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**R&D PLAN FOR THE
DEVELOPMENT OF ALTERNATIVES TO AFFF**

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EXECUTIVE SUMMARY

R&D PLAN FOR THE DEVELOPMENT OF ALTERNATIVES TO AFFF

BACKGROUND

- AFFF is a vital component of Navy and DoD fire protection for rapid extinguishment of fuel pool fires when
 - Pool threatens high value assets (such as an aircraft hangar)
 - Pool fire occurs under an occupied aircraft (must maintain fuselage integrity and rescue occupants)
 - Pool fire exposes weapons to potential “cook-off” (e.g., aircraft carrier flight deck)
- Use extends into civilian sector

ISSUES

- The use of AFFF may be restricted or eliminated in the future because of environmental regulations: potential categorization as “PBT”
 - Persistent
 - Bioaccumulative
 - Toxic
 - Secondary effects to air, water, and wastewater streams
 - Foaming
 - Biochemical and Chemical Oxygen Demand
 - Aquatic Toxicity
 - Hazardous Air Pollutants

- No currently available 1:1 replacement
 - Reduced performance for equal quantities and application rates
 - Space, weight, logistics to meet performance equivalent to AFFF
- EPA “A program to seek, test, and consider long-range alternatives to current fluorosurfactant-based AFFF would be prudent”

APPROACH

- Three task areas
 - Task 1 – Assess uses, inventory, required fire protection performance, appropriate environmental criteria
 - Prioritize uses and associated R&D efforts (e.g., aircraft carrier flight decks)
- Two – Phase R&D Effort
 - Task 2 – New Agent Development (Mid-to-Long-Term)
 - Physical modeling/scaling
 - Chemical formulations
 - Task 3 – Advanced Technology Development (Short-to-Mid-Term)

Task 1 – ASSESSMENT AND PRIORITIZATION

Objective – Outline rationale plan with priorities to replace AFFF

- Plan resources working with EPA
- Identify uses and required fire performance of agent based on ORDs
 - Where AFFF performance is required

- COTS alternatives or other engineering solutions to achieve acceptable level of risk
- Review environmental regulations affecting foam use and discharge
 - Develop policies and criteria where lacking
 - Update policies and criteria which are in-place

Task 2 – NEW AGENT DEVELOPMENT (MID-TO-LONG-TERM)

Objective – Develop a new, environmentally friendly foam with performance equal to or better than AFFF

- Physical modeling/scaling – understand fundamental extinguishment mechanisms
 - Refine model
 - Complete bench-scale foam drainage testing and establish foam spread parameters
 - Verify model performance
 - Correlate with intermediate- and large- testing
 - Evaluate new formulations
- Chemical Formulations
 - Nonfluorosurfactant film-formers
 - “Biodegradable” fluorosurfactants
 - Novel, “designer” chemicals

Task 3 – ADVANCED TECHNOLOGY DEVELOPMENT

Objective – Identify and develop hardware to improve effectiveness of COTS/readily available agents

- Performance of currently available agents
 - Intermediate-scale testing with full-scale verification testing
- Improved delivery devices
 - Air aspirating vs. non-air aspirating devices
- Proportioning equipment and associated system hardware
- Scenario specific evaluations
 - Flight deck firefighting
 - Shipboard systems
 - Crash firefighting rescue vehicles
 - Hangar suppression system alternatives
 - Training
- Mitigation and remediation technologies
- Criteria, specifications and technology transfer

OUTPUT

- Rationale approach to potential AFFF phase-out and replacement development
- Scientifically based agent development
- New agent and/or optimized use of existing agents
- New delivery system hardware
- Supporting criteria, policies, and specifications

I. BACKGROUND

A. Introduction

Aqueous film forming foam (AFFF) is a vital firefighting agent for controlling and extinguishing flammable liquid fires. Within the Navy and DoD, it is especially critical for fire scenarios where life safety is threatened, where ordnance is exposed, or high value assets are threatened.

There has long been recognition that AFFF has undesirable environmental characteristics. AFFF is formulated using a number of compounds, including fluorocarbon surfactants, hydrocarbon surfactants, solvents (e.g., glycol ether), and other minor additives plus water. Solvents in the foam concentrate are on the EPA list of hazardous air pollutants. AFFF discharged to waterways may exert a high biological oxygen demand, which affects aquatic life. Concentrates exhibit, to some degree, toxicity to fish. Foam solution discharge to wastewater treatment plants may shock load or foam the aerators in the treatment process, causing the plant to violate environmental laws.

While restrictions on AFFF use and discharge have increased, the Navy and DoD have adapted to these restrictions with modified or improved equipment, techniques and procedures (albeit in some cases at a high cost). Recently, the 3M Company, a major supplier of AFFF, has announced its voluntary phase-out of production of AFFF. The fluorocarbon surfactant in their AFFF degrades to perfluorooctyl sulfonate (PFOS). PFOS has been identified by EPA as environmentally persistent, bioaccumulative, and toxic to aquatic life and animals (the degree varies by species). As a result, they may be characterized as PBT (persistent, bioaccumulative, and toxic). On October 18, 2000, the EPA proposed a Significant New Use Rule (SNUR) under section 5(a)(2) of the Toxic Substances Control Act (TSCA). The SNUR would require manufacturers and importers to notify the EPA at least 90 days prior to commencing with the manufacture or import of the fluorosurfactants that 3M has voluntarily agreed to no longer produce. Other manufacturers of AFFF use a different chemical process to produce fluorosurfactants; EPA is currently evaluating other AFFFs to determine if the by-products

exhibit characteristics similar to PFOS. In a recent presentation to the DoD Fire and Emergency Services Workgroup, the EPA noted that non-PFOS based AFFF products may be affected by ongoing EPA reviews and may be subject to future regulatory actions. EPA suggested that a program to seek, test and consider long-range alternatives to current fluorsurfactant-based AFFF would be prudent.

A preliminary review of the issues was conducted at the Naval Research Laboratory (NRL) Technology Center for Safety and Survivability [1]. This meeting, cosponsored by the Naval Facilities Engineering Command (NAVFAC) and the Naval Air Systems Command (NAVAIR), was intended to assist NAVFAC in the development of a DoD design policy for AFFF systems in aircraft hangars and facilities to minimize adverse environmental impact. This policy and supporting documentation has been drafted [2]. The meeting also was used to obtain information to assist NAVAIR in finalizing their AFFF Environmental Safety and Health Need Assessment Summary (ESH NAS) and in preparing the follow-on Development Plan. The NAS and Development Plan has been completed [3,4]. The environmental issues associated with AFFF were identified in the NAS. The Development Plan communicated and documented a course of action for resolving the issue.

B. Development and Use of AFFF

AFFF was jointly developed by the 3M Company and the Naval Research Laboratory (NRL) [5] as an improvement to protein foam. AFFFs are synthetically formed by combining fluorine-free hydrocarbon foaming compounds with highly fluorinated surfactants. When mixed with water, the resulting solution achieves the optimum surface and interfacial tension characteristics needed to produce a film, which will spread across a hydrocarbon fuel. The foam produced from this agent extinguishes fuel fires in the same water-cooling and vapor-excluding fashion as other foams (e.g., protein or fluoroprotein foam). However, the solution which results from normal drainage or foam breakdown will quickly produce an aqueous "film" which spreads rapidly and is highly stable on the liquid hydrocarbon fuel surface. It is this film formation characteristic that is the significant feature of AFFFs.

The initial draft AFFF military specification (MIL SPEC) was included in test work reported by NRL and the Naval Sea Systems Command (NAVSEA) in 1969 [6]. The current MIL SPEC, MIL-F-24385F, includes fire performance, burnback, environmental (BOD/COD and fish toxicity) and quality control requirements [7]. Vendors are required to report fluorine content; there are no minimum or maximum quantities specified. The current custodian of the MIL SPEC is NAVSEA Code 03L.

The advantage of AFFF is its quick fire knockdown characteristics. For equivalent application rates (Lpm/m^2 , gpm/ft^2), AFFF extinguishes a fire more rapidly than other foams [8]. This is particularly important for military scenarios. For example, weapons exposed to fire 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 [9, 10].

A key characteristic of AFFF is its fluidity on fuel surfaces and the associated ability to discharge the agent using "non-air aspirating" equipment. This allows the use of nozzles/equipment originally intended for use with ^{water} AFFF. An AFFF solution typically has a low expansion ratio and a relatively quick drainage rate compared to protein-based foams. The non-air aspirating discharge technique has been used advantageously to increase the spray reach of AFFF from nozzles, monitors, and turrets, compared to protein foam. Combined with the inherent fluidity of the solution, this contributes to more rapid fire extinguishment. In contrast, air-aspirated nozzles are required with protein-based foams in order to aerate the foam solution sufficiently to float it on the fuel surface. Aerated foam does not spread well and must be "painted" onto the fuel surface, which contributes to longer extinguishment times versus AFFF.

Navy aircraft carrier flight decks and weapons staging areas rely on flushdeck and deck edge non-air aspirating nozzles. The performance of AFFF through non-air aspirating nozzles facilitated the conversion of the CBR countermeasure washdown system to firefighting use. NAVFAC has recently adopted the low-level technique to protect Navy aircraft hangars [11]. The technique is not limited to the Navy alone; in tests conducted by NRL for the US Air Force,

the non-air aspirating characteristics of AFFF discharged from crash firefighting and rescue (CFR) vehicle turrets contributed significantly to improved fire extinguishing capability compared to air-aspirated devices [12]. Also, tests by the USAF demonstrated that AFFF from non-air aspirating overhead sprinklers in hangars is more effective than air-aspirated AFFF [13]. The larger droplets of non-air aspirated AFFF provide better fire plume penetration. Where overhead AFFF sprinklers are currently specified in DoD hangars, non-air aspirating sprinklers are generally installed.

The effectiveness of AFFF for crash rescue firefighting is recognized by the international aviation community. The National Fire Protection Association (NFPA) *Standard on Aircraft Rescue and Firefighting Services at Airports* (NFPA 403) [14] references the MIL SPEC where AFFF is used as the primary firefighting agent. If protein or fluoroprotein foam is used, more agent is required. This results in larger or greater numbers of CFR vehicles.

Where speed of fire extinguishment/knockdown is not critical, other techniques and test methods may be used. For example, the petrochemical and marine industries generally reference Underwriters Laboratories, Inc. (UL) 162 *Standard for Foam Equipment and Liquid Concentrates* [15] or a similar standard.

C. Objective

While there is no immediate need to eliminate AFFF from Navy use, the EPA action calls into question the long-term viability of relying on the agent. The objective of this report is to provide a preliminary outline of a comprehensive R&D program to develop environmentally acceptable alternatives to AFFF for flammable liquid firefighting. This R&D plan provides a conceptual plan of action, with supporting references, to develop replacements for AFFF. An approach is presented to address near, mid, and long term goals. This allows R&D flexibility to respond to near-term opportunities while pursuing a long-term goal of developing an environmentally friendly firefighting foam. The emphasis of this R&D plan is on Navy fire protection applications and problems. The general plan may be applicable to many other DoD and civilian applications.

II. GENERAL TECHNICAL APPROACH

A two-path technical approach is proposed to develop alternatives: New Agent Development and New Technologies Development. Prior to initiating the full R&D effort, there would be a task-planning phase (Task 1) that would produce a roadmap for the research. This planning document would include detailed NASs for each distinct need area associated with AFFF as it is used by Navy activities. Subsequently, individual development plans, revised R&D plans (e.g., updates of this report), and a Technology Transition Plan would be prepared.

Under the general task area New Agent Development (Task 2), novel chemical and physical techniques will be investigated with the goal of creating a new, environmentally friendly flammable liquid firefighting agent. Chemical formulations will be evaluated to determine if compounds can be manufactured to be biodegradable and/or nontoxic. Alternatively, other surface-tension reducing technologies will be investigated. Concurrent with the chemical formulation effort, research will be conducted on the fundamental fire extinguishing theory of foam. Because the first principles of foam fire suppression of liquid fuels has not been established, it is believed that this understanding will lead to novel chemical and chemical/physical formulations and techniques. At the very least, this effort should result in bench-scale methods that correlate with full-scale results. These bench-scale methods could then be used to evaluate agent alternatives quickly and economically, instead of relying on the full-scale tests currently required.

The New Agent Development approach represents a moderate-to-high technical risk and will require a mid-to-long term (3-6 year) effort. To reduce the technical risk, there will be a parallel effort to develop New/Advanced Technologies (Task 3). In this effort, it is assumed that alternative commercial-off-the-shelf (COTS) agents and/or hardware will become available in the near term (1-3 years) that can be used to meet the operational requirements of certain Navy and DoD users and applications. Since there is no known one-for-one agent replacement currently available, any near-term replacement strategies would require adaptation of existing systems to use available foams. In this task, new delivery systems, equipment, and devices will be developed to optimize discharge of COTS agents to compensate for lower agent performance,

or optimized delivery systems as new agents are developed. Included in this task will be the development of mitigation technologies.

III. TASK 1 – ASSESSMENT OF THE PROBLEM AND PRIORITORIZATION

The NAS and Development Plan [3,4] summarized a strategy for identifying an AFFF replacement. The NAS recommended that:

1. An accurate, quantitative definition of the problem be developed, e.g., use, quantity, and environmental thresholds;
2. Guidance be developed on the definition of “environmentally friendly”;
3. Short and long term goals be established;
4. A coordinated plan/strategy with affected services and other users be established;
5. A coordinated implementation effort with affected organizations be used to assess the state-of-the-art and provide guidance on technologies appropriate to particular uses; and
6. Identify and apply best management practices to reduce/eliminate AFFF discharges into the environment.

To a limited extent, these tasks were initiated in the Development Plan prepared by NAVAIR [4]. These tasks will continue on through initial R&D efforts.

A. Task 1.1 – Problem Definition

This task would involve the characterization of the Navy inventory, quantities, concentrations, and locations of AFFF stores. It would also include the types of use, and, along with Task 1.2, provide an assessment of compliance with environmental regulations and policies. A similar approach was used in the initial assessment of halon alternatives.

B. Task 1.2 – Environmental Analysis

Task 1.2.1 – Environmental Definition

The goal of Task 1.2.1 will be to develop appropriate definitions of “environmentally friendly” so that researchers working on long-term solutions to the problem have appropriate goals/measures of performance. The definition would be cast both in terms of current and anticipated regulations. The definition will consider: persistence; biodegradability (e.g., BOD/COD); bioaccumulation; fish, animal, and human toxicity; volatilization of organic compounds (VOCs); effects on groundwater; effects on soil; and effects on wastewater treatment facilities. The NAS, the Development Plan, and a recent regulatory review [2] will serve as the starting point of this effort.

Additionally, the regulatory environment will be monitored. Newly released data will be assessed so that future trends and requirements can be anticipated. Prioritization of R&D tasks will be modified accordingly.

Task 1.2.2 – Environmental Criteria

Based on the definitions developed in Task 1.2.1, criteria will be developed that can be incorporated into agent specifications. In particular, current MIL SPEC requirements related to BOD/COD, fish toxicity, and fluorine content will be assessed in light of the current and anticipated regulatory environment. Test and measurement work may be required to fully develop these criteria; this would be performed in a Task 2 work area as described in Section IV.

Special requirements for Navy ships, particularly related to the Uniform National Discharge Standards (UNDS), will be considered in developing environmental criteria.

C. Task 1.3 – Establish Goals and Strategy

This task will be used to develop short, medium and long term goals and strategies for implementing options. The R&D efforts outlined in this report are considered the starting point for achieving mid and long term goals.

D. Task 1.4 – Prioritization of Navy/DoD Needs

Prioritization of Navy and military needs will help establish research and technology transfer priorities. In some situations, there may be an Operational Requirements Document (ORD) that establishes the level of fire protection required for a particular use. In some cases, quantitative and/or risk-based fire hazard analysis would need to be performed to assess priorities. As a first order approximation of priorities, rapid fire extinguishment of pool fires is considered critical when: high value assets are involved; aircraft occupant safety is a factor; and, weapons are exposed to potential cook-off.

Several examples already exist for establishing the level of fire protection required for a particular situation. The aircraft carrier flight deck scenario is a high priority example. During air operations, numerous aircraft loaded with ordnance may be exposed to an incident. The scenario is one of high value, hazard, and mission importance. Weapons cook-off may occur within 60 seconds following exposure of the ordnance to fire [9]. While the use of JP5 and JP8 have reduced the rate of flame spread on liquid pools, the time between ignition of a fire and radiant heat exposure that can cause cook-off may be relatively short (e.g., seconds). The fire extinguishing agent deployment/activation time plus extinguishment time will have to be on the order of one minute as is currently required. An increase in extinguishment time (e.g., using COTS non-AFFF agents) may result in an increased probability of weapons cook-off. This also assumes that flush deck nozzles currently used to discharge AFFF can be used for the replacement agent; in the near term this is unlikely as all non-AFFFs require air aspirating nozzles. The result is that the flight deck has a high priority both in terms of continued use of AFFF and need to develop alternatives if AFFF becomes unavailable.

Similar hazard assessments have been performed for US Navy aircraft hangars [16] and for USAF hush houses [17]. These hazard assessments were used to assess risk of loss, and impact of design changes such as the type of fuel used, ignition sources, detection time, and agent extinguishing effectiveness. These assessment techniques would qualitatively be used in a first order approximation of rank order of prioritization for Navy and DoD assets. A first-cut matrix is provided in Table 1.

Table 1. US Navy
Prioritized AFFF Applications (Preliminary)

Application	Relative Priority *	Rationale for Assigned Priority
Ship – Aircraft Carrier Flight Deck	1	- Weapons cook-off potential - Need for occupant rescue - Greatest potential for immediate multi-plane incident due to crash into pack of aircraft - Minimal separation distances between A/C, between ordnance items, and between A/C and ordnance - Proximity of threat area to occupied areas - High value asset - Potential for battle damage
Ship- Helicopter Flight Deck	2	- Same as flight deck, but: - Less potential for multi-plane incident - Lower parking density (greater separation distances) - Lesser amounts of ordnance
Ship- Aircraft Carrier Hangar	2	Same threat as flight deck, but less probability for sudden multi-plane incident and less ordnance
Ship- Helicopter Hangar on Large Deck Amphib	3	Less ordnance relative to aircraft carrier hangar
Ship- Single Helo Hangar on Small Ship	4	Single aircraft - Minimal ordnance - Negligible life safety threat
Ship- Machinery Spaces	3	High value asset, but no ordnance exposure and minimal life safety threat
Shore- CFR Apparatus	2	- Need for occupant rescue - Weapon cook-off potential
Shore-Aircraft Hangar	2	- Concentration of high value assets
Shore- Hot Refueling Stations	2	- Need for occupant rescue - Weapons cook-off threat
Shore-Hush Houses, Fuel Farms, Structural Pumps	4	- Physically separated assets - Minimal life safety threat

* Priority relative to need for rapid pool fire extinguishment

The rapid fire extinguishment requirement is not limited to DoD applications. One minute fire extinguishing time is used at civilian airports to determine the required CFR assets. This is based on the response time of vehicles and onset of hazardous conditions to people inside the incident aircraft. All major US airports currently use AFFF [18]. A change from AFFF to available alternatives could result in a substantial increase in the number of CFR vehicles required at airports. In special situations, the Navy or Air Force provides protection at civilian airfields.

IV. TASK 2 - NEW AGENT DEVELOPMENT

In anticipation of increasing restrictions on production of AFFF, NRL performed a review of the different approaches that might be used to develop alternatives [19]. Two fundamental approaches were identified. One approach is to identify alternative chemicals and formulate novel foam concentrates (i.e., the "chemical approach"). 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 as AFFF.

The alternative approach (i.e., "fire extinguishment fundamentals") assumes that chemical derivatives that combine both desirable firefighting and environmental characteristics are not readily available or identifiable. The contention is that a lack of a 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 agent performance. Small-scale apparatus would be used in support of this model. Having verified the extinguishment model, approaches that provide the required physiochemical properties could be investigated. This could lead to synthesis of agents that do not rely on the surface-tension reduction characteristics (for which fluorosurfactant chemicals are vital).

Since the development of an entirely new agent is considered a moderate-to-high technical risk, it is considered prudent to pursue both approaches.

A. Task 2.1 – Fundamentals of Fire Extinguishment

The limitations of using strictly the “chemical approach” for developing improved agents have been identified [19]. The total elimination of fluorosurfactants may not 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, Hughes Associates, Inc. (HAI) and the Federal Aviation Administration (FAA) indicates that there is no direct correlation between spreading coefficient and fire extinguishment/burnback resistance of firefighting foams [20, 21]. 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.

While AFFF is a rather “mature” technology, there is surprisingly limited documentation on the mechanisms of extinguishment of film-forming foams. In order to assess possible candidate agents, it seems reasonable to identify fundamental mechanisms that result in effective fire extinguishment; this theory is not currently available [22]. An understanding of the effect of a positive spreading coefficient (which results in film formation) may allow other avenues of investigation that are not dependent on an agent having a positive spreading coefficient. If this approach is successful, non-fluorinated surfactants might then be identified.

Based on an approach that a fundamental understanding of the extinguishment mechanisms is required, the objective in this task area will be to establish the theoretical parameters for developing a candidate agent that is environmentally friendly and can extinguish two-and/or three-dimensional hydrocarbon fuel fires. By establishing the governing equations, experimental apparatus will be designed that will be used to investigate the appropriate parameters. Experimental work can then establish the correlation between the governing equations and the small-scale test apparatus, from which candidate agents may be evaluated.

The output will be an analytical method to evaluate foam agent performance and the design of appropriate apparatus to measure relevant foam parameters. General formulations of

potential non-fluorinated, "environmentally friendly" formulations will be identified. Depending on the progress in Task Area 2.2 (Chemical Formulations), agents could be tested concurrently as the model/apparatus is developed.

HAI has proposed fundamental extinguishment parameters that form the basis of this extinguishment theory as shown in Figure 1. The fuel surface temperature, T_s , is very near the boiling point of the fuel, and the fuel vapor pressure will approach atmospheric. The fuel surface is subject to heat flux from both convection and radiation, with radiation dominating. Regardless of the spreading coefficient, a thin layer of water, the film, probably cannot survive on the fuel surface. Thus, "bulk" foam is required to flow over the fuel surface, halting fuel vaporization, and extinguishing fire. The mechanism of importance is the cessation of the fuel supply by a covering layer of foam. This intuitively seems reasonable: if a film alone could extinguish a fire, there would be no need for foam. The foam would only be needed as a reservoir source, and the film would spread in all directions and extinguish the fire. It is known, however, that even AFFF must be aspirated to some degree.

In order to put the fire out, the surface of the fuel must be covered with foam. If foam is being added to a fuel surface, it will begin to spread. The area the foam will cover will be a function of time and the spreading velocity of the foam. The spreading velocity of the foam will be a function of the foam thickness, density, viscosity, and surface tensions effects. The thickness of the foam is a function of the mass and density of the foam on the surface and the area covered. The mass of foam on the surface is a function of the addition rate, the loss rate due to vaporization, and the loss rate due to drop-through. The mass of foam loss to vaporization is a function of the surface area and the heat transfer to the foam surface. The mass of foam loss to drop-through is a function of draining time, foam depth, area, and surface tension effects.

The successful development and validation of a fire extinguishment model will, at the least, be useful for general foam evaluation. This would represent a significant leap in the technology, which is now reliant on moderate- to full-scale fire testing. Complete development of the scientific model could lead to the identification of a break-through agent.

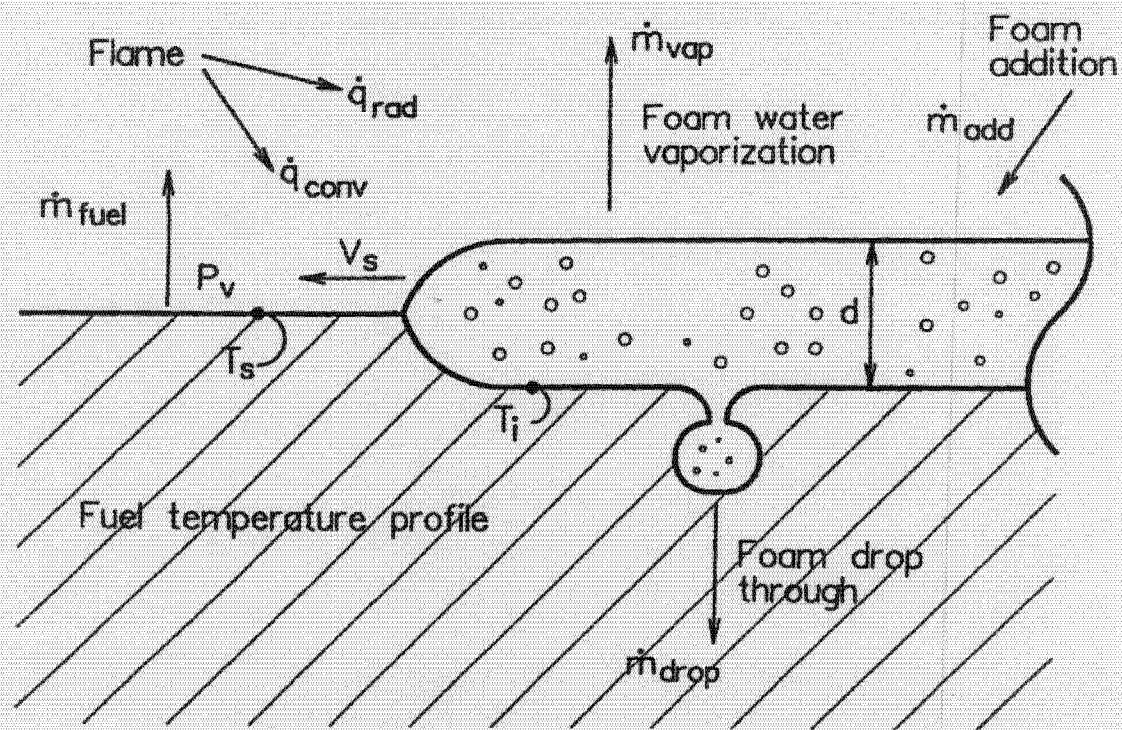


Figure 1 – Physical/chemical processes occurring with foam at the fuel surface

In a USAF-sponsored SBIR, HAI proposed the use of a fire extinguishment model to identify and evaluate new agents [23]. Preliminary results indicated that the model over-predicted the speed of a foam spread (i.e., more rapid-fire extinguishment), but the results were encouraging. NRL, HAI, and NAVAIR, through the Carrier Deck Firefighting Improvement Program, have made modest efforts to improve elements of the model [24, 25, 26] in recognition of its potential long-term utility. The following tasks would be used to validate the model, develop small/intermediate-scale apparatus, and test novel agents.

Task 2.1.1 – Model Refinement

The fire extinguishment model developed in previous efforts will be refined. A computer-based agent performance program will be written to execute calculations. A baseline fire extinguishment model will be the result. Consideration will be given to other modeling parameters such as three-dimensional fires and burnback resistance.

Task 2.1.2 – Bench-scale Apparatus

Bench-scale apparatus will be constructed. This will include apparatus for foam loss mechanisms. Experiments with existing formulations will be conducted (see Ref. [25]) for preliminary foam drainage results).

Task 2.1.3 – Foam Spread Apparatus

A small-scale foam spread apparatus will be constructed and experiments with existing formulations conducted as described in Ref. [26] (see Figure 2). The results will be used to modify the agent performance program as required. Results will be correlated with larger-scale spreading data available in the literature or conducted at a large-scale.

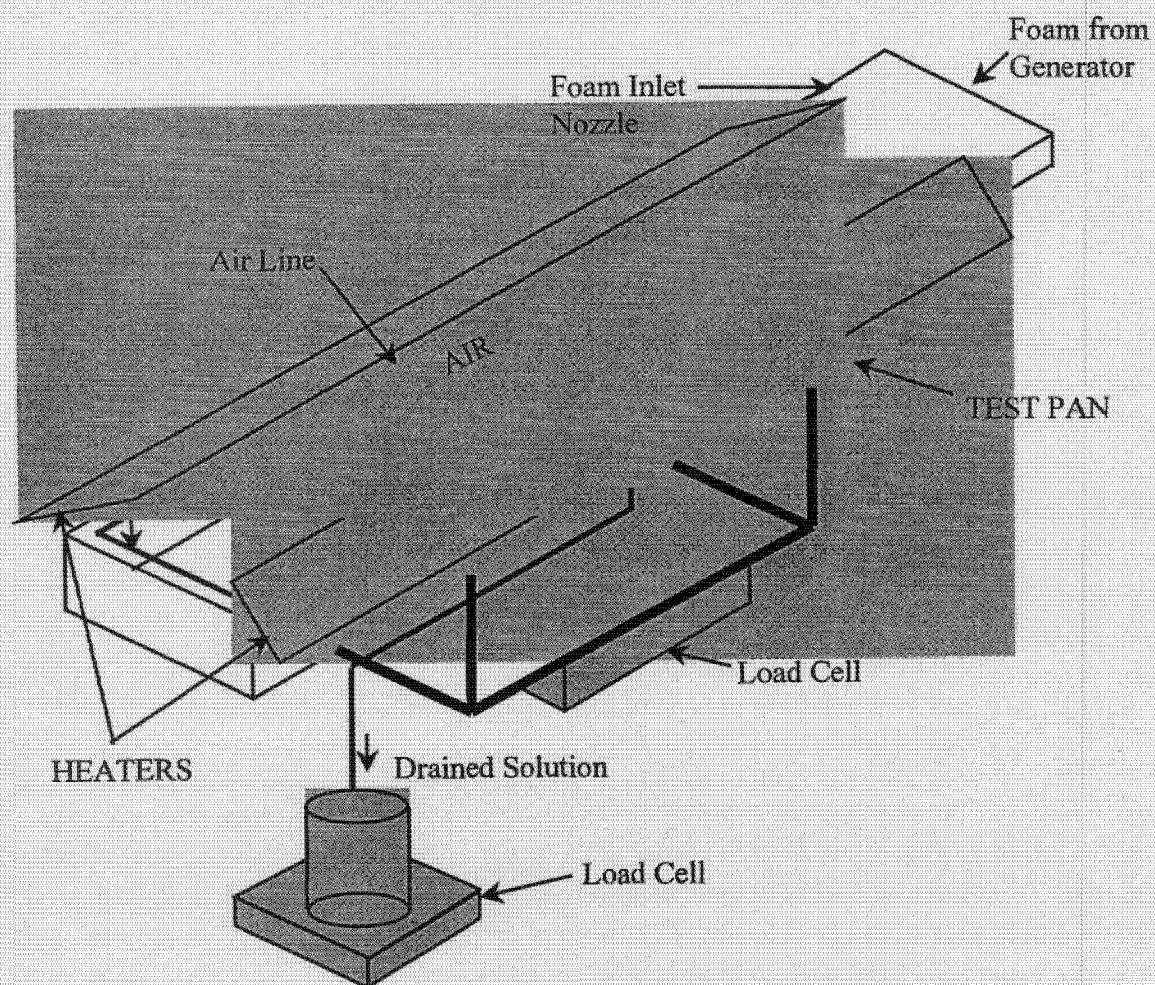


Figure 2 – Proposed small-scale foam spread apparatus

Task 2.1.4 – Agent Performance Modeling

From the agent performance program of Task 2.1.1 and data generated in Task 2.1.2 and 2.1.3, the extinguishment capabilities of foams will be calculated and compared to existing test data. New formulation work will be proposed based on the parameters that will improve performance and biodegradability of agents.

Task 2.1.5 – Integrate Environmental Criteria

Based on data/guidance from Tasks 1.2.1 and 1.2.2, criteria related to biodegradation and environmental issues related to firefighting foam and surfactants will be refined. Appropriate bench and intermediate-scale test methods and criteria will be developed and included in the overall performance approach (conducted in conjunction with Task 2.2.4).

Task 2.1.6 – Novel Agent Evaluation

From information learned in Tasks 2.1.4 and 2.1.5, various surfactants and chemicals to be evaluated in new formulations will be selected (also agents developed under Tasks 2.2.2 and 2.2.3). These surfactants and chemicals will be acquired from chemical manufacturers. Alternately, compounds that are not commercially available will be synthesized.

Task 2.1.7 – Performance of New Agents

The new firefighting foams will be formulated and their performance examined with the bench-scale drainage and foam spreading apparatus.

Task 2.1.8 – Correlation of Bench Tests With Model

The performance of the agents from Task 2.1.7 will be compared with predictions from the agent performance program developed in Task 2.1.4.

Task 2.1.9 – Intermediate-scale Fire Testing

Foam formulations that performed favorably in Tasks 2.1.7 and 2.1.8 will be fire tested using a 2.6 sq m (28 sq ft) MIL SPEC test at NRL (see Task 3.1).

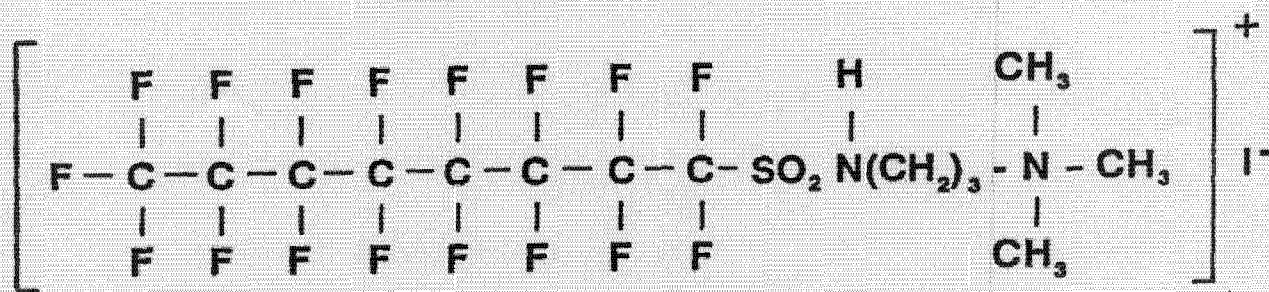
Task 2.1.10 – Define The Most Promising Formulations

Large-scale fire tests of the most promising agents will be conducted as appropriate (see Task 3.1).

B. Task 2.2 – Chemical Formulations

An understanding of foam chemical compositions is essential for evaluating candidate agents. In general, the surfactants used in aqueous foams are long chained compounds which have a hydrophobic (water repelling or water insoluble) group at one end and a hydrophilic (water soluble or water attracting) group at the other end [27]. The molecular structure of a typical AFFF fluorinated surfactant is shown in Figure 3. In this molecule, the perfluorooctyl group on the left is the hydrophobic group, while the propyltrimethylammonium group is the hydrophilic group. When these compounds are dissolved into solution with water, they will tend to group near the surface of the solution, aligned so that their hydrophobic ends are facing toward the air/solution interface. The advantage of this is that the perfluorooctyl group found in these compounds is also oleophobic (solutions containing this type of molecule are oil repelling) as well as hydrophobic.

AFFF concentrates also contain hydrocarbon surfactants. These compounds are less hydrophobic than those containing the perfluorooctyl group. However, they do provide greater stability once the solution is expanded into a foam. The net result of combining both of these compounds in an aqueous solution is the surface tension of the solution is reduced below that of water; the expanded foam produced from the solution is resistant to breakdown from heat, fuels, or dry chemical extinguishing agents; and the solution that drains out from the expanded foam is able to form a film on hydrocarbon fuels.



perfluorooctylsulfonamide - N - propyltrimethylammonium iodide

Figure 3 – Typical AFFF surfactant

The importance of both the film formation and foam bubble characteristics of AFFF, resulting from the combination of fluorocarbon and hydrocarbon surfactants, was evaluated in early work by Tuve et al. [28]. When a highly expanded, stiff formulation of AFFF was used, these experimenters found it difficult to obtain good fire extinguishment and vapor sealing characteristics. The foam resisted flow, and drainage of the aqueous solution (film) was slow. This was corrected by expanding the foam to a lesser degree. Foam agent with an expansion ratio of eight-to-one and a 25% drainage time of six minutes appeared to offer the best compromise characteristics. It provided a readily flowable foam which would seal up against obstructions, promoted the rapid formation of a surface-active film barrier on the fuel, and provided a sufficiently stable foam to resist burnback.

The composition is vital in achieving a balanced formulation using the strict "chemical" approach. Any formulation must create a stable foam bubble that will, over time, release an aqueous solution with the ability to form a vapor suppressing film on hydrocarbon fuels.

The challenge will be to identify potential formulations. A first-order requirement would be that the agent not be categorized as PBT (persistent, bioaccumulative, toxic). Additionally, fundamental measures of environmental impact contained in MIL-F-24385F must be assessed in terms of environmental definitions and goals established in Tasks 1.2.1 and 1.2.2. The current measures are chemical and biological oxygen demand (APHA Standard Methods for the Examination of Water and Waste Water) and fish toxicity (ASTM E729). These methods would be used to evaluate the environmental impact of candidate agents. Qualitative measures of reduced environmental impact might be used to make a "first cut" determination of the appropriateness of candidate agents. These qualitative measures are simply the reduction or elimination of fluorinated surfactants. It would also be desirable to reduce solvents in foam formulations. Some manufacturers add more solvent than is required to suspend solids. This additional solvent is used as a refractive index modifier, so that concentrations in proportioned solutions can be easily measured. Manufacturers have indicated that this additional solvent may contribute to reduced fire extinguishing performance.

The difficulty in modifying current formulations to address specific environmental impacts is evidenced in previous work performed by the USAF [29]. An effort was made to reduce AFFF solvents that were on the Hazardous Air Pollutant List of the 1990 Clean Air Act. The data presented indicated that the change of solvent could change other environmental factors such as BOD/COD and fish toxicity.

Work is ongoing in the private sector to reduce or eliminate fluorosurfactant compounds. NRL recently tested and qualified a product for the MIL SPEC qualified products list (QPL) that is reported to have reduced PFOS [30].

Task 2.2.1 – Literature Search and Vendor Survey

A review of the chemical literature of foam – based fire suppression agents would be performed. Additionally, vendors would be solicited for ideas and potential formulations.

Task 2.2.2 – Alternative Surfactants

Previous work by NRL and Hughes Associates, Inc. has identified potential surfactant combinations that may be worthy of investigating [19]. One potential group is the organosilicons, including cationic, anionic, and amphoteric siloxane surfactants. Synergistic behavior may result between fluorosurfactant and organic surfactants, which may result in a substantial decrease in required fluorosurfactant. Nonionic, low molecular weight surfactants from cosmetic-type applications may be used for interfacial tension reduction. These nontoxic, biodegradable materials will have to be combined with a suitable temperature-resistant foamer (e.g., lauryl sulfate matched with methoxy triglycol using polyethyleneoxide as the stabilizer). Alternative compounds that may be effective will be identified based on the environmental criteria established in Task 1.2.2.

Task 2.2.3 – Biodegradable Fluorosurfactants

Some researchers believe that fluorocarbon backbones can be synthesized to biodegrade. Novel techniques to implement this approach will be investigated.

Task 2.2.4 – Measurement Techniques and Criteria

New or modified measurement techniques may be required as new agents are developed and then fielded. During the development stage, new or more sensitive measuring techniques may be required to identify newly synthesized chemicals (it should be noted that the identification of environmental issues associated with fluorosurfactants is directly related to improved fluoronated by-product measurement techniques).

As a new agent is transferred to actual use, field measurement methods may need to be revised. For example, solvents such as butyl carbitol are currently used by some manufacturers as a refractive index modifier in AFFF. The refractive index of solutions is used to measure concentration. As noted, solvents may affect the fire extinguishing performance of the foam. Different chemical tracers may be used to track chemical concentration in a new agent. Alternately, new measurement techniques may be required to identify newly synthesized chemicals. Ultimately, this may lead to the elimination of refractive index requirements in the MIL SPEC.

This task will be used to develop and improve on measurement techniques used for new agent identification and assessment, including required environmental criteria that can be translated into updated MIL SPEC requirements.

Task 2.2.5 – Marketplace Assessment

Production costs of potential new agents, particularly for vital, high priority Navy and DoD applications, will be assessed and compared to limits in the marketplace.

Task 2.2.6 – Fire Testing

Chemical formulations developed under Task Area 2.2 will be assessed and tested using one of several approaches. If the bench-scale test apparatus and modeling techniques developed in Task Area 2.1 are available, agents will be assessed using those techniques. Otherwise,

intermediate-scale testing that correlates with full-scale performance will be used to assess fire extinguishment and burnback performance (See Task 3.1 for description of techniques).

V. TASK 3 – NEW TECHNOLOGIES

The Task 2 work areas have a moderate-to-high technical risk in terms of developing a new agent. Foam technology exists that does not require fluorocarbon surfactants, e.g., protein foam. The limitations of protein foam are well known. Alternatively, “floating foam” technology (i.e., not a film-former) may be developed to eliminate some of the undesirable characteristics of protein foam, e.g., limited shelf life. However, there still may be a requirement to aspirate the alternative agent. This inherently limits its utility and effectiveness. While aspirated or “floating foam” can be fielded with current technology, there are significant space, weight, and energy costs associated with providing protection equivalent to AFFF. In this task area, near and longer term protection needs will be addressed using new/advanced hardware and alternative agent technology that is currently available or will be available in the near term.

Associated with this task is near-term testing of available COTS agents for potential immediate application to particular use scenarios. For example, there may be available agents *that* can be combined with other loss control features to provide adequate protection. Test and evaluation scaling methods described in Task 3.1 will be used for these near-term assessments. Technologies needed to support the COTS foam approach will also be assessed.

This task area will also support technology transfer for any system/hardware requirements resulting from the development of a new agent in Task 2.

A. Task 3.1 – Current Agent State-of-the-Art Fire Testing

As a baseline of current performance, tests will be conducted of all available AFFFs and vendor proposed “environmentally friendly” agents to determine current foam technology performance. MIL SPEC 2.6 and 4.6 sq m (28 and 50 sq ft) fire testing will be used in this assessment. HAI has demonstrated the scaling relationship between these tests and full-scale performance up to 929 sq m (10,000 sq ft) [31]. The small tests are generally more challenging

than the larger tests, i.e., a ^{lower} ~~higher~~ fire extinguishment application density (l/sq m, gal/sq ft) is required for the 2.6 and 4.6 sq m (28-50 sq ft) test fires. This provides a factor of safety for correlating small- and large-scale results, and assures that successful extinguishment in small-scale will translate to either quicker extinguishment or extinguishment with less agent in full-scale.

The correlations described above are for "moving nozzle" scenarios, e.g., CFR or sweeping monitor nozzle situations. Intermediate-scale testing with fixed overhead nozzles, e.g., sprinklers, has also been performed, although not to the extent of "moving nozzle" tests. HAI/NRL used intermediate overhead nozzle testing with a 4.6 sq m (50 sq ft) pan fire as a precursor to large-scale hangar sprinkler tests, with reasonable success [32]. The UL 162 sprinkler test method, using four nozzles and a 9.3 sq m (100 sq ft) test pan, may also be used. While the correlations between overhead nozzle intermediate-scale tests and large-scale results are not as well established as with the "moving nozzle" tests, the available data suggest that these methods are adequate for reduced-scale screening tests prior to large-scale testing.

Large-scale testing on the order of 93-930 sq m (1000-10,000 sq ft) will be performed as "verification" tests at indoor or outdoor test facilities as described in Section VIII.

B. Task 3.2 – Improved Delivery Devices

Two approaches will be pursued in this task: low energy aeration to reduce stream projection losses, and high energy discharge devices to increase stream projection. Using the first approach, methods to aerate foam without energy loss will be investigated. Examples include the following:

- Gas injection into the foam solution, including use of foam with water mist systems; and
- Chemically generated aeration after foam is projected to fuel surface

The second approach would be an investigation of monitor nozzle and articulating boom technology to determine if foam, aerated using traditional techniques, can be projected using articulating boom or other novel techniques.

C. Task 3.3 – Proportioning Equipment

New agents may require proportioning and system storage/delivery modifications requiring engineering development. This work will be performed in this task area.

D. Task 3.4 – Scenario – Specific Evaluations

Specific Navy uses of AFFF will be evaluated in terms of agent and hardware needs. This task will be performed based on the priorities established in Task 1.4. The following task areas are anticipated.

Task 3.4.1 – Flight Deck Firefighting

The delivery and discharge of foam to aircraft carrier and air-capable ship flight decks will be evaluated. Monitors and turrets may be considered. Automated techniques, e.g., articulating boom technology, may be applicable. The evaluation will be performed considering proposed reduced damage control manning for flight deck operations. Systems evaluation and manned firefighting doctrine and tactics testing will be performed to verify performance.

Task 3.4.2 – Shipboard Systems

Shipboard systems, such as bilge sprinklers, will be considered. Technologies evaluated for this scenario will likely focus on proportioning and agent storage considerations.

Task 3.4.3 – Crash Firefighting Rescue Vehicles

Technology evaluations for the flight line/airport CFR use scenario will focus on monitor nozzle discharge techniques, proportioning, and storage requirements.

Task 3.4.4 – Hangar Fire Suppression System Alternatives

Hangar fire protection scenarios offer unique opportunities to investigate alternative techniques. High expansion foam is an alternative, but its equivalence to AFFF protection has not been quantified under all military conditions. The use of existing air aspirating and non-air aspirating sprinklers using COTS foam will be quantified to identify differences in performance.

Task 3.4.5 – Training

Training alternatives, both “live fire” and simulated, will be considered. Extension/improvement of current “training foams” [33] will be considered. Advanced simulations, perhaps utilizing virtual reality (VR) techniques, will be considered. Training alternatives which do not involve live fire scenarios will be evaluated against actual fires to verify adequacy of the simulation.

E. Task 3.5 – Mitigation and Remediation Technologies

The final disposition of foam effluent is typically included in any environmental assessment. Techniques and technologies that can be used to mitigate and remediate foam waste will be investigated in this task. There are different methods to mitigate AFFF waste. AFFF waste can be sequestered in a holding area where it can biodegrade to acceptable BOD levels. Anti-foaming agents or metering techniques may be required before it is discharged for treatment at a wastewater treatment plant: NRL and HAI have demonstrated that very low concentrations of AFFF will cause foaming [34]:

Other techniques include anaerobic fluidized bed reactor (FBR) systems to accelerate biodegradation. Air bubbling and air-sparged hydrocyclone techniques that reduce the amount of foaming have been demonstrated. Systems which can be installed at training facilities or on Navy ships will be considered. Chemical approaches will also be considered. For example, foams may be synthesized that fail to aerate within some time period after discharge.

F. Task 3.6 – Develop Near-Term COTS Foam Specification and Revised MIL SPEC

Criteria and specifications must be developed for near-term COTS and newly developed agents. These specifications will include fire extinguishment, burnback, environmental, hardware, and logistics requirements similar in scope to the current MIL SPEC. This may take the form of an amendment to the MIL SPEC, or, in the case of a totally new agent, a complete rewrite. The specifications may be “commercialized” following Navy/DoD policy; for example, the specification may ultimately reside as an NFPA or similar standard.

VI. OUTPUT

The output of the project will include:

- A rationale approach to potential AFFF phase-out and replacement development
- Scientifically based agent development
- New agent(s) and/or optimized use of existing agents
- New delivery system hardware
- Supporting criteria, policies and specifications

VII. SCHEDULE

The proposed schedule for the R&D project is shown in Figure 4. Interaction between tasks will occur to a greater degree than shown in Figure 4. Future updates of this plan will provide greater detail on task interaction.

VIII. LABORATORY CAPABILITIES

A. HAI

HAI has a 120 m² (12,000 sq ft) fire test laboratory in their Baltimore, MD headquarters. HAI has a wide range of instrumentation and equipment for conducting combustion and fire related experiments such as heaters, burners, flow meters, heat flux gauges, pressure transducers, PID controllers, etc. Other instrumentation related to chemical species measurements include standard gas analyzers, fourier transform infrared analyzer (FTIR), grab sample equipment and specific analyzers for replacement suppression agents.

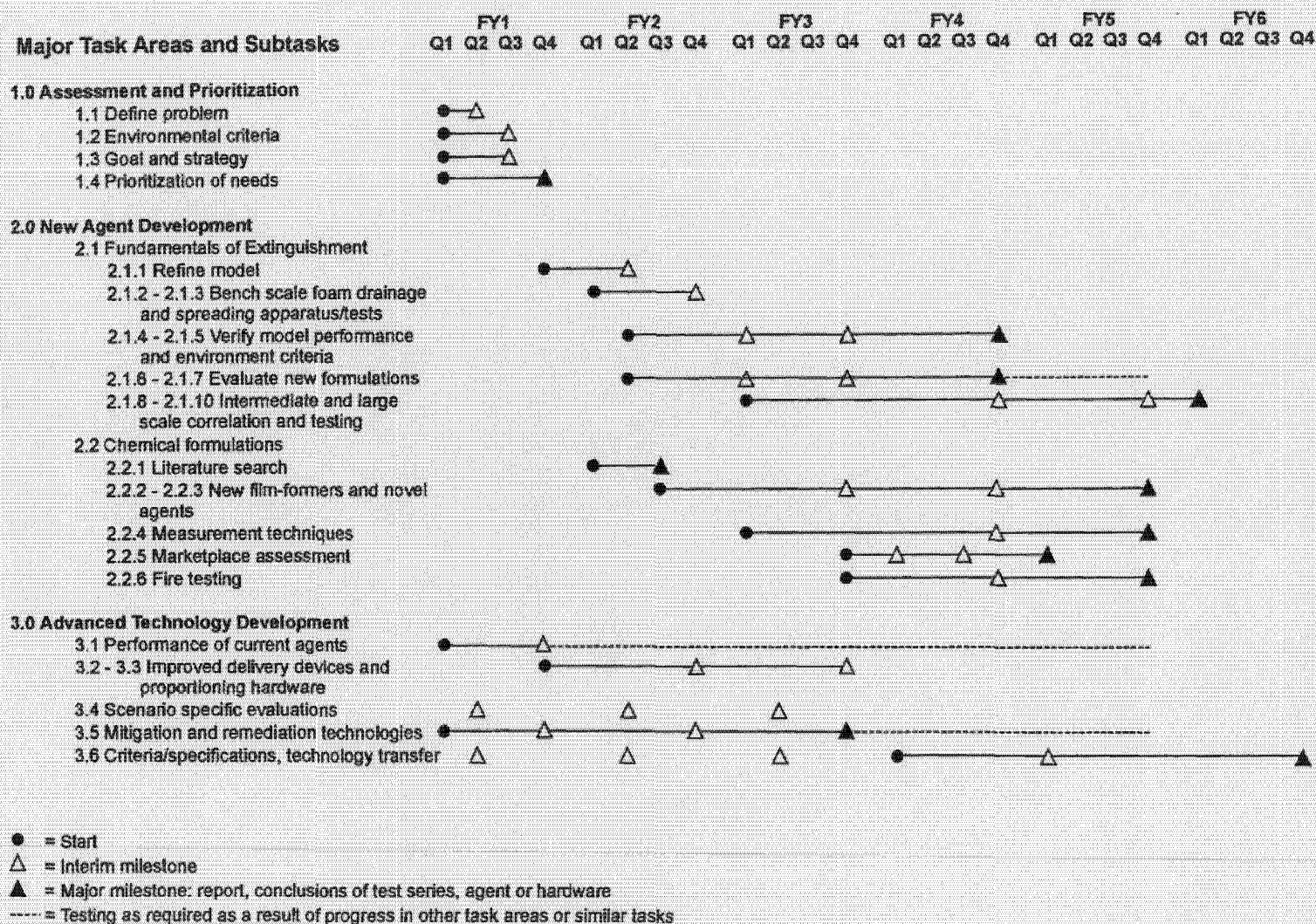


Figure 4 – Schedule

A radiant panel apparatus, used in prior experiments [25], is available for use to continue the foam modeling experimental work. HAI has a foam mixing apparatus to create foams having different expansion and drainage characteristics. This includes the standard 2 gpm MIL SPEC foam nozzle. Orifices are available for this nozzle to create flow rates of 2-6 gpm so that MIL SPEC and UL Standard 162 expansion and drainage tests can be performed.

B. NRL

The Navy uses the NRL Chesapeake Beach Detachment (CBD) to conduct MIL SPEC experimental and qualification testing. Two indoor test facilities are available to conduct 28 sq ft fire tests. Fifty square foot fire tests will be conducted outdoors on a concrete test pad. Associated physical/chemical properties tests needed for the MIL SPEC, including DuNoys tensiometer (to determine spreading coefficient in accordance with ASTM 1331), corrosion coupon apparatus, and ovens for accelerated aging, are available.

C. NAWCWD

The Naval Air Weapons Center China Lake facility (NAWCWD) will be used for large-scale testing. Two firefighting pads are available, including the 1022 sq m (11,000 sq ft) "mini-deck" firefighting facility used to develop much of the AFFF flight deck firefighting technologies. Additionally, the running fuel fire debris pile used to assess combined and three-dimensional firefighting agents is available. Reference [9] describes these facilities.

D. OTHER FACILITIES

Other small- and large-scale environmental and fire test facilities may be used during the research project. For example, large-scale indoor fire test facilities at Underwriters Laboratories Inc., Factory Mutual, or Southwest Research Institute may be utilized. Large outdoor fire research/training pads, such as that at Tyndall Air Force Base, may also be used.

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