

Fire Fighting Foam Coalition

September 2011

# Milspec Testing of AFFF and Fluorine-free Foam

### **Executive Summary**

At the 2011 SUPDET Conference in Orlando, the Naval Research Laboratories (NRL) presented the results of fire testing of AFFF agents and fluorine-free foam<sup>1</sup>. Although the testing was limited in scope, it provided clear evidence of the importance of film formation to foam performance. Extinguishment times for AFFF agents on 28ft<sup>2</sup> pool fires tested at full strength were on average 77% faster for gasoline, 88% faster for methylcyclohexane (MCH), and 70% faster for heptane when compared to fluorine-free foam. For isooctane, where the tested AFFF agents were unable to form a film, fluorine-free foam extinguished the fire about 10% faster.

AFFF agents extinguished all gasoline and heptane fires in less than 30 seconds, the time required to pass the military specification (milspec). The fluorine-free foam was unable to extinguish any gasoline or heptane fire in less than 30 seconds. Foam agents must meet the requirements of the milspec in order to be listed on the US Department of Defense qualified products database (QPD) and used for military applications. In addition the Federal Aviation Administration (FAA) requires all US airports to carry AFFF agents listed on the QPD<sup>2</sup>.

Burnback times were similar among the foams tested. AFFF agents performed on average 37% better on heptane and 28% better on gasoline. AFFF agents and fluorine-free foam performed almost identical on MCH and isooctane. It is difficult based on such limited data to draw any firm conclusions about the relationship between film formation and burnback performance.

### Introduction

AFFF is the premier fire fighting foam in the United States (US) and many parts of the world. Its ability to rapidly extinguish flammable liquid pool fires is unmatched by any other agent. AFFF agents are formulated by combining hydrocarbon surfactants used mainly as foaming agents with perfluorinated surfactants. When mixed with water, the resulting solution achieves the optimum surface and interfacial tension characteristics needed to produce an aqueous film that spreads across the surface of a hydrocarbon fuel. It is this film formation feature that provides superior fire extinguishment and is the source of the designation – Aqueous Film Forming Foam (AFFF).

Over the past decade, most foam manufacturers have developed fluorine-free foam products to offer as potential alternatives to AFFF in some applications. These foams usually contain higher concentrations of hydrocarbon foaming agents and other ingredients in order to make up for the lack of film forming fluorinated surfactants. Although they do not contain persistent chemicals, fluorine-free foams have an environmental profile related to biodegradation, acute toxicity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) that is similar to AFFF. A study of commercially available fire fighting foam agents indicates that some fluorine-free foams are at least an order of magnitude higher in aquatic toxicity than AFFF agents<sup>3</sup>.

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#### **Military Specification**

The US Department of Defense military specification (milspec) is one of the most rigorous and respected standards for fire fighting foams in the world. It is more difficult to meet than other standards such as ISO and UL, and there are many foam products that meet the requirements of those standards but do not meet the requirements of the milspec. These requirements include conformance to concentration as determined by refractive index and fluorine content; corrosivity (pH, total halides, general and localized corrosion); storage issues related to compatibility with other AFFF agents and stability based on aging of the agent; environmental impact as determined by biodegradability factors, specifically, chemical oxygen demand (COD) and biological oxygen demand (BOD), and aquatic toxicity (short term measurement for salt water Killifish); performance as a film forming agent (dry chemical compatibility, film formation and sealability, viscosity, spreading coefficient, and foamability); and, finally, fire performance on a 28 and 50ft<sup>2</sup> unleaded gasoline pool fire. As part of the fire performance testing foam agents must extinguish the 28ft<sup>2</sup> pool fire at half-strength4.

### **NRL Foam Testing**

Three commercially available foam agents, two AFFF agents listed on the QPD and fluorine-free foam that NRL has previously worked with, were tested on a 28ft<sup>2</sup> pool fire using four different fuels. All tests used the milspec nozzle, application rate, and test protocol with fresh water and the foam mixture at its full design strength.

Gasoline and heptane were tested to collect data comparing the two fuels for a possible changeover to heptane as the milspec test fuel in the future. The comparison of MCH, isooctane, and heptane was part of a mechanistic study to isolate the different factors influencing suppression and burnback. These three fuels were chosen to vary the spreading coefficient for AFFF agents while keeping the fuel flashpoint nearly constant. Previously NRL had looked at the influence of fuel flashpoint on the mechanism of burnback.

#### Results

Fire out times are presented in Table 1 and burnback times are presented in Table 2. In order to meet the milspec requirements, a foam agent must extinguish the 28ft<sup>2</sup> pool fire at full strength in 30 seconds or less and have a burnback time of at least 360 seconds.

Table 1. File Out Times (seconds)					
Fuel	AFFF (6%)	AFFF (3%)	Fluorine-free (6%)		
Gasoline	22	21	35, 41		
Heptane	23, 28	25	43		
МСН	22, 23	19, 20	33, 46		
Isooctane	32, 33	32, 33	29, 30		

Table 1: Fire Out Times (seconds)

AFFF agents extinguished the test fires in an average time of 21.5 seconds for gasoline, 25.3 seconds for heptane, 21 seconds for MCH, and 32.5 seconds for isooctane. The fluorine-free foam extinguished the test fires in an average time of 38 seconds for gasoline, 43 seconds for heptane, 39.5 seconds for MCH, and 29.5 seconds for isooctane. Extinguishment times for AFFF agents were on average 77% faster for gasoline, 88% faster for MCH, and 70% faster for heptane when compared to fluorine-free foam. For isooctane, where the tested AFFF agents were unable to form a film, fluorine-free foam extinguished the fire about 10% AFFF agents extinguished all gasoline and faster. heptane fires in less than the 30 seconds required to pass the milspec. The fluorine-free foam was unable to extinguish any gasoline or heptane fire in less than 30 seconds.

Table 2:	Burnback	Times	(seconds)
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Fuel	AFFF (6%)	AFFF (3%)	Fluorine-free (6%)	
Gasoline	652	657	512	
Heptane	878, 758	674	563	
МСН	522	499	503	
Isooctane	767	820	789	

Burnback times were similar among the foams tested. AFFF agents performed on average 37% better on heptane and 28% better on gasoline. AFFF agents and fluorine-free foam performed almost identical on MCH and isooctane. Both the AFFF agents and the fluorine-free foam had burnback times for gasoline and heptane that were well in excess of the 360 seconds needed to pass the milspec.

# Discussion

Although the limited scope of the NRL testing makes it difficult to draw many conclusions, it does confirm the already well-known fact that the ability of fluorosurfactant foams to form an aqueous film on hydrocarbon fuels is the key to exceptional extinguishing performance. AFFF agents performed significantly better than fluorine-free foam on fuels where they could form a film, but performed similar to fluorinefree foam when they could not form a film. It should be noted that AFFF agents form a film on most common flammable, hydrocarbon liquids such as gasoline and jet fuel that would be encountered in emergency situations. This is why they continue to be the only foam agents approved for military or airport use in the US.

In order to compensate for the lack of film formation, fluorine-free foams rely upon having a good enough foam blanket in terms of expansion ratio and drainage rate. Expansion ratios for foams generated using the milspec nozzle in this study were high, in the range of 9:1 to 10:1. These are much higher expansion ratios than would be expected from the equipment used by most firefighters in the field, which are likely to be 5:1 to 7:1 for air aspirated foam and 3:1 to 5:1 for non-aspirated foam. Expansion ratios of 9:1 and 10:1 would be expected to enhance the effectiveness of fluorine-free foam by producing a thick foam blanket that is unlikely to be achieved in real life situations. AFFF agents on the other hand actually perform better with lower expansion ratios similar to what would be expected in the field.

Additional testing on the 50ft<sup>2</sup> pool fire and the 28ft<sup>2</sup> pool fire at half-strength, as required under the milspec, could also be important in better defining foam performance and should be considered in future studies.

# References

<sup>1</sup> Extinguishment and Burnback Tests of Fluorinated and Fluorine-free Firefighting Foams with and without Film Formation, Bradley Williams, Timothy Murray, Christopher Butterworth, Zachary Burger, Ronald Sheinson, James Fleming, Clarence Whitehurst, and John Farley, Naval Research Laboratory, Washington, DC, presented on March 25, 2011, at the SUPDET Conference,www.nfpa.org/assets/files//PDF/Proceedings /SUPDET11WilliamsPaper.pdf.

<sup>2</sup> FAA Advisory Cautionary Non-directive (CertAlert), Aqueous Film Forming Foam meeting MIL-F-24385, No. 06-02, February 8, 2006 and Federal Aviation Administration, National Part 139 CertAlert No. 11-02, Identifying Mil-Spec Aqueous Film Forming Foam (AFFF), February 15, 2011

<sup>3</sup> 96-hour LC50 Value in Fathead Minnows (flow-through test), Report of tests on six fire fighting foam agents performed by Aqua Survey Inc., Flemington, New Jersey, USA and 96-hour LC50 Test in Fingerling Rainbow Trout, Report of tests on six fire fighting foams agents performed by Harris Industrial Testing Service Ltd., Nova Scotia, Canada

<sup>4</sup> United States Department of Defense Military Specification, Mil-F-24385, "Fire Extinguishing Agent, Aqueous Film Forming Foam"