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Improved Perfluoroalkylether Fluid Development

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PERFLUOROALKYLETHER FLUID DEVELOPMENT (NASA)
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SUMMARY

The feasibility of transforming a commercial linear perfluoroalkylether fluid into a material stable in the presence of metals and metal alloys in oxidizing atmospheres at 300 °C without the loss of the desirable viscosity-temperature characteristics was determined.

The approach consisted of thermal oxidative treatment in the presence of catalyst to remove weak links, followed by transformation of the thus created functional groups into phospho-s-triazine linkages. A dynamic process amenable to scale-up was developed. The experimental material obtained in 66 percent yield from the commercial fluid was found to exhibit, over an 8 hr period at 300 °C in the presence of Ti(4Al,4Mn) alloy, thermal oxidative stability better by a factor of 2.6×10^3 , based on volatiles evolved (0.4 mg/g) than the commercial product. The viscosity and molecular weight of the developed fluid were unchanged by the above exposure and were essentially identical with that of the commercial material. No metal corrosion occurred with the experimental fluid at 300 °C.

The material thus developed can be used as a lubricant, fluid, or grease, in applications where oxidizing atmospheres and extremes of temperature, -55 to +300 °C, are encountered in the presence of metals and metal alloys. No material exhibiting all these properties is available at present.

INTRODUCTION

Both in aeronautical systems and space applications there is a need for wide liquid range, high viscosity index fluids stable thermally and oxidatively above 300 °C, the applications being in hydraulics and lubrication, e.g., greases. Unbranched perfluoroalkylether fluids available today, as exemplified by Fomblin Z (Montedison Co. products) (ref. 1) of the general approximate formula $CF_3O(CF_2CF_2O)_n(CF_2O)_mCF_3$ possess the required liquid ranges but are unfortunately unstable in oxidizing atmospheres at elevated temperatures, particularly in the presence of metals (refs. 2 to 6).

This decomposition is accompanied by evolution of gaseous products and metal corrosion. These materials do exhibit high thermal stability, chemical inertness, and possess viscosity indices above 300 (refs. 7 and 8). The last property makes these compositions indispensable for applications where extremes of temperatures are encountered. Additives, phospho-s-triazines, and phosphines, have been developed (refs. 2 to 6 and 9) which virtually eliminate the

degradation of these fluids up to 288 °C for short periods of time. It would be preferable to have a fluid which does not require an additive and has even higher thermal oxidative stability than those attained to date. Thus, the objective of this work was to prove the feasibility of modifying Fomblin Z type of fluids to obtain a fluid with comparable temperature viscosity characteristics, yet stable in the presence of metals in oxidizing atmospheres at least to 300 °C.

EXPERIMENTAL DETAILS AND PROCEDURES

General

The perfluoroalkylether fluid employed in this study was Fomblin Z fluid, MLO-79-196; MW, 6400; viscosity 40 °C, 80.85 cS (product of Montedison), and was obtained through the courtesy of Dr. C. Tamborski and Mr. C.E. Snyder, Air Force Wright Aeronautical Laboratories.

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo.

Infrared spectra were recorded either neat (on liquids) or as gas spectra on gases and volatile liquids or in solution, the latter for the quantitative determinations, using a Perkin-Elmer Infrared Spectrophotometer Model 1330. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system.

Degradation Apparatus

Two systems were used. These are described below. In both instances, Ti(4Al,4Mn) metal coupons, (9.5 mm) o.d., 3.2 mm i.d., and 0.94 to 1.27 mm thick i.d. (obtained from Metaspec Company, San Antonio, Texas), were utilized. Prior to testing, these were polished using first Norton No-Fil Durite finishing paper Type 4 220A. This was followed by open coat Silicon Carbide papers grades 400A and 500A, respectively. Subsequently, the coupons were washed with Freon 113, dried, and weighed.

Sealed tube assembly. - This was a modified, scaled-down version of the AFML Micro-O-C-Test (ref. 10). It was described in detail previously (ref. 11). The schematics given in figures 1 and 2 show the reaction tube configuration and the rod assembly for holding the metal coupon specimens. For heating of sample tubes in a vertical position, a modified Lindberg Heavy-Duty box furnace, Type 51232, was utilized. In this arrangement, 180 mm of the 420 mm tube was at temperature; the fluid occupied at the most the lower 75 mm (see fig. 1); the extra gas reservoir was in the ambient environment.

In a typical experiment, the fluid was introduced into the degradation tube (see fig. 1) which was then evacuated and filled to a known pressure at a known temperature with oxygen. Inasmuch as the apparatus was calibrated and the fluid volume measured accurately, the quantity of gas thus introduced was known exactly. The degradation tube was then inserted into the preheated box furnace and kept there for a specified period of time; throughout this exposure, the temperature was continuously recorded. After removal from the furnace, the tube was allowed to cool to room temperature, attached to the high vacuum line, and opened. The liquid nitrogen noncondensibles were collected quantitatively, measured, and analyzed by gas chromatography. The liquid nitrogen condensibles were fractionated through -23 , -78 , and -196 °C traps. The -196 °C fractions were measured, weighed, and analyzed by infrared spectroscopy and mass spectrometry. The -23 and -78 °C fractions were weighed and analyzed by infrared spectroscopy. The fluid residue itself was weighed and subjected to infrared spectral analysis. This apparatus and procedure was used for determining the developed fluid stability and initially for preparing stable fluid precursors.

Flow systems. - For more controlled, larger scale preparation of the stable fluid precursors, the apparatus depicted in figure 3 was employed. The metal coupons used were the same as those utilized in the sealed tube except here the coupon rested on the bottom of the flask. In a typical operation, the fluid was introduced into the round bottom flask, the system assembled as shown, and evacuated with stopcocks A and C closed and D and B opened. Subsequently, stopcock D was closed and the system brought to atmospheric pressure with oxygen via stopcock A. At this stage, stopcock C was opened and oxygen flow adjusted to 30 ml/min. After cooling trap A to -78 °C and trap B to -96 °C, heating was commenced and continued for a specific period. At the conclusion of the test, the reaction flask was cooled to room temperature, oxygen flow stopped, stopcocks A, B, and C closed. Traps A, B, and C were then cooled to -196 °C, stopcock D was opened to vacuum, followed by stopcock B. After the whole system was evacuated, the volatile condensibles collected in trap C were separated by fractionation through -23 , -78 , and -196 °C cooled traps. All the fractions were measured and/or weighed and analyzed by infrared spectral analysis. The tests performed using both types of apparatus are summarized in table I.

Product Transformation

Methyl ester preparations. - All the -23 °C fractions were treated in an inert atmosphere with methanol, washed with water, dried over magnesium sulfate, and subjected to quantitative infrared spectral analysis. In a number of instances, molecular weights were determined using osmometry.

The involatile residues were likewise treated with methanol in inert atmospheres; the excess methanol was removed in vacuo. Viscosities, molecular weights, and quantitative infrared spectral analysis were performed on these materials.

Preparation of triazine ring-containing materials (ref. 12). - A portion of the involatile residue (12.70 g) from test number 16 (see table I), which was transformed into methyl ester using the procedure previously described, was treated in ether (30 ml) with ammonia at 0 °C. After removal of solvent and excess ammonia, the product containing amide groups (12.50 g) was heated

with phosphorus pentoxide (5.37 g, 37.8 mmol) for 5 hr at 220 to 240 °C. From the reaction mixture, the more volatile portion (3.23 g) was removed in vacuo at a bath temperature of 70 to 155 °C. The distillate exhibited strong nitrile absorption at 2260 cm^{-1} indicating that the major portion of the functional chains was in the distillate.

The above distillate (2.98 g) was subsequently transformed into the corresponding amidine by reaction with liquid ammonia (15 ml). Interaction of the amidine (2.58 g) with 1.56 mmol of a short chain nitrile, $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}$, afforded the imidoamidine (3.06 g). The amount of the short chain nitrile consumed, corresponded to an average molecular weight of 1700 for the functional amidine. To the resultant imidoamidine (2.86 g, 1.45 meq) in Freon 113 (10 ml) in the presence of triethylamine (0.75 g, 1.03 ml) was added diphenyltrichlorophosphorane (0.96 g, 3.20 mmol) in benzene (20 ml) and the mixture was heated at 50 °C for 16 hr. After solvent evaporation in vacuo, followed by washing with benzene, dissolution in Freon, and filtration through a 0.8 by 4 cm column of neutral alumina, final solvent removal gave a light tan liquid (1.99 g; MW, 1200 by osmometry) which exhibited the absorption at 1575 cm^{-1} characteristic of monophospha-s-triazine ring structure (ref. 11), identified as $[\text{T-16-RV-CN}][\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}][(\text{C}_6\text{H}_5)_2\text{PN}]$.

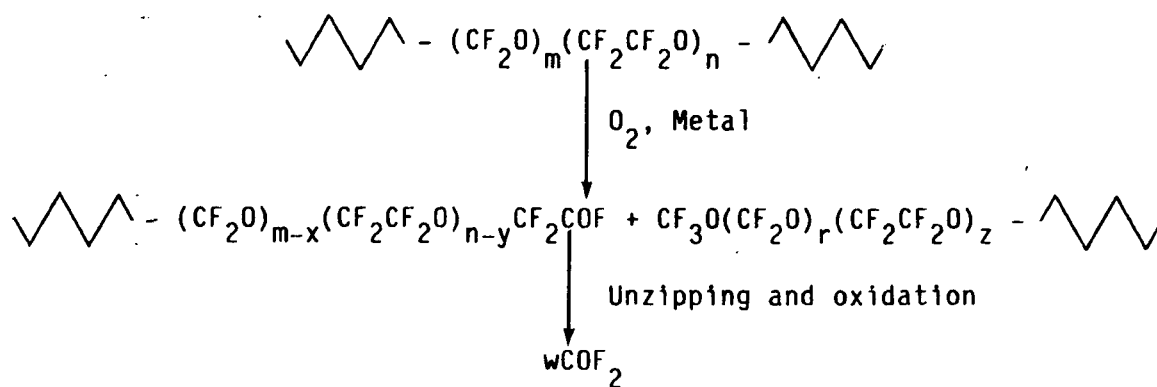
A parallel procedure was employed to prepare the phospho-s-triazine ring containing fluid from the involatile portion remaining after phosphorus pentoxide treatment and removal of the distillate described above. Functional molecular weight of the involatile material (based on $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}$ incorporation) was 17500. The product (6.75 g), MW (osmometry), 4800, viscosity at 40 °C, 61.7 cS, is identified as $[\text{T-16-RI-CN}][\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}][(\text{C}_6\text{H}_5)_2\text{PN}]$.

A modified procedure to that described for $[\text{T-16-RI-CN}][\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}][(\text{C}_6\text{H}_5)_2\text{PN}]$ was employed using the fluid from test number 15 (functional MW, 9000; average MW, 4150 (viscosity)). The portion used was the involatile fraction remaining after vacuum distillation following phosphorus pentoxide treatment. The functional molecular weight of the material was 8100 (from $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}$ uptake by the amidine). The triazine precursor imidoamidine was formed by interaction of equal amounts of the "nitrile" and corresponding "amidine." The final product after ring closure with diphenyltrichlorophosphorane, MW, 6750 (osmometry), viscosity at 40 °C, 80.8 cS, is identified as $[\text{T-15-RI-CN}]_2[(\text{C}_6\text{H}_5)_2\text{PN}]$.

RESULTS AND DISCUSSION

Fomblin Z fluid was found to undergo chain scissions when exposed to metals at 288 °C in oxygen. This was accompanied by unzipping and oxidation (refs. 2 to 5). The degradation products, involatile at -78 °C in vacuo, collected in the test where the alloy Ti(4Al,4Mn) was employed, amounted to 50 percent of the transformed fluid. From combined gas chromatography/mass spectrometry (ref. 5) and infrared spectral analyses, in agreement with the work of Gumprecht (ref. 13), it appeared that mainly acid fluoride terminated chains were formed, e.g.,

Scheme 1



Based on this scheme, it was postulated that at temperatures lower than 288 °C it should be possible to minimize the unzipping and to limit chain scissions only at the weakest links. In this way, the weak sites will be eliminated and the carbonyl end-groups created should be amenable to incorporation into phospho-s-triazine units, known to impart antioxidation and anticorrosion properties (refs. 2 to 5, 12, and 14) to perfluoroalkylethers.

Following the above reasoning, the series of tests summarized in table I was performed. Experiments 4 to 10 were carried out to establish the temperature at which the weak links degraded preferentially, with the unzipping held to a minimum. The extent of unzipping was determined from the quantity of carbonyl fluoride and its transformation products (silicon tetrafluoride and carbon dioxide) produced; these were collected as the -196 °C fraction. Using these criteria, it is apparent from tests number 4, 7, and 8 that a temperature around 220 to 240 °C will offer the best compromise. The catalyst used in all these investigations was Ti(4Al,4Mn) alloy since this metal was found to promote degradation of perfluoroalkylether fluids more readily than any other alloy or pure metal tested (refs. 4 and 5). Initially, as noted in table I, the sealed tube assembly developed for testing of fluid oxidative and corrosion behavior (ref. 11) was employed; subsequently, a flow system was utilized. The latter permitted the treatment of larger quantities of fluid in a controlled fashion.

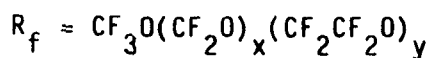
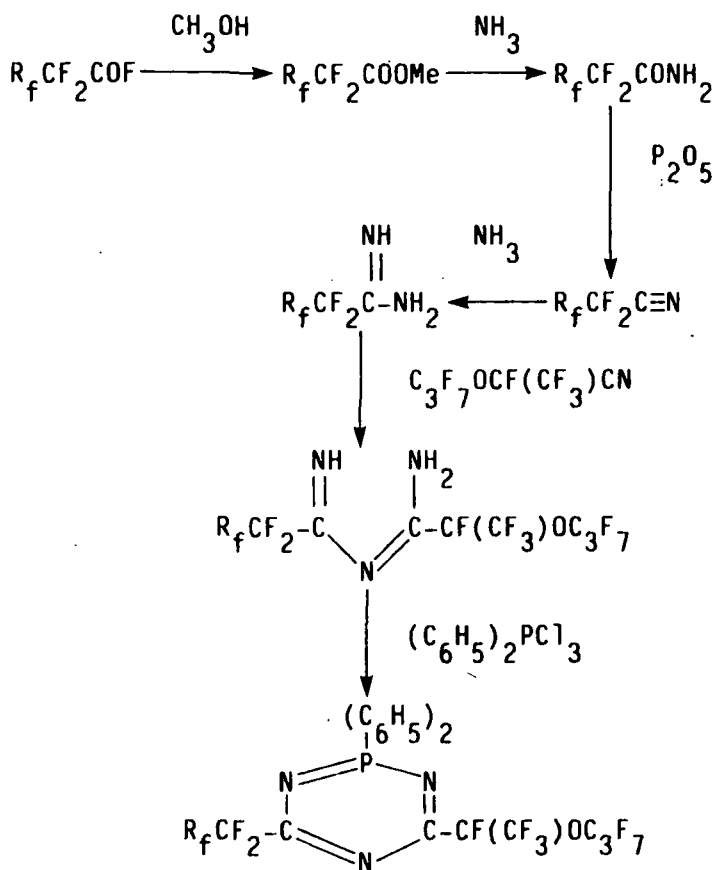
Quantitative infrared spectroscopy was employed to determine the concentration of functional groups (as methyl ester entities) in the involatile fluid, as well as the highly fragmented fluid collected in the -23 °C traps. The tabulated data and calibration curve are given in table II and figure 4, respectively. Initially, the number average molecular weights were determined by osmometry. For ease of comparison, a viscosity-molecular weight calibration curve was drawn and is given in figure 5. The actual values and "standards" are presented in table III. Although intrinsic viscosity is directly proportional to weight average molecular weight, not number average molecular weight, it is believed that if one assumes comparable molecular weight distributions it is valid to use the viscosity curve for molecular weight estimations.

It is apparent from the data listed in table I that the temperature and exposure duration greatly affected the extent of degradation, as shown by the relative proportion of the materials volatile at -78 °C and also by the molecular weight of the "involatile" fraction. This is illustrated by the results

of Test 10, where 44 percent material was in the form of COF_2 (-196°C fraction) and the "involatile" portion had the average molecular weight of ~ 1000 versus 6400 measured for the starting material, Fomblin Z (MLO-79-196). It should be noted that in the involatile portion, based on the functional and average molecular weights, only half of the chains were terminated by carbonyl groups. This is in agreement with the mechanism proposed by Gumprecht (ref. 13) for poly (hexafluoropropene oxide) fluids depicted by scheme 1. Thus, if a given chain undergoes only one scission, a functional and nonfunctional fragment will result. However, if the functional portion undergoes another cleavage, either a difunctional and a nonfunctional or two monofunctional fragments will be formed. Apparently, the difunctional species are predominantly of a relatively low molecular weight as indicated by the average and functional molecular weights of the -23°C fractions. Due to program considerations, the investigation of these materials was limited since most of the efforts were concentrated on the low volatility products inasmuch as the objective of this work was to prove the feasibility of transforming Fomblin Z type fluid to a fluid of corresponding characteristics insofar as viscosity and molecular weight were concerned, but of superior thermal oxidative stability. With respect to mechanistic implications, as well as a practical system design in any large scale production, flow of oxygen must be sustained. In a static system, as exemplified by test number 11, due to oxygen depletion, the reaction ceased. At this juncture it is worth mentioning that attempts at scale-up, from 5 to 20 g, as represented by test numbers 13 and 16, were successful. By extending the exposure time by 25 percent, an essentially identical product mix was obtained under otherwise parallel conditions.

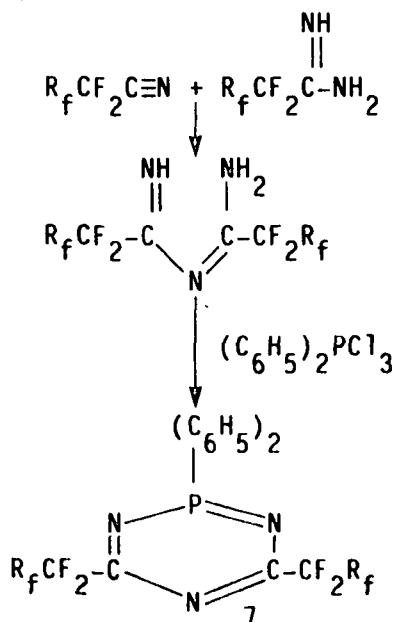
After completion of the series of experiments, delineated in table I, specific products were transformed into the phospho-s-triazine ring-containing materials. The procedure employed followed that described for the high molecular weight species derived from polymerizations of hexafluoropropene oxide (ref. 15). The reaction sequence is depicted below:

Scheme 2



To increase the molecular weight, a modification involving the interaction of the amidine with its precursor nitrile was also evaluated, i.e.,

Scheme 3



The products of test numbers 15 and 16 were selected for these studies since these differed significantly (factor of two) in molecular weights and in both instances enough materials were produced to permit evaluations of the final products. The materials prepared are listed in table IV. It should be emphasized that in the case of both test numbers 15 and 16, after treatment with phosphorus pentoxide, the material was separated into a 210 °C volatile and involatile portion. It is clearly evident from thermal oxidative stability and corrosive action evaluations, summarized in table V, that the best performance was exhibited by the product derived from the involatile portion of the test number 15 residue. Its thermal oxidative stability was better by a factor of 2.6×10^3 , based on the amount of volatiles formed. No metal corrosion was observed. Actually, the stability is probably much better than calculated since after the 8-hr test all the untreated fluid was degraded and this state more than likely was reached after a shorter period of time than the 8 hr exposure. Likewise, it is unknown whether or not more volatiles would have been produced if the phospho-s-triazine modified product had been exposed for a period longer than the 8 hr.

From the data given in table V, it can be deduced that the higher molecular weight materials exhibit better stability than those of lower molecular weights (compare tests 17B and 18). Furthermore, the incorporation of the short side chain $C_3F_7OCF(CF_3)-$ in the phospho-s-triazine ring results in greater volatiles productions. It is gratifying to report that the material [T-15-RI-CN]₂[(C₆H₅)₂PN], which exhibited the best stability, was also obtained in the best overall yield, 66.1 percent (based on the starting material Fomblin Z, MLO-79-196). The still relatively low yield is due partially to the formation of lower molecular weight functional species which provide potentially useful by-products. In addition, it is strongly believed that the process can be significantly improved and better yields attained without sacrificing the fluid properties. This applies, in particular, to the step involving phosphorus pentoxide treatment (see scheme 2).

It must be understood that the concentration of the actual phospho-s-triazine ring-containing chains in the final product is relatively low (0.12 percent of (C₆H₅)₂PN) since the functionality of the fluid prior to transformations via scheme 3 was low. The final fluid, [T-15-RI-CN]₂[φ₂PN], exhibited essentially the same viscosity and molecular weight as the starting material (see table III). Thus, one could assume that its temperature viscosity profile was also comparable. Within the scope of the current program it was not possible to assess the stability at 300 °C with respect to exposure duration, nor to compare it with an additive fluid formulation since none were tested at 300 °C under previous programs.

SUMMARY OF RESULTS

The results of this study are summarized below.

1. The development of perfluoroalkylether fluid of vastly improved thermal oxidative stability (~3 orders of magnitude at 300 °C) and corrosion behavior as compared to the presently available material, Fomblin Z, has been accomplished. The viscosity and molecular weight are essentially identical to that of the starting material, Fomblin Z fluid (MLO-79-196).

2. The stabilization was accomplished via removal of weak links by treatment at 235 to 240 °C in oxygen followed by transformation of the formed functional groups into phospho-s-triazine linkages.

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TABLE II. - METHYL ESTER GROUP CONCENTRATION,
INFRARED SPECTRUM ANALYSIS DATA LISTING

Material ^a	Conc. mg/ml	A	$[-CO_2CH_3]$ mmol/ml	MW
(HFPO) ₃ CO ₂ CH ₃ ^b	27.2	0.1299	0.0533	510
(HFPO) ₃ CO ₂ CH ₃	59.8	.2944	.1172	510
(HFPO) ₄ CO ₂ CH ₃ ^c	23.1	.0826	.0342	680
(HFPO) ₄ CO ₂ CH ₃	38.9	.1434	.0575	680
(HFPO) ₄ CO ₂ CH ₃	53.8	.2031	.796	680
T-4 -23 °C fraction	31.6	.3178	.1262	250
T-4 involatile fraction	174.3	.2470	.0982	1 800
T-8 involatile fraction	240.7	.1230	.0493	4 900
T-9 -23 °C fraction	114.4	.4579	.1815	630
T-9 involatile fraction	272.4	.0214	.0092	29 700
T-10 -23 °C fraction	46.9	.2234	.0889	530
T-10 involatile fraction	92.3	.1506	.0602	1 500
T-11 -23 °C fraction	45.8	.2914	.1157	400
T-11 involatile fraction	200.1	.1150	.0461	4 300
T-12 -23 °C fraction	34.5	.1709	.0682	510
T-12 involatile fraction	152.5	.2478	.0985	1 600
T-13 -23 °C fraction	46.3	.2061	.0821	560
T-13 involatile fraction	225.0	.1941	.0773	2 900
T-14 -23 °C fraction	40.6	.1887	.0752	540
T-14 involatile fraction	212.7	.1248	.0500	4 300
T-15 -23 °C fraction	63.0	.2913	.1157	540
T-15 involatile fraction	257.8	.0710	.0287	9 000
T-16 -23 °C fraction	54.2	.2642	.1050	520
T-16 involatile fraction	236.8	.1803	.0719	3 300

^aAll the stable fluid precursors were in the form of methyl esters.

^bC₃F₇OCF(CF₃)CF₂OCF(CF₃)CO₂CH₃.

^cC₃F₇O[CF(CF₃)CF₂O]₂CF(CF₃)CO₂CH₃.

TABLE I. - RESULTS OF EXPOSURE OF FOMBLIN 2 FLUID TO ELEVATED TEMPERATURES IN THE PRESENCE OF OXYGEN AND Ti(4Al, 4Mn) ALLOY^a

Test no.	Amt of fluid, g	Temp., °C	Temp., hr	Condensable volatiles								Involatile fraction					Comments ^c
				-196 °C		-79 °C		-23 °C				g	%	MW			
				mg	%	mg	%	mg	%	MW				OSM	IR ^b	Visc	
										OSM	IR ^b						
4	4.08	250	8	838.4	20.5	2.5	0.1	576.0	14.1	530	250	2.57	63.0	1500	1 800	----	Fluid level at coupon Fluid level above coupon Fluid level below coupon No fluid in bottom of tube
7	3.35	200	8	2.0	.1	-----	---	-----	----	----	---	3.28	97.9	----	-----	----	
8	3.46	235	8	306.3	8.9	183.5	5.3	-----	----	----	---	2.93	84.7	2900	4 900	----	
9	3.60	235	16	1297.8	36.0	164.0	4.6	1117.9	31.1	1500	630	1.27	35.3	6000	29 700	----	
10 ^d	3.61	235	16	1592.0	44.1	150.6	4.2	1615.1	44.7	1100	530	.70	19.4	990	1 500	----	
11	5.09	235-250	16	559.8	11.0	46.3	0.9	382.5	7.5	870	400	4.10	80.6	2400	4 300	----	
12	4.98	240	7	780.5	15.7	116.0	2.3	1239.3	24.9	1100	510	2.65	53.2	1250	1 600	----	
13	5.00	↓	4	399.5	8.0	62.3	1.2	668.2	13.4	----	560	3.56	71.2	----	2 900	2000	
14	10.00	↓	4	596.2	6.0	20.2	0.2	822.5	8.2	----	540	8.42	84.2	----	4 300	2750	
15	20.00	↓	4	539.5	2.7	90.1	0.5	759.9	3.8	----	540	18.52	92.6	----	9 000	4150	
16	20.00	↓	5	1555.8	7.8	230.7	1.2	2444.0	12.2	----	520	15.02	75.1	----	3 300	2100	

^aThe tests 4 to 10 were performed in sealed tubes following the procedure described in reference 4. Test 11 was performed in a static system on the vacuum line. Tests 12 to 16 were performed also on the vacuum line in an oxygen flow system. All products, prior to evaluation by infrared spectral analysis and osmometry, were treated with methanol. This assured that all COP end-groups were transformed into methyl ester.

^bThis is the molecular weight based on methyl ester functionality.

^cThe level observed is at the exposure temperature.

^dIn this test, the alloy coupon rested on the bottom of the tube.

TABLE III. - MOLECULAR WEIGHT-VISCOSITY CORRELATIONS^a

Material	Viscosity cS at 40 °C	MW, osr	MW, visc
Fomblin Z (MLO-79-196)	80.85	6 400	6 400 (std) ^b
T-11 involatile fraction ^c	23.95	2 400	2 400 (std)
T-14 involatile fraction ^c	28.92		2 750
T-12 involatile fraction ^c	4.45	1 250	1 250 (std)
T-13 involatile fraction ^c	18.00		2 000
Fomblin Z (FMZ-83-BJ)	148.0	11 000	11 000 (std)
T-15 involatile fraction ^c	49.10		4 150
T-16 involatile fraction ^c	19.43		2 100
[T-16-RI-CN][C ₃ F ₇ OCF(CF ₃)CN][φ ₂ PN]	61.71	4 800	5 050
[T-15-RI-CN] ₂ [φ ₂ PN]	80.80	6 750	6 350

^aAll the viscosities were measured at 40 °C using Cannon-Manning semi-microviscometers.

^bThese materials were used as standards in developing the curve.

^cThese precursor fluids, obtained from the denoted tests, were treated with methanol (to esterify the COF groups) prior to molecular weight and/or viscosity determination.

TABLE IV. - REPRESENTATIVE FLUIDS DEVELOPED

Product identification ^a	Starting material	Yield ^b %	MW	Viscosity cs at 40 °C
[T-15-RI-CN] ₂ [φ ₂ PN]	Involatile frac. test number 15	71.4 (8.9)	6750	80.8
[T-16-RV-CN][C ₃ F ₇ OCF(CF ₃)CN][φ ₂ PN]	Involatile frac. test number 16	17.15 (70.4)	1200	n.d.
[T-16-RI-CN][C ₃ F ₇ OCF(CF ₃)CN][φ ₂ PN]	Involatile frac. test number 16	66.5 (25.8)	4800	61.7
Fomblin Z, MLO-79-196 ^c	not applicable	not applicable	6400	80.9

^aThe involatile fractions denoted in table I, following treatment with phosphorus pentoxide (see Scheme 1), could be separated into materials volatile and involatile at 210 °C at 10⁻³ mm. The I corresponds to involatile, the V to volatile.

^bYields are given with respect to the original room temperature involatile fraction of the given test. The values given in the parenthesis are the proportion of either the involatile (at 210 °C at 10⁻³ mm) or the corresponding volatile fraction depending which one was utilized in preparing the product.

^cThis has been included for comparison.

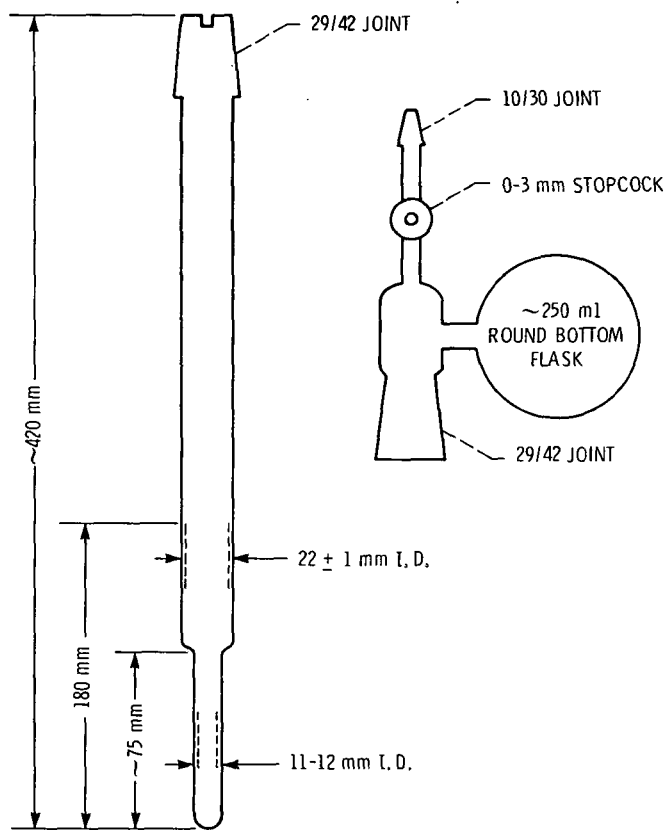


Figure 1. - Decomposition tube and adapter .

TABLE V. - EVALUATION OF THERMAL OXIDATIVE STABILITY OF FLUIDS OVER 8 HR PERIOD
IN OXYGEN IN THE PRESENCE OF Ti (4Al, 4Mn) ALLOYS^a

Test no.	Fluid ^b	Temp., °C	Amt of fluid, g	Viscosity cS at 40 °C	Condensibles	
					mg	mg/g ^c
19	Fomblin Z (MLO-79-196), as received (MW, 6400)	300	2.12	80.8	2250	1060
17A	[T-16-RV-CN][C ₃ F ₇ OCF(CF ₂)CN][φ ₂ PN] (MW, 1200)	288	.99	----	30.4	30.7
17B ^d	[T-16-RV-CN][C ₃ F ₇ OCF(CF ₂)CN][φ ₂ PN] (MW, 1200)	300	.96	----	12.6	13.1
18	[T-16-RI-CN][C ₃ F ₇ OCF(CF ₂)CN][φ ₂ PN] (MW, 4800)	300	2.02	61.7	4.9	2.4
20	[T-15-RI-CN] ₂ [φ ₂ PN] (MW, 6750)	300	1.12	80.8	.5	.4

^aThe apparatus consisted of a sealed glass tube in which the metal coupon was suspended in the fluid; the test was conducted in pure oxygen. At the conclusion of the test, oxygen was measured and the products were collected and measured.

^bThe experimental fluids are denoted by the number of the test they were produced in and which fraction of the fluid was used (R = residue; V = volatile; I = involatile). If co-reactant was employed, it is listed; φ₂PN corresponds to the phosphorus portion of the end of bridging triazine unit.

^cProducts formed in mg/g of fluid employed.

^dIn this test the residue from 17A was utilized.

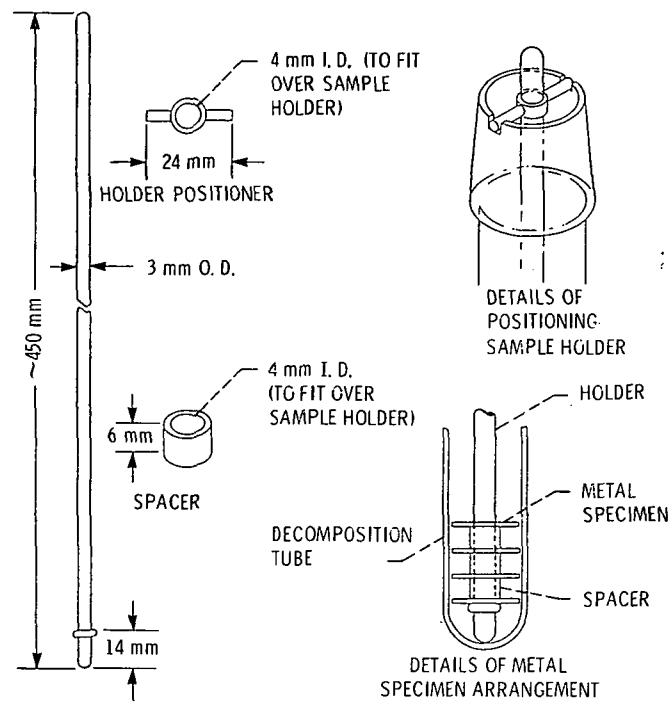


Figure 2. - Metal specimen holder arrangement.

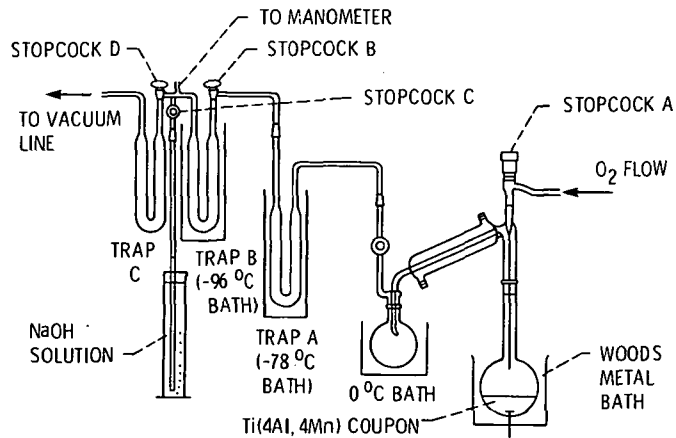


Figure 3. - Schematic of apparatus used to prepare stable fluid precursors.

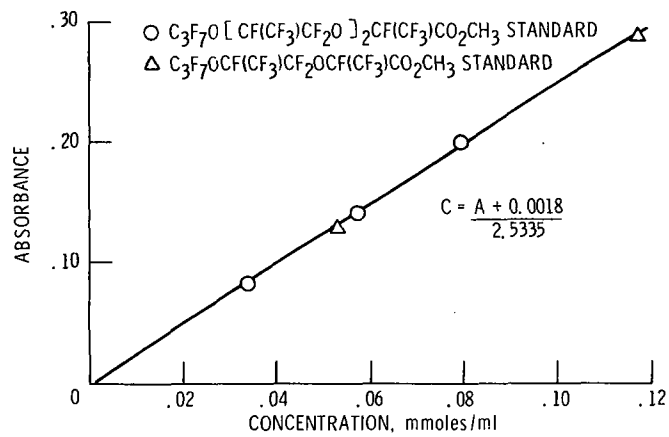


Figure 4. - Calibration curve for methyl ester group concentration determination using infrared spectral analysis.

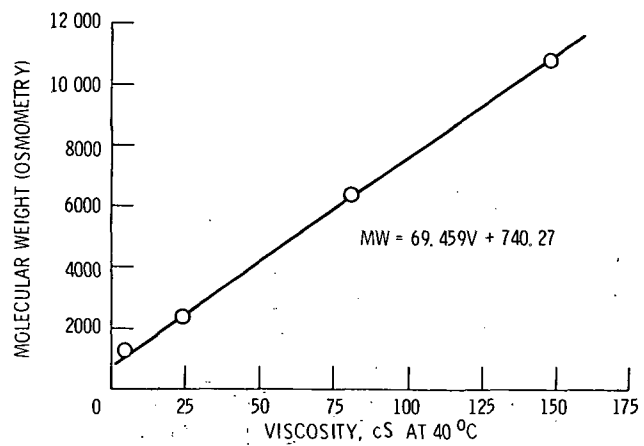


Figure 5. - Viscosity-molecular weight relationship for linear perfluoroalkyl ether fluids.

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16. Abstract The feasibility of transforming a commercial linear perfluoroalkylether fluid into a material stable in the presence of metals and metal alloys in oxidizing atmospheres at 300 °C without the loss of the desirable viscosity-temperature characteristics was determined. The approach consisted of thermal oxidative treatment in the presence of catalyst to remove weak links, followed by transformation of the thus created functional groups into phospho-s-triazine linkages. The experimental material obtained in 66 percent yield from the commercial fluid was found to exhibit, over an 8 hr period at 300 °C in the presence of Ti(4Al,4Mn) alloy, thermal oxidative stability better by a factor of 2.6×10^3, based on volatiles evolved (0.4 mg/g) than the commercial product. The viscosity and molecular weight of the developed fluid were unchanged and were essentially identical with that of the commercial material. No metal corrosion occurred with the experimental fluid at 300 °C.					
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