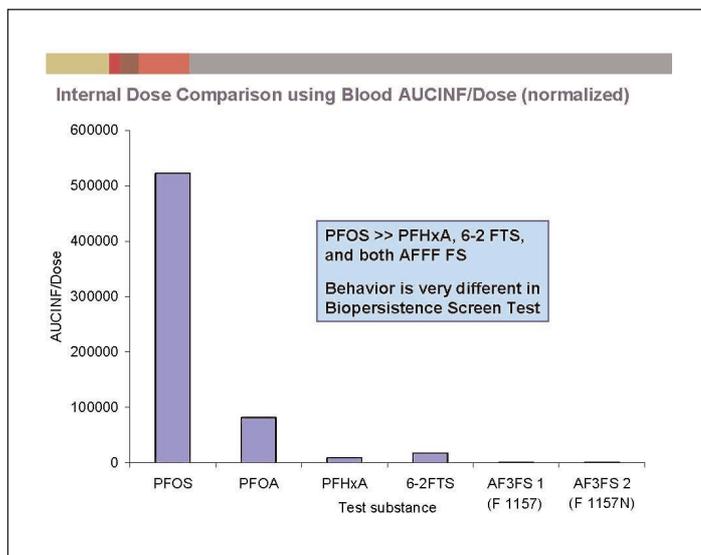
purport the 6:2 FtS to be a PFOS analog (sometimes incorrectly referred to as H-PFOS), the scientific data do not support this allegation. The physical, chemical, biopersistence and toxicological properties of 6:2 FtS are not similar to PFOS.

Toxicology

A second part of the debate seems to focus on the potential hazards of PFHxA and the 6:2 FtS. These two compounds can be both contaminants in the final products as well as potential degradants once the AFFF agents are used. Extensive data on PFHxA were presented at a US Environmental Protection Agency (EPA) PFOA Information Forum in June 2006 that gave a very favorable initial toxicology (hazard) profile³. Additional information was presented in September 2007 at a major foam conference in the UK (Reebok) that further supported the favorable toxicology profile of PFHxA⁴. Preliminary data were shared on four major toxicology end points: sub-chronic toxicity in rats, reproductive toxicity in rats, developmental toxicity in rats, and genetic toxicity. It was noted at this conference that PFHxA was neither a selective reproductive nor a selective developmental toxicant. In addition it was clearly shown to be neither genotoxic nor mutagenic. Combining these data with those presented in June 2006 provides significant evidence that this particular end product has a low hazard profile based on current data.

Based on recent groundwater studies, the 6:2 FtS has been shown to be the likely ultimate degradation product of the C6 fluorotelomer-based surfactants used in today's AFFF agents. The screening study cited above (Figure 2) indicated that the 6:2 FtS had a low relative biopersistence potential. The 6:2 FtS had a high NOEC (no observed effect concentration, the higher the NOEC the lower the concern for toxicity) in the 90-day early life stage trout study. Results presented at the Reebok foam conference provided preliminary new results on environmental effects as well as bioconcentration (BCF) and bioaccumulation (BAF) in rainbow trout. Although the data were preliminary in nature, the results were clear and compelling. Moreover both the BCF and the BAF values suggest low concern for bioaccumulation from water or diet. The data strongly suggested that 6:2 FtS is not bioaccumulative according to

Figure 2. Biopersistence Screening Study Results



published regulatory criteria and affirmed that it does not behave like PFOS.

Biopersistence

The results of a 6:2 FtS biopersistence screening study were also presented at the Reebok foam conference. The data presented are shown in Figure 2 (publication in preparation). This screening study involves oral dosing of male rats for 10 days followed by an 84-day recovery period. The study determined total organic fluorine levels in plasma, liver, and fat. It provides a screening measure of what toxicologists refer to as biouptake and bioclearance. The AUCINF, or area under the curve integrated to infinity, provides a relative integrated measure of the absorbed dose of the compound studied. A compound that is absorbed and quickly eliminated or is simply not absorbed will have a low relative AUCINF. It is very clear from Figure 2 that the 6:2 FtS, the C6 acid (PFHxA), and the two commercial fluorotelomer-based fire fighting surfactants have extremely low values when compared to PFOS. In this study, PFOA is also lower when compared to PFOS.

PFOA global stewardship program

Although they are not made with PFCAs, fluorotelomer-based fluorosurfactants may contain trace levels of PFOA. Fluorotelomer producers are working toward the elimination of trace levels of PFOA, PFOA precursors, and related higher homologue chemicals from finished products by 2015 as part of the US EPA global stewardship program. Under the program, EPA asked fluorotelomer producers to make two commitments:

- Reduce by 95% by 2010 (based on a 2000 year baseline) facility emissions and product content levels of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals.
- Commit to working towards elimination of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals from emissions and products by 2015.

The recent announcements by fluorochemical manufacturers of the introduction of short-chain fluorotelomer products means that the AFFF industry is in position to meet the EPA goal well in advance of the 2015 target date.

Fire Fighting Foam Coalition

In May 2001, AFFF and fluorosurfactant manufacturers met in Washington DC with representatives of the US EPA, the US military, and major foam users to discuss the

fallout from 3M's decision to stop production of PFOS-based AFFF due to environmental concerns. It quickly became clear that users and agency staff did not fully understand the differences in chemistry between PFOS-based and fluorotelomer-based AFFF agents. It was also evident that speculation about the future regulation of AFFF agents was causing problems for the industry. As a result of this meeting, the Fire Fighting

Foam Coalition (FFFC) was formed to ensure that accurate information about fluorotelomer-based AFFF agents is disseminated to appropriate audiences.

FFFC is a non-profit corporation that represents the AFFF industry's interests on all issues related to the environmental acceptability of fire fighting foams. The coalition provides a focal point for industry technical reviews, development of industry positions, and interactions with the EPA and other relevant organizations. Members of are AFFF manufacturers, fluorosurfactant manufacturers, and distributors.

FFFC has provided extensive information on AFFF to environmental agencies in the US, Europe, and Canada that includes the following:

- Amount of fluorosurfactant actives used in the manufacture of AFFF in the US
- Chemical structure of the fluorosurfactants used in major fluorotelomer-based AFFF formulations
- Mechanics of film formation
- Groundwater monitoring data from US military fire training areas
- U.S. Inventory of PFOS-based and fluorotelomer-based AFFF
- Overview of the different types of foams, the market channel for their distribution, and the environmental fate once they are used
- Aquatic toxicity of fire fighting foams

Existing stocks of PFOS foams

Although production of PFOS-based foams ended in 2002, significant stocks of PFOS-based foams are still in service in many industries throughout the world. A study by Hughes Associates of AFFF inventories in the US showed that there were 4.5 million gallons of PFOS-based AFFF concentrate in stock in 2004⁵. While US regulations do not restrict the use of these stocks, regulations in Europe and Canada would ban the use of existing stocks of PFOS-based foams within 3-5 years.

A European Union directive on PFOS was published in December 2006 that requires existing stocks of PFOS-based foams to be removed from service by June 27, 2011. To facilitate tracking and adherence to the directive, EU member states must provide the European Commission with an inventory of existing stocks of PFOS-based foam



agents by December 27, 2008.

A proposed regulation was published by Environment Canada in December 2006 that would require existing stocks of PFOS-based AFFF to be removed from service 5 years after the regulation comes into force. During the 5-year exemption period, those stocks could not be used for testing or training purposes. (In other words, they could only be used to extinguish emergency fires.) The final regulation should be published this year, which means that the restrictions on PFOS foams would begin in 2013 or 2014.

Fluorine-free foams

As a result of the concerns raised by the PFOS issue, foam manufacturers continue to evaluate many types of potential products that do not contain fluorosurfactants, but efforts to date have not yielded working products with fire performance across all fuels and in all operational circumstances equal to film-forming foams. Some fluorine-free foams can provide an alternative to AFFF in some applications, but they are not currently able to provide the same level of fire suppression capability, flexibility, scope of usage, and independent validation. A recent paper from the University of Newcastle that shows that even the best available fluorine-free foam would need to be replenished three times as often as AFFF to provide the same level of fire protection⁶.

Fluorine-free foams are often championed as "environmentally-friendly" alternatives to AFFF. Although such foams may not contain fluorine, their environmental profile related to biodegradation, acute toxicity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) is typically no better than fluorine-containing products and in many cases is not as environmentally responsible in use as AFFF. A recent study of commercially available fire fighting foam agents indicates that fluorine-free foams are at least an order of magnitude higher in aquatic toxicity than AFFF agents⁷.

FFFC assists in wastewater treatment

Another issue that has been brought to the forefront in recent years is the containment and

treatment of wastewater from foam discharges. FFFC and its member companies have been actively involved in this issue, and recently provided assistance to an oil refinery in Missouri that was looking for help in dealing with a wastewater disposal issue. The company had a fire at a bulk plant that resulted in 1.1 million gallons of wastewater containing gasoline, diesel fuel, and fire fighting foam agents used to extinguish the fire.

FFFC put the company in touch with one its members, Martial Pabon of DuPont, who had done research on the use of activated carbon to treat water that contained fluorosurfactants similar to those used in AFFF. Based in part on the information provided by Dr. Pabon, the company successfully treated 1.1 million gallons of wastewater in 15 days using granular activated carbon (GAC) in a trailer-mounted system with two pressure vessels each containing 5,000 pounds of GAC⁸. Dr. Pabon has done additional research on other methods to treat wastewater, including nanofiltration, ultrafiltration, and reverse osmosis⁹.

Conclusions

Fluorotelomer-based AFFF agents are the most effective agents currently available to fight flammable liquid fires in military, industrial, and municipal settings. They do not

contain or breakdown into PFOS and are not likely to be significant sources of PFCAs. They do contain fluorosurfactants that are persistent, but are not generally considered to be significant environmental toxins. AFFF and fluorosurfactant manufacturers are in position to meet the goals of the EPA global stewardship program years ahead of the target date with a new family of fluorosurfactants that provide the same fire protection characteristics with reduced environmental impacts. **APF**

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