PFAS Use in Fire Fighting Foams
Current Environmental and Regulatory Trends and Impact

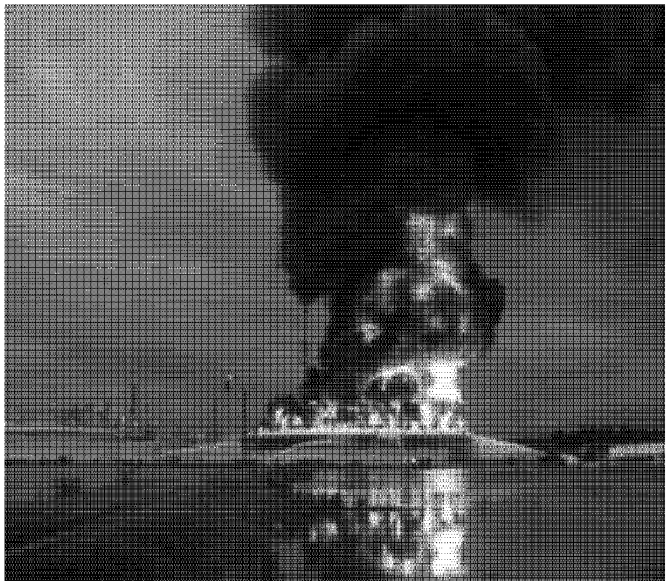
DoD MERIT

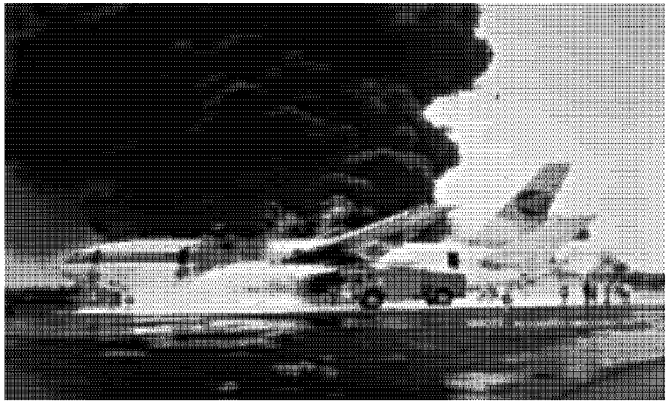
Crystal City, VA 19 July 2016

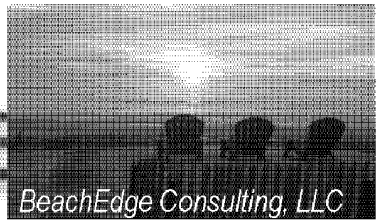
Stephen Korzeniowski

Agenda Overview

- Introduction
- Emerging Issues
- Historical Perspective
- Transition to Short-chains
- Regulatory Update
  - United States
  - Australia
- Fluorine-free Foams
- Foam Legacy Consequences
- Best Practice Guidance - FFFC
- Current Events & Summary





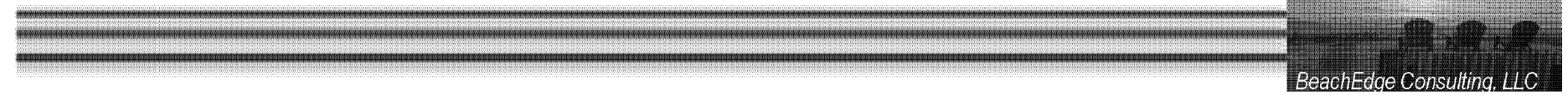

BeachEdge Consulting, LLC

Steve Korzeniowski Background

- 37+ Years at DuPont/Chemours
- Organic Chemist by Training - PhD; MBA – Finance
- 26 Years in Fluorochemical Technology & Business Roles
- 15 Years in AFFF Fluorochemcials (2001 – Present)
- Led DuPont Fluorotelomer technology & plant transition from long to short chains and in US EPA Stewardship Program
- Founding Member and Past Chairman and Board Member of FFFC
- Founding Member and Previous Chair of Telomer Research Program (TRP: 2000-2011) and FluoroCouncil Member (2011 – Present)
- Co-author of 45+ Papers & Articles in Organic Synthesis, Analytical, Toxicology and Fluorotechnology
- Started BeachEdge Consulting one year ago following Chemours exit
  - Consult for various companies and teach at local university

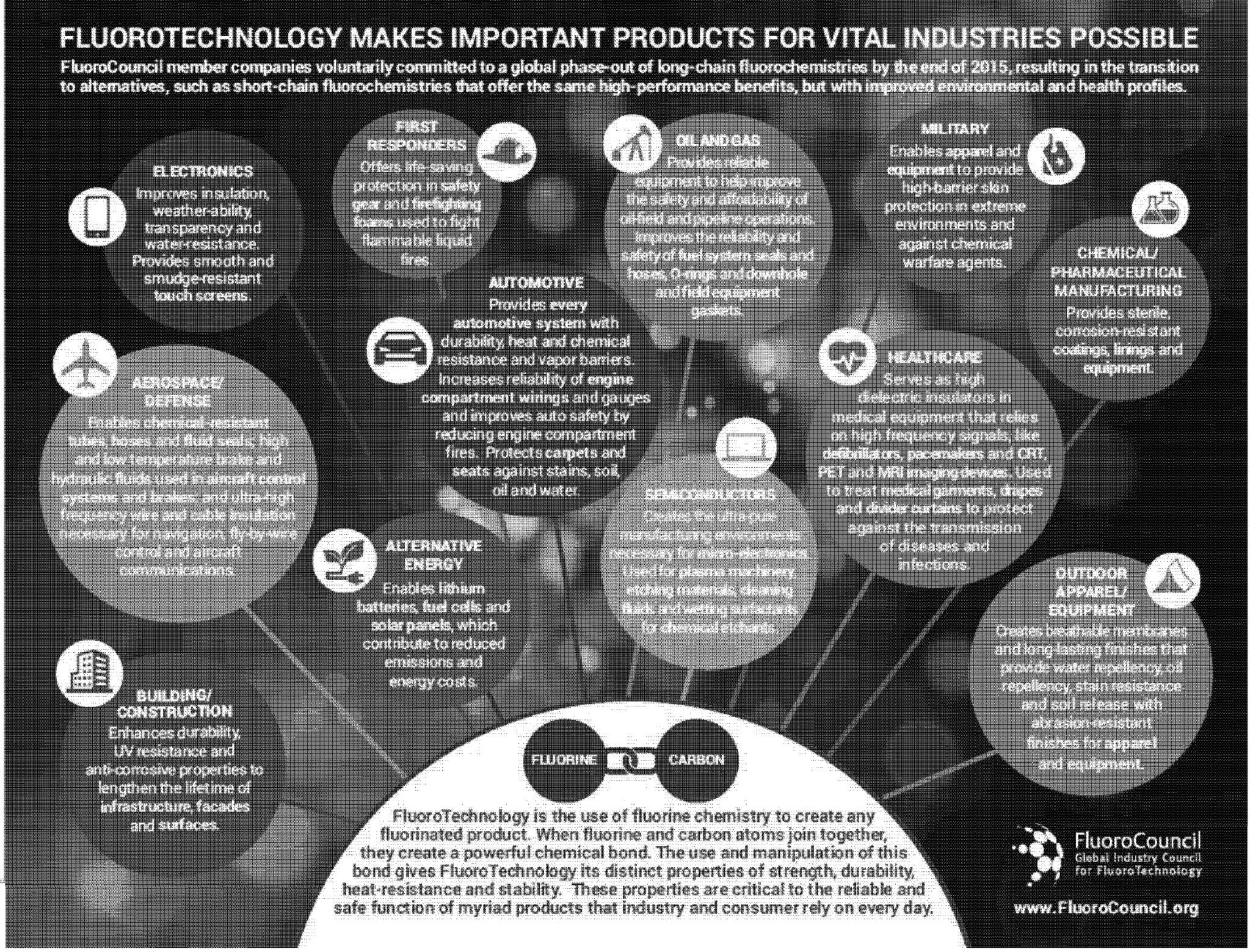
Industry Primary Engagement Points for FFFC and FluoroCouncil

- US Department of Defense
- Federal Aviation Administration
- European Commission
- Environment Canada
- Canadian Department of National Defence
- Belgian Environment Agency
- Queensland Department of Environment
- Western Australia Department of Environment
- China Ministry of Environmental Protection
- Stockholm Convention on POPs
- UK Civil Aviation Authority
- Global approval bodies: US EPA, METI, UBA



FLUOROTECHNOLOGY MAKES IMPORTANT PRODUCTS FOR VITAL INDUSTRIES POSSIBLE

FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemistries by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemistries that offer the same high-performance benefits, but with improved environmental and health profiles.



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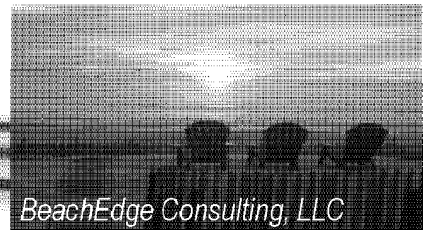
P's and P's & Q's

- In Business it is the 4 P's of Marketing:
  - Product, Place, Price, Promotion
  - Other P's are Positioning, People, Profit

- In Fluorochemistry (PFAS's) the P's have evolved as the chemistry has changed from long-chains to short chains
  - The discussion/debate has shifted away from PBT as the chemistry has changed
- The 4 P's of Fluorochemistry:
  - Potential, Precaution, Presence, Persistence (or vP)
- A critical P that must always be added to this equation is: Performance

2016 Emerging Issues

- Need to better understand the degradants or metabolites from the short chain C6 chemistry: PFHxA plus……
- Misconception that all PFASs are the Same – long chain, short chain – all have CF Bond
  - Simplistic view by some Parties is they are all the same *(which they are clearly not)* and should be treated as such
- Drinking Water
  - Evolving situation primarily as a result of the US EPA Health Advisory on PFOS and PFOA
  - Military bases
  - "Flint, Michigan" effect
- Criteria Changing
  - Heightened focus on Precautionary Principle
  - Set aside "risk based" approach and assessments
  - Development of new criteria of concern: PMT and vP vs PBT
  - Overt focus on Mobility and Persistence as critical criteria
    - Not T & B as in PBT



Transition to Short-chains: Emerging Issues

Headlines: Precautionary Principle and "Reversibility of Exposure"

- Both Australia QLD DEHP and Cousins et al have invoked the precautionary principle as the basis for their published positions
- Germany and Cousins et al are also focusing on PMT vs PBT with P being given significant weight and Mobility (M) replacing B in the evaluation process
- Reversibility of Exposure: Environment & Human Body
- Precautionary Principle vs Risk-based Approach

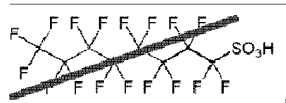
- Madrid & Helsingor Statements: Blum & Cousins
- Green Science Policy Institute: Blum

NGO/Academic Focus on Persistence

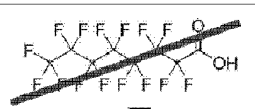
Industry phase-outs and replacements

Stockholm University

Products (low molecular weight and polymers) containing long-chain perfluoroalkyl moieties



PFSAs (≥ 6 perfluorinated carbons)



PFCAs (≥ 7 perfluorinated carbons)

8:2 FTOH

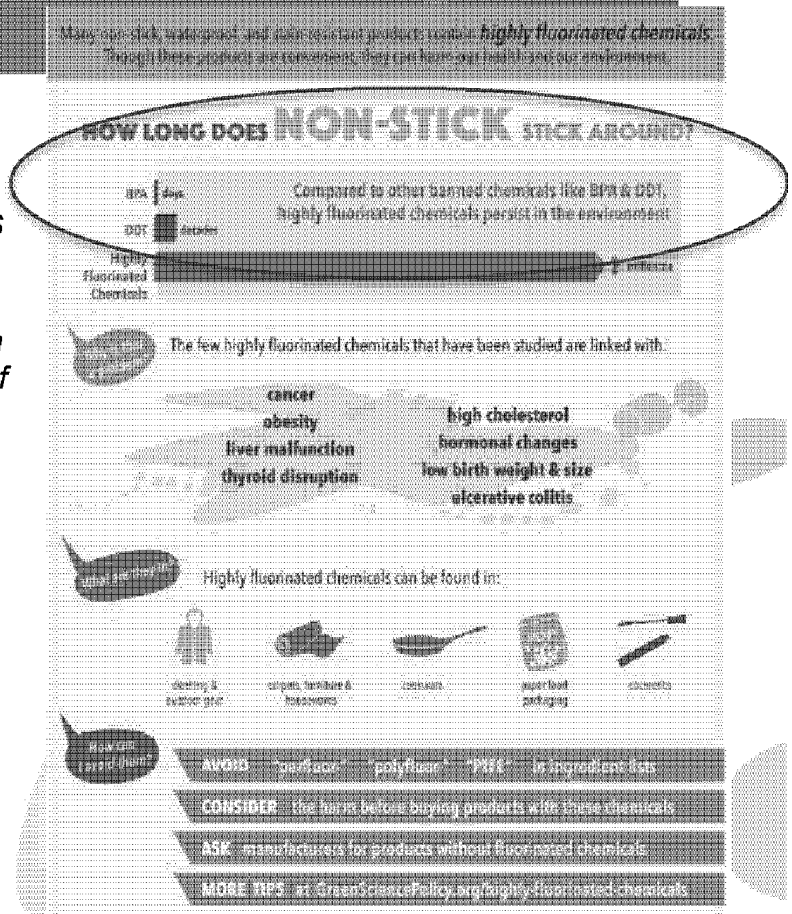
Mainly replaced with alternative products containing or degrading to form

Short-chain PFAS moieties	Perfluoro(poly)ether moieties
PFCA < 7 perfluorinated carbons PFSA < 6 perfluorinated carbons	

vP and LRTP

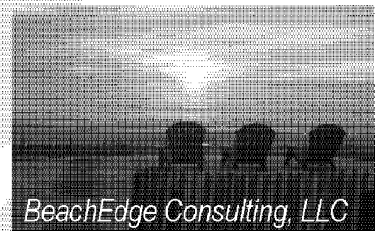
15

- From presentation by Ian Cousins at May 2016 Helsinki Chemicals Forum and June 2016 Workshop "Strategy for a Non-toxic Environment of the 7th Environmental Action Programme (EAP)"

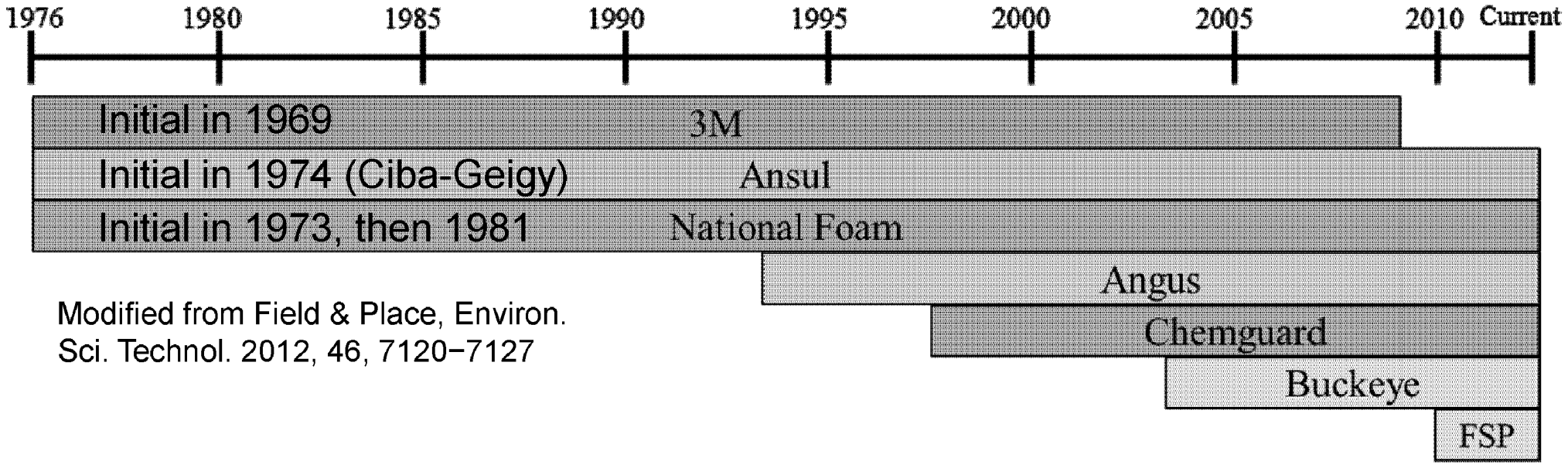


"To protect groundwater resources for future generations, society should consider a precautionary approach to chemicals management and prevent the use and release of highly persistent and mobile chemicals such as PFASs."

- Green Science Policy Institute (author of Madrid Statement)



QPL Products and Suppliers



Modified from Field & Place, Environ. Sci. Technol. 2012, 46, 7120−7127

QPL History: Nov 1969 Spec MIL-F-24385 Issued. First QPL Approval to 3M's FC-196. The first AFFF for Naval Fire Service was 3M's FC-183, Introduced in 1964. FC-183 was Later Replaced with FC-194 and then FC-195

From NRL Report 7437

Fire Fighting Foam Coalition Members:

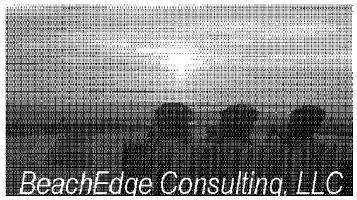
FFFC BOARD MEMBERS

ANGUS FIRE · ANSUL · CHEMGUARD · Chemours · dynax · NATIONAL FOAM

FFFC GENERAL MEMBERS

Fire Service Plus · fomtec · ICL · KIDRON · KV FIRE · Dr. STHAMER

The Industry Has Changed



Fluorotelomer and ECF Products : Different Chemistry

Fluorotelomers (Telomerization)

$CF_2=CF_2$ (TFE)

↓

$F(CF_2)_nI$ Perfluoroalkyl Iodide

n = 4,6,8,10,12, even

↓

$F(CF_2)_nCH_2CH_2I$ Fluorotelomer Iodide

→ $F(CF_2)_nCH_2CH_2SO_3X$: FT Sulfonate

→ AFFF Surfactants

↓

$F(CF_2)_nCH_2CH_2OH$ Fluorotelomer Alcohol

↓

Sales Products

Even number, straight chains, No Branching
Polymers n≥ 8 ; Surfactants n=6 primarily
By YE 2015 n ≤ 6

ECF (ElectroChemical Fluorination)

$H(CH_2)_nSH$

↓

$F(CF_2)_nSO_2F$ → $F(CF_2)_nSO_3X$

PASF = Perfluoroalkylsulfonates

PFOS n = 8;
PFH_xS n = 6
PFBS n = 4

↓

$F(CF_2)_nSO_2N(R)CH_2CH_2OH$

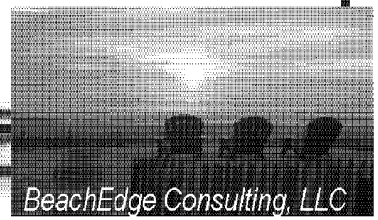
↓

Perfluoroalkyl sulfonamido ethanol

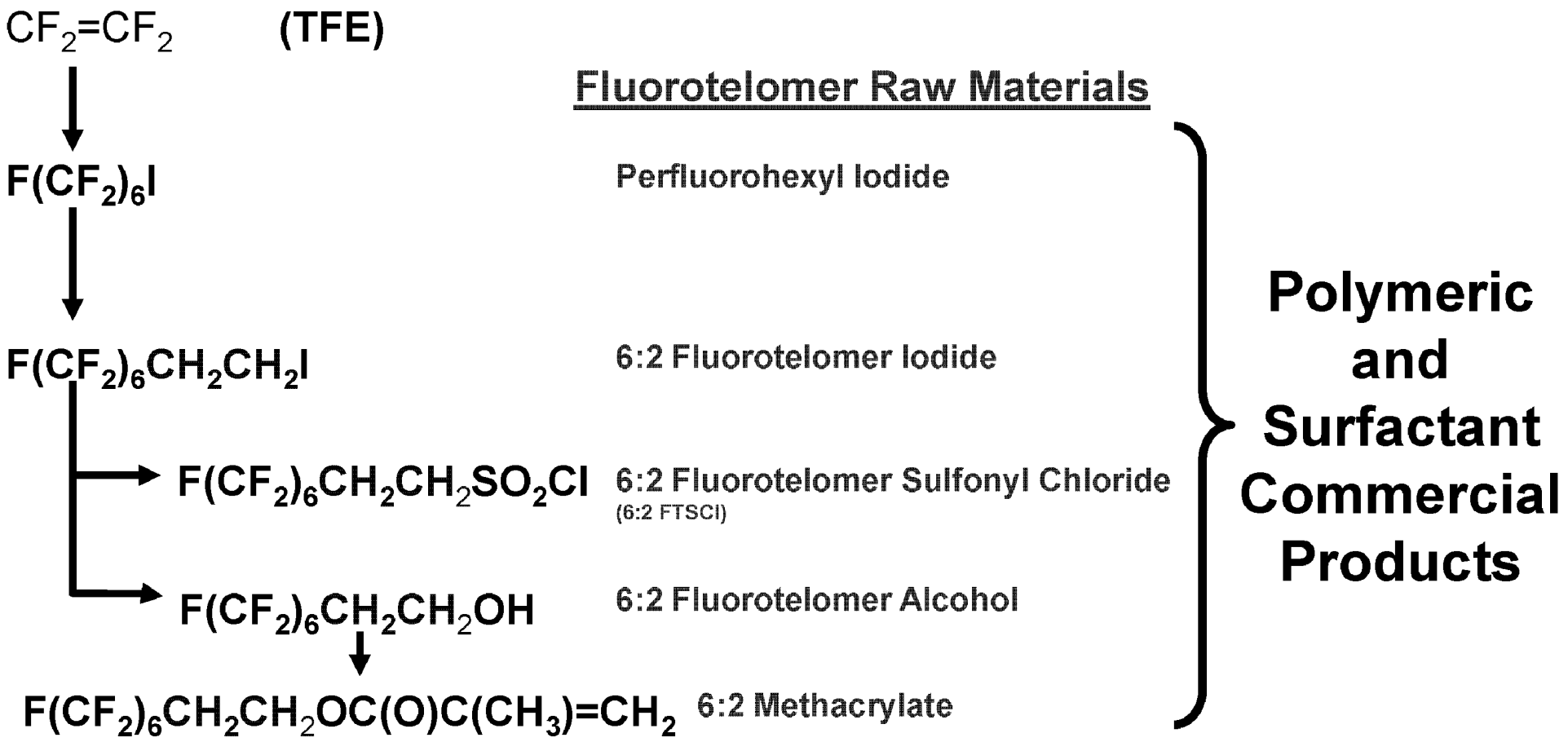
↓

Sales Products

ECF produced materials have up to 30% branched isomers at the fluorinated chain end and contain odd and even carbon chain lengths

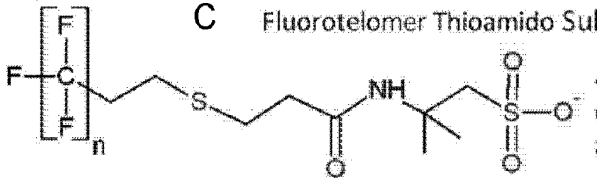


Synthesis: Short-chain Fluorotelomer-based products



The Chemistry: 1960's - Present

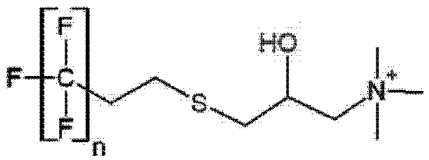
C Fluorotelomer Thioamido Sulfonates[N]



4:2 FtTAoS	n = 4	Qi
6:2 FtTAoS	n = 6	Sq
8:2 FtTAoS	n = 8	Qi

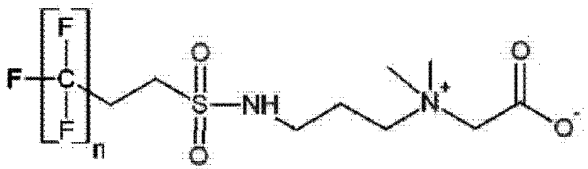
Fluorotelomer Thiohydroxy Ammonium[N]

D



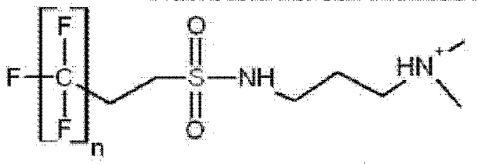
6:2 FtTHN+	n = 6	Sq

A Fluorotelomer Sulfonamido Betaines[N]



6:2 FtSaB	n = 6	Sq
8:2 FtSaB	n = 8	Qi
10:2 FtSaB	n = 10	Qi
12:2 FtSaB	n = 12	Qi

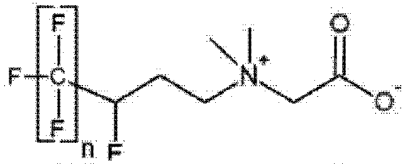
B Fluorotelomer Sulfonamido Amines[N]



6:2 FtSaAm	n = 6	Sq
8:2 FtSaAm	n = 8	Qi

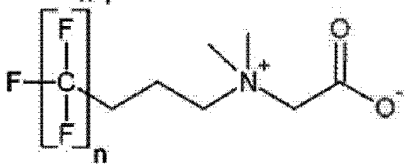
Fluorotelomer Betaines[N]

F



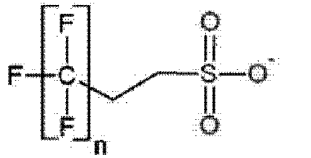
5:1:2 FtB	n = 5	Sq
7:1:2 FtB	n = 7	Sq
9:1:2 FtB	n = 9	Sq

G



5:3 FtB	n = 5	Sq
7:3 FtB	n = 7	Sq
9:3 FtB	n = 9	Sq

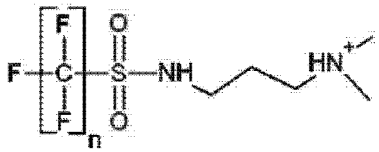
Fluorotelomer Sulfonates[L]



4:2 FtS	n = 4	Qn
6:2 FtS	n = 6	Qn
8:2 FtS	n = 8	Qn

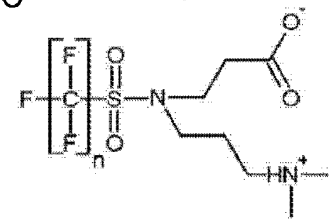
Fluorotelomer -Based: A-G

D Perfluoroalkyl Sulfonamido Amines[N]



PFBSaAm	n = 4	Qi
PFPeSaAm	n = 5	Qi
PFHxSaAm	n = 6	Qi
PFHpSaAm *	n = 7	Qi
PFOSaAm	n = 8	Qi

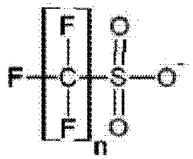
B, C Perfluoroalkyl Sulfonamide Amino Carboxylates[N]



PFBSaAmA	n = 4	Qi
PFPeSaAmA	n = 5	Qi
PFHxSaAmA	n = 6	Qi
PFHpSaAmA *	n = 7	Qi
PFOSaAmA	n = 8	Qi

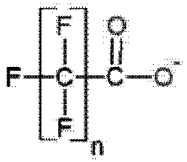
Perfluoroalkyl Sulfonates[L]

A



PFBS	n = 4	Qn
PFPeS *	n = 5	Qi
PFHxS	n = 6	Qn
PFHpS	n = 7	Qn
PFOS	n = 8	Qn
PFNS *	n = 9	Qi
PFDS	n = 10	Qn

Perfluoroalkyl Carboxylates[L]

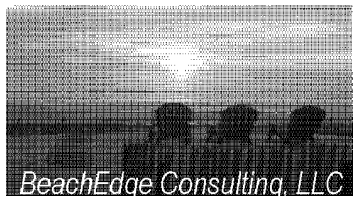


PFBA	n = 4	Qn
PFPeA	n = 5	Qn
PFHxA	n = 6	Qn
PFHpA	n = 7	Qn
PFOA	n = 8	Qn
PFNA	n = 9	Qn
PFDA	n = 10	Qn
PFUdA	n = 11	Qn
PFDoA	n = 12	Qn
PFTrA	n = 13	Qn
PFTeA	n = 14	Qn

ECF-Based: A-D

Backe, Day & Field; Environ. Sci. Technol., 2013, *47* (10), pp 5226–5234

ID Letters from: B.J. Place and J. A. Field, *Environ. Sci. Technol.* 2012, 46, 7123



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Dynax Fluorotelomer Betaine

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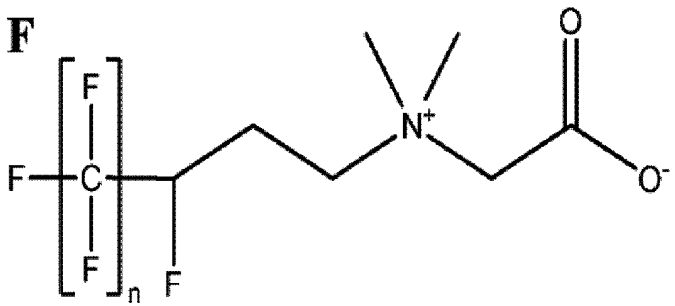

n = 5,7, 9

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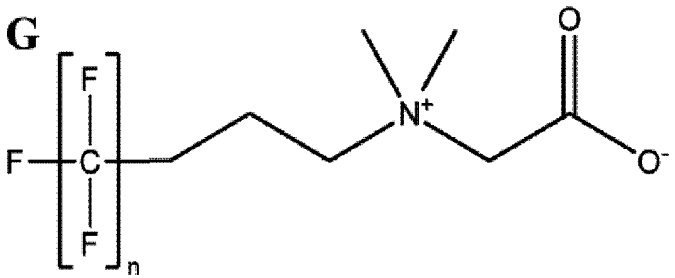


n = 5, 7, 9

DX3001*:

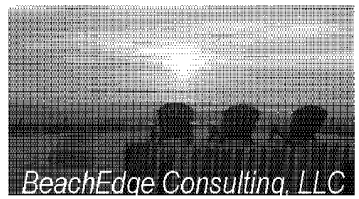
$RfCHFC_2H_4N^+(CH_3)_2CH_2COO^-$	~80%
$RfCH_2C_2H_4N^+(CH_3)_2CH_2COO^-$	~20%

Rf Distribution (average):

C5	C7	≥C9
45.4%	40.8%	~13.8%

***Production phased out in 2014**

Ref: Fig. F&G: B.J. Place and J. A. Field, *Environ. Sci. Technol.* 2012, 46, 7123



Transition to Short-chains

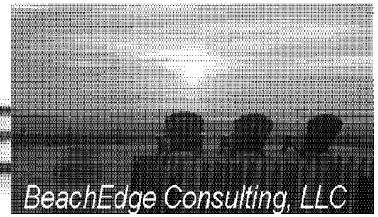
Is short-chain chemistry new?

No, key component of some foams since the 1970s

- AFFFs with >95% short-chain fluorotelomer-based fluorosurfactants have been on market for >30 years and exceed the most challenging industry standards
- AFFFs with >95% short-chain fluorotelomer-based fluorosurfactants have been primary foams used for last decade by US, Australian, and European armed services
- New mil-spec AFFF agents from ICL, National Foam, Solberg, and Tyco containing only short-chain fluorotelomer-based fluorosurfactants

From PFOS/PFOA to 6:2 Fluorotelomer Surfactants

Year	Events	Reference/Note
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 used; 134 dead/62 injured/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) **(C6 purity > 95-97%)**
1973	First AR-AFFF launched by National Foam	
1978	DC-10 Aircraft Fire at LAX	3M's Light Water used 196 lives saved out of 200
1982–	Large selections of 6:2 FT-Surfactants available to AFFF agent producers for US Mil-spec applications	6:2 FT-surfactants: **C6 (> 95-97%) + C4 & C8**



Fluorosurfactants for Firefighting Foams

Key Events 1990 – 2015

Year	Events
1991	Dynax is founded and starts fluorotelomer surfactant R&D.
1993-1995	Dynax introduces C5/C7/C9-based fluorotelomer surfactant (DX3001), and 1st and 2nd generation all C6 (≥99%) foam stabilizers: DX4302 & DX5011.
2000-2002	3M and Solberg exit PFOS-based AFFF agents market.
2001	FFFC (Fire Fighting Foam Coalition) is formed to represent the firefighting foam industry's interests on all issues related to the environmental acceptability of AFFFs.
2002	DuPont acquires Atofina's fluorotelomer surfactant business, including C6 fluorosurfactants.
2003	Chemguard acquires Ciba Specialty Chemicals' Lodyne fluorosurfactant business.
2006	EPA announces the 2010/2015 PFOA Voluntary Stewardship Program.
2011	Tyco acquires Chemguard.
2014	Dynax phases out its C5/C7/C9-based fluorosurfactant, and its only C8-fluorotelomer surfactant (DX2200)
2015	All VSP Fluorotelomer manufacturers exit long chain production by year end DuPont spins out Fluoroproducts Business into Chemours

Transition to Short-chains

- US EPA PFOA Voluntary Stewardship Program (VSP) 2010/2015
  - Started in 2006 with 8 fluorochemical manufacturers
  - By the end of 2010, 95% elimination…products & plants
  - By the end of 2015, "*work towards the total elimination*…"

- VSP fluorochemical manufacturers ended production of long-chain chemicals (≥C8) during or before 2015

- In response, most foam manufacturers have transitioned to the use of pure short-chain (C6) fluorosurfactants in Class B foams

- Environmental authorities consider perfluorinated chemicals containing less than eight carbons to have a lower potential for toxicity and bioaccumulation
  - Short Chains such as C6 Fluorotelomers have regulatory approvals in many global jurisdictions

US Environmental Protection Agency

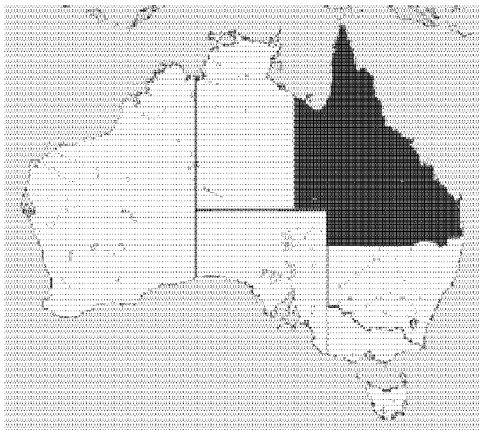
- TSCA Reform & Impact
- PMN Process, Innovation & Impact
- Health Advisory on PFOS and PFOA
  - Level: 70 ppt
  - Additivity: sum of PFOS & PFOA!!
  - Derivation
  - Implications
  - Contrast to Australia's enHealth June 2016 Recommendations: PFOA – 5 ppb and PFOS – 0.5 ppb and
  - Health Canada's 200 ppt MAC for PFOA

Queensland Foam Policy

Draft policy (now Final) on management of fire fighting foam published by the Queensland Department of Environment and Heritage Protection (DEHP)

Queensland Government

Restricts	use of fluorinated foams *
Permits	use of fluorine free alternatives



** by requiring "complete" containment of all discharges and disposal as a regulated waste and justification of C6 Agent usage vs FF*

Issue Number	Consultation Date
1st draft	December 2013
2nd draft	December 2014
3rd draft - Final	*None: 7 July 2016- Final!!***

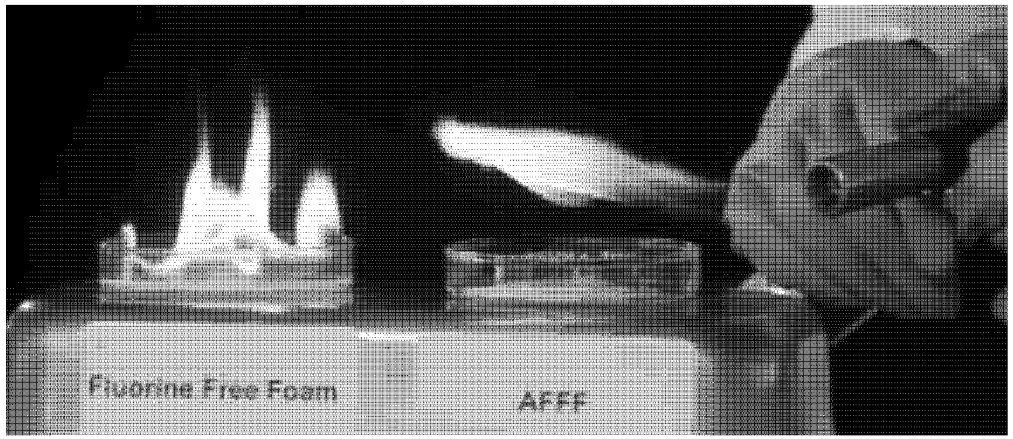
**Significant Objections raised by FPAA

Fluorine Free Foams

- Most foam manufacturers have developed fluorine-free (FF) foams that provide an alternative to fluorinated agents in some applications
- Do not have fire performance across all fuels and in all operational circumstances equal to fluorinated products
- 2011 paper by Naval Research Labs showed that AFFF agents extinguished gasoline and heptane fires about 70-80% faster than FF
- 2016 ACS presentation by NRL showed performance of an AFFF to be superior to a FF product:
  - Extinguishment: AFFF = 18 sec, FF = 40 sec
  - Foam Degradation: FF = 1-2 min, AFFF = 35 min

Fluorine Free Foams

- Fluorine-free foams are inherently oleophilic (fuel attractive)
- In the absence of oleophobic (fuel-repelling) fluorosurfactants, fluorine-free foam can easily pick up fuel and the contaminated foam degrades quickly and becomes flammable
- This fuel contamination problem compromises the fire performance and severely limits the application of fluorine-free foams



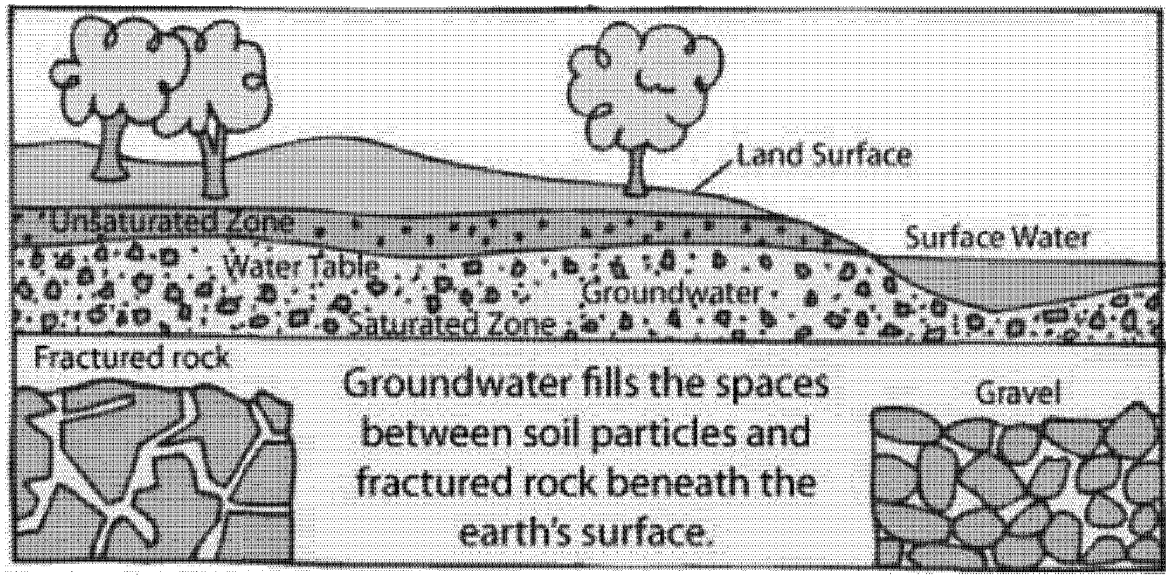
Source: "Flammability & Degradation of Fuel – contaminated Fluorine Free Foams " by Chang Jho, International Fire Fighter, 41, Issue 36 – November, 2012

Fluorine Free Foams: SERDP Project

- Strategic Environmental Research and Development Program Project Proposal 29 Oct 2015
  - WPSON 17-01 Fluorine Free Aqueous Film Forming Foam
- Proposal Reviews Completed Spring 2016
  - Administered by Noblis
- Project focused on Performance & Compatibility, EF&E and Toxicology including both ST and LT Research
- Outcome….

Foam Legacy - Contamination

- Groundwater and soil studies from fire training areas show multiple releases over many years results in long-term contamination
- Major issue at some military bases & some airports



Source: "What is Groundwater?" by The Groundwater Foundation, 2016

- Any facility where uncontrolled discharges of foam have taken place could have groundwater and soil contamination
- Growing concerns in US, Europe, Australia, Canada

Foam Legacy

- 3M or other PFOS-based foams contain and/or degrade into:
  - PFOS, PFHxS (C6 homologue of PFOS)
  - PFOA, PFHxA (C6 homologue of PFOA)

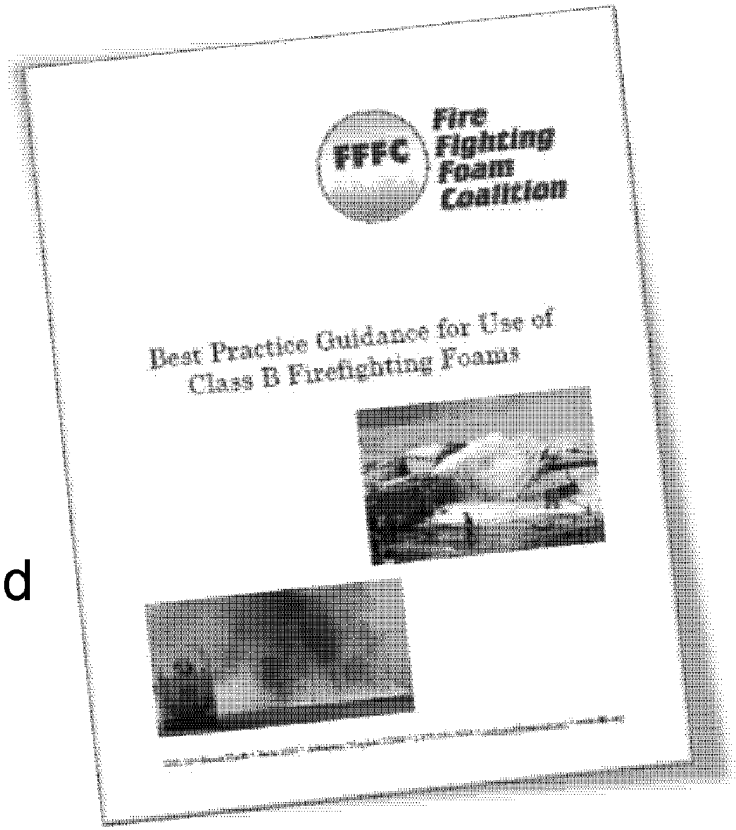
- Fluorotelomer-based foams contain and/or degrade into :
  - 6:2 Fluorotelomer Sulfonate (6:2 FtS), 8:2 FtS
  - PFHxA, PFOA, resp. (minor breakdown products)
  - Do not contain or breakdown to PFOS or PFHxS
  - Misconception to refer to fluorotelomer-based foams as “PFOA foams” and 6:2 FtS is not THPFOS!!
  - Not made with PFOA; PFOA is not an ingredient in the foam; only contain trace quantities of PFOA as an inadvertent byproduct of the fluorotelomer manufacturing process

Minimize Emissions - FFFC

- The vast majority of foam discharges result from the use of foam for training or testing of systems and equipment
- FFFC has developed best practice guidance that focuses on using alternative fluids and methods for testing and non-fluorosurfactant foams for training
- Also contains detailed guidance on containing and treating foam discharges
- Included as additions to NFPA 11, Appendix F

FFFC Best Practice Guidance

- Use fluorinated Class B foams only in situations that present a significant flammable liquid hazard
- Before deciding to use fluorinated Class B foam for a specific hazard, investigate whether other non-fluorinated techniques can achieve the required extinguishment and burnback resistance
- Be aware of the shortfalls of these alternative methods including no film formation, potential for longer extinguishments and reduced after-fire protection



FFFC Best Practice Guidance

- Use **training foams** that do not contain fluorosurfactants for training and testing purposes
- Provide for **containment**, treatment, and proper disposal of foam solution – do not release directly to the environment
- Develop firewater **runoff collection plans** if not already in place
- Plan system testing so as to properly contain and dispose of foam solution effluent generated by the tests

- With a live fire there are an unlimited number of circumstances, therefore, any and all actions should consider fire fighter and public safety first and in some cases property protection
- Develop plans for dealing with unplanned releases of foam concentrate or foam solution so as to minimize the environmental impact

Current Events

- Willow Grove - Horsham
- DuPont/Chemours
- AUS Senate & QLD DEHP
- New York
- VT
- NH
- CA
- AL
- MN
- US EPA HA & TSCA Reform
- EU Regs
- New York Times
- Air Force Solicitation Number:

FA8051-16-R-3004

Summary

- Regulatory agencies in Canada, Europe, and the United States have proposed regulations on the use of long-chain perfluorinated chemicals
- Emerging Issues at forefront of conversations
- The science debate has been reframed: The Fluorochemistry P's
- Foam legacy contamination issues are likely to be a growing concern
- Fluorinated fire fighting foams are the most effective agents currently available to fight flammable liquid fires (Class B)
- Fluorosurfactants provide exceptional extinguishing capability, but also an additional environmental challenge – persistence & mobility
- Environmental impact is being reduced further with the transition to short-chain (C_6) fluorosurfactants
- Industry is promoting use of best practices to reduce environmental impact of foam

Thank you an

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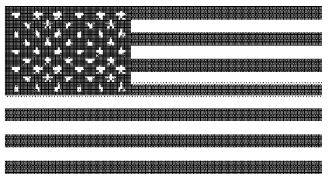
d questions?

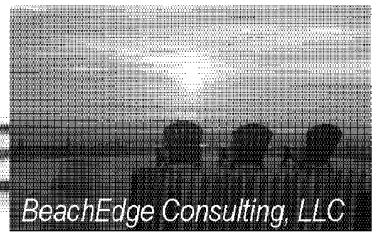
Back Up Charts

US Environmental Protection Agency



- US Environmental Protection Agency (EPA) has proposed a Significant New Use Rule (SNUR) on long-chain perfluoroalkyl chemicals (LCPFACs)
- SNUR is intended to provide a regulatory backstop to the US EPA 2010/2015 PFOA Stewardship Program
- As proposed, the SNUR would be expected to have minimal impact on the production and use of fire fighting foams

Prohibits	manufacture and import of LCPFACs for new uses and existing uses that are not ongoing
Permits	sale and use of LCPFACs



Synthesis: Fluorotelomer-based sulfonyl chemistry

$F(CF_2)_6CH_2CH_2SO_2Cl$ 6:2 Fluorotelomer Sulfonyl Chloride (6:2 FTSCl)

↓

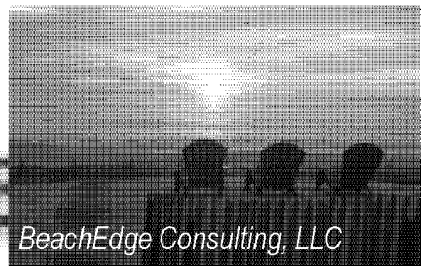
$F(CF_2)_6CH_2CH_2SO_2R$ **AFFF Surfactant Products**

↓ biodegradation

$F(CF_2)_6CH_2CH_2SO_3^-$ 6:2 Fluorotelomer Sulfonate (6:2 FTSA or 6:2 FTS)
6:2 FTS ≠ THPFOS

↓ biodegradation

6:2 biodegradation pathways



6:2 Fluorotelomer Sulfonate (FtS)

- It has been determined based on groundwater and soil monitoring studies that the 6:2 fluorotelomer sulfonate (6:2 FtS) is likely the primary breakdown product of the C_6 fluorosurfactants contained in telomer-based AFFF - $C_6F_{13}CH_2CH_2SO_3^-$

- Broad range of existing data indicate that 6:2 FtS is **not** similar to PFOS in either its physical or toxicological properties

  - Low in acute and sub-chronic toxicity
  - Low in aquatic toxicity
  - Negative for genetic and developmental toxicity
  - Not bioaccumulative according to regulatory criteria
  - Significantly lower than PFOS in biopersistence

Perfluorohexanoic Acid (PFHxA)

- Telomer-based foam products may contain trace levels of perfluorohexanoic acid (PFHxA), which is not being addressed by the EPA stewardship program
- Telomer-based foams (C_6 chemistry) may break down in the environment to PFHxA – research continues
- Extensive testing has provided a favorable toxicology profile for PFHxA
  - Low aquatic toxicity
  - Low acute oral toxicity
  - Not damaging to DNA, not genotoxic or mutagenic
  - Not a selective developmental or reproductive toxicant
  - Low biopersistence and *not bioaccumulative*