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Development of an analytical AFFF formulation for the evaluation of alternative surfactants

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**Abstract:** Following criteria set by MIL-F-24385F for firefighting foams, we are developing an analytical aqueous firefighting foam (AFFF) formulation to be used for laboratory testing in place of proprietary commercial AFFF formulation. An aqueous reference foam solution containing 0.15% Capstone (fluorocarbon surfactant), 0.05% Triton X-100 (hydrocarbon surfactant), and 0.95% diethylene glycol butyl ether, by weight and was found to meet MilSpec criteria for aqueous film formation, which was inferred to be essential for improved fire extinction. However, the reference AFFF extinguished the 28 ft2 gasoline pool fire in 54 seconds, exceeding the maximum 30 second qualification standard. Despite similar surface tensions and spreading coefficients between the reference and commercial AFFF indicating adequate film formation, the fire extinction time criterion could not be met. However, we found that the reference AFFF and a commercial AFFF degraded in 30 and 45 minutes respectively when the foams were placed over 50°C n-heptane fuel at bench-scale consistent with burn-back Milspec test results. Differences in foam degradation may prove to be more valuable to fire extinction than the role of film formation.

***Keywords: Fire extinction, firefighting foams, environmental, foam degradation***

1. **Introduction**

 Aqueous film forming foam (AFFF) is used to suppress pool fires worldwide. Fluoro-surfactants in AFFF lower the surface tension of water, enabling a thin film to spread on top of the fuel pool surface. Film formation is assumed to be a critical component for improved fire suppression, so much so that film formation is a current requirement of MIL-F-24385F, the standard military test for the use of firefighting foams (MilSpec) [1]. However, fluoro-surfactants that enable film formation have been heavily regulated due to environmental hazards [2] and require hazardous waste mitigation when used.

 Current efforts are being undertaken to find an environmentally friendly surfactant. Progress would benefit from an analytically defined reference formulation since developments have been stifled by proprietary information concerning commercial AFFF composition. Dlugogorski [3] provides some information on AFFF composition for a specific brand of commercial AFFF, but hundreds of AFFF formulations exist with research citing different companies with differing formulations (AFFF FC-206CF by Lattimer [4], National and Buckeye by Williams [5]). Researchers have made fluorine-free analytical foam solutions, but little focus has been given to designing a fluorinated foam solution since they exist commercially [6, 7].

 To provide consistency to AFFF research at the U.S. Naval Research Laboratory, we are developing an analytically defined AFFF formulation comprised of 3-4 well defined components that can be reproduced by other research organizations. We have designed a reference formulation that matches properties of commercial AFFF that most relate to film formation. This formulation was then tested in the 28 ft2 pool fire extinction and burn-back test detailed in MIL-F-24385F [1].

# Methods / Experimental

Materials used for the reference AFFF formulation were the following: Capstone (a 6:2 fluorotelomer sulfonamide alkylbetaine surfactant, DuPont Inc.), Triton X-100 (Sigma Aldrich), and diethylene glycol butyl ether (DGBE, Sigma Aldrich). We compare the reference AFFF with National 3% commercial foam in-lab because both formulations contain the same fluoro-surfactant (Capstone, DuPont Inc.) Foam solutions were characterized by dynamic surface tension (using a bubble tensiometer), static surface tension and spreading coefficient (using a DuNoy ring tensiometer) at room temperature. The spreading coefficient was determined using Eq. (1) [1].

$Spreading Coefficient= σ\_{cyclohexane}-σ\_{foam solution}-σ\_{interfacial}$ (1)

In Eq. (1), *σcyclohexane* and *σfoam solution* are surface tensions, and *σinterface* is the interfacial surface tension between cyclohexane and the foam solution. A positive spreading coefficient is needed for film formation; MIL-F-24385F requires the spreading coefficient be greater than 3.



Figure 1. Diagram of in-lab foam generation method.

Figure 1 shows a foam generator consisting of a plastic container filled with 375 mL of foam solution, a porous sparger to form bubbles (pore size 25-50 µm) placed 2 cm from the bottom of the container, and a lid with a plastic dispensing nozzle, 2 cm in diameter [8]. Nitrogen flows through a flow controller (Sierra Instruments, Inc.) to produce a foam flow rate of 500 mL/min. Humidified nitrogen then flows into the plastic container, bubbling nitrogen through the foam solution producing foam which is then dispensed through the outlet nozzle.

The foams were characterized by initial expansion ratio, initial bubble diameter, and 25% liquid drainage time (time for 25% of the liquid contained in the foam to drain out) from the foam. The expansion ratio, which describes the liquid content of the foam, was measured by weighing 250 mL of freshly generated foam and dividing the volume of foam by the volume of water in the foam (weight of the foam multiplied by density of water). MIL-F-24385F requires an expansion ratio between 5 and 10. The bubble diameter was measured by taking a picture of freshly generated foam and using Image-J to measure the diameter of 300 bubbles. The 25% liquid drainage time was measured by recording foam in a graduated cylinder and measuring the volume of liquid collected at the bottom of the cylinder over time. MIL-F-24385F specifies that foam have a 25% drain time over 150 seconds.

Foam degradation was measured by monitoring the volume of foam above heated n-heptane over time. 60 mL of pre-heated n-heptane was poured into a beaker, 4.5 cm in diameter. Heating tape was coiled around the beaker, up to the 60 mL mark, to maintain temperature and ensure that only the fuel was being heated. Foam was generated onto the fuel surface and the foam volume was then recorded over time. The foam volume is inclusive of any large bubble that span across the entire fuel surface or “gap” that forms between the foam-fuel interface, leading to values over 100% for changes in foam layer thickness.

Fire extinction, burn-back performance, and the film and seal test were conducted using a 28 ft2 pool fire detailed in MIL-F-24385F. Fire suppression criteria is extinction under 30 seconds and burn-back lasting over 360 seconds. Burn-back time is the time for a small fire placed on a foam covered pool to spread to 25% of the pool area due to degradation of the foam. The film and seal test (pass/fail) determines if a film forms over cyclohexane.

Initial expansion ratio, liquid drainage, and initial bubble diameter were collected during large-scale MilSpec testing to compare to in-lab results. We were only able to characterize and compare FomTec 3% commercial foam with the reference AFFF for MilSpec testing. We expect differences between in-lab generated National and FomTec to be relatively small, but these differences have not be quantified. MilSpec testing also uses an air aspirated nozzle to generate foam which may produce foam properties different from in-lab results.

1. **Results and Discussion**

In order to produce a reference AFFF suitable for laboratory testing, the reference foam formulation was created by matching properties of commercial AFFF related to film formation.

Figure 2. Dynamic surface tension of Capstone, Triton X-100, National AFFF 3%, and the reference AFFF formulation (0.2 % 3:1 Capstone, Triton, 1% DGBE).

We measured the dynamic surface tension of AFFF 3% (National Inc.) foam solution and compared it to an aqueous solution of Capstone and Triton X-100 at their experimentally determined critical micelle concentrations (CMC), 0.27 wt% and 0.3 wt%, respectively. Figure 2 shows the initial response of Capstone is greater than that of Triton X-100 and AFFF, closer to the value of water at low surface ages. Triton X-100 has a smaller initial surface tension than AFFF, but never reaches a low surface tension at longer surface ages. Therefore, the reference AFFF needed to be a mixture of the two surfactants to take advantage of the low initial surface tension of Triton X-100 and the low surface tension of Capstone at longer surface ages. The formulation that proved most similar to the dynamic surface tension of AFFF was a 3:1 mixture of Capstone and Triton X-100 at its CMC concentration (0.2 wt. %) in a 1% by vol. DGBE aqueous solution.

The foam solution properties for the reference AFFF formulation were measured and compared to National 3% foam solution. The results are tabulated in Table 1.

Table 1: Measured foam solution property data for reference AFFF and National 3%.

|  |  |  |
| --- | --- | --- |
| Property | National 3% | Reference AFFF |
| Surface Tension (mN/m) | 16.5 | 16.31 |
| Spreading Coefficient | 6.30 | 4.89 |

The solutions have similar surface tensions but different interfacial tensions (3.75 and 1.2 for reference AFFF and National 3% respectively). The spreading coefficient between the two foams differ by 22%; however, the reference AFFF exceeds the criteria (>3) for MilSpec qualification.

 Foam properties were measured during MilSpec testing and compared to the in-lab generation method. MilSpec data was collected for FomTec 3% instead of National 3% foam. Table 2 tabulates the initial expansion ratio, initial bubble diameter and 25% liquid drainage time.

Table 2. Measured foam property data from in-lab and MilSpec foam generation.

|  |  |  |  |
| --- | --- | --- | --- |
| Foam | Initial Expansion Ratio | Initial Bubble Diameter (mm) | 25 % Liquid Drainage Time (s) |
| In-Lab | Ref AFFF | 10.32 | 0.35 ± 0.08 | 105 |
| Commercial (National) | 8.46 | 0.55 ± 0.14 | 98 |
| MilSpec | Ref AFFF | 7.35 | 0.16 ± 0.04 | 213 |
| Commercial (FomTec) | 7.6 | 0.18 ± 0.04 | 254 |

Table 2 shows that the two foams have similar properties when generated in-lab or during MilSpec testing, but disagree between the two generation methods. In-lab generation produced dryer foams with the reference AFFF not passing MilSpec criteria for expansion ratio (5-10), but meeting the criteria during MilSpec generation. The bubble diameters produced in-lab were also larger than those compared to MilSpec generation and drained faster, but the bubble diameters and liquid drainage rate of the two foams in MilSpec generation were very similar.

 Despite similarities between the foam solution and foam properties of the reference and commercial AFFF’s, the reference AFFF could not meet MilSpec criteria for fire extinction or burn-back in the 28 ft2 gasoline pool fire test. Fire performance results are tabulated in Table 3.

Table 3. MilSpec fire performance results for the reference AFFF and FomTec 3%

|  |  |  |  |
| --- | --- | --- | --- |
| Test | MilSpec Criteria | FomTec | Ref AFFF |
| Extinction Time (s) | < 30  | 23 | 54 |
| Burn-back Time (s) | > 360  | 496 | 295 |
| Film and Seal (s) | No flame | No flame | No flame |

The reference AFFF extinguished the flame in 54 seconds while the commercial AFFF extinguished the flame in 23 seconds. However, the reference AFFF passed the film and seal test indicating a film was present. Because the foams showed film formation but different extinction times, extinction may be impacted by mechanisms other than film formation.

 We examined foam degradation of the reference AFFF and National 3% over n-heptane, heated to 50°C. Figure 3 below plots the change in foam layer thickness over time. A -100% change in foam thickness indicates the foam has completely degraded from the fuel surface.

Figure 3. Percent change in foam thickness over time for the reference AFFF and National 3% foam generated in-lab over 50°C heated n-heptane.

As seen in Figure 3, the reference AFFF has a foam lifetime of 30 minutes while the commercial AFFF has a foam lifetime of 45 minutes over heated n-heptane. This is consistent with degradation observed in burn-back times shown in Table 3. Foam degradation can impact a foams ability to effectively cover a fuel surface, creating a physical barrier between the fuel and the flame. Without effective foam cover, the fire cannot be suppressed, leading to differences in fire suppression due to differences in foam degradation. To improve the reference AFFF formulation, we must focus on properties that effect foam degradation instead of only focusing on properties that impact film formation.

1. **Conclusions**

To assist laboratory testing, a reference AFFF foam solution was made. The reference AFFF formulation was 0.15 wt. % Capstone, 0.05 wt. % Triton X-100, and 1% by vol. DGBE in aqueous solution. The reference AFFF foam solution dynamic surface tension, static surface tension, and spreading coefficient were similar to a commercial AFFF foam solution, National 3%. The spreading coefficient for the reference AFFF and commercial AFFF met MilSpec criteria.

Foam properties for the reference AFFF were measured and compared to commercial AFFF’s in-lab (National 3%) and in large-scale MilSpec testing (FomTec 3%). In-lab foams were dryer, had larger bubbles, and drained faster than foams generated in MilSpec testing. However, both foams had similar initial expansion ratios, initial bubble diameters, and 25% liquid drainage times that met MilSpec criteria when generated for MilSpec testing.

Despite similarities, the reference AFFF extinguished a 28 ft2 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.

We recorded differences in foam degradation over n-heptane at 50°C for the reference AFFF and National 3% generated in-lab. The reference AFFF degraded in 30 minutes while the commercial AFFF degraded in 45 minutes. This improvement in degradation could explain the superior firefighting abilities of the commercial AFFF over the reference AFFF. Future work in developing a reference AFFF will investigate composition/molecular structure of surfactant formulations that effect foam properties including degradation.

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