Fire Fighting Foams:

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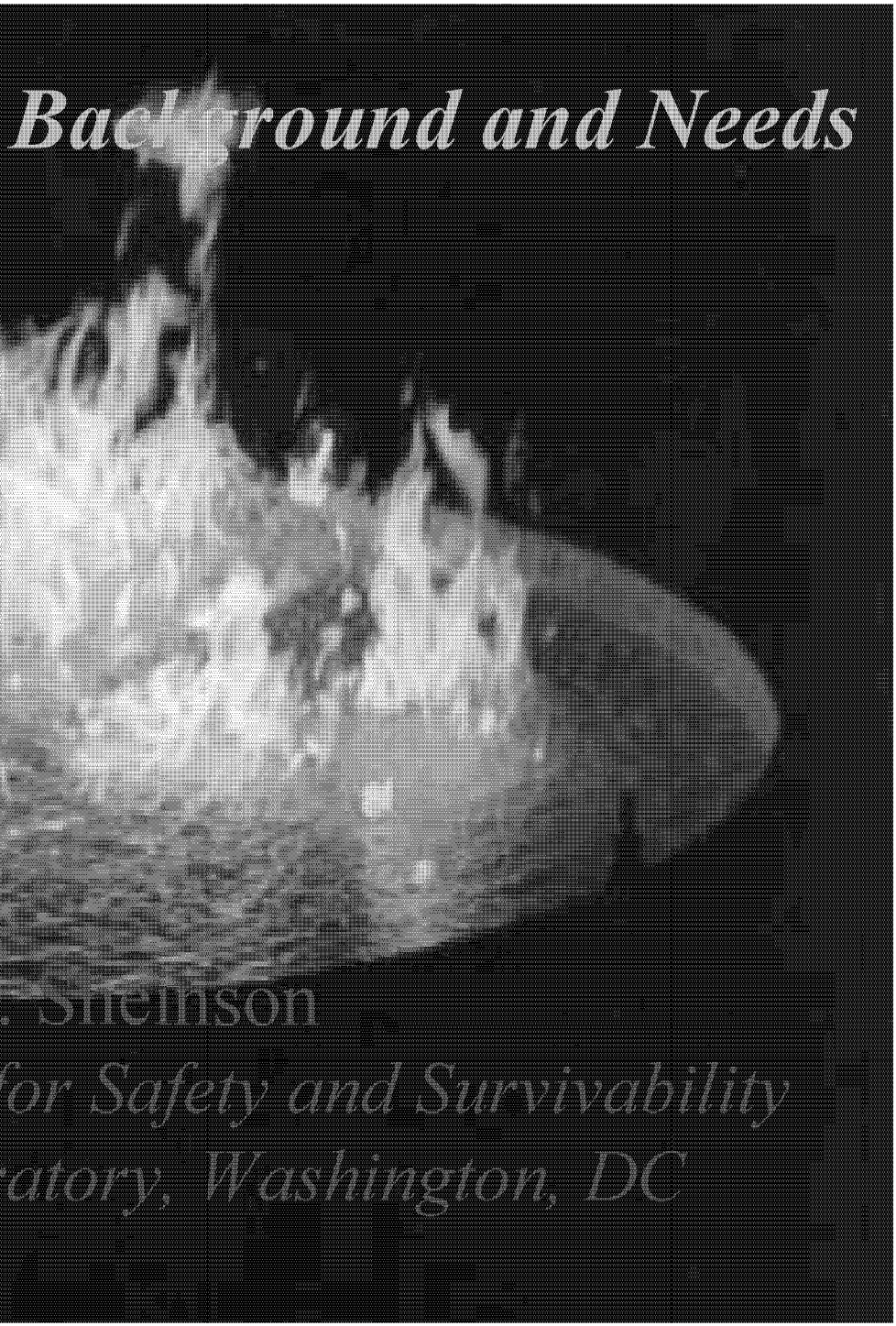
Background and Needs



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for Safety and Survivability

ratory, Washington, DC

What kinda foam do you want with those fries?

There are a variety of needs and a variety of standards

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Foam Flavors

Protein: "Processed" waste stream proteins

FP: FluoroProtein, i.e., protein + fluorosurfactant

FFFP: Film Forming FluoroProtein

AFFF: Aqueous Film Forming Foam

MilSpec AFFF: AFFF passing DoD qualification testing

AR (Alcohol Resistant) Variants

Sticky foams – 3-D capability for Class A fire scenarios

AFFF Importance to US Navy (Aircraft)

Ship – Aircraft Carrier Flight Deck	1*	Weapons cook-off potential Need for occupant rescue Greatest potential for immediate multi-plane incident from 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), and lesser amounts of ordnance
Ship- Aircraft Carrier Hangar & Amphib Well Deck	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- Machinery Spaces	3	High value asset. But no ordnance exposure and minimal life safety threat
Ship- Single Helo Hangar on Small Ship	4	Single aircraft, minimal ordnance, negligible 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, weapon cook-off potential
Shore- Hush Houses, Fuel Farms, Structural Pumpers	4	Physically separated assets, minimal life safety threat

* Priority relative to need for rapid pool fire extinguishment

Background and Basics

- AFFF developed in the early 1960's by NRL and 3M to provide better fire protection than was provided by protein foam
- Class B (liquid fuel) fires in "pools," 2-D, not 3-D
- Hydrocarbon foaming agents
- Fluorinated surfactant (required by MilSpec)
- Specification includes a number of performance and physical property requirements

The Need for AFFF

- Many applications worldwide depend on the capabilities of the US military developed AFFF
- The US military performance requirements for life safety and critical national security asset protection cannot be reduced
- Many worldwide applications, as well as some military applications, may be able to be satisfied with other than MilSpec qualified products, depending on threat scenario specific protection requirements

Background

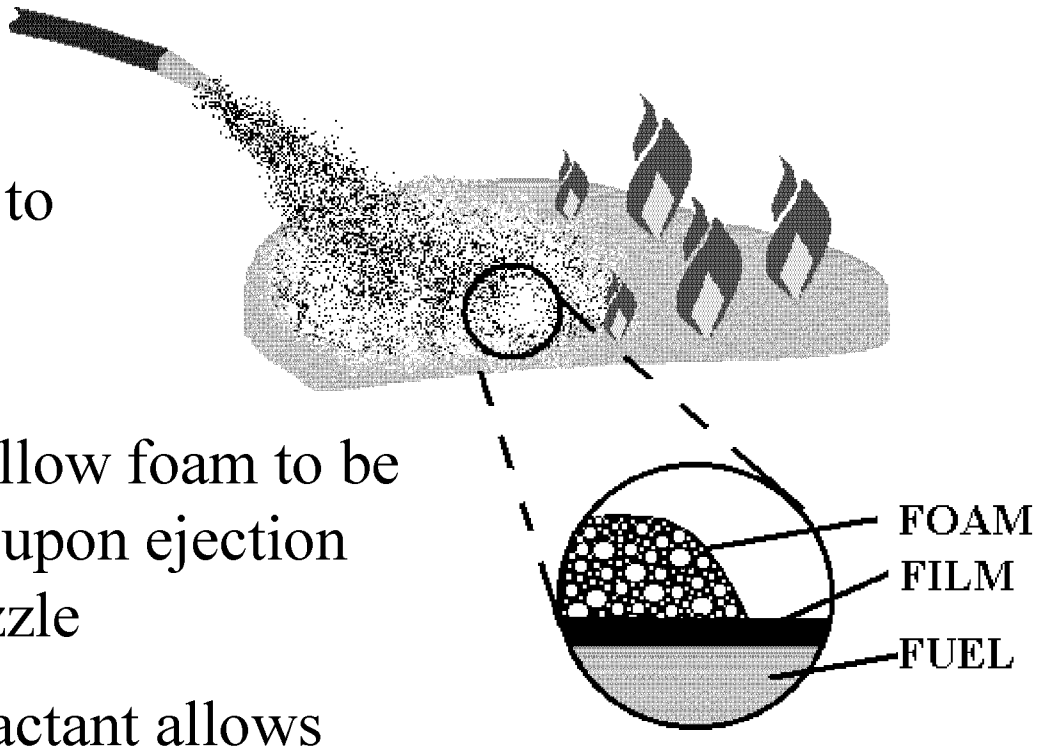
- AFFF is a vital component of Navy and DoD fire protection for rapid extinguishment of fuel pool fires when a
  - Pool fire threatens high value assets (such as multiple aircraft and / or aircraft carrier)
  - Pool fire occurs under an occupied aircraft (must maintain fuselage integrity and rescue occupants)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

Issues

- The use of AFFF in the future may become more restricted or some uses eliminated because of environmental regulations: potential categorization as "PBT"
  - Persistent
  - Bio-accumulative
  - Toxic
  - Effects to air, water, and wastewater streams
    - Foaming
    - Biochemical and Chemical Oxygen Demand
    - Aquatic Toxicity
    - Hazardous Air Pollutants

Surfactant Role in AFFF

Purpose of surfactants is to reduce surface tension



Fluorinated surfactants allow foam to be produced spontaneously upon ejection from a non-aspirated nozzle

Even without foam, surfactant allows aqueous layer to cover fuel, even though the water is more dense, and has higher intrinsic surface tension.

What are surfactants?

- Surfactant = SURFace ACTive AgeNT
- Compound properties
  - Soluble (usually in water, but also oils and other organic solvents)
  - Changes surface activities between materials
    - Surface tension
    - Interfacial tension
- Most common examples are soaps and detergents

Why do we need surfactants?

- Surfactants can accomplish many small-scale tasks due to their unique structure and physical properties
- Surfactants are used for
  - Drug Delivery
  - Textiles and Cleaning
  - Electronics Substrates
  - Film Handling
  - Agriculture
  - Mining
  - Fire Protection

Why are surfactants so special?

- Present in very small quantities, but have significant effect on properties of the bulk
- Surfactant theory involves both transport and thermodynamic considerations
- Especially important in situations where phase boundary area is large relative to system volume (e.g. films, puddles, bubbles)
- Many surfactants of different structures can produce similar physico-chemical effects

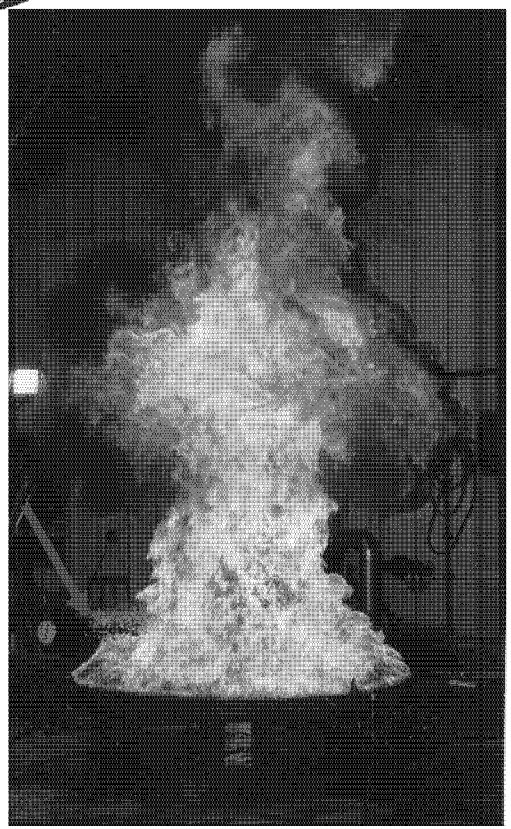
AFFF Surfactants

- Are long chained with hydrophobic and hydrophilic ends
- Reduce water surface tension
- Reduce hydrocarbon surface tension
- Effective in presence of dry chemical agents
- Solution that drains out from foam is film-forming on hydrocarbon fuels

What's In A Name?

- US DoD AFFF MilSpec requires the use of a fluorinated surfactant
- PFAS Main AFFF example is PFOS (8 carbon skeleton) from 3M
  - Persistent, Bioaccumulative and Toxic (PBT)
  - Manufacturer phase out
  - EPA SNUR ban future manufacture and import.
- PFAA E.g., PFOA – C-8, PFHxA – C-6 (Not used in manufacture of AFFF)
  - Similar concerns and regulatory review as PFOS
- Telomerization Process Used to make fluorosurfactants for AFFF
  - Usually C-6; No / Little PFOA or PFOS (But C-6 may degrade to PFHxA)
  - Persistent
  - Industry and regulatory review of bio-accumulation and toxicity of perfluorosurfactant telomers and degradation products

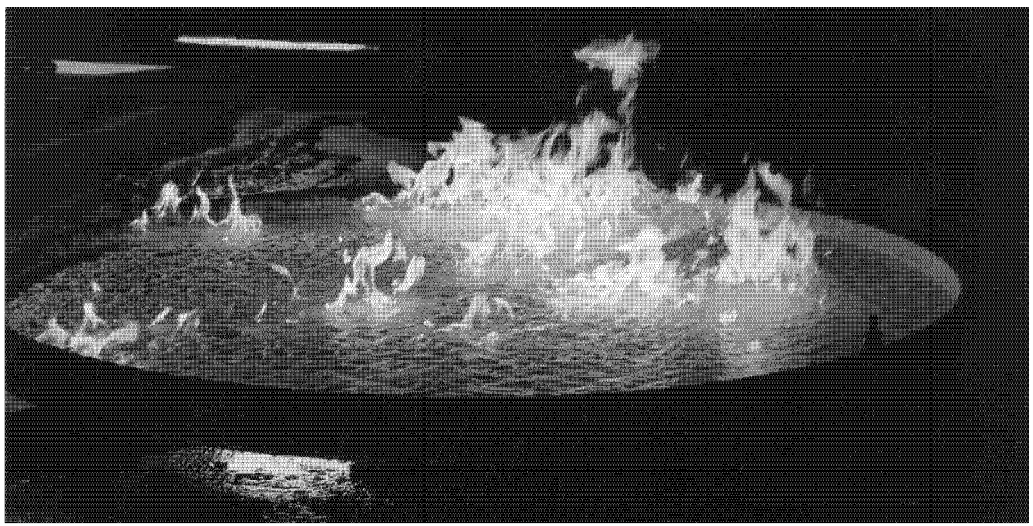
Fire Performance Evaluation



Applying AFFF

Photos show qualification testing of AFFF in 28 ft^2 gasoline pan fire. Requirement for extinguishment is 30 seconds.

Other tests include salt water dilution of concentrate, ½ strength solution, simulated aging, and 50 ft^2 pan fire.



Almost Extinguished

AFFF Performance

- Prevents radiation from reaching fuel
- Retards pyrolyzates and fuel from reaching flame
- Absorbs heat
- Cools fuel
- Rapidly spreads, covers and reseals fuel surface

Key Properties

- Surface Tension
- Viscosity
- Foam quality
  - Drainage
  - Thermal stability
- Film fire protection

Understanding Aqueous Film Forming Foam

- Simplistic model uses two interacting fluids
  - AFFF is less dense and more viscous
  - Use oil over water principles
- Very simplistic model does not accurately determine spreading
- Reality: non-Newtonian behavior greatly complicates modeling
- Surfactant diffusion, adsorption, and solubility further complicates modeling
- Need model complicated enough to capture essential behaviors, but still manageable

MilSpec AFFF Capabilities

- No other agent can equal its ability to rapidly extinguish a pool fire
  - Rapidly spreads, covers and reseals fuel surface
- Vital to confronting:
  - Potential ordnance cook-off
  - Pool fires threatening aircraft crew
  - Threat to concentrated high value assets

We **NEED** effective foam, and

It must be **environmentally acceptable**

AFFF Uses

Rapid extinguishment of pool fires

- Flight decks, bilge spaces of Halon (and Halon replacement) protected areas
- Flight lines
- Facilities
- Training

AFFF used for a hierarchy of needs, from **Critical**, to lower threat level applications

Extinguishment with AFFF

- The foam blanket covers the fuel surface
  - Prevent radiation from reaching fuel
  - Prevent pyrolyzates from reaching flame
- Water drains out and cools the fuel
- Film self-seals the fuel surface, eases foam spread
- Functions with salt or fresh water
- Does not work well for three-dimensional fires

Fate of Surfactants in AFFF

- Biodegradation
  - Straight-chain hydrophobic groups decompose better than branched-chain or ring-containing groups, although they are less soluble in water and/or hydrocarbons than branched chains or rings
  - Fluorocarbon chains are resistant to biodegradation even when straight

Wastewater Treatment Plant

- Generally recognized that the water reaching the treatment plant cannot have a greater concentration of AFFF than 1700 ppm*
- 6-million gallons per day plant can handle 7 gpm of solution.
  - Medium Sized City
  - Can take days or weeks to process foam depending on the discharge.

*Department of the Army Technical Letter No. 1110-3-481, 23 May 1997

Operational Restrictions

- Limitations already exist
- Training and ship testing protocols have been changed in response
- Restrictive regulations continue to evolve (UNDS)
- Need to anticipate impact of future regulations

Where Are We?

Research on firefighting foams is ongoing

Only recently has literature become available for review to begin to fully understand surfactant solution properties when spreading on liquid substrates

Some avenues of research are only now beginning to be possible

Environmentally Friendly Foams

- Physical modeling/scaling - understand fundamental extinguishment mechanisms
  - Create, refine models
  - Verify model performance
  - Correlate with intermediate and large scale testing
  - Evaluate new formulations
- Chemical formulations
  - Non-fluorosurfactant film-formers
  - "Biodegradable" fluorosurfactants
  - Novel, "designer" chemicals

Conclusions

- AFFF is a fast and efficient way to extinguish two-dimensional liquid hydrocarbon pool fires
- DoD, especially US Navy, has long record of being proactive in protecting the environment
- Continuing accumulation of information on harmful effects and international concerns and restrictions make it prudent to explore future options
- Better definition of user needs, as opposed to desires, will enable more options to be considered
- Improved understanding of AFFF action will lead to design of less environmentally threatening products, while maintaining required fire protection capabilities

Onward for Environmentally Friendly Fire Fighting Foams

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Composition and Proposed Film Structure of AFFF

AFFF composition is a complicated proprietary mixture unique to each manufacturer. Concentrate is mostly water, glycol ethers to increase viscosity => extend foam lifetime. Contains both fluorocarbon and hydrocarbon surfactants.

Chemical composition of 3M AFFF concentrate

chemical name	percent of total composition
water	69.0–71.0
diethylene glycol butyl ether (butyl carbitol)	20.0
amphoteric fluoroalkylamide derivative	1–5
alkyl sulfate salts	1.0–5.0
perfluoroalkyl sulfonate salts	0.5–1.5
triethanolamine	0.5–1.5
tolyltriazole (corrosion inhibitor)	0.05

Fluorocarbon surfactant thought to predominate at water/air interface, hydrocarbon surfactant at water/fuel interface.