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From: Commanding Officer, Naval Research Laboratory
To: Commander, Naval Air Systems Command (Code 4.3.T Sinwell)

Subj: STATUS REPORT ON THE DEVELOPMENT OF AN ENVIRONMENTALLY IMPROVED AFFF

Encl: (1) Two copies of subject report

1. Enclosure (1) is forwarded for your information. This work was accomplished under Naval Air Systems Task 2221-J19.

2. Aqueous film-forming foam (AFFF) is the most effective foam agent for combating two-dimensional fuel spill fires. The Naval Air Systems Command (NAVAIR) relies on AFFF systems to protect its assets. The current formulation of AFFF concentrates includes compounds which are nonbiodegradable and which have potential toxic impact to the environment.

There are different approaches for developing an environmentally improved suppression agent. This report outlines the feasibility of formulating an environmentally benign AFFF, the current direction and status of R&D and technical risks and probabilities of success for different approaches. Recommendations for continued development of an environmentally improved AFFF are proposed, including the development of a fire suppression model.

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Subj: STATUS REPORT ON THE DEVELOPMENT OF AN ENVIRONMENTALLY IMPROVED AFFF

## BACKGROUND

The U.S. Navy is one of the world's largest consumers of aqueous film-forming foam (AFFF). AFFF is the agent of choice for suppressing two-dimensional combustible/flammable liquid fuel fires resulting from aviation and shipboard accidents and battle induced damage. The Naval Air Systems Command (NAVAIR) uses AFFF in essential fire suppression systems protecting aircraft assets. Mobile vehicles (both shipboard and shoreside) use AFFF which is discharged through turrets and handlines. Aircraft carrier flight deck washdown systems can discharge AFFF in the event of a serious flight deck mishap.

The importance of AFFF to the Navy is evident by the rapid control, cooling, and extinguishment times required when accidents involve weapons. When exposed to fire, weapons may "cook-off" and explode in as little as 60 seconds. The control of any weapons exposure fire on air-capable ships is reliant on the suppression capability of AFFF. AFFF systems have been specifically designed to control and suppress flight deck fires to reduce the chance of weapons cook-off [1,2]. Any reduction in AFFF performance would result in substantially increased risks of catastrophic shipboard fires. The role of AFFF in protecting Naval assets should not be underestimated.

NAVAIR is by no means the sole Navy user of AFFF. The Naval Sea Systems Command (NAVSEA), the technical manager for the AFFF procurement specification, MIL-F-24385 [3], specifies AFFF to protect surface ship and submarine machinery spaces through handlines and fixed sprinkler systems. Deluge sprinkler systems are used to protect aircraft carrier hangar decks. The Naval Facilities Command (NAVFAC) specifies AFFF sprinklers for shoreside hangars and other flammable liquid hazards.

The formulation of foam concentrates currently requires the use of nonbiodegradable materials and chemicals which may have toxicological effects. There is now heightened awareness of the impact of these materials. As a result of recently enacted Federal environmental legislation and specific local waste treatment issues, there is a need to evaluate foam in terms of environmental impact. Environmental issues which have been raised include persistence of AFFF fluorosurfactants, discharge of glycols used in foam formulations, and the potential for upsetting the balance of biodegradation mechanisms in wastewater treatment facilities when foams are discharged and treated in this manner. These issues affect training of

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Ser 3905
6180/0060

Navy personnel, discharge testing of foam from flight deck fixed and mobile systems, and the installation of fixed foam systems, for example, in hangars.

Environmental issues associated with AFFF have and will continue to impact NAVAIR specifically and the Navy in general. For example, the new P-25 flight deck firefighting vehicle was proposed to have a 3780 L (1000 gal) premix tank of AFFF. For maintenance and testing, the tank contents must be discharged. Environmental restrictions limit the ability to discharge the premix solution overboard. As a result, a less reliable and more maintenance-intensive proportioning system is being considered instead of the premix tank. Environmental concerns also limit the ability to test and maintain the flight deck AFFF washdown system. At shoreside facilities, NAVFAC must now consider the disposition of effluent from AFFF system discharges resulting from testing, maintenance, and accidental trips of the system.

Other military users, notably the U.S. Air Force, have also encountered environmental concerns with AFFF. They have sponsored research currently geared primarily toward the elimination of glycol ethers from AFFF formulations.

The Navy continues to act in a leadership role in the development, analysis, and specification of AFFF. Navy representatives participate in a National Fire Protection Association (NFPA) Task Group to evaluate AFFF environmental issues. The prominence of the AFFF MIL SPEC has recently been broadened to include the national and international commercial aviation sectors by its adoption in NFPA Standard 403, "Aircraft Rescue and Fire Fighting" [4].

AFFF is widely recognized as the most effective foam agent for suppressing hydrocarbon pool fires. When mixed with water, the resulting solution achieves surface and interfacial tension characteristics needed to produce a film which will spread across a hydrocarbon fuel. The foam produced from this agent extinguishes fires by halting fuel vaporization in the same fashion as other foams (e.g., protein or fluoroprotein foam). However, the foam has film formation capabilities and is a very fluid foam that rapidly spreads across the fuel surface. The compounds used to create the desired film formation characteristics of AFFF do not readily breakdown in the environment. Thus, the very elements which make AFFF an effective agent have a potentially detrimental impact on the environment.

## OBJECTIVE

The objective of this status report is to outline the feasibility of formulating an environmentally benign AFFF. The current direction and status of R&D is described. Technical risks and probabilities of success are assessed. Recommendations for continued development of an environmentally improved AFFF are proposed.

## ISSUES AND SCOPE

AFFF is discharged to combat fires, suppress vapors resulting from a spill, train firefighters, and test/maintain fire suppression systems. AFFF may also be inadvertently discharged as a result of a false trip of a fixed system. In each of these situations, there are potential mitigating strategies. For example, a "training foam" might be used as a surrogate for actual AFFF for training scenarios. Likewise, simulants or plain water could potentially be used for system discharge testing or maintenance. For firefighting, an agent with less environmental impact could be used. This could take the form of an existing agent, e.g., fluoroprotein or protein foams. Alternately, a new, environmentally benign agent could be developed. Fluoroprotein foams may not contain glycol esters, but still contain fluorosurfactants. The fluorosurfactant persistence issue would not be solved. A protein foam might be used, but at a great sacrifice to extinguishment performance, e.g., 50 percent increase in extinguishment time compared to AFFF. Given the additional requirement to change out equipment to be air-aspirating, the fallback to protein-based foams is not a practical approach. No commercially available foam has been found to be as effective as AFFF [5].

For NAVAIR, it is undesirable to introduce a separate, "surrogate" agent for testing and training. For example, crash firefighting and rescue (CFR) vehicles used in a training scenario are often in a standby mode for an actual incident. The unit would respond in the event of an aircraft incident. The introduction of a less effective AFFF training surrogate would eliminate the vehicle from its active "standby" status. The introduction of such an agent also increases the risk of misuse of the agent in an actual fire, i.e., through failure to flush and refill the concentrate tank with genuine AFFF.

The development of a new firefighting agent, an environmentally benign foam, offers the most attractive solution for NAVAIR. While it is the most technically challenging, it offers the optimum long-term answer to the environmental issue. This report focuses on the feasibility of developing such an agent.

## ENVIRONMENTAL ISSUES

The discussion of potential approaches to developing an acceptable AFFF should be made in the context of the environmental issues. Scheffey [6] outlined foam environmental considerations, which are summarized here.

Quantitative data and methods to evaluate environmental impact are not widely published or well developed. The issue is not a new or unique development, but has received increased notice as a result of increased attention to environmental impact of firefighting agents. Factors related to the impact of firefighting foam on the environment include the following:

- Discharge of foam solutions and fuel-contaminated foam solutions to waterways and the potential toxicity to aquatic life;

- Effects on water treatment facilities; and

- Persistence and biodegradability of chemicals in foam concentrates and solutions including potential toxicity to humans.

In order to assess the impact of foam on the environment, the likely scenarios under which AFFF may be discharged should be considered. Based on these scenarios, the overall impact can be assessed and, where appropriate, potential mitigation strategies can then be developed. Likely scenarios include uncontrolled fire situations, potential hazardous situations, firefighting training evolutions, and fixed or mobile vehicle suppression system discharge testing (including intentional and accidental).

**Biodegradability**

The primary component of AFFF solution is water. Other components include non-fluorinated surfactants (e.g., hydrocarbon surfactants), glycol ethers, and fluorinated surfactants. The fluorinated surfactants are particularly resistant to biodegradation. Conversely, the less effective protein-based foams were largely assumed to be non-polluting because of their "natural" organic base. An early review of the available literature by Factory Mutual [7] indicated that both types of agents present inherent environmental issues and that effluents containing either should be processed in some form of sewage treatment facility or diluted prior to discharge into a stream.

A conventional method used to determine the biodegradability of a material is comparison of the Chemical Oxygen Demand (COD) of the material with its Biological Oxygen Demand (BOD). This is particularly important for waste treatment facilities where the stability of the treatment process may be upset. A compilation of test methods is found in "Standard Methods for the Examination of Water and Wastewater [8]." The BOD measures the amount of oxygen consumed by microorganisms in breaking down a hydrocarbon. The COD measures the maximum amount of oxygen that could theoretically be consumed by microorganisms. Therefore, a BOD/COD ratio is representative of the ability of the microorganism to biodegrade the components in a foam. The higher the BOD/COD ratio, the more biodegradable the foam. Results reported for BOD/COD of AFFF range from 0.60 to 0.99. The U.S. Military Specification requires a maximum COD of 500,000 mg/L and a minimum 20-day BOD/COD ratio of 0.65 for 6 percent concentrate. AFFF agents have been reported to have higher BOD and COD values than protein foams [9]. AFFF solutions are high BOD materials compared to the normal influent to treatment plants. Large quantities can "shock load" wastewater treatment facilities.

The fluorochemical based surfactants in AFFF have a carbon-fluorine chain that apparently does not break down in either the BOD or the COD test. If the rest of the hydrocarbons in the AFFF that are consumed in the COD are also consumed in the BOD then the BOD/COD ratio would be one. The AFFF would appear to be completely biodegradable, even though the remnant carbon-fluorine chain would remain.

If non-biodegradability concerns are based on the persistence of the fluorochemical surfactants, then the environmental impact tests currently used to assess foams do not address this concern. There is speculation that the undegradated material is biologically inert, but there are no published data to confirm this.

**Foaming and Emulsification of Fuels**

The surfactants in AFFF solutions can cause foaming in treatment aeration ponds. This foaming process may suspend high BOD solids in the foam. If these are carried over to the outfall of the treatment facility, nutrient loading in the outfall waterway may result. Foam aeration may also cause foam bubble backup in sewer lines.

In uncontrolled fires, spills, and live fire training scenarios, foams may contain suspended fuels. The fuel may become emulsified in the foam water solution.

**Toxicity**

In sufficient concentrations, foams may affect aquatic life. A number of fish toxicity studies have been performed. In tests using fathead minnows, the U.S. Air Force found that these fish could live in a simulated effluent stream containing 250 ppm (V/V) AFFF without fatality for up to eight days. $LC_{50}$ values at 96 and 24 hours were 398 and 650 ppm, respectively [9]. The U.S. MIL SPEC requires AFFF toxicity testing in accordance with ASTM E-729 using dynamic procedures with the Killiefish. An $LC_{50}$ of 1000 mg/L for 6 percent concentrate is permitted.

By themselves, these values may be considered as having a low degree of fish toxicity using environmental regulation rating scales. Localized concentrations in ponds or streams may exceed the values cited if there is no water movement.

There are no published data on the phytotoxicity of foam solutions, but there have been no published reports of plant kills resulting from foam solution discharges.

Manufacturers report that thermal decomposition products from AFFF do not present a health hazard during firefighting. Again, there are no data published in the literature. Manufacturers' product environmental data for AFFF include references to a test where a layer of AFFF was burned in a pan of gasoline inside an enclosure. Two measurements of HF recorded above the sample were 0.23 and 0.16 ppm [10].

## Current Regulatory Environment

*Glycol Ethers*

As a result of the 1990 Clean Air Act, the U.S. Environmental Protection Agency now requires the reporting of certain chemical uses and releases. Among these, glycol ethers are subject to reporting under Section 313 of the Emergency Planning and Community Right-to-Know (EPCRA) list. Additionally, the glycol ether category was placed on the list of hazardous air pollutants (HAP) under the 1990 Clean Air Act amendments. The HAP listing results in the designation of the chemical as a "hazardous substance" under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA).

The inclusion of glycol ethers on the HAP list had automatically set a default reportable quantity requirement of one pound per day for CERCLA reporting. This resulted in the requirement to report every time one pound of glycol ether entered the environment in a twenty-four hour period. For AFFF, this equated to a discharges as low as 15 gallons of solution (not concentrate). The EPA has since revised the reporting requirement (June 12, 1995, final rule 60 CFR 30926). Currently there is no reportable quantity for the glycol ethers. Thus, foams containing glycol ethers are not subject to EPA reporting.

Summarizing, the trend at this time includes an effort by industry to permit greater amounts of agent which could be discharged before they become reportable. Continued use of the glycol ethers in the longer term may be problematic if future EPA toxicological analysis suggest continued or greater restrictions on this product.

*Fluorosurfactants*

To date, no regulations related to the reporting or restriction of fluorosurfactants have been identified. There is concern in the industry that these elements will eventually be targeted for regulation by virtue of their persistence in the environment. Toxicity effects have not been well established, and there are difficulties in detecting fluorosurfactant elements in waste systems.

The elimination of fluorosurfactants as a general class of elements available for use in fire extinguishing agents would have a significant effect. For example, reliance on non-fluorosurfactant foam, e.g., protein foam, would reduce fire extinguishment effectiveness by a factor of roughly 2:1 [11]. Critical Navy systems, e.g., aircraft carrier flight deck washdown systems, are currently not readily adaptable to protein foams, which require air-aspiration.

*Wastewater Treatment Plants*

Effluent from AFFF streams may ultimately be processed through wastewater treatment plants. Problems may result from large quantity discharge of AFFF to these facilities.

Foaming at the plant can cause suspension of high biological oxygen demand (BOD) solids in the foam. This may upset the treatment facility balance and cause nutrient loading at the outfall of the treatment plant. Because AFFF solutions are high BOD materials, they can cause wastewater treatment plant "shock loading" or overload. Bacteria used in plants may also be killed by shock loading. As a result of these factors, treatment plants may operate outside nutrient and water quality permit limits regulated by local environmental agencies. In extreme cases, local authorities may severely restrict or prohibit the discharge of AFFF into the local wastewater stream. This is currently the case with the Hampton Roads Sanitation District (HRSD), located adjacent to the Norfolk Naval Station. Treatment plant upsets have reportedly occurred as a result of fire training facility AFFF use and AFFF system discharge tests from aircraft carriers. Requirements for wastewater limits to treatment plants may include BOD, COD, pH, oil, and grease, total suspended solids, and a measurement of surfactant quantity. These parameters are described in the *Military Handbook for Firefighting School Facilities*, MIL-HDBK-1027/1.

## APPROACH TO THE DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY AFFF

Two fundamental approaches have been proposed to develop a new AFFF. One approach is to identify alternative chemicals and formulate novel foam concentrates. These novel foam concentrates would first be screened to see if they form a positive spreading coefficient. They may also be fire tested at a relatively small scale. This approach assumes that a positive spreading coefficient on a hydrocarbon fuel is necessary for a candidate agent to have similar if not equal fire extinguishment and burnback performance to AFFF.

The alternative approach assumes that chemical derivatives are not readily available or identifiable which combine both desirable firefighting and environmental characteristics. The contention is that a lack of fundamental theoretical understanding of foam spreading and extinguishment mechanisms limits the ability to investigate novel concepts/formulations. This approach relies on the development of a foam spreading and extinguishment model to predict foam performance. Small-scale apparatus might be used in support of this model. Having verified the extinguishment model, approaches which provide the required physiochemical properties could be investigated. This could lead to an approach which does not rely on the surface-tension reduction characteristics (for which fluorosurfactant chemicals are vital).

This report will discuss the known work in this area (limited in both cases), the pros and cons of each approach, technical risks, and the ultimate payoff.

## INVESTIGATION OF CHEMICAL ALTERNATIVES

The direct investigation of chemical alternatives offers the potential to reduce or eliminate two of the chemicals which do or could be considered to have an environmental impact: glycol ethers and fluorosurfactants. The known work in this area is reviewed here. The primary sources of information are vendor information, chemical and fire test data from the Naval Research Laboratory and Hughes Associates, Inc., and preliminary data from work conducted by the U.S. Air Force.

### Elimination of Glycol Ethers

*Vendor Information*

Discussions with vendors supplying MIL SPEC AFFF on the Qualified Products Lists [12] have informally indicated that alternatives may exist for the glycol ethers used in AFFF. In the near term, the use of reduced quantities of glycol ethers appears to be technically feasible. One vendor has successfully tested a MIL SPEC agent with less glycol ether. The new compound reduced the glycol ether content from 30 percent by volume to 20 percent. Understandably, these vendors, for proprietary reasons, are hesitant to discuss specific chemical formulations. The market place, particularly customer requirements for Material Safety Data Sheets (MSDS) will require partial if not full disclosure of the alternative formulations. Based on this information alone, the reduction of glycol ethers in AFFF formulations appears to be feasible and of low-to-moderate technical risk. This is supported by experimental data by NRL as described in the next section. The technical feasibility of the total elimination of glycol ether in the near-to-mid term is subject to debate. Some vendors indicate that this may not be possible, particularly to the extent that the one pound reportable quantity level can be met. Others indicate that they are nearly ready to submit a glycol ether-free MIL SPEC agent.

*NRL and Hughes Associates Data*

A one-quarter scale fire test apparatus was created to evaluate novel foam formulations. This was a 1 $m^2$ (7 $ft^2$) circular test pan with nozzles and foaming apparatus to control foam expansion and solution flow and pressure. Surface tension measurements were performed with surfactants obtained from different manufacturers. Organosilicon and fluorosurfactant combinations were evaluated. Although the nonionic organosilicon and nonionic fluorosurfactant chemicals provided the requisite surface tension reduction, their formulations did not foam. However, an anionic and cationic fluorosurfactant combination, which provided the lowest surface tensions, showed fire knockdown characteristics in small-scale test evaluations. From Table 1, it can be seen that, with less volume of chemicals, comparable burnback and extinguishment times were achieved. For example, average concentrations for the novel formulations was 2.6-2.9 percent in distilled and hard tap water (see Table 2). The tests indicate that the expansion ratio of the air to liquid volume was obtained without the

refractive index modifier, butyl carbitol, which is present at 15 percent concentration in 3M-FC206CE.

These data suggest that agents with reduced concentrations of glycol ethers or with replacement ethers are technically feasible. The exact chemicals used would have to be compared against the chemicals on the CERCLA reporting requirements listing. There are technical challenges to overcome since butyl carbitol is used as a refractive index modifier and for freeze protection in non-MIL SPEC agents. The refractive index is used for field testing of AFFF proportioning systems. The current refractive index

Table 1. Fire Performance Characteristics of AFFF and Novel Foam Agents Using a 1 $m^2$ (7 $ft^2$) Small-scale Test Platform

| Agent | Application Rate (Lpm/$m^2$ (gpm/$ft^2$)) | 100% Extinguishment Time (s) | Extinguishment Density (L/$m^2$ (gal/$ft^2$)) | Burnback Times (s) | |
|---|---|---|---|---|---|
| | | | | 25% | 50% |
| 3M MIL SPEC 6% AFFF (Lot #159, 6/90) | 1.7 (0.041) | 39 | 1.1 (0.027) | 476 | 506 |
| | 1.5 (0.036) | 52 | 1.3 (0.031) | 490 | 519 |
| | 2.4 (0.058) | 41 | 1.6 (0.040) | 428 | 467 |
| | 2.2 (0.055) | 39 | 1.5 (0.036) | 453 | 495 |
| | 2.4 (0.060) | 39 | 1.6 (0.039) | 411 | 468 |
| | 2.5 (0.062) | 36 | 1.5 (0.037) | 416 | 466 |
| | 2.0 (0.048) | 35 | 1.1 (0.028) | 761 | 810 |
| | 3.2 (0.079) | 40 | 2.1 (0.052) | 510 | 530 |
| | 3.1 (0.077) | 39 | 2.0 (0.050) | 571 | 586 |
| Batch #1 DuPont/3M Fluorosurfactants | 3.1 (0.075) | 67 | 3.4 (0.084) | 452 | 477 |
| Batch #2 DuPont/3M Fluorosurfactants | 3.1 (0.075) | 94 | 4.8 (0.118) | 467 | 486 |
| | 3.1 (0.075) | DNE[1] | --- | --- | --- |
| Batch #5 DuPont/3M Fluorosurfactants | 3.1 (0.077) | 57 | 3.0 (0.073) | 446 | 470 |
| | 3.1 (0.077) | DNE[1] | --- | --- | --- |

[1]DNE did not extinguish.

Table 2. Contents of Anionic - Cationic Fluorosurfactant Agent in 20 Liters

| Manufacturer/Product | Surfactant Type | Percent by Volume |
|---|---|---|
| 3M / FC-135 | Cationic: Perfluoroalkyl quaternary ammonium iodide | 0.31 |
| DuPont / FEA | Anionic: Lithium (fluoroalkyl) thio propionate | 0.20 |
| Mona Industries / ADA | Amphoteric: Cocamidopropyl betaine | 0.31 |
| Stepan Company / Maprosyl 3 | Anionic: Sodium lauroyl sarcosinate | 0.63 |
| Union Carbide / Polyox Aldrich / STG | Nonionic: 5% poloxyethylene, triethyleneglycol monomethylether | 0.49 |

measurement techniques are dependent on sufficient quantities of butyl carbitol in the concentrate. Alternative benign solvents or compounds may provide the requisite refractive index modification. For example, urea may be added to a formulation for refractive index modification. Alternatively, the electrical conductivity method might be used for field testing of AFFF proportioning systems [13]. However, electrical conductivity measurements are non-linear in seawater solutions. Application of this method for Navy shipboard situations is questionable.

*U.S. Air Force Information*

The U.S. Air Force, in current work to reduce the environmental impact of AFFF, has proposed formulations for a revised MIL SPEC [14]. These formulations are to include "solvents not on Hazardous Air Pollutant List of the 1990 Clean Air Act nor subject to SARA Title 11, Section 313 regulations." This suggests that Air Force researchers believe that replacement solvents are technically feasible, but no specific agents, formulations, or test data have been reported. It has been proposed that the refractive index will be lower for a modified agent compared to MIL SPEC agents. Again, no specific data have been reported.

**Elimination of Fluorosurfactants**

*Vendor Information*

No QPL vendor has, to date, indicated that fluorosurfactants can be reduced or eliminated from MIL SPEC AFFF. Market and regulatory forces play at least a partial role in this issue. On one hand, there are no regulations or requirements to eliminate fluorosurfactants. On the other hand, the vendors appear to understand that, by virtue of its persistence, fluorosurfactants may potentially be regulated. Vendors have indicated that the AFFF market is very competitive. Since the fluorosurfactants are one of the most expensive components of AFFF, this suggests that the levels of fluorosurfactants are already at a

minimum. If an alternative was readily available, it probably would already have been proposed for use. It is unlikely that such a replacement chemical is readily available. One vendor has stated that no other known class of material has the capability of producing solutions of sufficiently low surface tension to permit the formulation of an aqueous film on hydrocarbon fuels. At least one manufacturer of fluorosurfactant compounds has initiated a research program to develop a "biodegradable" fluorosurfactant.

*NRL and Hughes Associates Data*

A review of potential candidate chemicals based on their physical performance criteria is summarized in an SBIR Phase I report on environmentally friendly AFFF prepared by Hughes Associates, Inc. for the U.S. Air Force [15]. Previous patents were consulted for information on chemical components and their behavior as extinguishing agents. One group of surfactant chemicals was the organosilicons. Most of the organosilicon chemicals produced commercially are used in polymer, paint and textile processing, and enhanced oil recovery. As such, most of these organosilicon compounds, manufactured by Dow Corning and Union Carbide, are derived from polydimethysiloxanes and are too viscous for foams. However, patent information revealed that there existed some siloxanes with charged functional groups that foam at low concentrations. In fact, one company, Union Carbide, claimed to have invented cationic, anionic, and amphoteric siloxane surfactants that extinguished hydrocarbon fires. Coincidentally, these inventions occurred just after the original patent for extinguishing hydrocarbon fires using fluorosurfactants was issued to researchers from NRL [16].

Another potential avenue for reevaluation is the synergistic behavior of fluorosurfactant and organic surfactants. When the decrease in surface tension of a mixture of anionic and cationic fluorosurfactants together was found to be lower than each separately, new formulations were investigated to demonstrate this phenomena [17]. Fluorosurfactants were obtained from DuPont and Minnesota Mining and Manufacturing (3M) for this purpose.

Next, in the process of choosing chemicals to use for interfacial tension reduction, a stable but biodegradable, non-toxic group of surfactant chemicals was chosen for their ability to foam and enhance the spreading of non-hydrocarbon surfactants over the hydrocarbon fuel surface. A range of manufacturers sent samples to Hughes Associates, Inc., including, Stepan, Co., Shell, Rohm and Haas, Rhône Poulenc, Mona Industries, BASF, Dow, and Union Carbide Corp. The foamers contain ingredients that are used for cosmetic type applications. Their stability in a high temperature type situation depends on the stabilizers used to strengthen the bubble lamellae. For this purpose nonionics were employed of low molecular weight with low vapor pressure ethers of chain length similar to the surfactant foamer. For instance, a typical foamer of eleven carbons, lauryl sulfate, was matched with methoxy triglycol using polyethyleneoxide as the foam stabilizer.

The surfactant formulations were evaluated on the basis of surface tension for their ability to attain low surface tensions separately and as synergistic combinations. The surfactant combinations of Table 3 from Reference 15 are examples of the method used for novel agent formulation. The choice of surfactant concentration was based on the critical micelle concentration of the surfactant. This is the point where the surface tension changes very little as one increases the concentration in the solution.

Preliminary fire testing of the novel agents using the 1 $m^2$ small-scale fire test apparatus showed that none of the organosilicon compounds worked as extinguishing agents. As noted earlier, their surface tension reduction is comparable to the fluorosurfactant surface tension reduction in water at similar concentrations. However, these foams, when applied to a fire, were destroyed. Different fluorosurfactant combinations were successfully created which could extinguish the fire. Applications of theoretical assumptions from research and texts to new and old surfactant technology provided products with interesting results. For example, a cationic-anionic blend of fluorosurfactants showed lower surface tension than either one by itself. This indicates that, besides increased surface pressure and spreading capability on hydrocarbon surfaces, there is similarity to their behavior with hydrocarbon surfactants.

It was shown that cationic organic ammonium bromides displayed lower surface tensions with an anionic fluorosurfactant, i.e., surface tensions lower than each exhibit separately [18]. It was also well documented that amphoteric and anionic fluorosurfactant blends worked well together. The problem with this approach is that amphoteric fluorosurfactants were used at much greater than necessary concentrations. They were being used in combination with anionic organic interfacial tension reducers as well as with the anionic fluorosurfactant moiety [19].

It was concluded that an organic amphoteric surfactant mixed with anionic fluorosurfactant and anionic organic surfactant mixed with a cationic fluorosurfactant performed as an extinguishing agent. Because the organic-fluorosurfactant combinations synergistically reduce surface tensions to lower values at lower concentrations of all components involved, it may be possible to use less fluorosurfactant to achieve similar results. The data to date do not support the use of a nonfluorinated surfactant to achieve the desired surface tension reduction properties.

*U.S. Air Force Information*

The U.S. Air Force has sponsored a Phase II SBIR project with the goal of chemically developing an environmentally friendly AFFF. The research proposes three levels of AFFF performance as shown in Table 4 [14]. The proposal implies that the fluorine content can be reduced, but not eliminated. This is consistent with the NRL/Hughes Associates findings. The proposed level of decrease in fluorine content is not identified. No decrease in

Table 3. Example Surface Tension Measurements of Novel Agents [16]

| Surfactant Chemical | Charge | Apparent Surface Tension $\gamma$(dynes $cm^{-1}$) | Concentration (% in deionized distilled $H_2O$ |
|---|---|---|---|
| FSA (DuPont)<br>Lithium 3-[(1H,1H,2H,2H<br>-Fluoroalkyl) thio]<br>propionate | Anionic | 17.75 | 0.01 |
| FSA (DuPont)<br>(UC) L7607-Polyalkylene oxide<br>polydimethylsiloxane | Anionic<br>nonionic | 20 | 0.2 |
| FC-135 (3M)<br>1 - Propanaminium<br>3 [[[(heptadecafluoroctyl)<br>sulfonyl] amino] -<br>N N -trimethyl] | Cationic | 16.8 | 0.01 |
| FC-135 (3M)<br>FSA (DuPont) | Cationic<br>Anionic | 15.85 | 0.2 |
| FC-135 (3M)<br>FSA - DuPont<br>Silwet-L7607-Union Carbide | Cationic<br>Anionic<br>Nonionic | 16 | 0.3 |
| FC-135 (3M)<br>FSA (DuPont)<br>L7607 (Union Carbide)<br>Pluronic-Polyoxyethylene<br>(propylene)<br>(BASF) - copolymer<br>MTG (Aldrich)<br>Ethanol,<br>(2-(2-(2-methoxy-ethoxy)ethoxy) - | Cationic<br>Anionic<br>Nonionic<br><br>Nonionic<br><br>Nonionic | 16 | 0.38 |

firefighting performance is proposed while a goal of improved burnback performance has been established.

Table 4. Fire Performance Parameters Proposed for the USAF Environmentally Improved AFFF Agents [14]

| 3% AFFF-EMB Parameters | Type A 3% AFFF-EMB | Type B 3% AFFF-EMB | Type C 3% AFFF-EMB | MIL-F-24385F 3% AFFF |
|---|---|---|---|---|
| Fluorine content limited to | low level | med. level | max. 1% | not limited |
| Environmental impact improvement | very much | much | limited | --- |
| Burnback resistance improvement | limited | much | very much | --- |
| 28 ft² fire - Foam application time to extinguish, seconds, maximum | | | | |
| Half strength | 45 (3/4) | MIL-F | MIL-F | 45 |
| Full strength | MIL-F | MIL-F | MIL-F | 30 |
| 5 x strength | MIL-F | MIL-F | MIL-F | 55 |
| Burnback time of resulting foam cover, seconds, minimum | | | | |
| Half strength | 300 (3/4) | MIL-F | 360 | 300 |
| Full strength | 360 | 420 | 480 | 360 |
| 5 x strength | 240 | 300 | 360 | 200 |
| 50 ft² fire - Foam application time to extinguish, seconds, maximum | MIL-F | MIL-F | MIL-F | 50 |
| Burnback time of resulting foam cover, seconds, minimum | 360 | 420 | 460 | 360 |
| 40 second summation | 320 | 340 | 360 | 320 |

The Air Force also found that commercially available agents which may exhibit improved biodegradable characteristics (BOD/COD ratios), e.g., protein or fluoroprotein foams, were not as effective as MIL SPEC AFFF in terms of fire extinguishment and burnback resistance. This is consistent with previous NRL and Hughes Associates studies which showed MIL SPEC AFFF to be the most effective Class B firefighting foam currently available [5,15,20].

*Summary*

The limitations of the "chemical approach" for developing improved agents have been identified. Glycol ether content may be totally or substantially reduced; the total elimination of these solvents appears to be a moderate technical risk. The total elimination of fluorosurfactants does not appear to be technically feasible, at least in the near term. The

fluorosurfactants provide the necessary surface tension reduction of solutions to create a positive spreading coefficient on hydrocarbon fuels. Yet, research and evaluation of test data by NRL and Hughes Associates indicate that there is no direct correlation between spreading coefficient and fire extinguishment/burnback resistance of firefighting foams [5]. There is a lack of correlation between chemical/physical properties typically measured for foams and fire performance. This limitation impedes the evaluation of novel concepts, elements, and chemical formulations since the required suppression theory has not been fully developed.

## FOAM SUPPRESSION MODELING

The mechanisms of foam fire extinguishment on two-dimensional pool fires have not been completely elucidated. Usually, the fire extinguishment is described simply as a factor of the cessation of fuel vaporization at the fuel surface. As the fuel vapor decreases, the size of the combustion zone decreases. When the area is totally covered, extinguishment occurs. Hanauska et al. [15] have proposed fundamental extinguishment parameters, summarized below.

### Foam Loss Mechanisms

Fire extinguishment by foams can be summarized as shown in Figure 1. Foam having a temperature, $T_f$, and depth, h, spreads at a rate of V, along a fuel of temperature, $T_s$, and vapor pressure, $P_v$. Fuel is volatized by the fire at a rate of $\dot{m}_{fuel}$, which is a function of the radiative feedback, $\dot{q}_{rad}$. The foam is added by the discharge application, $\dot{m}_{add}$, and lost through evaporation, $\dot{m}_{vap}$, and drop through, $\dot{m}_{drop}$.

The total mass loss of the foam is a function of the loss due to drop through and the mass loss due to evaporation. The mass loss due to drop through is at least partially dependent on the drainage of liquid from the foam. Evaporation of the liquid occurs primarily from radiant energy from the fire. Assuming that most of the radiation results in direct evaporation of the foam, the evaporation of foam can be characterized by

$$\dot{m}''_{evap} = \frac{\dot{q}''_{evap}}{\Delta H_v} \qquad (1)$$

where $\Delta H_v$ is the combined latent and sensible heat of vaporization. Using a rough estimate of $\dot{q}''$ from large pool fires of 45-185 kW/m$^2$ yields an evaporation rate of 18-72 g/m$^2$s assuming a heat of vaporization of 2563 kJ/kg. To account for reflective and absorbed losses, Persson [22] has proposed a calculation method:

$$\dot{m}''_{evap} = \dot{q}''_{rad}\, k_e \qquad (2)$$

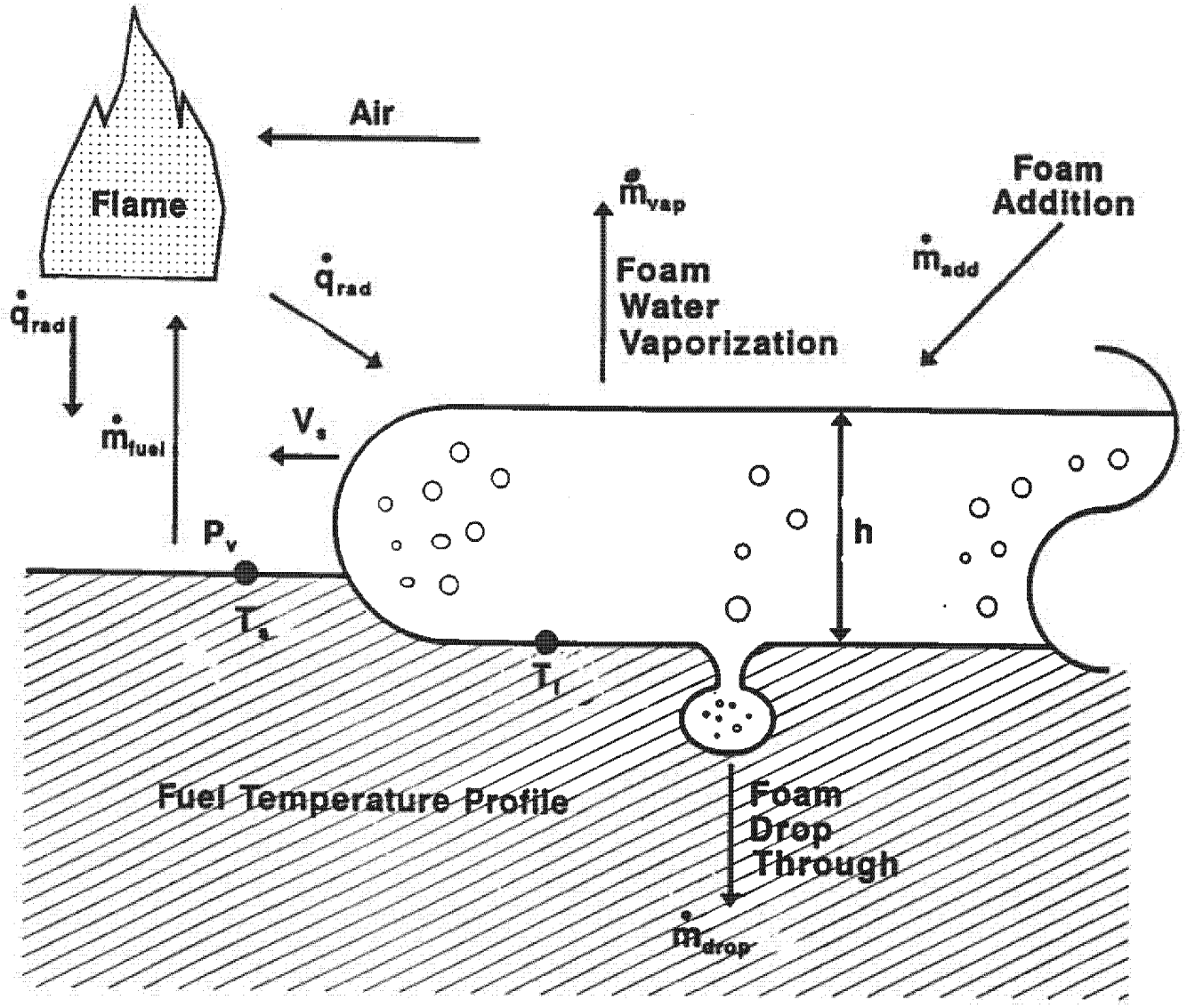


Fig. 1 - Parameters affecting foam fire extinguishment [16]

where $k_e$ is an experimentally derived constant using different fluxes from a radiant exposure. For $\dot{q}''_{rad}$ values of 45 and 185 kW/m$^2$, equation 2 yields values for $\dot{m}''_{evap}$ of 11 and 46 g/m$^2$s, respectively. The estimated $\dot{m}''_{evap}$ based on equation 1 at the same heat fluxes were 18 and 72 g/m$^2$/s. The mass loss rates from the experimental results are about 62 percent lower than the theoretical loss. The difference between values is attributable to neglecting the reflected and absorbed losses in equation 1. This indicates that about 48 percent of the radiant flux to the foam surface is either reflected from or absorbed into the foam blanket. The division between these two heat transfer mechanisms is not clear and is an area for further study.

Foam loss can likewise be described theoretically based on the downward force of gravity and the opposing forces due to surface tension and buoyancy. Alternatively, a model from mass loss due to drainage can be expressed as a time-averaged constant:

$$\dot{m}''_{drain} = k_d \qquad (3)$$

where $k_d$ is an experimentally determined drainage coefficient. From the data of Persson, the drainage coefficient can be estimated to be 17 to 25 g/s/m$^2$. The drainage rate was found to be relatively independent of the radiant heat flux to the foam, but highly dependent on the expansion ratio. Foams with lower expansion ratios will drain faster. For example, decreasing the expansion ratio by about half (11.3 to 5.3) increased the drainage rate by a factor of about 2 (55 to 105 g/min). Decreasing the expansion ratio changes fundamental parameters of the foam, which allows it to drain faster.

**Foam Spread Over Liquid Fuels**

In order to predict the extinguishment of a liquid pool fire by firefighting foam, it is necessary to describe the process of spreading the foam over the liquid fuel surface. This process of foam spread on a liquid fuel is similar to the spread of a less dense liquid (such as oil) on a more dense liquid (such as water). This phenomenological approach to the spread of foam on a liquid pool is appropriate to the extent that foam can be treated as a liquid. Kraynick [22] characterizes foams macroscopically as being Bingham fluids with a finite shear stress and a non-Newtonian viscosity. That is, foam displays an infinite viscosity up to some initial shear rate above which they display a shear rate dependent viscosity.

Since fuels typically have low viscosities (especially compared to foam viscosities at relatively low shear rates), it may be appropriate to model foam spread across a fuel surface using models developed for oil spread on water. These models assume that the oil spreads as a fluid with a viscosity much larger than the water on which it is spreading. The process of oil spread on water has been described in detail by Fay [23], and Fay and Hoult [24]. Their phenomenologically based model describes three regimes of spread as characterized by combinations of spreading forces and retarding forces. The first regime is the gravity-inertia regime where the outward spread of the oil is driven by a gravity force and retarded by the

inertia required to accelerate the oil. The second regime is the gravity-viscous regime, where the gravity-induced spreading is retarded by viscous dissipation in the water. Since the oil is much more viscous than the water, they assume that there is slug flow in the oil and that the viscous drag force is dominated by the velocity gradient in the water. The final regime is characterized by a surface tension spreading force opposed by the viscous retarding force. By setting the spreading and retarding forces equal in each of the regimes, they developed equations to estimate the length of the spread as a function of time.

By treating the spread of foam on fuel as similar to the spread of oil on water, the equations developed by Fay and Hoult might be used to describe the spread of a foam blanket over a fuel pool as a function of time. Since foam generally has a much higher viscosity than the fuel on which it is spreading, the assumption of slug flow made for the oil by Fay and Hoult should be reasonably valid for foam spread on fuel as well. The equations are

$$\textit{gravity-inertia regime:}\quad l = (\Delta g V t^2)^{1/4}$$

$$\textit{gravity-viscous regime:}\quad l = \left[\frac{\Delta g V^2 t^{3/2}}{\nu^{1/2}}\right]^{1/6} \qquad (4)$$

$$\textit{surface tension-viscous regime:}\quad l = \left[\frac{\sigma^2 t^3}{\rho^2 \nu}\right]^{1/4}$$

where

| | | |
|---|---|---|
| $l$ | = | length of spread (cm), |
| $\Delta$ | = | $(\rho_{fuel} - \rho_{foam})/\rho_{fuel}$, |
| $g$ | = | acceleration of gravity (981 cm/s$^2$), |
| $V$ | = | foam volume (cm$^3$), |
| $t$ | = | time (s), |
| $\nu$ | = | kinematic viscosity of fuel (cm$^2$/s), |
| $\sigma$ | = | spreading coefficient (dynes/cm), and |
| $\rho$ | = | density of fuel or foam (g/cm). |

Equation (4) represents an untested theoretical model of foam spread. The equation includes the parameters which are known or suspected to affect foam spread.

## Prediction of Foam Spread

Persson and Dahlberg [25], working independently from U.S. researchers, developed a foam spread prediction model using the same "oil on water" theory used by Hanauska et al. [15]. Viscous friction, described as a friction constant or friction factor, is assumed to be the dominant mechanism in opposing foam spread. The spreading process is decoupled from mass transport due to evaporation and drainage of water contained in the foam. Preliminary experiments with foam spreading on a 20 m diameter circular pan of water were used to determine the friction coefficient. The model fits reasonably well with the experimental results for a wide range of volume flow rates and foam expansion numbers as shown in Figures 2 and 3. This work constitutes the first step in an attempt to develop a model describing foam spread on a burning surface.

## Modeling of Fire Extinguishment

At this point, modeling of foam extinguishment cannot be performed because of the large number of remaining uncertainties. A model would have to take into account the addition of foam to the fuel surface, the spread of foam on the fuel surface, and the foam loss mechanisms of evaporation and drop through. The foam spread length equations can be used to estimate the area of foam coverage at a specific time and for a specific quantity of foam. Modeling at this time is now limited because of the lack of established values for $k_e$ (Equation 2) and $k_d$ (Equation 3). Also, the yield stress and viscosity relationships for firefighting foams have not been quantified.

Preliminary modeling of fire extinguishment has been performed using assumed fire heat fluxes and spreading factors [15]. The modeling used the MIL SPEC 2.6 $m^2$ (28 $ft^2$) fire pan and application rate. The model predicted extinguishment on the order of 6 seconds. Tests with MIL SPEC AFFF generally have extinguishment times on the order of 25 seconds, with a maximum of 30 seconds permitted. Modeling with larger fire areas also predicts critical application rates of approximately one-half of the critical rates based on actual data.

The model is overpredicting the speed of foam spread, but the results are encouraging given the level of assumptions now being used. Experimental work is clearly needed, particularly in the area of foam breakdown as a function of radiant heat flux from a pool fire. It is anticipated that bench-scale test apparatus can be constructed to develop foam loss factors. Combined with more precise spreading friction factors, the modeling of foam fire extinguishment appears to be technically feasible.

## Advantages in Developing Foam Suppression Theory

Preliminary work by both the Navy and Air Force demonstrate the difficulties in developing nonfluorosurfactant compounds and glycol ether-free mixtures. The lack of correlation between spreading coefficient data and fire test results also indicates a lack of

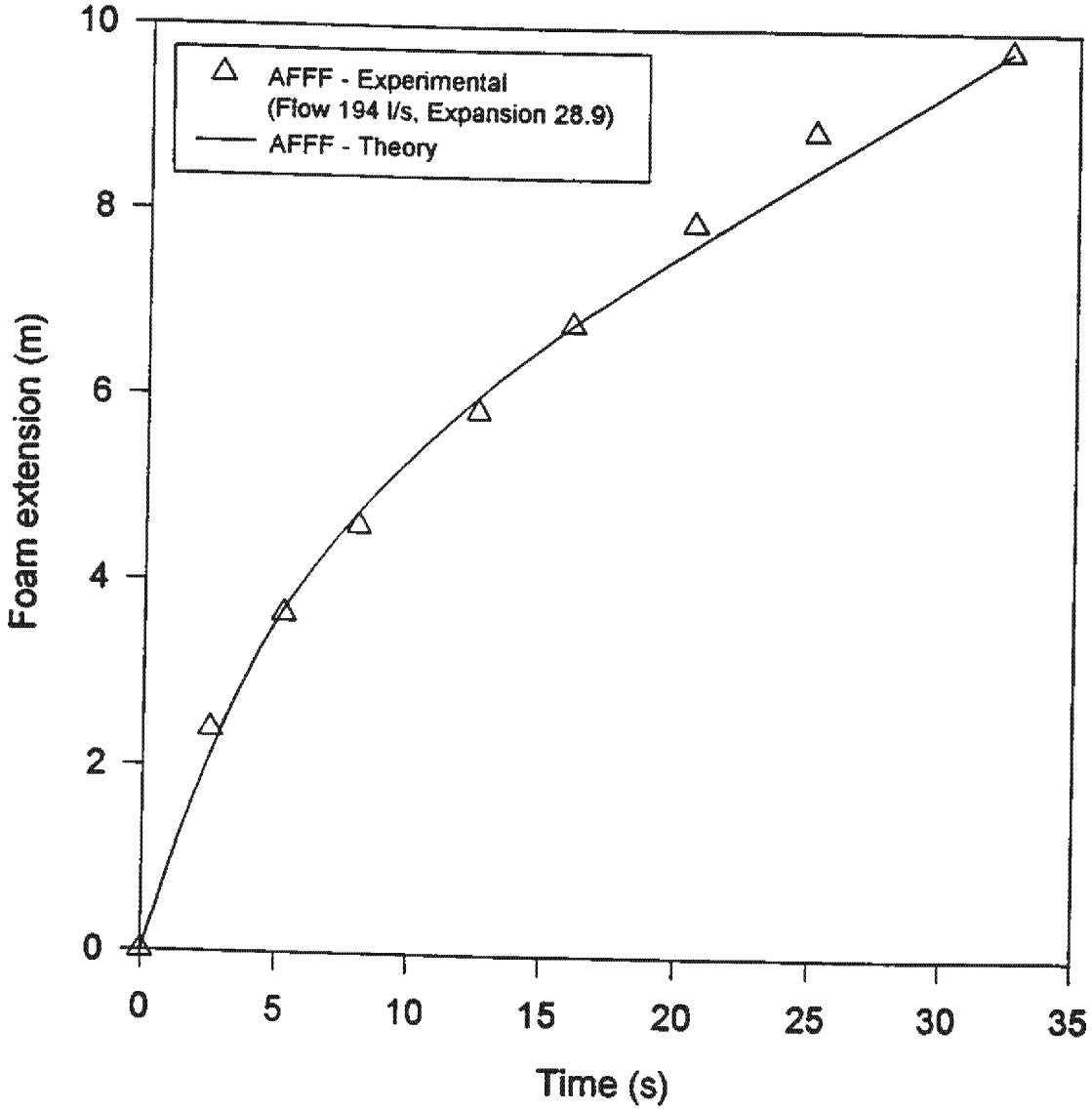


Fig. 2 - Comparison between predicted and measured extension for detergent foam having a friction factor of 0.1 $N/m^3$ (from Ref 25)

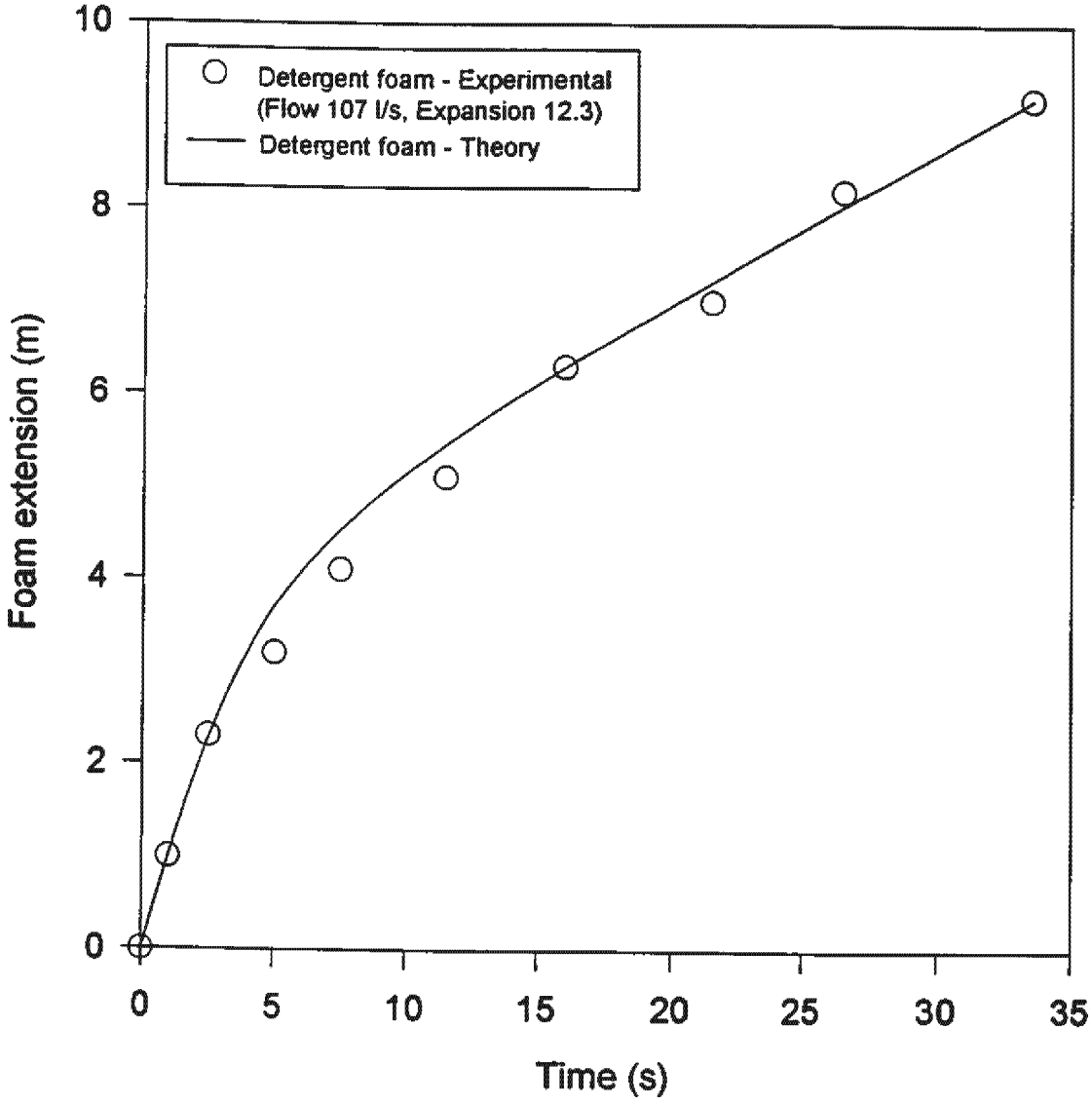


Fig. 3 - Comparison between predicted and measured extension for AFFF having a friction factor of 0.1 N/m$^3$ (from Ref 25)

fundamental understanding of foam suppression mechanisms. In order to generate the next generation of foam agents, i.e., environmentally benign, new approaches/techniques will probably be required. These concepts might be derived from outside the traditional fire suppression chemical field, e.g., from the coatings technology field. To apply techniques/mixtures/approaches from other disciplines, fundamental scientific relationships must be in place. These relationships would be established through the development of a foam fire extinguishment model. In the near term, this modeling combined with bench-scale, correlatable test methods could be used to evaluate novel formulations to address environmental issues. In the longer term, advanced fire suppression agents, with perhaps double the extinguishment effectiveness of currently available AFFF, could be evaluated at a substantially reduced cost and effort compared to current approaches.

Even if efforts to improve the environmental characteristics fall short of goals, a successfully developed and validated fire extinguishment model would still be useful for general foam evaluation. This would represent a significant advance in the technology which is now reliant on moderate- to full-scale fire testing.

## CONCLUSIONS

1. AFFF is a vital component for the protection of Naval aviation assets. This protection, particularly as it applies to weapons cook-off, requires an agent with rapid control, cooling, and suppression capability. Reduction of fire suppression capability through the use of existing, environmentally more favorable agents would increase the risk of catastrophic fires and probably require significant hardware modifications to accommodate the agent.

2. Regulations related to the discharge of chemicals in AFFF require reporting for relatively small amounts of solution. The trend is toward more strict regulation of the chemicals in AFFF and of the discharge of AFFF into the environment.

3. There are several potential options to address issues related to AFFF impact on the environment. The best option for the long term is to develop an agent that is totally biodegradable.

4. It appears to be technically feasible to reduce the quantities of chemicals which exert an impact on the environment. It is not clear that these elements can be totally eliminated in near-term reformulations of AFFF.

5. Suppression mechanisms of hydrocarbon pool fires by foam are not fully understood. This inhibits the investigation of alternative approaches to developing an environmentally benign AFFF.

6. It appears to be technically feasible to develop a fire suppression model which could be used to assess alternative methods for developing an environmentally friendly agent. This model could form the basis for the development of the next generation foam agent.

## RECOMMENDATIONS

1. Continue to monitor the trends of regulations affecting the discharge of AFFF.

2. Continue to monitor the near-term development of any AFFF reformulations which reduce the amount of non-biodegradable or regulated compounds in AFFF.

3. Adopt the approach of developing a long-term solution which would address all aspects of the environmental issue, i.e., a next generation biodegradable fire suppression agent.

4. Develop the fire suppression model which would be used to support the formulation of the next generation agent. A work plan for the development of the fire suppression model is included in Appendix A.

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# Appendix A

## Work Plan to Develop a Fire Suppression Model

Work Plan to Develop a Fire Suppression Model

| | |
|---|---|
| Task 1 | Refine the fire extinguishment model developed in previous efforts. Write computer-based agent performance program to execute calculations. Develop as a baseline the fire extinguishment model. Consider other modeling parameters such as three-dimensional fires and burnback resistance. |
| Task 2 | Construct bench-scale apparatus. This would include apparatus for critical foam thickness and foam loss mechanisms. Conduct experiments with existing formulations. |
| Task 3 | Construct small-scale foam spread apparatus. Conduct experiments with existing formulations. Use results to modify agent performance program as required. Correlate results with larger scale spreading data. |
| Task 4 | From the agent performance program of Task 1 and data generated in Tasks 2 and 3, calculate the extinguishment capabilities of foams and compare to existing test data. Propose new formulation work based on the parameters that will improve performance and biodegradability of agents. |
| Task 5 | Define biodegradation and environmental issues related to firefighting foam and surfactants. Select or develop appropriate test methods and criteria. |
| Task 6 | From information learned in Tasks 4 and 5, select various surfactants and chemicals to evaluate in new formulations. Acquire these surfactants and chemicals from chemical manufacturers. |
| Task 7 | Formulate new firefighting foams and examine performance with the bench-scale and foam spreading apparatus. |
| Task 8 | Evaluate the performance of the agents from Task 7 with the agent performance program. |
| Task 9 | Test foam formulations that performed favorably in Tasks 7 and 8 using a 28 $ft^2$ MIL SPEC test at NRL CBD. |
| Task 10 | Define the most promising formulations. Perform large-scale fire tests as appropriate. |