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TECHNICAL REPORT SUMMARY

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POSF reviewed
vs PFOS fate.

SEP 14 1983

TO: TECHNICAL COMMUNICATIONS CENTER – 201-2C-12

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Division Environmental Laboratory (EE&PC) - 21-2W-05	Dept. Number 0535
Project Commercial Chemicals Division	Project Number 9970012600
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To R. L. Bohon - Environmental Labortory - 21-2W-05	Period Covered or Date Sept. 1, 1983
Author(s) E. A. Reiner - Environmental Laboratory - 21-2W-05	Employee Number(s) 47816
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3M CHEMICAL REGISTRY ▶ ☐ Check box if new chemicals are reported. Use Chemical Registry Form 6092 to report all new substances.

KEYWORDS:
Lab Code
LEE&PC

Other Keywords

CURRENT OBJECTIVE:

The objective of this report (written in July, 1982) was to predict the environmental properties of POSF (FM-3168) and evaluate its environmental risk.

REPORT ABSTRACT: This abstract information is distributed by the Technical Communications Center to alert 3M'ers to Company R&D. It is Company confidential material.

POSF (perfluorooctane sulfonyl fluoride) is not a significant environmental hazard because very little of the POSF manufactured reaches the environment.

A review of the manufacture and processing of PCSF shows that less than 2% of that synthesized reaches the environment. Of this, 1/2 is discharged with wastewater, 1/4 is lost to the atmosphere, and 1/4 is landfilled. Some of the material which undergo treatment could be adsorbed by waste treatment sludge and eventually land applied with this sludge. A fraction of the sewered POSF is also likely to be volatilized from waste treatment during aeration and dispersed in the atmosphere. No biodegradation and very little hydrolysis of POSF is expected in wastewater treatment.

At Full capacity for design
24 to 28 Ton/yr POSF
lost to sewer
from process
6/26/98
Discothem design
John Hunter letter

Information Liaison
Initials AM

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Exhibit
1292
State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

1 7-6-82

ENVIRONMENTAL ASPECTS OF POSF

I. SUMMARY

POSF (perfluorooctane sulfonyl fluoride) is not a significant environmental hazard because very little of the POSF manufactured reaches the environment.

POSF is not a product. It is an intermediate used in the manufacture of other fluorochemicals. POSF is made from OSF (octane sulfonyl fluoride) in electrochemical fluorinate cells. The cell products are purified by distillation and the distillate is reacted to form a variety of fluorochemical intermediates and products.

A review of the manufacture and processing of POSF shows that less than 2% of that synthesized reaches the environment. Of this, 1/2 is discharged with wastewater, 1/4 is lost to the atmosphere, and 1/4 is landfilled. Some of the material which undergo treatment could be adsorbed by waste treatment sludge and eventually land applied with this sludge. A fraction of the sewered POSF is also likely to be volatilized from waste treatment during aeration and dispersed in the atmosphere. No biodegradation and very little hydrolysis of POSF is expected in wastewater treatment.

II. ENVIRONMENTAL ENTRY

A. Manufacturing

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A review of the manufacturing process indicates the POSF will enter the environment by 3 routes: 1) disposal of cell tars; 2) maintenance of cell electrolite composition; and 3) distillation of cell products. Table 1 shows the maximum estimated environmental releases of POSF from manufacture assuming an annual production 1,000,000 lbs of POSF per year.

Table 1 - Environmental Release of POSF From Manufacture

Process Causing Release	POSF Release (lbs/yr)	
Removing tars from cells	<45 (to wastewater treatment)	underestimated for PFOS based on disco therm design
Cell electrolite maintenance	<2000 (to landfill)	
Cell product distillation	<900 (to landfill) <7500 (to wastewater treatment) <2500 (to atmosphere)	
Total release	<13,000	24-28 Tons/yr. per JSH 6/26/98
% release	<1.3%	

1. Disposal of Cell Tars

High molecular weight tarry materials that accumulate in the electrochemical fluorination cells are washed from the cells by high pressure water streams and sewered. Additional tars are sewered after removal by bubbling steam through the cells in water filled boil-vats. Finally,

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tars which fall off the cells in the housing units (cell bodies) are sewered, or landfilled when large volumes are present.

Cleaning of the cells is done approximately once every 6 weeks, and approximately 100-200 lbs of tars are disposed at each cleaning. Tars are estimated to contain 1-2% POSF. Based on this estimate <5 lbs of POSF enter the environment through this route every 6 weeks (<45 lbs/year) and the majority of this would go to wastewater treatment.

2. Maintenance of Cell Electrolite Composition

A second manufacturing process route of loss results from maintenance of the electrolite within the cells. Typically 2,500 lbs of electrolite is withdrawn from the cells 2 times per week and distilled to recover HF. Approximately 60% of this withdrawn material (HF) is returned to the cells. The remainder which contain approximately 2% POSF is landfilled. Approximately 2,000 lbs of FOSF per year is landfilled because of this cell maintenance process.

3. Distillation of Cell Products

The third route of POSF environmental entry is at the cell products distillation step. POSF is purified primarily by a single plate distillation, but some is fractionally

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distilled. Materials distilling at higher or lower temperatures contain some POSF, but this is consumed in the manufacture of other products.

Three percent of the cell products remain as bottoms after distillation. These consist mostly of very high boiling materials and have little POSF (probably <3%). Assuming the manufacture of 1,000,000 lbs of cell products, <900 lbs of POSF per year would be landfilled with these bottoms.

During distillation 0.5-1% of POSF is lost to volatilization. Based on estimates that the scrubbers are 75% efficient, 1200-2500 lbs/year would be lost to the atmosphere and 3800-7500 lbs/yr would be discharged with scrubber water to the wastewater treatment system as a result of the distillation process.

B. Usage

Very little POSF is wasted as a result of its use in the synthesis of other fluorochemicals. POSF is the most expensive component in these synthesis reactions, and because of this cost, it is reacted with excesses of other reactants. Also, tests are frequently made to make sure the POSF is completely consumed. It can be assumed that less than .5% of POSF is lost in usage.

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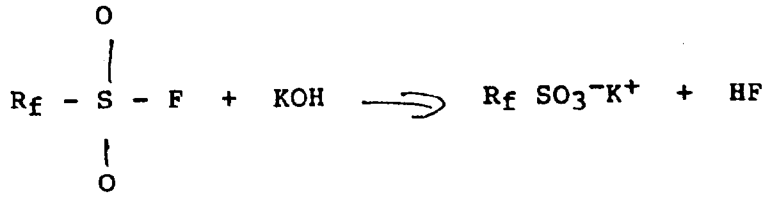
POSF is transported by pipeline within the plant. These pipelines are cleaned by purging them with N_2, which forces POSF to return to the tank or reactors. As a result, no POSF is normally lost from within plant transportation. Little (<5%) POSF is shipped off the plant site. Almost all is shipped in steel drums lined with blow-molded polyethylene, and most is sent to 3M's Chemolite plant. Due to its low viscosity, POSF can be nearly completely removed from the drums. The POSF remaining in the drums (approximately 0.2%) is normally destroyed with the drums in the Chemolite Incinerator.

III. ENVIRONMENTAL FATE

A. Persistence

Under strongly basic conditions (pH >10) POSF will react to form the sulfonic acid salt.



$$R_f - \overset{\displaystyle O}{\overset{|}{\underset{\underset{\displaystyle O}{|}}{S}}} - F + KOH \longrightarrow R_f\,SO_3^-K^+ + HF$$

At neutral pH this reaction is very slow. For example, POSF can be steam distilled or stored for extended periods in the presence of water without detectable degradation. Nevertheless, the perfluorosulfonic acid and its salts will be the eventual hydrolysis products of POSF, although the halflife of POSF may be weeks, months, or even years be longest under acidic conditions.

Biodegradation is not expected to occur with POSF. Laboratory testing shows no biodegradation of its sulfonic acid hydrolyses product. This lack of biodegradability is predicted since all perfluorochemicals are resistent to biodegradation.

B. Mobility

No direct measurements of the environmental mobility of POSF have been made. Rough estimates however can be made based on its physical chemical properties (Table 2).

Table 2 - Physical Chemical Properties of POSF

Vapor pressure	1.6 mm Hg at 20°C 2.5 mm Hg at 25°C
Molecular weight	502
Boiling range	154-155°C
Specific gravity	1.838
Heat of vaporization	20.3 cal/g
Solubility in water	Very low*

*No actual measurements of water solubility have been made. It is known to be very low and is estimated to be in the same range as that of inert fluorochemical liquids (1-10 ppm). (Calculations confirming this very low solubility are attached in an appendix.)

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These physical chemical properties suggest that volatilized POSF would tend to stay in the atmosphere, and would not be removed at a significant rate by rain or deposition.(1) POSF would also tend to move from water into sediments or the atmosphere, and would tend to be immobile in soil.

IV. EFFECTS

No actual environmental effects data exists on POSF. Based on the limited toxicology data and our experiences with other non-water soluble perfluorochemicals, no significant toxicity to terrestrial plants or aquatic organisms is expected. While the material could bicconcentrate, this is unlikely to be of significance since so little POSF enters the environment.

Appendix - Calculated Solublity of POSF

The following shows how the solubility of POSF ($C_8F_{17}SOF$) can be calculated from the measured solubility of $C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$ (Ethyl FOSE Alcohol).

The structure activity relationships used here, however, may not be valid for use with perfluorochemical like POSF. The probable reason for this is that perfluorochemicals are both hydrophobic and oleophobic. An example of this problem is work done with tri-perfluorohexylamine which revealed a 5 order of magnitude discrepancy between the measured partition coefficient (K_{ow}) and that calculated from its water solubility of 0.76 mg/l. Its calculated K_{ow} was 1.25×10^6 while its measured K_{ow} was 1.1×10^1.

The water solubility of Ethyl FOSE Alcohol has been measured 2 times with the following results: 0.05 mg/l and 0.16 mg/l. The average value of 0.1 mg/l will be used in this calculation. This is equivalent to a molar solubility (S) of 0.18 u moles/l. Using the regression equation of Banerjee et al.(2) and its melting point of approximately 45°C, one can calculate the log octanol water partition coefficient (log K_{ow}) for Ethyl FOSE Alcohol.

$$\log K_{ow} = 6.5 - 0.89 \log S - 0.015 (MP)$$

$$\log K_{ow} = 6.5 - 0.89 (-.74) - 0.015 (45)$$

$$\log K_{ow} = 7.2$$

1

coefficients, (3) one can calculate the log K_{OW} for (POSF) from the log K_{OW} of Ethyl FOSE Alcohol

$R - SO_2F$ = POSF

$R - SO_2N\begin{smallmatrix}CH_2CH_3\\CH_2CH_2OH\end{smallmatrix}$ = Ethyl FOSE Alcohol

The fragment constant for $-SO_2F$ (f_{SO_2F}) when attached to aromatics is 0.30. Its fragment constant to an aliphatic is not listed (3) but aliphatic fragment constants for fragments without carbon or hydrogen are always lower. On an average they are lower by .87. This calculation assumes that the aliphatic fragment constant for $-SO_2F$ is 0.30-0.87 = -0.57.

The fragment constant for $-SO_2N\begin{smallmatrix}CH_2CH_3\\CH_2-CH_2\end{smallmatrix}-OH$ is calculated from the sum of its fragment constants (f) and binding and branching factors (F) as follows.

The factor for SO_2N = has only been measured for aromatics as -2.09. Again this calculation assumes the fragment constant for aliphatics as (-2.09 - 0.87) = -2.96 = $f_{SO_2N=}$

The bonding factor F_B is calculated by multiplying the number of bonds, not counting those from hydrogen or within fragments, minus 1 (n-1 = 4) times the bond factor. Here, as described in the method, a bond factor of -0.20 is used since 3 hydrophobic chains radiate from a tetrahedral atom (the N). Therefore $F_B = 4(-0.20) = -.80$. Another factor for branching F_{Br} is calculated by multiplying the number of branches times -0.13.

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The fragment constant for $-SO_2N(CH_2CH_3)CH_2CH_2OH$ is thus

$1f_{CH_3} + 3f_{CH_2} + f_{SO_2N=} + f_{-OH} + F_B + F_{Br}$

$= 0.89 + 3(0.66) - 2.96 - 1.64 - .80 - .13$

$= -2.66$

The log K_{ow} for POSF is then calculated as:

log K_{ow} = log K_{ow} for Ethyl FOSE Alcohol -

$f_{SO_2N(CH_2CH_2)CH_2CH_2OH} + f_{SO_2F}$

Log $K_{ow} = 7.2 - (-2.66) + (-0.57)$

log $K_{ow} = 9.29$

The solubility of POSF can be calculated by using the regression equation of Banerjee et al. (2)

log S = 7.3 - 1.12 log K_{ow} - 0.017 (MP)

Since POSF is a liquid, 25°C is used instead of the actual melting point.

= 7.3 - 1.12 (9.29) - 0.017 (25)

log S = -3.5

S = .0003 u moles/l

S = .15 ug/l

This is an extremely low water solubility. Due to the lack of experience in applying these methods to perfluorochemicals and the number of assumptions made the reliability of this calculation is low. The calculation, however, does confirm the low solubility of POSF.

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REFERENCES

1. Cupitt, Larry T. Fate of Toxic and Hazardous Materials in the Air Environment. EPA 600/3-80-084, August (1980), NTIS #PB80-221948.

2. Ref: Banerjee, S., Yalkowsky, S. H., and Valvani, S. C.; Water Solubility and Octanol-Water Partition Coefficients of Organics. Limitations of the Solubility-Partition Coefficient Correlation. Environmental Science and Technology Vol. 14(10) p. 1227-1229 (1980).

3. Hansch, C. and A. Leo, Substitutent Constants for Correlation Analysis in Chemistry and Biology, John Wiley & Sons, 1979.

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