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William R. Jones, Jr.
Lewis Research Center
Cleveland, Ohio

and

K. J. L. Paciorek, T. I. Ito, and R. H. Kratzer
Ultrasystems, Inc.
Irvine, California

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SUMMARY

Thermal and thermal oxidative stability studies have been performed on linear perfluoroalkylether fluids. The effect on degradation by metal catalysts (M-50 steel and Ti(4 Al, 4 Mn) alloys) and degradation inhibitors (a monophospha-s-triazine and a perfluorophenyl phosphine) are reported.

The linear perfluoroalkylethers are inherently unstable at 316° C in an oxidizing atmosphere. This instability is not due to the presence of hydrogen chain termination or peroxide linkages. The metal catalysts greatly increased the rate of degradation in oxidizing atmospheres. In the presence of these metals in an oxidizing atmosphere, the degradation inhibitors were highly effective in arresting degradation at 288° C. However, the inhibitors had only limited effectiveness at 316° C. The metals promote degradation by chain scission.

Based on elemental analysis and oxygen consumption data, the linear perfluoroalkylether fluids have a structural arrangement based on difluoroformyl ($-CF_2O-$) and tetrafluoroethylene oxide ($-CF_2CF_2O-$) units, with the former predominating.

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INTRODUCTION

Perfluoroalkylethers are a class of fluids which exhibit excellent thermal and oxidative stability (refs. 1 and 2). Combined with good viscosity characteristics (ref. 3), good elastohydrodynamic film forming capabilities (ref. 4), good boundary lubricating ability (refs. 3 and 5), and nonflamability properties (ref. 6) make these fluids promising candidates for high temperature lubricant applications.

Basically, there are two types of perfluoroalkylethers, a linear (ref. 7) and a branched class (ref. 1). The general structures of these classes are shown in figure 1. The most important representatives of the branched materials (fig. 1(a)) are based on the polymerization of hexafluoropropylene oxide (HFPO). These compositions suffer some deficiencies. In order to satisfy low temperature fluidity, volatility problems are encountered (ref. 8). In addition, the poly(hexafluoropropene oxides) were found to exhibit poor compatibility with ferrous and titanium alloys above 260° C (ref. 3).

The mechanism responsible for the low temperature (<316° C) incompatibility has been studied by Paciorek et al. (ref. 9) and was found to be due to the presence of ~3 percent unstable chains. These chains have been subsequently shown to be hydrogen (rather than fluorine) terminated. Exposure of HFPO fluids at 343° C in oxygen resulted in removal of these chains by volatilization. The resultant fluid was not degraded by oxygen at 343° C nor by M-50 and Ti(4 Al, 4 Mn) alloys at 316° C. However, degradation did occur with these alloys at 343° C.

A new class of perfluoroalkylethers based on the photo-oxidation of fluoro-olefins (ref. 7) has been developed. This class of materials, whose general chemical structure appears in figure 1(b), has a linear structure. These fluids have better viscosity-temperature properties than the branched (HFPO) class (ref. 8). However, the linear fluid class has exhibited lower thermal oxidative stability compared to the HFPO fluids (ref. 8). This is surprising since the chemical bonding in both classes is very similar. In fact, it has been shown (ref. 10) that tertiary carbon-fluorine bonds are less stable than those involving primary or secondary carbon atoms. This would lead one to conclude that the HFPO fluids (which contain tertiary carbon atoms) should be less stable than the linear fluids.

Therefore, the objective of this work was to conduct a study of the thermal oxidative degradation processes of the linear class of perfluoroalkylether fluids. Tests were conducted with the neat fluid and also in the presence of M-50 or Ti(4 Al, 4 Mn) alloys. Test atmospheres included air, oxygen, and nitrogen. Test temperatures ranged from 288° C to 343° C. Selected tests were conducted in the presence of a degradation inhibitor (a phospha-s -triazine or a perfluorophenyl-phosphine).

EXPERIMENTAL FLUIDS

Two types of perfluoroalkylether fluids were employed in this study. One class is believed to have a linear structure and is manufactured by Montecatini Edison under the trade name Fomblin Z. Two different batches of this class were studied which are designated MLO-72-22 and MLO-79-129. The second class has a branched structure and is manufactured by E. I. Dupont de Nemours and Co. under the trade name Krytox (MLO-71-6). These are Air Force designations where the first two numbers refer to the year the fluid was received.

DEGRADATION INHIBITORS

Two different degradation inhibitors were used in these studies. One was a perfluoroalkylether substituted perfluorophenyl phosphine (fig. 2(a)). Results with this additive have been previously reported (ref. 11) where it was designated as P-3. The second additive was a perfluoroalkylether substituted monophospha-s-triazine (fig. 2(b)) (ref. 12). This additive will be designated as C_2PN_3 for convenience.

OXIDATION - CORROSION APPARATUS

The micro-oxidation corrosion apparatus is a modified version of the type reported by Snyder and Dolle (ref. 3). The decomposition tube configuration and the rod assembly for holding the metal corrosion catalysts are schematically shown in figures 3 and 4, respectively. The metal catalysts (M-50 steel or Ti(4 Al, 4 Mn) alloys) were 9.5 mm (3/8 in.) OD and 3.2 mm (1/8 in.) ID. These were obtained from Metaspec Co., San Antonio, Texas. For heating sample tubes in a vertical position, a modified Lindberg Heavy-Duty box furnace, Type 51232 (fig. 5) was used. In this arrangement, 180 mm of the 420 mm of tube length were at test temperature; the fluid occupied, at most, the lower 75 mm (fig. 3). The extra gas reservoir was in the ambient environment.

Prior to testing the metal catalysts 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 catalysts were washed with Freon 113, dried, weighed, and suspended in the test apparatus (see fig. 4). After the completion of a given experiment, the metal catalysts were washed with Freon 113, dried in an inert atmosphere chamber, then weighed and visually inspected. The used catalysts were subsequently sealed in Mylar envelopes.

In a typical experiment, the fluid was introduced into the decomposition tube (see fig. 2) which was then evacuated and filled to a known pressure at a known temperature with a selected gas (air, N_2, or O_2). Inasmuch as the apparatus was calibrated and the fluid volume measured accurately, the quantity of gas thus introduced was exactly known. The decomposition 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 vacuum line, and opened. The liquid nitrogen noncondensibles were collected quantitatively, measured, and analyzed by gas chromatography and infrared spectroscopy. The liquid nitrogen condensibles, which were volatile at room temperature, were measured, weighed, and analyzed by infrared spectroscopy and mass spectrometry. The fluid residue itself was weighed and subjected to infrared spectral analysis; in selected instances, molecular weight and nuclear magnetic resonance (NMR) determinations were performed.

The degradation rate is calculated from the amount of liquid nitrogen condensibles formed and is reported as milligrams of condensible product per gram of original fluid per hour.

THERMAL DECOMPOSITION APPARATUS (TENSIMETER)

The tensimeter apparatus is shown in figure 6. The basic function of the tensimeter consists of heating a liquid sample and of plotting either the vapor pressure or the isothermal time rate of increase of vapor pressure due to thermal decomposition as a function of temperature.

The sample cell is a glass bulb having a 5-milliliter (5×10^{-6} m^3) volume with a stem extending through the oven wall to a valve and pressure transducer mounted outside the oven. Three to four milliliters (3×10^{-6} to 4×10^{-6} m^3) of test fluid are placed in the sample cell. The cell is attached to the cell assembly and the fluid is degassed and refluxed under vacuum. The cell assembly is then placed in the oven. The sample is heated to an initial temperature about 50° C below the suspected decomposition temperature. After a 5-minute stabilization period, the increase in vapor pressure, if any, is recorded as a vertical bar during a fixed time interval. Then the programmer raises the sample temperature by a preset amount, usually 5° C, and the previous process is repeated.

This yields a plot of the logarithm of the isothermal rate of vapor pressure increase as a function of reciprocal absolute temperature. A straight line is drawn connecting the tops of the recorded bars at higher temperatures. The intersection with the temperature reference axis is the thermal decomposition temperature (T_d). The temperature axis corresponds to a pressure rise of 50 torr per hour, which defines the T_d.

RESULTS AND DISCUSSION

This investigation involves mainly the linear class of perfluoroalkylether fluids. This class of materials is prepared from tetrafluoroethylene and oxygen under ultraviolet radiation (ref. 7). This process introduces peroxide linkages which are then removed by subsequent heat treatment.

Some limited data is presented for the branched class of fluids. These are prepared by telomerization of hexafluoropropylene oxide (HFPO) (ref. 10). The termination reaction is well documented (ref. 10) and theoretically should yield only perfluoroalkyl end groups. No such information is available for the linear fluids, although based on published data (ref. 13) it can be concluded that the grouping is $-CF_2H$. The nature of these end-groups and the presence of structural irregularities are factors which limit the inherent stability of the perfluoroalkylether systems. Thus, any study of thermal oxidative behavior must take into account structural considerations.

DEGRADATION STUDIES

Thermal and thermal oxidative studies performed on the two batches of linear perfluoroalkylethers are summarized in tables I (MLO-72-22) and II (MLO-79-196). The effect of metal catalysts and degradation inhibitors on fluid MLO-72-22 appear in tables III and IV, respectively. The distribution of condensible volatiles appears in table V.

Nonoxidizing atmospheres. - The presence of heat "removable" species was determined in tests 1 (MLO-72-22) and 2, 3, and 7 (MLO-79-196) which were performed in nitrogen atmospheres. Tests 1 and 2 were run under identical test conditions (3 hr at 150° C, 2 hr at 200° C, and finally 2 hr at 250° C). The total condensible products for test 2 was about 50 times that of test 1. This indicates that batch MLO-72-22 is thermally more stable than MLO-79-196. However, further heat treatment at 250° C of the MLO-79-196 residue from test 2 yields a much lower degradation rate (test 3). One can conclude that some unstable species were removed during the initial heat treatment. These data are illustrated in figure 7.

Thermal tests on MLO-79-196 using another device (the tensimeter) were performed. A typical result is shown in figure 8. Early evolution of volatiles is evident well below the thermal decomposition temperature (T_d) of 361° C. A rerun of the residue from this test appears in figure 9. There is less lower temperature decomposition and the T_d is elevated (365° C). This supports the prior statement that some unstable species are removed after exposure at high temperatures in the absence of oxygen.

In contrast, the thermal decomposition data (tensimeter) for a HFPO fluid (Krytox PR 143AB) appears in figure 10. There is almost no low temperature decomposition and the T_d is almost 30° C higher than the linear fluid.

Oxidizing atmospheres. - In oxidizing atmospheres at 316° C, initial exposure of the MLO-72-22 fluid (test 5) promoted considerable degradation. However, subsequent exposures of the residue from test 5 at 316° C, results in less degradation (tests 6, 9, and 10). This is illustrated in figure 11. These rates are more than an order of magnitude greater than a comparable test of the MLO-79-196 fluid in nitrogen (test 7).

At higher temperatures in oxygen, the degradation rate increases about 1.5 times for each 10° C rise in temperature. This is illustrated in figure 12. A similar temperature rate increase (1.3 times per 10° C rise) occurred in nitrogen (tests 3 and 7).

It became evident that sample size was affecting the degradation rate in some of the tests. For example, tests 17 and 19 run with less than 3 grams of fluid yielded rates of approximately 2.6 to 2.7 mg/g-hr. In contrast, tests 21, 30, and 39 run with large samples (>19 g) yielded considerably lower rates (0.72 to 0.90 mg/g-hr). A plot of rate of condensible product formation for MLO-72-22 as a function of sample size appears in figure 13. The reduction in rate at large sample sizes is not due to oxygen depletion since calculations show that only 5 percent of the available oxygen was consumed in test 21 and 12 percent in test 39. One explanation could be that the degradation is diffusion limited for large sample sizes. This effect is not a factor for small samples (~3g) since halving the fluid quantity (tests 17 and 19) did not alter the rate.

The residue from large sample test 21 was used for small sample tests 31 and 40. Both of these tests yielded rates which appear anomalously high compared to figure 12. It seems likely that the pretreatment (test 21) was not complete. As a point of interest, previous tests on HFPO fluids in the absence of metal catalysts indicated that sample size did not affect degradation rates (ref. 9).

The thermal oxidative degradation behavior of MLO-79-196 fluid (table II) was similar to that of MLO-72-22 (table I). The degradation rate of MLO-79-196 as a function of temperature appears in figure 14. A reference curve for MLO-72-22 (from fig. 12) is shown for comparison. The rates of degradation for the two batches are very similar. The nature and relative concentration of the condensible volatiles (table V) formed by these two fluids are also similar.

Metal Catalysis. - Only fluid MLO-72-22 was evaluated in the presence of metal catalysts and degradation inhibiting additives. The test series involving the metal catalysts M-50 steel and Ti(4 Al, 4 Mn) alloys is compiled in table III.

The presence of the metal catalysts greatly accelerated fluid degradation in O_2. At 288° C, M-50 and Ti(4 Al, 4 Mn) alloys increased the degradation rate by factors of 28 and 73, respectively. A test with M-50 at 316° C yielded a rate about 30 times that of the uncatalyzed fluid. However, in the absence of oxygen, neither catalyst promoted fluid degradation (tests 43, 44, and 45). These data are illustrated in figure 15.

Degradation Inhibitors. - The effect of inhibitors on the degradation rate are compiled in table IV. Both a monophospha-s-triazine (C_2PN_3) and a perfluorophenyl phosphine (P-3) were studied at a concentration of 1 weight percent. Both additives were effective in reducing the degradation processes in the presence of metal catalysts. At 288° C, rates were reduced by factors of 700 to 2000. At 316° C the inhibitors were still effective but to a much lesser degree (less than an order of magnitude). It appears that on a weight basis the C_2PN_3 additive is about twice as effective as the P-3 additive. The data for M-50 are illustrated in figure 16.

Earlier work (ref. 9) on HFPO fluids showed that inhibitors also arrested fluid degradation in the absence of metal catalysis. A similar result was obtained for a linear fluid (test 33) where the degradation rate was reduced by a factor of 8.

Nuclear magnetic resonance (NMR) measurements. - The ^{19}F NMR spectra of the fluid residue from test 19 appears in figure 17. Expanded sections of figure 17 labeled A, B, C, and D appear in figure 18. Proton NMR spectra for the residues from tests 19 and 21 appear in figure 19. The CCl_3F reference peak and the peaks associated with the solvent, C_6F_6, are identified in figure 17.

The fluid appears to contain CF_3O-, $-OCF_2$, $-OCF_2CF_2-$, and $-OCF_2CF_2CF_2CF_2-$ groups arranged randomly. Area "A" may be assigned to CF_3O-, $-OCF_2O-CF_2O-$, $-OCF_2OCF_2CF_2$, etc.; areas "B" and "C" may be assigned to $-OCF_2CF_2O-$, $-OCF_2CF_2CF_2CF_2-$ groups depending on what is attached to the oxygen, e.g., $-OCF_2CF_2OCF_2O$ is different from $-OCF_2CF_2OCF_2CF_2O-$. Area "D" is due to a $-CF_2-$surrounded by other CF_2 groups, e.g., $-OCF_2CF_2CF_2CF_2O-$.

No peaks were found in the 0 to +100 ppm region (not shown) indicating an absence of -COF groups. The spectra are different from those reported by Sianesi, et al. (ref. 13). Significantly, there are no doublets with 50-70 Hz splitting characteristic of $-OCF_2H$ or $-OCFH$ or $-CF_2H$ groups, etc. In other words, the ^{19}F NMR is consistent with the ^1H NMR (fig. 19) indicating the absence of protons.

The absence of protons in the pretreated fluid is in agreement with the experimental data (i.e., the lack of stabilization after exposure to oxidizing atmospheres for prolonged periods of time). The experimental degradation data thus indicates that either all the chains are hydrogen-terminated, which was not revealed by proton NMR, or such termination is insignificantly low and is not responsible for the observed thermal oxidative behavior of the fluids. It is unlikely that residual peroxide linkages are causing the observed thermal oxidative instability since the rate of degradation failed to decrease after prolonged exposure at elevated temperatures. Metals, in the absence of oxygen, did not cause any fluid degradation, supporting further that there are no residual peroxide linkages. Consequently, it must be concluded that the arrangement of the units in the chains or the end-groups is responsible for the observed degradation behavior.

Elemental analysis. - Elemental analyses of the fluid, both "lightly" thermally stressed (test 21) and after extensive exposure to oxygen at elevated temperature (test 19), differ somewhat as evident from the tabulation given in table VI. On the other hand, the variation in carbon content is within acceptable limits and it has been usually found that in these type of compositions, fluorine values are generally lower than those actually present. Thus, it is unknown whether the calculated increased oxygen content in the residue of test 19 is real. However, the C:O ratio which is lower for both of the samples than the theoretical 2:1 value for $(CF_2CF_2O)_x$ polymer is definitely real. Consequently, it would appear from these data that the ratio of CF_2O entities to CF_2CF_2O groups greater than 1:1. This would further imply that the concentration of $-O(CF_2)_xO$units wherein x is greater than 2 is low. All these stipulations do not contradict the NMR spectral findings; unfortunately the latter do not provide information regarding the concentration of specific groups, i.e., $-OCF_2O-$, $-O(CF_2)_2O-$, $-O(CF_2)_4O-$, etc.

From the calculations of the ratios of fluid volatilized to oxygen atoms consumed (given in table VII) for the different segments, it appears that the content of $-OCF_2O-$ units is higher than that denoted by $-CF_2OCF_2CF_2O-$ arrangement. Tests 16, 19, 21, and 31 were carried out in the absence of metal catalysts. In these tests only traces of materials non-volatile at -78° C were formed. Based on the nature of the collected volatiles, it can be deduced that COF_2 was the initial product formed. SiF_4, CO_2, and BF_3 are the products of COF_2 interactions with constituents of glass at the elevated temperatures. Since some COF_2 survived the treatment, one would expect to see CF_3COF or related acid fluorides if there was substantial content of $-O(CF_2)_xO-$ units where x is greater than 2. It should be noted that CF_3COF was found in the volatiles formed by HFPO derived polyethers (ref. 9), but none was detected in the linear fluid investigations.

Metals definitely promoted scission of the chain bonds as shown by the increased ratio of the volatilized fluid to oxygen consumed and by the type of products formed. This is especially significant in the case of Ti(4 Al, 4 Mn) alloy wherein at 288° C almost half of the products were in the form of relatively nonvolatile, predominantly -COF terminated chains as determined by infrared spectral analysis.

SUMMARY OF RESULTS

Based on thermal-oxidative degradation studies of linear perfluoroalkylether fluids the following results were obtained.

1. Linear perfluoroalkylether fluids are inherently unstable at 316° C in oxidizing atmospheres. This instability is not due to hydrogen chain termination or residual peroxide linkages.

2. In the presence of M-50 steel or Ti(4 Al, 4 Mn) catalysts at 316° C in oxidizing atmospheres, the linear perfluoroalkylether fluids exhibit much greater degradation than in uncatalyzed tests. These catalysts do not promote degradation at 316° C in inert (nitrogen) atmospheres.

3. Two inhibitors, a monophospha-s-triazine and a perfluorophenyl phosphine were highly effective in arresting degradation at 288° C, but had only limited effectiveness at 316° C.

4. The metal catalysts promote degradation by chain scission.

5. Based on elemental analysis and oxygen consumption data, the linear perfluoroalkylether fluids have a structural arrangement based on difluoroformyl ($-CF_2O-$) and tetrafluoroethylene oxide ($-CF_2CF_2O-$) units with the former predominating.

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TABLE I. - THERMAL AND THERMAL OXIDATIVE BEHAVIOR

OF LINEAR PERFLUOROALKYLETHER (MLO 72-22)

Test	Sample size, g	Atmosphere	Temperature, °C	Degradation rate, mg/g-hr
1	26.33	N_2	150,200,250	0.005
5	3.44	Air	316	2.0
6[a]	3.26	O_2	↓	.93
9[a]	3.16	↓	↓	1.2
10[a]	3.07	↓	↓	.81
12[a]	3.02	↓	332	1.1
17[a]	2.95	↓	343	2.7
19[a]	1.76	↓	↓	2.6
21[b]	19.51	↓	↓	.90
30	24.15	↓	↓	.75
39	54.54	↓	↓	.72
31[c]	4.27	↓	316	2.7
40[c]	3.74	↓	288	1.0

[a]Involatile residue from previous test.
[b]Involatile residue from test 1.
[c]Combined residue from tests 21 and 30.

TABLE II. - THERMAL AND THERMAL OXIDATIVE BEHAVIOR

OF LINEAR PERFLUOROALKYLETHER (MLO 79-196)

Test	Sample size, g	Atmosphere	Temperature, °C	Degradation rate, mg/g-hr
2	35.29	N_2	150,200,250	0.24
3[a]	32.71	↓	250	.003
7[a]	5.03	↓	288	.017
		↓	316	.027
8[a]	5.03	Air	288	.013
11[a]	3.90	Air	316	.67
13[a]	3.82	O_2	316	.66
14[a]	3.77	↓	316	.70
15[a]	3.71	↓	332	1.39
16[a]	3.46	↓	332	1.63

[a]Involatile residue from previous test.

TABLE III. - EFFECT OF METAL CATALYSTS ON THE THERMAL AND THERMAL OXIDATIVE BEHAVIOR OF LINEAR PERFLUOROALKYLETHER (MLO 72-22)

Test[a]	Atmosphere	Temperature, °C	Catalyst	Degradation rate, mg/g-hr
40	O_2	288	None	1.0
38	O_2	288	M-50	28
41	O_2	288	Ti(4 Al, 4 Mn)	73
31	O_2	316	None	2.7
32	O_2	316	M-50	80
43	N_2	316	None	0.093
44	N_2	316	M-50	.095
45	N_2	316	Ti(4 Al, 4 Mn)	.099

[a]All fluids were pretreated at 343° C in O_2 for 24 hours.

TABLE IV. - EFFECT OF INHIBITORS ON THE THERMAL OXIDATIVE BEHAVIOR OF LINEAR PERFLUOROALKYLETHER (MLO 72-22) IN AN OXYGEN ATMOSPHERE

Test[a]	Temperature, °C	Catalyst	Inhibitor 1% wt	Degradation rate, mg/g-hr
36	288	M-50	C_2PN_3 [b]	0.014
37	288	M-50	P-3[c]	.040
42	288	Ti(4 Al, 4 Mn)	P-3	.047
33	316	None	P-3	0.12
34	316	M-50	P-3	12
35	316	M-50	C_2PN_3	6.6

[a]All fluids were pretreated at 343° C in O_2 for 24 hours.
[b]Monophospha-s-triazine.
[c]Perfluorophenyl phosphine.

TABLE V. - PRODUCT DISTRIBUTION OF

THERMAL OXIDATIVE DEGRADATION OF

LINEAR PERFLUOROALKYLETHERS

Test	Fluid	Volatile products, percent			
		CO_2	COF_2	SiF_4	BF_3
5	MLO 72-22	65	3.1	22	9.5
6	↓	60	3.7	26	9.8
9	↓	63	2.2	26	9.8
10	↓	60	2.0	28	9.9
12	↓	66	2.2	22	10.3
17	↓	52	.4	36	11.7
19	↓	55	1.5	34	9.0
21	↓	66	.4	27	6.6
31	↓	61	6.6	25	7.0
32[a]	↓	54	19.7	21	5.2
33[b]	↓	47	.9	52	.5
34[c]	↓	49	13.6	30	6.9
38[a]	↓	67	13.9	13	5.8
40	↓	70	14.9	9	6.4
41[d]	↓	64	23.3	11	2.0
13	MLO 79-196	68	5.2	16	10.6
14	↓	73	4.0	11	12.0
15	↓	53	.9	41	5.0
16	↓	46	1.3	46	6.8

[a]M-50 catalyst.
[b]P-3 inhibitor.
[c]M-50 and P-3.
[d]Ti(4 Al, 4 Mn).

TABLE VI. - ELEMENTAL ANALYSIS OF PERFLUOROALKYL ETHERS

Material	C,%	F,%	C:F:O
MLO 72-22 (test 21)	20.03	61.21	2.85:5.50:2
MLO 72-22 (test 19)	19.63	60.09	3.86:7.48:3
$(CF_2CF_2O)_x$	20.69	65.52	2:4:1
$(CF_2OCF_2OCF_2CF_2O)_x$	19.37	61.29	4:8:3
$(CF_2OCF_2CF_2O)_x$	19.80	62.64	3:6:2

TABLE VII. - INFLUENCE OF METAL CATALYSTS ON RATIOS OF VOLATILIZED FLUID TO OXYGEN CONSUMED

Test	Atmosphere	Temperature, °C	Catalyst	Products, mg	Ratio mmol fluid lost to O atoms consumed	
					Segm,116[a]	Segm,182[b]
16	O_2	332	None	272	2.1:1	1.3:1
19	↓	343	↓	216	2.6:1	1.5:1
21		343		426	2.1:1	1.3:1
31		316		279 (4)[c]	2.0:1	1.2:1
32		316	M-50	2666 (10)	2.6:1	1.7:1
38		288	M-50	1117 (22)	3.7:1	2.3:1
41		288	Ti(4 Al, 4 Mn)	2235 (47)	4.6:1	2.9:1

[a]Segment $-CF_2CF_2O-$.
[b]Segment $-CF_2OCF_2CF_2O-$.
[c]Values in brackets correspond to the percentage of products which were involatile at -78° C.

$C_3F_7O(CFCF_2O)_nR_f$

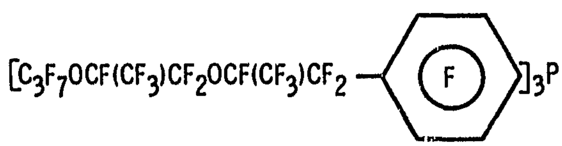
CF_3

(a) Hexafluoropropylene oxide (HFPO) based fluids.

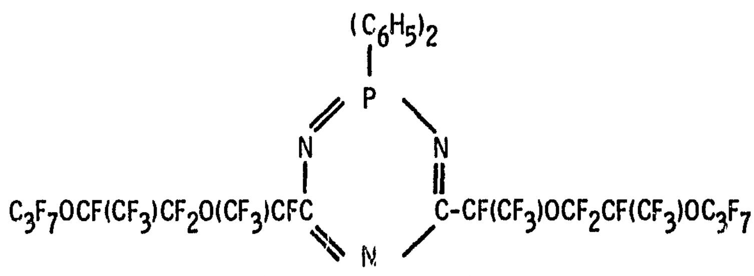
$R_fO(CF_2CF_2O)_m(CF_2O)_nR_f$

(b) Linear perfluoroalkylether fluids.

Figure 1. - Chemical structures of perfluoroalkylether fluids (R_f = CF_3 or C_2F_5).



(a) Perfluoroalkylether perfluorophenyl phosphine.



(b) Monophospha-s-triazine.

Figure 2. - Chemical structures of degradation inhibitors.

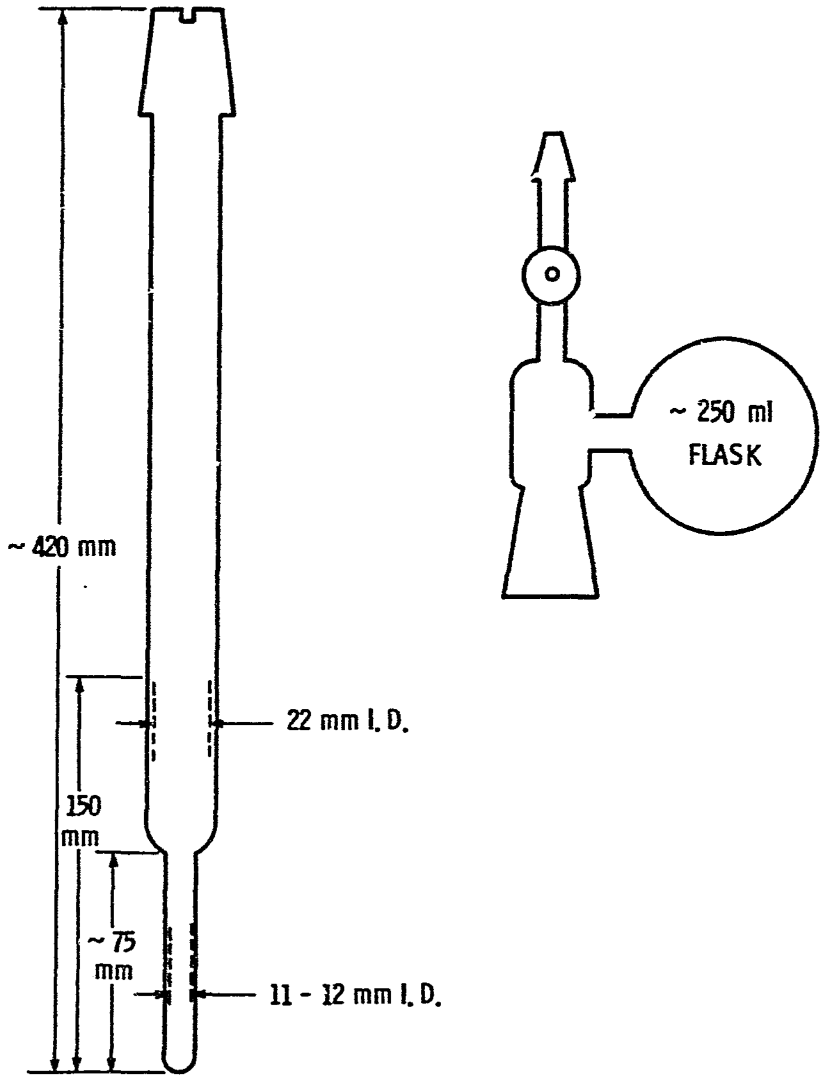


Figure 3. - Decomposition tube and adapter.

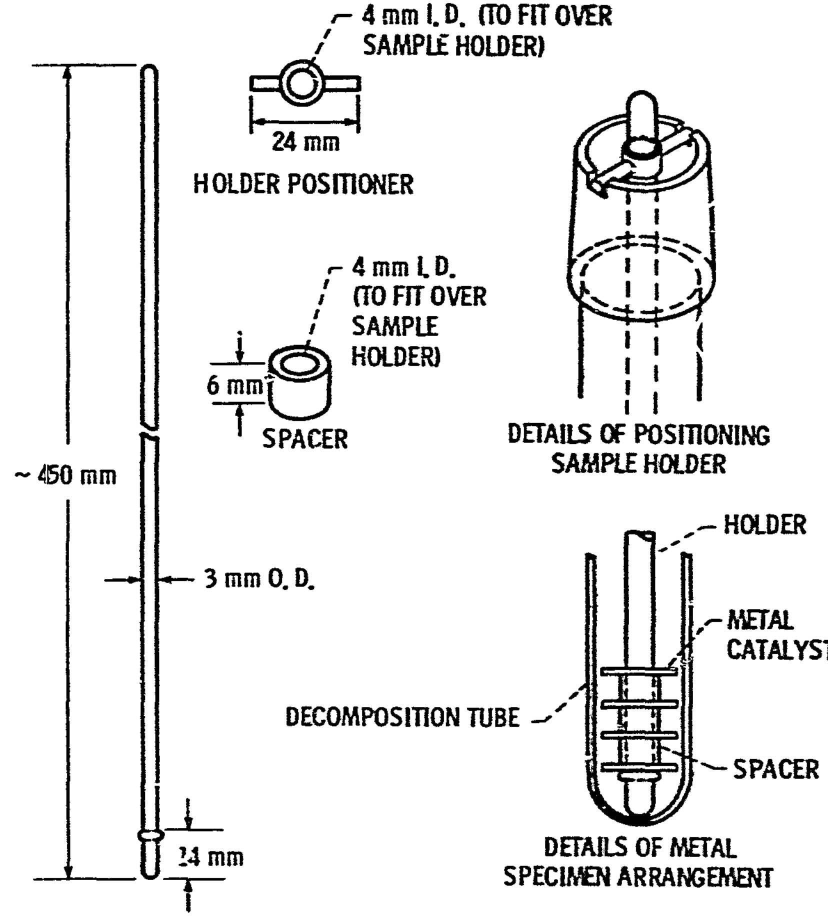


Figure 4. - Metal specimen holder arrangement.

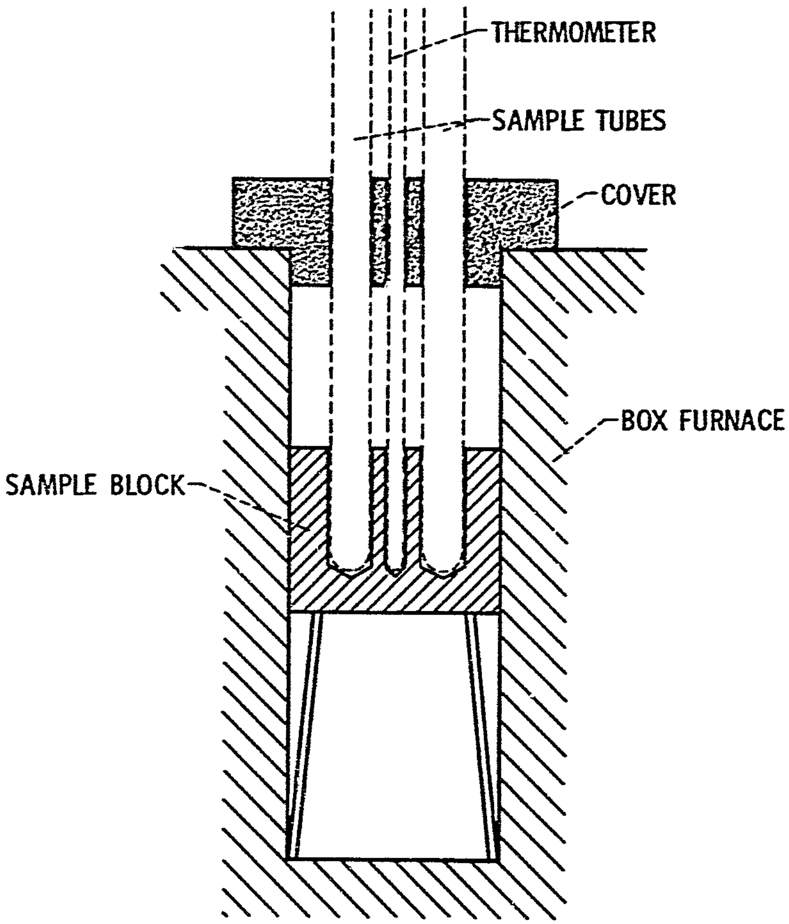


Figure 5. - Box furnace arrangement.

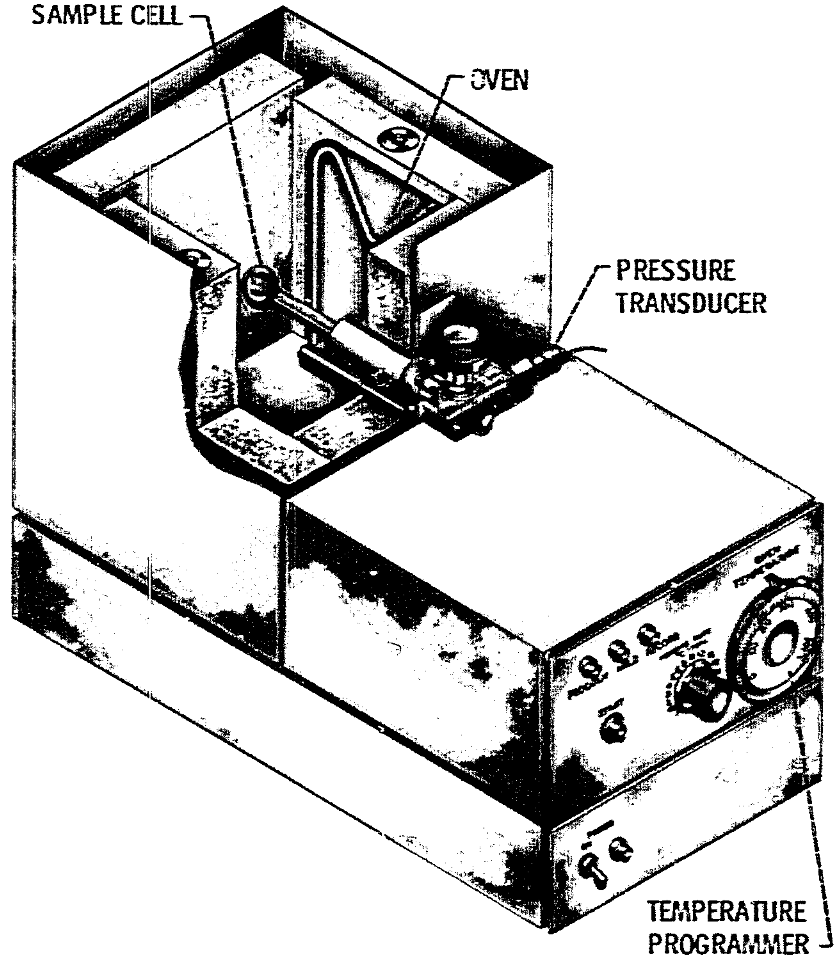


Figure 6. - Thermal decomposition apparatus (tensimeter).

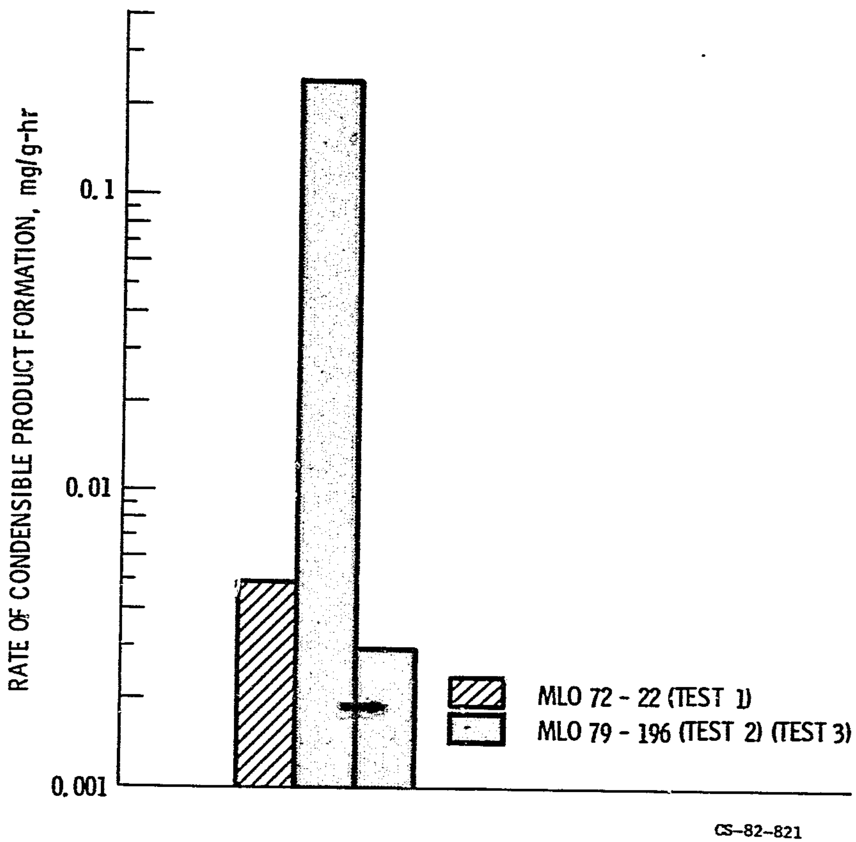


Figure 7. - Rate of condensible product formation for linear perfluoroalkylethers at 250^{0} C in nitrogen.

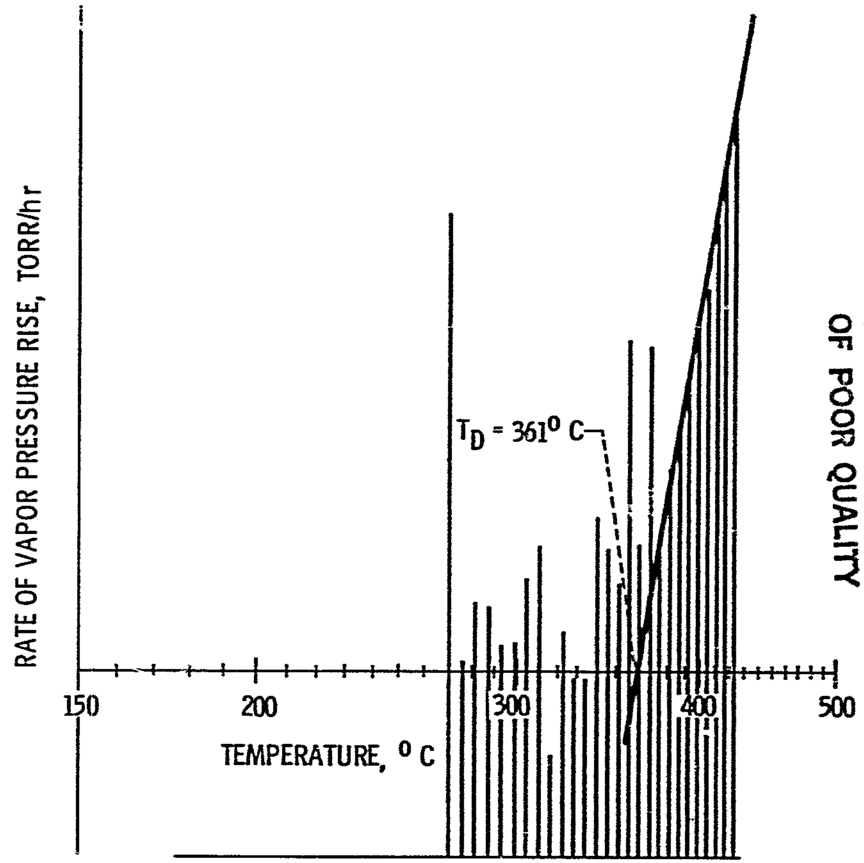


Figure 8. - Thermal decomposition of Fomblin Z (MLO 79-196).

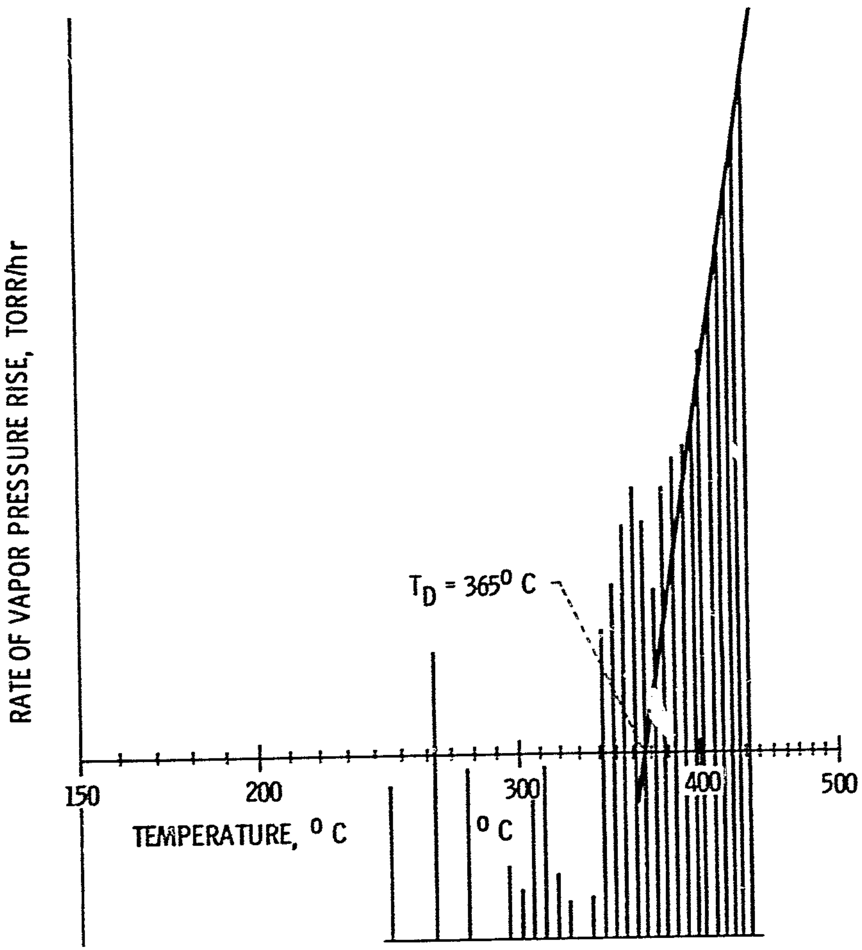


Figure 9. - Thermal decomposition of Fomblin Z (MLO 79-196) after thermal pretreatment.

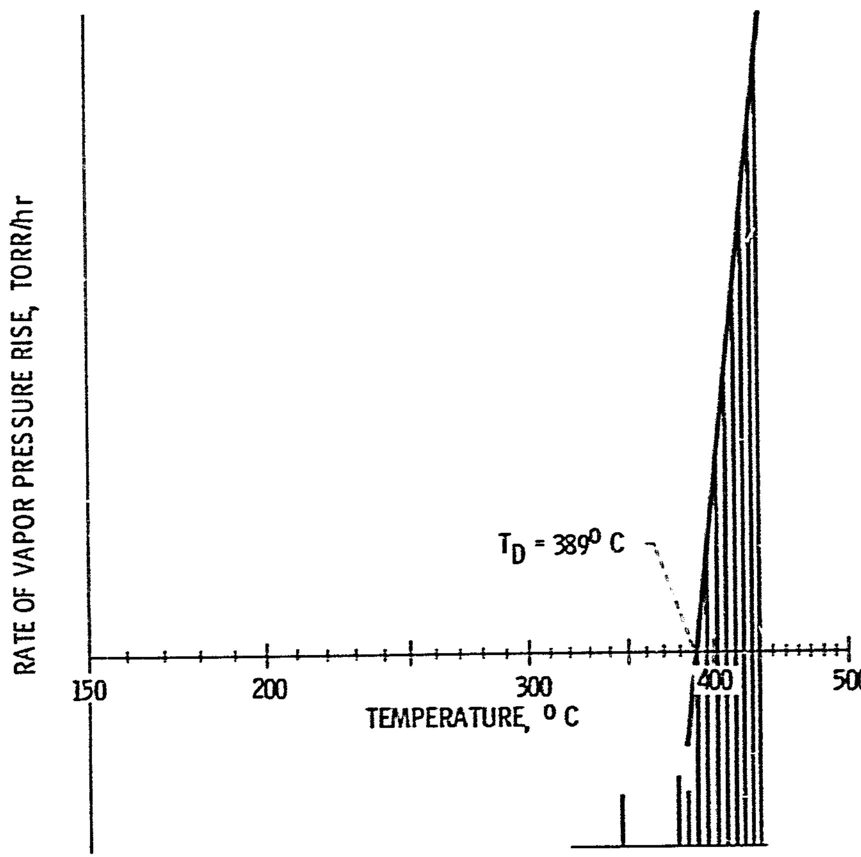


Figure 10. - Thermal decomposition of KRYTOX (PR143AB).

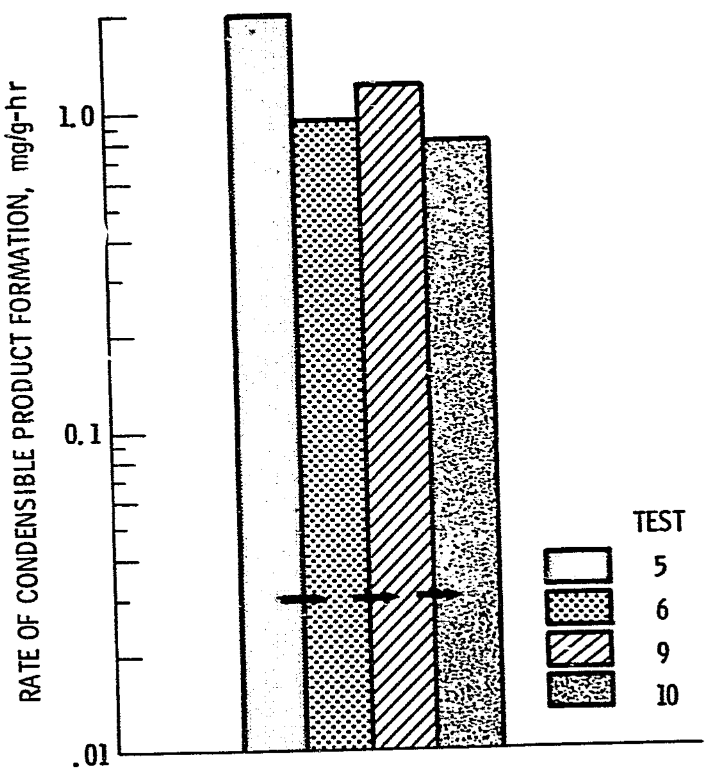


Figure 11. - Rate of condensible product formation for linear perfluoroalkylether (MLO 72-22) in oxidizing atmospheres at 316° C.

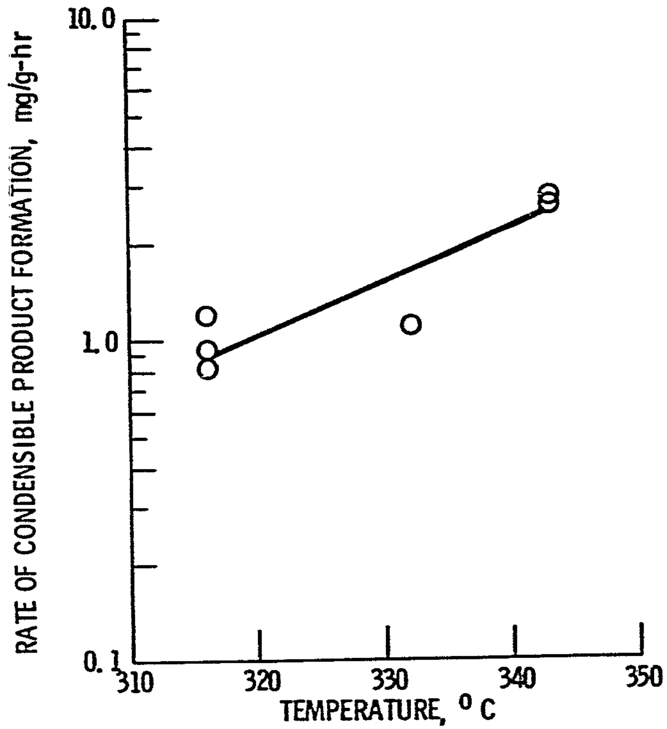


Figure 12. - Rate of condensible product formation for linear perfluoroalkylether (MLO-72-22) in oxygen as a function of temperature (small sample size).

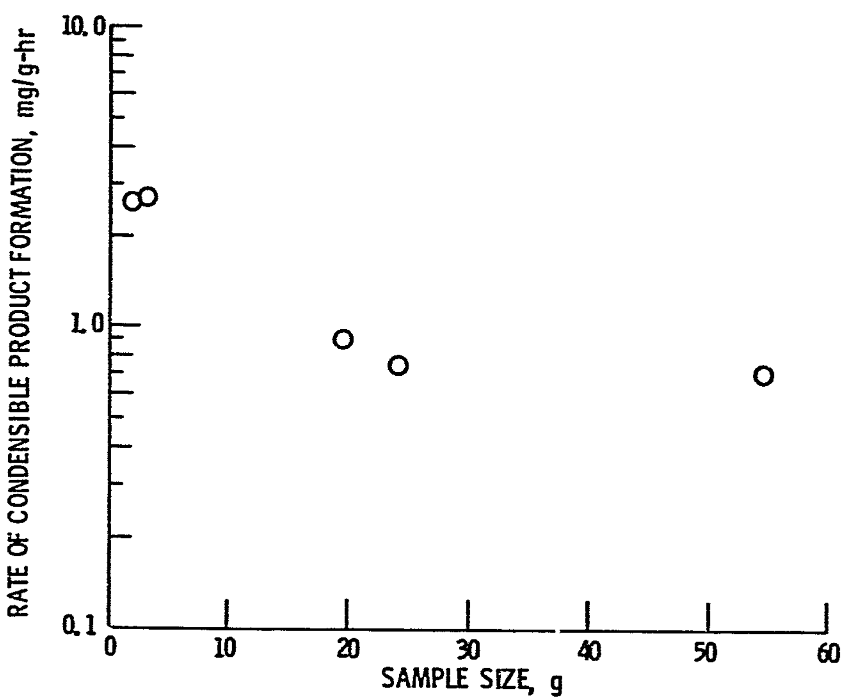


Figure 13. - Rate of condensible product formation for linear perfluoroalkylether (MLO 72-22) in oxygen at 343° C as a function of sample size.

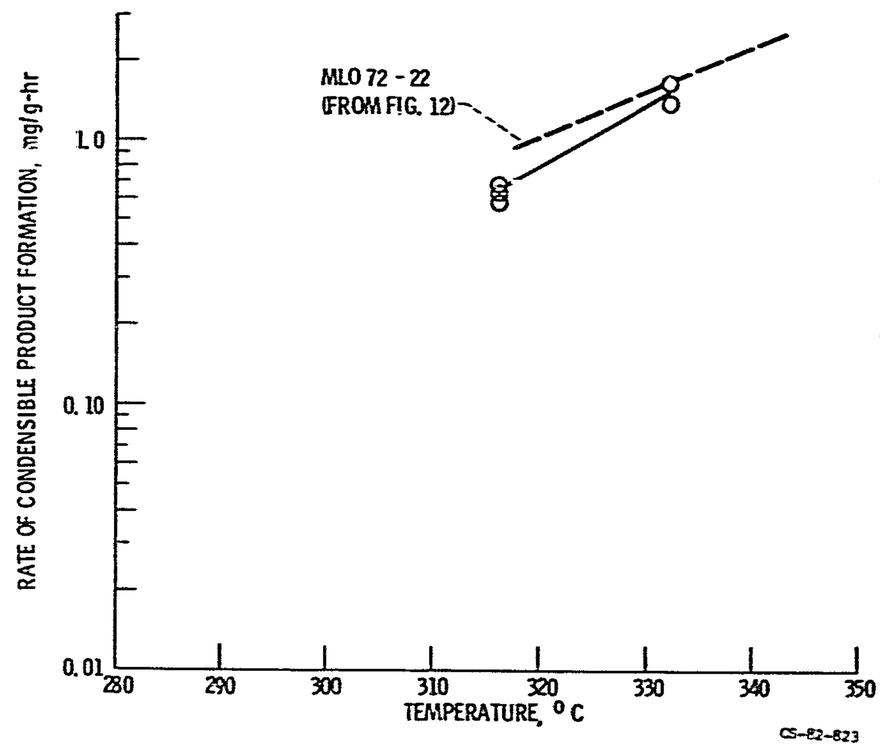


Figure 14. - Rate of condensible product formation for linear perfluoroalkylether (MLO 79-196) in oxidizing atmospheres as a function of temperature (small sample size).

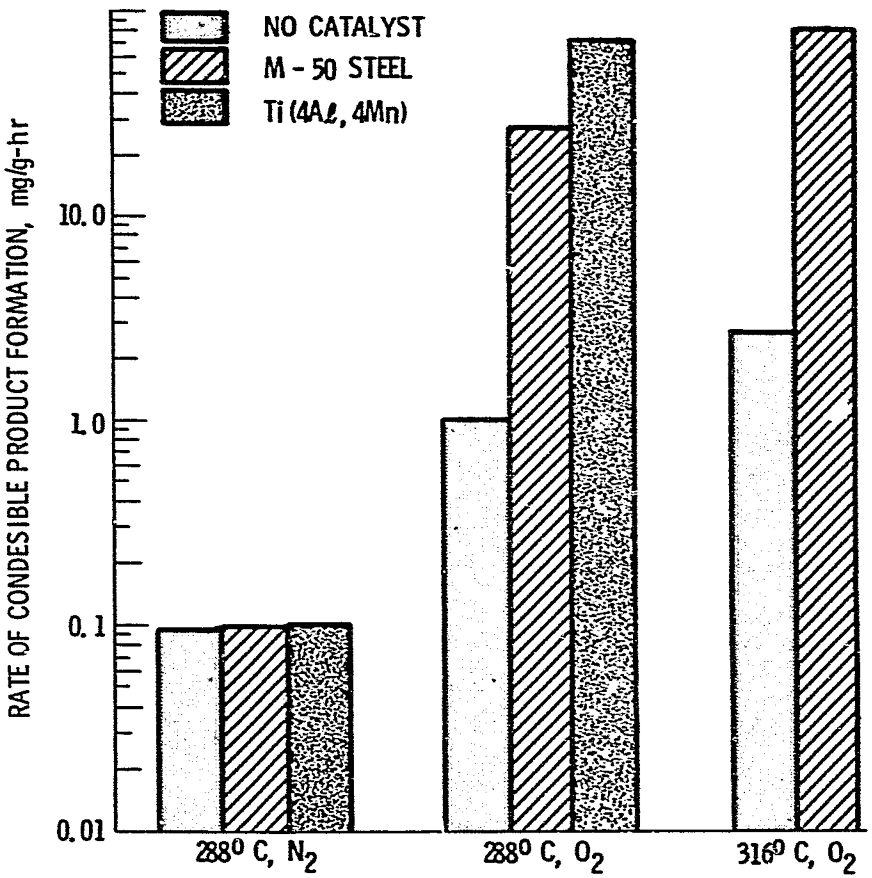


Figure 15. - Rates of condensible product formation for linear perfluoroalkylether (MLO 72-22) in the presence of metal catalysts.

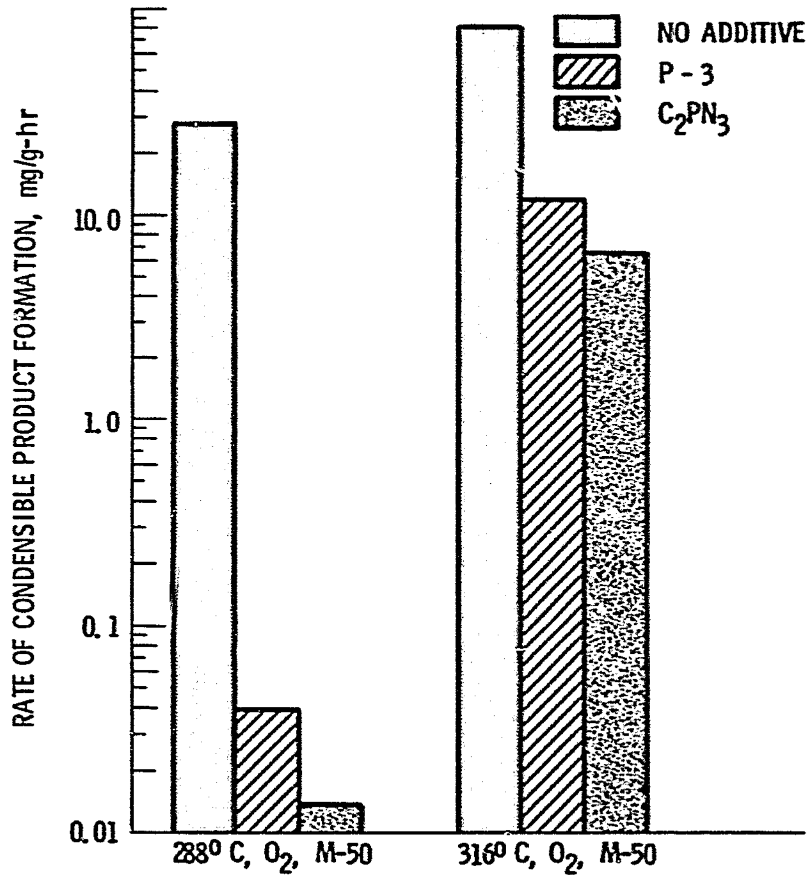


Figure 16. - Effect of degradation inhibitors on the rate of condensible product formation of linear perfluoroalkylether (MLO 72-22).

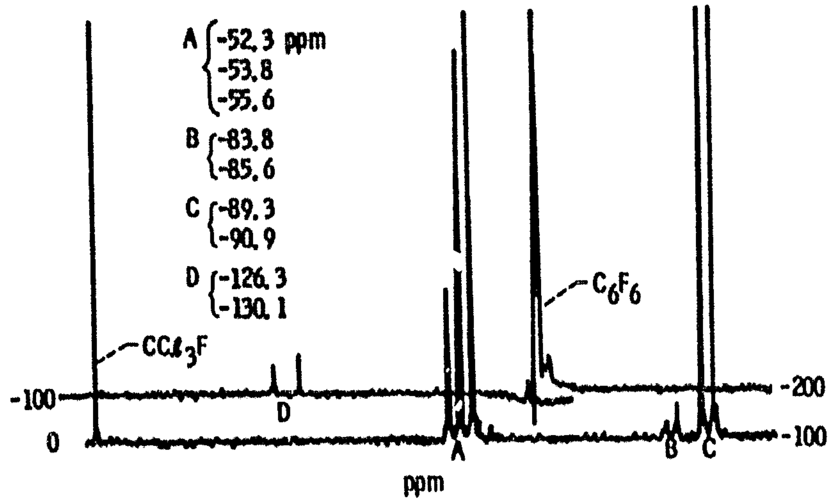


Figure 17. - [19]F NMR spectrum of linear perfluoralkylether fluid MLO-72-22.

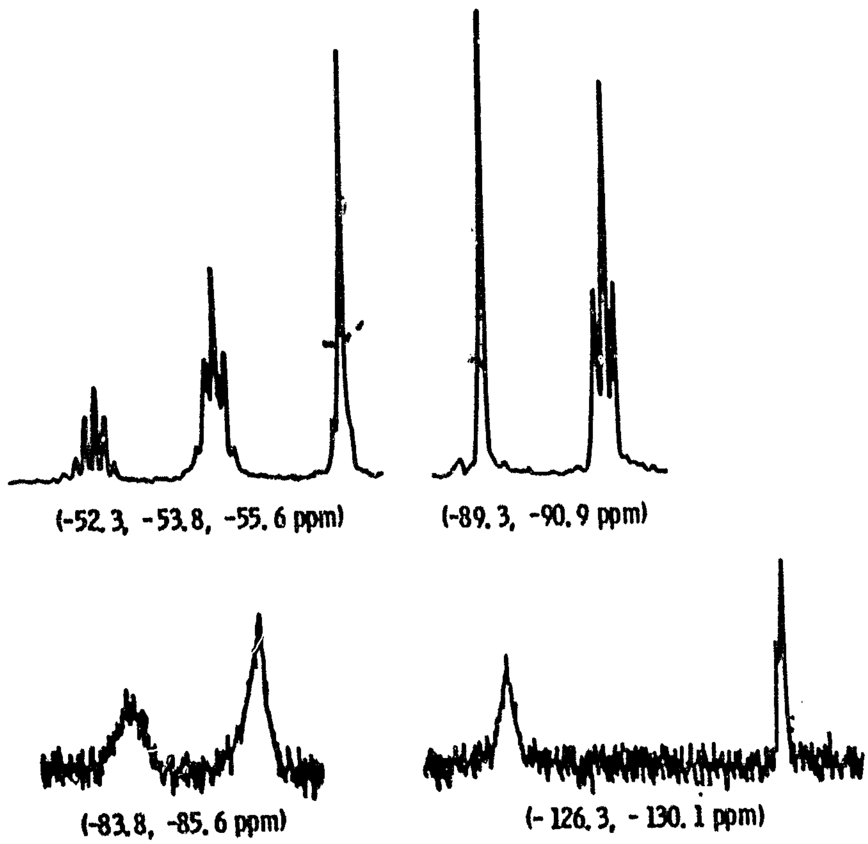


Figure 18. - [19]F NMR spectrum of fluid MLO-72-22, expanded sections A, B, C, and D.

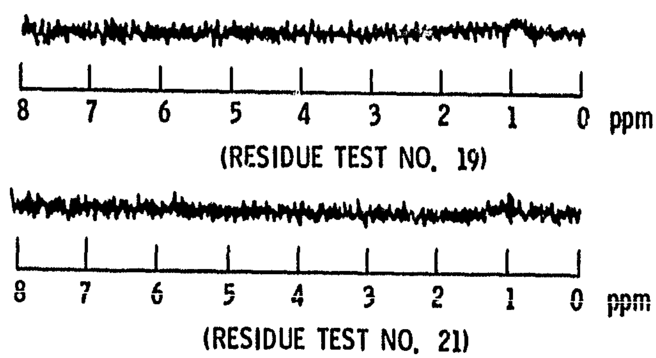


Figure 19. - Proton NMR spectra of fluid MLO 72-22.