Comparison of Firefighting Performance between Commercial AFFF and Analytically Defined Reference AFFF Formulations

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Abstract

In an effort to develop an environmentally benign surfactant for firefighting foam, an analytical aqueous film forming foam (AFFF) formulation was developed for use in laboratory research in place of commercial AFFF with proprietary formulations. Our original reference formulation (Reference 1) consisting of 0.15 % fluorocarbon surfactant (Capstone, DuPont), 0.05 % hydrocarbon surfactant (Triton X-100, Sigma-Aldrich), and 0.95 % diethylene glycol butyl ether, by weight, met MilSpec criteria for spreading coefficient, film and seal, expansion ratio, and liquid drainage rate. However, this initial reference AFFF formulation extinguished the 28-ft^2 gasoline pool fire in 54 seconds and had a burnback time of 295 seconds; both measurements do not meet U.S. military specification (MilSpec) extinction time criteria of under 30 seconds and a burnback time of over 360 seconds. We increased the surfactant concentration in a Reference 2 formulation and replaced Triton X-100 with an alternative hydrocarbon surfactant in a Reference 3 formulation, and following MIL-F-24385F, we evaluated Reference 2 and 3 for 28-ft^2 pool fire extinction, burnback, film and seal, expansion ratio, and liquid drainage rate. We identified one formulation that met the specified MilSpec requirements and compares favourably to the performance of commercial AFFF.

Keywords: fire extinction, environmental, surfactant

Introduction

Aqueous film forming foams (AFFF) are used worldwide to suppress Class B pool fires which occur because the vapor above a pool of liquid fuel ignites and forms a fire that is continuously refueled by the pool below. The U.S. Naval Research Laboratory developed AFFF to be a more effective fire suppressant than protein foams in combating liquid pool fires [1]. Foams are generated from aqueous solutions containing a mixture of surfactants in conjunction with other additives that influence suppression performance and conform to requirements set in the U.S. MilSpec. AFFF floats on the pool surface and forms a barrier between the fuel pool and the fire, which is suppressed as fuel vapors are unable to resupply the flame above. The barrier provided by AFFF is composed of two parts: the foam bubbles and a thin aqueous film formed over the fuel surface. The utilization of fluorocarbon surfactants in foam solutions lowers the surface tension to 16-18 mN/m (at 20°C) so that a thin aqueous film forms on the hydrocarbon fuel pool beneath the foam. It is assumed that aqueous film formation is critical to improved fire suppression; so much so that the U.S. military specification for firefighting foams (MIL-F-24385F, also referred to as MilSpec) tests for film formation [2].

Current AFFF meets stringent military extinction performance requirements, which include extinguishing a 28-ft^2 gasoline pool fire in under 30 seconds [2]. Although AFFF has been very effective at suppressing pool fires, fluorocarbon surfactants, required for aqueous film formation, have been regulated by the U. S. Environmental Protection Agency (EPA) [3] due to their environmental toxicity and bio-accumulative health hazards. Ongoing research to find an environmentally benign replacement foam have used commercial AFFF foam formulations as references to measure fire suppression performance and to understand the role of film formation [4], surface cooling [5], and foam degradation [6] on fire suppression. However, different studies use different commercial AFFF formulations, all of which have proprietary information concerning the composition of the foam formulation. Although, partial information on composition is available on a specific brand of commercial AFFF [7], many proprietary AFFF formulations exist making comparison with replacement formulations difficult. Research and development efforts would benefit from a reference foam formulation containing a minimum of 3-4 components, which are analytically well defined or pure and are readily available commercially. Our goal is to design a simplified reference formulation that passes the 28-ft^2 fire extinction test defined in MIL-F-24385F if even by only a small margin relative to a commercial AFFF. Herein we describe our previous results from MilSpec testing on an initial design of an AFFF reference formulation and how the formulation was improved in recent work to meet specific MilSpec criteria.

Experimental

Materials

Capstone 1157N, a 6:2 fluorotelomer sulfonamide alkylbetaine surfactant, supplied by DuPont, Inc., was used as the fluorinated surfactant [8]. Triton X-100, a hydrocarbon surfactant [9], and diethylene glycol butyl either (DGBE) were purchased from Sigma

Aldrich. An alternative hydrocarbon surfactant was procured through a commercial source; however, we have not fully characterized the surfactant and chose to withhold its detailed information. The reference AFFF formulations were compared to a commercial AFFF, FomTec 3 %. Reference 1-3 formulations were prepared by wt% in distilled water as follows in Table 1 below. FomTec 3 % was prepared by mixing 3 vol% foam concentration with distilled water.

Table 1. Reference AFFF formulation compositions.

Material	**Reference 1**	**Reference 2**	**Reference 3**
Capstone 1157N	0.15%	0.3%	0.3%
Triton X-100	0.05%	0.2%	N/A
Alternative Hydrocarbon Surfactant	N/A	N/A	0.2%
DGBE	0.95%	0.5%	0.5%

Individual quantities of components in Reference 1 were determined by matching film-forming properties (surface tension and spreading coefficient) of the solution with those of commercial FomTec 3 %. Triton X-100 was used to lower the surface tension of the Capstone surfactant as a mixture of the two produced a lower solution dynamic surface tension than a solution with Capstone alone. Many commercial foam formulations list fluorocarbon and hydrocarbon surfactants in the formulation due to the beneficial synergistic effects between the two surfactants. Research by Osei-Bonsu et al. [10] further confirmed the beneficial effects when a mixture of surfactants was used over a single surfactant through improved foam degradation rates. We also used DGBE to act as a solvent in the formulation. To improve upon the formulation, we examined the role of surfactant concentration and the utilization of an alternative hydrocarbon surfactant (undisclosed at this time) that was more polar than Triton X-100, with hydroxyl groups in the surfactant head structure. Reference formulations were evaluated in the MilSpec 28-ft^2 pool fire extinction test outlined in MIL-F-24385F [2].

Methods

Surfactant solution and foam properties were measured for the three reference AFFFs and compared to measured properties of the commercial AFFF. The spreading coefficient, defined in Eq.(1) below, was determined using a DuNoy ring tensiometer to measure the surface tension.

$$Spreading\ Coefficient = \sigma_{cyclohexane} - \sigma_{foam\ solution} - \sigma_i \qquad \text{(Eq.1)}$$

The first two terms, $\sigma_{cyclohexane}$ and $\sigma_{foam\ solution}$ are surface tensions, and σ_i is the interfacial tension between cyclohexane and the foam solution. MIL-F-24385F requires a spreading coefficient greater than 3.

Foam properties were measured during MilSpec testing. Foam was generated using an air-aspirated nozzle in which foam solution and air mix near the nozzle outlet and exit the nozzle in a fan-like pattern. Expansion ratio (volume of foam/volume of liquid), bubble diameter, coarsening with time, and liquid drainage time were measured. We measured expansion ratio by weighing 250 mL of foam, generated by directing the aspirated nozzle on to a vertical aluminum panel (MIL-F-24385F). The weight of foam is essentially equal to the weight of liquid water in the foam and is used to determine the volume of liquid in the foam. MIL-F-24385F requires an expansion ratio between 5 and 10. Even though MIL-F-24385F has no requirement on bubble diameter and coarsening, we measured bubble diameter by pouring freshly generated foam into a rectangular column affixed with a ruler and taking a picture. Image processing software (ImageJ) was used to measure the diameter distributions for 300 bubbles. The time for a 50 % increase in average bubble diameter was measured by taking an image of foam at different times within the rectangular column and measuring the bubble diameter distribution at each time. We measured the volume of liquid drained to the bottom of a 500 ml graduated cylinder over time until the foam drained 25 % of its liquid volume. MIL-F-24385F specifies that foam have a 25 % drain time of over 150 seconds.

MilSpec pool fire extinction was performed using a 28-ft^2 circular pan filled with gasoline (specific to time of year [2]). The gasoline is ignited and pre-burned for 10 seconds after which a trained firefighter attempts to suppress the fire holding an aspirated nozzle, spraying the pool fire with foam. After the fire has been extinguished, the firefighter continues to apply foam to the pool surface. The duration of foam application from when the foam begins to extinguish the fire and the continuous application after extinction is limited to 90 seconds total. A small container holding a gasoline flame is then placed in the center of the foam pool. Once 25 % of the 28-ft^2 pool surface has reignited, the time is recorded reflecting the burnback time. A burnback test is performed to assess the ability of foam to maintain a suppressive barrier over the fuel and prevent re-ignition. MIL-F-24385F requires a burnback time lasting longer than 360 seconds. A film and seal test, per MIL-F-24385F, which determines the formation of a film on the fuel was also conducted. The film and seal test involves spreading foam over a small pool of cyclohexane (flash point, -4 °C) at room temperature, carefully removing the foam layer with a spatula, and exposing the pool to a propane flame within 60 seconds after the foam is generated [2]. Lack of ignition shows presence of an aqueous film floating on the less dense fuel pool. This is a pass/fail test.

Results / Discussion

The spreading coefficients between FomTec 3 % and Reference 1 (0.15 % Capstone, 0.05 % Triton X-100, and 0.95 % DGBE) are tabulated in Table 2 below.

Table 2. Foam solution properties for reference AFFF and FomTec 3%.

Property	FomTec 3%	Reference 1
Surface Tension (mN/m)	16.03	16.31
Spreading Coefficient	6.50	4.89

Both the commercial AFFF and Reference 1 have similar surface tensions, but the commercial AFFF has a larger spreading coefficient due to differences in the interfacial tension of the commercial AFFF and Reference 1 over cyclohexane. FomTec 3 % has a lower interfacial tension (1.6 mN/m) over cyclohexane compared to Reference 1 (3.1 mN/m). The spreading coefficient is indicative that energetics are favourable for film formation and a higher value may insinuate a better fire extinction performance. However, both FomTec 3 % and Reference 1 meet MilSpec criteria for spreading coefficient (>3). The foam properties measured for FomTec 3 % and Reference 1 during MilSpec testing are tabulated below in Table 3.

Table 3. Measured foam properties during MIL-F-24385F.

Measured Property	MilSpec Criteria	FomTec 3%	Reference 1
Initial Expansion Ratio	5-10	7.6	7.35
Initial average Bubble Diameter (mm)	N/A	0.18	0.17
50% increase in average Bubble Diameter (s)	N/A	540	420
25% Liquid Drainage Time (s)	> 150	254	213

In Table 3, the expansion ratio was measured within one minute of generating foam however the bubble diameter was measured at different times for the two foams (within 1 minute for Reference 1 and within 7 minutes for the commercial AFFF). Table 3 shows both Reference 1 and the commercial AFFF pass the liquid drainage test and meet the criteria for expansion ratio. Due to camera difficulties, we were unable to secure an adequate image of the commercial AFFF for bubble diameter processing within 1 minute. From the captured images, only the image taken after 7 minutes was useful for image processing. We were better able to measure the bubble size for Reference 1 taking a useful image within one minute. We found that Reference 1 exhibited a narrow bubble diameter distribution with average bubble diameter of 0.17 mm at one min. FomTec 3 % bubble size at 7 minutes is 0.18 mm;

the bubble diameter could initially be much smaller due to coarsening indicating differences in initial bubble diameter. Furthermore, Reference 1 has a 22 % shorter coarsening time (time for 50 % increase in average bubble size) than the commercial foam. Hinnant et al. [6] showed that changes in bubble diameter can effect foam degradation which in turn can effect fire suppression. Kennedy et al. [11] showed that differences in coarsening rates can effect liquid drainage from the foam which could also impact foam degradation and fire suppression. These differences in bubble diameter and bubble diameter distributions could lead to differences in extinction performance between the two foams.

The fire extinction performance results of the commercial AFFF and Reference 1 are tabulated in Table 4 below.

Table 4. Fire extinction performance results for FomTec 3% and Reference 1.

Measured Property	MilSpec Criteria	FomTec 3%	Reference 1
Extinction time (sec)	<30 seconds	23	54
Burnback time (sec)	>360 seconds	496	295
Film and Seal	Pass	Pass	Pass

Despite containing only 3 components, the initial reference formulation performance compares favorably to the commercial AFFF (> 6 components), Table 4 shows that both Reference 1 and the commercial AFFF form an aqueous film and pass the film and seal test. Even with a film present, Reference 1 does not meet MilSpec criteria for extinction or burnback time. The commercial AFFF extinguishes the fire in 23 seconds while Reference 1 extinguishes it in 54 seconds. Because both foams form films, yet have significant differences in extinction time, extinction may also be impacted by a mechanism other than film formation. Differences in foam properties such as bubble diameter and coarsening rates could contribute to differences in fire extinction performance.

Table 4 also shows large differences in burnback time which is likely due to differences in foam degradation. Previously, we showed that fuel can cause foams to degrade significantly and are affected by the foam formulation and bubble diameter [6]. Foam degradation affects the ability of the foam to act as a barrier between the fuel pool and flame above. Without an effective barrier, fuel vapors resupply the fire, increasing fire extinction time. The challenge in designing a reference AFFF formulation is identifying the correlation between changes in surfactant and foam formulation to changes in foam properties including foam degradation. Our initial approach attempted to relate changes in surfactant (concentration and mixture with hydrocarbon surfactants) to foam solution properties specific to film formation. Subsequent attempts focused on enhancing foam properties and how the foam, not just the film, impact fire suppression.

In our initial reference formulation, we aimed to match commercial AFFF formulation properties in which the commercial AFFF solution is at its critical micelle concentration (CMC). We therefore kept Reference 1 at its CMC. With so few components, the reference AFFF cannot be compared directly to a commercial product that aims to reduce cost; we decided to increase the surfactant concentration to 5 times the CMC to improve extinction performance.

In the Reference 2 formulation, we increased the total amount of surfactant in the formulation as well as increasing the ratio between the hydrocarbon surfactant and the fluorocarbon surfactant and decreased the amount of solvent to further determine if extinction is driven primarily by the surfactant make-up.

Aside from changes in surfactant concentration, we also changed the type of hydrocarbon surfactant to generate Reference 3. We exchanged Triton X-100 with a more polar hydrocarbon surfactant, but kept the ratios the same. The Reference 2 formulation was 0.3 % Capstone 1157N, 0.2 % Triton X-100, and 0.5 % DGBE in aqueous solution. Reference 3 was 0.3 % Capstone 1157N, 0.2 % alternative hydrocarbon surfactant, 0.5 % DGBE in aqueous solution. For these two additional formulations, we measured the extinction performance, burnback time, film and seal, expansion ratio, and liquid drainage time. The MilSpec results comparing the commercial AFFF and Reference 1-3 are tabulated in Table 5 below.

Table 5. Fire extinction properties for additional formulation testing.

Measured Property	**FomTec 3%**	**Reference 1**	**Reference 2**	**Reference 3**
Extinction (sec)	23	54	37	26
Burnback (min)	8:16	4:55	6:00	9:22
Film and Seal	Pass	Pass	Fail	Pass
Expansion Ratio	7.6	7.35	7.41	7.46
25% Drainage (min)	4:41	3:59	4:55	5:17

As seen in Table 5, the formulation with the alternative surfactant met all MilSpec criteria tested and matched favorably to the values measured for the commercial AFFF. The formulation with the alternative surfactant extinguished the pool fire in 26 seconds while both formulations with Triton X-100 had extinction times over 30 seconds.

Increasing the surfactant concentration between Reference 1 and Reference 2 appears to have decreased extinction time dropping extinction time from 54 seconds to extinction in 37 seconds, narrowly failing the MilSpec requirement of under 30 seconds. Surprisingly, the 0.3 % Capstone 0.2 % Triton X-100 did not pass the film and seal test;

however, we believe an additional test may discredit this result as each result was conducted only once due to the nature of large-scale testing. Increased surfactant concentration also increased burnback time to where the 0.3 % Capstone 0.2 % Triton X-100 formulation passed MilSpec criteria for burnback.

Changing the hydrophobicity of the hydrocarbon surfactant resulted in the most significant impact on extinction and burnback time. Initial lab-scale testing of the Reference 2 and 3 formulations show similar CMCs so both are at 5 times the CMC. We believe fire suppression performance differences between the two formulations may exist due to differences in foam degradation and fuel transport through the foam. Studies are underway to provide this additional information that will allow us to identify the correlation of surfactant properties in the foam to overall foam performance leading to the development of environmentally benign and effective surfactant alternatives.

Summary

To assist laboratory measurements and future research looking into environmentally benign firefighting foams, we have designed three reference AFFF foam solutions. The initial formulation, Reference 1, was 0.15 % Capstone, 0.05 % Triton X-100, and 0.95 % by wt. DGBE in aqueous solution. Reference 1 foam solution spreading coefficient was similar to a commercial AFFF, FomTec 3 %. The commercial AFFF had a lower interfacial tension over cyclohexane compared to Reference 1, but both met the MilSpec criteria for spreading coefficients (>3).

Foam properties including expansion ratio, 25 % liquid drainage time, bubble diameter, and time to 50 % bubble size increase were measured using the MilSpec method of foam generation: an air-aspirated nozzle. The commercial AFFF and Reference 1 had similar expansion ratios and liquid drainage times, but appeared to differ in initial bubble size and bubble coarsening rate. Reference 1 coarsened faster than the commercial AFFF and the initial bubble size of the commercial AFFF was only able to be collected 7 minutes after generation due to camera difficulties. These differences in foam properties could relate to differences in extinction performance [6, 11].

Despite similarities in foam solution properties, Reference 1 extinguished a 28 ft^2 gasoline pool fire in 54 seconds, failing MilSpec criteria, while FomTec 3 % extinguished the fire in 23 seconds. Similar surface tensions, spreading coefficients, and the passing of the film and seal test show that both foams are able to form films, but film formation is not sufficient for rapid fire extinction.

In an effort to improve upon the initial reference AFFF formulation, we tested two additional formulations. Both had increased amounts of surfactant with a ratio of 0.3 % Capstone to 0.2 % hydrocarbon surfactant and decreased solvent concentrations. In Reference 2, Triton X-100 was used as the hydrocarbon surfactant, in Reference 3: an alternative hydrocarbon surfactant, more polar than Triton X-100 with hydroxyl groups in the surfactant head structure. These two formulations were compared to the commercial AFFF and Reference 1 through extinction performance, burnback time, film and seal, expansion ratio, and 25 % liquid drainage time.

The foam formulation with the alternative hydrocarbon surfactant, Reference 3, met the specified MilSpec criteria with an extinction time of 26 seconds, comparable to the 23 second extinction of the commercial AFFF. Reference 2, with a higher concentration of surfactant and Triton X-100 displayed improved extinction with 37 seconds, but it did not meet MilSpec criteria for extinction time, burnback time, or film and seal. Based on the additional formulations, it appears the hydrocarbon surfactant plays an important role in fire suppression. The change in hydrocarbon surfactant did not appear to alter foam solution properties significantly, but additional research must be conducted to see how differences in foam properties that relate to foam degradation and fuel transport through the foam may be present between the solutions with different hydrocarbon surfactants.

We believe the Reference 3 formulation with the alternative hydrocarbon surfactant meets specific MilSpec criteria important for fire suppression and matches those of commercial AFFF well enough to use it as a reference formulation. We do not expect the Reference 3 formulation to be used as a DOD firefighting foam that meets full MilSpec criteria, but is intended for research and development purposes only so that we may attribute cause and effects clearly. In future research, we will replace the fluorocarbon surfactant in the mixture with an environmentally benign surfactant to better relate surfactant properties to fire extinction.

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