

Environmental Status and Use of Telomer Based Fluorosurfactants

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OUTLINE

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 - HISTORY OF PFOA/PFOS ISSUES
 - •TELOMER BASED FLUOROSURFACTANTS
 - •REACH REGULATIONS AND REQUIREMENTS
- •FLUOROSURFACTANT CHARACTERISTICS
- •FLUOROSURFACTANT APPLICATIONS



ENVIRONMENTAL ISSUES WITH PFOS/PFOA BASED PRODUCTS

What are the longterm prospects for fluorosurfactants in industrial applications?

Due to the decision by 3M to withdraw their <u>Perfluorooctyl</u> <u>Sulfonate</u> (PFOS) based products from the market, the only viable products left are produced from Perfluoro Telomer.

Recently, Perfluorooctanoic Acid (PFOA) has also come under considerable fire.

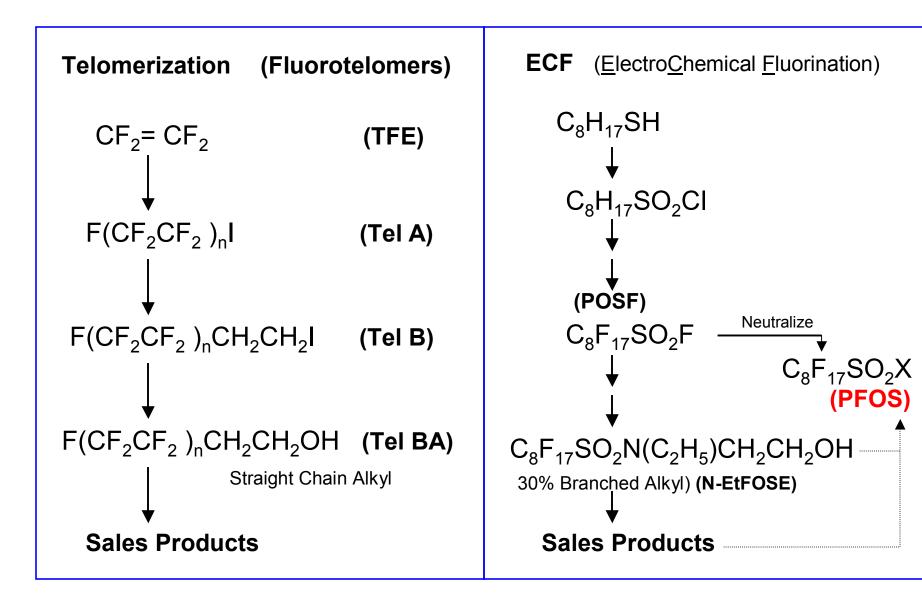


Why did 3M agree to phase out 90 Perfluorooctyl (FC95, FC120, FC135, FC430, ETC.) Sulphonate (PFOS) based products by 2003?

- Data indicate PFOS chemicals are Persistent
 - •PFOS is a very stable chemical that does not break down or degrade in the environment
- Data indicate PFOS chemicals are Bioaccumulative
 - •PFOS can build up over time; its half-life in human blood may be about 4 years
- Data indicate PFOS chemicals are Toxic
 - •PFOS is only moderately toxic via acute oral exposure; *rat LD*₅₀ *of 251 mg/kg*
 - •In repeat oral dose systematic and reproductive toxicity studies, however, serious effects are seen
 - Post-natal deaths in rats at 3.2 and 1.6 mg/kg/day
 - In repeat-dose treated Rhesus monkeys, death within 3 weeks at 10 mg/kg/day; within 7 weeks at 4.5 mg/kg/day.



Comparison : Telomerization vs. ECF Intermediate Products



ENVIRONMENTAL ISSUES WITH TELOMER BASED PRODUCTS

What are the longterm prospects for fluorosurfactants in industrial applications?

Telomer manufacturers have been required to do large quantities of research on the environmental properties and fate of Perfluoro Telomers.

To date, this research has indicated that Perfluoro Telomers, although Persistent, do not appear to Bioaccumulate or be Toxic as was PFOS. A positive result!



Why does Chemguard see Telomer Based Fluorosurfactants safe from EPA's action in the near future?

In October 2003, the EPA Telomer Technical Workgroup determined that telomer-based AFFF fire fighting foam is not likely to be a source of PFOA in the environment and will not have to be tested in the current enforceable consent agreement (ECA) process.

The EPA has concluded that existing data "provided no evidence that these fluorosurfactants (C6 perfluoro- telomer) biodegrade into PFOA or its homologs..."

The March 2005 Fire Fighting Foam Coalition (FFFC) states "there is no known pathway for the C6 fluorosurfactants used in AFFF to breakdown into PFOA."



Chemguard uses the same fluorochemical intermediate for the coatings, wetting and leveling market for as AFFFs!

Telomer fluorosurfactants in AFFF sold to the U.S. military:

Precursor - C₆F₁₃CH₂CH₂SH normally made from C₆F₁₃CH₂CH₂I, or 6-2 Telomer B iodide

Type of telomer surfactants - All contain group C₆F₁₃CH₂CH₂S- or C₆F₁₃CH₂CH₂SYCH₂CH-

Degradation products found in groundwater -

6:2 telomer sulfonate

C₈F₁₃CH₂CH₂SO₃⁻

Perfluorooctyl sulfonate (PFOS)

C₈F₁₇SO₃⁻X⁺

Perfluorooctanoic Acid (PFOA)

C₇F₁₆CO₂H

Perfluorohexanoic Acid (PFHA)

Conclusion - 6:2 telomer sulfonate is the likely biodegradation product of the C_s fluorosurfactants contained in AFFF sold to the U.S. military

Telomer based fluorosurfactants do not contain PFOA, PFOS or any of its derivatives or breakdown products.



REACH is the new European Community (EU) regulation governing the "Registration, Evaluation, Authorization and restriction of CHemicals"

It came into force on June 1st 2007 and replaces multiple European directives and legislation with a single regulation. All EU members are required to enforce it.

Its primary aim is to protect human health and the environment.

REACH will have major impact on the entire chemicals sector since manufacturers and importers of chemical substances made in or imported into the EU in annual volumes of 1 ton or more must register them with the European Chemicals Agency (ECHA).

It is estimated that more than **30,000** substances industry-wide will be affected by REACH.



REGISTRATION TIMELINE

PRE-REGISTRATION: JUNE 1, 2008- DECEMBER 1, 2008

REGISTRATION: 3 PHASES DEPENDING ON VOLUME

IMPORTED

1-100 TONS PER YEAR: JUNE 1, 2018 100-1000 TONS PER YEAR: JUNE 1, 2013

1000 TONS PER YEAR: NOVEMBER 30, 2010

REACH requires manufacturers and importers of chemical substances to obtain information on the physico-chemical, health and environmental properties of their substances and use it to determine how these substances can be used safely. Each manufacturer and importer must submit a registration dossier documenting data and assessments.

If substances are not registered correctly in time, they **cannot** be manufactured, imported or sold.

EVALUATION PROCESS

Dossier evaluation - ECHA decides whether REGISTRATION information complies with requirements and examines testing proposals made by registrants.

Substance evaluation – ECHA in coordination with the competent authorities of the Member States assesses the risk of substances to human health or the environment and determines the possible need for additional information and/or proposes further testing.



AUTHORIZATION PROCESS

Companies applying for authorization must demonstrate that any risk associated with uses of a substance is adequately controlled or that the socioeconomic benefits of use outweigh potential risk.

Restriction

The EU can impose restrictions and prohibit or set conditions for the manufacture, placing on the market or use of certain dangerous substances when unacceptable risks to humans or the environment have been identified.



BOTTOM LINE

It will cost more to sell into the EU and this law will likely spawn similar laws in other countries.

It is likely many chemicals will be discontinued due to the cost of testing.



MORE INFORMATION

REACH USA 2008 April 15-17 2008, Boston, Massachusetts, USA

http://www.rapra.net/products_and_services/Conferences/REACH_US A_2008.asp



FLUOROSURFACTANTS MAJOR ADVANTAGES

- Best known products for wetting
- Superior interfacial tension reduction which speeds up emulsion
- Can perform all vital surfactant jobs
- High cost can be offset by lower use levels

Characteristics vital to use

- Wetting ability
- Emulsification
- Corrosion inhibition
- Leveling

- Dispersing ability
- Foaming
- Pore penetration
- Anti-blocking



Fluorosurfactant Product Examples

Product	Туре	C6-perfluoro	Polymer Y/N	Mixture Y/N	
FS1	Amphoteric	> 50%	No	No	
FS2	Anionic	95% or >	No	No	
FS3	Cationic	95% or >	No	No	
FS4	Nonionic	> 50%	Yes	No	
FS5	Nonionic	95% or >	Yes	No	
FS6	Slightly Cationic	95% or >	No	Yes	
FS7	Slightly Cationic/Silicone	95% or >	No	Yes	
FS8	Anionic/Silicone	95% or >	No	Yes	



Fluorosurfactant Product Examples

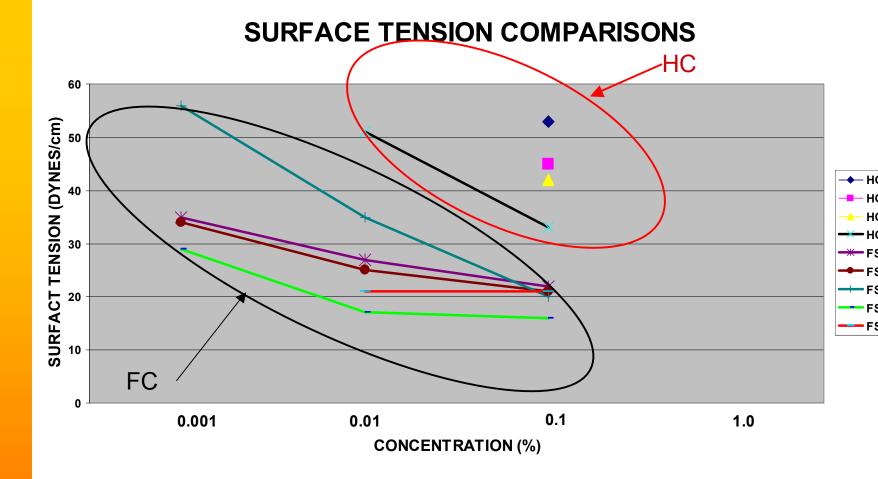
			_		Surface Tension (dynes/cm)*		
Product Name	Туре	Description	Solvent	Actives	0.1%	0.01%	0.001%
					(1,000ppm)	(100ppm)	(10ppm)
					(Actives Concentration)		
FS1	Amphoteric	Alkyl amino acid fluorosurfactant	Hexylene Glycol 10% tetramethylene sulfone 3% water 62%	25.0%	21	21.3	35.7
FS2	Anionic	Alkyl sodium sulfonate fluorosurfactant	Hexylene Glycol 15% magnesium sulfate 1.7% water 38.3%	45.0%	19.9	35.2	56.1
FS3	Cationic	Alkyl ammonium chloride fluorosurfactant	Hexylene Glycol 10% sodium chloride 3% water 57%	30.0%	28.6	46.6	55
FS4	Nonionic	Polyoxyethylene fluorosurfactant	Isopropanol 34% alkyl polyoxyethylene 18% water 3%	45.0%	21.2	24.6	34.3
FS5	Nonionic	Polyalkyl ether fluorosurfactant	Polyoxyethylene - polyoxypropylene 15%	85.0%	21.6	26.6	35.4
FS6	Cationic Blend	Alkyl ammonium chloride fluorosurfactant Blend	Hexylene glycol 10% Water 55%	45%	16.2	17.3	
FS7	Cationic/Silicone Blend	Blend of fluoro and silicone surfactants	Hexylene glycol 10% Water 55%	45%	16.4	16.4	
FS8	Anionic/Silicone Blend	Blend of fluoro and silicone surfactants	Hexylene Glycol 9.5% water 39%	48.4%	15.9	16.7	28.5



KRUSS TENSIOMETER







Fluorosurfactants (FC) impart 10 to 100 times lower surface tension than typical hydrocarbon Surfactants (HC) on water based solutions.



Chemguard Fluorosurfactant Product Line

PRODUCT TYPE	WETTING AGENT	FOAMING AGENT	SOLUBLE IN NONPOLAR	SOLUBLE IN POLAR	ANHYDROUS	CORROSION INHIBITOR	STABLE IN		
			SOLVENTS	SOLVENTS			HEAT	ACID	ALKALIES
S-100 AMPHOTERIC	X	X	-	X	-	-	X	X	X
S-111 AMPHOTERIC	X	X	-	X	-	-	X	X	X
S-103A ANIONIC	X	X	-	X	-	X	X	X	X
S-228M ANIONIC	X	-	-	X	-	X	X	X	X
S-106A CATIONIC	X	X	-	X	-	X	X	X	X
S-208A CATIONIC	X	X	-	X	-	X	X	X	X
S-216A CAIONIC	X	-	-	X	-	-	X	X	X
S-107B NONIONIC	X	-	X	X	-	-	X	X	X
S-222N NONIONIC	X	-	X	X	X	-	X	X	X







Specialty Chemicals & Equipment

Chemguard Fluorosurfactant Product Line

APPLICATION GUIDE

PRODUCT	S-100 amphoteric	S-111 AMPHOTERIC	S-103A ANIONIC	S-228M ANIONIC	S-106A CATIONIC	S-208 CATIONIC	S-216 CATIONIC	S-107B NONIONIC	S-222N NONIONIC
PAINTS WAXES POLISHES AND COATINGS Wetting Leveling Antisoiling	0.1 0.1 -	0.1 0.1 -	0.05 0.05 -	0.05 0.05 -	0.05 0.05 -	0.05 0.05 -	0.05 0.05 -	0.05 0.05 0.1	0.05 0.05 0.05
ADHESIVES Wetting Semi-Release Additive Nonaqueous formulas	0.1	0.1	0.05 0.1	0.05 0.1	0.05 0.1 -	0.05 0.1 -	0.05 0.1 -	0.05 0.1 0.1	0.05 0.05 0.05
GRAPHIC ARTS Leveling Wicking Decrease Emulsion Wetting	- - -	- - -	-		- - -	- - -	- - -	0.05 0.1 0.1	0.05 0.05 0.05
METALWORKS Plating Bath Aid Anticorrosion Cleaning and Scale Removal Degreasing	- - - -		0.05 0.05 0.05	0.05	- - - -		- - - -	0.1 0.1	0.05 0.05 0.05 0.1
CLEANING Alkaline Cleaners Glass Cleaner and Defogging Solvent Degreasing	0.1	0.1		-	- - -		- - -	0.1 0.1 0.1	0.05 0.05 0.05
FOAMING Hydrocarbon Foamer Aqueous Foamer Acid (HCI) Foaming	0.1	- 0.05 -	- 0.05 -	- - -	0.05 0.3	0.05 0.3	- - -	- - -	0.5



CONCLUSIONS

- •Telomer based fluorosurfactants are safer than PFOS/PFOA based products.
- •Telomer based fluorosurfactants offer similar characteristics to what the old PFOS based products imparted to formulations.
- •Concentrations can be low enough to make fluorosurfactants cheaper than hydrocarbon surfactants for many applications.
- •Lower concentrations equate to less product ultimately released into the environment.



QUESTIONS?

