

**STATUS REPORT ON ENVIRONMENTAL CONCERNS RELATED TO AQUEOUS  
FILM FORMING FOAM (AFFF)**

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## Abstract

AFFF is the primary firefighting agent used on crash rescue fire fighting vehicles to provide protection at major U.S. airports. Recently, the 3M Company, a major producer of AFFF, announced its decision to cease manufacturing of "PFOS" based products. AFFF is one of these products. Production is being halted because of "PBT" concerns, that is, concerns related to chemical persistence, bioaccumulation, and toxicity. Other manufacturers use a different process to make AFFF. The U.S. Environmental Protection Agency is currently assessing these chemicals.

This paper provides an update of the current status of fire fighting foam environmental issues, including the latest position of the EPA. Environmental factors related to foam are identified, and their relationships with current PBT concerns reviewed. The fire performance requirements of foam for aircraft/airport protection are outlined so that users can select appropriate alternatives to 3M AFFF. Current and future R&D efforts in the field are identified, including efforts to reduce fluorosurfactant chemicals in AFFF, improve biodegradation of formulations, and predict the performance of foam through modeling.

## Background

Foam fire protection has been utilized in the aviation industry for many years to provide vital fire protection at airports. In the 1970s a substantial improvement was made in the effectiveness of foam fire protection with the development of fluorosurfactant based foams. The fluorosurfactants are unique in their ability to reduce surface tension. These foams are now the standard used in aircraft crash fire rescue (CFR) operations at U.S. airports.

The fluorosurfactant based foams include the following concentrates: Aqueous Film-Forming Foam (AFFF), Film-Forming Fluoro-Protein (FFFP), and Fluoro-Protein (FP). These agents are used for rapid suppression and extinguishment of jet fuel fires resulting from an aircraft crash. A survey conducted in 1990 by Hughes Associates, Inc. and the U.S. Navy indicated that the twenty-four largest airports in the United States use AFFF for airport protection [1]. While not in common usage, non-fluorosurfactant containing foams such as protein foams may be used.

Protein-based foams were the standard for many years. In the 1960s, chemists at the 3M Company, working with the Naval Research Laboratory, developed agents that provided surface tension properties that allowed a thin film of water to float on hydrocarbons. This substantially improved the fire knockdown performance of foams. From this work, the AFFF agents were developed. It was also found that the performance of protein foam could be enhanced with the addition of these fluorocarbon surfactants. If the surfactants are added in high enough quantity, film formation is also possible.

The formulations of these foam concentrates are based on performance, not on the constituents. In the U.S., the two most widely used foam specifications are Underwriters Laboratories Inc. (UL) "Foam Equipment and Liquid Concentrates" (UL 162) [2] and the U.S.

Military Specification (MIL SPEC, MIL-F-24385) for AFFF [3]. These specifications require that certain performance requirements be met in medium scale fire tests (28 and 50 square foot pans), along with other requirements. The manufacturer determines the exact constituents that make up a concentrate. Many U.S. airports reference the MIL SPEC when purchasing AFFF. It has been recommended that the MIL SPEC is an appropriate standard for FAA certification purposes [4].

Foam concentrates come in 6%, 3%, and 1% products, being mixed with 94%, 97% and 99% water respectively. The foam solution that is formed generally contains the following:

- Water, 98%-99%
- Surfactants (fluorosurfactants and hydrocarbon surfactants), 0.03%-0.45%
- Butyl Carbitol<sup>1</sup> (glycol ether), 0.5%-1.1%
- Ethylene Glycol (not in all formulations), 0.34%-0.60%
- Urea (not in all formulations), 0.2%-0.4%
- Xantham gum (in alcohol resistant formulations).

While mostly water, the actual firefighting solution is a mixture of a number of chemicals. The potential environmental impacts and regulatory issues are many. An excellent review of these issues is presented by Ruppert et al. [5] and Darwin et al [6]. The issue that has caused the most significant problems, and occasionally has resulted in limiting the use of foam, is the upsetting of a wastewater treatment plant. This effect is caused by the foaming, and as a result efforts should be made to reduce the foaming of effluent solutions prior to release into the treatment facility. This can be achieved by de-foaming or metering the solution. The generally recommended disposal method is metering the solution into a wastewater treatment plant. If done incorrectly this can result in the plant becoming dysfunctional and releasing improperly treated sewage. The method of properly metering the solution can be found in the National Fire Protection Association (NFPA) Standard for Low Expansion Foam (NFPA 11) [7].

More traditional environmental concerns exist with foam. The Biochemical and Chemical Oxygen Demands (BOD/COD) are important in defining how well the concentrates biodegrade. It may also be possible to remove oxygen from a watercourse too fast, resulting in a fish kill, but in most releases this is unlikely. The acute toxicity of the foam is also a potential concern, generally determined relative to aquatic animals. Much work was done in the 1990s to change the solvents used in the formulations because some solvents were on the list of Hazardous Air Pollutants and required release reporting to the U.S. Environmental Protection Agency (EPA) when foam was used. Also, the act of foaming is an environmental issue and is regulated. While these issues have existed for long time, a new issue has drawn attention.

The fluorochemical surfactants, the key ingredients that make foam so effective, have long been known not to biodegrade completely. The fluorochemical surfactants used in foam have a 6 to 10 carbon chain that is fully fluorinated and is impervious to biological, and most chemical, assault. Recently, 3M discovered that the fluorochemical surfactants used in the Light Water™ products biodegrade to a compound that is also bioaccumulative and toxic. This

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<sup>1</sup> Not contained in all agents

combination of persistence, bioaccumulation, and toxicity (PBT) is considered a significant environmental problem.

### The PFOS Issue

On May 16, 2000 3M unexpectedly announced it was phasing out fluorocarbon surfactant manufacturing which effected a number of product lines, including the Light Water™ firefighting foams. The foams made up about 5% of the production of a business based on fluorocarbon surfactants and similar chemistries that also included the ScotchGuard™ fabric protectors, ScotchBan™ food wrapping paper treatments, and many other industrial uses. This business represented about \$300,000,000 worth of business, or slightly less than 2% of 3M's total revenues.

The chemistries for these products are based on electrochemical fluorination (ECF), a method 3M uses to create heavily fluorinated molecules. 3M was the only major manufacturer in the U.S. using this method, and one of only a few in the world. 3M had pioneered ECF in the 1950s and has had many product lines based on it over the years.

The chemical of interest from the ECF process is perfluorooctanesulfonyl fluoride (POSF),  $C_8F_{17}SO_2F$ . When POSF, and the derived products, are biologically degraded the final chemistry is perfluorooctane sulfonate (PFOS),  $C_8F_{17}SO_3$ . This molecule is not believed to be further degraded under any natural conditions except combustion. PFOS is persistent.

PFOS has been found to have a tendency to bioaccumulate. As part of 3M's regular monitoring of employees, new and more sensitive methods of detection of PFOS in serum were developed. The levels in relatively highly exposed workers are found to be in the few parts per million. Studies using these methods have also found PFOS in small quantities, tens of parts per billion, in the blood of the general U.S. population [8]. These tests were conducted using pooled samples from multiple blood banks. Essentially, everyone in the U.S. may be carrying low levels of PFOS in their body.

Low levels of PFOS were also found in fish and birds from various locations including albatross on Midway Island in the Pacific. PFOS has a widespread presence and has been shown to bioaccumulate.

Toxicology studies show that PFOS is absorbed orally and distributes primarily in serum and the liver. Numerous repeat dose oral toxicity studies have been conducted with rats and monkeys [9]. Toxic effects are seen at levels believed to be at least two orders of magnitude higher than the exposed 3M workers, and four orders of magnitude higher than the general population. These toxic effects are considered significant.

PFOS is considered to be a PBT, persistent-bioaccumulative-and toxic. The levels in the general population are low and are not believed to present an imminent hazard. However, concern is raised that with the continued production and release of these compounds, eventual adverse effects on people and the environment are possible. At the time of 3M's announcement

of withdrawal from the market of the POSF derived products, they were in consultation/ negotiation with the EPA. Since that time, the EPA has proposed a Significant New Use Rule (SNUR).

If this problem was only associated with PFOS and 3M's agents, despite some temporary market chaos, it would not be particularly significant. 3M's withdrawal has drawn much attention and this attention has spilled over to the other manufacturers agents. With 3M definitely out of the business, and the focus turning to the other agents, this has the potential to be a serious fire protection issue. The SNUR does specifically identify the other agents as the focus of continued investigation and evaluation.

### **The Proposed SNUR**

On October 18, 2000 the EPA published a proposed rule for PFOS [10]. The intent of the proposed SNUR was to "shut the door" on any other manufacture or importation of the chemicals 3M was voluntarily withdrawing. In the U. S., this would effectively end the production and ultimately the release of chemicals that biodegrade to PFOS. The proposed SNUR would have no effect on existing stocks of foam.

Along with the proposed SNUR, EPA accepted the voluntary phase-out schedule of the chemicals. 3M proposed a graduated phase out, with very limited manufacturing continuing for some applications into 2003. However, for the foam fluorosurfactants, 3M has stopped production in the fall of 2001 and is merely taking orders from remaining stocks in the supply chain.

The proposed SNUR is not a ban, rather it would require companies to file notice with the EPA if they planned to manufacture or import the listed chemicals. EPA would look at the proposed use and could grant, deny, or impose conditions on the intended use.

A public meeting was held on March 27, 2001 to address comments EPA received on the proposed SNUR. All the significant comments were from PFOS users outside of fire protection. The final rulemaking for the SNUR has not yet been issued as the comments and new information on those uses is being examined by the EPA.

### **The Telomers**

Of the many producers of firefighting foam, 3M was unique in at least two aspects. First, they were the only company basic in the fluorochemicals that also produced foam concentrates; all other manufacturers purchase the fluorochemical surfactants or intermediates from an outside source, typically a major chemical company. Second, 3M's foams were the only ones using fluorochemicals from the electrofluorination process; the others all used fluorochemical surfactants derived from the telomerization process.

The telomerization process produces a molecule for surfactants distinctly different than that produced by electrofluorination. The product from the telomerization process predominantly used for foam is perfluorohexyl iodide,  $C_6F_{13}I$  [11]. Further chemistry is performed on this molecule by replacing the iodide with various groups to get the desired surfactant properties. This chemistry is distinctly different than the PFOS chemistry and does not biodegrade down to the PFOS molecule.

The telomer based surfactants do biodegrade down to a molecule that contains the highly fluorinated carbon chain and this molecule is not expected to further biodegrade. But what molecule this is has not been established and is currently a subject of contention. Two possibilities apparently exist; the molecules biodegrade down to perfluorohexanoic acid,  $C_5F_{11}COOH$ , or the biodegradation product is unknown.

Perfluorohexanoic acid is a shorter chain homologue of perfluorooctanoic acid (PFOA),  $C_7F_{17}COOH$ . There is not a lot known about perfluorohexanoic acid, but PFOA is a commercial chemical with a major use as a processing aid in manufacturing. What is known is that different chain length homologues have many similar properties.

PFOA was also found in some of the pooled serum samples 3M was testing for PFOS, but at even lower levels of a few parts per billion. The bioaccumulation potential of PFOA has not been examined as thoroughly as PFOS and it is not yet known if the presence of PFOA in some of the serum samples represents a wider problem.

If the telomer based surfactants do biodegrade to the PFOA homologues, and if PFOA is confirmed to bioaccumulate, then the telomers may become the focus of regulatory efforts. The EPA has repeatedly indicated that the PFOA and the telomers are subjects of interest to them. EPA is currently performing a hazard assessment on PFOA with the results expected in early 2002. This hazard assessment was expected in June, but due to additional information being made available and the need to have it reviewed at high levels within the EPA, it has been delayed.

Environmental and toxicological information on the telomers is being voluntarily submitted by the manufacturers to the EPA. In response, five of the producers (Asahi Glass, Atofina, Clariant, Daikin, and DuPont) have formed the Telomer Research Program (TRP) Group and presented a research program to the EPA in October of 2000. The multi-year multi-million dollar study is expected to produce definitive results on the fate of the telomers and assess the toxicological hazards.

### **The Current Situation**

The largest U.S. supplier of firefighting foam for the aviation industry has ceased production. Other manufacturers can supply foam with similar or better fire extinguishment performance. All of the other foams containing fluorocarbon surfactants come from the telomer manufacturing process. While these have not been shown to biodegrade to a chemical that bioaccumulates and is toxic (it will however be persistent), there is much regulatory interest and

ongoing research. Aviation industry users must be prepared to request and understand the listings and approvals of any new agent being offered to insure its performance will meet their requirements. To date, no non-fluorocarbon containing foam has been able to demonstrate the performance that is achieved by high quality fluorosurfactant based foams [12].

Users who currently use 3M AFFF for CFR applications may have questions regarding purchase of foam as stocks of existing foam are depleted through normal or emergency use. This should not be a significant problem. The earlier survey of major airports [1] indicated that the majority used the MIL SPEC as the procurement specification when purchasing foam. Since the MIL SPEC requires compatibility between all agents on the Qualified Products List (QPL), users can simply purchase another product from the QPL. All others are the telomer-based AFFFs. Users who do not use the MIL SPEC should verify compatibility before mixing AFFFs from different vendors.

The relatively small quantity of telomer chemicals used in foam may not prevent potential regulation by the EPA. The EPA has identified the release of surfactants in foam (and other products) to the water as one of the possible routes of human exposure for PFOS [13]. While the precise exposure route(s) is not known, releases to watercourses and subsequent ingestion are being investigated. Also being investigated is intake from food wrapped with treated paper and inhalation from airborne sources.

The historical environmental issues with foam have always called for a high standard of care with its use, whether for actual fire fighting, training, or system discharge testing. The additional concern over the environmental fate and effects of the fluorocarbon surfactants should be considered by users when assessing the responsible storage, handling and discharge of foam. Even if the disposal guidelines recommended by most foam manufacturers are followed (e.g., metered input to a wastewater treatment plant), this will not change the fluorocarbon surfactant impact as they pass through the plant into the watercourse.

The recognition of the potential environmental impact of the fluorocarbon surfactants and their uncertain future has led to calls for research on replacement chemicals and technologies. The EPA, in a presentation to the U.S. Department of Defense Fire and Emergency Services Workgroup, has noted that "a program to seek, test, and consider long-range alternatives to current fluorosurfactant-based AFFF would be prudent" [14].

### **Potential Impact on Aviation CFR**

If current fluorochemical-based foams become unavailable, there are two potential approaches for addressing the needs of the aviation industry. The first is to develop new agents with similar performance. Alternatively, agents having lower performance could be used, recognizing that greater quantities would be required for protection equivalent to AFFF.

In anticipation of increasing restrictions on production of AFFF, the Naval Research Laboratory (NRL) performed a review of the different approaches that might be used to develop alternatives [15]. Two fundamental approaches were identified. One approach is to identify

alternative chemicals and formulate novel foam concentrates (i.e., the "chemical approach"). These novel foam concentrates would first be screened to see if they form an aqueous film on fuel surfaces. They might also be fire tested at a relatively small scale. This approach assumes that a positive spreading coefficient (i.e., the formation of a film) on a hydrocarbon fuel is necessary for a candidate agent to have similar if not equal fire extinguishment and burnback performance as AFFF.

An alternative approach, which would be pursued in parallel with efforts to identify new chemicals, is designated as "fire extinguishment fundamentals." This approach assumes that chemical derivatives that combine both desirable firefighting and environmental characteristics are not readily available or identifiable. The contention is that a lack of a fundamental theoretical understanding of foam spreading and extinguishment mechanisms limits the ability to investigate novel concepts/formulations. This approach relies on the development of a foam spreading extinguishment model to predict agent performance. Small-scale apparatus would be used in support of this model. Having verified the extinguishment model, approaches that provide the required physiochemical properties could be investigated. This could lead to synthesis of agents that do not rely on the surface-tension reduction characteristics (for which fluorosurfactant chemicals are vital).

Since the development of an entirely new agent is considered a moderate-to-high technical risk both approaches would be pursued as there is much technical cross-over in both efforts. Currently, no near-term substitute agent has been identified which has performance equal to AFFF.

The alternative would be to use existing protein-based foams. The FAA, NFPA, and ICAO recognize the use of protein-based foams for CFR use. Where protein foam is used as substitute for AFFF, the FAA requires the volume of water carried by CFR vehicles to be increased by roughly fifty percent [16]. Consider the situation where an FAA Index E airport is required to have CFR vehicles with a total of 6,000 gallons of AFFF discharged at a total rate of 1,200 gallons per minute (gpm). If protein foam was used, the CFR vehicles would have to have a capacity of 9,000 gallons and a total discharge rate of 1,800 gpm. If 2,500 gallon/500 gpm CFR vehicles are used, the number of required vehicles would have to be increased from three to four.

The increased equipment requirements become more exaggerated if NFPA 403 guidelines [17] are used by an airport. For the same FAA Index E (NFPA Category 9) airport, 9,570 gallons of AFFF at 1,200 gpm is recommended by NFPA. Approximately 13,000 gallons of foam at about 3,500 gpm is the protein-based foam equivalent. In this case, the number of required vehicles would be increased from four to six or seven.

There are also practical considerations in converting CFR vehicles from AFFF to protein foam. Proportioning systems would have to be modified to account for higher flow rates and differences in foam concentrate viscosity. Non-air aspirated foam discharge nozzles would have to be replaced with air-aspirating nozzle.

If the current fluorochemical based foams become unavailable, and new agents with similar performance are not developed, airport operators are likely to see a large increase in the

cost of protection if they are required to use currently available protein-based foam. It should be emphasized that this is not expected in the near term.

### **Future Developments**

The most significant near-term future developments related to AFFF environmental issues are the PFOA hazard assessment and the definitive determination of the biodegradation product(s) of the telomer based surfactants. If the PFOA hazard assessment turns out to not indicate significant environmental concerns, then perhaps the fluorocarbon surfactants will not be regulated or controlled.

If the fluorocarbon surfactants do not biodegrade to the homologues of PFOA, then the actual biodegradation products will need to be defined and studied. This process would likely take several years. In the interim, direct regulatory action would be unlikely.

If the telomer surfactants are found to biodegrade to the PFOA homologues, future regulatory action may occur. The degree of regulation would be dependent on the PFOA hazard assessment. The regulations could be developed under the rules of the Toxic Substances Control Act (TSCA). TSCA uses an "unreasonable risk" standard in an attempt to balance hazard, exposure, benefits, costs, and availability of alternatives at the time of the proposal. The actions that could be taken include: testing requirements (Section 4); SNURs and new chemical reviews (Section 5); manufacturing, use and disposal rules (Section 6); and, information submittals (Section 8).

Invoking Section 6 and developing use and disposal rules would have the most direct and immediate impact on the fire protection community. Because the use of foam is almost always emissive and the surfactants end up in the environment, it may be relatively high on the list of regulatory issues. In general, the EPA prefers to negotiate with industry and have them take voluntary action rather than regulate (i.e. 3M and PFOS). The regulatory process, if effectively contested by industry, can take several years and result in significant costs to both parties.

Unless the biodegradation products pose an immediate risk to human health or the environment, any regulatory activity is unlikely to affect existing stocks of foam. Rather, regulators will likely focus on future production and use. The objective would be to stop the production, and hence cap the quantity in the environment, at a level not believed to be hazardous. The logistics and costs of trying to collect and destroy (by incineration) the existing stocks would be prohibitive.

A potential option for the fire protection community would be to ask for exemptions from regulations on the basis that the increased risk from loss of life, major property damage, and disruption of portions of the economy outweigh the risks from continued use of the fluorosurfactant based foams. This strategy would probably only be effective if it was very specific: AFFF at airports for crash fire rescue, aircraft carrier flight deck firefighting, extinguishment of large storage tank fires, etc.

The percentage of foam production used to fight fires is relatively low, estimated to be 5% to 10%, but is not validated with data. The other 90% or so is used for training, system testing, accidental discharge, replacement of contaminated or obsolete stock, or stored in new systems. While an exemption may be made for actual firefighting it is highly unlikely to be acceptable for training, testing, accidental release etc. The fire protection community may need to develop technologies and codes of practice to reduce these releases to the absolute minimum feasible. This is both to enhance the position relative to any future regulations but also for good stewardship of the environment. Some manufacturers already use alternative, non-foaming agents for system testing, as well as for FM and UL approvals.

## **Conclusions**

The fluorocarbon surfactants used in foam are being scrutinized because of concern over their ultimate environmental fate. The fluorocarbon surfactants used by 3M biodegrade to PFOS, a chemical that is persistent, bioaccumulates and is toxic. 3M has ceased manufacturing these chemicals. Other foam manufacturers use fluorocarbon surfactants from the telomerization process and these surfactants are currently being scrutinized by the EPA. The biodegradation products of the telomer chemistries are known to be persistent and are being tested and examined for their bioaccumulation potential and toxicity.

Currently, there are no regulations limiting the use of fluorocarbon based foam because of the biodegradation products concern. Even though the 3M foams are no longer in production, foams which provide equivalent protection are available from a number of other manufacturers. Users should be aware of these environmental issues when assessing the responsible storage, handling, and discharge of foam. If the telomer-derived surfactants biodegrade to a chemical that is a PBT, then product withdrawals and regulation of the existing foams may occur.

While replacement agents that do not contain fluorocarbon surfactants will become more available, these agents do not currently have the same performance as existing foams. The lack of capability could be compensated for by increased agent volumes and applications rates. While this may provide an equivalent level of performance, it will be at a substantially increased cost.

## **Recommendations**

In the near-term, the aviation industry should closely monitor the activities of EPA related to the PFOA and telomer assessments. These activities are having an impact on foam fire protection. Already we are seeing proposals from vendors of "environmentally friendly" foams to accept their products for aviation fire protection. NFPA 403 requires that agents used at the AFFF flow rate and agent quantity meet the MIL SPEC performance criteria. This technical position was validated and recommended for adoption by FAA in 1994 [4]. Yet, to date, this recommendation has not been implemented. A recent performance analysis of foam agents required to combat aviation-related fuel fire hazards reaffirms that the MIL SPEC provides an appropriate level of performance [18]. If alternative foams are to be evaluated, a baseline of

performance needs to be established and in place. FAA should adopt the MIL SPEC performance for AFFF as previously recommended.

Proponents of alternative foam test methods, particularly international standards, which are less restrictive than the MIL SPEC, argue that many U.S. airports use protein-based foams. This contradicts the findings of the 1990 study which indicated that all of the 24 largest U.S. airports in the U.S. use AFFF [1]. It would be useful to update this study to determine if this is still accurate. At the same time, a survey of typical CFR foam capacity, discharge and pumping equipment could be performed to determine the impact of a potential transition to protein foams or foams having similar performance characteristics. It would be in the interest of FAA and airports to have this information available should further restrictions be proposed on the use of AFFF.

Just as the fire extinguishment and burnback performance of foam needs to be quantified (e.g., by adoption of MIL SPEC criteria), so should acceptable environmental criteria and associated test methods. It is clear that environmental criteria in the MIL SPEC needs to be updated to reflect current concerns. Vendors are already advertising environmental improvement through the reduction of fluorosurfactant content. It is unclear to what extent this mitigates environmental impact in terms of the EPA assessments. For example, efforts have been proposed to develop screening models that predict bioconcentration of chemicals in organisms. These methods could then be adopted in appropriate foam specifications. The aviation industry should support such efforts.

As noted, the development of a non-fluorosurfactant based foam will be a challenging endeavor. There is an opportunity to advance the science of fire protection in an effort to identify new, environmentally improved agents. The aviation industry could take a leadership role in this effort; alternately, the FAA and industry should support efforts by the U.S. military and others in the international community in these efforts.

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