Replacement of Fluorinated Aqueous Fire-Fighting Foams (AFFF)

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What is AFFF

- Aqueous Fire Fighting Foam (AFFF)
  - Also referred to as a Film Forming Foam (FFF)

- Used for Class B Liquid fuel Fires
    - Gasoline
    - Diesel/Jet Fuels

- Contains Fluorocarbon Surfactants
  - Per- and Polyfluoroalkyl Substances (PFAS)
  - Perfluorooctanesulfonic sulfonate (PFOS)
  - Perflouroalkane sulfonates (PFSAs)
  - The foam forms a film that suppresses fire.

- Most foam manufacturers have now transitioned to the production of only short-chain (C6) fluorotelomer-based fluorosurfactants.
  - These are still PFAS!

The Problem with AFFF

- It contains Per- and Polyfluoroalkyl Substances (PFAS)
  - Persistent in the environment
  - Bioaccumulates
  - Human and Environmental Health Impacts

Stakeholders

- Federal Aviation Administration
- U.S. Department of Defense
  - Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP)
- Fire Service
  - Local fire departments
- Petroleum Industry
  - Large Atmospheric Storage Tank Fires (LASTFIRE)
  - American Petroleum Institute

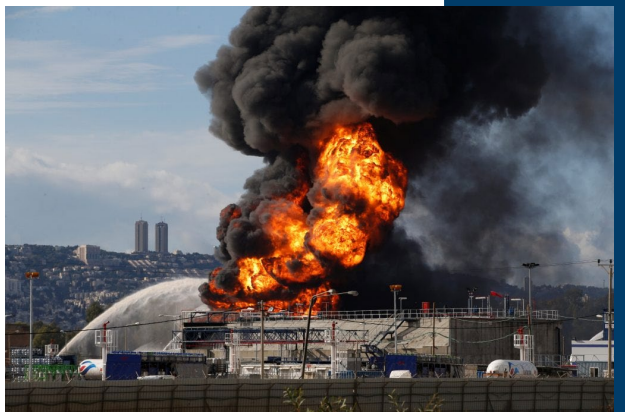

Image Links
https://tinyurl.com/2hx64kha
https://www.strategypage.com/military_photos/military_photos_2010032023550.aspx

Development

- Pre-AFFF Days (1940s to 1960s)
  - Primary agent for flammable liquid fire fighting was Protein Foam
    - Derived from the hydrolysis of protein products
    - Delivered as aspirated foam
    - Had to cover entire top surface of fuel – no film formation
- Fluorocarbon Surfactants (1962)
  - Surfactants could form a coating that was “grease and oil resistant”
  - Can they be used as fire extinguishing agents for flammable liquid fires?
- Introduction of Hybrid AFFFs (1970s)
  - Film Forming Fluoroprotein
  - Alcohol Type AFFF (needed for alcohol and polar solvents)
- 1980s and 1990s
  - AFFF incorporated in national and international standards
  - Mil Spec expanded to include Type 3 (3 %) AFFF
  - Widespread deployment

Darwin, Robert L., “ 1960 – 2020”, Jensen Hughes, presented at the NFPA Research Foundation Workshop, FireFighting Foams: Fire Service Roadmap, October 12-14,2021

Current MIL-PRF-24385F Fire Performance Testing Requirements

- Uses both a 28 square foot (6-foot diameter) and 50 square foot (8-foot diameter) pan
  - A shallow layer of water is placed in the pan to protect the pan bottom and complete coverage of the area with fuel.
  - Fuel is added (10 gallons in a 28 ft^2 pan, and 15 gallons in a 50 ft^2 pan)
  - 2 Gallon per minute foam flow rate
- Test 1: Extinguishment Test
  - Fuel allowed to burn freely for 10 seconds
  - Fire attacked and extinguished in an expeditious manner.
  - Measure the time to extinguish the fire.
  - Foam applied for a total of 90 seconds.
- Test 2: Burnback Test
  - Place a 1-foot diameter pan containing 1 gallon of ignited gasoline in the test pan within 60 seconds of completion of foam application and start timer.
  - Remove the burn back pan when the fire has spread outside the pan
  - Determine the time for fire to spread to 25 percent of the larger pan.

Other Current MIL-PRF-24385F Testing Requirements

- Two Classes
  - Type 3 - To be used as three parts concentrate to ninety-seven parts water by volume solution.
  - Type 6 - To be used as six parts concentrate to ninety-four parts water by volume solution
- Refractive Index (minimum)
- Hydrogen Ion Concentration (pH)
- Viscosity: Maximum at 5 C and Minimum at 25C
- Spreading Coefficient – based surface and interface tensions of the foam to cyclohexane
- Foamability
  - Foam Expansion
  - Foam drainage time
- Perfluorooctanoic acid (PFOA) content, 800 ppb, maximum
- Perfluorooctane Sulfonate (PFOS) content, 800 ppb, maximum
- Corrosion Rate
- Environmental Impact
  - 20-day Biochemical Oxygen Demand (BOD)
  - Chemical Oxygen Demand (COD)
  - Killiefish (Fundulus herteroclitus) LC_{50}

Historical Review of the AFFF Military Performance Specification

Specification Version	Specification Date	Fire Area (ft^2)	Flow Rate (gpm)	Extinguishment Time (sec)	Burnback Time (sec)
24385	11/21/1969	28	2	84	240
Amendment 3	7/7/1971	28	2	65	240
24385A	5/2/1977	28	2	45	320
24385B	5/25/1978	28	2	30	320
24385C	3/12/1981	28	2	30	360

John Farley & Stanley Karwoski, WP20-5373: Fluorine-Free Military Specification Development

Recognized Advantages

- Enhanced fire fighting effectiveness
- Fire Prevention: protective film on fuel spills
- Long term stability/shelf life
- Relatively low corrosion on metals
- Ease of proportioning
- Inter-agent compatibility (if Mil Spec)
- No need for air-aspirated nozzles

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2020 National Defense Appropriations Act (NDAA)

SEC. 322. REPLACEMENT OF FLUORINATED AQUEOUS FILM-FORMING FOAM WITH FLUORINE-FREE FIRE-FIGHTING AGENT.

(a) USE OF FLUORINE-FREE FOAM AT MILITARY INSTALLATIONS.

(1) MILITARY SPECIFICATION.—Not later than January 31, 2023, the Secretary of the Navy shall publish a military specification for a fluorine-free fire-fighting agent for use at all military installations and ensure that such agent is available for use by not later than October 1, 2023.

(b) LIMITATION.—No amount authorized to be appropriated or otherwise made available for the Department of Defense may be obligated or expended after October 1, 2023, to procure fire-fighting foam that contains in excess of one part per billion of perfluoroalkyl substances and polyfluoroalkyl substances.

(c) PROHIBITION ON USE.—Fluorinated aqueous film-forming foam may not be used at any military installation on or after the earlier of the following dates:

(1) October 1, 2024.

(d) EXEMPTION FOR SHIPBOARD USE.—Subsections (b) and (c) shall not apply to firefighting foam for use solely onboard oceangoing vessels.

Replacement Candidates

- Non-Fluorinated Foams (15 candidates tested to date)
  - Protein Foams
  - Siloxane Foams
  - Wetting Agents
  - 13 of 15 foams/agents extinguish Jet A in <30 sec with 2 gpm
  - Some (5) could not extinguish gasoline
- Foam Additives
  - Stabilizers
  - Fire suppressants
- Foam Delivery Systems
  - Use existing equipment?
  - Compressed air foam (CAF)
  - Ultra-high Pressure (UHP)

Back, J., Assessment of Commercially Available Fluorine-Free Firefighting Foams and Agents, SERDP & ESTCP Webinar Series, October 22, 2020

Issues In Selecting Replacement Candidates

- Performance Testing
  - Mil-Spec tests are large scale, expensive to perform.
  - Need bench scale fire performance screening test to downselect candidates for full scale test.
- Compatibility of the Foams
  - Can foams be mixed?
- Foam Shelf Life
- Environmental Tests
  - What Parameters are needed?

Environmental Testing of Replacement Candidates

- Acute Toxicity Testing
  - Aquatic: Freshwater algae, Water Fleas (Ceriodaphniadubia, Daphnia magna), Midge (Chironomus dilutus), Amphipod (Hyalellaazteca), Mud Snail (Tritiaobsoleta), Jefferson's salamander, American toad, Western chorus frog, Gray tree frog, Northern leopard frog, Wood frog, Fathead minnow, Sheepshead minnow
  - Terrestrial: Bobwhite Quail, Brown Anole
- Biochemical Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)

Moore, D., Hoverman, J. and Suski, J., Assessing the acute toxicity of PFAS-free AFFF alternatives to aquatic and terrestrial species, SERDP/ESTCP AFFF Project Meeting, August 2021

Additional Testing of Replacement Candidates

- Fate
  - Sorption on Soil
  - Biodegradation in wastewater and mixing zone
- Biological Treatment
  - Activated Sludge
  - Anaerobic Digestor
- Physicochemical Treatment
  - Activated Carbon
  - Membrane Filtration
  - Chlorination
  - UV Irradiation

- Are there other tests/evaluations that can be performed?

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Thank you for your attention!
Any Questions?
What are we missing?