

THE FUTURE OF AQUEOUS FILM FORMING FOAM (AFFF): PERFORMANCE PARAMETERS AND REQUIREMENTS

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INTRODUCTION

Aqueous film forming foam (AFFF) is a highly efficient type of fire suppressant agent, used by itself to attack flammable liquid pool fires, and in conjunction with Halon 1301 to attack fires in Navy vessel machinery spaces. Gaseous halon replacements for machinery spaces will likewise operate in conjunction with AFFF systems. Also, portable AFFF extinguishers have been manufactured as alternatives to handheld Halon extinguishers for both conventional and marine applications. AFFF used by the U. S. military must meet the requirements set forth in Military Specification MIL-F-24385F, which is under the control of the Naval Sea Systems Command, Code 05P9. The Naval Research Laboratory is the designated institution for certification evaluation for the Department of Defense (DoD) AFFF Qualifying Products List (QPL).

AFFF is used in the U.S. military, and in most civilian applications worldwide, as either a 3% or a 6% concentrate. The numbers refer to the percentage of the foam concentrate mixed with either fresh or sea water by a proportioning nozzle. The foam forms spontaneously upon ejection of the concentrate/water mix from the nozzle. An aspirating nozzle is not needed nor used. The AFFF coats a pool of hydrocarbon fuel with a layer of foam, which acts as a thermal and evaporation barrier to inhibit and eventually extinguish combustion. The "film-forming" characteristic refers to the fact that, even after the foam has dissipated, the aqueous layer formed from the water/concentrate mixture can coat a liquid hydrocarbon surface. The MilSpec AFFF formulations are effective against a wide variety of liquid hydrocarbon fire threats. Special formulations exist for use against alcohol and other water-miscible fuels.

The AFFF concentrates are themselves mostly water, with other components such as glycol ethers and ethylene or propylene glycol added to extend the lifetime of the foam. The lowering of surface tension to allow formation of foam and of a coverage film of water on hydrocarbon, is accomplished by use of both fluorocarbon and hydrocarbon surfactants. Recently the fluorinated surfactants that are used in all current AFFF formulations (and in fact explicitly mandated by MIL-F-24385F) have been the topic of environmental scrutiny.

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The fluorinated surfactants used in AFFF are produced by one of two synthetic processes [1]. One class of fluorosurfactants used in AFFF formulations is based on perfluorooctyl sulfonate (PFOS) and structurally related compounds. These are prepared by direct electrochemical fluorination. The current scrutiny of AFFF formulations began when the PFOS based surfactants were voluntarily removed from the market, following the finding that these chemicals were environmentally persistent and widely distributed throughout the environment, as well as having some degree of toxicity. Alternate surfactant formulations, synthesized by telomerization (a polymerization process producing extremely short chains) were not directly affected by the phase out of PFOS. Since the telomer-based surfactants are also highly fluorinated, they may be, like PFOS, environmentally persistent and bioaccumulative. Thus, they are currently being scrutinized by the Environmental Protection Agency.

Given this background, exploration of alternatives to the current generation MilSpec AFFF products is prudent. The situation regarding AFFF resembles that of Halon 1301 in that, until environmental concerns were raised, little needed to be done to understand and improve its performance. Now, however, increasing United States and international environmental concerns regarding AFFF must be addressed as use restrictions can seriously impact operations. Generating formulations that will satisfy DoD fire protection needs and be more environmentally friendly requires an understanding of how AFFF functions. The unique surfactant properties of the film, protected and regenerated by the foam, provide the tremendous effectiveness and usage envelope advantages over other types of foam formulations. Identifying and understanding the key parameters for successful AFFF extinguishment will guide development of replacement foams.

This paper examines the properties of AFFF that provide for rapid and efficient fire extinguishment, highlights operational restrictions of employing AFFF for DoD applications, and critiques the requirements of MIL-F-24385F. Identifying and understanding the key parameters for successful AFFF extinguishment will guide development of replacement foams. Possible modification of specification requirements in MIL-F-24385F may engender broader options for possible compositions, thus increasing the likelihood of a successful AFFF alternative without sacrificing fire suppression performance.

MILITARY SPECIFICATION AFFF

The requirements of MIL-F-24385F, as well as their rationale and revisions since the AFFF MilSpec was formulated in 1963, are summarized in Ref. [2]. Of the MilSpec requirements, fire suppression performance is paramount. Successful performance in field tests is needed to assure capability to perform the mission, in addition to the safety of the personnel and viability of the platform. Relaxing the fire suppression performance requirements for AFFF for the sake of environmental or logistics considerations is not desirable. Specification performance tests need to rigorously capture the range of challenging threat scenarios that have significant possibility of occurring. A representative, but not overly burdensome, set of tests and success criteria must be employed to ascertain field performance with suitable safety factors.

One of the tests specified in MIL-F-24385F involves fire suppression by AFFF concentrate/water mixtures with the concentrate at one-half and five times its nominal proportion. This requirement originated from concerns regarding the accuracy of the proportioning equipment. It is reasonable to reevaluate that basis for the requirement given improved proportioning system performance envelopes. Note, however, that the half-strength test is likely to be a more rigorous requirement than the full strength test, and may therefore assure a more capable product, by providing a safety factor for unforeseen difficult challenge scenarios. In this event, the elimination of the half-strength test would mean accepting a decrease in AFFF performance.

There are several requirements in the Military Specification in addition to fire suppression performance. Some (e.g., foamability, foam lifetime, and film sealability) are needed to ensure meeting the stringent DoD fire protection requirements and should remain. Other specification items enable implementation, facilitate usage, or associated monitoring. These latter requirements need to be explored, as modification may be possible without adversely impacting AFFF fire protection performance. Appropriate modification of these requirements, where feasible, will expand the possibilities for foam formulations. Government – industry interactions can help formulate possible modifications to MIL-F-24385F.

FILM FORMATION AND SURFACE TENSION

Film properties are crucial to AFFF performance capabilities. The ability of a water/AFFF film to coat the surface of a lower density fuel, can be characterized by the spreading parameter (or spreading coefficient):

$$\text{Spreading parameter} = (\text{surface tension of fuel}) - (\text{surface tension of AFFF}) \\ - (\text{interface tension between AFFF and fuel}).$$

MIL-F-24385F specifies that the spreading parameter of AFFF on cyclohexane (surface tension @ 20 C: 25 dynes/cm) must be at least 3 dynes/cm. Fluorinated surfactants are capable of reducing the surface tension of water (surface tension @ 20 C: 73 dynes/cm) to approximately 15 dynes/cm, while a typical interfacial tension between a hydrocarbon and an aqueous layer containing AFFF concentrate is approximately 2-5 dynes/cm [3]. Thus, meeting the MilSpec requirement for the spreading parameter requires the surfactants used in AFFF to lower both the surface and interfacial tension of the aqueous phase as much as possible, since the spreading parameter reflects small differences in large numbers. This is a very severe requirement on surfactant performance. In AFFF formulations, both hydrocarbon and fluorocarbon surfactants are used: the hydrocarbon surfactants produce a low energy interface with the chemically similar fuel surface, while the fluorocarbon surfactants minimize the energy of the upper surface of the film.

A negative spreading coefficient implies that the water/surfactant layer will not coat a fuel surface because this would increase the surface energy, and buoyancy cannot play a role because the aqueous phase is denser. The converse, however, does not always hold: examples are known of systems that have positive (equilibrium) spreading coefficients but which do not exhibit spreading [3,4]. This behavior is ascribed to non-equilibrium surface tension effects in the aqueous layer [4].

Fluorinated surfactants have uniquely served in providing the specification-mandated film properties. Understanding of film properties is limited however, as only static - equilibrium behavior has been considered to date. In the past decade, non-equilibrium dynamics have been shown to exert a strong influence on various aspects of the behavior of surfactant-mediated fluids. The so-called "dynamic surface tension" arises from the inability of surfactants to instantaneously coat a newly created surface. This lag is caused by the need for surfactants dissolved in the bulk fluid to diffuse to the surface. For some surfactant/solvent systems, an Arrhenius dependence of the surface coverage on temperature has been reported, ascribed to an energy barrier to the surfactant molecules properly orienting themselves on the surface. [5]

NON-EQUILIBRIUM BEHAVIOR

The dynamic surface tension is manifested by the dependence of the surface tension on time after creation of a fresh surface. At time = zero, the value of the surface tension is that of the pure solvent. For long times the value asymptotically approaches the value of the equilibrium surface tension for the surfactant/solvent system. For processes taking place on sufficiently short time scales, the "effective" (instantaneous) value of the surface tension can greatly exceed the equilibrium value. Typical time scales for surfactant/surface equilibration are on the order of seconds to minutes. Thus non-equilibrium surface tension will influence behavior of surfactant-mediated systems on time scales shorter than this.

Foam formation following AFFF concentrate/water ejection from a nozzle occurs on a time scale of less than a second. The existence of foam is necessarily a non-equilibrium phenomenon, because virtually all foams are thermodynamically unstable [6]. Mil-F-Spec 24385F specifies only the equilibrium surface tension of the AFFF concentrate. Dynamic surface tension, which can influence the film spreading rate [7] as well as the foaming properties of the AFFF formulation, is not mentioned in the MILSPEC. However, dynamic surface tension will likely influence the results of fire suppression performance tests.

Studies have shown that the time required for the dynamic surface tension to approach its asymptotic value depends on the surfactant concentration in the bulk fluid: a higher concentration reduces the equilibration time [8,9]. Use of a high concentration of a surfactant, which lowers the surface tension far more than is actually required for a given application, is one strategy for avoiding undesirable effects of non-equilibrium surface tension. This is generally not feasible for AFFF formulations, because the low surface tensions of hydrocarbon fuels relative to water already place a severe requirement on surfactant performance. Additionally, the current environmental drivers regarding fluorinated surfactants may require the use of surfactants with somewhat higher equilibrium surface tensions, as well as encouraging minimization of surfactant concentrations in future AFFF formulations.

Furthermore, the spreading rate of the AFFF foam across an uncoated fuel surface is clearly a property that can be expected to impact the performance of an AFFF formulation in a fire suppression test. Foam spread can be modeled as two interacting fluids (similar to oil spreading on water), but since foam is not an ideal fluid, this approach cannot accurately determine spreading for this non-Newtonian system. Thus, better understanding of the principles governing

AFFF behavior, and validation of predictive models against empirical data, will help to clearly define the relationship between physical properties and fire suppression performance.

Similar consideration needs to be given to dynamic viscosity; only static – equilibrium characteristics are included in Mil-F-Spec 24385F. In addition, other specified requirements such as determination of concentrations from refractive index information may be better-handled using dyes or other approaches.

SUMMARY

AFFF is a fast and efficient way to extinguish two-dimensional liquid hydrocarbon fires, but current and increasing environmental restrictions need to be addressed. If a new AFFF formulation is required, a drop-in replacement is the goal. Enabling broader options for possible compositions increases the likelihood of success. The directions of possible changes and indeed, the search for new products, need to be guided by a better understanding of AFFF functioning.

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