

Perfluorooctyl Ethanol Biodegradation Transformation Products & Pathway

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Presentation Outline

- Background - Chemistry
- Environmental Fate Studies
 - Physical - Chemical Properties
 - 8-2 Telomer B Alcohol Biodegradation
 - Cold Studies
 - Radiolabel Studies
- Summary & Conclusions



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Fluorotelomer Chemistry

Telomerization (Fluorotelomers)



(TFE)

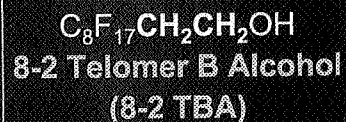


$n = 3 - 6$

Straight Chain Alkyl Only



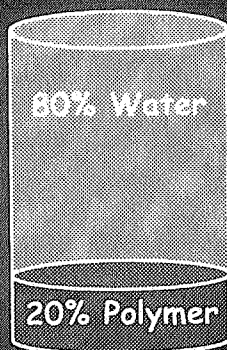
Sales Products



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A Typical Fluorotelomer-Based Polymeric Product



- Aqueous Dispersion of....
- 100-200 nm Polymeric Particles, > 10,000 Daltons MW, dispersed with...
- Hydrocarbon Surfactant(s)
- What happens to
 - the raw materials ? LIKE 8-2 TBA
 - the polymer ?
 - They are not likely to be the same

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Physical-Chemical Properties

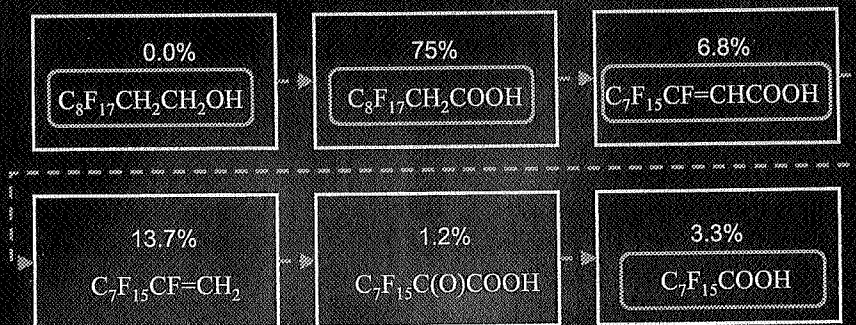
8-2 Telomer B Alcohol (8-2 TBA)

- | | |
|--------------------------------|--|
| – UV Absorption | Does not absorb visible light |
| – Low water solubility | $\sim 150 \mu\text{g}\cdot\text{L}^{-1}$ |
| – Vapor pressure | 3 Pa at 21 °C |
| – Adsorption | rapid and potentially irreversible |
| – a "difficult" test substance | |

Microbial Biodegradation : $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$

- Theoretical Model Prediction
- Standards
- Experimental
 - Cold Studies
 - Radiolabel Studies

CATABOL® Biodegradation *Prediction*



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Chemical Standards

To achieve *unequivocal quantitative accuracy and precision*

- **Isotopically - Labeled Standards**

- M+5 : $\text{C}_7\text{F}_{15}^{13}\text{CF}_2\text{CD}_2\text{CD}_2\text{OH}$ (internal standard)
- M+2 : $\text{C}_6\text{F}_{13}^{13}\text{CF}_2^{13}\text{COOH}$

- **“Cold” Standards**

- $\text{C}_8\text{F}_{17}\text{CH}_2\text{COOH}$
- $\text{C}_7\text{F}_{15}\text{CF}=\text{CHCOOH}$
- $\text{C}_5\text{F}_{11}\text{COOH}$, $\text{C}_8\text{F}_{17}\text{COOH}$

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Summary "Cold" Biodegradation Screening Studies

- Additional transformation products may have been formed
- Mass Balance was not achieved



Major Product in
"Ready" Study



Major Product in
"Inherent" Study



Minor Product(s)



Not Observed

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Radiolabel Studies : $\text{C}_7\text{F}_{15}^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

- Radiolabel
 - Identify & Quantify Transformation Products
 - Achieve Mass Balance
- Ready Biodegradability
- Accelerated Biodegradability

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Ready Biodegradation
Modified OECD 301D
of
 $\text{C}_7\text{F}_{15}^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Sponsored by the
Telomer Research Program
Asahi Glass, Clariant, Daikin, DuPont

Ready Biodegradation : Methods

- Modified OECD 301D Closed Bottle Test - 28 Days
 - 337 $\text{mg}\cdot\text{L}^{-1}$ dispersed in mineral medium
 - 13 $\text{mg}\cdot\text{L}^{-1}$ of ethanol (as co-solvent)
 - Inoculum : Municipal, Non-acclimated, 5 mL sludge $\cdot\text{L}^{-1}$
- Analytical
 - Parent $\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{OH}$ quantified by GC/MS
 - LC/ARC : separation and quantification of ^{14}C -labeled parent and transformation products
 - Transformation products identified by TOF-MS
 - Spike recovery of ^{14}C -parent and ^{14}C -transformation products from the sample matrices by liquid scintillation counting and LC/MS/MS, respectively

Spike Recovery from Sample Matrices

Substance spiked (dosed)	% Recovery*
$\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	92 ± 7
$\text{F}(\text{CF}_2)_7\text{CF}_2\text{CH}_2\text{COO}^-$	100 ± 20
$\text{F}(\text{CF}_2)_7\text{CF}=\text{CHCOO}^-$	81 ± 21
$\text{F}(\text{CF}_2)_7\text{COO}^-$	104 ± 14
$\text{F}(\text{CF}_2)_5\text{COO}^-$	120 ± 11

*: Average value for days 0, 7, 14 and 28.

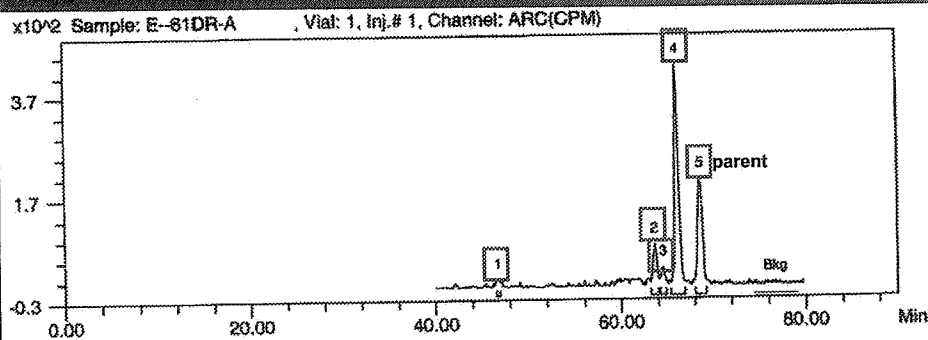


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Results - Day 28 biodegradation sample

LC/ARC analysis of ^{14}C -labeled transformation products



Peaks 1, 2, 3, & 4 are observed transformation products and peak 5 is the parent.



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Accurate Mass Measurement Observed Transformation Products

Determined mass	¹⁴ C-labeled transformation products	Elemental composition	Calculated mass	Error in ppm
478.9803	$\text{CF}_3(\text{CF}_2)_6^{14}\text{CF}_2\text{CH}_2\text{COO}^-$	$^{12}\text{C}_9^{14}\text{CH}_2\text{O}_2 \text{ F17}$	478.9816	-2.6
458.9764	$\text{CF}_3(\text{CF}_2)_6^{14}\text{CF}=\text{CHCOO}^-$	$^{12}\text{C}_9^{14}\text{CHO}_2 \text{ F16}$	458.9753	+2.3
414.9771	$\text{CF}_3(\text{CF}_2)_6^{14}\text{COO}^-$	$^{12}\text{C}_7^{14}\text{O}_2 \text{ F15}$	414.9691	+19.3
443.0037	$\text{C}_7\text{F}_{15}^{14}\text{CH}_2\text{CH}_2\text{COO}^-$ <i>proposed structure</i>	$^{12}\text{C}_9^{14}\text{H}_4\text{O}_2\text{F15}$	443.0004	+7.4

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Transformation Products Mass Balance Day 28

Transformation Products	% Total
Peak 1 - $\text{F}(\text{CF}_2)_7^{14}\text{COO}^-$	2.0
2 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}=\text{CHCOO}^-$	5.9
3 - $\text{F}(\text{CF}_2)_7^{14}\text{CH}_2\text{CH}_2\text{COO}^-$	2.3
4 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{COO}^-$	26.6
5 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ (parent)	16.1
$\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ (parent) adsorbed to test vessel surfaces	~ 40
Sum	93*

* Other unidentified minor transformation products together accounted for < 10% of mass balance, with each of them accounted for < 1% of mass balance.

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Ready Biodegradation Potential Biotransformation Route



Major Transformation
Product



Other fluorinated substances ?



New, Previously Unidentified
Transformation Product



Not Observed

(Does Not include unidentified minor transformation products)

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Accelerated Biodegradation 90 Days

Acclimated Sludge



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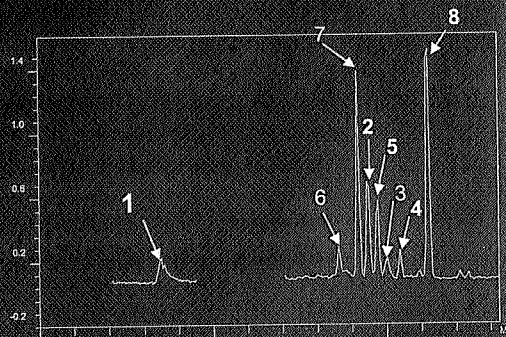
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Accelerated Biodegradation : Methods

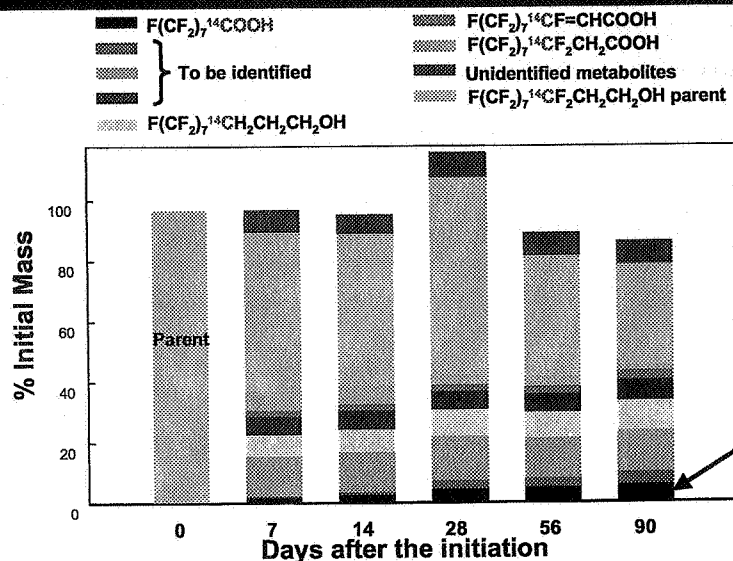
- Closed bottles
- Additional Carbon sources
 - 0.1% yeast extract and $\sim 50 \text{ mg}\cdot\text{L}^{-1}$ ethanol
- Inoculum
 - Industrial sludge adapted 8-2 Telomer B alcohol prior to the test
- Experimental Duration: 90 days at room temperature
- Analysis
 - fluoride selective electrode $[\text{F}^-]$
 - LC/ARC and Q-TOF-MS for ^{14}C -transformation products, and LC/MS/MS for PFHA.

Results - Day 90 Sample

- 1 - $\text{F}(\text{CF}_2)_7^{14}\text{COOH}$
- 2 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}=\text{CH}-\text{COOH}$
- 3 -
- 4 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2-\text{COOH}$
- 5 - $\text{F}(\text{CF}_2)_7^{14}\text{CH}_2\text{CH}_2-\text{COOH}$
- 6 -
- 7 -
- 8 - $\text{F}(\text{CF}_2)_7^{14}\text{CH}_2-\text{CH}_2-\text{OH}$
(parent)



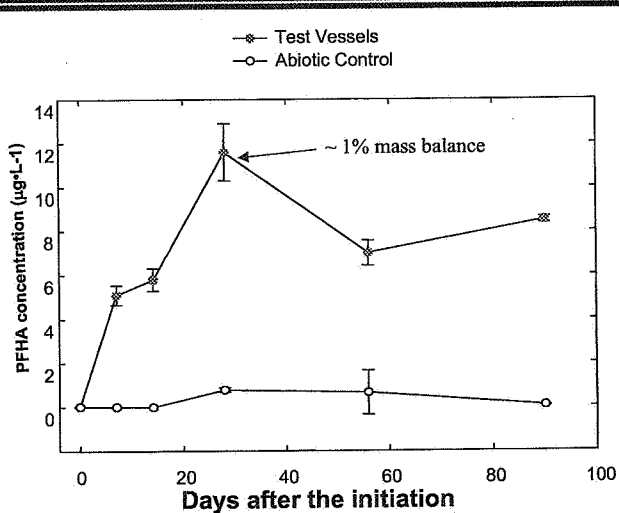
Time Course of Biotransformation



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Time Course of Perfluorohexanoic Acid $\text{F(CF}_2)_5\text{COOH}$ Formation



Spike Recovery (%)

Day 0	113
Day 7	102
Day 14	482?
Day 28	134
Day 56	177
Day 90	177

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Inherent Biodegradation - 90 Day Study

$C_7F_{15}^{14}C F_2CH_2CH_2OH$

- Many Additional ^{14}C containing transformation products
 - structural identification in-progress
- $^{14}CO_2$ observed
- $C_5F_{11}COO^-$ is a transformation product
- $C_7F_{15}COO^-$ is not formed rapidly or in great amount nor is it the primary transformation product
- Results suggest a transformation route or route(s) where more than one $-CF_2-$ group is "degraded"



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Summary & Conclusions

- Many transformation products observed in tests conducted
 - 8-2 Telomer B Acid and α - β unsaturated acid are stable transformation products; others need to be structurally verified
 - $C_7F_{15}COO^-$ is a *minor* transformation product
 - no $C_8F_{17}COO^-$ observed
- Transformation of multiple $-CF_2-$ groups was observed
 - $^{14}CO_2$ and $C_5F_{11}COO^-$
- Results suggest additional investigations
 - understand actual environmental partitioning
 - transformations in other environmental compartments



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