Interactions of Fir
With Hydroc
Some Fundame

Chang Jho, Ph.D.
Dynax Corporation, NY USA

Singapore, July 20 – 22, 2016

re-fighting Foam
arbon Fuel -
ɘntal Concepts

dynax
FLUOROSURFACTANTS

USS Forrestal Fire Disaster – July 29, 1967
Protein foam (Fluorine-free) used; 134 dead/62 injured/21 aircraft destroyed

dynax
FLUOROSURFACTANTS

DC-10 (Continental FL 603) Crash Fire at LAX (March 1, 1978)
AFFF (Light water) used; 196 lives saved out of 200!!)

dynax
FLUOROSURFACTANTS

Engine Fire, May 27, 2016
KAL FL 2708, 18 injured /319 people on board

dynax
FLUOROSURFACTANTS

Engine Fire, June 27, 2016
FL SQ368, 222 passengers/19 crew all safely evacuated

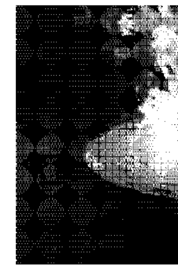
dynax FLUOROSURFACTANTS

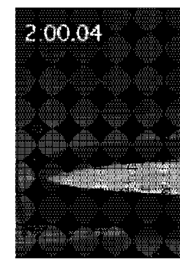
Fuel contamination problem:

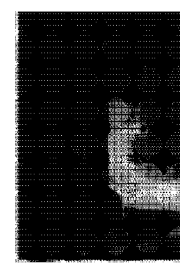
A serious, unavoidable issue, particularly under direct or forceful app

Fuel contamination problem leads to:

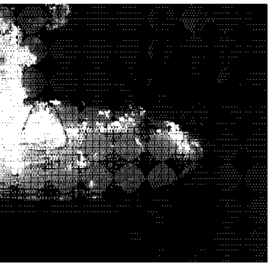
- Premature breakdown of foam blankets
- Flickers, Flashovers
- Ghosting, Re-ignition (Flashback)

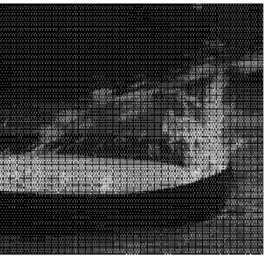


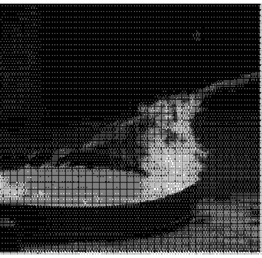




plications







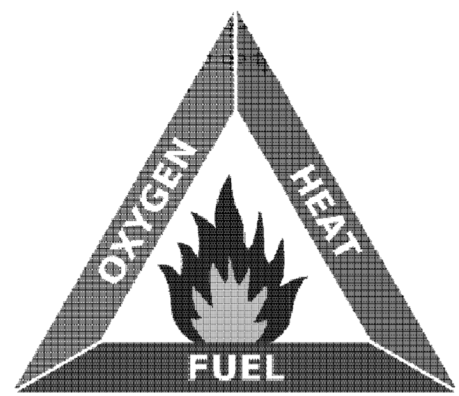
dynax
FLUOROSURFACTANTS

Fire-fighting Foam: Basics

"An aggregate of air-filled bubbles formed from aqueous solutions and is lower in density than flammable liquids" – NFPA 11

Fire-fighting foams work by:

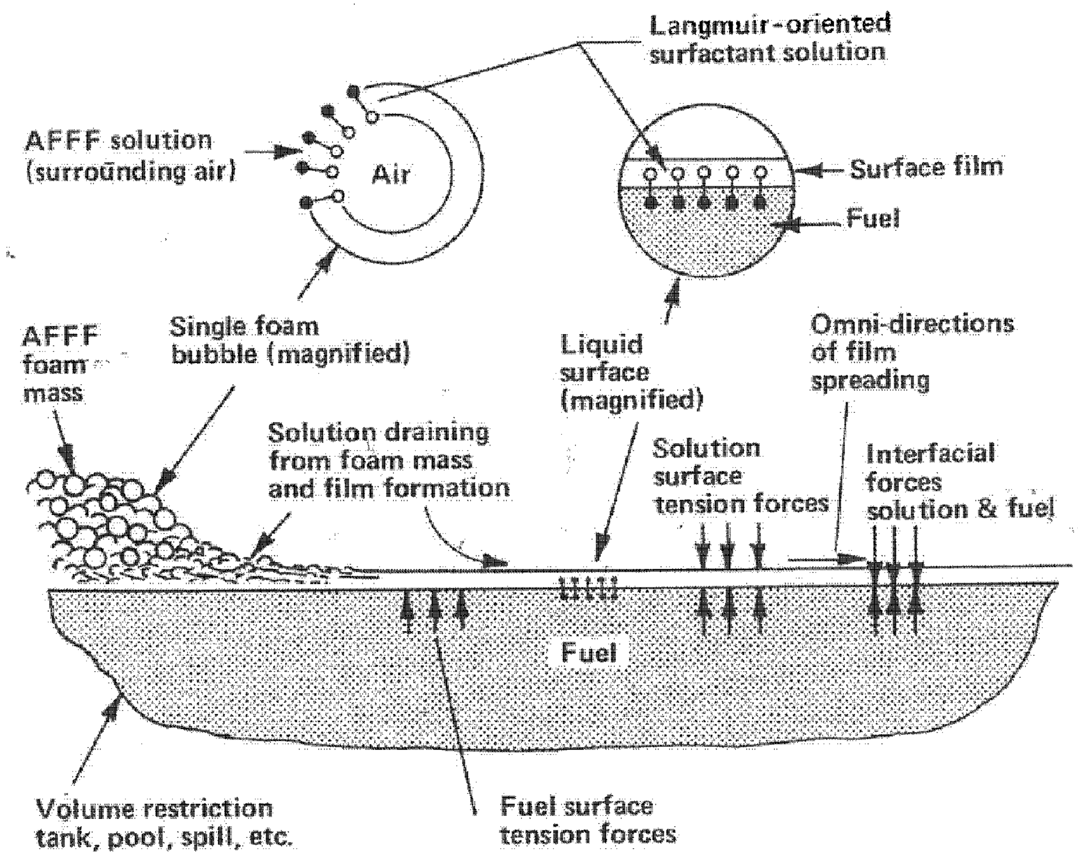
- Separating fuel from air (Oxygen).
- Suppressing the fuel vapor by physical & chemical barriers (*what burns is not the liquid fuel but its vapor!!*)
- Cooling the fuel.
- Separating the flames from the fuel surface.



The Fire Triangle

Fire-fighting Foam – Basics
AFFF (Aqueous Film-forming Foam)

The mechanism of film formation on a fuel surface
by aqueous film-forming foams -
from "*Principles of Fire Protection Chemistry*" (1976) by Richard L. Tuve



dynax FLUOROSURFACTANTS

US00002754

Fire-fighting Foam: Basics

"An aggregate of air-filled bubbles formed from aqueous solutions and is lower in density than flammable liquids" – NFPA 11

Fire-fighting Foam Characteristics (Low Expansion Foam)

Expansion Ratio	Density (g/cc)	%Air (by volume)
1	1 (Solution)	0
2	0.50	50%
2.8*	0.36*	64%*
4	0.25	75%
6	0.17	83%
8	0.13	88%
10	0.10	90%
12	0.08	92%
14	0.07	93%
16	0.06	94%
20	0.05	95%

**Critical Point: air bubbles are completely spherical and they touch each other at one point.*

Density of Hydrocarbon Fuels (@25°C):

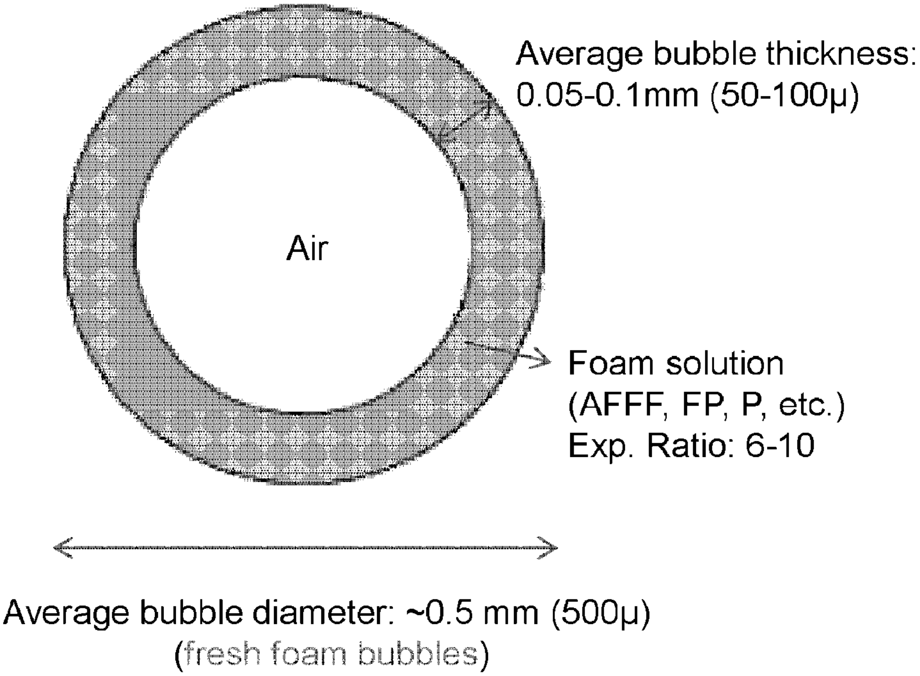
Octane: 0.70; Heptane: 0.68; Gasoline: 0.73

Foam Class	Expansion Ratio*
Low Expansion Foam	2 - <20
Medium Expansion Foam	20-200
High Expansion Foam	>200

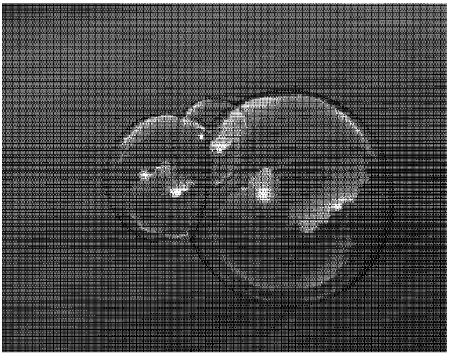
***Expansion ratio** = Volume of foam generated/Volume of liquid used

dynax FLUOROSURFACTANTS

Fire-fighting Foam: Basics
Anatomy of a Foam Bubble



Reference: ***FOAMSPEX: Large Scale Foam Application – Modeling of Foam Spread and Extinguishment, SP Report 2001:13***



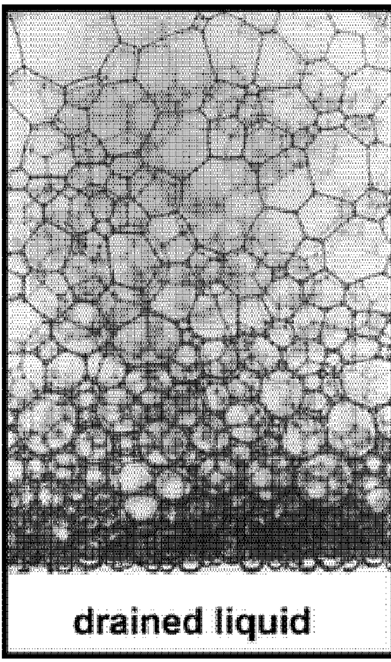
Soap Bubble film thickness: 0.2 – 1 μ

$P_i - P_o = 4\Upsilon/r$ (LaPlace eq.)

P_i: pressure inside
P_o: pressure outside
Υ: surface tension
r: radius of bubble

Gibbs-Marangoni Stabilization:
(Restoring force)
Elasticity = 2A(dΥ/dA)

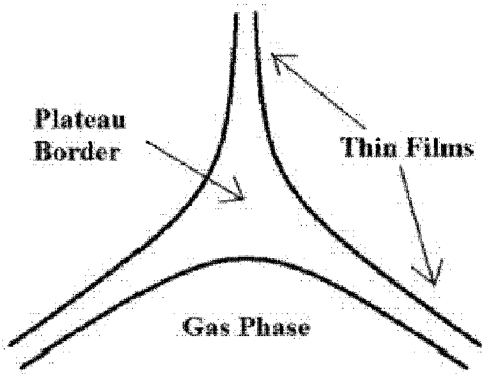
Fire-fighting Foam: Basics
Anatomy of Foam



Polyhederschaum: thin fi

Kugelschaum: thick film

Reference: ***Arnaud Saint-Jalmes****, "Physical chemistry in foam drainage and coarsening," Soft Matter, 2006, 2, 836-849* lm

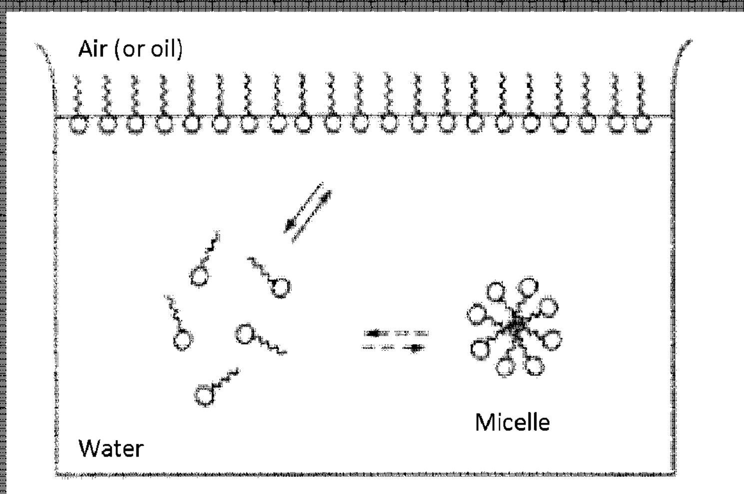


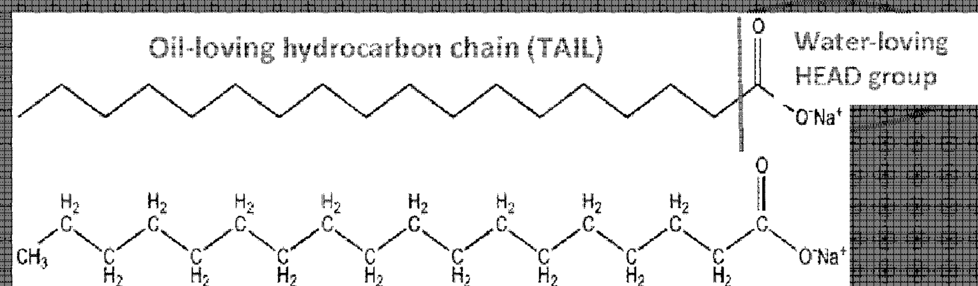
Drainage occurs through
Plateau borders and nodes
by gravity and capillary force.

Surfactants: Basics

Pure liquids cannot foam: No foam stabilizing mechanisms exist. To create a stable foam, foam solution must contain a foaming agent which is a SURFACTANT (Surface Active Agent).

Surfactant: A chemical substance containing a balance of both oleophilic (oil-loving) and hydrophilic (water-loving) groups. Due to this structural property, surfactant molecules adsorb (migrate) spontaneously onto air/water and oil/water interfaces and reduce the surface tension of the medium (water).





Surfactants: Basics

Two Types of Surfactants Used in Fire-fighting Foams:

- Hydrocarbon Surfactants **(used mainly as foaming agent)**

  Examples: "Man-made" Hydrocarbon Surfactants: Synthetic detergents
  "Natural" Hydrocarbon Surfactants: Alkyl polyglycosides, Protein hydrolysates

  Adsorb preferentially at the oil/water interface and affect the interfacial tension.

- Fluorosurfactants***(used mainly in AFFF)**

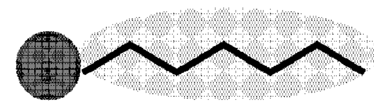
  Examples: PFOS- & PFOA-related fluorosurfactants; C6 fluorotelomer surfactants

  Adsorb preferentially at the air/water surface and dominantly affect the surface tension.

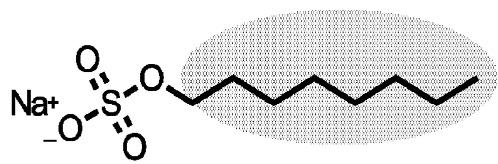
*contain Oleophobic (oil-repellent) and Hydrophilic groups

Examples of Hydrocarbon- and fluoro-surfactants Used in Fire-fighting Foams

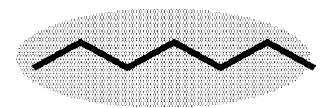
Hydrocarbon Surfactants (Foaming Agents)



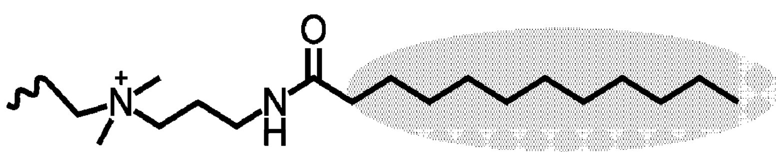
Oleophilic (oil loving) hydrocarbon **"tail"**
Hydrophilic "head" group



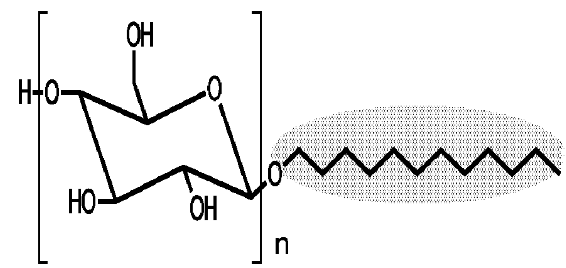
Sodium Octyl Sulfate
(Anionic surfactant)



Heptane
(hydrocarbon fuel)



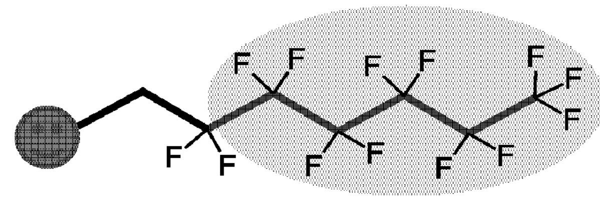
Cocamidopropyl Betaines and Hydroxy Sultaines
(Amphoteric surfactants)



Lauryl Polyglycosides
(Nonionic surfactant)

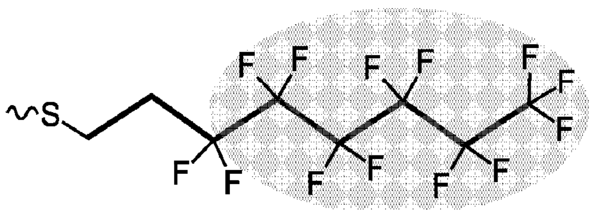
Examples of Hydrocarbon- and fluoro-surfactants Used in Fire-fighting Foams

Fluorotelomer surfactants (Fuel repellent)



Oleophobic (oil/fuel repellent) fluorinated **"tail"**

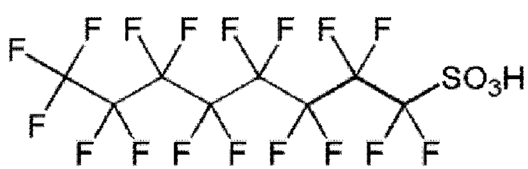
Hydrophilic "head" group



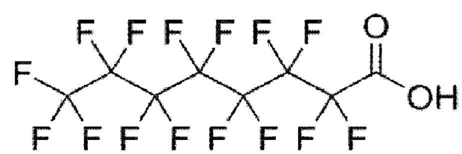
C6 (6:2) Fluorotelomer surfactant

Currently available:
C6 Purity: >99%
PFOA: trace (ppb levels)
PFOA precursors: trace (ppb levels)
PFOS: None

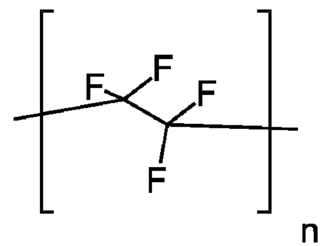
versus



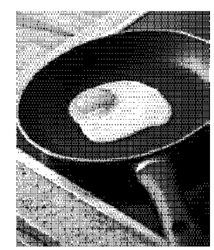
PFOS (C8)



PFOA (C7)("C8")



"Teflon" Polymer
(Repeating units)



AFFF (Aqueous Film Forming Foam) – Basics

Major components in AFFF: Fluorosurfactants & Hydrocarbon surfactants (other components: solvents, water, etc.)

Fluorosurfactants:

- Their inherent oleophobicity (oil/fuel hating) provides fuel repellency to foam.
- Their low surface tensions make it possible for the foam solution (16 -18 dyne/cm) to spread spontaneously on hydrocarbon fuel ($S_{S/F} > 0$)
- Impart heat resistance to foam.

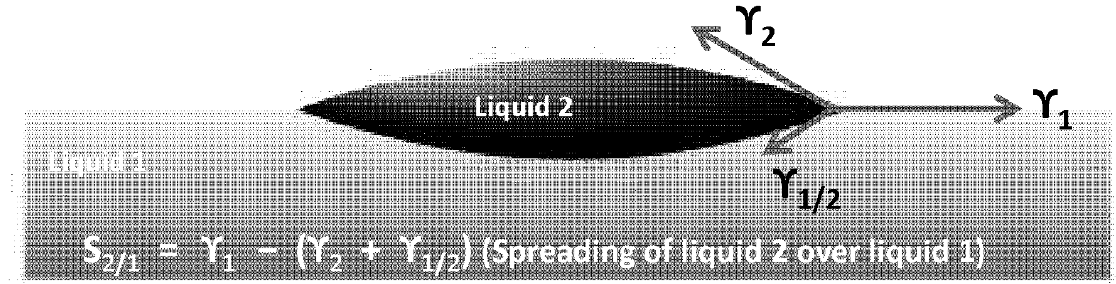
Hydrocarbon Surfactants:

- Used mainly as a **foaming agent**. (Remember pure liquids don't foam!)
- Inherent **oleophilicity** (oil/fuel loving) leads to easy fuel contamination of foam.
- Provides **low interfacial tension** between foam solution and fuel to meet the positive spreading conditions.

AFFF (Aqueous Film Forming Foam) – Basics

The Spreading Coefficient Concept (W.D. Harkin (1922))

(A measure of the driving force for one liquid to spontaneously spread across another.)



$S_{2/1} > 0$: Liquid 2 spreads spontaneously on liquid 1:
$S_{1/2} > 0$: Liquid 1 spreads spontaneously on liquid 2

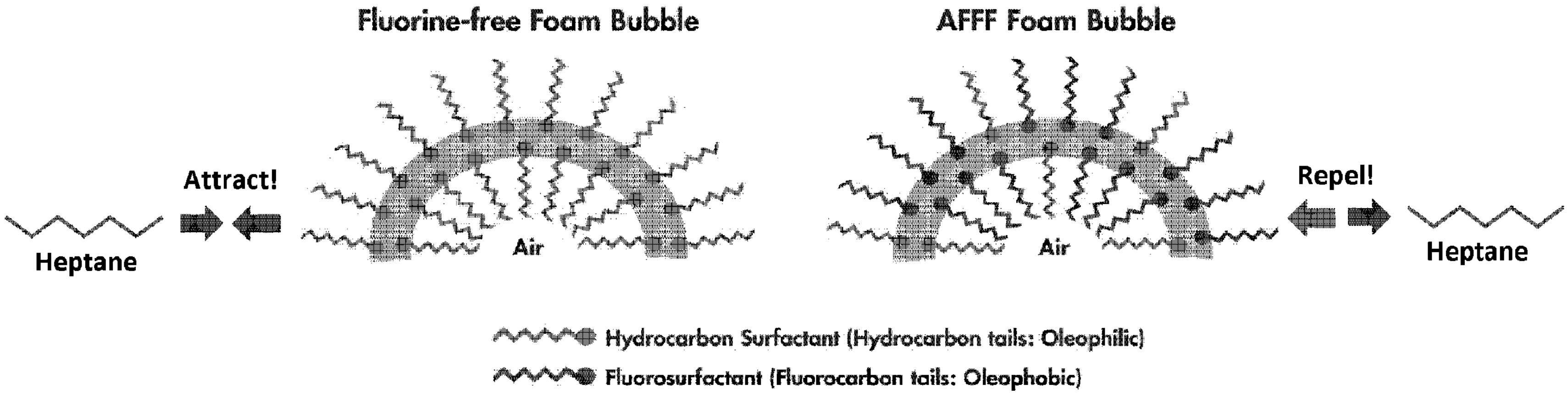
Example: AFFF foam solution (d=1.0) spontaneously spreads on the surface of cyclohexane (d=0.78) forming a duplex film (~10-20μ thick).

Foam	Υ_F (Cyclohexane)	Υ_S (Foam)	$\Upsilon_{S/F}$	$S_{S/F}$	$S_{F/S}$
AFFF	24	16.4	4.3	+4.3	-11.9
F3 (RF6)	24	26.4	2.4	-4.8	0

Surface tension unit: dyne/cm

Reference: **Bogdan Z. Dlugogorski, Ted H. Schaefer and Eric M. Kennedy, "Performance of Replacements for Fluorine-containing AFFF," 3rd Reebok Foam Seminar (2007)*

Interactions of Fuel with Surfactant Molecules on the Foam Bubble Surface



Hydrocarbon surfactants attract hydrocarbon fuels

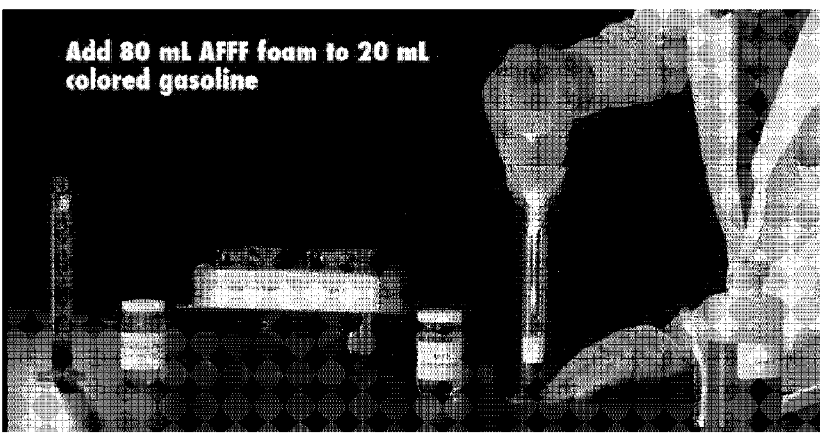
Fluorosurfactants repel hydrocarbon fuels

Laboratory Experiments: Two Effe

of
Fuel-contaminated Foams

Products Tested:
- Five F3 Agents
- Four Fluorinated: AFFF (1)

Test Fuels:

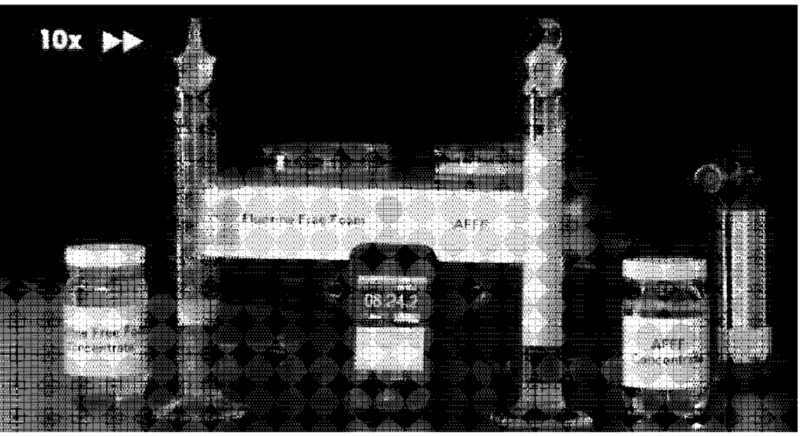


www.youtube.com: “Flammable Firefighting Foams”

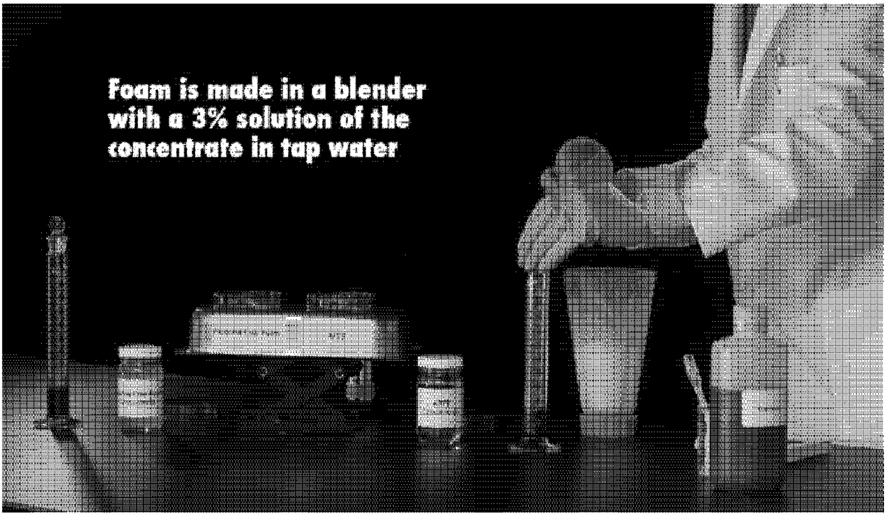
ects of Fuel Contamination

of
Fuel-contaminated Foams

/AR-AFFF (3) Agents

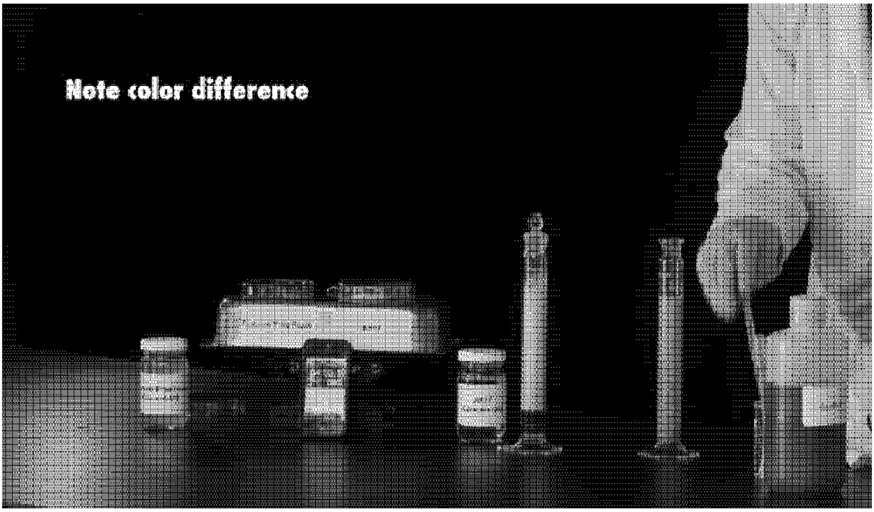


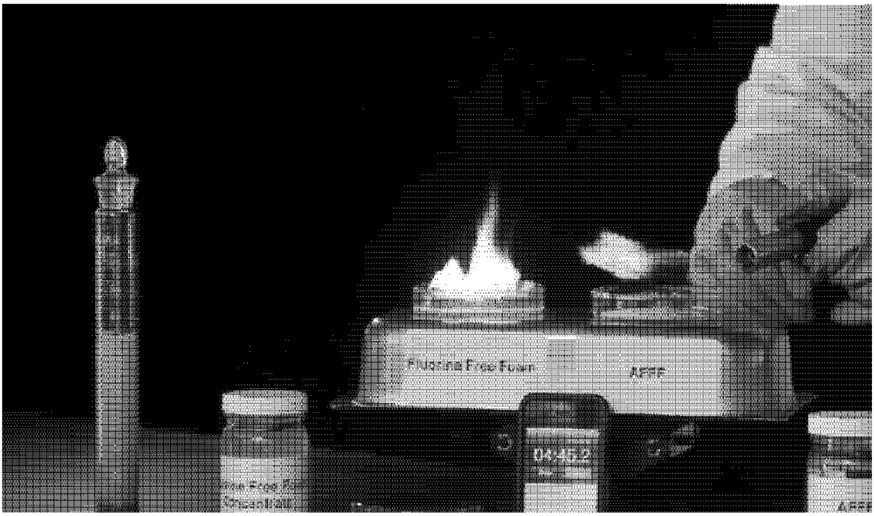
AFFF Foam

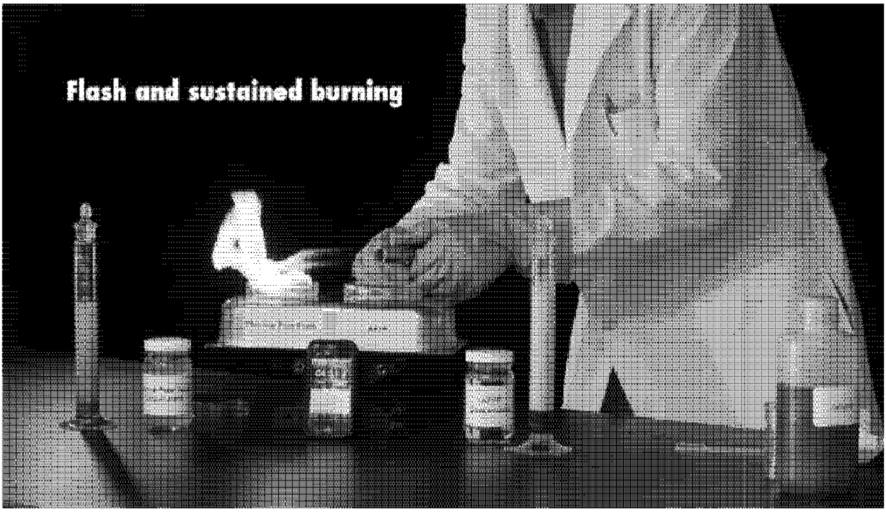

Foam is made in a blender
with a 3% solution of the
concentrate in tap water

dynax FLUOROSURFACTANTS

F3 Foam







dynax
FLUOROSURFACTANTS

Foam Flammability Test Results

Table 1. Comparison of Flammability of Fuel-Contaminated Fluorine-free Foams and AFFF/AR-AFFF				
Test Foam Agent	Flammability and Sustained Burning			
	Iso-Octane	Gasoline	n-Heptane	Cyclohexane
Fluorine-Free Foam (F3) Agents				
Product A (6%) Product B (3%/6%) Product C (3%) Product D (3%/3%) Product E (3%/6%)	All ignited and burned away			
AFFF/AR-AFFF Agents				
Product 1 (AFFF-3%) Product 2-AR-AFFF-3%/3% Product 3-AR-AFFF-3%/3% Product 4-AR-AFFF-1%/3%	None ignited or burned at all			

Note: Due to its high (>38°C) flash point, Jet A1-contaminated foams could not be ignited at ambient temperature.

Reference: Chang Jho, International Fire Fighter, 41, Issue 36 (2012)

Foam Flammability Test Results

Spike Exp.: Effect of C6 Fluorotelomer surfactant on Flammability of F3 Foams

Test F3 Foam	%F from DX1025	Flammability (Cyclohexane) Flash/Sustained Burning?
Produc 1 (3% AFFF Base)	None	Yes/Yes
Base + DX1025* (0.035%F in concentrate)	0.035	Yes/No
Base + DX1025 (0.042%F in concentrate)	0.042	No/No
Product B (3%/6% AR Product)	None	Yes/Yes
Product B + DX1025 (0.42%F in concentrate)	0.42	Yes/Yes
Product B + DX1025 (0.60%F in concentrate)	0.60	Yes/Yes
Product B + Dx1025 (0.65%F in concentrate)	0.65	No/No
Product F (3%/6% AR Product)	None	Yes/Yes
Product F + DX1025 (0.50%F in concentrate)	0.50	Yes/Yes
Product F + DX1025 (0.60%F in concentrate)	0.60	Yes/yes
Product F + DX1025 (0.65%F in concentrate)	0.65	No/No

*DX1025: All C6 (>99%) Fluorotelomer surfactant from Dynax

dynax FLUOROSURFACTANTS

Foam Stability (Degradation) Test Results

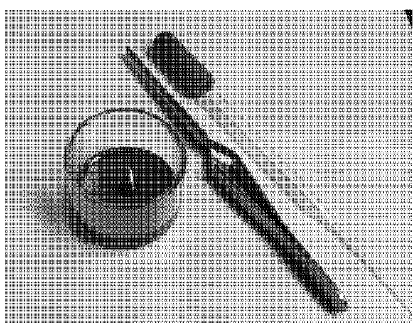
Table 2. Stability Test Results of Fuel-Contaminated Foams					
Test Foam Agent	50% Foam Collapse Time (min)				
	Iso-Octane	Gasoline	n-Heptane	Cyclohexane	Jet A1
Fluorine-Free Foam (F3) Agents					
Product A (6%)	>30	4.6	13.4	9.5	>30
Product B (3%/6%)	>30	9.5	7.1	6.3	>30
Product C (3%)	>30	4.5	23.0	8.7	>30
Product D (3%/3%)	12.8	5.5	3.7	7.4	>30
Product E (3%/6%)	14.1	6.7	9.3	8.7	20
AFFF/AR-AFFF Agents					
Product 1 (AFFF-3%)	>30				
Product 2 (AR-AFFF-3%/3%)					
Product 3 (AR-AFFF-3%/3%)					
Product 4 (AR-AFFF-1%/3%)					

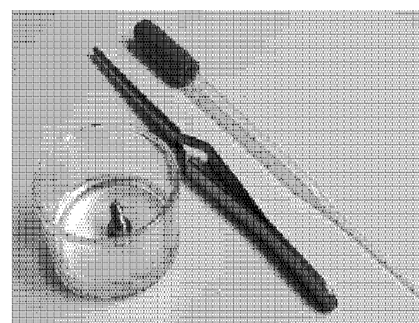
Reference: ***Chang Jho, International Fire Fighter, 41, Issue 36 (2012)***

Why did all the Fluorine-free Foams become flammable when contaminated with hydrocarbon fuel while all AFFF/AR-AFFF Foams did not??

Spreadability of Foam Solution over Fuel:
$S_{S/F} = \Upsilon_F - (\Upsilon_S + \Upsilon_{S/F})$

Spreadability of Fuel over Foam Solution:
$S_{F/S} = \Upsilon_S - (\Upsilon_F + \Upsilon_{S/F})$





"Upside Down Screw Test"

Spreading and Sealability Test Results: Foam Solution over Fuel

Table 3. Spreading and Sealability Tests of Foam Solution over Fuel

Test Foam Agent	Foam Solution over Fuel				
	Gasoline	n-Heptane	Iso-Octane*	Cyclohexane	Jet A
Fluorine-Free Foam (F3) Agents					
Product A (6%) Product B (3%/6%) Product C (3%) Product D (3%/3%) Product E (3%/6%)	None of the foam solutions spread or sealed (All burned)				
AFFF/AR-AFFF Agents					
Product 1 (AFFF-3%) Product 2 (AR-AFFF-3%/3%) Product 3 (AR-AFFF-3%/3%) Product 4 (AR-AFFF-1%/3%)	All foam solutions spread and sealed (No burning)				

*Spreading on Iso-Octane was hard to detect, but sealing was confirmed by no burning.

AFFF Foam Solution
Fuel

F3 Foam Solution
Fuel

Reference: ***Chang Jho, International Fire Fighter, 41, Issue 36 (2012)***

Spreading Test Results: Fuel over Foam Solution

Table 4. Spreading Tests of Fuel over Foam Solution

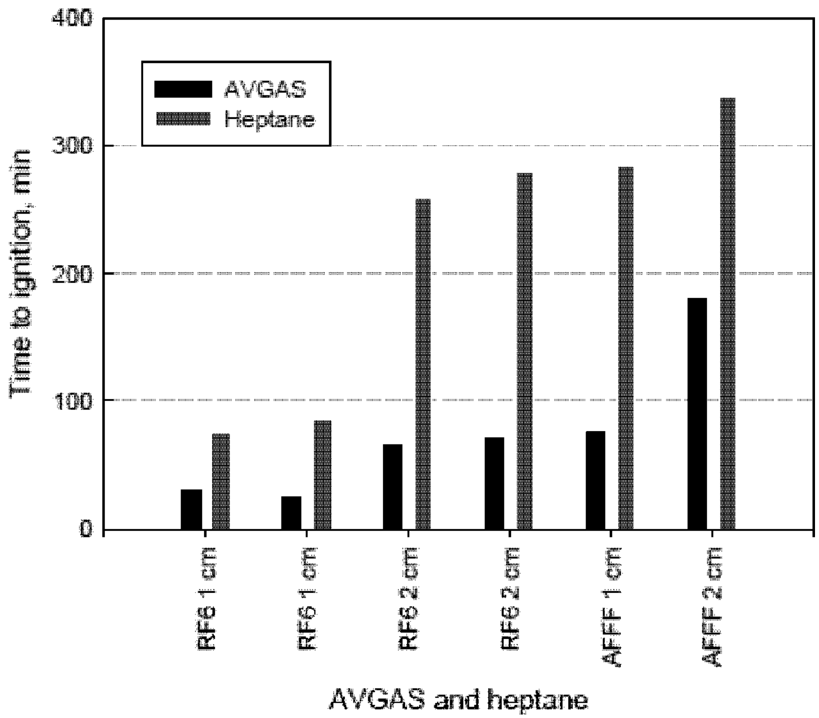
Test Foam Agent	Fuel over Foam Solution				
	Iso-Octane	Gasoline	n-Heptane	Cyclohexane	Jet A1
Fluorine-Free Foam (F3) Agents					
Product A (6%)	Spreading (30%)*	Spreading (100%)	Spreading (40%)	Spreading (20%)	Spreading (20%)
Product B (3%/6%)	Spreading (40%)	Spreading (80%)	Spreading (20%)	Spreading (15%)	No Spreading
Product C (3%)	Spreading (20%)	Spreading (100%)	Spreading (20%)	Spreading (20%)	Spreading (20%)
Product D (3%/3%)	Spreading (40%)	Spreading (80%)	Spreading (20%)	Spreading (15%)	Spreading (15%)
Product E (3%/6%)	Spreading (20%)	Spreading (80%)	Spreading (15%)	Spreading (15%)	No Spreading
AFFF/AR-AFFF Agents					
Product 1 (AFFF-3%)	None of the fuels spread over foam solution				
Product 2 (AR-AFFF-3%/3%)					
Product 3 (AR-AFFF-3%/3%)					
Product 4 (AR-AFFF-1%/3%)					

* Numbers in parentheses Indicate % spread area.

Fuel	Fuel
F3 Foam Solution	AFFF Foam Solution

*Reference: **Chang Jho, International Fire Fighter, 41, Issue 36 (2012)***

Vapor Suppression Properties of Foams:
AFFF vs Fluorine-free Foams - Sealability Test based on DEF (AUST) 5706 (2003)*

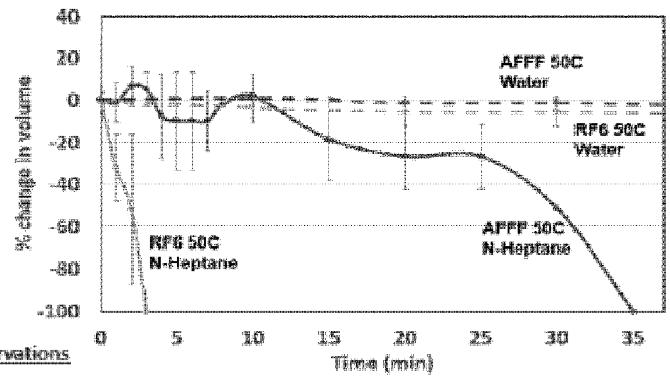


***Foam Sealability Test (Annex A):**
Pan: 59.5 cm dia/10.2 cm depth w/conical bottom
Fuel: Avgas

Conclusion: "…best-performing FfreeF formulation (RF6) provided about 30% of the durability of an AFFF for protection against evaporation of low-flashpoint flammable liquids."

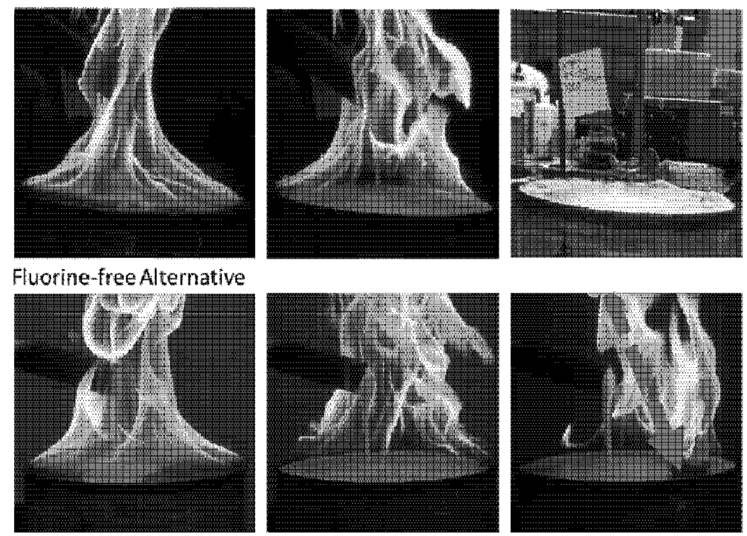
*Reference: **Bogdan Z. Dlugogorski, Ted H. Schaefer and Eric M. Kennedy**, "Performance of Replacements for Fluorine-containing AFFF," 3rd Reebok Foam Seminar (2007) & Fire Technology, 44(3), 297-309 (2008)*

Effect of Flammable Vapor on Foam Degradation:
AFFF vs Fluorine-free Foams – NRL Test*



AFFF

Extinction



18 seconds

Fluorine-free Alternative

40 seconds

Observations

- AFFF had a much longer foam lifetime than fluorine-free, RF6, when exposed to n-heptane, fluorination appears to reduce degradation
- The presence of fuel influences foam degradation with RF6 foam lifetime changing from over an hour on water to 3 minutes on n-heptane, degradation seen during extinction may be caused by fuel and not pool temperature
- RF6 degradation time scale relevant to extinction time scales (1-2 minutes), could be effecting extinction performance

*Reference: ***Katherine Hinnant, Ramagopal Ananth, Michael Conroy, and Bradley Williams***, *"Evaluating the Difference in Foam Degradation between Fluorinated and Fluorine-free foams for Improved Pool Fire Suppression," ARL-TARDEC Fire Protection Information Exchange Meeting, Aberdeen Proving Ground, MD, October 14, 2015*

Takeaway: AFFF vs F3 Foams

Foam Property	Advantage	AFFF	F3
Fuel Repellency *	Yes	Yes	No
Fuel Shedding	High	High	Low
Fuel Pickup	Low	Low	High
Film Formation*	Yes	Yes	No
Foam spreading on fuel*	Yes	Yes	No
Fuel spreading on foam*	No	No	Yes
Fuel emulsification	Low	Low	High
Flammability of contaminated foam	Low	Low	High
Degradation of contaminated foam	Low	Low	High
Heat resistance of foam	High	High	Low

*Fundamental differences between AFFF and F3 foams

Takeaway: AFFF vs F3 Foams

Is Fluorine-free Foam (F3)
a viable alternative to
C6 Fluorotelomer surfactant-based AFFF?

Thank you!

Dynax Contact Info:
Chang Jho, 79 Westchester Avenue, PO Box 285, Pound Ridge, NY 10576 USA
Tel: 914 764-0202 Fax: 914 -764-0533 e-mail: chang.jho@dynaxcorp.com