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**THE DEVELOPMENT OF NEW, LOW-COST PERFLUOROALKYLETHER
FLUIDS WITH EXCELLENT LOW AND HIGH-TEMPERATURE PROPERTIES**

FINAL REPORT

May 1988

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7N-27

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Lewis Research Center

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16. Abstract A series of perfluoroalkylether (PFAE) fluids were synthesized by direct fluorination. Viscosity-temperature properties, oxidation stabilities, oxidation-corrosion properties and lubricity were determined. The fluids were tested in the presence of common elastomers to check for compatibility. The bulk modulus of each was measured to determine if any could be used as nonflammable aircraft hydraulic fluid. It was determined that as the carbon to oxygen ratio decreases, the viscometric properties improve, the fluids may become poor lubricants, the bulk modulus increases, the surface tension increases and the fluid density increases. The presence of difluoromethylene oxide units in the polymer does not seriously lower the oxidation and oxidation-corrosion stabilities as long as the difluoromethylene oxide units are separated by other units.					
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1. SUMMARY

A series of perfluoroalkylether (PFAE) fluids were synthesized by direct fluorination. Viscosity-temperature properties, oxidation stabilities, oxidation-corrosion properties and lubricity were determined. The fluids were tested in the presence of common elastomers to check for compatibility. The bulk modulus of each was measured to determine if any could be used as a nonflammable aircraft hydraulic fluid. It was determined that as the carbon to oxygen ratio decreases, the viscometric properties improve, the fluids may become poorer lubricants, the bulk modulus increases, the surface tension increases and the fluid density increases. The presence of difluoromethylene oxide units in the polymer does not seriously lower the oxidation and oxidation-corrosion stabilities as long as the difluoromethylene oxide units are separated by other units.

2. INTRODUCTION

With the advent of newer and more sophisticated aerospace systems, new fluids and lubricants are needed which can survive the severe temperatures and oxidative environments to which the systems are often subjected.

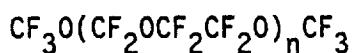
Perfluoropolyethers as a class of fluids exhibit excellent thermal and oxidative stability¹⁻³ and when combined with good viscosity-temperature characteristics,³ good elastohydrodynamic film forming capabilities,⁴ good boundary lubricating ability³⁻⁶ and nonflammability properties⁷ make these fluids promising candidates for high temperature lubricant applications.

A series of perfluoroalkylether fluids were prepared and studied which contain difluoromethylene and/or tetrafluoroethylene oxide units. Fluids based on these structures were expected to perform well at very low temperatures due to the abundance of oxygen in the polymer backbone. In addition to studying the low temperature properties, we hoped to demonstrate that fluids could be made which also

have adequate high temperature properties. A successful objective of the program was the demonstration that a fluid having a composition nearly identical to that of Fomblin Z could be made which would be substantially more oxidatively stable than Fomblin Z.

3. EXPERIMENTAL DETAILS

3.1 Preparation of Perfluoropolydioxolane #1



A 300 g sample of 1,3-dioxolane (distilled over sodium) was mixed with 300 g methylene chloride (washed with sulfuric acid and distilled over P_2O_5) and polymerized using a catalytic amount of trifluoromethane sulfonic acid. Following a five minute induction period, the solution began to thicken as the 1,3-dioxolane polymerized. The reaction was complete in approximately four hours. A trace of triethyl amine was added to the polymer to deactivate the catalyst once the reaction was complete.

The polymer (300 g) was fluorinated in a 48-hour reaction to give 370 g fluid (50% yield) and 148 g of elastomeric solids (20% yield). A total of 1500 g of fluid prepared in several reactions was treated with 30% fluorine at 250 °C to remove any residual hydrogens. The sample was distilled to give the following fractions:

<u>Sample #</u>	<u>Wt. of Sample (g)</u>	<u>% of Total</u>	<u>b.p. range (°C)</u>
101	325	21	< 200 °C @ 100 mm
102	395	26	> 200 °C @ 100 mm, < 245 °C @ 10 mm
103	300	19	> 245 °C @ 10 mm, < 288 °C @ 0.1 mm
104	176	11	> 288 °C @ 0.1 mm, < 340 °C @ 0.05 mm
105	352	23	> 340 °C @ 0.05 mm

^{19}F NMR of the fluid (sample #104) gave the following results: δ 48.8 (m, e), 51.5 (p, 11.1 Hz, g), 54.0 (q, 9.6 Hz, b), 55.8 (t, 9.1 Hz, i), 57.6 (t, 9.6 Hz, a), 87.3 (s, c), 88.7 (m, d), 90.0 (7, 11.1 Hz, f) and 90.4 (q, 9.1 Hz, h).

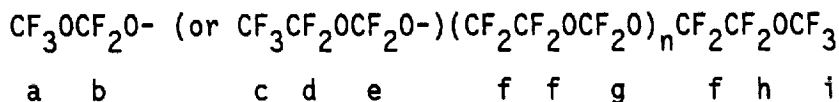


Table 1 Perfluoropolydioxolane #1 Fractions and Properties

Fraction						
Property		<u>101</u>	<u>102</u>	<u>103</u>	<u>104</u>	<u>105</u>
	-40 °C	23.2	125	646	2660	12,900
	20 °C	2.83	7.92	23.0	50.8	238
Kinematic	40 °C	1.88	4.78	12.5	26.4	113
Viscosity	60 °C	1.33	3.14	7.68	15.5	63.0
(cst.)	80 °C	0.99	2.18	5.13	10.0	39.3
	95 °C	0.81	1.69	3.78	8.11	30.3
	149 °C	0.46	0.87	1.79	3.61	13.0
ASTM slope (ASTM D341)		.901	.758	.604	.527	.417
Pour point (°C)		-107	-96	-87	-73	-66
Density (20 °C, g/ml)		1.768	1.801	1.830	1.845	1.855
Surface Tension (dyne/cm)		15.7	16.9	19.0	18.9	18.3
Boiling point range °C (mm/Hg)		<200(100)	>200(100) <245(10)	>245(10) 288(0.05)	>288(0.05) <343(0.05)	>343(0.05)

Anal. Calcd. for $\text{C}_3\text{F}_6\text{O}_2$: C, 19.78; F, 62.64. Found: C, 19.86; F, 62.72.

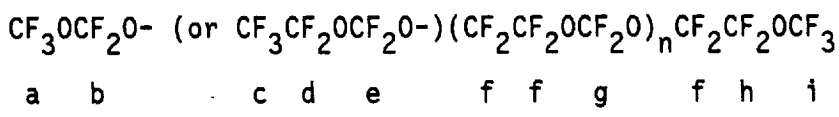
3.2 Preparation of Perfluoropolydioxolane #2



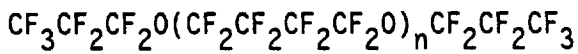
The structure of perfluoropolydioxolane #2 is essentially identical to that of perfluoropolydioxolane #1 with one exception. Perfluoropolydioxolane #2 was made using a newly developed fluorination procedure which gives a fluid which is essentially linear with a negligible number of branch sites. Perfluoropolydioxolane

#1 was made using older technology and as a result some molecules have one or several short branch sites which appear to decrease the oxidative stability of the fluid by approximately 50 °F.

¹⁹F NMR of a fraction having a boiling point greater than 288 °C and less than 340 °C at 0.05 mm/Hg gave the following results (84.87 MHz, CFC1₃): δ 48.8 (m, e), 51.5 (p, 11.1 Hz, g), 54.0 (q, 9.6 Hz, b), 55.8 (t, 9.1 Hz, i), 57.6 (t, 9.6 Hz, a), 87.3 (s, c), 88.7 (m, d), 90.0 (t, 11.1 Hz, f) and 90.4 (q, 9.1 Hz, h).

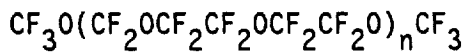


The ¹⁹F NMR spectrum also showed small peaks at 55.7 (t), 81.9 (t), 83.3 (s), 84.3 (m), 87.3 (s), 88.5 (p), 125.7 (s) and 130.0 (s) corresponding to an impurity in the fluid having the following structure:



The origin of the impurity is not known with certainty; however, we suspect that the impurity was present in some sodium fluoride powder used to remove hydrogen fluoride from the fluid (hydrogen fluoride is a by-product of the direct fluorination process). The sodium bifluoride formed in the reaction of sodium fluoride with hydrogen fluoride is typically reused after regeneration at 600 °C. We suspect that some perfluoropolytetrahydrofuran (a fluid prepared for Air Force Contract No. F33615-87-C-5307) which was present on the sodium fluoride powder survived the regeneration process and remained as a contaminant in the sodium fluoride.

3.3 Preparation of Perfluoropolytrioxocane #1



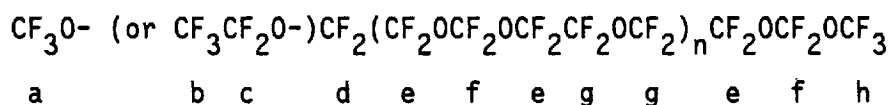
Into a one liter stirred flask equipped with a water separator were placed 500 g diethylene glycol (4.7 mol), 225 g paraformaldehyde (7.5 mol), 150 ml toluene and 5 g ion exchange resin (H⁺ form). The mixture was refluxed for several hours to remove

the water formed during the reaction. The solution was first filtered to remove the ion exchange resin, then distilled to 150 °C at 0.05 mm/Hg to remove the toluene and other lights. A nearly quantitative yield of polymer was obtained.

The polymer (400 g) was fluorinated in a 48-hour reaction to give 379 g of fluid (37.5% yield) and 320 g of an elastomeric solid (31.7% yield). Approximately 1150 g of fluid, the product of several reactions, was treated with 30% fluorine at 250 °C for 12 hours, then distilled to give the following product distribution:

<u>Sample #</u>	<u>Wt. of Sample (g)</u>	<u>% of Total</u>	<u>b.p. range (°C)</u>
201	277	26	< 200 °C @ 100 mm
202	238	22	> 200 °C @ 100 mm, < 245 °C @ 10 mm
203	234	22	> 245 °C @ 10 mm, < 288 °C @ 0.05 mm
204	202	19	> 288 °C @ 0.05 mm, < 370 °C @ 0.05 mm
205	112	11	> 370 °C @ 0.05 mm

¹⁹F NMR of the sample #204 (84.87 MHz, CFC1₃): δ 52.0 (p, 11 Hz, f), 56.0 (t, 8.9 Hz, a), 57.8 (t, 8.9 Hz, h), 87.3 (s, b), 88.9 (s, g), 90.7 (t, 11 Hz, d), 90.8 (t, 11 Hz, e) and 90.9 (m, c).

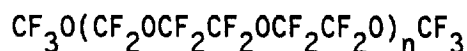


Anal. Calcd. for C₅F₁₀O₃: C, 20.13; F, 63.76. Found: C, 20.12; F, 63.50.

Table 2 Perfluoropolytrioxocane #1 Fractions and Properties

Fraction						
Property		<u>201</u>	<u>202</u>	<u>203</u>	<u>204</u>	<u>205</u>
Kinematic Viscosity (cst.)	-40 °C	33.9	382	2750	11,500	84,100
	20 °C	3.04	10.7	37.4	105	502
	40 °C	1.94	5.90	12.7	46.0	210
	60 °C	1.36	3.67	10.0	24.5	105
	80 °C	1.01	2.49	6.30	14.7	59.7
	95 °C	0.84	1.98	4.85	11.2	45.3
	149 °C	0.43	0.96	2.11	4.45	17.3
ASTM slope (ASTM D341)		.945	.769	.648	.560	.440
Pour point (°C)		-100	-83	-70	-65	-55
Density (20 °C, g/ml)		1.766	1.806	1.832	1.848	1.858
Surface Tension (dyne/cm)		15.4	16.8	18.2	18.6	18.6
Boiling point range °C (mm/Hg)		<200(100)	>200(100) <245(10)	>245(10) <288(0.05)	>288(0.05) <370(0.05)	>370(0.05)

3.4 Preparation of Perfluoropolytrioxocane #2

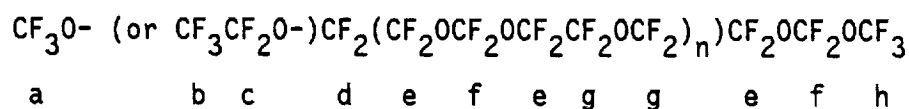


A 450 g sample of 1,3,6-trioxocane was polymerized in one liter of dry methylene chloride at room temperature using 0.04 ml of trifluoromethane sulfonic acid as a catalyst. The polymerization was complete in 24 hours. Sodium methoxide (1 g) dissolved in 50 ml of dry methanol was added to the polymer to neutralize the acid catalyst.

Approximately 400 g of the polymerized 1,3,6-trioxocane was fluorinated in a 24-hour reaction to give 425 g of fluid (42.2% yield) and 85 g of solids (8.4% yield). Approximately 1150 g of fluid was distilled to give the following product distribution:

<u>Sample #</u>	<u>Wt. of Sample (g)</u>	<u>% of Total</u>	<u>b.p. range (°C)</u>
301	337	31	< 200 °C @ 100 mm
302	358	33	> 200 °C @ 100 mm, < 245 °C @ 10 mm
303	174	16	> 245 °C @ 10 mm, < 288 °C @ 0.05 mm
304	112	10	> 288 °C @ 0.05 mm, < 370 °C @ 0.05 mm
305	111	10	> 370 °C @ 0.05 mm

¹⁹F NMR of sample number 304 (84.87 MHz, CFC1₃): δ 52.0 (p, 11 Hz, f), 56.0 (t, 8.9 Hz, a), 57.8 (t, 8.9 Hz, h), 87.3 (s,b), 88.9 (s, g), 90.7 (t, 11 Hz, d), 90.8 (t, 11 Hz, e), 90.9 (m, c).

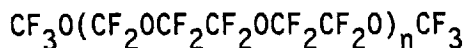


Anal. Calcd. for C₅F₁₀O₃: C, 20.13; F, 63.76. Found: C, 19.88; F, 63.63.

Table 3 Perfluoropolytrioxocane #2 Fractions and Properties

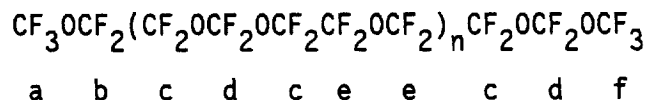
Fraction						
Property		<u>301</u>	<u>302</u>	<u>303</u>	<u>304</u>	<u>305</u>
	-40 °C	33.6	382	2545	7480	36,900
	20 °C	3.22	11.8	38.9	83.3	291
Kinematic	40 °C	2.06	6.56	19.2	38.3	125
Viscosity	60 °C	1.44	4.13	11.1	21.1	65.7
(cst.)	80 °C	1.07	2.84	7.08	13.1	39.6
	95 °C	0.88	2.24	-	10.1	29.7
	149 °C	0.48	1.15	-	4.17	11.9
ASTM slope (ASTM D341)		.901	.725	.615	.549	.451
Pour point (°C)		-100	-83	-70	-65	-55
Density (20 °C, g/ml)		1.765	1.808	1.829	1.849	1.857
Boiling point range		<200(100)	>200(100)	>245(10)	>288(0.05)	>370(0.05)
°C (mm/Hg)			<245(10)	<288(0.05)	<370(0.05)	

3.5 Preparation of Perfluoropolytrioxocane #3

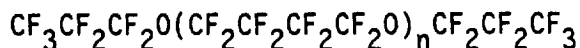


A third sample of perfluoropolytrioxocane was prepared using the newer technology which has been demonstrated to give linear fluid with essentially no cross-linking and branching. Like perfluoropolydioxolane #2, perfluoropolytrioxocane #3 is slightly more stable than perfluoropolytrioxocane #1 or #2 which are believed to contain some branch sites.

^{19}F NMR of a fraction having a boiling point above 288 °C and less than 370 °C at 0.05 mm/Hg gave the following results: ^{19}F NMR (84.87 MHz, CFCl_3) δ 52.0 (p, 11 Hz, d), 56.0 (t, 8.9 Hz, a), 57.8 (t, 8.9 Hz, f), 88.9 (s, e), 90.7 (t, 11 Hz, b) and 90.8 (t, 11 Hz, c).



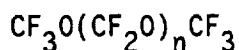
The NMR spectrum also showed small peaks at 55.7 (t), 81.9 (t), 83.3 (s), 84.3 (m), 87.3 (s), 88.5 (p), 125.7 (s) and 130.0 (s), corresponding to an impurity (7%) in the fluid having the following structure:



We have ruled out the possibility that the impurity is a result of a side reaction in the preparation of the fluid and believe that the impurity was present in some sodium fluoride used to remove hydrogen fluoride from the sample (see Section 3.2).

Anal. Calcd. for $\text{C}_5\text{F}_{10}\text{O}_3$: C, 20.13; F, 63.76. Found: C, 19.88; F, 63.61.

3.6 Preparation of Perfluoropoly(methylene oxide)



A poly(methylene oxide) polymer was prepared by copolymerizing 200 g 1,3,5-trioxane (2.8 mol) and 1,3-dioxolane (0.3 mol) in methylene chloride using

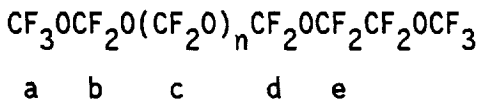
trifluoromethane sulfonic acid as a catalyst (2.6×10^{-3} mol). Following a short induction period, the solution became cloudy and a fine precipitate began to form. The reaction products were allowed to stand for 12 hours, then filtered and washed with dilute sodium methoxide in methanol to give a nearly quantitative yield of the polymer.

The powder (300 g) was fluorinated in a 48-hour reaction to give 265 g of fluid (40.1% yield). Approximately 1 kg of the fluid was distilled to give the following fractions:

<u>Sample #</u>	<u>Wt. of Sample (g)</u>	<u>% of Total</u>	<u>b.p. range (°C)</u>
401	204	21	< 210 °C @ 100 mm
402	182	19	> 210 °C @ 100 mm, < 223 °C @ 15 mm
403	195	20	> 223 °C @ 15 mm, < 275 °C @ 0.05 mm
404	155	16	> 275 °C @ 0.05 mm, < 335 °C @ 0.05 mm
405	224	23	> 335 °C @ 0.05 mm

The undistilled sample was analyzed by ^1H NMR and was shown to have no detectable hydrogens. The fluid was shown by ^{19}F NMR to contain 95.4% CF_2O units and 4.60% $\text{CF}_2\text{CF}_2\text{O}$.

^{19}F NMR of sample #404 (84.87 Hz, CFCl_3): δ 57.7 (t, 8.8 Hz, a), 53.3 (m, b), 55.0 (s, c), 55.7 (m, d), 90.3 (t, 10.8 Hz, e).

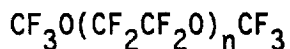


Anal. Calcd. for CF_2O : C, 18.18; F, 57.58. Found: C, 18.09; F, 57.49.

Table 4 Perfluoropoly(methylene oxide) Fractions and Properties

Fraction		401	402	403	404	405
Property						
Kinematic Viscosity (cst.)	-40 °C	9.01	27.6	54.5	128	305
	20 °C	2.18	4.89	8.78	18.4	41.3
	40 °C	1.49	3.38	5.99	12.3	27.1
	60 °C	1.12	2.49	4.32	8.81	19.1
	80 °C	0.88	1.91	3.24	6.60	14.1
	95 °C	0.72	1.55	2.59	5.25	11.0
	149 °C	0.46	0.94	1.55	2.97	6.29
ASTM slope (ASTM D341)		.837	.629	.523	.418	.352
Pour point (°C)		-120	-120	-119	-118	-115
Density (20 °C, g/ml)		1.794	1.822	1.840	1.846	1.852
Surface Tension (dyne/cm)		16.4	17.9	20.1	19.8	18.3
Boiling point range °C (mm/Hg)		<210(100)	>210(100) <223(15)	>223(15) <275(0.05)	>275(0.05) <335(0.05)	>335(0.05)

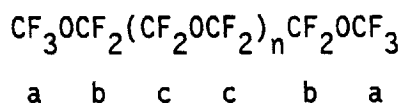
3.7 Preparation of Perfluoropoly(ethylene oxide)



A 1000 MW polyethylene glycol (400 g) was fluorinated to give approximately 850 g of perfluoropoly(ethylene oxide) which was distilled to give the following fractions:

<u>Sample #</u>	<u>Wt. of Sample (g)</u>	<u>% of Total</u>	<u>b.p. range (°C)</u>
501	111	13	< 200 °C @ 100 mm
502	341	40	> 200 °C @ 100 mm, < 245 °C @ 10 mm
503	304	36	> 245 °C @ 10 mm, < 288 °C @ 0.05 mm
504	62	7	> 288 °C @ 0.05 mm, < 343 °C @ 0.05 mm
505	31	4	> 343 °C @ 0.05 mm

^{19}F NMR of sample #504 gave the following results (84.87 MHz, CFCl_3): δ 56.0 (t, 9.6 Hz, a), 89.0 (s, b) and 91.0 (q, 9.6 Hz, c).



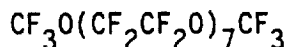
Anal. Calcd. for $\text{C}_2\text{F}_4\text{O}$: C, 20.69; F, 65.17. Found: C, 20.77; F, 65.29.

Table 5 Perfluoropoly(ethylene oxide) Fractions and Properties

Fraction						
Property		<u>501</u>	<u>502</u>	<u>503</u>	<u>504</u>	<u>505</u>
	-40 °C	-	-	-	-	-
	20 °C	3.32	13.2	33.9	127	447
Kinematic	40 °C	2.07	7.21	16.1	51.9	173
	60 °C	1.43	4.25	9.05	26.7	82.9
Viscosity (cst.)	80 °C	1.05	2.80	5.73	15.5	44.9
	95 °C	0.85	2.09	4.19	11.1	-
	149 °C	0.46	1.07	1.93	4.27	11.4
ASTM slope (ASTM D341)		.934	.725	.681	.538	.488
Pour point (°C)*		-	-	-	-	-
Density (20 °C, g/ml)		1.7484	1.7650	1.7883	1.8133	1.8234
Boiling point range °C (mm/Hg)		<200(100)	>200(100) <245(10)	>245(10) <288(0.05)	>288(0.05) <343(0.05)	>343(0.05)

*Perfluoropoly(ethylene oxide) has a melting point between 0 °C and 20 °C, depending upon the average molecular weight of the sample.

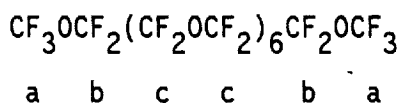
3.8 Preparation of Perfluoroheptaglyme



Heptaglyme was prepared by reacting the sodium salt of 2-(2-methoxyethoxy)-ethanol with 1,2-bis(2-chloroethoxy)ethane. Vacuum distillation of the crude product gave heptaglyme in about a 50% yield.

Fluorination of 300 g of heptaglyme in a 24-hour reaction resulted in 670 g of fluid (82%) being produced from which 557 g of perfluoroheptaglyme (68%) could be isolated via an atmospheric distillation (d 1.709 g/ml).

^{19}F NMR (84.87 MHz, CFC_3): δ 56.0 (t, 9.6 Hz, a), 89.0 (s, b) and 91.0 (q, 9.6 Hz, c).

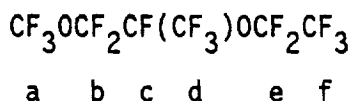


3.9 Preparation of $\text{CF}_3\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_3$

Into a three liter stirred flask were placed 1.2 liters tetrahydrofuran and 159 g of 60% sodium hydride dispersion in mineral oil (3.97 mol). To that mixture was added 270 g propylene glycol monomethyl ether (3.0 mol). After refluxing for 30 minutes, 520 ml diethyl sulfate (3.97 mol) was slowly added. Distillation of the product gave 150 g of liquid boiling at 109 °C.

Fluorination of 60 g of the product gave 70 g of a perfluorinated fluid with the desired structure. b.p. 58.8 °C.

^{19}F NMR (84.87 MHz, CFC_3): δ 56.0 (t, 9.5 Hz, a), 86.0 and 86.3 (m, b), 145 (t, 22 Hz, c), 80.7 (m, d), 85.4 (m, e), and 87.5 (s, f).



3.10 Preparation of $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$

Sodium hydride dispersion (4.0 mol) was added to 500 ml dry tetrahydrofuran in a two liter flask. While refluxing, 100 g 1,3-propanediol (1.32 mol) was slowly added. After refluxing for an additional 30 minutes, 616 g diethylsulfate (4.0 mol) was added. The solution was distilled to give a 60% yield of a product boiling at 208 °C.

Fluorination of 63 g of the product gave 72 g of a perfluorinated fluid having the above structure. b.p. 80.3 °C

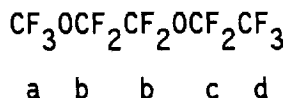
^{19}F NMR (84.87 MHz, CFC_3): δ 87.7 (s, a), 88.7 (m, b), 83.7 (m, c) and 129.4 (s, d).

3.11 Preparation of $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$

Approximately one liter of ethylene glycol monoethyl ether was reacted with 64 g sodium metal (2.78 mol) in a two liter flask. The addition of 262 ml (2.78 mol) of dimethylsulfate to the refluxing solution yielded 281 g (97%) of a product boiling at 104 °C.

Fluorination of 60 g of the product in a 40-hour reaction gave 67 g of a perfluorinated fluid. b.p. 39.7 °C.

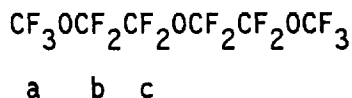
^{19}F NMR (84.87 MHz, CFCl_3): δ 56.0 (t, 8.7 Hz, a), 87.4 (s, d), 88.7 (s, b) and 91.0 (q, 8.7 Hz, c).



3.12 Preparation of $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$

Diglyme (65 g) was fluorinated in a 48-hour reaction to give 75 g of perfluoro-diglyme. b.p. 67.5 °C.

^{19}F NMR (84.87 MHz, CFCl_3): δ 58.7 (t, 9.5 Hz, a), 93.7 (q, 9.5 Hz, b) and 91.7 (s, c).



3.13 Investigation of Thermal Oxidative Behavior

The thermal oxidation tests were conducted in an apparatus similar to the one described in NASA CR-165516 (Ultrasystems). For most of the tests the furnace was held at 343 °C or 371 °C \pm 0.5 °C using a programmable temperature controller. For each test, a preweighed amount of fluid was placed in the decomposition apparatus along with a known amount of oxygen (typically 200 or 400 mm of oxygen). The apparatus then placed in a preheated furnace. Upon removal from the furnace, the

tube was allowed to cool to room temperature, attached to a high vacuum line, and the liquid nitrogen-condensable material was trapped in a U-tube and transferred to a flask for weighing. Routinely, the sample was left in the tube, additional oxygen was added and the tube was placed back in the furnace to allow additional degradation to take place. See Table 6 for the results of the tests.

Table 6 Oxidative Stability of Several Perfluoropolyethers

<u>Test No.</u>	<u>Fluid</u>	<u>Temp. (°F)</u>	<u>Amt. Used</u>	<u>Duration (hr.)</u>	<u>Amt. Cond. (mg)</u>	<u>mg/g/day</u>
1 ^a	PDO-104	650	2.075	24	254	122
2	PDO-104*	650	1.821	24.5	110	59.6
3	PDO-104*	650	1.711	24.5	84.7	48.7
4	Triox-204	650	1.973	25.7	137.9	65.1
5	Triox-204*	650	1.835	24.4	99.1	53.4
6	Triox-204*	650	1.736	24.0	71.0	40.9
7	Triox-204*	650	1.665	58.3	118	29.2
8	Triox-304	650	1.910	23.5	47.9	25.6
9	Triox-304*	650	1.860	24.1	38.3	20.5
10	Triox-304*	650	1.820	24.7	44.4	23.7
11	Z-25 P-28	650	1.93	24.0	71.6	37.0
12	Z-25 P-28*	650	1.86	25.1	41.8	21.3
13	Z-25 P-51	650	1.92	24.9	38.8	19.5
14	Z-25 P-51*	650	1.88	24.2	26.0	13.7
15	Z-25 P-21	650	1.95	24.2	75.8	38.6
16	Z-25 P-21*	650	1.87	24.0	56.0	29.9
17	Z-25 P-21	650	1.906	24.0	86.0	45
18	Z-25 P-21*	650	1.870	24.0	60.1	33
19	Z-25 P-21*	700	1.760	24.3	257.9	145

Table 6 Oxidative Stability of Several Perfluoropolyethers (continued)

<u>Test No.</u>	<u>Fluid</u>	<u>Temp. (°F)</u>	<u>Amt. Used</u>	<u>Duration (hr.)</u>	<u>Amt. Cond. (mg)</u>	<u>mg/g/day</u>
20 ^b	PEO-504	650	1.939	24.2	33.5	17.2
21	PEO-504*	650	1.906	24.0	14.7	7.7
22	PEO-504*	700	1.890	24.2	40.4	21.4
23	PDO-104 [‡]	700	2.2507	24.0	314	139.6
24	PDO-104*	700	1.937	24.0	161	83.2
25	PDO #2	700	1.911	24.0	206	107.2
26	PDO #2*	700	1.705	24.8	97.8	55.5
27	Triox #3	700	1.974	24.0	158	80.0
28	Triox #3*	700	1.816	24.0	53.7	29.6

[‡]Fluid refluorinated at 275 °C for 12 hours.

*Fluid from previous test.

^a200 mm oxygen used in tests 1-19.

^b400 mm oxygen used in tests 20-28.

3.14 Oxidation-Corrosion Behavior of Perfluoroalkylethers

An oxidative-corrosion test similar to that described by others³ was used to evaluate the oxidative stability of the fluids and their compatibility with various metals. Metal washers, 1.91 mm x 0.635 mm I.D., purchased from Metaspec (San Antonio, Texas) were polished with 600 grit sandpaper, rinsed with Freon 113 in an ultrasonic bath, then quickly dried with compressed air. The compounds were weighed then positioned on a 6 mm glass rod with FEP spacers between the coupons. The glass rod containing the metal specimens was positioned in the bottom of a 24 mm O.D. glass tube and 20 ml of a perfluoroalkylether fluid was added. The tube was evacuated for approximately 30 minutes, then backfilled with either 400 mm oxygen or nitrogen. The

tube was then placed in an aluminum-block furnace. Following the test, the coupons were rinsed with Freon 113 for two minutes in an ultrasonic bath, dried for five minutes at 80 °C, then weighed. The test fluid was removed from the tube, filtered and the viscosity was checked following each test.

Table 7 Perfluoropolydioxolane Oxidation-Corrosion Test (Nitrogen)

Perfluoropolydioxolane #103: b.p. > 245 °C @ 10 mm and < 288 °C @ 80 μ

Temperature: 218 °C

Gas: 400 mm nitrogen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.7544	1.7543	-0.03
402-K titanium A70	0.9673	0.9677	+0.13
402-4917 titanium 4A1 4Mn	1.2967	1.2971	+0.13
402-A copper	1.7500	1.7498	-0.06
402-Ni nickel	1.5463	1.5464	+0.03

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	12.5	13.5	5.9
80.0 °C	5.1	5.5	6.7

Table 8 Perfluoropolydioxolane Oxidation-Corrosion Test (Oxygen)

Perfluoropolydioxolane #103: b.p. > 245 °C @ 10 mm and < 288 °C @ 80 μ

Temperature: 218 °C

Gas: 400 mm oxygen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.7442	1.7441	-0.03
402-K titanium A70	0.9594	0.9592	-0.06
402-4917 titanium 4A1 4Mn	1.2881	1.2880	-0.03
402-A copper	1.7304	1.7305	+0.03
402-Ni nickel	1.5369	1.5366	-0.10

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	12.48	13.06	4.4
80.0 °C	5.12	5.42	5.5

Table 9 Perfluoropoly(ethylene oxide) Oxidation-Corrosion Test (Nitrogen)

Perfluoropoly(ethylene oxide) #503: b.p. > 245 °C @ 10 mm and < 288 °C @ 0.05 mm

Temperature: 218 °C

Gas: 400 mm nitrogen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.6137	1.6138	+0.03
402-K titanium A70	0.9548	0.9547	-0.03
402-4917 titanium 4A1 4Mn	1.3602	1.3602	0.00
402-A copper	1.7435	1.7434	-0.03
402-Ni nickel	1.5087	1.5087	0.00

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	16.1	16.1	0.0
80.0 °C	5.73	5.71	-0.3

Table 10 Perfluoropoly(ethylene oxide) Oxidation-Corrosion Test (Oxygen)

Perfluoropoly(ethylene oxide) #503: b.p. > 245 °C @ 10 mm/Hg and < 288 °C @ 0.05 mm

Temperature: 218 °C

Gas: 400 mm oxygen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.6822	1.6826	+0.12
402-K titanium A70	0.9405	0.9407	+0.06
402-4917 titanium 4A1 4Mn	1.2668	1.2671	+0.09
402-A copper	1.6566	1.6569	+0.09
402-Ni nickel	1.5044	1.5044	0.00

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	16.1	16.1	0.0
80.0 °C	5.73	5.69	-0.7

Table 11 Perfluoropolytrioxocane #1 Oxidation-Corrosion Test (Nitrogen)

Perfluoropolytrioxocane #204: b.p. > 288 °C and < 370 °C @ 75 μ

Temperature: 218 °C

Gas: 400 mm nitrogen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.7064	1.7064	0.00
402-K titanium A70	0.9425	0.9427	+0.06
402-4917 titanium 4A1 4Mn	1.2702	1.2706	+0.13
402-A copper	1.6676	1.6675	-0.03
402-Ni nickel	1.5088	1.5090	+0.06

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	46.8	48.3	+4.8
80.0 °C	14.7	15.2	+3.3

Table 12 Perfluoropolytrioxocane #1 Oxidation-Corrosion Test (Oxygen)

Perfluoropolytrioxocane #204: b.p. > 288 °C and < 370 °C @ 75 μ

Temperature: 218 °C

Gas: 400 mm oxygen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.7095	1.7098	+0.09
402-K titanium A70	0.9440	0.9442	+0.06
402-4917 titanium 4A1 4Mn	1.2718	1.2720	+0.06
402-A copper	1.6764	1.6770	+0.18
402-Ni nickel	1.5120	1.5122	+0.06

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	46.0	50.1	+8.2
80.0 °C	14.7	15.2	+3.3

Table 13 Perfluoropolytrioxocane #2 Oxidation-Corrosion Test (Nitrogen)

Perfluoropolytrioxocane #303: b.p. > 245 °C @ 100 μ and < 288 °C @ 75 μ

Temperature: 218 °C

Gas: 400 mm nitrogen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.7313	1.7313	0.00
402-K titanium A70	0.9531	0.9531	0.00
402-4917 titanium 4A1 4Mn	1.2812	1.2814	+0.06
402-A copper	1.7067	1.7065	-0.06
402-Ni nickel	1.5293	1.5291	-0.06

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	19.2	19.5	1.6
80.0 °C	7.1	7.2	1.4

Table 14 Perfluoropolytrioxocane #2 Oxidation-Corrosion Test (Oxygen)

Perfluoropolytrioxocane #303: b.p. > 245 °C @ 10 mm and < 288 °C @ 75 μ

Temperature: 218 °C

Gas: 400 mm oxygen

Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.7234	1.7239	+0.16
402-K titanium A70	0.9496	0.9501	+0.16
402-4917 titanium 4A1 4Mn	1.2773	1.2776	+0.09
402-A copper	1.6967	1.6960	-0.22
402-Ni nickel	1.5217	1.5217	0.00

<u>Temperature</u>	<u>Viscosity</u>		<u>Change (%)</u>
	<u>Before</u>	<u>After</u>	
40.0 °C	19.2	19.5	1.5
80.0 °C	7.1	7.2	1.1

Table 15 Perfluoropoly(methylene oxide) Oxidation-Corrosion Test (Nitrogen)

Perfluoropoly(methylene oxide) #404: b.p. > 275 °C @ 0.05 mm and < 335 °C @ 0.05 mm
 Temperature: 204 °C
 Gas: 400 mm nitrogen
 Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.6208	1.6256	-0.16
402-K titanium A70	0.9542	0.9600	+0.16
402-4917 titanium 4A1 4Mn	1.3617	1.3675	+0.16
402-A copper	1.7530	1.7580	-0.09
402-Ni nickel	1.5105	1.5155	-0.09

Table 16 Perfluoropoly(methylene oxide) Oxidation-Corrosion Test (Oxygen)

Perfluoropoly(methylene oxide) #404: b.p. > 210 °C @ 100 mm and < 235 °C @ 10 mm
 Temperature: 177 °C
 Gas: 400 mm oxygen
 Duration: 72 hours

<u>Coupon</u>	<u>Weight (g)</u>		<u>Weight Change (mg/cm²)</u>
	<u>Before</u>	<u>After</u>	
402-M50 tool steel	1.6763	1.6779	+0.51
402-K titanium A70	0.9380	0.9385	+0.16
402-4917 titanium 4A1 4Mn	1.2642	1.2647	+0.16
402-A copper	1.6469	1.6468	-0.03
402-Ni nickel	1.4975	1.4980	+0.16

3.15 Determination of Common Elastomer Compatibility With Perfluoroalkylether Fluids

A series of tests were carried out to determine over what temperature range the more common elastomers can be used in the fluids being prepared for this contract. Due to a lack of sophisticated equipment, the success or failure of a particular elastomer in a specific fluid was judged on the following criteria:

- (1) A visual inspection was carried out to see if there was a change in appearance or an obvious change in strength or elasticity.
- (2) The elastomers, in the form of O-rings, were checked for swelling by carefully recording their dimensions before and after each test.
- (3) The weight of each O-ring was recorded before and after each test.

All of the elastomers tested were in the form of commercial O-rings (size 110 which were positioned on a 9 mm glass rod with Teflon spacers being placed between the O-rings. A sufficient amount of fluid was placed in the apparatus to completely cover the O-rings. The Pyrex apparatus, the same one used for the metal compatibility tests, was evacuated and backfilled with 400 mm nitrogen prior to being placed in a furnace for 72 hours. Following each test, the O-rings were removed, rinsed 10 seconds in Freon 113 in an ultrasonic bath, then dried for five minutes at 70 °C in a convection oven. Upon removal from the oven, the O-rings were allowed to cool in air, then their weights and dimensions were immediately recorded. The following results were obtained.

Table 17 Elastomer Compatibility With Perfluoropolydioxolane

Fluid: Perfluoropolydioxolane #103
 b.p. > 245 °C @ 10 mm, < 288 °C @ 0.05 mm

<u>O-ring</u>	<u>Temperature (°F)</u>	<u>Weight Change (%)</u>	<u>Volume Change (%)</u>
Silicone	200	+0.8	+1.9
Silicone	300	+1.5	+0.5
Silicone	400	-2.6	+7.5
Neoprene	200	-4.8	-3.4
Neoprene	300	-7.4	-5.5
EPDM	200	+2.0	+1.4
EPDM	300	+0.2	+1.3
EPDM	400	-5.5	-5.3
Viton	200	+0.1	+0.5
Viton	300	+0.3	0.0
Viton	400	-0.1	-0.5
Buna-N	200	-	-
Buna-N	300	-3.2	-3.1

Table 18 Elastomer Compatibility With Perfluoropolytrioxocane #1

Fluid: Trioxocane #203
 b.p. > 245 °C @ 10 mm, < 288 °C @ 0.05 mm

<u>O-ring</u>	<u>Temperature (°F)</u>	<u>Weight Change (%)</u>	<u>Volume Change (%)</u>
Silicone	200	+3.1	+3.1
Silicone	300	+4.6	+3.1
Silicone	400	+4.6	+1.3
Neoprene	200	-4.0	-2.3
Neoprene	300	-8.5	-5.8
EPDM	200	+1.9	+0.8
EPDM	300	<0.1	-0.4
EPDM	400	-4.6	-4.8
Viton	200	+0.3	-0.5
Viton	300	-0.8	-1.3
Viton	400	-1.3	-0.2
Buna-N	200	-1.4	-1.2
Buna-N	300	-5.2	-3.4

Table 19 Elastomer Compatibility With Perfluoropoly(methylene oxide)

Fluid: Perfluoropoly(methylene oxide) #404
 b.p. > 275 °C @ 0.05 mm, < 335 °C @ 0.05 mm

<u>O-ring</u>	<u>Temperature (°F)</u>	<u>Weight Change (%)</u>	<u>Volume Change (%)</u>
Silicone	200	+6.4	+2.0
Silicone	300	+7.8	+3.1
Silicone	400	+2.3	+2.8
Neoprene	200	-3.8	-3.6
Neoprene	300	-8.9	-7.9
Neoprene	400	-23.1	-19.1
EPDM	200	+4.3	+1.8
EPDM	300	+0.2	-0.5
EPDM	400	-2.8	-1.4
Viton	200	+1.7	+1.0
Viton	300	+0.5	-0.2
Viton	400	+0.6	-0.3
Buna-N	200	+0.4	-0.9
Buna-N	300	-7.7	-7.2
Buna-N	400	-6.9	-7.4

Table 20 Elastomer Compatibility With Perfluoropoly(ethylene oxide)

Fluid: Perfluoropoly(ethylene oxide) #503
b.p. > 245 °C @ 10 mm, < 288 °C @ 0.05 mm

<u>O-ring</u>	<u>Temperature °C (°F)</u>	<u>Weight Change (%)</u>	<u>Volume Change (%)</u>
Silicone	93 (200)	+0.8	+1.1
Silicone	149 (300)	+2.8	+1.0
Silicone	204 (400)	+0.2	-1.3
Neoprene	93 (200)	-3.5	-6.2
Neoprene	149 (300)	-5.7	-4.3
EPDM	93 (200)	+2.0	+0.9
EPDM	149 (300)	+2.3	+1.1
EPDM	204 (400)	-9.1	-12.5
Viton	93 (200)	<0.1	+0.7
Viton	149 (300)	+0.4	+0.8
Viton	204 (400)	-0.2	-1.5
Buna-N	93 (200)	-1.8	-2.5
Buna-N	149 (300)	-4.8	-6.0

3.16 Determination of Bulk Modulus

The bulk modulus of a fluid becomes an important variable if the fluid is to be considered for use as a hydraulic fluid. Perfluoropolyethers are considered by most to be too compressible (bulk modulus too low) to be of general interest as hydraulic fluids while other fluorinated fluids such as CTFE-base telomers are much less compressible. By measuring the bulk modulus of each of the fluids prepared, we had hoped to determine if the oxygen in the perfluoroalkylethers was responsible for the comparatively high compressibilities.

Isothermal secant bulk moduli were measured using an apparatus developed at Exflour capable of compressing fluids to 5000 psi over a temperature range of 38 °C

to 204 °C. Water was used as a standard to calibrate the apparatus. Bulk moduli were measured using both degassed fluids and aerated fluids with the two giving almost identical results.

Table 21 Comparative Bulk Modulus Values

(Isothermal Secant Values at 3,000 psi and 100 °F)

<u>Fluid</u>	<u>Bulk Modulus - PSI</u>
Perfluoropoly(ethylene oxide) (#502)	112,760
Perfluoropolytrioxocane (#302)	117,850
Perfluoropolydioxolane (#102)	123,290
Perfluoropoly(methylene oxide) (#402)	129,270
Perfluorokerosene	132,170

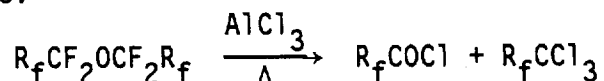
To determine the effect of temperature and pressure on the bulk modulus, a series of measurements were made using perfluoropolytrioxocane #203. The values obtained for this fluid are generally about 7% higher than those obtained for #302 (Table 21). Fluid #203 has a higher average molecular weight than does #302 and for that reason should be less compressible (higher bulk modulus).

Table 22 The Effects of Temperature and Pressure on the Bulk Modulus of Perfluoropolytrioxocane #203

<u>°F/PSI</u>	<u>1000</u>	<u>2000</u>	<u>3000</u>	<u>4500</u>	<u>5000</u>
100	118,700	122,250	126,650	129,880	132,550
150	101,650	100,560	103,400	104,150	106,120
200	70,897	74,532	78,268	80,154	83,357
250	58,561	61,357	65,388	69,288	69,074

3.17 Determination of Lewis Acid Stability

Perfluoroalkylethers, because of their superior chemical inertness over hydrocarbon oils, have found many uses in the aerospace and electronics industries. Although perfluoroalkylethers are inert to most chemicals, they are degraded at elevated temperatures by some Lewis acids. For example, when exposed to aluminum chloride, chlorine replaces fluorine on a carbon adjacent to an oxygen resulting in cleavage of the molecule.⁸



In the manufacture of semiconductors, perfluoroalkylether fluids are often used in a variety of different types of pumps including diffusion, turbomolecular and rotary vane pumps. Unfortunately, aluminum chloride is a common contaminant in semiconductor manufacturing. Chlorine and chlorinated organics react with aluminum surfaces in the manufacturing process to generate aluminum chloride.

Little is known concerning the reaction of perfluoroalkylethers with Lewis acids. Fluids which contain difluoromethylene oxide such as Fomblin Z are known to be much more reactive towards aluminum chloride than fluids such as Krytox which do not. Most of the fluids prepared during this study contain some difluoromethylene oxide units. By doing a comparative reactivity study with aluminum chloride we had hoped to better understand how perfluoroalkylethers interact with Lewis acids.

Approximately 20 g of fluid was placed in a 25 ml flask along with 2 g of freshly sublimed $AlCl_3$. A 15 cm long air-cooled condenser was placed on top of the flask. The flask, which was kept under a nitrogen atmosphere, was placed in a constant temperature oil bath for 24 hours. Following the test, the contents of the flask were weighed and a percent weight loss was calculated.

Table 23

Lewis Acid Stability of Perfluoropolyethers in the Presence of Aluminum Chloride (24-hour Test)

Sample	Weight (g)		Temperature (°C)	Weight Loss (%)
	Fluid	AlCl ₃		
Heptaglyme (F)	20.00	2.10	100	2.0
Heptaglyme (F)	20.10	1.99	130	5.0
Triox #202	20.00	1.95	100	2.5
Triox #202	20.01	2.01	130	100
Triox #302	20.00	1.75	100	1.3
Triox #302	20.00	2.00	130	7.1
Triox #302	20.01	2.00	160	19.8
PEO #502	20.01	1.99	100	1.4
PEO #502	20.01	1.95	130	2.2
PEO #502	20.01	1.99	160	100
PDO #102	20.00	1.95	100	1.8
PDO #102	20.01	2.09	130	8.9
PDO #102	20.13	2.00	160	100
PMO #402	20.01	2.02	50	20.0
Fomblin Z-25	20.00	2.02	50	2.6
Fomblin Z-25	20.00	2.09	100	36.1
Fomblin Z-25	20.00	2.00	130	100
Fomblin Z-25	20.00	2.83	160	100
Demnum 100	20.00	1.95	100	1.2
Demnum 100	19.97	2.00	130	1.6
Demnum 100	19.97	1.99	160	9.5
Krytox AD	20.00	1.87	100	1.8
Krytox AD	20.16	1.94	160	5.7
Poly THF (F)	19.67	2.00	160	3.2
DPG/CH ₂ O	20.01	2.04	160	9.7

3.18 Evaluation of Fluid Lubricity

The lubricity of each of the fluids prepared was measured using a Faville LeValle Four-Ball Wear Tester. Each fluid was tested at 75 °C using a 40 kg load, at 1200 RPM for 60 minutes. The following results were obtained.

Table 24 Four-Ball Wear Test Data (ASTM 2266)

<u>Fluid</u>	<u>Average Wear Scar (mm)</u>
Perfluoropoly(ethylene oxide) #503	0.52
Perfluoropolytrioxocane #303	0.65
Perfluoropolydioxolane #103	0.69
Perfluoropoly(methylene oxide) #403	1.82

3.19 The Effect of Temperature on Fluid Density

The density of perfluoropolytrioxocane (#203) was checked over a range of temperatures to determine the effect of temperature on fluid density. The following results were obtained.

Table 25 The Effect of Temperature on the Density of Perfluoropolytrioxocane #203

<u>Temperature (°C)</u>	<u>Density (g/ml)</u>
38 (100 °F)	1.797
66 (150 °F)	1.742
93 (200 °F)	1.684
121 (250 °F)	1.626
149 (300 °F)	1.568
177 (350 °F)	1.509

4. DISCUSSION OF RESULTS

4.1 Thermal-Oxidative Stability

Thermal oxidative tests were carried out on three types of samples. The initial tests were done on perfluoropolydioxolane (PDO-104), perfluoropolytrioxocane #1 (Triox-204) and perfluoropolytrioxocane #2 (Triox-304). These fluids, being copolymers of tetrafluoroethylene oxide and difluoromethylene oxide, exhibit very similar oxidative stabilities when tested at 343 °C (200 mm oxygen). Each sample, when reused in subsequent tests showed improved stability. The second series of samples tested were Fomblin Z-25 samples acquired from NASA. The oxidative stability of each of these samples was comparable to those of the previously tested fluids. The final three fluids tested were prepared using slightly different fluorination procedures which we now believe gives a fluid which is essentially free of any branching or cross-linking. Perfluoropoly(ethylene oxide) (PEO-504), perfluoropolydioxolane #2 (PDO #2) and perfluoropolytrioxocane #3 (Triox #3) appear to be at least 30 °C more stable than the fluids produced by the older method and as much as 30 °C more stable than the Fomblins tested. For example, perfluoropolydioxolane #2, when tested at 371 °C with 400 mm oxygen present, resulted in a weight loss of 55.5 mg/g/day while Fomblin Z-25 P-21 showed a weight loss of 145 mg/g/day at 371 °C. A perfluoropolydioxolane sample prepared for the Air Force showed still lower decomposition rates giving a weight loss of only 31.0 mg/g/day.⁹ At this time it is unclear why the Air Force sample appears to be more stable than the sample prepared for this contract.

The oxidative stability of perfluoropolydioxolane #2 and perfluoropolytrioxocane #3 exceed that of Fomblin Z-25 because of the well defined structures of the Exfluor fluids which do not contain difluoromethylene oxide units adjacent to other difluoromethylene oxide units. Tests were made on three Fomblin Z-25 samples having slightly different compositions. Each of the fluids tested showed considerable improvement

when the fluid was reused in a second test. The numbers obtained from the second tests are probably better indicators of the bulk fluid stability since the higher decomposition rates obtained for the initial oxidation could be due to a minor component of the fluid which is less stable. The following order of stability can be assigned where P-51 is most oxidatively stable (13.7 mg/g/day) followed by P-28 (21.3 mg/g/day) with P-21 being least stable (29.9 mg/g/day). A ^{19}F NMR study was carried out in order to ascertain the cause of instability in P-28 and P-21. The following results were obtained.

Table 26 Fomblin Z-25 ^{19}F NMR Results

Structure	δ ppm	Relative Intensity (%)		
		P-51	P-21	P-28
$\text{OCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{CF}_2\text{O}$	53.2	9.7	6.8	7.3
$\text{OCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{O}$	55.0	15.7	20.5	19.4
$\text{OCF}_2\text{OCF}_2\text{OCF}_2$	56.5	6.5	16.4	14.6
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{O}$	57.3	0.5	0.7	0.5
$\text{CF}_3\text{OCF}_2\text{O}$	59.2	0.5	0.7	0.5
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}$	82.7	1.6	1.4	1.0
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}$	84.3	1.8	1.7	2.4
$\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{O}$	90.7	27.7	16.4	18.5
$\text{OCF}_2\text{OCF}_2\text{CF}_2\text{O}$	92.5	33.7	32.9	32.6
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}$	127.3	1.4	1.4	1.4
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}$	131.2	0.9	1.0	1.0

The average composition of each of the fluids can be estimated and is summarized below.

Table 27 **Composition of Fomblin Z-25 Fluid**

<u>Structure</u>	mole % present in polymer chain		
	<u>P-51</u>	<u>P-21</u>	<u>P-28</u>
-CF ₂ O-	49.7	62.4	60.2
-CF ₂ CF ₂ O-	47.8	35.3	37.3
-CF ₂ CF ₂ CF ₂ CF ₂ O-	1.4	1.0	0.9
-CF ₂ CF ₂ CF ₂ O-	1.2	1.3	1.6

The fluid which is most oxidatively stable, P-51, contains the lowest concentration of CF₂O (56.7%) while the least stable fluid, P-21, contains the highest CF₂O concentration (62.4%). Small differences in the CF₂O and CF₂CF₂O ratio result in significant changes in fluid stability for Fomblin Z because of the random nature of the structure. An increase in CF₂O content of only several percent increases the ¹⁹F NMR resonance at 56.5 ppm markedly (OCF₂OCF₂OCF₂O) and to a lesser extent the resonance at 55.0 ppm is increased (OCF₂CF₂OCF₂OCF₂O). These two structures clearly appear to be weak links in Fomblin Z with OCF₂OCF₂OCF₂O representing the least oxidatively stable of the two. The concentration of the unstable structure in Fomblin Z-25 P-21 is more than twice as high as that seen in P-51. As a result, Fomblin Z-25 P-21 decomposes at a rate more than twice that of Fomblin Z-25 P-51 at 343 °C in an oxygen atmosphere.

4.2 Oxidation-Corrosion Study

Oxidation-corrosion tests were carried out at 218 °C using an inert atmosphere and then in oxygen. The metal coupon weight change in almost every case was minimal while the fluid changed little in physical appearance. Two fluids, perfluoropolydioxolane #1 and perfluoropolytrioxocane #1, each showed an appreciable increase in fluid viscosity (3 to 5%) during the test. Although we lack an explanation, both fluids are suspected of having an unacceptable level of residual hydrogen. For instance, PDO #104 showed a comparable level of decomposition at 343 °C (test #1,

Table 6) as it did at 371 °C following refluorination at 275 °C (test #23).

Perfluoropolytrioxocane #1 has performed poorly in every test including oxidation tests and Lewis acid stability tests.

4.3 Elastomer Compatibility

In general, all of the elastomers tested were suitable for use in each of the fluids at 93 °C with one possible exception. The silicone O-ring became stiffer in the perfluoropoly(methylene oxide) fluid. At 149 °C, silicone, Viton and EPDM were suitable in perfluoropoly(ethylene oxide), perfluoropolydioxolane and perfluoropolytrioxocane fluids. Only EPDM and Viton were not changed appreciably in perfluoropoly(methylene oxide) at 149 °C. At 204 °C, only Viton survived the test in each of the fluids.

4.4 Bulk Modulus

As expected, each of the fluids tested was very compressible and gave comparatively low bulk modulus values. These findings can be attributed to the low internal cohesion forces which give the perfluoropolyethers many of their unique properties such as their low surface tensions. As the carbon to oxygen ratio increased, a decrease in the bulk modulus was observed. For example, perfluoropoly(ethylene oxide), having the least amount of oxygen, exhibited the lowest bulk modulus (112,760 psi) while perfluoropoly(methylene oxide), having a 1:1 carbon to oxygen ratio, was the least compressible. Based on these results one is tempted to conclude that the presence of covalently bonded oxygen in fluorocarbons increases the bulk modulus; however, there are exceptions. In general, fluorocarbon fluids such as perfluorokerosene, which do not contain oxygen, give bulk moduli values which are comparable to or exceed those of the perfluoropolyethers. In addition, fluorocarbon fluids which show relatively high bulk moduli also are relatively dense while the more compressible fluids have lower specific gravities.

4.5 Lewis Acid Stability

The Lewis acid study supports the theory that difluoromethylene oxide units in a polymer generally represent weak points in the polymer which are susceptible to attack by Lewis acids. However, there is strong evidence that isolated difluoromethylene oxide units are substantially more stable than adjacent difluoromethylene oxide units. In fact, isolated difluoromethylene oxides have a Lewis acid stability comparable to that of tetrafluoroethylene oxide units. For example, weight losses of 2.2, 7.1, 8.9, 100 and 100%, respectively were obtained for perfluoropoly(ethylene oxide), perfluoropolytrioxocane #302, perfluoropolydioxolane, Fomblin Z-25 and perfluoropoly(methylene oxide) at 130 °C. Perfluoropolytrioxocane and perfluoropolydioxolane fluids with isolated difluoromethylene oxide units showed nominal weight loss as did perfluoropoly(ethylene oxide) while Fomblin Z, a fluid which contains some sequential difluoromethylene oxide units, decomposes completely in the test. Perfluoropoly(methylene oxide), a fluid which contains essentially 100% difluoromethylene oxide, decomposes violently even at 100 °C.

In addition to these findings, we found that very stable difluoromethylene oxide-containing polymers can be prepared. For example, a perfluorinated 1:1 copolymer of dipropylene glycol and formaldehyde, designated as DPG/CH₂O in Table 23, is considerably more stable than perfluoropoly(ethylene oxide)--a fluid which does not contain any difluoromethylene oxide units.⁹ In this case, the difluoromethylene oxide is sterically protected from Lewis acid attack by the pendant trifluoromethyl group of the propylene oxide. A similar fluid, Fomblin Y, which contains a much lower concentration of difluoromethylene oxide units which are randomly distributed with hexafluoropropylene oxide, is much more reactive towards Lewis acids.¹⁰ The problem with Fomblin Y is similar to that of Fomblin Z--it contains sequential difluoromethylene oxide units.

In addition to these findings concerning difluoromethylene oxide reactivity, there also appears to be a correlation between the carbon to oxygen ratio (in the backbone) and the Lewis acid stability. For example, perfluoropoly(ethylene oxide) (2:1 carbon to oxygen ratio), Demnum 100 (3:1 ratio) and perfluoropoly(tetramethylene oxide) (4:1), designated as Poly THF (F) in Table 23, have markedly different reactivities with $AlCl_3$ at 160 °C. Perfluoropoly(ethylene oxide) decomposes completely, Demnum 100 lost 9.5% of its weight while Poly THF (F) lost only 3.2%.⁹ The difference in reactivity seen were too large to be attributed solely to the variations in concentration of the "weak links" (the ether linkages) in the polymers.

Perfluoropolytrioxocane #202, which has been ignored until this point in the discussion, gave unexpected results which do not correlate with the observations made with the other fluids. We strongly suspect that sample #202 was not perfluorinated and the anomalous behavior of the fluid can be attributed to an appreciable hydrogen content.

4.6 Fluid Lubricity

Fluids having nearly identical molecular weights were selected for four-ball wear tests. Unfortunately, we did not have sufficient quantities of fluid to run multiple tests and the results shown should be viewed with caution since they represent the results of a single test. The findings suggest that perfluoroalkyl-ethers in general are good lubricants. It is interesting to note that as the carbon to oxygen ratio increases so does the average wear scar. Evidently the best lubricants are those containing the least amount of oxygen. With the exception of difluoromethylene oxide which is a comparatively poor lubricant, all of the fluids tested appear to be slightly better lubricants than is Fomblin Y-25. An average wear scar of 0.86 has been reported by its manufacturer.¹ Additional studies are needed to determine if linear perfluoropolyethers are inherently better lubricants than branched fluids.

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