FLUOROETHERS AND FLUOROAMINES

1. Introduction

Fluoroaliphatic ethers and perfluorotertiary amines together with the perfluoroalkanes and cycloalkanes comprise a class of unreactive materials known in the industry as inert fluids. These fluids are colorless, nearly odorless, essentially nontoxic, nonflammable, dense, and extremely nonpolar. In the electronics industry, the lower molecular weight compounds find application in such areas as thermal management, testing, cleaning solvents, and solvents for coating applications. Higher molecular weight polymers and oligomers are used in a variety of applications, including hazardous-duty vacuum pump fluids, specialty greases, and various specialty cosmetics and lubricants.

Many perfluoroaliphatic ethers and tertiary amines have been prepared by electrochemical fluorination (1-6), direct fluorination using elemental fluorine (7-9), or, in a few cases, by fluorination using cobalt trifluoride (10). Examples of lower molecular weight materials are shown in Table 1. In addition to these, there are three commercial classes of perfluoropolyethers prepared by anionic polymerization of hexafluoropropene oxide [428-59-1] (11,12), photooxidation of hexafluoropropene [116-15-4], or tetrafluoroethene [116-14-3] (13,14), or by anionic ring-opening polymerization of tetrafluorooxetane [765-63-9] followed by direct fluorination (15).

More recently, the new class of hydrofluoroethers has been commercialized. These ethers comprise a perfluorinated portion separated by oxygen from a hydrocarbon portion and are prepared by alkylation of perfluorinated acyl fluorides. Their structure gives these ethers extremely useful properties including enhanced solvency and the ability to form many useful nonflammable azeotropes with a variety of hydrocarbon cosolvents. In addition to these hydrofluoroethers, a recent class of hydrofluoropolyethers has been commercialized. These materials contain hydrogen atoms at the alpha and omega positions of a perfluoropolyether chain and have properties intermediate between the perfluorinated fluids and the hydrofluoroethers. These ethers are prepared by oxidative polymerization of tetrafluoroethene followed by reduction.

2. Physical Properties

Perfluorinated compounds boil at much lower temperatures and have lower heats of vaporization than the corresponding hydrocarbon analogues even though they have considerably higher molecular weights. This holds true not only for the perfluoroalkanes and cycloalkanes, but for the perfluorinated ethers and tertiary amines as well. The latter compounds have boiling points very close to the perfluoroalkanes having the same number of carbon atoms; the heteroatoms contribute little polarity to the molecules. In-chain oxygen and nitrogen atoms have marked effects on the freezing points and on the viscosity at low temperatures. Note the extremely low pour point of the Du Pont K7 fluid despite its high molecular weight. This effect is believed to be due to the increased flexibility

Table 1. **Physical Properties of Some Fluorinated Liquids**

Name	CAS Registry number	Molecular formula	bp, °C	d^{25}	Viscosity, cps/25°C	Pour point, °C
perfluoro-4-methylmorpholine	[382-28-5]	$CF_3N(CF_2)_2O(CF_2)_2$	50	1.70	0.68	−80
perfluorohexane	[355-42-0]	C_6F_{14}	58	1.68	0.64	−74
Galden HT 170[a]			170	1.77	3.2	−97
Fluorinert FC-75	[11072-16-5]	$C_8F_{16}O^b$ (cyclic)	103	1.76	1.3	−93
perfluoroctane	[307-34-6]	C_8F_{18}	103	1.77	0.71	−30
perfluorotripropylamine	[338-83-0]	$(C_3F_7)_3N$	128	1.82	1.40	−50
perfluorotributylamine	[311-89-7]	$(C_4F_9)_3N$	178	1.86	4.7	−50
perfluoro(diethylamino) ethyl ether	[108709-75-7]	$[(C_2F_5)_2NC_2F_4]_2O$	178			−80
perfluorohexyl ether	[424-20-4]	$(C_6F_{13})_2O$	181	1.81		−90
K7 Fluid	[59884-34-3]	$C_3F_7O[C_3F_6O]_5C_2F_5$	250	1.82		−80
methoxyheptafluoropropane	[375-03-1]	$C_3F_7OCH_3$	34	1.40	0.45	−122
Novec Engineered Fluid HFE-7100[c]		$C_4F_9OCH_3$	61	1.52	0.58	−135
Novec Fluid HFE-7200[d]		$C_4F_9OC_2H_5$	76	1.43	0.58	−138
Novec Fluid HFE-7500	[297730-93-9]	$C_3F_7CF(OC_2H_5)CF(CF_3)_2$	130	1.61	1.24	−110
H-Galden ZT 180		$HCF_2O(CF_2O)_n(C_2F_4O)_mCF_2H^e$	178	1.69	2.53	−110
H-Galden ZT 85		$HCF_2O(CF_2O)_n(C_2F_4O)_mCF_2H^e$	85	1.60	0.94	−123

[a] Mixture of perfluorinated polyethers marketed by Solvay Solexis.

[b] $C_8F_{16}O$ represents a mixture of isomers of cyclic perfluoroaliphatic ethers, primarily perfluoro-2-butyltetrahydrofuran [355-36-4].

[c] HFE-7100 is a mixture of methoxynonafluorobutane [163702-07-6] and methoxynonafluoroisobutane [163702-08-7] marketed by 3M.

[d] HFE-7200 is a mixture of ethoxynonafluorobutane [163702-05-4] and ethoxynonafluoroisobutane [163702-06-5] marketed by 3M.

[e] Mixture of hydrofluoropolyethers with varying values of n and m.

that in-chain oxygen or nitrogen atoms contribute to the perfluorinated chain (16) and is also observed for the higher molecular weight perfluoropolyethers that have relatively low pour points at relatively high molecular weights.

Many of the unusual properties of the perfluorinated inert fluids are the result of the extremely low intermolecular interactions. This is manifested in, eg, the very low surface tensions of the perfluorinated materials (on the order of 9–19 mN/m = dyn/cm) at 25°C, which enables these liquids to wet any surface including polytetrafluoroethene. Their refractive indexes are lower than those of any other organic liquids, as are their acoustic velocities. They have isothermal compressibilities almost twice as high as water. Densities range from 1.7 to 1.9 g/cm^3 (17). The absolute viscosities of the perfluorinated inert liquids are higher than the analogous hydrocarbons but the kinematic viscosities are lower due to the higher density of the perfluorinated compounds. The viscosity index, ie, the change in viscosity with temperature, is generally higher for the perfluorinated liquids than for hydrocarbons.

Hydrofluoroethers and hydrofluoropolyethers also have low surface tensions in the range of 13–16 dyn/cm at 25°C. Their densities are slightly lower than the corresponding perfluorinated analogues and range from 1.4 to 1.7 g/cm^3.

Hydrofluoroethers have boiling points that fall between the hydrocarbon and perfluorinated analogues. For example, HFE-7100, $C_4F_9OCH_3$, boils at 61°C, $C_4F_9OCF_3$ boils at 35°C and $C_4H_9OCH_3$ boils at 71°C. Hydrofluoropolyethers have higher boiling points than the corresponding compounds with the nonpolar CF_3 end group but the difference decreases with increasing number of chain carbon atoms (18). Both hydrofluoroethers and hydroperfluoropolyethers exhibit low pour points typical of the perfluorinated analogues.

2.1. Thermal Stabilities. The perfluoroethers have thermal stabilities comparable to those of the perfluoroalkanes. Typically, although this depends somewhat on structure, they do not undergo significant decomposition until ~400°C. Perfluorotertiary amines are less stable thermally and begin to decompose at temperatures of ~250°C (19). Generally, this slight instability is not a significant problem during use.

Hydrofluoroethers and hydrofluoropolyethers are stable up to 275°C for short time periods, but recommended long term use temperatures are generally ~150°C. (20, 21).

2.2. Electrical Properties. The low polarizability of perfluorinated liquids makes them excellent insulators. Their dielectric strengths are ~40 kV (ASTM D877); dissipation factors are ~0.0001 at 1 MHz; dielectric constants are ~1.8; volume resistivities are $\sim 1 \times 10^{15} \Omega \cdot$ cm (ASTM D257) (17).

Hydrofluoroethers and hydrofluoropolyethers also are excellent insulating fluids. The electrical properties vary with structure but dielectric strengths range from 30 to 40 kV, dielectric constants from 3 to 7 and volume resistivity from 10^8 to 10^{10} $\Omega \cdot$cm. (20,21).

3. Chemical Properties

The inert character of the perfluoroethers and tertiary amines is demonstrated by their lack of basicity or reactivity as compared with their hydrocarbon analogues. Both classes of compounds are nonflammable. The perfluorotertiary amines do not form salts with any protic acid nor do they form complexes with boron trifluoride. Neither class reacts with most oxidizing or reducing agents nor with strong acids or bases. As with the perfluoroalkanes, perfluoroethers and tertiary amines may, under some conditions, react violently with fused alkali metals. In contrast to the perfluoroalkanes, both classes of compounds react with aluminum chloride or bromide at elevated temperatures (~90–200°C) (22). The $-OCF_2O-$ linkage is especially vulnerable to this attack (23,24).

In contrast to the perfluorinated ethers, the hydrofluoroethers are more reactive. Their properties tend to be a blend of those expected from a fluorinated ether combined with a hydrocarbon ether. Thus the hydrofluoroethers are significantly better solvents than the perfluorinated ethers. If the ratio of hydrogen to fluorine in the molecule is high enough, hydrofluoroethers can have a flash point although the commercially available materials do not have a flash point. The hydrofluoroethers can be more susceptible to chemical reagents including strong amine bases such as piperidine with which some of them may be reactive. The presence of hydrogen in the molecules is beneficial in rendering the hydrofluoroethers and hydrofluoropolyethers reactive toward atmospheric oxidation and removal, which leads to a short atmospheric lifetime (25).

3.1. Solvent Properties. In comparison to the more familiar hydrocarbon systems, the solvent properties of the perfluorinated inert liquids are also unusual due to their nonpolar nature and low intermolecular forces. They are generally very poor solvents for most organic compounds. Water and hydrocarbon alcohols are nearly completely insoluble in them. Lower aliphatic hydrocarbons, lower molecular weight ethers, and some highly chlorinated solvents such as carbon tetrachloride are relatively soluble. As the molecular weight of the perfluorinated compound increases, the hydrocarbon solubility decreases. Partially fluorinated compounds such as benzotrifluoride or bis(trifluoromethyl)-benzene are soluble in perfluorinated liquids. Aliphatic highly fluorinated compounds containing hydrogen such as $C_7F_{15}H$ are also miscible with perfluorinated liquids. The hydrofluoroethers and hydrofluoropolyethers display solvent

Table 2. **Solubility of Various Solvents in Fluorinated Ethers and Amines**[a]

Solvent	$C_8F_{16}O$	$(C_4F_9)_3N$	$C_4F_9OCH_3$	$C_3F_7CF(OC_2H_5)CF(CF_3)_2$	$HCF_2O(C_2F_4O)_m(CF_2O)_nCF_2H$[b]
acetone	1.8	0.8	miscible	miscible	miscible
benzotrifluoride	miscible	miscible	miscible	miscible	miscible
heptane	6.1	5.0	miscible	miscible	
octane	1.5	1.3	miscible	miscible	<5
2-propanol	0.6	0.2	miscible	15	miscible
methanol	<0.1	0.3	miscible	0.9	<8
methyl ethyl ketone	1.9	1.5	miscible	miscible	miscible
toluene	2.8	2.5	miscible	miscible	
water	0.0013	0.0011	0.0095	0.0045	

[a] Solubility of solvent in fluorinated compound, percent by weight at 20°C.

[b] Molecular weight = 611, functionality >1.9.

Table 3. **Azeotropic Mixtures Containing Hydrofluoroethers**

Binary azeotropes with $C_4F_9OCH_3$				
Second component	Bp of azeotrope, °C	$C_4F_9OCH_3$ in mixture, wt%		
2-propanol	54.7	93.3		
trans-1,2-dichloroethylene	40.8	50.3		
ternary azeotrope with $C_4F_9OCH_3$	bp of azeotrope °C	$C_4F_9OCH_3$ in mixture, wt%	*trans*-CHClCHCl in mixture, wt%	ethanol in mixture, wt%
	39.6	52.7	44.6	2.7

properties that are intermediate between their fully fluorinated and hydrocarbon analogues. Many lower molecular weight organic solvents exhibit appreciably greater solublility in the partially fluorinated ethers as compared to the perfluorinated ethers and amines. Halogenated hydrocarbons are highly soluble and often completely miscible with the hydrofluoroethers. However, as with the perfluorinated ethers, the hydrofluoroethers and hydrofluoropolyethers demonstrate reduced solubility as their molecular weight increases. Typical solubility data are shown in Table 2.

These solubility relationships are consistent with the predictions based on the Hildebrand solubility parameter (26). For perfluorinated liquids, the solubility parameters are on the order of 10–12 $J^{1/2}/cm^{3/2}$ (5–6 $cal^{1/2}/cm^{3/2}$), which are the lowest known values for liquids. The solubility parameters for the hydrofluoroethers are somewhat higher than those of the perfluorinated liquids at 11–14 $J^{1/2}/cm^{3/2}$. The hydrofluoroethers also exhibit a tendency to form azeotropic mixtures with a number of organic solvents (27–30). Examples of commercially available azeotropic mixtures are listed in Table 3. The increased solvency of these mixtures broadens the utility of hydrofluoroethers in many precision cleaning and coating applications.

The solubilities of gases such as oxygen, nitrogen, and carbon dioxide are generally high as shown in Table 4 (31). The oxygen and carbon dioxide solubilities of related compounds has led to their use as specialized synthetic blood substitutes.

Table 4. **Solubility of Gases in Fluorinated Ethers and Amines at 25°C and 101 kPa (1 atm)**[a]

Solvent	$C_8F_{16}O$	$(C_4F_9)_3N$	$C_4F_9OCH_3$	$C_4F_9OC_2H_5$
argon			67.5	60.5
oxygen	48.8	38.9	72.7	58.0
nitrogen	33.4	28.4		
air	40.5	33.1	38.6	
carbon dioxide	192	152		

[a] mL gas/100 mL solvent.

4. Methods of Preparation

4.1. Electrochemical Fluorination. In the Simons electrochemical fluorination (ECF) process the organic reactant is dissolved in anhydrous hydrogen fluoride and fluorinated at the anode, usually nickel, of an electrochemical cell. This process has been reviewed (6). Essentially all hydrogen atoms are substituted by fluorine atoms; carbon–carbon multiple bonds are saturated. The product phase is heavier than the HF phase and insoluble in it and is recovered by phase separation.

$$(C_4H_9)_3N + 27\ HF \xrightarrow{ECF} (C_4F_9)_3N + 27\ H_2$$

With an amine reactant, it has been shown that roughly one-third of the current passed makes liquid product, one-third gas, and one-third goes to HF-soluble polyfluorinated products (32). The ether perfluoro(2-butyltetrahydrofuran) [335-36-4] is made from a cyclization process during the ECF of perfluorooctanoyl chloride; other cyclic ethers have been prepared from certain ester reactants by a similar cyclization (33). Perfluoroaminoethers have been prepared by ECF (34).

Electrochemical fluorination leads to fragmentation, coupling, and rearrangement reactions as well as giving the perfluorinated product. In addition, small amounts of hydrogen can be retained in the crude product. The products are purified by treatment with base to remove the hydrogen-containing species and subsequently distilled.

Electrochemical fluorination can also be used in the preparation of functional compounds including perfluorinated acyl fluorides that are important intermediates in the synthesis of the hydrofluoroethers.

4.2. Direct Fluorination. Another method for the synthesis of perfluorinated compounds is direct fluorination using elemental fluorine (7–9) (see FLUORINE COMPOUNDS, ORGANIC, DIRECT FLUORINATION). Direct fluorination is especially useful for the preparation of perfluoroethers. Multiple ether oxygen atoms can be present in the molecule. Cleavage and coupling reactions occur with direct fluorination although to a lesser extent than with ECF.

4.3. Polymerization. The higher molecular weight perfluoropolyethers are prepared by distinctly different technology. The anionic polymerization of hexafluoropropene oxide is carried out using cesium or potassium fluoride as catalyst in a polar aprotic solvent such as diglyme (11). This leads to repeating units (n can vary widely) of the perfluoroisopropoxy group in the oligomeric chain which is terminated with an acyl fluoride.

$$CF_3CF{-}CF_2(O) \xrightarrow{F^-} F[CF(CF_3)CF_2O]_nCF(CF_3)COF$$

This reactive end group must be removed to render the final compound inert using one of several methods. The lower molecular weight members of this family have been marketed by Du Pont as their K-Series fluids.

The photooxidation of hexafluoropropene or tetrafluoroethene or mixtures thereof leads to perfluoro polyether peroxides of varying molecular weights

(14). The peroxidic links are subsequently decomposed by thermal treatment, the presence of base is optional, to give lower molecular weight fragments containing a variety of end groups. The polymers are then stabilized by removal of the functional group via direct fluorination. The final products of the photooxidation of hexafluoropropene have the following structure where the ratio q/p can vary between 0 and 0.1:

$$CF_3O[(CF(CF_3)CF_2O)_p(CF_2O)_q]CF_3$$

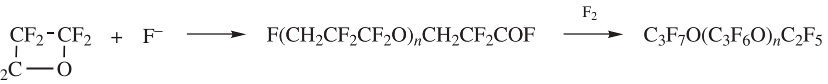
The lower molecular weight fractions from this process have been marketed by Solvay Solexis under their trade name Galden.The final products for the photooxidation of tetrafluoroethene have the following structure where the ratio m/n is between 0.6 and 1.5 and is typically ~0.8 (14). The average molecular weight of these polyethers is between ~1,000 and 40,000.

$$CF_3O(C_2F_4O)_m(CF_2O)_nCF_3$$

Hydrofluoropolyethers are obtained from the oxidative polymerization of tetrafluoroethene with or without ultraviolet (uv) irradiation (21). The initially obtained polyperoxides are reduced by reaction with hydrogen over a catalyst to afford essentially difunctional perfluoropolyether acyl fluorides. These acyl fluorides are then converted by standard chemistry, decarboxylation in the presence of a proton donor, to the desired hydrofluoropolyethers.

$$HCF_2O(CF_2O)_n(C_2F_4O)_mCF_2H$$

Perfluoropolyethers with the linear perfluoropropoxy repeat unit have been commercialized (35). They are prepared by the anionic oligomerization of tetrafluorooxetane followed by direct fluorination to remove the acyl fluoride end group as well as to fluorinate the remaining CH_2 groups; n can vary widely.



All the processes give perfluoropolyethers with a broad distribution of molecular weights. They are typically separated into fractions by vacuum distillation.

4.4. Alkylation of Perfluoroacyl Fluorides. Hydrofluoroethers are prepared by alkylation of perfluorinated alkoxides which themselves are prepared by reaction of a perfluoroacyl fluoride or perfluorinated ketone with an anhydrous alkali metal fluoride (eg, potassium or cesium fluoride) in an anhydrous polar, aprotic solvent. The reaction scheme is shown below.

$$n+i-C_3F_7COF+KF \xrightarrow{\text{diglyme}} n+i-C_3F_7CF_2O^-K^+$$

$$n+i-C_3F_7CF_2O^-K^+ + (RO)_2SO_2 \longrightarrow n+i-C_4F_9OR; R=CH_3, C_2H_5$$

5. Economic Aspects

Information on the production levels of the perfluoroethers and perfluorotertiary amines is not disclosed, but the products are available commercially and are marketed, eg, as part of the Fluorinert Electronic Liquids family by 3M Co. (17). These liquids have boiling points of 30–215°C with molecular weights of ~300–800. Perfluoropropene oxide polyethers are marketed by Du Pont with the trade name Krytox (36). The linear perfluoropropene oxide polyethers are marketed by Daikin under the trade name Demnum (35). The perfluoropolyethers derived from photooxidation are marketed by Solvay Solexis under the trade names of Fomblin (37) and Galden. The hydrofluoroether liquids have boiling points from 34–130°C and are marketed with the trade name Novec Engineered Fluids by 3M. The hydrofluoropolyether liquids have boiling points from 85 to 180°C and are marketed under the trade name of H-Galden by Solvay-Solexis.

6. Health and Safety Factors

All of the fluorinated compounds discussed above have an ozone depletion potential of zero because they do not contain either chlorine or bromine, which take part in catalytic cycles that destroy stratospheric ozone (38). In addition, the commercially available compounds do not contribute to the formation of ground level ozone and as a result, most are exempt from VOC regulations (39). The lack of reactivity of the perfluorinated compounds results in resistance to degradation in the lower atmosphere and long atmospheric lifetimes similar to those of the perfluoroalkanes (40). These long atmospheric lifetimes result in high global warming potentials for these compounds.

By contrast, the partially fluorinated hydrofluoroethers and hydrofluoropolyethers are reactive in the lower atmosphere, resulting in significantly shorter atmospheric lifetimes (41). While these compounds still absorb infrared radiation, their shorter atmospheric lifetimes produce significantly lower global warming potentials as indicated in Table 5 (41–45).

Over the years animal studies have repeatedly shown that perfluorinated inert fluids are non-irritating to the eyes and skin and practically nontoxic by ingestion, inhalation, or intraperitoneal injection (17,31). The commercially available hydrofluoroethers and hydrofluoropolyethers have also been shown to be low in toxicity (21,46). The LC_{50} values (inhalation) for the hydrofluoroethers and hydrofluoropolyethers are >90,000 ppmV (or greater than the maximum attainable vapor concentration, 4-h exposure in the rat). As with all fluorinated compounds, thermal degradation of the fluorinated ethers and amines can produce toxic decomposition products including hydrogen fluoride and perfluoroisobutene, which has a reported LC_{50} of 0.5 ppm (6-h exposure in rats) (47). This decomposition generally requires temperatures >200°C. All of the commercially available fluorinated ethers and amines are nonflammable, exhibiting no open or closed cup flash point.

Table 5. **Atmospheric Lifetime and Global Warming Potential (GWP) of Fluorinated Ethers and Amines**

Atmospheric lifetime (years)	GWP (100 year integration time horizon)	
$N(C_4F_9)_3$	2000	7200
$CF_3O(CF(CF_3)CF_2O)_m(CF_2O)_nCF_3$	3200	7400
$C_3F_7OCH_3$	4.7	400[a]
$C_4F_9OCH_3$	3.8	300[b]
$C_4F_9OC_2H_5$	0.8	55
$C_7F_{15}OC_2H_5$	2.2	100[c]
$CHF_2OCF_2OC_2F_4OCHF_2$	6.3	1800
$CHF_2OCF_2OCHF_2$	12.1	2700
$CHF_2OCF_2CF_2OCHF_2$	6.2	1500

[a] Calculated using the data of Ninomiya and co-workers and the IPCC 2001 method.

[b] Calculated using the data of Oyaro and co-workers, Wallington and co-workers and the IPCC 2001 method.

7. Uses

The unique combination of properties of the perfluorinated fluids makes them useful in a variety of applications in the electronics industry (48). The lower molecular weight materials are used in two principal areas in this industry: heat transfer, both direct and indirect, and testing applications. Perfluorinated liquids have been used as the total immersion coolant for supercomputers. This fluid is used to cool the power supplies, memory boards, logic circuits, and main processors. Testing applications include liquid burn-in testing, gross and fine leak testing, and electrical environmental testing.

The higher molecular weight perfluoropolyethers are useful as specialty lubricants. They provide good lubrication under boundary conditions in systems in which the mechanical parts are exposed to high temperatures or aggressive chemical environments. They are typically used as the working fluid in hazardous duty vacuum pumps used in plasma etching. Specialty greases, used in high temperature environments in which a hydrocarbon-based grease fails, have also been formulated by blending perfluoropolyethers with fluorinated polymers. Additionally, perfluoropolyethers are used as lubricants for magnetic media, lubricant and sealing agent for oxygen service, inert hydraulic fluids, etc (14). They have also found application in cosmetics (49) and as a protective coating for outdoor stone art and masonry (50). Perfluorinated compounds are also potentially useful as inert reaction media, particularly when one of the reactants is gaseous. The high solubility of oxygen and carbon dioxide in perfluorinated liquids has allowed their use as blood substitutes (51) and as oxygenation media for biotechnology (52). One product, Fluosol DA (53) (Green Cross Corp.), has been commercialized, and there is an abundant patent art in this area (see BLOOD SUBSTITUTES).

The hydrofluoropolyethers have begun to find use as heat-transfer fluids. The hydrofluoroethers are used in a number of applications as replacements for ozone-depleting chlorofluorocarbons (CFCs). These applications include electronics and precision cleaning as well as solvents for the deposition of lubricants and coatings on computer hard disks, electronic components and medical devices. Hydrofluoroethers are also employed as heat transfer fluids in the manufacture of semiconductors and electronic components. In addition, they are used in a number of specialty applications such as an alternative to flammable solvents in fingerprint development and a component in some cosmetic formulations.

BIBLIOGRAPHY

"Fluoro Ethers and Amines" under "Fluorine Compounds, Organic" in *ECT* 1st ed., Vol. 6, pp. 762–763, by L. J. Hals and W. H. Pearlson, Minnesota Mining & Manufacturing Co.; in *ECT* 2nd ed., Vol. 9, pp. 753–754, by L. J. Hals and W. H. Pearlson, Minnesota Mining & Manufacturing Co.; in *ECT* 3rd ed., Vol. 10, pp. 874–881, by R. D. Danielson, Minnesota Mining & Manufacturing Co.; "Fluoroethers and Fluoroamines" under "Fluorine Compounds, Organic" in *ECT* 4th ed., Vol. 11, pp. 525–534, by Richard M. Flynn, 3M Company; "Fluoroethers and Fluoroamines" in *ECT* (online), posting date: December 4, 2000 by Richard M. Flynn, 3M Company.

CITED PUBLICATIONS

1. J. H. Simons and co-workers, *J. Electrochem. Soc.* **95**, 47 (1949).
2. J. H. Simons, ed., *Fluorine Chemistry*, Vol. 1, Academic Press, Inc., New York, 1950, pp. 414–420.
3. S. Nagase, in P. Tarrant, ed., *Fluorine Chemistry Reviews*, Vol. 1, Marcel Dekker, Inc., New York, 1967, pp. 77–106.
4. T. Abe and S. Nagase, in R. E. Banks, ed., *Preparation, Properties and Industrial Applications of Organofluorine Compounds*, Ellis Horwood, Chichester, U.K., 1982, p. 19.
5. I. N. Rozhkov, in M. M. Baizer and H. Lund, eds., *Organic Electrochemistry*, 2nd ed., Marcel Dekker, Inc., New York, 1983, p. 805.
6. W. V. Childs and co-workers, in H. Lund and M. M. Baizer, eds., *Organic Electrochemistry*, 3rd ed., Marcel Dekker, New York, 1991, p. 1103.
7. U.S. Pat. 5,093,432 (Mar. 3, 1992), T. R. Bierschenk and co-workers (to Exfluor Research Corp.).
8. World Pat. 90,06296 (June 14, 1990), M. G. Costello and G. G. I. Moore (to Minnesota Mining & Mfg. Co.).
9. R. J. Lagow, *Prog. Inorg. Chem.* **26**, 161–210 (1979).
10. R. D. Chambers and co-workers, *J. Fluorine Chem.* **29**, 323 (1985).
11. J. T. Hill, *J. Macromol. Sci.-Chem.* **A8**(3), 499 (1974); P. Tarrant and co-workers, in P. Tarrant, ed., *Fluorine Chemistry Reviews*, Vol. 5, Marcel Dekker, New York, 1971, pp. 77–113.
12. H. S. Eleuterio, *J. Macromol. Sci.-Chem.* **A6**(6), 1027 (1972).
13. D. Sianesi and co-workers, *Chim. Ind. (Milan)* **55**(2), 208 (1973).
14. G. Caporiccio, in R. E. Banks, D. W. A. Sharp, and J. C. Tatlow, eds., *Fluorine: The First Hundred Years (1886–1986)*, Elsevier Sequoia, New York, 1986, pp. 314–320.
15. Y. Ohsaka, *J. Jpn. Pet. Inst.* **8**(9), 2 (1985).

16. U.S. Pat. 3,810,874 (May 14, 1974), R. A. Mitsch and J. L. Zollinger (to Minnesota Mining (Mfg. Co.).
17. *Fluorinert Liquids*, technical notebook, 3M Co., St. Paul, Minn., 1987.
18. G. Marchionni, M. Bassi, G. Fontana, P. Maccone, and G. Ajroldi, *J. Fluorine Chem.* **98**, 41 (1999).
19. H. G. Bryce, in J. H. Simons, ed., *Fluorine Chemistry*, Vol. 5, Academic Press, Inc., New York, 1964.
20. P. Tuma and L. Tousignant, SEMI Technical Symposium, SEMICON West, July 16, 2001.
21. G. Marchionni, R. Silvani, G. Fontana, G. Malinverno, and M. Visca, *J. Fluorine Chem.* **95**, 41 (1999).
22. G. V. D. Tiers, *J. Am. Chem. Soc.* **77**, 4837, 6703, 6704 (1955).
23. P. Kasai and P. Wheeler, *Appl. Surface Sci.* **52**, 91 (1991).
24. P. Kasai, W. Tang, and P. Wheeler, *Appl. Surface Sci.* **51**, 201 (1991).
25. J. Owens, Proceedings of the Joint IPCC/TEAP Expert Meeting on Options for the Limitation of Emissions of HFCs and PFCs, Energieionderzoek Centrum Nederland, Petten, The Netherlands, May 1999.
26. J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York, 1970, p. 207.
27. U.S. Pat. 5,814,595 (Sep. 29, 1998), R. Flynn (to Minnesota Mining and Manufacturing Company).
28. U.S. Pat. 5,827,812 (Oct. 27, 1998), R. Flynn (to Minnesota Mining and Manufacturing Company).
29. U.S. Pat. 6,008,179 (Dec. 28, 1999), R. Flynn (to 3M Innovative Properties Company).
30. U. S. Pat. 6,030,934 (Feb. 29, 2000), J. Owens (to 3M Innovative Properties Company).
31. J. W. Sargent and R. J. Seffl, *Fed. Proc.* **29**, 1699 (1970).
32. A. Dimitrov, St. Rudiger, and M. Bartoszek, *J. Fluorine Chem.* **47**, 23 (1990).
33. T. Abe and co-workers, *J. Fluorine Chem.* **12**, 359 (1978).
34. G. G. I. Moore and co-workers, *J. Fluorine Chem.* **32**, 41 (1986).
35. *Demnum, Demnum Grease Technical Bulletin*, Daikin Industries, Ltd., Osaka, Japan, Jan. 1987.
36. *Krytox, Technical Bulletins No. E74823*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., Aug. 1985.
37. *Fomblin y Fluorinated Fluids*, Montedison SpA, Milan, Italy, 1971.
38. M. J. Molina and F. S. Rowland, *Nature London* **249**, 810 (1974). J. W. Clayton, Jr., in Ref. 3, pp. 225–232.
39. *Fed. Reg.* **57**(22), 3945 (Feb. 3, 1992).
40. P. Tuma and L. Tousignant, *Solid State Technolo.*, June 2000.
41. IPCC (Intergovernmental Panel on Climate Change), Climate Change 2001 : The Scientific Basis, J. Houghton, ed., Cambridge University Press, Cambridge, U.K., 2001.
42. Y. Ninomiya, M. Kawasaki, A. Guschin, L. Molina, M. Molina, and T. Wallington, *Environ. Sci. Technolo.* **34**, 2973 (2000).
43. T. Wallington, W. Schneider, J. Sehested, M. Bilde, J. Platz, O. Nielsen, L. Christensen, M. Molina, L. Molina, and P. Wooldridge, *J. Phys. Chem. A* **101**, 8264 (1997).
44. N. Oyaro and C. Nielsen, *Asian Chem. Lett.* **7**, 119 (2003).
45. M. Goto, Y. Inoue, M. Kawasaki, A. Guschin, L. Molina, M. Molina, T. Wallington, and M. Hurley, *Environ. Sci. Technol.* **36**, 2395 (2002).
46. J. Owens, in B. Kanegsberg, and E. Kanegsberg, eds., *Handbook for Critical Cleaning*, CRC Press LLC, Boca Raton, Flor., 2000.
47. J. W. Clayton, Jr., in Ref. 3, pp. 225–232.

48. D. Slinn and S. Green, in Ref. 4, pp. 45–82.
49. Eur. Pat. Appl. 390,206 (Oct. 3, 1990), F. Brunetta and G. Pantini (to Ausimont SRL).
50. *Fomblin MET Technical Bulletin*, Montefluos, Milan, Italy, Oct. 1987.
51. *Science* **206**, 205 (1979).
52. B. Mattiasson and P. Adlercreut, *Trends Biotechnol.* **5**, 250 (1987).
53. *Chem. Eng. News* **12** (Nov. 26, 1979).

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