Class B Foams…Is It Time To Innovate?

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ABSTRACT

The objective is to explain the progress and remove the confusion associated with the 16 May, 2000, announcement by 3M Company on the discontinuation of Perfluoro Octyl Sulphonate (PFOS) chemistry. After more than 40 years 3M is transitioning out of PFOS formulations of 3M™ Light Water™ AFFF and AFFF/ATC fire fighting foams. The 3M announcement cited the environmental persistence of PFOS as the reason for discontinuation of this product. Could a company that prides itself on innovation manage its way around this hurdle and develop fire fighting foam technology that was not environmentally persistent?

Statement of findings:

All modern flammable liquid fire fighting foams contain fluorochemical surfactants. 3M use the electro-fluorination process that results in the formation of PFOS, which is the building block for some 3M fluorosurfactants. Most other fluorosurfactant manufacturers use a chemical reaction process known as a telomer process and produce different molecules that do not contain PFOS. All other fluorosurfactant manufacturers have been asked by the US EPA to scientifically prove that their fluorosurfactants are different from 3M's PFOS based chemistry by the end of 2002. Has it become time to reflect on the chemistry of Class B foams? To this point there have been no long term directions or conclusions. Is it time to innovate?

INTRODUCTION

3M Company established its role as a supplier of fire fighting foams with the innovation of fluorosurfactants and the invention of AFFF technology through a joint development program with the US Naval Research Laboratories in the early 1960's. Fluorosurfactant use in fire fighting foam technology was one of the most important innovations in the past 100 years in fire protection chemistry for the rapid control and extinguishment of flammable liquid fires. The resulting product was named 3M™ Light Water™ Aqueous Film Forming Foam (AFFF). AFFF foam technology has become known for its:

-rapid knockdown and extinguishment
-use for tank fires with all application devices
-long shelf life
-self-healing
-protection of fuels from reignition
-excellent compatibility with dry chemical
-easy to foam (can use conventional nozzles)
-ability to work through standard sprinkler heads

Part of the success of the AFFF products is the rapid draining foam, which provides a supply of an aqueous film containing a mix of water, hydrocarbon surfactants and fluorosurfactants. This aqueous film has a very low surface tension, near 16 mN/m, which allows it to rapidly float across the flammable liquid surface. The fluorosurfactants also have high temperature resistance, which means the film can progress against the flame front.

FOAM CHEMISTRY

The fluorosurfactants have a unique structure such that a perfluorinated molecule has been combined with a hydrocarbon molecule. The result is a surface active agent, or surfactant, that has a water soluble end (hydrophilic) and a perfluorinated end that is non-water soluble (hydrophobic) end. The hydrophobic part of the fluorinated surfactant not only repels water, but also repels hydrocarbon liquids and oil (lipophobic). Fluorosurfactants are capable of reducing the surface tension of water from 60 mN/m to near 16 mN/m. This characteristic allows the formation of a thin aqueous film on top of solvents. The thin film promotes the spreading of the

foam and suppression of solvent vapour. The fluorinated end is chemically inert. It also adds heat resistant film at the fire front and reduced solvent solubilization in the foam.

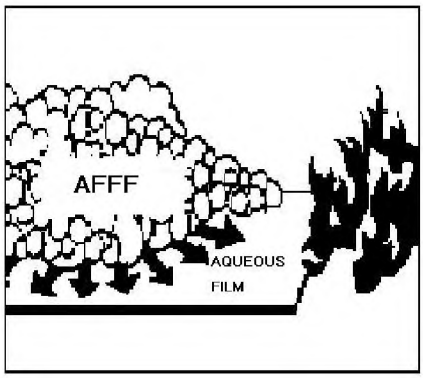

Figure 1 Diagram depicting aqueous film formation from 3M™ Light Water™ AFFF

3M Company made its fluorosurfactants a special way using the Simon's electro-fluorination cell. The best fire fighting surfactants had primarily a perfluorinated eight carbon chain that was sulfated with an organic functional group attached. They can generically be of the structure $C_8F_{17}SO_2R$. The result was called a perfluorooctanyl sulphonate, or PFOS surfactant. Straight PFOS salts like $C_8F_{17}SO_3K$ were also used. The following is an example of a PFOS molecule:

$$C_8F_{17}SO_2N(C_2H_4COOH)C_2H_4CONH_2$$

Fluorochemistry had created a fire fighting foam that had unrivaled performance. The combination of fluorosurfactants and surfactants was called AFFF.

AFFF = Flurorosurfactants + Hydrocarbon Surfactants

AFFF foam could now put out a flammable hydrocarbon liquid fire so quickly that the functionality of protein foam was in question. Fluorosurfactants were then added to improve the performance of protein foams to improve their flow characteristics. So what better way to improve the performance of protein foam than to add a fluorosurfactant. This created the category of fluoroprotein foams (FPF).

FPF = Fluorosurfactants + Hydrolysed Protein

In the 1970's we saw the alcohol resistant AFFF technology evolve that included 3M™ Light Water™ AFFF/ATC that used the same fluorosurfactants and hydrocarbon surfactants plus a polymer. Then film forming fluoroproteins (FFFP) and the alcohol resistant version (FFFP/AR) were developed.

AFFF/ATC = Flurorosurfactants + Hydrocarbon Surfactants + Polymer

FFFP = Fluorosurfactants + Hydrolysed Protein + Hydrocarbon Surfactants

FFFP/AR = Fluorosurfactants + Hydrolysed Protein + Hydrocarbon Surfactants + Polymer

The common factor was inclusion of fluorosurfactants in all of the new categories of flammable liquid fire fighting foams.

FLUOROSURFACTANTS

3M Company made all of their fluorosurfactants by electro-fluorination and based a lot of product chemistry on the PFOS molecule. Other chemical companies also could make fluorosurfactants based on other chemical paths like perfluorooctanic acid (PFOA) and telomers. All other fire fighting foam manufacturers relied on 3M and other chemical companies to provide their fluorosurfactants.

Typically the fluorinated end of the molecule was eight carbons long for fluorosurfactants used in fire fighting foams. This is also true for PFOS, PFOA and PFOA based telomers. Other telomers can use seven or six carbon fluorinated starting point. It is this portion of the molecule that gives the unique surface chemistry characteristics, including heat resistance. The fluorinated end moiety of these surfactants are called inert. Inertness was considered to be a good thing for a harsh environment like fire.

During biodegradation of fluorosurfactants what happens to the molecule? The organic end seems to biodegrade quite rapidly, leaving the fluorinated end of the chain, which was thought to remain as an inert and unreactive chain. This means no significant degradation. This fractured moiety was man made and did not occur naturally in the environment. [Kissa, 1994]

Back in 1966, before AFFF was on the market, scientists had already observed that humans had low concentrations of organic and inorganic fluorides in their blood. The inorganic fluorides came from fluorinated potable water and toothpaste, but what about the organic fluorides? Tests of production workers in plants that manufactured fluorosurfactants were conducted and found concentrations of 1 to 71 ppm in their blood. [Kissa, 1994] However, no ill health effects were determined at these low concentrations.

The concentration of fluorosurfactants in the environment could not be determined, since the organic fluorides could be measured only as low as parts per million. In the late 1990's, 3M Company's analytical laboratories developed a method for determining organic fluorides in parts per billion. 3M had determined that the PFOS molecule was still around. The analytical method was passed on to the US EPA, and it commissioned a study by Oregon State University. The result was a study of two disused military fire training facilities. About a decade after they stopped fire training, they could still find fluorosurfactants in the water around the training ground. The authors, Moody and Field, had found several types of organic fluorides, including PFOA. [Moody and Field 2000]

3M ANNOUNCEMENT

On 16 May, 2000, 3M Company announced that it would be discontinuing PFOS based chemistry due to concerns with its environmental persistence. The discontinuation was not due to any health issues. 3M stated it would cease the manufacture of the PFOS based chemicals by 31 December, 2000. In 2003 3M would voluntarily phase out 90 PFOS based chemicals. Some of the many effected products were Scotchgard ^{TM} and industrial fluorosurfactant related chemistry, and Light Water^{TM} AFFF and ATC fire fighting foams. From a fire fighting foam perspective, 3M will cease selling AFFF to non-military customers before 2003. Sales of Light Water^{TM} ATC to industry and AFFF sales to military customers will cease when 3M runs out of PFOS based stock, which will be during 2003. This is not a recall or ban on the use of the existing PFOS chemicals on the market. However, there will be no more PFOS made by 3M. With 3M withdrawing voluntarily, the US EPA has started discussions with other fluorosurfactant manufacturers about PFOA and telomer based surfactant chemistry. [Hanauska, 2001] The US EPA has started a hazard assessment. The initial report on PFOA and its telomers has been published in April 2002 (corrected version), with a second report expected near September 2002. [US EPA, 2002] There is no final ruling at this time, but we already know that PFOA is persistent. The report on other telomers is pending.

The future seems uncertain. Fluorosurfactants are under great scrutiny in any application that allows easy escape into the environment. This means fluorosurfactant based fire fighting foams are being examined in great detail.

WHAT ARE THE CHOICES?

This scenario of chemical phase out seems all too familiar to those of us in the fire protection industry. Not long ago Halons were identified as depleting the ozone layer. Ten years on we are still waiting for a Halon alternative that is a sustainable solution. To find such a chemical, it will take a great deal of research and investment. The same may be true for replacements for fluorosurfactant foams. If all the current chemistry is persistent and does not meet other criteria set by the US EPA, then what will we do to retain technologies like AFFF, FPF, FFFP and alcohol resistant foams? Dlugogorski (2002) identified a strategy to take two approaches in replacing the current foam chemistry: (i) Identify new fluorinated surfactants that do not contain perfluorinated chains but display film forming properties. This approach was proposed by Robin (2001) to establish structure-performance relationships on suitable replacement molecules. These surfactants would still be fluorine containing, but not have the inert perfluorinated tail that is the current concern to the environment. (ii) Examine the properties of fire fighting foams to achieve the performance of an AFFF, FFFP or FPF. Next link these properties with the fundamental behaviour of surfactant solutions, foams, surface tensions, foam drainage, foam coarsening, foam bulk viscosity and foam yield stress (without the use of fluorosurfactants).

Historically, non-fluorochemical foams fall under the categories of protein foam; high expansion foam; medium expansion foam; synthetic foams (Europe); specialty foams, and Class A/CAFS foams. With the exception of protein foam, the above listed foam technologies are primarily designed for Class A type fires, but have been extended for use into Class B flammable liquid fires. However, they have often suffered a credibility problem due to reduced Class B performance. Based on history, the only alternative for flammable liquid fire fighting could be protein foam? This would be stepping back 60 years for the fire protection industry.

IS IT TIME TO INNOVATE?

On 16 May, 2000, 3M labs were at a stand still. In disbelief we listened to the news of the day. PFOS chemistry was going to disappear. The message was clear, any environmentally persistent chemistry would not have a long commercial life in today's environmentally focussed society. This was not restricted to fire fighting foams as it also had broad implications in the industrial and consumer markets.

For a corporation to survive it needs to rely on its key competencies, and 3M's key competency is innovation. By 1 June, 2000, we were doing what 3M does best, innovating. 3M had now given us a challenge to change the chemistry of our products. So in the fire protection labs we looked at two main approaches: (i) New fluorochemical surfactants that satisfied US EPA requirements; and (ii) Fluorochemical free foams. Some of our best scientists made major contributions to fluorosurfactant chemistry working on new molecules. However, the application of fire fighting foams remains dispersive and the risk of failure seemed greater than the financial gain. Approach (i) seemed to lose its appeal, and the funding decreased. Non-fluorochemical approaches were studied, but success avoided the main R&D labs. Despite the vast technologies inside and outside 3M, no potential products emerged. One by one the labs were dismantled. The key competency of these labs was the ability to formulate fluorochemical based fire fighting foams.

There was one other lab that existed in a rather isolated location, the 3M Australia subsiduary. Its key competency was formulating with organic surfactants to give support to the main labs. In addition to supporting the other labs, 3M Australia was the leading lab for non-fluorosurfactant foams like training foams, high expansion foam, and Class A foam technologies. We set out to

develop a fluorochemical free class B flammable liquid fire fighting foam with the fire control, extinguishment, and burn back similar to an AFFF. And we did it.

3M Australia has discovered, through it's process of innovation, how to make high performance fluorosurfactant free foams that are fully capable of extinguishing flammable liquid fires. However, the absence of fluorosurfactants also means the absence of the formation of an aqueous film. To get the needed performance, it is then necessary to mimic the aqueous film with layers of bubble walls. A bubble wall is a thin aqueous film; therefore many bubble layers will give a performance not unlike an aqueous film. The foam works on the principle of forming a flowing low yield stress foam structure that has a significantly longer drain time than an AFFF. So the generated foam moves freely and quickly, and the foam has good heat resistance that allows fast fire securement. If the foam structure is broken, the bubbles flow back to fill the hole such that it is capable of repairing punctures and structural damage. The foam has been observed during burn back tests to move toward an open ignited fuel surface, reducing the area of the fire and sometimes extinguishing it completely. The performance of this type of agent is reliant on the existence of functional layers of bubbles.

A FLUOROCHEMICAL FREE FOAM

3M Australia Pty Ltd proudly announces the RF series of fluorosurfactant free Class B fire fighting foam concentrates. It is 100% biodegradable, and contains no persistent chemicals. It is the first non-fluorosurfactant foam to meet the International Civil Aviation Organization level B fire performance specification. This is the first fluorine free foam to meet the high performance aviation AFFF specification. The following test result for the 3M™ Foam RF6 were witnessed by Det Norske Veritas (the table includes the test results of fluorosurfactant containing AFFF products):

Table of ICAO Level B Fire Performance (4.5 m^2 pan) Test Results

	ICAO Level B Spec	3M™ Foam RF6	3M™ FC-206CF*	3M™ FC-3003*
Test witnessed by		DNV (Norway)	SP (Sweden)	ASA (Australia)
Solution Strength	3 or 6%	6	6	6
90% Control	-	30 s	38 s	-
Extinguishment	<60 s	46 s	46 s	50 s
Burn Back Time	> 5:00	> 8:00	> 8:00	7:06

Note: * Indicates fluorosurfactant based foam

Testing was carried out at RAF Manston on 22 July, 2002, to demonstrate the performance of this new fluorine free chemistry on a large fire. The Royal Air Force have a 81 m^2 brick lined pit that is used as a proving ground for fire fighting foams. The pit was filled with 675 litres of AVTUR. After a 60 second pre-burn, a 225 litre per minute air aspirating nozzle was used by a RAF fire fighter to apply the foam for 110 seconds. The results were as follows:

Table of RAF Manston Fire Performance (81 m^2) Test Result

Product Tested	3M™ Foam RF6
Foam Induction Percent	6%
Foam Application Time	110 s
90% Control	11 s
Full Extinguishment	21 s
25% Burn Back	16:30

The test proved highly successful and resulted in an invitation to do further testing at the same RAF facility. The 3M™ Foam RF6 had surprising control, extinguishment and burn back properties. Plus the RF6 foam survived plunging and variable operator technique. RF6 is a 6% foam concentrate that can be described as a amber viscous liquid. The viscosity of the

concentrate is about 2000 cps. The physical properties of the RF6 product are listed in the following table.

Table of 3M™Foam RF6 Physical Properties

Nominal use concentration	6%
Specific Gravity @ 20°C	1.06
Viscosity (Kinematic) @25°C	Approx 2000
Minimum use temperature	1.7°C
pH @ 20°C	7.0-8.5
Surface Tension (6% solution)	Approx. 30 mN/m
Interfacial Tension (6% solution) with cyclohexane	Approx 3.0 mN/m
Foam Expansion	8.0-12.0
Foam Drainage (25%)	Approx 18:40

CONCLUSIONS

3M Company is ceasing the manufacture of fluorosurfactant based fire fighting foams. 3M used PFOS based chemistry in the formulation of its AFFF and ATC fire fighting foam products. PFOS has been identified as a persistent chemical and it is no longer manufactured. The availability of PFOS based foams will cease during 2003.

The US EPA has now turned its attention to PFOA and telomer based fluorosurfactants that are also used in fire fighting foams. The initial US EPA report has been published with a second report due later in 2002. PFOA and its telomers have been identified as persistent. Other telomer based fluorosurfactants are also being studied by the US EPA. A likely outcome is further restrictions, or even the discontinuation of their use in dispersive applications such as fire fighting foams.

All modern class B flammable liquid fire fighting foams contain fluorosurfactants. If fluorosurfactants are no longer environmentally acceptable, then a sustainable alternative chemistry must be found. We must be innovative and find a solution. 3M Australia has innovated and developed a sustainable chemistry to act as an AFFF alternative. The 3M RF series of foams are 100% biodegradable. 3M™ Foam RF6 is the first product of this series and it meets the highest standards of the aviation industry with an ICAO level B performance certificate from DNV. It is a versatile product that could also be used by fire brigades for Class B hydrocarbon fires.

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