THE SCIENCE OF ORGANIC FLUOROCHEMISTRY

3M
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The Science of Organic Fluorochemistry

Introduction

The science of fluorochemistry begins with fluorine. Fluorine is the most abundant member of the halogen family and is one of the most reactive of all the elements. It is capable of combining with nearly every other element in the periodic table, which is why elemental fluorine is rarely if ever found in nature. The strength of the fluorine bond with other elements also made the discovery of elemental fluorine a difficult task. Elemental fluorine was not isolated until 1886, a relatively late date, as chemical discoveries go. Therefore, the science of fluorochemistry is relatively young. Because of its strong electronegative properties, ionic fluorine will form weak bonds with other electronegative atoms and very strong bonds with electropositive atoms. Ionic metal fluorides are the most common chemical forms of fluorine found in nature, such as fluorspar (CaF_2). Naturally occurring fluorinated hydrocarbon molecules rarely occur in nature because of the energy required to make or break the carbon-fluorine bond in biological systems. However, partially and fully fluorinated organic molecules can be synthesized.
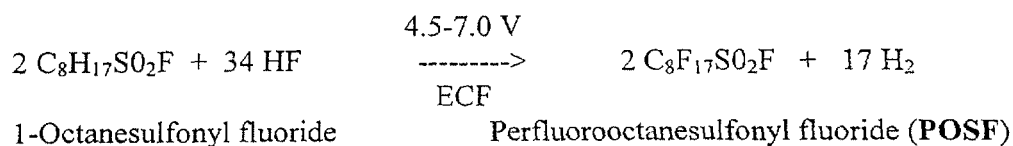
3M Experience in Fluorochemistry

3M Company began its history in fluorochemistry with the licensing of specific intellectual property from Dr. Simons of Penn State University in 1945. Dr. Simons had developed a process, now referred to 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 component of the products produced by this process have the same carbon skeletal arrangement as the feedstock used 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 perfluoroorganic molecules where all of the hydrogen atoms of the hydrocarbon feedstock have been replaced by fluorine atoms. 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, MN, Cordova, IL, and Decatur, AL).

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). The starting feedstock for this reaction is 1-octanesulfonyl fluoride. (Reaction 1)

Reaction 1

$$2\ C_8H_{17}SO_2F\ +\ 34\ HF\ \xrightarrow[ECF]{4.5\text{-}7.0\ V}\ 2\ C_8F_{17}SO_2F\ +\ 17\ H_2$$

1-Octanesulfonyl fluoride ⠀⠀⠀⠀⠀ Perfluorooctanesulfonyl fluoride (**POSF**)

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It is important to understand that perfluorooctane sulfonic acid (**PFOS**) will result from the chemical or enzymatic hydrolysis of POSF. Under appropriate conditions, the perfluorooctane sulfonate anion can form salts with monovalent metallic cations. Current information strongly supports that PFOS or its salts cannot be broken down further chemically. Therefore PFOS is the ultimate degradation product from POSF derived fluorochemicals and will persist in that form.

The electrochemical fluorination process yields about 35%-40% straight chain (normal) POSF, and a mixture of biproducts and waste of unknown and variable composition comprised of the following:

1)   higher and lower straight-chain homologs, i.e., n-$CnF_{2n+1}SO_2F$, e.g., $C_6F_{13}SO_2F$, $C_7F_{15}SO_2F$, $C_9F_{19}SO_2F$ which comprise about 7% of the process output

2)   branched-chain, perfluoroalkylsulfonyl fluorides with various chain lengths, about 18-20% of the output

3)   straight-chain, branched, and cyclic (non-functional) perfluoroalkanes and ethers, which comprise about 20-25% of the output

4)   "tars" (high molecular weight fluorochemical byproducts) and other byproducts, including molecular hydrogen, which comprise about 10-15% of the output.

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. The commercialized POSF derived products are a mixture of approximately 70% linear POSF derivatives and 30% branched POSF derived impurities.

During production, byproducts and waste products are formed. The volatile waste products, such as perfluoromethane, have been vented to the atmosphere in the past, but improvements are underway to capture and destroy these releases by thermal oxidation. The tars are incinerated at an in-house, 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 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, but is primarily an important intermediate in the synthesis of substances used in many other 3M fluorochemical products. The majority is used to produce functionally derivatized fluorochemicals and high molecular weight polymeric products. Table 1 identifies some fluorochemicals, their acronyms, chemical name, 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. PFOS is also a commercialized product for a variety of specific applications.

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. Chart 1 outlines the general classes of fluorinated materials made by 3M. The major intermediates are represented by the trunk of the "tree". 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).
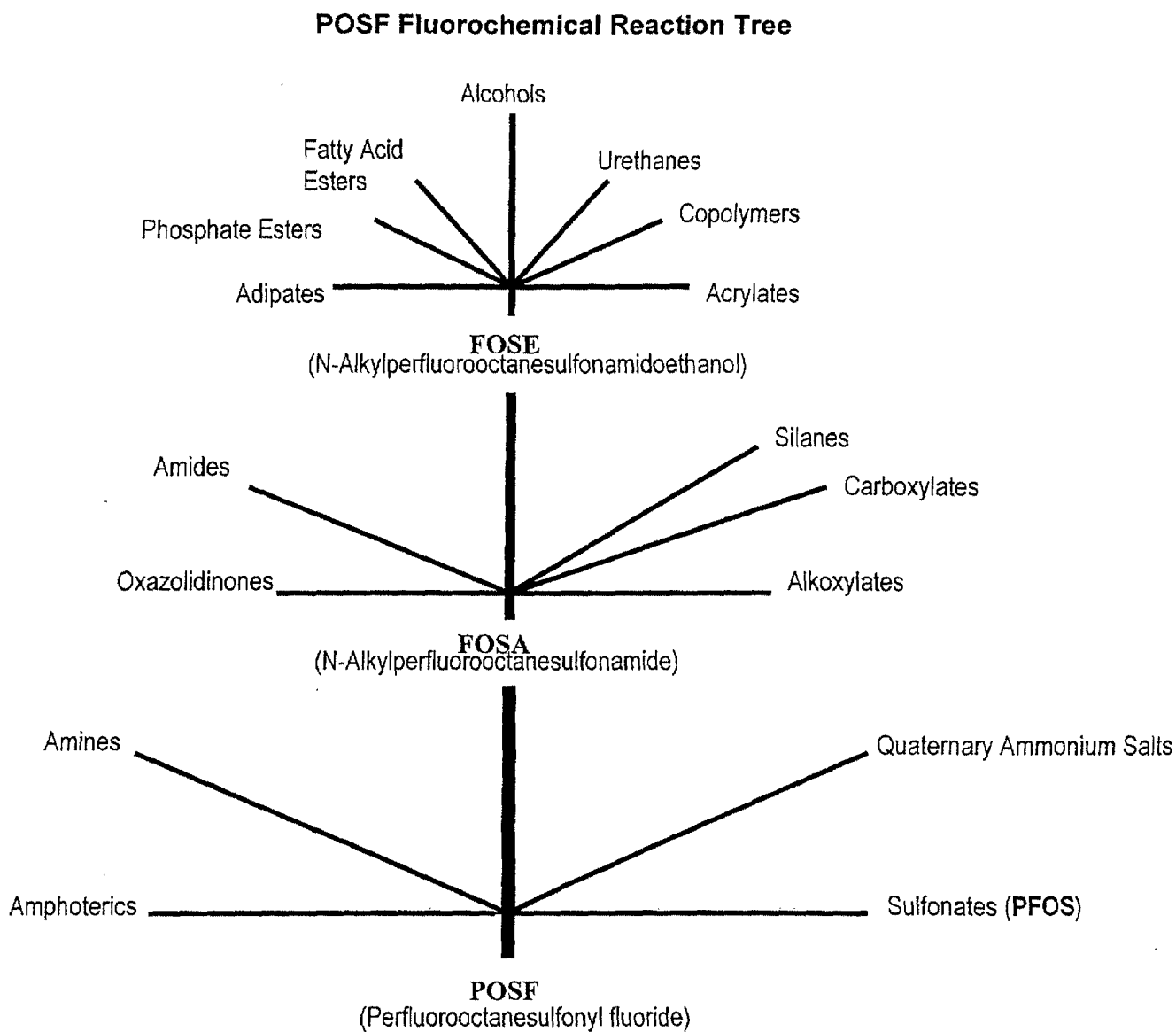
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Chart 1

POSF Fluorochemical Reaction Tree

Alcohols

Fatty Acid
Esters

Urethanes

Phosphate Esters

Copolymers

Adipates ——————————————— Acrylates

FOSE
(N-Alkylperfluorooctanesulfonamidoethanol)

Silanes

Amides

Carboxylates

Oxazolidinones —————————————— Alkoxylates

FOSA
(N-Alkylperfluorooctanesulfonamide)

Amines

Quaternary Ammonium Salts

Amphoterics ——————————————— Sulfonates (**PFOS**)

POSF
(Perfluorooctanesulfonyl fluoride)

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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.NH₄ 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	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OCOCH=CH_2$	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)

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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, such as FOSA or FOSE) that are carried forward to the final product. Typically, these residuals are present at a concentration of 1% or less. Such processes are under a continuous improvement plan to reduce or eliminate the presence of unnecessary residuals in the production of commercializable product. It is important to understand that the non-fluorochemical moieties added to the sulfoniyl fluoride group of POSF can also be removed through a variety of degradation processes (chemical, environmental, and metabolic). Again, the terminal product of such degradation will be PFOS.

Physical-Chemical Properties

Fluorinated organics are less well described in the scientific literature than organic molecules bearing other halogens, i.e. bromine, and chlorine, which have been more thoroughly investigated by many researchers in published reports. To understand fluorinated organic properties, it is necessary to describe in more detail the properties of fluorine. Fluorine has several characteristics which differ from the other halogens and contribute to the unusual properties of fluorochemicals.

Fluorine has a van der Waals radius of 1.35 Å, more comparable to that of oxygen and smaller than other halogens, and is isosterically similar to a hydroxyl group. Fluorine has the highest electronegativity (4.0 – Pauling scale) of all the halogens, and the highest in the periodic table. This confers a strong polarity to the carbon-fluorine bond. The carbon-fluorine bond is one of the strongest in nature (~110 kcal/mol). See Table 2 and 3. This very strong, high energy bond contributes to the stability of fluorochemicals. Such stability may also lead to the persistence of certain fluorochemicals. That stability confers a variety of unique properties to fluorocarbons as described in Table 4.

TABLE 2
Fluorocarbon Structure
Considerations

Structure	Bond Length A°	Atomic Van Der Waals' Radius A°	Bond Strength Kcal/Mole
H_3C-H	1.11	1.20	101
H_3C-F	1.385	1.35	107
H_3C-Cl	1.78	1.80	81
H_3C-Br	1.93	1.95	67
H_3C-I	2.13	2.15	55

TABLE 3
Effect of Increasing Fluorination

Structure	Bond Length A°	Bond Strength Kcal/Mole
H_3C-F	1.385	107.0
H_2FC-F	1.358	109.6
HF_2C-F	1.332	114.6
F_3C-F	1.317	116.0

TABLE 4
Stability of Fluorocarbons

Chemical
- Unaffected by any normal reagent
- React with alkali metals at high temperatures

Thermal and Oxidative
- Stable in air at high temperatures
- Non-flammable

Electrical
- High electric strength
- Low dielectric constant

The high ionization potential of fluorine (401.8 kcal/mole) and its low polarizability leads to weak inter- and intramolecular interactions. This is demonstrated in the low boiling points of fluorochemicals relative to molecular weight, and their extremely low surface tension and low refractive index. Table 5 compares the physical properties of a perfluoroalkane with its hydrocarbon analog to demonstrate the effect of low polarizability.

TABLE 5
Physical Properties
(Effect of Low Polarizability)

|	C_8F_{18}	C_8H_{18}
Low Boiling Point:		
MW	438	114
Bp (°C)	97	125
Low Heat of Vaporization		
G-Cal/Gram	20	86.8
Low Refractive Index		
N_D20	1.280	1.3975
Low Surface Tension		
Dynes/cm	15.0	21.8

The partitioning behavior of perfluoroalkanes is also unique. Some perfluoroalkanes, when mixed with hydrocarbons and water, form three immiscible phases, demonstrating that perfluorinated chains are both oleophobic and hydrophobic. A charged moiety, such as carboxylic acid, sulfonic acid, phosphate or a quaternary ammonium group, when attached to the perfluorinated chain, makes the molecule more water soluble because of the hydrophilic nature of these charged moieties. Therefore, such functionalized fluorochemicals can have surfactant properties.

A conventional hydrocarbon surfactant generally may be represented as:

R_H------------------------------------X
Insoluble Tail
Hydrophilic Group
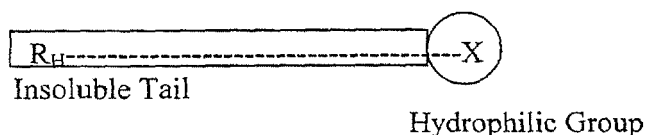
Where R_H....represents the hydrocarbon "tail" and ····X represents a solubilizing group.

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In a similar fashion, fluorochemical surfactants can typically be described by the following chemical structure:

R_F ———————————————————— X
Insoluble Tail

Hydrophilic Group
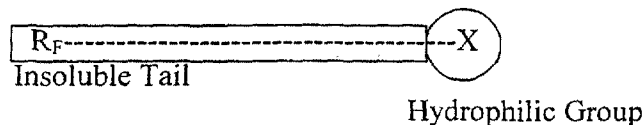
Where the R_F.... portion is the stable fluorocarbon tail, ˝X represents a solubilizing group. It is this unique fluorochemical "tail", modified in length and structure to meet end use needs, which provides the exceptional resistance to thermal and chemical attack characteristic of the fluorochemical. This fluorochemical portion of each is basically responsible for its capability to dramatically reduce surface tension, as well as being the major difference between these materials and conventional surfactants.

The solubilizing group, ˝X is commonly water soluble, but can be designed to be oil soluble for use in nonaqueous systems.

R_F ———————————————————— X
Insoluble Tail
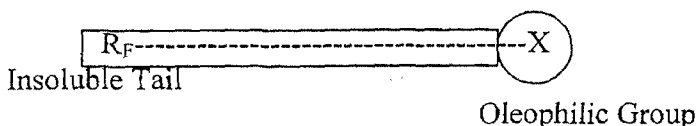
Oleophilic Group

The nature of the oleophilic group varies among the fluorochemical surfactants. By altering it, fluorochemical surfactants have been prepared which are extremely surface active in a number of environments, including many systems which would degrade hydrocarbon or silicone surfactants.

Physical properties available on 3M fluorochemical products are principally those parameters needed for quality control use and material handling. It is important to remember that these physiochemical properties have been obtained from products that are not highly refined, and that may have more than one fluorochemical component. Some products may have nonfluorochemical components which contribute to the determination of the values. One observes a wide range in values for physiochemical parameters among low molecular weight, POSF based, fluorochemicals. Typically these low molecular weight chemistries tend to have higher water solubility and lower vapor pressure than polymeric products containing them. In addition to being intermediates in the formation of products, some of these low molecular weight fluorochemicals are also likely intermediates in the degradation of polymeric compounds.

3M Sulfonyl-based Fluorochemical Products

The 3M 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 their final product. (Product lines using fluorochemicals which contain no sulfonyl groups are not listed.)

Surface Treatments
Fabric/Upholstery Protector (High molecular weight [MW] polymers)
Carpet Protector (High MW polymers)
Leather Protector (High MW Polymers)
Paper and Packaging Protector (High MW phosphate esters or high MW polymers)

Surfactants (Low MW chemical substances)
> Specialty Surfactants
> Household Additives
> Electroplating and Etching Bath Surfactants
> Coatings and Coating Additives
> Chemical Intermediates
> Carpet Spot Cleaners
> Fire Extinguishing Foam Concentrates
> Mining and Oil Surfactants

Other Uses
> Insecticides (Low MW chemical substances)

Some of the POSF derived chemistries are relatively low molecular weight (< 500 daltons). These fluorochemicals can be intermediates that 3M or our customers use in making other finished products. Such fluorochemical intermediates can be covalently bound to a variety of polymeric hydrocarbon backbones to make products with unique performance characteristics. The majority of 3M fluorochemicals produced for commercialization are used in such polymeric form for treatment of surfaces and materials. For example, fluorochemical containing polymers (urethane and acrylate) plus fluorochemical adipates can provide soil, stain, and water resistance to personal apparel and home furnishings. Such protective products function through the fluorocarbon moiety on the polymer lowering the surface energy of the material to which they are applied.

The 3M paper protectors can be divided into two general classes of chemistries. One class is based on phosphate esters of N-EtFOSE. The other class is a N-MeFOSEA-acrylate copolymer. Applied to paper, the perfluorocarbon moiety in these products has the previously described 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.

As previously described, the POSF-derived fluorochemical products have surfactant properties. Such fluorochemical surfactants 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 these other types. 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 6 summarizes the features of fluorochemical surfactants.

Table 6
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 materals, 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.

Many applications involve more than just air-liquid interfaces where surface tension alone might be important. More often liquid-liquid or solid-liquid systems are encountered. In these cases, interfacial tension, as well as surface tension, plays a significant role in the wetting or leveling process. Quite often in these cases, a combination of a suitable hydrocarbon surfactant can produce a degree of wetting which cannot be accomplished by either type alone. Normally, in such a combination, it is the fluorochemical surfactant which reduces the surface tension, while the hydrocarbon material aids in the reduction of the interfacial tension. The net result can be a system that easily wets and spreads on otherwise hard to wet surfaces.

Another unique physical characteristic of fluorochemicals is their ability to form tough, yet resilient foams. Such foams 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.

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