

Next Generation Fluorine-Free Firefighting Foams

Rajesh R. Melkote
Engineering Director – Global Firefighting
UTC Climate, Controls, and Security
9 Farm Springs Rd
Farmington, CT 06032
USA
Phone: (860) 284-3104
rajesh.melkote@fs.utc.com

Liangzhen Wang & Nicolas Robinet
Kidde France
UTC Climate, Controls, and Security
Rue Aloys Senefelder
BP 1008
51683 Reims Cedex 2
France
liangzhen.wang@fs.utc.com

Abstract

Fluorosurfactants, critical to the performance of aqueous film-forming foams, have come under environmental pressure in the past few years. Those with eight or more carbons (C₈) in the perfluorinated chain have been shown to degrade to perfluorooctanoic acid (PFOA) in the environment. The latter is bioaccumulative and biopersistent. There are numerous PFOA regulations coming into force globally, including an EPA directive to phase these materials out by 2015. The majority of manufacturers have responded by reformulating with shorter chain length (C₆) fluorosurfactants, which do not degrade to PFOA.

Foams which eliminate fluorosurfactants entirely, and are thus PFOA-compliant, have steadily gained momentum in the last few years. Most of the commercially available fluorine-free foams achieve their properties at the expense of increased acute toxicity, due to higher hydrocarbon detergent levels. This paper presents a novel approach to formulating a fluorine-free foam, which simultaneously achieves high performance and low toxicity. The approach can be readily extended to foams suitable for proportioning at 3% and 6% ratios. The paper includes detailed results of comparative fire extinguishing performance tests as well as details of environmental toxicity and long-term stability data.

Introduction: Regulatory Climate

Firefighting foams have traditionally been formulated based on fluorochemicals—as either fluorinated polymers, or as surfactants. Fluorosurfactants, in particular, serve to reduce surface tension—allowing the applied foam to spread across the fuel and form a film, rather than sink into the fuel. Fluoropolymers have the property of oleophobicity—resistance to oil, and therefore resist wicking and contamination of the foam layer by fuel. In particular, Aqueous Film Forming Foams (AFFF) are heavily reliant on fluorosurfactants for their fast knockdown of hydrocarbon fuel fires, which has led to their widespread use across multiple segments.

Fluorochemicals have received much regulatory attention over the past two decades. An entire class of AFFF which contained and/or degraded to perfluorooctanesulfonate (PFOS), has been discontinued by a major manufacturer since 2002. PFOS is considered by environmental authorities to be persistent, bioaccumulative and toxic (PBT). Regulations in the United States, Canada, European Union, Australia, and Japan effectively serve as a ban on new production of

PFOS-based products including foams, whereas these products can be and are produced yet in certain countries.

A major switch to the so-called telomer-based chemistry took place in the early 2000s, concurrent with the PFOS phaseout. Telomer-based AFFF agents not only contain less fluorine by mass, they do not break down into PFOS, and are not made with any chemicals currently considered to be PBT. The EPA has indicated that some telomer-based fluorochemicals can break down in the environment into perfluorooctanoic acid (PFOA) or other perfluorocarboxylic acids (PFCAs). The EPA has further indicated that the concern is chiefly on chemicals containing eight carbons or more in the perfluorinated chain (C₈, C₁₀, C₁₂). Current data shows that shorter-chain compounds (C₆ and below) have a lower potential for toxicity and bioaccumulation.⁽¹⁾

On the basis of this data, in 2006 the EPA introduced a voluntary directive to dramatically reduce PFOA emissions and content. Eight fluorochemical manufacturers signed on to the PFOA Stewardship Program, which called for a 95% reduction by 2010, and 100% reduction by 2015.⁽²⁾ It is notable that four of the eight have met the 2010 milestone.⁽³⁾ In the drive to comply with the 2015 deadline, all major fluorosurfactant manufacturers have begun to retool their plants, equipment, and processes to be able to produce C₆-based products. This has created huge pressure on AFFF manufacturers to convert their formulations to be able to use C₆ fluorosurfactants, far in advance of the deadline.

It should be noted that the C₆ counterparts of the historically used C₈ surfactants are not “drop in” replacements, in terms of replicating the fire performance, foam quality, and maintenance of 3rd party listings. Hence the AFFF manufacturer faces a multitude of options to meet the 2015 directive.

Introduction: Fluorine-Free Foams

One such option is to develop a foam which is free of fluorochemicals entirely, and therefore cannot undergo degradation to PFOA. To replicate the aforementioned properties of AFFF (particularly the surface tension and fuel resistance) without the use of fluorosurfactants represents a considerable technical challenge. The first true fluorine-free foam was launched in 2002.⁽⁴⁾ Since then, it is well known that a number of offerings have hit the marketplace, with the pace of introduction increasing since 2009.

The technical approach to reformulation adopted by many of the entrants has been to increase the hydrocarbon surfactant levels to compensate for the removal of fluorine. This approach has two deficiencies—a general decrease in performance, particularly burnback characteristics on polar fuels, and a worsening of short term toxicity markers. While many of these Fluorine-Free Foams (F3) are neither biopersistent nor bio-accumulative, they do exhibit extremely high aquatic toxicity, up to an order of magnitude more toxic than AFFFs.⁽⁵⁾ These first generation F3s are therefore not environmentally benign.

From a performance standpoint, the heretofore available F3s suppress vapors for approximately 70% less time than AFFFs. This requires greater application quantities in order to maintain equivalent vapor suppression performance.

2nd Generation F3 – Fire Performance

This presentation will discuss the introduction of a novel next generation F3, based on a different approach vs. the past. This will be shown to result in (a) an enhanced environmental profile and (b) equivalent or better fire fighting performance, when compared to 1st generation F3s.

The technical approach taken was to use ingredients not previously used in firefighting foams, and achieve the best balance of properties, enabling a reduction in the detergent level. In particular, the balance between extinguishment, burnback, and viscosity is critical; test results will be presented to illustrate this.

The F3 formulations, which have been developed in both 6% and 3% versions, were able to achieve excellent ratings per the EN 1568:2008 standard, as shown in Table 1. In the presentation, we will illustrate that these ratings compare very favorably vs. the available F3s on the market.

Foam Master 6% (launched 2011):

Fuel type:	FW	SW
Hydrocarbon	I-A	I-A
Acetone	I-A	I-A
IPA	II-C	II-A

Foam Master 3% (to be launched 2012):

Fuel type:	FW	SW
Hydrocarbon	I-A	II-A
Acetone	I-A	I-B
IPA	I-B	II-B

Table 1: EN 1568:2008 ratings for 2nd generation F3 (MPA Dresden)

Finally, long-term aging studies were conducted to ensure compatibility with materials of storage. These results, obtained per the USDA Forest Service test protocols, indicate very low corrosivity.

2nd Generation F3 - Environmental Profile

The novelty of this work lies in the fact that comparable performance is achieved, relative to 1st generation F3s, but with a superior environmental profile. Some key characteristics of the latter are highlighted in Table 2.

Property	Protocol	3% version	6% version	Comments
Biodegradation	28 day (OECD 301A)	97%	100%	
Acute aquatic toxicity	96 hr LC50 – various species (OECD 203)	> 100 mg/l	> 100 mg/l	Low toxicity
Mammalian toxicity	Oral, LD50 Dermal, LD50 Eye	> 5000 mg/kg > 5000 mg/kg Category 2	> 5000 mg/kg > 5000 mg/kg Category 3	
Waste water treatment compatibility	BOD/COD ratio (OECD 209)	40%	46%	> 30%; “easy to treat”
Fluorine content	O2 combustion + ISE Perfluorinated compounds via LC/MS	Below detection limit (< 5 ppm) < 0.05 µg/g	Below detection limit (< 5 ppm) < 0.05 µg/g	Zero fluorine Not biopersistent

More insight into these results, and how they compare with published values for 1st generation F3s, will be presented.

Conclusions

Due to increasing regulatory focus on fluorosurfactants, critical to the performance of firefighting AFFFs, many foam manufacturers have introduced F3s to the market, especially since 2009. Most of the 1st generation F3s have shown lower performance, and breadth of listings, relative to AFFFs, as well as higher acute toxicity. In this paper, we present a novel 2nd generation F3. While it still has significant performance gaps vs. AFFFs, it does not suffer from the same tradeoffs as the 1st generation products. We have shown it is possible to build an F3 platform, for at least certain applications, which has neither the biopersistence issue associated with PFOAs, none of the discharge concerns associated with even C₆-based AFFFs, and has excellent biodegradability and short-term toxicity.

References

1. Fact Sheet on AFFF Fire Fighting Agents, published by FFFC, 2001.
2. US EPA 2010/2015 PFOA Stewardship Program website, <http://www.epa.gov/opptintr/pfoa/pubs/stewardship/index.html>.
3. US EPA press release, “Industry Progressing in Voluntary Effort to Reduce Toxic Chemicals / Companies have successfully developed over 150 alternatives to long-chain perfluorinated chemicals”, issued Feb 10, 2012.
4. Angus Syndura datasheet, ref. 5420/3/02.10, Angus Fire Company.
5. “Aquatic Toxicity of Firefighting Foams,” paper posted on Fire Industry Association website <http://www.fia.uk.com>.