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Extinction Performance Summary of Commercial Fluorine-free Firefighting Foams over a 28 ft^2 Pool Fire Detailed by MIL-PRF-24385

Katherine M. Hinnant
Ramagopal Ananth
John P. Farley
Clarence L. Whitehurst

Navy Technology Center for Safety and Survivability
Chemistry Division

Spencer L. Giles
William A. Maza

Materials Chemistry Branch
Chemistry Division

Arthur W. Snow

Volunteer Emeritus
Chemistry Division

Stanley Karwoski

Jensen Hughes
Baltimore, MD

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Katherine M. Hinnant, Ramagopal Ananth, John P. Farley, Clarence L. Whitehurst, Spencer L. Giles William A. Maza, Arthur W. Snow, and Stanley Karwoski*

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*Jensen Hughes, 3610 Commerce Drive, Suite 817, Baltimore, MD 21227

14. ABSTRACT

Commercial fluorine-free firefighting foams were evaluated at conditions relevant to military qualification testing. Extinction and burnback times were quantified over a 28 ft2 pool fire using heptane and gasoline as test fuels, and for varying foam solution flow rates: 2, 2.5, and 3 gallons per minute (gpm). Foam and solution properties detailed by military qualification testing were also measured and compared to a commercial AFFF. Solberg RF3 (2018) and Fomtec Enviro 2-3% USP extinguished a gasoline pool fire in 49 and 78 seconds at a solution flow rate of 2 gpm. Commercial AFFF extinguished under the same conditions in under 30 seconds. Performance of the fluorine-free foams improved when the fuel was switched to heptane and when the solution application rate was increased from 2 gpm to 2.5 gpm with both fluorine-free foams extinguishing the fire in 31 seconds. Both fluorine-free foams had slower drainage and slower bubble coarsening than the commercial AFFF. However, foam properties collected do not appear to correlate well with extinction performance. Solberg RF3 and Fomtec Enviro 2-3% USP had concentrate viscosities of 26,000 and 16,000 cP, exhibited shear thinning of the concentrate, and had negative spreading coefficients. The inability of the foams and concentrates to meet critical extinction and property metrics for military qualification testing indicate the difficulties of utilizing these commercial products for Navy operations.

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INTRODUCTION

Aqueous film forming foams (AFFFs) suppress liquid pool fires by spreading over and covering the fuel surface, acting as a physical barrier between fuel vapors and the flame above. Fluorocarbon surfactants used in commercial AFFF formulations lower the surface tension of the foam solution significantly. This allows a thin film of liquid to spread on the fuel surface, despite the aqueous solutions' higher density. Fluorocarbon surfactants also produce stable foams that can remain over the fuel pool for long periods of time and limit the transport of fuel vapors through the foam layer [1-3]. Although fluorocarbon surfactants in firefighting foams have rapid fire suppression, the surfactants are known to bio-accumulate and accumulate in the environment [4]. Degradation products of fluorocarbon surfactants in AFFF, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), have been regulated by the U.S. Environmental Protection Agency (EPA) with more perfluorinated compounds potentially being regulated in the future [5]. It is therefore critical to replace fluorocarbon surfactants in firefighting foams, but maintain the rapid fire suppression capability. Commercial fluorine-free replacements are available, but their fire suppression capabilities and ability to maintain safety remain unknown.

Fluorocarbon surfactants were introduced into firefighting foams in the 1960's, proving more effective than previous protein-based firefighting foams. Developed at the Naval Research Laboratory in conjunction with the 3M Company, the superior performance of these new surfactants was attributed to their ability to significantly lower the surface tension of aqueous solutions, from roughly 72 mN/m of water down to 15-16 mN/m [6, 7]. Tuve et al. [6] deemed this film formation as unique to these solutions compared to protein-based foams which were unable to form "films" due to the high surface tension of its solution. Current military qualifications for use of firefighting foam specifies the need for the foam to form an aqueous film by having a spreading coefficient with cyclohexane greater than 3 [8].

MIL-PRF-24385 qualifications for firefighting foams include other specific foam solution properties such as refractive index and viscosity to ensure compatibility with Navy hardware [8]. More importantly, MilSpec qualification involves a rigorous series of fire extinction tests that test foams with fresh and salt water, aged and unaged concentrates and solutions, and mixes the test foam solution with MilSpec qualified products to test compatibility [8]. We propose a baseline performance metric outlined by MilSpec qualifications to be an extinction test of unaged foam, mixed at the appropriate amount with fresh water, over a 28 ft^2 gasoline pool fire, applied at a liquid solution rate of 2 gallons per minute (gpm). Under these conditions, MilSpec requires the foam to extinguish the fuel pool in under 30 seconds [8]. Film formation is considered key to rapidly suppressing a fire in under 30 seconds. Although fluorocarbon surfactants provide improved fire suppression capabilities besides film formation, the focus of fluorocarbon replacement in firefighting foams has been maintaining film formation and eliminating harmful environmental contaminants.

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Foam industry efforts to develop a film forming replacement for fluorocarbon surfactants are unknown as their research is not publically available, but academic efforts have been conducted to identify such surfactants. Hetzer et al. [9] synthesized a siloxane surfactant, mixed with a polyglycoside hydrocarbon surfactant, to produce a foam solution with a surface tension of 20 ± 5 mN/m. This foam was compared to a commercial AFFF in a 0.66 m^2 (roughly 7 ft^2) F-34 pool fire at a foam application rate of 1.5 kg/(min*m^2) (0.26 gpm given 0.66 m^2 pool size). Hetzer et al. [9] report extinction times of 131 seconds for the siloxane based foam and 103 and 136 seconds for a commercial AFFF. However, the surfactants patented by Hetzer et al. have not yet been developed into a commercial fluorine-free product. Research efforts at the Naval Research Laboratory have also focused on surfactant replacement in AFFF, examining firefighting effectiveness of commercial siloxane surfactants as well as synthesizing new surfactants. Ananth et al. [10] report fire suppression performance for a mixture of a commercial trisiloxane surfactant (DuPont 502W), a commercial polyglycoside surfactant (Glucopon 225 DK), and solvent (diethylene glycol butyl ether). On a 28 ft^2 pool fire, using an active firefighter, and the MilSpec nozzle at a solution flow rate of 2 gpm, Ananth et al. [10] show extinction times of 51 seconds on heptane, but no extinction on gasoline for the formulation.

Film formation is believed to aid in fire suppression through the formation of a liquid barrier that cools the fuel and reduces fuel transport to the fire above. As few efforts have developed surfactants to form this film thermodynamically, the industry approach has been to "mimic" film formation through slow liquid drainage from the foam. Based on available composition data from safety data sheets of fluorine-free foam concentrates, many use hydrocarbon or sulfonated surfactants and a number of solvents, stabilizers and thickeners. Using thickeners such as gums and starches increases the viscosity of the liquid, slowing liquid drainage from the foam over time [11]. Slower drainage results in a pseudo liquid layer at the foam-fuel interface throughout the extinction event which is thought to improve fire suppression capabilities.

Thicker fluorine-free concentrates have shown some promise as fluorinated surfactant concentrate replacements. Many commercial products have passed European test series ICAO Level B and Solberg RF3 (2018) has passed ICAO Level C, considered the closest test equivalent to U.S. military testing [12, 13]. However, these tests series do not use gasoline, utilize different pools sizes, and use passive versus active fire suppression compared to requirements detailed in MIL-PRF-24385. Snow et al. [14] has shown the differences in fire suppression performance for commercial fluorine-free foams over gasoline and heptane in a bench-scale pool fire. In a 19-cm bench-scale pool fire, commercial fluorine-free products from Chemguard (Ecoguard 3% F3) and National Foam (Universal Green 3-3%, alcohol resistant synthetic foam packed August, 2018) showed superior performance on heptane compared to gasoline. Commercial fluorine-free products from Solberg (Rehealing foam RF3-LV, viscosity 30-60 cP) and Fomtec (Enviro ARC 3x6) showed improved fire suppression over heptane at low foam applications rates, but over a gasoline pool fire performed equal to or better than heptane at high foam application rates. Snow et al. [14] showed almost no dependency on extinction time between the two fuels for commercial AFFF consistent with 28 ft^2 data.

While it is unclear whether these foams are able to suppress a fire under MilSpec qualifications, the high viscosity of the concentrates disqualifies them for military use. MIL-PRF-24385 specifies a foam concentrate must have a viscosity above 2 cSt at room temperature, but below 20 cSt at 5°C [8]. This specification ensures adequate flow and proportioning of concentrate into solution on board military ships with existing hardware. Higher viscosities would require a change in infrastructure, which would only be for consideration of fluorine-free products that match the safety level of current fluorinated AFFF while simultaneously mitigating environmental concerns. At this time it is unclear whether these commercial products are limited only by their viscosity or if they are also limited in their fire suppression performance.

Objective. The objective of this report is to assess the fire suppression capabilities of commercial fluorine-free firefighting foams for a limited set of MIL-PRF-24385 extinction tests using a 28 ft^2 pool fire, an active firefighter, heptane and gasoline fuels (given differences observed by Snow et al. [14] and the different requirements between foam test standards), and at various liquid foam solution application rates (2, 2.5, and 3 gpm). Evaluation over heptane and at flow rates higher than 2 gpm are not specified in military testing, but are conducted in this report in order to relate performance over a standardized fuel and to assess performance enhancement at higher foam solution flow rates. In addition to extinction tests, foam properties were measured to determine consistencies in foam generation using different orifices in the MilSpec nozzle for various liquid flow rates and foam solutions. Foam properties were also measured with time to see how components within the foam affected liquid drainage from the foam as well as bubble coarsening with time.

APPROACH AND METHODOLOGY

Materials

Fuels. Commercial grade heptane and alcohol-free unleaded gasoline were purchased from Tilley Chemical Company (Middle River, MD).

Commercial AFFF Concentrates. A commercial AFFF product, submitted by a manufacturer for MilSpec MIL-PRF-24385 evaluation (packaged in 2016) was used in this test series. This product passed MilSpec qualification testing and is currently on the Qualified Products List for military firefighting foams. The identity of this product cannot be disclosed in this report and is referred to as AFFF-1 when data is presented.

Commercial Fluorine-free Concentrates. Two commercial fluorine-free concentrates were purchased and evaluated: Solberg Re-Healing Foam RF3% (Solberg Scandinavian AS) packaged in 2018, and Fomtec Enviro 2-3% USP Synthetic Foam Fresh Water Only (Dafo Fomtec AB) packaged in 2019. Neither foams have been evaluated for full MilSpec certification, but Solberg RF3 meets European testing specifications, ICAO Level B and C, Fomtec Enviro USP 2-3% ICAO meets ICAO Level B. Technical data provided by the manufacturers is compiled in Table 1 [12, 13].

Table 1. Technical Data for commercial firefighting foam concentrates.

	Solberg RF3	**Fomtec Enviro 3% ICAO**
Appearance	Brown Liquid	Clear to yellow liquid
Freezing Point (°C)	-5	-11
Storage Temperature (°C)	< 49	< 55
pH	7.0-8.0	6.5-8.5
Viscosity at 20°C (cP)	4900-5300	1500
Specific Gravity at 20°C (g/mL)	1.06-1.10	1.04 ± 0.01
Suspended Sediments (vol/vol)	< 0.05	< 0.2

Liquid and Foam Property Measurements

Concentrate Testing. Viscosity of the liquid concentrate at room temperature (20°C) was independently measured using an HR-2 TA Instruments Hybrid Rheometer. A sample of concentrate was pressed between two plates, then a shear rate increasing with time was applied. Initial shear rate was 1 s^{-1} and ended at 100 s^{-1}. Refractive index was measured by pipetting a small drop of concentrate onto a MISCO hand-held refractometer, measurements were repeated twice using visible light at 20°C.

Solution Testing. Concentrates were diluted into premix foam solutions with distilled water at a 3% proportioning rate by weight. The DuNoüy ring method was used to measure surface and interfacial tensions with a platinum-iridium ring (20 mm in diameter) in a tensiometer (Sigma 701, Biolin Scientific Inc., Gothenburg, Sweden) at 20°C. Interfacial tension measurements were measured between foam solutions, heptane, and gasoline.

Foam Property Testing. Foams were generated using the MIL-PRF-24385 described nozzle with various orifices to generate foams at different foam solution flow rates. Foam properties were assessed in two ways. First, protocol dictated in MIL-PRF-24385 for expansion ratio and 25% liquid drainage time were followed. Second, foam was analyzed using a Dynamic Foam Analyzer (DFA, Kruss, Hamburg, Germany). Foam was collected off of a backboard (detailed in MIL-PRF-24385) into a column fitted with a triangular prism. This column was then placed in the DFA and the system began recording bubble radius with time and liquid drainage from the foam with time. Data was collected for 20 minutes. Due to the slow drainage rate of the Fomtec Enviro 2-3% USP, no significant liquid drainage was recorded in the 20 minute time period of the DFA measurement.

Large-Scale Fire Testing

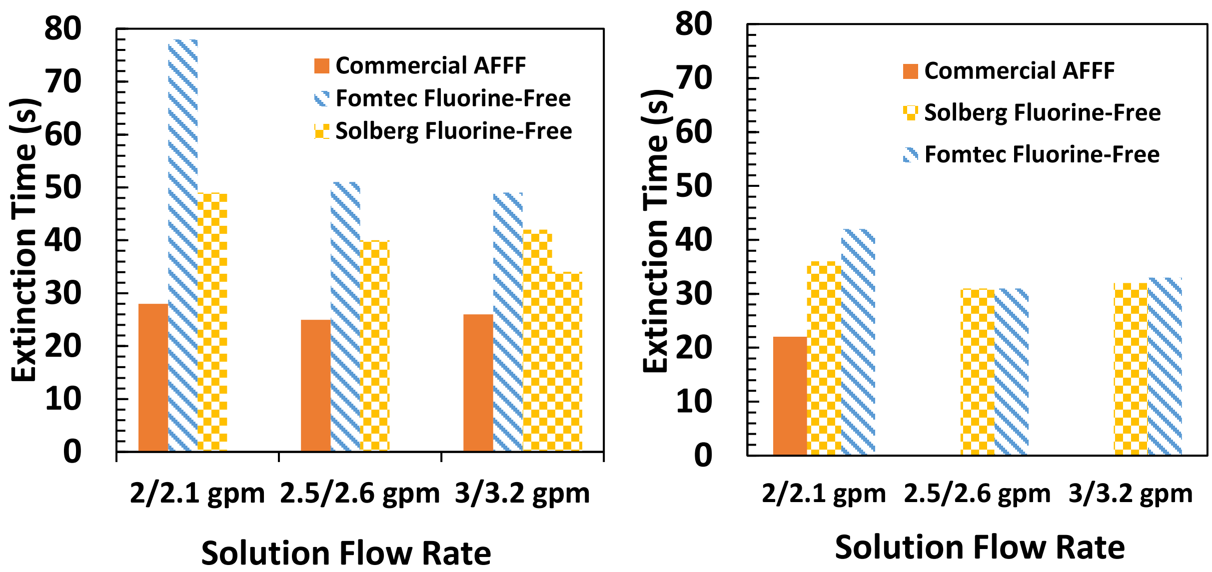
Varying Foam Flow Rate. MIL-PRF-24385 testing specifies a specific nozzle and orifice for firefighting foams that makes foam using a foam solution flow rate of 2 gpm. In this test series, the orifice was changed to examine extinction performance at solution flow rates of 2, 2.5, and 3 gpm. Changes in solution flow rate were measured by spraying foam into a 5 gallon bucket and monitoring the time to fill the bucket. The bucket was then weighed to determine the liquid content of the foam and the subsequent solution flow rate.

Heptane and Gasoline Pool Fire Testing. Extinction test protocol detailed in MIL-PRF-24385 for the 28 ft^2 pool fire were followed in this report. Water was first placed in the pan and topped with 10 gallons of the fuel to be analyzed. Testing was conducted for pool fires of alcohol-free unleaded gasoline as well as commercial grade heptane. Once the fuel was in the pan, it was ignited and pre-burned for 10 seconds. The firefighter then extinguished the flame and continued to apply additional foam to the pool surface for a total of 90 seconds, inclusive of extinction time. After the 90 seconds, a burnback test was conducted in which a small 1 ft diameter pan of fuel was ignited and lowered into the center of the 28 ft^2 pan. With time, the flame in the small pan spreads into the larger one, reigniting the fuel beneath the foam layer. Burnback time is defined as the time between the small pool deposition and 25% re-ignition of the 28 ft^2 pool fire. Two firefighters alternated between tests and are designated as FF-1 and FF-2 for each test.

RESULTS AND DISCUSSION

The fire suppression performance of AFFF-1 and two fluorine-free firefighting foams (Solberg RF3 and Fomtec Enviro 2-3% USP) were compared on a 28 ft^2 pool fire using heptane and gasoline, at three different solution flow rates: 2, 2.5, and 3 gpm. This was done in an effort to test whether commercial fluorine-free products are able to meet MilSpec requirements by varying the fuel and foam flow rate.

Extinction Results. Figure 1 plots the extinction results of gasoline (a) and heptane (b) in bar graph form to compare trends in extinction performance based on solution flow rates. Table 2 summarizes the extinction times shown in Fig. 1 along with the firefighter associated with the extinction and burnback time for a given test. The RF3 3 gpm gasoline test shown in Table 4 was conducted twice: FF-1 attempted to extinguish the fire, but was skeptical with the technique employed to fight the fire, FF-2 repeated the test with a slightly different technique which resulted in a shorter extinction time. The burnback time reported is for the second test with FF-2. Both times are listed in Table 2 and are shown side-by-side in Fig. 1.



(a) (b)

Figure 1. Bar graph of large-scale extinction results over (a) gasoline and (b) heptane for AFFF-1, Fomtec fluorine-free foam, and Solberg fluorine-free foam. For x-axis label "A/B gpm", "A" refers to the expected solution flow rate based on the orifice plate, "B" is the actually measured solution flow rate using a 5 gallon bucket.

Table 2. Extinction and burnback results for three foams, at three different solution flow rates, on two different fuels, fought by two separate firefighters, FF-1 and FF-2.

Applied Liquid Flow Rate (gpm)	**Fuel**	**Foam**	**Firefighter**	**Extinction Time (s)**	**Burnback Time (s)**
2	**Heptane**	AFFF-1	FF-2	22	697
		RF3	FF-2	36	1020
		Enviro 3%	FF-2	42	778
	Gasoline	AFFF-1	FF-1	28	433
		RF3	FF-1	49	463
		Enviro 3%	FF-1	78	362
2.5	**Heptane**	RF3	FF-2	31	1049
		Enviro 3%	FF-2	31	780
	Gasoline	AFFF-1	FF-1	25	549
		RF3	FF-1	40	690
		Enviro 3%	FF-1	51	482
3	**Heptane**	RF3	FF-1	32	1221
		Enviro 3%	FF-2	33	816
	Gasoline	AFFF-1	FF-1	26	609
		RF3	FF-1/FF-2	42/34	938
		Enviro 3%	FF-1	49	555

Suppression performance varies by foam type, fuel type, and slightly by solution flow rate. There also appears to be some dependence on firefighter form or dispensing technique as we noticed a significant difference in extinction time between FF-1 and FF-2 for RF3 at 3 gpm over gasoline. AFFF-1 is able to suppress a fire in under 30 seconds at MilSpec requirements of 2 gpm over gasoline, unlike the two fluorine-free foams which extinguish in 49 seconds and 78 seconds for the Solberg and Fomtec fluorine-free products respectively. Increasing the flow rate to 2.5 gpm over gasoline, AFFF-1 maintains rapid fire suppression, suppressing in 25 seconds. The fluorine-free products have improved fire suppression performance, but still not comparable to AFFF-1, extinguishing at 40 and 51 seconds for the Solberg and Fomtec foams respectively. The change in fire suppression performance between 2.5 and 3 gpm is not as significant for the fluorine-free foams as it is for the change between 2 and 2.5 gpm. Increasing the flow rate to 3 gpm still did not produce comparable suppression performance between AFFF-1 and the two fluorine-free foams. Interestingly, AFFF-1 does not appear to have a significant dependence on solution flow rate, the change in extinction performance is negligible between 2, 2.5 and 3 gpm.

Extinction performance is improved at all three flow rates for the fluorine-free foams when the fuel is changed from gasoline to heptane. At 2 gpm, Solberg foam extinguishes a gasoline pool in 49 seconds, but in 36 seconds on a heptane pool. Similarly, the Fomtec foam extinguishes a gasoline pool in 78 seconds, but a heptane pool in 42 seconds. Although an improvement in suppression is observed, neither fluorine-free foam is able to match the performance of AFFF-1 at 2 gpm over heptane, which extinguishes the fuel pool in 22 seconds. Performance over heptane is improved for the fluorine-free foams when the solution flow rate is increased leading to fire extinction times just above 30 seconds on a 28 ft^2 pool fire. At 2.5 gpm, both fluorine-free foams extinguish the heptane pool fire in 31 seconds; however, additional improvement is not seen when the solution flow rate is increased to 3 gpm.

Burnback performance varied significantly from extinction performance. Over gasoline, Solberg fluorine-free had the longest burnback times at all three flow rates compared to AFF-1 and Fomtec fluorine-free foams. Because burnback tests are conducted on a foam blanket 90 seconds after foam is applied, the foam blanket thickness varies for each test depending on differences in fire extinction time and foam properties. For example, at 2 gpm over gasoline, AFFF-1 extinguishes in 28 seconds and therefore had 62 seconds of applied foam to build up a thick foam blanket. The Solberg fluorine-free foam extinguished in 49 seconds, leaving only 41 seconds of applied foam to build up the foam blanket. Despite this difference, the Solberg fluorine-free has a longer burnback time than AFFF-1. AFFF-1 does have longer burnback times than the Fomtec fluorine-free foam over gasoline for all 3 solution flow rates. Despite the longer burnback time of Solberg's foam, it takes longer to extinguish heptane and gasoline fires compared to AFFF-1.

Burnback times over heptane are expected to be longer than times over gasoline due to differences in vapor pressure between the two fuels. Gasoline with a higher vapor pressure produces a larger concentration of vapors below the foam that can potentially travel through the foam blanket compared to heptane. Because less fuel vapors are penetrating the blanket with time, more time is required to build up a flammable concentration of vapors over the foam layer. This is seen for the fluorine-free foams at the 3 flow rates and for AFFF-1 at 2 gpm: burnback times are longer on heptane compared to gasoline. At 2 gpm over heptane, Fomtec fluorine-free foam has a longer burnback time than AFFF-1, despite large differences in extinction time. This demonstrates further fuel dependency on performance as Fomtec foam had shorter burnback times compared to AFFF-1 on gasoline, but longer burnback times on heptane. At 2.5 and 3 gpm over heptane, both fluorine-free foams had similar extinction times, but the Solberg foam had longer burnback times than the Fomtec foam, indicating superior foam stability.

Foam Property Measurements. Foam solution components can affect the structure of the foam produced, which may also impact extinction and burnback performance. In Table 3, we tabulate the measured expansion ratios, 25% liquid drainage time, and initial bubble diameter recorded for foams generated from the MilSpec nozzle at solution flow rates of 2, 2.5, and 3 gpm.

Table 3. Expansion ratio, 25% liquid drainage time, and initial bubble diameter for different firefighting foams at various liquid foam solution flow rates.

	Applied Liquid Flow Rate (gpm)	Expansion Ratio, MilSpec	25% Liquid Drainage Time (min)	Initial Bubble Diameter (μm)
AFFF-1	2 (2.1)*	7.7 (8.3)*	5.4	66
	2.5 (2.4)	6.8 (7.3)	5.4	62
	3 (3.0)	6.5 (7.3)	4.9	62
Solberg RF3	2 (2.1)	7.9 (7.6)	21.3	66
	2.5 (2.6)	7.5 (8.4)	19.1	64
	3 (3.2)	6.4 (7.9)	28.0	62
Fomtec Enviro 3% ICAO	2 (2.0)	12.3 (10.5)	58.2	70
	2.5 (2.5)	10.6 (9.4)	47.3	80
	3 (3.1)	10.6 (8.9)	42.9	72

*Numbers in parentheses are measured by foam collection in a 5 gallon bucket.

Some variations in expansion ratio and liquid drainage time are seen between AFFF-1 and the two fluorine-free foams. However, initial average bubble diameter (measured with the DFA) appear to be uniform between foams and solution flow rates with the Fomtec fluorine-free having slightly larger bubbles on average. AFFF-1 has expansion ratios similar to Solberg fluorine-free foam at the 3 liquid flow rates examined. Variation between the two at each flow rate are 2.6, 9.8, and 1.6 % for 2, 2.5, and 3 gpm. Although the expansion ratios are similar, the Solberg fluorine-free foam drains much slower than AFFF-1. AFFF-1 also shows less variance in 25% liquid drainage time compared to the Solberg fluorine-free foam; however, the 25% liquid drainage time observed for Solberg RF3 at 3 gpm may be an outlier as the other foams indicate a trend in faster drainage as the solution flow rate is increased.

The Fomtec fluorine-free foam displays a larger expansion ratio than the other two foams, between 10 and 12, outside of the accepted MilSpec expansion ratio range of 5-10. Fomtec foam drainage times are also longer than the two foams, lasting nearly an hour compared to the roughly 20 and 5 minutes of the Solberg foam and AFFF-1. Differences in drainage time may be related to foam solution properties or concentrate composition. Drainage time can be affected by solution viscosity [12], but also initial liquid content of the foam (expansion ratio) [15]. Magrabi et al. [15] noted faster drainage in wetter foams compared to drier foams. It is possible that the higher expansion ratio of Fomtec fluorine-free foam slows liquid drainage from the foam. It is unclear as to what component or property of the foam solution affects the expansion ratio.

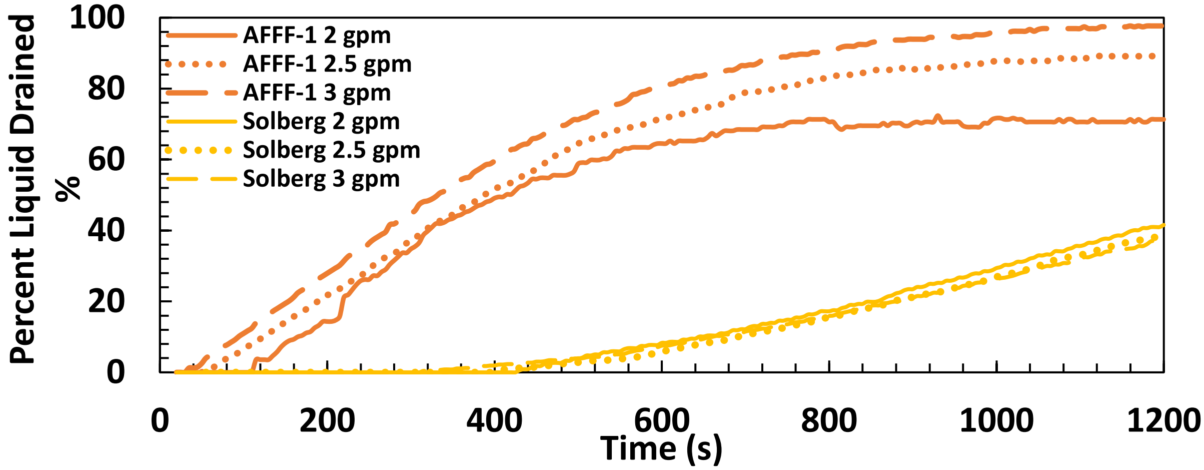


Figure 2. Percent liquid drained from the foam with time, calculated using the expansion ratio values measured in Table 2. Data is presented for AFFF-1 and Solberg fluorine-free foam at 3 different solution flow rates.

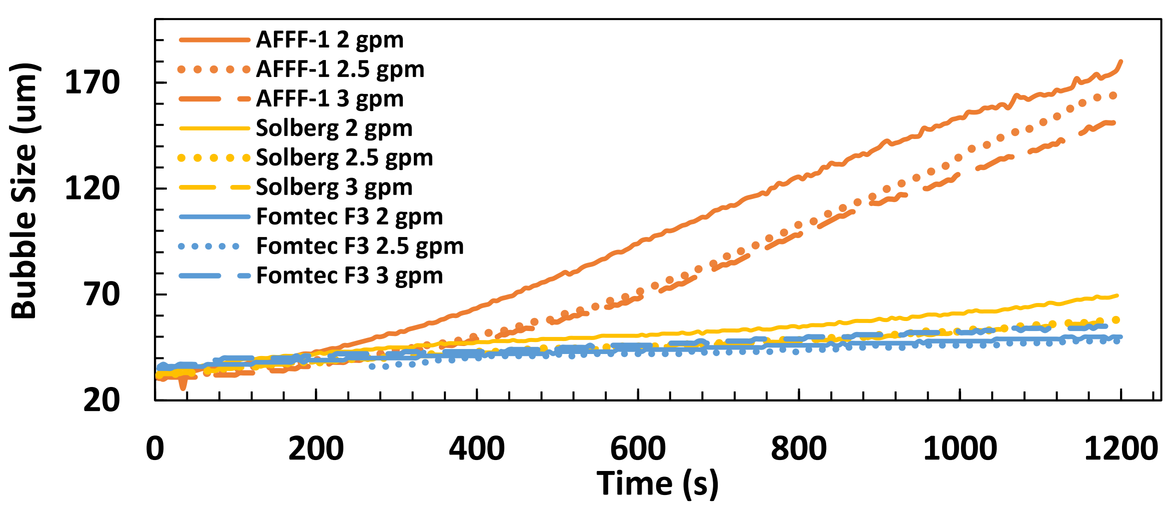


Figure 3. Bubble coarsening with time represented by the change in arithmetic bubble size with time. Data is presented for AFFF-1, Solberg fluorine-free, and Fomtec fluorine-free foam at 3 different solution flow rates.

DFA data for liquid drainage rates and bubble coarsening rates are shown in Figures 2 and 3 respectively. Figure 2 plots the drainage data for AFFF-1 and Solberg fluorine-free foam at all 3 solution flow rates examined. Fomtec fluorine-free foams were also analyzed, but no significant drainage (less than 5%) was measured within the 20 minute time frame of the dynamic foam analyzer test, therefore no data is reported. This is in agreement with the 25% drainage time collected through MilSpec testing which indicates a 25% drainage time between 40 and 50 minutes for the Fomtec fluorine-free foam across the three solution flow rates. However, bubble coarsening rates for Fomtec fluorine-free foams were able to be measured at the three separate solution flow rates and are plotted in Fig. 3.

Drainage data shown in Fig. 2 indicate a difference in drainage performance between AFFF-1 and Solberg fluorine-free. This is also observed in the 25% drainage time collected through MilSpec specification. The AFFF-1 shows some variance in drainage rate with solution flow rate: AFFF-1 at 2 gpm drains slower over a longer period of time compared to 2.5 gpm and 3 gpm which results in faster drainage rates. Solberg fluorine-free shows no difference in drainage rates based on the three solution flow rates. A statistical analysis could not be done as multiple trials were not completed for the same test. Therefore, it is unclear whether differences in the AFFF-1 drainage rates are statistically significant. However, it is likely that the large differences in drainage rates between AFFF-1 and the two fluorine-free foams is a result of drastic differences in concentrate and solution viscosity, with the higher viscosity fluorine-free foams slowing the drainage from foam compared to the lower viscosity AFFF-1. Concentrate viscosity values are presented later in Table 4 of this report.

After 20 minutes, AFFF-1 has an average arithmetic bubble size of roughly 170 µm whereas the two fluorine-free foams have bubble sizes of only 50 µm. AFFF-1 shows some variance in bubble coarsening rates based on solution flow rate with the foam produced from 2 gpm coarsening faster than AFFF-1 foam at the two other flow rates. A statistical analysis could not be done because multiple trials were not completed for each test. Therefore, it is unclear whether the differences in AFFF-1 bubble coarsening rates are statistically significant. Differences in bubble coarsening are not seen for the two fluorine-free foams in Fig. 3. However, given the lengthy time required to lose 25% liquid from the foams, the test may not have been conducted long enough to observe these differences.

Foam properties appear to have mixed effects on firefighting performance. AFFF-1 and Solberg fluorine-free foam have similar expansion ratios, but AFFF-1 drains and coarsens faster than Solberg fluorine-free foam. Despite the fast drainage and coarsening, AFFF-1 extinguishes faster on gasoline and heptane at 2 gpm. Foam properties may not be effecting extinction, but Solberg fluorine-free foam, with superior drainage and bubble coarsening, has longer burnback times than AFFF-1. These enhanced foam properties may indicate why Solberg fluorine-free foam has longer burnback times regardless of solution flow rate and fuel compared to AFFF-1. Fomtec fluorine-free foam has even slower drainage than Solberg fluorine-free, but has a higher expansion ratio which may be negatively impacting its suppression and burnback performance; however, a relationship between expansion ratio and firefighting performance is not well established. Other properties related to interactions between the foam and fuel may better explain extinction and burnback results rather than foam properties.

Foam Solution Measurements. Concentrate and foam solution measurements were made to correlate solution behavior to foam properties and potentially fire suppression. Solution properties are also analyzed for MilSpec requirements and have strict guidelines on solution performance. Military requirements specify the refractive index of the concentrate, viscosity of the concentrate at room temperature, and the spreading coefficient between the foam solution and cyclohexane. In this report, we quantify aspects of the spreading coefficient (solution surface tension, interfacial tension) over gasoline and heptane. Viscosity values reported in Table 4 are the values recorded at a shear rate of 1 s^{-1} in the hybrid rheometer. Figure 4 plots the change in viscosity of the concentrates as a function of shear rate applied by the rheometer.

Table 4. Concentrate (C) and foam solution (S) properties measured at 20°C. Error between measurements for surface and interfacial tensions is 0.5 mN/m.

	AFFF-1	**Solberg RF3**	**Fomtec Enviro 3% ICAO**
Refractive Index (C)	1.3693	1.3880	1.3740
Viscosity, cP (C)	3.52	26,320	16,120
Surface Tension, mN/m (S)	15.3	25.6	24.0
Int. Tension Gasoline, mN/m (S)	1.17	0.84	0.9
Int. Tension Heptane, mN/m (S)	1.53	3.06	2.0

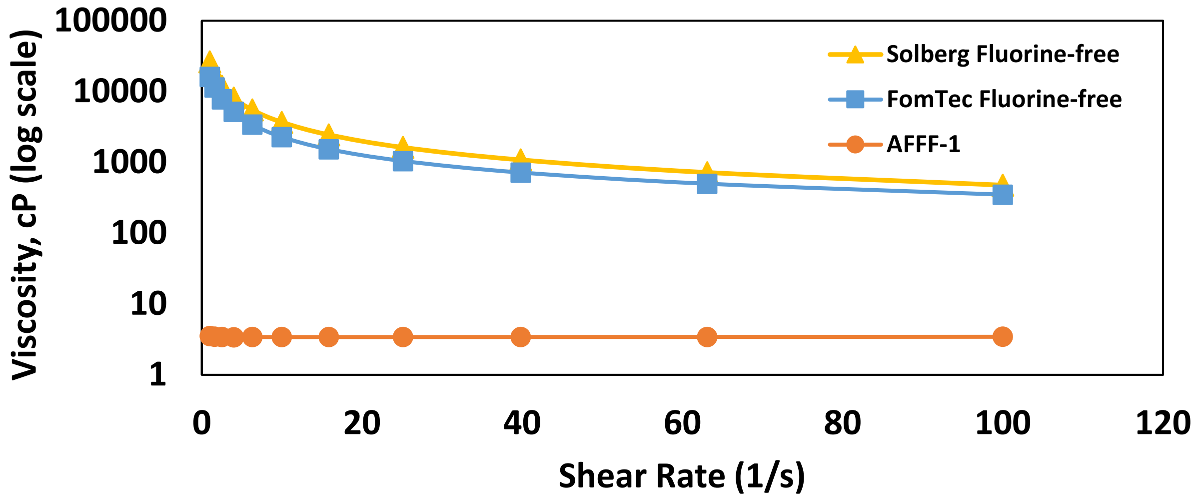


Figure 4. Viscosity of AFFF-1, Solberg fluorine-free, and Fomtec fluorine-free foam concentrates as a function of applied shear rate in a plate rheometer. Y-axis is on a log-scale.

One of the largest differences between the fluorinated and fluorine-free concentrates is the viscosity. The reported viscosities in Table 1 are lower than the values reported at a shear rate of 1 s^{-1}. It is suspected that manufacturers are reporting the viscosity averaged across the shear rate tests. The viscosity significantly changes for the fluorine-free concentrates as the shear rate is increased. The averaged viscosities across a test for the two foams are 7220 and 4500 cP for Solberg fluorine-free and Fomtec fluorine-free foam concentrates which are closer to those values reported by the manufacturer. The high viscosities of the concentrates would lead to slowed liquid drainage from the foams, which is what is seen for the fluorine-free foams compared to AFFF-1. Solberg fluorine-free and Fomtec fluorine-free foam concentrates show viscosities of the same order a magnitude, but Fomtec fluorine-free still drains slower. This could be due to differences in the generated expansion ratios between the two foams as Fomtec fluorine-free was dryer than Solberg fluorine-free foam.

The fluorine-free foam concentrates exhibit shear thinning, meaning as the applied shear rate is increased, the viscosity decreases. This is not true for the AFFF-1 concentrate that has a similar viscosity regardless of the applied shear rate. During the test, the viscosities of the two fluorine-free concentrates dropped from roughly 10,000 cP to 100 cP. Considering the components of the fluorine-free foams detailed by the foam manufacturers, the shear thinning behavior of these materials is not that surprising. Safety data sheets report Solberg RF3 containing starch and sucrose, both in excess of 1%. Fomtec Enviro 2-3% USP does not list any identifiable gums or starches on their Safety Data Sheet [16, 17], but the listed components only account for a maximum of 36% of the formulation. Polysaccharide gums and starches have been shown to be shear-thinning materials and can effect initial viscosities and shear-thinning rates of aqueous solutions. Mrokowska et al. [18] demonstrated that solutions of xanthan gum ranging from 0.25 to 1.4 g/L in water display shear-thinning behavior under shear rates from 0.1 s^{-1} to 1000 s^{-1}. The initial viscosity of the solution increased with increasing concentration. Additionally, Cengiz et al. [19] reported on the shear-thinning behavior of tapioca starch and a specific gum in binary-mixtures with roughly 3-4 % starch and gum in solutions. Given the similar concentrations between the studies and available component data for fluorine-free firefighting foams, the presence of these gums and starches must be influencing the initial viscosity and the shear-thinning abilities of these concentrates.

Other significant differences in solution properties for the 3 formulations tested are the surface tension and interfacial tensions. However, the effect of these differences on foam properties and fire extinction is unclear. AFFF-1 solution has a surface tension of roughly 15 mN/m whereas the fluorine-free solutions have surface tensions of 24 and 25.6 mN/m as seen in Table 4. Surface tension is expected to impact film formation (which can thermodynamically occur for AFFF-1 but not the fluorine-free foams), but also bubble size. Lower surface tensions can produce smaller bubbles, maintaining larger pressure differences between the inside and outside of the bubble. The lower surface tension of AFFF-1 does not appear to impact initial bubble size as the three foams have similar initial bubble sizes. The three foam solutions also have similar interfacial tensions under heptane, roughly 1 mN/m. However, over gasoline, the interfacial tension of the fluorine-free foams increases to 2 or 3 mN/m while the AFFF-1 solution has a similar interfacial tension to that under heptane. This shows some fuel dependency for the fluorine-free foam solutions examined, but not the AFFF-1 solution examined.

SUMMARY

Commercial fluorine-free foams Solberg RF3 and Fomtec Enviro 2-3% USP were compared to a commercial fluorinated foam, AFFF-1, through extinction and burnback performance in a 28 ft^2 pool fire, foam properties, and liquid solution properties. The foams were tested on gasoline and heptane pool fires, at various foam solution flow rates (2, 2.5, and 3 gpm). Although MilSpec testing specifies gasoline with a solution flow rate of 2 gpm, we wanted to explore the possibility that performance could be improved by using a different, more standardized, fuel and varying the solution flow rate. The purpose of this test series was to quantify differences between the foam performances and assess performance gaps.

Extinction results confirmed the superior performance of AFFF-1 on gasoline pool fires. AFFF-1 extinguished a gasoline pool fire in 28 seconds compared to the 49 and 78 seconds of the Solberg and Fomtec fluorine-free foams at 2 gpm. AFFF-1 showed no change in fire suppression performance on gasoline when the liquid application rate increased to 2.5 and 3 gpm. However, improvement was seen for the fluorine-free foams between 2 and 2.5 gpm. The extinction over a gasoline pool fire was 40 and 51 seconds for the Solberg and Fomtec fluorine-free foams respectively. A significant improvement in fire suppression over gasoline was not seen for the fluorine-free foams when the liquid application rate increased from 2.5 to 3 gpm. The most noticeable improvement to extinction was observed when heptane was used as the fuel. These differences in performance were already shown at bench-scale by Snow et al. [14] and were confirmed at large-scale for commercial fluorine-free foams. The comparisons with Snow et al. can only be qualitative because of differences in scales and in the identity (or formulation) of commercial fluorine free foams used. However, the fluorine-free foams were both able to extinguish a heptane pool fire in 31 seconds at a solution flow rate of 2.5 gpm at the large scale.

The Solberg fluorine-free foam exhibited longer burnback times compared to AFFF-1 over both heptane and gasoline at the three liquid foam solution flow rates examined. Fomtec fluorine-free had shorter burnback times over gasoline, but a longer burnback time over heptane compared to AFFF-1 after a liquid application rate of 2 gpm. We attribute differences in burnback performance to differences in foam properties between the three foams. The fluorine-free foams had slow drainage compared to AFFF-1. Solberg fluorine-free had a 25% drainage time of 20 minutes and Fomtec fluorine-free drained 25% of its liquid in 40 minutes compared to the roughly 5 minute 25% drainage time for AFFF-1. Although Fomtec fluorine-free foam had slower drainage than Solberg fluorine-free foam, the foam was dryer, with an expansion ratio of 10-12 compared to the 6-7 expansion ratio for both AFFF-1 and Solberg fluorine-free foam. This difference in expansion ratio and effects related to interactions with different fuels may explain observed differences in burnback performance. Although the fluorine-free foams exhibit superior burnback performance and can achieve rapid extinction on a heptane pool fire at a higher solution flow rate, they display poor performance on gasoline and could not meet the baseline extinction described in the Introduction of this reported, detailed by MIL-PRF-24385.

Differences in liquid drainage from the foam appear to be driven by differences in concentrate viscosity between the three foams. Solberg and Fomtec fluorine-free foam concentrates have viscosities of roughly 26,000 and 16,000 cP at a shear rate of 1 s^{-1}. AFFF-1 has a viscosity of roughly 3 cP at the same shear rate. Higher viscosities can slow drainage through the foam, increasing the stability of the foam, which is seen in the collected data for the fluorine-free foams. The collected data confirms issues with solution and concentrate properties, such as viscosity, for compatibility with Navy operations as well as limitations on fire extinction performance.

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