FLUOROCHEMICAL USE, DISTRIBUTION AND RELEASE OVERVIEW

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FLUOROCHEMICAL USE, DISTRIBUTION AND RELEASE OVERVIEW

Introduction

This paper and accompanying appendices provide an overview of the use, distribution and environmental release of sulfonyl-based fluorochemicals (FCs) produced by 3M Company. The paper and appendices are intended to present a preliminary review of FC pathways for human and environmental exposure from the time these materials leave the control of 3M through their end-use and/or disposal. This assessment is primarily *qualitative* and is based on available information within 3M and the experience and judgment of 3M's FC marketing and technical support personnel.

3M undertook this review for two purposes: (i) to support initial judgments about the exposure scenarios of greatest significance and set priorities for in-depth quantitative evaluation of the use and disposal profile of selected FC products; and (ii) to guide and set priorities for product reformulation, customer communication and other product stewardship activities. Although the review is preliminary and qualitative, it may be useful in providing EPA and other agencies with an introduction to FC exposure issues.

3M has already taken a range of actions based on this preliminary review. These include product and environmental stewardship initiatives to reduce FC exposures and releases at 3M and downstream manufacturing locations. In addition, 3M is in the process of developing a comprehensive exposure assessment plan which will include further modeling, monitoring and product use simulations. Preliminary work to support this assessment is already underway. A summary of 3M's stewardship initiatives and exposure assessment workplan is presented in the final section of this paper.

Because the information in this paper and appendices is preliminary and qualitative, it contains some worst-case estimates of potential exposure and release levels. For this reason, the information in the paper should be used with caution. 3M expects that more realistic estimates of human exposure and environmental release levels will be available once its exposure assessment plan is implemented.

The 3M ECF Process

FCs are components of several important 3M product lines due to their unique and useful properties. As components of products, they repel both water and oil, reduce surface tension much lower than other surfactants, act as catalysts for oligomerization and polymerization, and function where other products would rapidly degrade.

3M Company utilizes a process known as Simons Electro-Chemical Fluorination (ECF) to synthesize organofluorine molecules. In this process, organic feedstocks are dispersed in liquid, anhydrous hydrogen fluoride, and an electric current is passed through the solution, causing the hydrogen atoms on the molecule to be replaced with fluorine. The predominant components of the products created by this process have the same carbon skeletal arrangement as the feedstock used, but with all of the hydrogen atoms replaced by fluorine. However, fragmentation and rearrangement of the carbon skeleton can also occur and significant amounts of cleaved, branched and cyclic structures may be formed. The degree of fluorination of the organic feedstock is also dependent upon the specific carbon chain length of the feedstock and parameters of the ECF process such as electrical current and the length of time the process is run. It is possible to synthesize fully fluorinated or perfluorooganic molecules where all of the hydrogen atoms of the hydrocarbon feedstock have been replaced by fluorine atoms. Using these perfluorooganic molecules as basic building blocks, unique chemistries can be created by further reactions with functionalized hydrocarbon molecules.

3M built the first manufacturing pilot scale ECF process in 1949 and has continued to develop and improve the Simons ECF process for the production of fluorochemical products. Currently, 3M has three manufacturing sites in the United States using the ECF process (Cottage Grove (pilot production only), MN, Cordova, IL, and Decatur, AL). FC production using the ECF process occurs outside the United States at 3M's facility in Antwerp, Belgium.

3M Production of Sulfonyl-based Fluorochemicals

3M has produced sulfonyl based fluorochemicals commercially for over 40 years using the ECF process. A basic building block of such products and the highest production volume fluorochemical 3M manufactures is perfluorooctanesulfonyl fluoride (POSF). POSF is produced in the United States primarily at 3M's Decatur facility in quantities of around *3.5 million pounds* per year (1997). The starting feedstock for producing POSF is 1-octanesulfonyl fluoride.

Reaction 1

$$C_8H_{17}SO_2F + 34HF \xrightarrow{ECF} C_8F_{17}SO_2F + 17\,H_2$$

1-Octanesulfonyl Fluoride — Perfluorooctanesulfonyl fluoride (POSF)

The electrochemical fluorination process yields about 34%-40% straight chain (normal) POSF, and a mixture of byproducts and waste of variable composition. Because of slight differences in process conditions, raw materials, and equipment, the mixture produced by the electrochemical fluorination process varies somewhat from lot-to-lot and from plant-to-plant. The product that results from electrochemical fluorination is thus not a pure chemical but rather a mix of isomers and homologues.

During production, byproducts and waste products are formed. The volatile waste products, such as perfluoromethane, are vented to the atmosphere, but a program is underway to capture and destroy these releases by thermal oxidation. The tars formed in the process are incinerated at 3M corporate hazardous waste incinerator. The byproducts, many of which are incompletely fluorinated with hydrogen atoms still present, can be recycled back into the ECF process or are partially degraded in stabilization processes, and eventually discharged to controlled, in-house, wastewater treatment systems. The treatment sludge is either landfilled or land-incorporated. Some of the non-POSF byproducts are recovered and sold for secondary uses.

POSF is itself a commercially viable product, and in 1997 was sold in quantities of approximately *84,000 pounds* for use as an industrial raw material (mainly outside the US). However, the primary use of POSF is within 3M, where it functions as an important intermediate in the synthesis of substances used in many other 3M fluorochemical products. The majority of internally-consumed POSF is used to produce functionally derivatized fluorochemicals and high molecular weight polymeric products. **Table 1** identifies POSF-based fluorochemicals, their acronyms, chemical names, and formulas. To a lesser extent, some homologues of POSF, [$C_nF_{(2n-1)}SO_2F$ where n=other than 8], principally perfluorohexanesulfonyl fluoride, are also intermediates in the formation of other 3M products.

Perfluorooctane sulfonic acid (PFOS) will result from the chemical or metabolic hydrolysis of POSF-derived FCs. Under appropriate conditions, the perfluorooctane sulfonate anion can form salts with monovalent metallic cations. Current information indicates that PFOS or its salts cannot be broken down further chemically under normally occurring environmental conditions. Therefore PFOS is the ultimate degradation product from POSF derived fluorochemicals and will generally persist in that form. PFOS is also a commercialized product used for a variety of surfactant applications (mainly fire-fighting foams and coating additives). 3M sells approximately 50,000 lbs/year of-PFOS salts.

Using POSF as a basic building block, unique chemistries can be created by derivatizing POSF through the sulfonyl fluoride moiety of the molecule using conventional hydrocarbon reactions. Charts 1 and 2 outline the general classes of fluorinated materials made by 3M. The major intermediates are represented by the trunk of the "tree" in Chart 1. POSF is reacted with methyl or ethyl amine to produce either N-methyl or N-ethylperfluorooctanesulfonamide (FOSA). FOSA is subsequently reacted with ethylene carbonate to form either N-methyl or N-ethylperfluorooctanesulfonamidoethanol (FOSE). The FOSA and FOSE intermediates are the principal building blocks of 3M's product lines. By poundage, methyl-fose based intermediates and products slightly predominate over ethyl-fose-based materials.

The secondary reactions producing all of these derivatives are single or sequential batch processes that do not necessarily produce pure products. There may be varying amounts of fluorochemical residuals (unreacted or partially reacted starting materials or intermediates) that are carried forward to the final product. Examples of such residuals include PFOS, n-methyl and n-ethyl FOSA and N-MeFOSE and N-Et FOSE alcohols. Typically, where present, these residuals can be found at a concentration of 1-2% or less in final products and, in the aggregate, represent roughly 1-2% of total FC production volume. (FC residuals in 3M products have the potential to degrade or metabolize to PFOS.) In addition, during product use or disposal, the non-fluorochemical moieties added to the sulfonyl fluoride group of POSF can also be removed through a variety of degradation processes (chemical, environmental and metabolic). In such instances, the fluorochemical species which is ultimately produced as a result of such degradation will generally be PFOS as well.

3M Sulfonyl-based Fluorochemical Products

The 3M Chemical product lines that use POSF-based fluorochemicals are summarized below. In some cases, 3M manufactures the final commercialized product. In other cases, 3M sells a fluorochemical which another company incorporates into its final product. (Product lines using fluorochemicals which contain no sulfonyl groups are not listed).

POSF-derived fluorochemicals (polymers and monomers) are formulated with water or solvent, with the FC component (or FC solids) representing 20-35 percent of the formulation. Total U.S. production of FC solids across 3M's product lines is about 4 *million pounds.* 3M produced FC solids represent 95% plus of the total production of sulfonyl based fluorochemicals in the U.S. The breakdown of 3M FC production into different product categories is shown in **Table 2.**

Surface Treatments (High Molecular Weight (MW) polymers or formulated products with low percentages of non-polymeric FC solids)

Carpet Protector
Fabric/Upholstery Protector
Apparel and Leather Protector
Protective Products for After Markets and Consumer Application

Paper and Packaging Protectors (Phosphate esters or high MW polymers)

Food Packaging

Paper Products

<u>Performance Chemicals</u> (Low MW chemical substances)
Fire Extinguishing Foam Concentrates
Mining and Oil Surfactants
Electroplating and Etching Bath Surfactants
Household Additives
Chemical Intermediates
Coatings and Coating Additives
Carpet Spot Cleaners
Insecticides Raw Materials

Surface treatment products for carpets, textiles and apparel are typically sold under the Scotchgard® tradename; 3M markets its paper and packaging protective products under the Scotchban® tradename; and some performance chemicals are sold under the Fluorad® tradename.

*Surface Treatment Products.*3M fluorochemicals produced for surface treatment applications provide soil, stain, and water resistance to personal apparel and home furnishings. The great bulk of these products are manufactured as high-molecular weight polymers although some surface treatment products used for aftermarket and consumer spray application contain a significant fraction of unpolymerized FC components. Polymeric surface treatment products are primarily N-MeFOSEA-based; the fluorochemical is polymerized with urethane, acrylate and/or adipate reactants. Such protective products function through the fluorocarbon moiety on the polymer lowering the surface energy of the material to which they are applied.

Paper Protectors. The 3M paper protectors are used in food packaging and commercial applications. They can be divided into two general classes of chemistries. One class consists of mixtures of mono-, di- and tri-phosphate esters of N-EtFOSE alcohol, roughly in the proportions of 10%, 85% and 5% percent, respectively. The other class is N-MeFOSEA-acrylate copolymer. Applied to paper, the perfluorocarbon moiety in these classes of products has the effect of lowering the surface energy of the individual paper fibers. This lowered surface energy greatly contributes to the holdout of low surface energy liquids such as greases and oils.

Performance Chemicals. POSF derived chemistries used as performance chemicals are relatively low molecular weight (<500 daltons) surface active materials and monomers. Some of these chemicals are sold by 3M, or incorporated by 3M customers into formulated products, for use as surfactants in a range of industrial or consumer applications. Other performance chemicals are used as intermediates from which 3M or its customers make other finished products. Such fluorochemical intermediates can be covalently bound to a variety of polymeric hydrocarbon backbones to make higher molecular oligomeric or polymeric products with unique performance characteristics.

POSF-derived performance chemicals with fluorochemical surfactant properties differ greatly from conventional hydrocarbon and silicone surfactants. In most systems they are far more efficient in reducing surface tension to levels that are unreachable with other types of surfactants. In some aqueous systems, surface tensions as low as 15 to 16 dynes/cm can be attained. The fluorochemical surfactants normally produce these extremely low values at concentrations as low as 100 parts per million, or less. Equally important is the fact that certain of these fluorochemical surface active agents are stable and effective in many extremely hostile environments, including strongly acidic, strongly alkaline and even strongly oxidizing systems. **Table 3** summarizes the features of fluorochemical surfactants.

Another unique physical characteristic of certain POSF-based performance chemicals is their ability to form tough, yet resilient foams. Such foams usually contain low molecular weight fluorochemicals (including PFOS) and have been formulated to resist the action of high temperature or aggressive chemicals and vapors. These formulations have found commercial application in suppressing flammable liquid, chemical and organic fires or toxic and obnoxious vapors and odors.

Profile of Major Product Categories

The Appendices to this paper provide detailed profiles of each of the major use categories for sulfonyl-based FCs. For each use category, the Appendices present:

- Chemical composition information for 3M products.
- A description of the relevant business, including the scope of FC usage and distribution and location of key customers.
- A synopsis of use and distribution patterns, including potential exposure pathways during the initial application of FCs by 3M's customers, potential environmental release scenarios and opportunities for exposure during end-use of products to which FCs are applied.

Key information about each use category is highlighted below.

Surface Treatment Products

- These products provide soil resistance and repellency (fluorochemical products). Industrial, non-retail customers for products in this class consist of (i) carpet manufacturers and fiber producers who serve the markets for residential, commercial and transportation flooring; (ii) textile mills and commission finishers who produce upholstery fabric for residential furniture, home decor items such as slipcovers, mattress pads and shower curtains, and automotive, truck and van interiors or produce non-woven fabrics for use in medical or industrial applications; and (iii) textile mills, leather tanneries, finishers and chemical formulators who treat fabric and leather used for garments, footwear, accessories and non-garment functional fabrics.
- These products consist of polymeric FCs (mainly acrylates, urethanes and adipates) with high molecular weights. Industrial, commercial and consumer exposure is primarily to polymeric substances, although most of the 3M products contain low amounts of monomeric FC residuals (typically at 1 percent or lower levels) to which some exposure may occur.
- Upon distribution to mills, fiber manufacturers or other customers, the 3M surface treatment product is typically mixed with other additives and diluted. It is then applied to uncut fiber, textile or leather raw materials. Application methods include spray, foam, pad or co-application. Depending on the market segment, the application process occurs in an enclosed or open operation. In the latter case, mill production workers could have inhalation and/or dermal exposure to FCs although such exposure would be predominantly to

polymers. Some additional exposure may occur during processing operations such as drying, shearing, cutting and shipping although exposure levels should be low.

- Losses of FC polymers to the environment are expected during 3M customer operations. These losses could involve discharges of process wastewater and air releases during initial application of surface treatment formulations to uncut carpet, fiber, fabric or leather. Additional wastes (typically solids coated with FC polymers) are created during cutting, shearing and other packaging operations and are typically landfilled or recycled. Total FC losses during downsteam operations will vary by application but it is estimated that they could range between 10 and 25 percent.

- The end-use of consumer articles is another source of FC losses to the environment. For example, vacuuming and cleaning of carpets is estimated to result in substantial removal of the FC treatment over time; carpet containing FC coatings is also landfilled upon end-of-life disposal. Similarly, FC losses to the environment are also expected in wastewater from dry cleaning and laundering of garments, upholstery and leather goods and from landfilling of these items after they are discarded.

- 3M surface treatment products have extensive aftermarket applications and are distributed through retail and commercial channels for direct treatment of upholstery, carpet, auto interiors, apparel and leather by individual consumers or professional applicators.

- Retail products in this category are aerosol can spray cleaners and protectors for residential use. These products are manufactured by independent non-3M facilities under contract with 3M and are distributed through grocery, hardware and autoparts stores and other retail outlets. A variety of formulations are manufactured for this market. Typically, they include non-polymeric fluorochemical salts and residuals at levels of between 1.5 and 5%. These have the potential to degrade to PFOS. These products are intended for occasional home use only.

- Commercial 3M surface treatment products are marketed to (i) commercial cleaning services and (ii) commercial film processing facilities. Products in the first category are liquid, water-based materials applied through low-pressure or paint-type spray equipment to upholstery, carpet and other surfaces in homes, commercial buildings or retail furniture outlets. These products contain non-polymeric FC solids and residuals in concentrations of between 3 and 12 percent. The second class of products includes liquid, photocurable coating for film negatives which is typically machine-applied at commercial film processing facilities.

Paper and Packaging Protectors

* 3M markets fluorochemical sizing agents to the packaging and paper industries. These products impart grease, oil and water resistance to paper and paperboard substrates. They are used for food contact applications (plates, food containers, bags and wraps) and non-food applications (folding cartons, containers and carbonless forms and masking papers).

* Fluorochemical sizing agents are applied to paper and paperboard substrates predominantly by paper mills which treat paper fibers and, to a much lesser extent, by converters who transform paper and/or paperboard into wraps, bags or cartons for desired end-uses.

Application methods vary but approximately 75 percent of paper mill use of these products occurs via the size press. The fluorochemical product received by 3M customers is typically diluted in a starch/ water solution and applied in a 0.5 % concentration to the paper web, which is then dried to evaporate the water and converted into rolls for shipment. Mix preparation, treatment of the paper web, and conversion are all carried out in open systems although fluorochemical exposure to workers is generally considered to be limited because of the dilute form of the sizing mixture and predominance of high molecular weight FC esters or polymers. Some loss of the fluorochemicals to the environment occurs as a result of spillage, cleanup and releases during the opening, rinsing and recovery of FC totes or drums. Environmental media for FC releases include wastewater and air (for losses during papermaking) and landfills (for disposal of end-use paper products).

* 3M's food packaging products include a high molecular weight phosphate ester produced using N-EtFOSE and an acrylate copolymer based on N-MeFOSEA. Both of these products are regulated by the Food and Drug Administration (FDA) for direct food contact under 21 C.F.R. 176.170. The first product has been subject to considerable dialogue between FDA and 3M as a result of a petition for approval for microwave popcorn applications filed by 3M. In a risk assessment recently submitted to FDA in connection with this petition, 3M presented analyzes indicating that PFOS could be formed *in vivo* as a result of the hydrolysis of certain product components and the metabolic conversion of FC residuals. [1]

* 3M's grease, oil and water repellant products for non-FDA applications are similar in composition to its food contact products. Consumer exposure to the FC residuals is expected to be minimal because use scenarios for paper and packaging products containing them involve very occasional dermal contact.

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[1]Environ Corporation, *Revised Interim Safety Assessment of FC-807 and 807A: Two Fluorochemical-based Indirect Food Additives,* January 25, 1999.

Performance Chemicals

* Products in this category are distributed for a variety of specialized industrial, commercial and consumer applications, often where the surfactant properties of fluorochemicals offer significant benefits. Many of these products are low molecular weight POSF-derived chemistries; some are fluorochemical intermediates covalently bonded to a variety of polymeric hydrocarbon backbones. Since these products tend to serve niche markets, volumes are generally small.

* *Fire Fighting Foams*. Light Water® and ATC® are trademarks for 3M products that are aqueous film forming foams (AFFF) and alcohol-resistant concentrate (AR-AFFF) used to suppress and/or extinguish flammable liquid fires and suppress flammable liquid and toxic chemical vapors. The great bulk of these products are sold to "fire fighters" who mix the concentrate with water to form a foam and apply it to the fire or flammable liquid either manually or through an automated system. User categories for the foams include chemical and petroleum plants, fire departments, vessels, off-shore drilling platforms, the military, and environmental remediation companies. The 3M foam products contain low concentrations (0.5 to 3%) of potassium perfluoroalkyl sulfonate (potassium salt of PFOS), which is typically present at levels of 150-900 ppm in the foam as applied. After application, the foam is disposed of, typically through wastewater treatment, but uncontrolled releases to surface water or land are known to occur.

* *Mining and Oil Surfactants*. 3M sells surfactants to copper and gold mines to increase wetting of the sulfuric acid or cyanide that leaches the ore, enhancing the amount of metal recovery. Oil well service firms and oil companies also use these surfactants in a "well stimulation" formulation that is injected into wells to enhance oil or gas recovery. These products contain low molecular weight FCs (fluorinated alkyl ethoxylate, fluorinated alkyl quaternary ammonium iodides, fluorinated alkyl esters, fluoroaliphatic polymeric esters and fluorinated alkyl quaternary chlorides) present at low levels in the range of 100-1000 ppm.

* *Metal Plating and Electronic Etching Baths*. Users of 3M surfactants in this category include chrome and plastic preplate etchant platers seeking to suppress oxidizing mist for purposes of worker protection. 3M surfactants are sold either as powders to formulators or as liquids directly to platers. Electronics manufacturers also add 3M surfactants as strong acids in order to etch precise patterns in a silicon wafer or a printed circuit board. The 3M products are lithium perfluoroalkyl/ potassium perfluoroalkyl sulfonates, amine perfluoroalkyl sulfonates and ammonium perfluoroalkyl sulfonates. As distributed to formulators, these products typically contain FC solids at levels of 25% or higher but are diluted down to concentrations of 30-50 ppm when added to metal plating or electronic etching baths. Because of the presence of strong acids and other corrosive materials, workers who prepare and apply the baths normally use personal protective equipment. Disposal of the spent baths is either to wastewater treatment facilities or to hazardous waste landfills or incinerators when the baths qualify as hazardous waste for purposes of RCRA.

* *Household Additives*. 3M surfactants are now (or previously have been) sold to a variety of formulators to improve the wetting of water-based products marketed as alkaline cleaners, floor polishes, photographic film, denture cleansers and shampoos. Several of these products (alkaline cleaners, floor polishes, shampoos) are (or previously were) marketed to consumers; some products are also sold to janitorial and commercial cleaning services. Some of the alkaline cleaners are spray-applied and could result in inhalation or ingestion exposure. The primary exposure route for other products is dermal. The 3M surfactants are potassium fluorinated alkyl carboxylates and lithium perfluoroalkyl and amine perfluoroalkyl sulfonates (alkaline cleaner and floor polish) and fluorinated alkyl quatenary ammonium iodides (shampoo and floor stripper). As supplied to formulators, the 3M products contain in the range of 25-50% FC solids but are then heavily diluted and are present in final products at extremely low levels (10-100 ppm).

* *Intermediates*. 3M sells limited quantities of fluorochemical intermediates which are combined with other monomers to produce polymers. The intermediates sold by 3M in the U.S. include, fluorinated alkyl acrylate and fluorinated alkyl alcohol. Polymers produced by 3M customers are believed to have trace levels of FC residuals.

* *Coatings and Coating Additives*. 3M sells fluorochemical polymer coatings and coating additives (fluorinated alkyl polyoxyethylene ethanols) which are used as received or diluted with water or butyl acetate to impart soil or water repellency to surfaces (including printed circuit boards or photographic film). These polymers contain FC residuals in low levels (typically 4% or less). Other formulators add 3M fluorochemical polymers as a thickener to aqueous coatings used to protect tile, marble and concrete. Products in this class have some distribution to commercial and consumer channels.

* *Carpet Spot Cleaner*.3M supplies a non-polymeric fluorochemical to formulators of carpet spot cleaners in which the fluorochemical provides stain and soil resistance. These products are marketed to consumers in pump and aerosol cans for spray application to carpets. The FC component of these products is present at levels of 0.5 to 1 percent.

* *Insecticides Raw Materials*. The 3M products (fluorinated alkyl sulfonamide and lithium perfluoroalkyl sulfonate) are processed by 3M customers into active ingredients in bait stations for leaf cutter ants, pharoah ants, cornfield ants and a variety of household ants. These products are used mainly in commercial and industrial applications. (The lithium perfluoroalkyl sulfonate is used in consumer insecticide bait stations outside the U.S.) The fluorochemicals are present in the pesticide formulation at levels of 0.5 to 1 %.

Ongoing and Proposed Exposure Assessment and Stewardship Initiatives

Based on the results of its initial product use, distribution, and release overview, 3M has undertaken or is planning a variety of stewardship and exposure assessment initiatives intended to better characterize the highest priority human and environmental exposure pathways while taking initial steps to minimize exposure and release levels for products containing PFOS or PFOS precursors.

3M has undertaken extensive research and development programs to reengineer POSF-based products to reduce PFOS and precursor residuals and ultimately to transition to chemistries with lower accumulation potential.

3M has updated fluorochemical based MSDS's and has begun an industrial hygiene program with customers aimed at helping to promote improved use and handling of fluorochemicals and reduction of occupational exposures where appropriate. As part of this program, 3M has volunteered to make available its industrial hygiene professionals for qualitative workplace assessments at customer facilities. 3M is also conducting use simulation studies to determine potential consumer exposure levels for FCs released during spray application of surface treatment products marketed to consumers.

Exposure Assessment Plan Overview

Building on 3M's initial assessment a plan also has been developed to assess potential environmental exposure pathways associated with the manufacture, use and disposition of major 3M fluorochemical products. A detailed description of all the exposure/product stewardship initiatives is beyond the scope of this paper but the four principle components are as follows:

1) The characterization of fate and transport properties is being addressed in multiple steps. The specific projects planned and/or initiated to characterize fate and transport properties of fluorochemicals are:

   a) Physical/chemical properties testing of persistent fluorochemical degradation products as well as selected fluorochemical products. This includes (where applicable): melting point, boiling point, vapor pressure, disassociation constant, hydrolysis, water solubility, air/water partition coefficient, octanol/water partition coefficient, soil/water partition coefficient, bioconcentration in fish.
   b) Photodegradation studies
   c) Atmospheric chemistry evaluation
   d) Studies to assess aerobic and anaerobic biodegradability
   e) Development of appropriate models for the prediction of physical/chemical properties of fluorochemicals not tested.

2) Using the initial estimates in the attached assessment and sales data from 1997, releases from manufacturing, the supply chain, use and disposal at all steps are being estimated for the products identified as important. Release data is also being determined by sampling and analyses of 3M manufacturing plant process wastes and effluents. In addition to providing the information necessary to assess distribution and exposure, release estimates will aid in determining sampling sites and substantiate results from sampling. It is anticipated that this effort may also identify those fluorochemicals which require further analysis of fate, transport and exposure.

3) Modeling and sampling is being undertaken to estimate fluorochemical concentrations and better characterize the distribution of FCs in the environment. These activities are to be conducted in an iterative fashion and will become refined and focused as more data become available. The specific projects planned and/or initiated to characterize environmental distribution are:

   a) Sample and analyze environmental media in the region of 3M fluorochemical manufacturing facilities.

b) Sample and analyze environmental media and market baskets of food from selected cities.
c) Sample and analyze environmental media from geographically diverse regions.
d) Analyze selected animal tissues to characterize food chain concentrations.
e) Utilize multi-media models to estimate environmental concentrations.
f) Utilize data from mammalian toxicology studies to estimate releases to the environment from metabolism of fluorochemicals.

4) Exposure levels for all possible pathways that could lead to human ecological exposure from the prioritized products will be estimated. When release and distribution data become available, the most important pathways will be hypothesized. Iterative sampling and modeling will be employed to test these hypotheses and determine the important pathways to be used in risk assessment. The specific projects planned and/or initiated to estimate exposure are:

1) Utilize data from mammalian toxicology studies to estimate exposure from fluorochemical metabolism.
2) Determine foot traffic releases from 3M fluorochemical-treated carpets and assess potential human exposures by using a sampling design which will differentiate between inhalation, dermal penetration and ingestion.
3) Conduct studies to determine the extent of migration of FDA regulated indirect fluorochemical food additives from paper packaging products to food.
4) Analyze human sera samples to determine the extent of fluorochemical concentrations in human populations and to identify metabolic fingerprints of specific fluorochemicals.

SUMMARY

Efforts are underway at 3M to assess the risk of POSF based 3M fluorochemicals to both human health and the environment. To augment 3M's initial review an exposure assessment plan for POSF based fluorochemicals is being implemented. As new information becomes available it will be summarized and communicated to the EPA. A POSF based fluorochemical environmental "white paper" is currently being prepared and will be submitted upon completion.

Chart 1

POSF Fluorochemical Reaction Tree

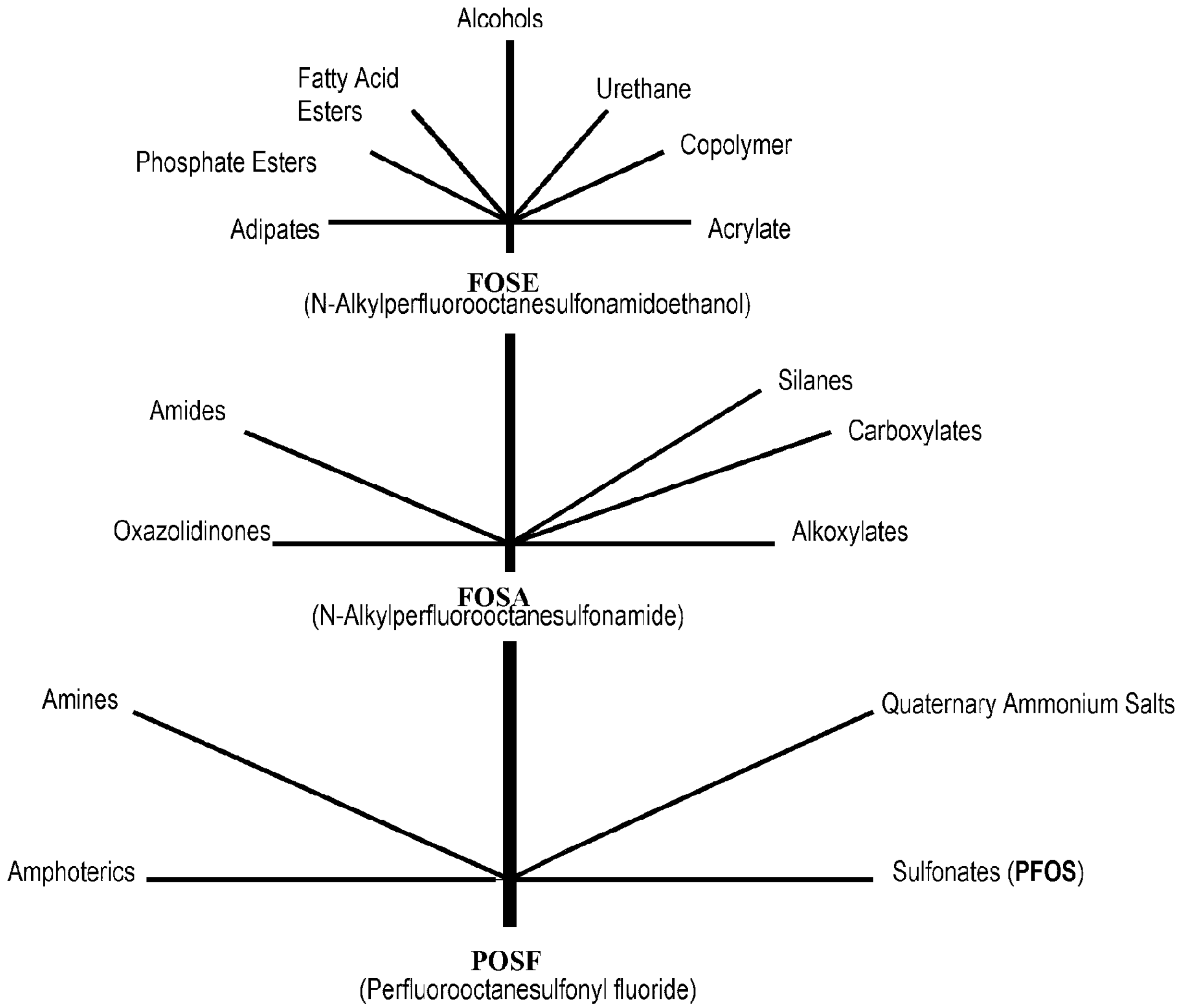

Table 1. Fluorochemical Glossary

Designation	Molecular Formula	Technical Name (CAS Name)
POSF	$C_8F_{17}SO_2F$	Perfluorooctanesulfonyl fluoride (1-Octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-)
PFOS	$C_8F_{17}SO_3^-$	Perfluorooctanesulfonate (1-Octanesulfonic acid anion, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-)
PFOSH	$C_8F_{17}SO_3H$	Perfluorooctanesulfonic acid (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-)
PFOS.NH_4 salt	$C_8F_{17}SO_3NH_4$	Ammonium perfluorooctanesulfonate (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt)
PFOS.DEA salt	$C_8F_{17}SO_3NH(CH_2CH_2OH)_2$	Perfluorooctanesulfonate, diethanolamine salt (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1))
PFOS.K salt	$C_8F_{17}SO_3K$	Potassium perfluorooctanesulfonate (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt)
PFOS.Li salt	$C_8F_{17}SO_3Li$	Lithium perfluorooctanesulfonate (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt)
FOSA	$C_8F_{17}SO_2NH_2$	Perfluorooctanesulfonamide (1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-)
N-EtFOSGE	$C_8F_{17}SO_2N(CH_2CH_3)CH_2COO^-$	N-perfluorooctylsulfonyl-N-ethylglycinate (Glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl]-, anion)
N-EtFOSA	$C_8F_{17}SO_2NHCH_2CH_3$	N-Ethylperfluorooctanesulfonamide (1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-)
N-MeFOSA	$C_8F_{17}SO_2NHCH_3$	N-Methylperfluorooctanesulfonamide (1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-methyl-)
N-EtFOSE	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$	N-Ethylperfluorooctanesulfonamidoethanol (1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-)
N-MeFOSE	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	N-Methylperfluorooctanesulfonamidoethanol (1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-N-methyl-)
N-EtFOSEA	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OCOCH{=}CH2$	N-Ethylperfluorooctanesulfonamidoethyl acrylate (2-Propenoic acid, 2-[ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl ester)
N-EtFOSEMA	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OCOC(CH_3){=}CH2$	N-Ethylperfluorooctanesulfonamidoethyl methacrylate (2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl ester)
N-MeFOSEA	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OCOCH{=}CH2$	N-Methylperfluorooctanesulfonamidoethyl acrylate (2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulfonyl]methylamino]ethyl ester)

Chart 2
Product Building

Electro-Chemical Fluorination Cells
(Octanesulfonyl fluoride + HF + electrical energy)

↓

Perfluorooctane sulfonyl fluoride (POSF)

↓

Secondary Reactors

↓

Perfluorooctane sulfonic acid (PFOS)

Surfactants
↓
Various commercialized intermediates and surfactants
↓
Amphoteric surfactants (Fire Fighting Foams)

N-ethyl (and methyl) perfluorooctane-sulfonamide
↓
N-ethyl (and methyl) perfluorooctane-sulfonamide ethanol
↓

Phosphate esters (Paper &

Acrylate polymers
Adipate adducts
Urethane polymers
(Carpet and

Various commercialized intermediates and surfactants

Table 3
Features of Fluorochemical Surfactants

SURFACE ACTIVITY

AQUEOUS SYSTEMS

Some of these surfactants can lower surface tension to less than 16 dynes/cm and function at low concentrations. They are effective in dramatically reducing surface tension in a wide variety of aqueous media, including acidic and basic systems.

NON AQUEOUS SYSTEMS

Fluorochemical Surfactants have been developed which uniquely reduce surface tensions of many organic media to about 20 dynes/cm, including solvents such as esters, alcohols and ethers and resin systems including epoxies, polyesters, urethanes and acrylics.

WETTING

Reduced surface tensions result in the ability to improve the wetting of a variety of materials, including such hard to wet surfaces as plastics and oily metals.

BETTER SPREADING

Low surface tension in combination with low interfacial tension affects spontaneous spreading of a liquid over various surfaces. This is important in reducing pinholes, craters, and edge crawling of coatings applied to unclean surfaces.

REDUCED WATER SPOTTING

Because of reduced droplet formation, the need for distilled or deionized water in rinsing operations may be eliminated.

SMALLER GAS BUBBLES

These smaller gas bubbles produced at the surface of metal during chemical etching will have less tendency to adhere, grow and cause surface imperfections.

SMALLER DROP FORMATION

Smaller drops are desired in fine aerosol mists.

BETTER LIQUID PENETRATION

The force required to cause liquids to move through small pore spaces can be greatly reduced.

IMPROVED FILM UNIFORMITY

Smoother, more even films are produced from polishes, finishes and coatings.

LEVELING

Emulsion coatings applied to difficult to wet surfaces can show greatly improved leveling with the addition of small quantities of these materials.

FOAMING

Stable foams can be produced in hostile media such as chromic acid or sodium hydroxide, where conventional surface active agents would be destroyed.

EMULSIFICATION

While generally not effective as emulsifiers in water-organic systems, these materials can be quite efficient emulsifiers in specialty applications, where fluorinated materials comprise either the continuous or the dispersed phase.

STABILITY

Chemical

Some of these surface active agents are stable in such rigorous environments as hot chromic acid, anhydrous hydrazine, hot concentrated sulfuric acid, hot concentrated hydrofluoric acid and hot concentrated sodium hydroxide solutions.

Thermal

While all of these materials have very good stability at moderate temperatures, a few can withstand temperatures in excess of 300°F in air.

LOW CONCENTRATION

These materials are normally effective at extremely low concentrations, and often are utilized at concentrations of 100 parts per million active solids or less.

Table 2
Estimated Fluorochemical (FC) Usage by Application

MARKET	Estimated Pounds of FC Solids Sold/Year in U.S. (1997 Data)(3)	Estimated Polymer Pounds (2)	Estimated Non-Polymer Pounds (2)
Protective Materials Division			
Carpeting (Mill Applied)	764,000	764,000	0
Home Furnishings (Upholstery, Mill Applied)	270,000	270,000	0
Home Fashions (Mill Applied)	41,000	41,000	0
Automotive (Mill Applied)	97,000	97,000	0
Medical Fabrics – Non-Wovens (Surgical gowns/drapes and wraps)	119,000	119,000	0
Apparel and Leather (Mill Applied)	330,000	330,000	0
Retail (Consumer) Spray Cans	90,000	74,000	16,000
Commercial Care (Professionally Treated Upholstery and Carpet)	135,000	92,000	43,000
Paper and Packaging (Mill Applied)	1,450,000	440,000	1,010,000
Intermediate	84,000	0	84,000
Performance Materials Division			
Mining and Oil	69,000	19,000	50,000
Metal Plating	9,000		9,000
Household Additives	69,000		69,000
Other Intermediates	3,000		3,000
Coating/Coating Additives	198,000	142,000	56,000
Carpet Spot Cleaner	77,000		77,000
Insecticides	26,000		26,000
Fire Fighting Foams	179,000		179,000
Other 3M Divisions			
Use in Production of 3M Articles (1)	160,000	(est.) 80,000	(est.) 80,000
TOTAL	4,170,000	2,468,000	1,702,000

(1) Includes processing aids or manufacturing components for articles including Tape, Traffic Control products, Commercial Graphics and non-woven textiles produced and distributed by other 3M business.
(2) These columns indicate if the FC solids in each market are sold as polymers or non-polymers.
(3) 1998 Production figures are very similar (± 10-15%) to the data shown above.