

Recent Developments in 6:2 Fluorotelomer Surfactants and Foam Stabilizers

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From

PFOS/PFOA Fluorosurfactants

to

6:2 Fluorotelomer Surfactants,

which biodegrade into

6:2 Fluorotelomer Sulfonate (6:2 FTS),

used as

Film Formers (Non-polymeric)

Fuel Repellents (Polymeric)

Foam Stabilizers (Polymeric)

From PFOS/PFOA to 6:2 Fluorotelomer Surfactants

Year	Events	Reference
1963	Tuve + Jablonsky, US NRL, 3M/NRL Collaboration PFOS + PFOA type fluorosurfactants Light Water + Purple K (Twin Agents) (no hydrocarbon surfactants) MIL-F-23905 (11/1/63) (Fresh water only)	US 3,258,423 (filed 9/4/63) GB 1,070,289 (filed 9/3/64)
1964	Ratzer, Chemical Concentrates: Use of Hydrocarbon Surfactants with fluorosurfactants in AFFF	Campobello Foam Meeting (10/11-13/64), Published in "Foam" Oct. 1964, Nr. 24
1967	USS Forrestal Fire	Protein Foam; 134 dead and 21 aircrafts destroyed
1969	3M Francen Patents: Use of Hydrocarbon Surfactants with Fluorosurfactants in AFFF	US 3,562,156 (filed 6/12/69) US 3,772,195 (filed 2/5/71): Invalidated 1980
1969	MIL-F-24385 (6% AFFF) (Fresh & Seawater)	Seawater tests introduced
1972–75	Atochem, France & Ciba-Geigy, USA: 6:2/8:2 and 6:2 FT-Surfactants for AFFF Agents Pilot plant production for AFFF agent tests at Eau et Feu (Atochem) and Ansul (Ciba-Geigy)	"Forafac" (Atochem) and "Lodyne" (Ciba-Geigy)
1978	DC-10 Crash Fire at LAX (First major use of 3M Light Water)	196 lives saved out of 200
1982–	Large selections of 6:2 FT-Surfactants available to AFFF agent producers	6:2 FT-surfactants: C6 (~95 to 97%) + C4 & C8
1992	MIL-F-24385F (3% & 6% AFFF)	3% requirements introduced

USS Forrestal Fire – 29 July 1967



DC-10 Crash Fire at LAX – 1 March 1978



Environmental Studies of AFFF Agents

Sampling Site	Source of AFFF	Major Components ¹
2004 US Study (ground water)*		
Naval Air Station, Fallon, NE	3M	PFOS + PFOA
Tyndall AFB, FL	3M + Ansul	PFOS + PFOA +
Wurtsmith AFB, MI	3M + Ansul	6:2 FTS²/4:2 & 8:2 FTS
2008 Norwegian Study (soil)**		
Mongstad Oil Refinery	National Foam + 3M	PFOS + PFOA + 6:2 FTS
Solberg Scandinavian AS	3M + DuPont(?)	
Gardermoen Airport	3M + DuPont (?)	
Rygge Air Station	3M	PFOS + PFOA

*Jennifer Field, et. al., Environ. Sci. Technol. 2004, 38, 1828.

**Norwegian Pollution Control Authority (SFT) Report (2008)

¹PFOS and PFOA include other homologs.

²Ansul AFFF derived from Lodyne fluorosurfactants (Ciba-Geigy) contained >95% 6:2 FT-surfactants.

6:2FTS was never used in AFFF agents.

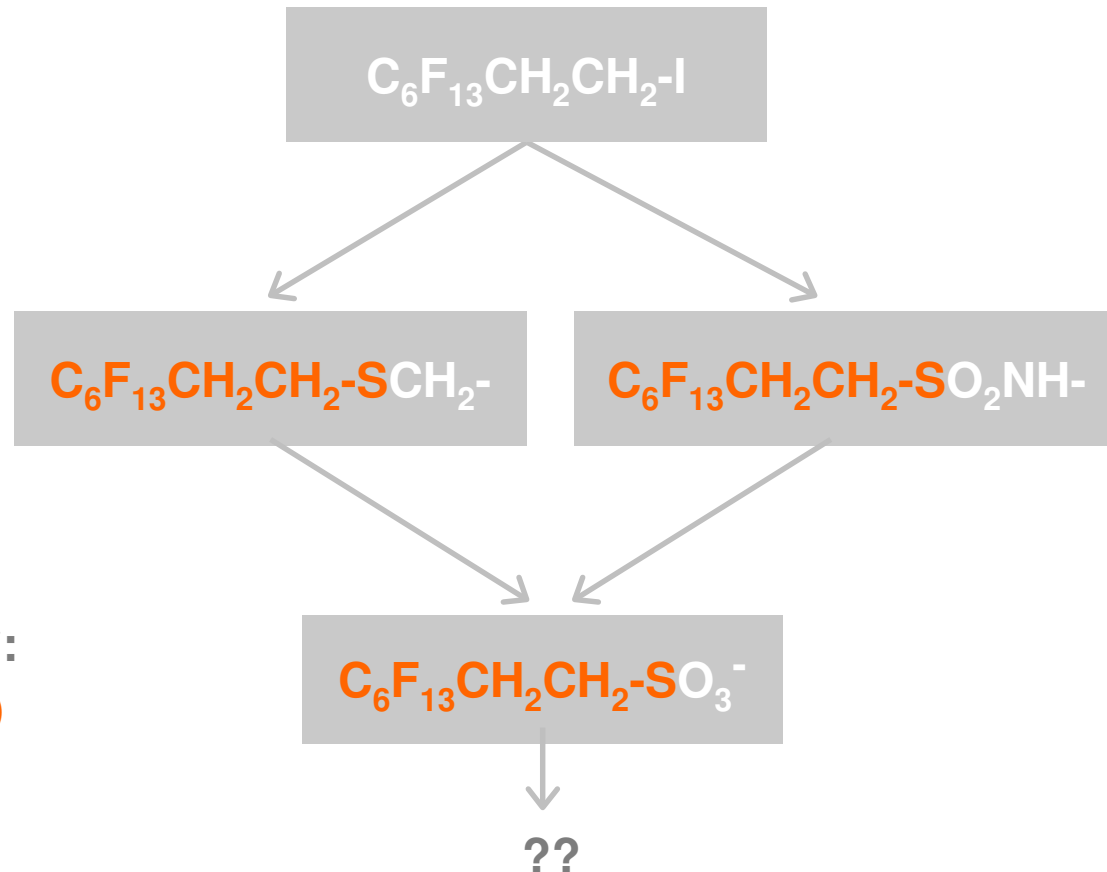
Chemistry and Biodegradation of 6:2 Fluorotelomer Surfactants

Starting Material:
6:2 FT-Iodide

Type of
6:2 FT-Surfactants

Biodegradation Products*:
6:2 FT-Sulfonate (6:2 FTS)

*Based on environmental studies.



Foam Stabilizers for AR-AFFF/AR-FFFP Agents

Year	Producer	Foam Stabilizer	AR-AFFF/AR-FFFP
1973	National Foam	Polysaccharides (PS)	3x6 (High viscosity)
1990	Ciba-Geigy	Lodyne K90'90*	3x3 (Low viscosity) AR-AFFF/AR-FFFP
1995	Dynax	DX5011 6:2 Fluorotelomer Polymeric Surfactant	3x3 (Lower viscosity) AR-AFFF & AR-FFFP
1998-99	DuPont	Forafac 1210* Forafac 1268*	AR-FFFP AR-AFFF
2000	Ciba Specialty Chem	Lodyne 5100*	AR-AFFF/AR-FFFP
2008	Dynax	DX5022 Only 6:2 Fluorotelomer Foam Stabilizer that biodegrades to 6:2 FTS	3x3, 1x1, 0.5x0.5 Development of semi-Newtonian AR-AFFF & AR-FFFP agents without PS

* Fluorotelomer polymeric surfactant

Fluorosurfactants for Fluoroprotein Foam Agents

Year	Events
1968	Chubb Fire introduces FP foams based on ICI Monflor MD 313: Used by all FP agent producers.
1973	Regular Ministry Supply Contracts for Monflor MD 313-based FP agents
1980	Ciba-Geigy introduces Lodyne K78'220(B) as drop-in replacement for Monflor MD 313. ICI withdraws Monflor MD 313. K78'220(B) becomes THE ONLY GAME IN TOWN!
1990	Lodyne K78'220B, an 8:2 FT-Surfactant, used as fuel repellent in AFFF and FFFP agents.
2009	Dynax DX2200 and Chemguard FS-220B (successors of Lodyne K78'220B): STILL THE ONLY GAME IN TOWN!
2009	No Fluorine-free FP yet!!
2010/15	Phase-out period for 8:2 FT-Surfactants.

Note: Use levels of K78'220B (40%) in 3% FP: 0.3 – 0.6% (0.02 – 0.05%F)

Fluorosurfactants – Key Events 2002 – 2015

Year	Events
2002	DuPont acquires the Atofina fluorotelomer business.
2003	Chemguard acquires Ciba Specialty Chemicals Lodyne fluorosurfactant business.
2004	Dynax introduces 6:2 Lodyne fluorosurfactants with > 99.5% C6
2005	Chemguard introduces modified Lodyne fluorosurfactants with ~72% C6 and ~28% C8/C10.
2008	Dynax introduces DX5022, a second generation foam stabilizer.
2008	DuPont announces introduction of short-chain fluorochemicals meeting US EPA Global 2010/2015 PFOA Stewardship Program objectives.
2009	DuPont announces that 45 Capstone products are on the market by mid-2009
2010/15	EPA's Global 2010/2015 PFOA Stewardship Program: PFOA and higher homolog acids and their precursor chemicals should be reduced by 95% no later than 2010, and eliminated no later than 2015 from facility emissions and in product content.

6:2 FT-Surfactants for Fire Fighting Foam Agents

Film Formers for AFFF/FFFP:

- § Non-polymeric
- § Fast equilibrating (high diffusion rate) (C6 vs C8)
- § Low equilibrium & dynamic surface tension (C6 vs C8)

Fuel Repellents for FP:

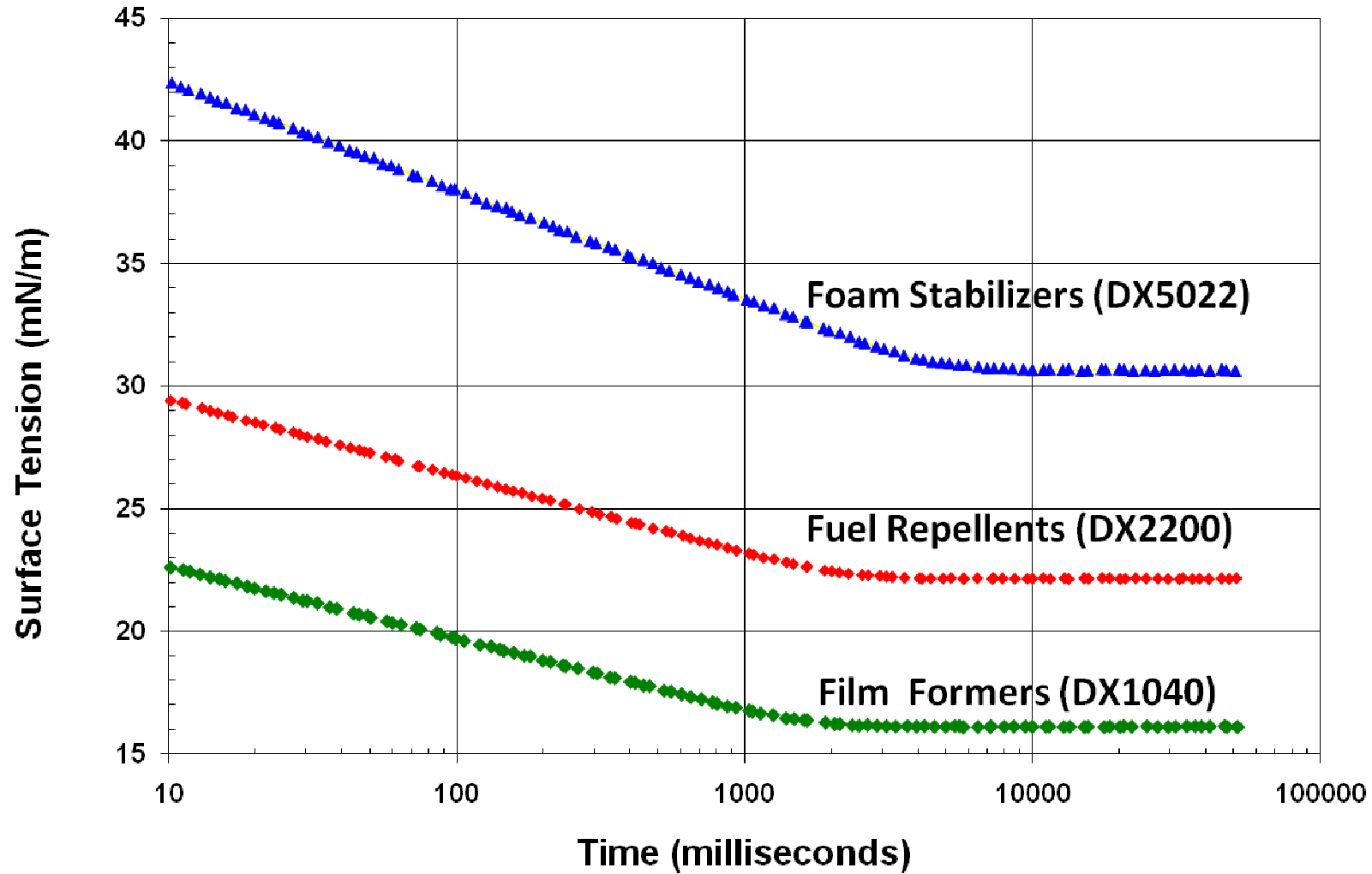
- § Polymeric (oligomeric)
- § Oleophobicity (fuel repellent) (C8 vs C6)
- § Slow equilibrating (low diffusion rate)

Foam Stabilizers for AR-AFFF/FFFP

- § Polymeric
- § Solvophobicity (solvent repellent)
- § Slow equilibrating (low diffusion rate)

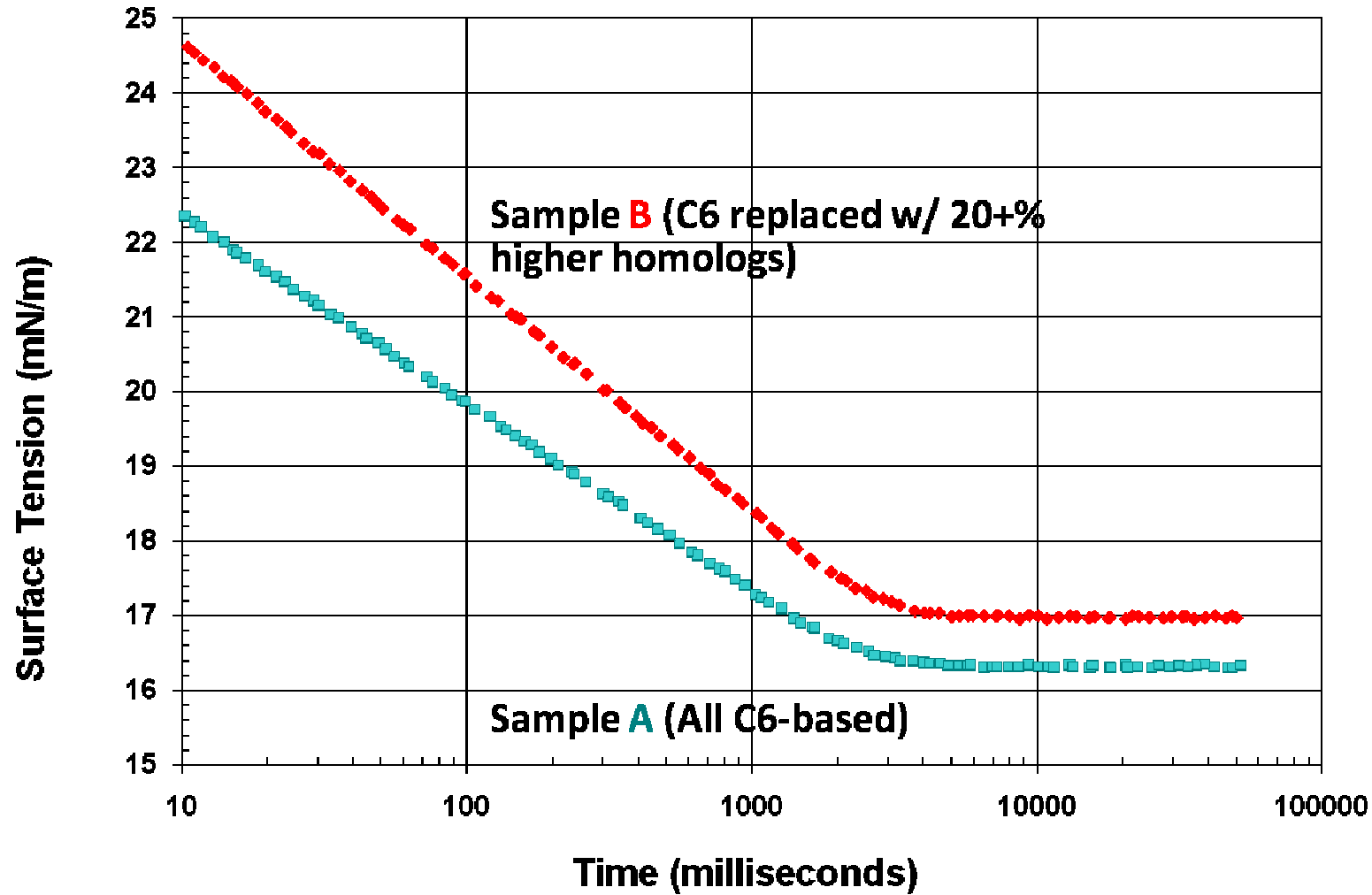
Three Types of Fluorosurfactants

Dynamic Surface Tension Profile (0.1% Actives in Water)



C6 vs C6/C8-based Non-ionic Fluorotelomer Surfactants

Dynamic Surface Tension Profile (0.1% actives in water)



US Air Force SBIR Phase 1 & 2 Contracts Awarded to Dynax in 1993 & 1994

“Improved Formulation of Fire Fighting Agents for Hydrocarbon Fuel Fires”

- Improved Extinguishment
 - + Improved Foam Life and Burnback Resistance
 - + Lower Levels of Fluorosurfactants
 - + Lower Toxicity on Aquatic Life Forms
 - + Elimination of Butyl Carbitol (SARA Title III Section 313)
-

= **Environmentally More Benign (EMB) AFFF Agents**

3% AFFF Agents on US QPL List in 1993:

Highest Fluorine Content: 1.8%F (3M Light Water FC-203CF)

Lowest Fluorine Content: 0.85%F (NF Air-O-Water 3EM)

Proposed MIL-F-24385 Specification Changes

Maximum Fluorine Content	0.85%
Spreading Coefficient	Increase (3.0 5.0)
Toxicity, LC₅₀, mg/L (Min)	Increase (50 750)
COD, mg/L (Max)	Decrease (1,000K 600K)
BOD₂₀/COD (Min)	Leave at 0.65*

*Subject to definition of BOD/COD ratio

In 1993, the issues of PFOS/PFOA and C6 vs C8/C10 telomer type fluorosurfactants did not exist.

Dynax Proposal for New MIL-F-Fire Performance Specifications Based on US Air Force SBIR Contract Report (1996)

3% AFFF Agents	Solution	MIL-F-24385F	Proposed Spec*
Foam Expansion (min)	3.0%	5.0	6.5
	1.5%	None	6.0
¼ Drain Time (min, min)	3.0%	2.5	4.0
	1.5%	None	3.0

28 ft² Fire Tests (Fresh & Seawater)

Extinguishment time (sec, max)	3.0%	30	Delete
	1.5%	45	40
Burnback (sec, min)	3.0%	360	Delete
	1.5%	300	360

50 ft² Fire Tests (Seawater only)

Extinguishment time (sec, max)	3.0%	50	45
Burnback (sec, min)	3.0%	360	420

*This proposal is based on a Dynax “Environmentally More Benign” 3% AFFF formulation containing 0.85%F (vs. 1.8%F for 3M Light Water FC-203CF)

Dynax 6:2 Fluorotelomer Surfactants and Foam Stabilizers

Dynax Product	Ionic Type	Agent Application Guide			
		AFFF	AR-AFFF	FFFP	AR-FFFP
Fluorosurfactants					
DX1030	Anionic	•	•		
DX1040	Anionic	•	•		
DX1080	Nonionic	•	•	•	•
DX1090	Nonionic	•	•	•	•
DX1025*	Anionic	•	•		
Foam Stabilizers					
DX5011	Anionic		•		•
DX5022	Anionic		•		•
DX5065**	Anionic		•		•
DX5066**	Anionic		•		•

*Blends of fluorosurfactants **Blend of Fluorosurfactants and Foam Stabilizers

4th Reebok Foam Seminar, Bolton, UK 6 – 7 July 2009

Thank you!

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FLUOROSURFACTANTS