



THE EFFECTS OF METALS AND INHIBITORS ON THERMAL OXIDATIVE
DEGRADATION REACTIONS OF UNBRANCHED PERFLUOROALKYLETERS

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ABSTRACT

Thermal oxidative degradation studies were performed on unbranched perfluoroalkylethers at 288° C in oxygen. Metals and alloys studied included Ti, Al, and Ti (4 Al, 4 Mn). The mechanism of degradation was by chain scission. Ti and Al promoted less degradation than Ti (4 Al, 4 Mn). The two inhibitors investigated (a perfluorophenyl phosphine and a phosphatriazine) reduced degradation rates by several orders of magnitude. Both inhibitors were effective for the same duration (75 to 100 hr). The phosphatriazine appeared to provide more surface protection.

SUMMARY

Thermal oxidative degradation studies were performed on an unbranched class of perfluoroalkylethers (Fomblin Z). Tests were conducted in oxygen at 288° C with the neat fluid and in the presence of pure titanium, pure aluminum, or a Ti (4 Al, 4 Mn) alloy.

The mechanism of degradation of the unbranched perfluoroalkylethers in the presence of metals was chain scission. The pure metals (titanium and aluminum) promoted less degradation than the alloy, Ti (4 Al, 4 Mn).

Two inhibitors (a perfluorophenyl phosphine and a phosphatriazine) reduced degradation rates in the presence of metals (based on the quantity of volatile products formed) by several orders of magnitude. Both inhibitors were effective for the same duration (75 to 100 hr) at a 1 percent by weight concentration. However, the phosphatriazine provided more protection to the metal surfaces.

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 nonflammability properties (ref. 6) make these fluids promising candidates for high temperature lubricant applications.

Basically, there are two types of perfluoroalkylethers, an unbranched (ref. 7) and a branched class (ref. 1). The most important representatives of the branched materials (fig. 1(a)) are derived from hexafluoropropene 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 (ref. 9) and was found to be due to the presence of ~3 percent unstable chains. These chains were 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. These materials, whose general chemical structure appears in figure 1(b), are unbranched and have better viscosity-temperature properties than the branched (HFPO) products (ref. 8). However, the unbranched fluids exhibit 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 normally 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 unbranched materials.

A preliminary thermal oxidative stability study has been performed on these fluids (ref. 11). The effects of metals (M-50 steel and Ti (4 Al, 4 Mn) alloy) and inhibitors (a monophospho-s-triazine and a perfluorophenyl phosphine) on degradation were reported.

The unbranched fluids were found to be inherently unstable at 316° C in an oxidizing atmosphere. This instability was not due to the presence of hydrogen chain termination or peroxide linkages. Metals greatly increased the rate of degradation in oxidizing atmospheres; however, degradation inhibitors were highly effective in arresting degradation at 288° C. At 316° C the effectiveness was limited.

The objective of this work was to continue the study of the thermal oxidative degradation processes of the unbranched type of perfluoroalkylether fluids, in particular to determine the influence of alloys versus pure metals upon degradation and to assess the effectiveness of the degradation inhibitors both with respect to concentration and test duration.

EXPERIMENTAL FLUID

The unbranched perfluoroalkylether fluid used in this study is manufactured by Montecatini Edison under the trade name Fomblin Z. Two different batches of this fluid were studied which are designated MLO-72-22 and MLO-79-196. These are Air Force designations where the first two numbers refer to the year in which 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. 12) where it was designated as P-3. The second additive was a perfluoroalkylether substituted monophospha-s-triazine (fig. 2(b)) (ref. 13). This additive will be designated as C₂PN₃ 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 coupons are schematically shown in figures 3 and 4, respectively. The coupons 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 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 coupons were polished using first, Norton No-Fil Durite finishing paper Type 4 220A, followed by open coat silicon carbide papers grades 400A and 500A, respectively. Subsequently, the metal coupons 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 coupons were washed with Freon 113, dried in an inert atmosphere chamber, then weighed and visually inspected. The used coupons 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 oxygen. Since the apparatus was calibrated and the fluid volume measured accurately, the quantity of gas introduced was exactly known. The decomposition tube was then inserted into the preheated box furnace for a specified period of time; during 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.

DEGRADATION STUDIES

Effect of Metals

Previous work (ref. 11) has shown that the unbranched perfluoroalkylether fluids are inherently unstable at 316° C in oxidizing atmospheres. In addition, the presence of certain metal alloys (M-50 steel and Ti (4 Al, 4 Mn)) greatly accelerated this degradation. In the present study, the behavior of the fluid in oxidizing atmospheres at 288° C in the presence of pure metals and alloys was evaluated. Tests were run neat and with Ti (4 Al, 4 Mn), pure titanium (Ti) and pure aluminum (Al) coupons. Rates of condensible product formation for these tests appear in figure 5.

The batch employed in this test series (MLO-79-196) behaved similarly to the previous batch (MLO-72-22) reported in ref. 11. Repeat tests in the absence of metals and with Ti (4 Al, 4 Mn) yielded comparable degradation rates. The arrows in figure 5 indicate continuations of the same test. Tests with the pure metals yielded definitely lower degradation rates compared to the alloy (Ti (4 Al, 4 Mn)). It is noteworthy that the degradation rate increased with time for titanium but decreased for aluminum.

Effect of Degradation Inhibitors

Previously reported work (ref. 11) had shown that two inhibitors, a perfluorophenyl phosphine (P-3) and a phosphatriazine (C_2PN_3) were highly effective in arresting degradation of the fluids in the presence of metals and oxygen at 288° C, but had only limited effectiveness at 316° C. In the present study, a series of tests were run for a different time duration at 288° C in oxygen using a 1 percent (wt) inhibitor concentration. Data for P-3 and C_2PN_3 appear in figures 6 and 7, respectively. Both series of tests afforded similar results showing the additives' effectiveness of 75 to 100 hr.

Finally, a third series of tests with C_2PN_3 were performed under the same conditions except that a lower concentration (0.2 percent wt) was used. These data appear in figure 8. Here degradation increased gradually with test duration time, but surprisingly, the loss of effectiveness occurred in the same exposure range as that observed for the 1 percent concentration tests (~ 100 hr). A summary of these three sets of data appears in figure 9, which more clearly illustrates the similar behavior.

Metal Corrosion

In the absence of inhibition, extensive corrosion of the surface occurred. This is illustrated in the scanning electron micrograph of an M-50 coupon surface shown in figure 10. In contrast, little surface corrosion occurred in the presence of inhibitor (P-3) (Figure 11) (Note the change in magnification).

Comparison of the as received M-50 coupon and the M-50 coupons from the two different inhibitor tests appears in figure 12. It appears that the phosphatriazine was more effective than the perfluorophenyl phosphine in protecting the M-50 surface, even though the fluid degradation was about the same.

Metal Surface Analysis

A scanning electron micrograph of the M-50 coupon from test 37 (P-3 inhibitor) is shown in figure 13. The surface has a pocked appearance consisting of small dark spots and larger light areas. Results of local energy dispersive X-ray analyses (EDX) of these areas also appear on figure 13. Atomic ratios for chromium and vanadium (ratioed to iron) appear for both areas. Also included are the Cr-V ratios for an M-50 standard.

It appears that local depletion of chromium and vanadium has occurred in the light areas while an enhancement has occurred in the dark areas. The results for large area EDX analyses for each M-50 metal surface for tests 36, 37 and 38 as well as an unused specimen appear in table II.

It is obvious that all specimens have the same overall chromium and vanadium surface composition. Apparently, the perfluorophenyl phosphine additive causes or allows some surface etching to occur with the M-50 metal which exposes local concentrations of chromium and vanadium.

Degradation Mechanism

Results reported earlier (ref. 13) indicated that, in the presence of metals and oxygen, the unbranched perfluoroalkylethers are degraded via chain scissions. This parallels the findings of Gumprecht (ref. 10) in his studies of branched perfluoroalkylethers. The mechanism postulated (ref. 10) leads to the formation of COF and C₂F₅ terminated chains and is illustrated in figure 14. Analysis of the products obtained from the unbranched perfluoroalkylethers, by combined gas chromatography and mass spectrometry, showed that this mechanism also applies. To facilitate analysis, the acid fluoride end-groups were transformed into methyl ester species. Unfortunately, the unbranched materials undergo extensive fragmentation when subjected to electron impact. This associated with the absence of molecular ions prevented the identification of compounds other than those presented in figure 14.

SUMMARY OF RESULTS

Thermal oxidative degradation of unbranched (Fomblin Z) perfluoroalkylethers was investigated in the presence of selected metals and alloys.

1. Chain scission was the mechanism of degradation by metals and alloys
2. Pure metals (Ti and Al) promoted less degradation than alloys (Ti (4 Al, 4 Mn))
3. Inhibitors (perfluorophenyl phosphine and phosphatriazine) retarded degradation by several orders of magnitude
4. Both inhibitors were effective in the unbranched fluids for about the same time period (75 to 100 hr), but the phosphatriazine yielded better protection of the metal surfaces.

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TABLE I. - EFFECT OF METALS AND INHIBITORS ON THE THERMAL OXIDATIVE BEHAVIOR OF UNBRANCHED PERFLUOROALKYLETHER IN OXYGEN

Test ^a	Sample size, g	Temperature, °C	Metal	Inhibitor	Degradation rate, mg/1g-hr
41	3.84	288	Ti (4 Al, 4 Mn)	None	72.8 (8) ^f
42	3.67	288	Ti (4 Al, 4 Mn)	1 percent P-3b	0.047 (24)
46A	3.60	288	Ti (4 Al, 4 Mn)	1 percent P-3b	0.032 (72)
46B	3.58	288	Ti (4 Al, 4 Mn)	1 percent P-3b	5.0 (48)
55A	4.94	288	Ti (4 Al, 4 Mn)	1 percent P-3b	0.026 (86)
55B	4.92	288	Ti (4 Al, 4 Mn)	1 percent P-3b	0.11 (16)
55C	4.91	288	Ti (4 Al, 4 Mn)	1 percent P-3b	0.19 (8)
55D	4.90	288	Ti (4 Al, 4 Mn)	1 percent P-3b	1.72 (16)
54A	3.81	288	Ti (4 Al, 4 Mn)	1 percent C ₂ PN ₃	0.028 (24)
54B	3.81	288	Ti (4 Al, 4 Mn)	1 percent C ₂ PN ₃	0.014 (48)
54C	3.80	288	Ti (4 Al, 4 Mn)	1 percent C ₂ PN ₃	3.37 (28)
56A	4.03	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.040 (24)
56B	4.02	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.043 (24)
56C	4.02	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.066 (24)
56D	4.01	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.13 (8)
56E	4.01	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.10 (8)
56F	4.01	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.13 (8)
56G	4.00	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	0.24 (8)
56H	4.00	288	Ti (4 Al, 4 Mn)	0.2 percent C ₂ PN ₃	27.2 (24)
61	2.82	292	None	1 percent C ₂ PN ₃	0.035 (24)
63 ^d	30.17	343	None	None	0.39 (24)
64 ^e	3.20	288	None	None	3.45 (24)
69 ^e	3.54	288	Ti	None	48.2 (8)
70 ^e	3.64	288	Al	None	30.2 (8)
71 ^d	30.00	343	None	None	0.42 (24)
72A ^d	3.15	288	None	None	0.51 (24)
72B	3.10	288	None	None	0.45 (24)
73 ^d	3.67	288	Ti (4 Al, 4 Mn)	None	75.9 (8)
74A ^d	3.56	288	Ti	None	5.6 (8)
74B	3.42	288	Al	None	29.6 (16)
75A ^d	3.50	288	Al	None	12.3 (8)
75B	3.16	288	Al	None	7.9 (8)
75C	2.93	288	Al	None	4.13 (16)

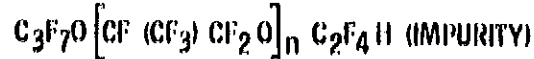
- a. All the fluids used, unless otherwise indicated, were pretreated at 343° C in oxygen for 24 hr; in the series of runs denoted by consecutive letters of the alphabet, the residue of the preceding test was employed after removal of the volatiles and oxygen replenishment; in the experiments up to the Run 61 the batch MLO-72-22 was employed; starting with the Test No. 63 MLO-79-196 was used.
- b. MLO-80-279 (perfluorophenyl phosphine).
- c. 1-diphenylphospha-3,5-bis[C₂F₇OCF(CF₃)CF₂OCF(CF₃)]-2,4,6-triazine.
- d. In these tests, the MLO-79-196 fluid was used as received.
- e. In these tests, the residue of Test No. 63 was utilized.
- f. The value in parentheses corresponds to the time of exposure in hr.

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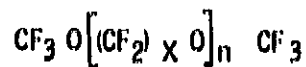
TABLE II. -- CHROMIUM AND VANADIUM CONCENTRATION
(RATIOED TO Fe) FOR M-50 METAL DETERMINED
BY ENERGY DISPERSIVE X-RAY ANALYSIS

Test	Inhibitor	Cr	V
Unused M-50		0.105	0.043
36	Monophospha-s-triazine	.103	.045
37	Perfluorophenyl phosphine	.104	.044
38	None	.102	.045

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(a) Branched fluids (Krytox).

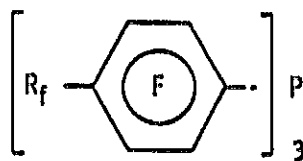


WHERE $x = 1, 2, \dots, m$

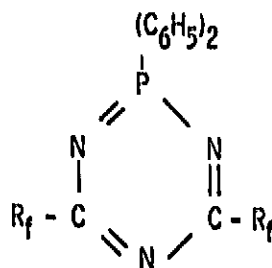


(b) Unbranched fluids (Fomblin Z).

Figure 1. - Chemical structures of perfluoroalkylether fluids.



(a) Perfluorophenyl phosphine (P - 3).



(b) Monophosphazene (C₂PN₃).

Figure 2. - Chemical structures of degradation inhibitors.

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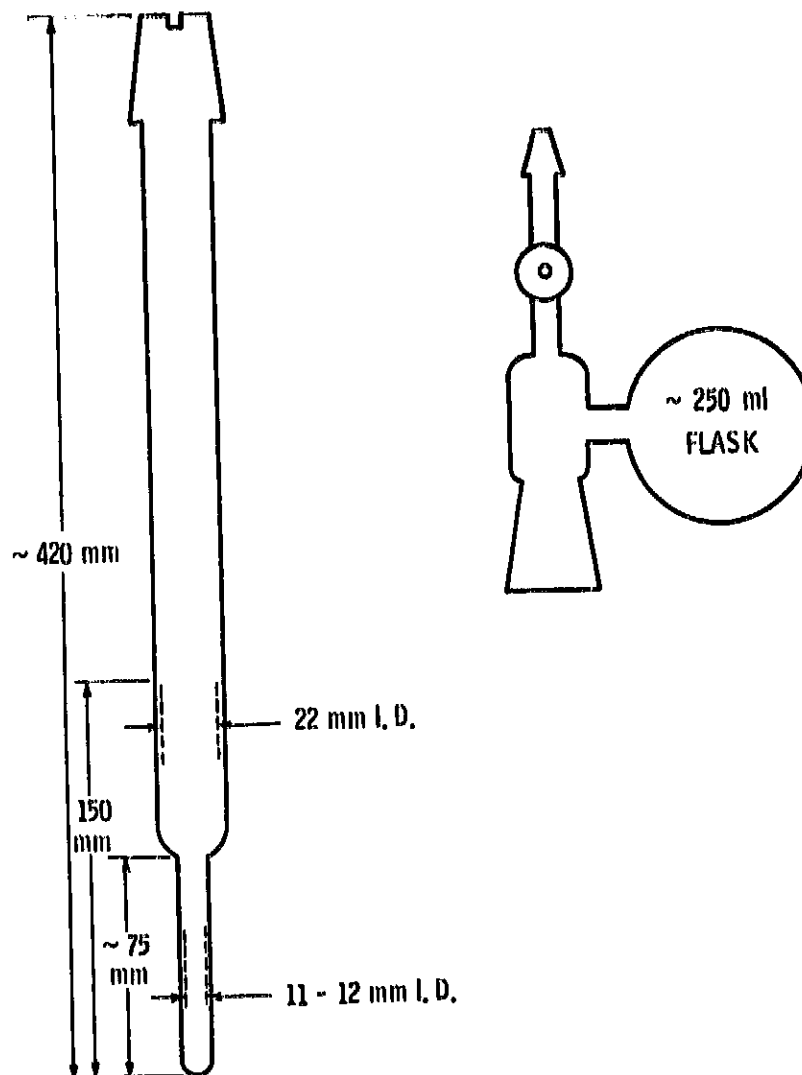


Figure 3, - Decomposition tube and adapter.

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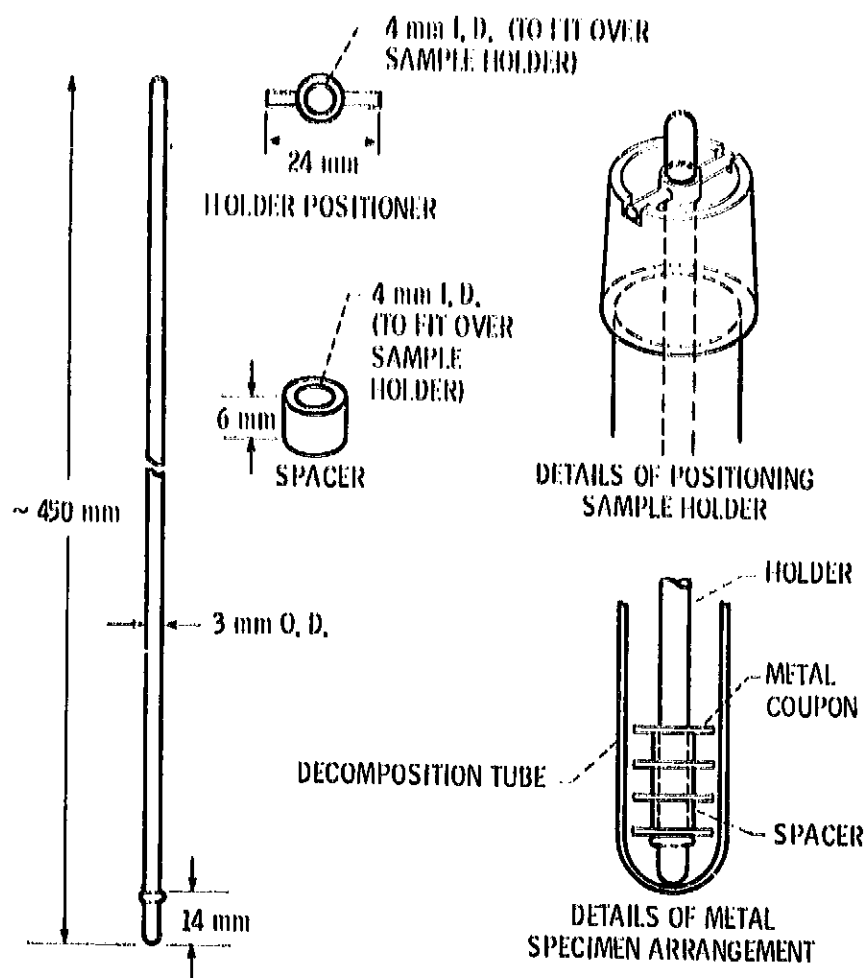


Figure 4. - Metal specimen holder arrangement.

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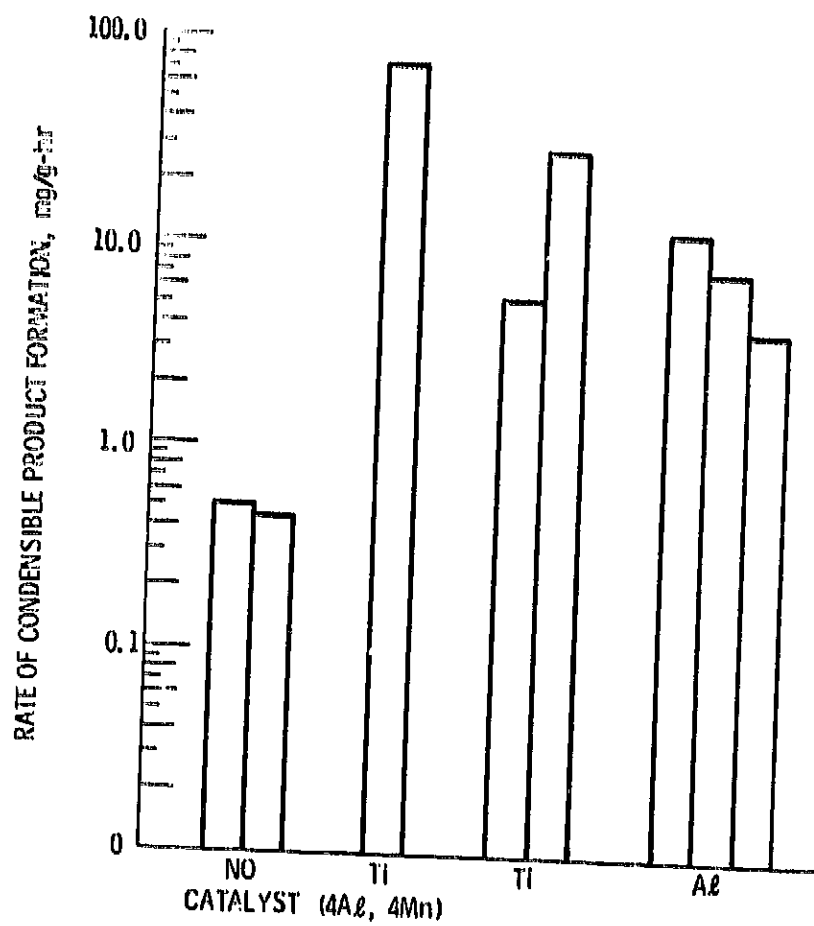


Figure 5. - Effect of metals on the degradation of unbranched perfluoroalkylether (MLO 79-196) (288° C, O₂).

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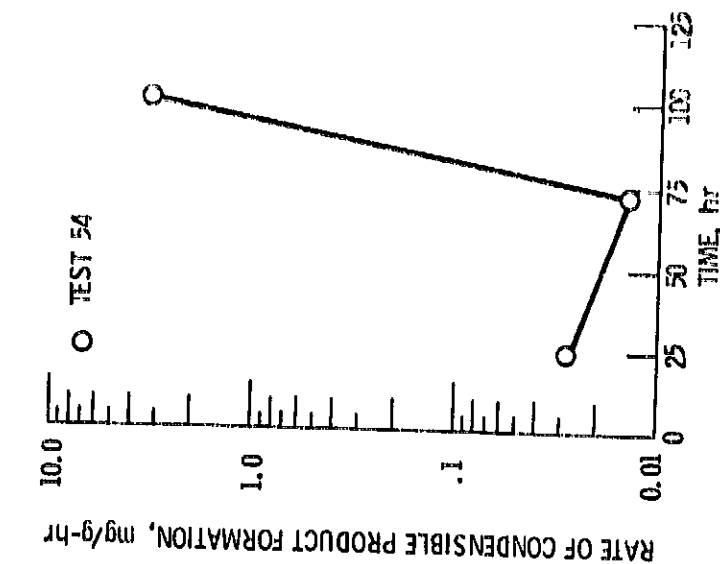


Figure 6. - Effect of inhibitor (perfluorophenyl phosphine, P-3) on degradation of unbranched perfluoroalkylether, 288° C, O₂, inhibitor concentration 1% wt, Ti (4A1, 4Mn) alloy.

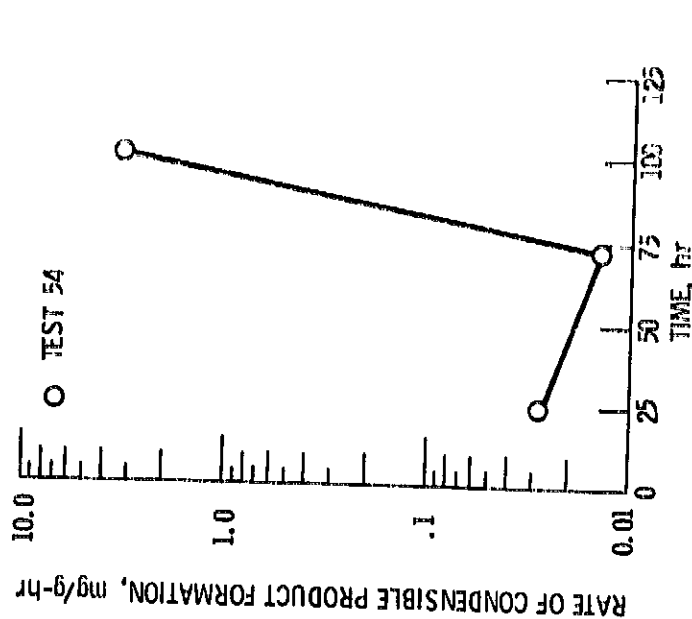


Figure 7. - Effect of inhibitor (phosphine, P-3) on degradation of unbranched perfluoroalkylether, 288° C, O₂, inhibitor concentration 1% wt, Ti (4A1, 4Mn) alloy.

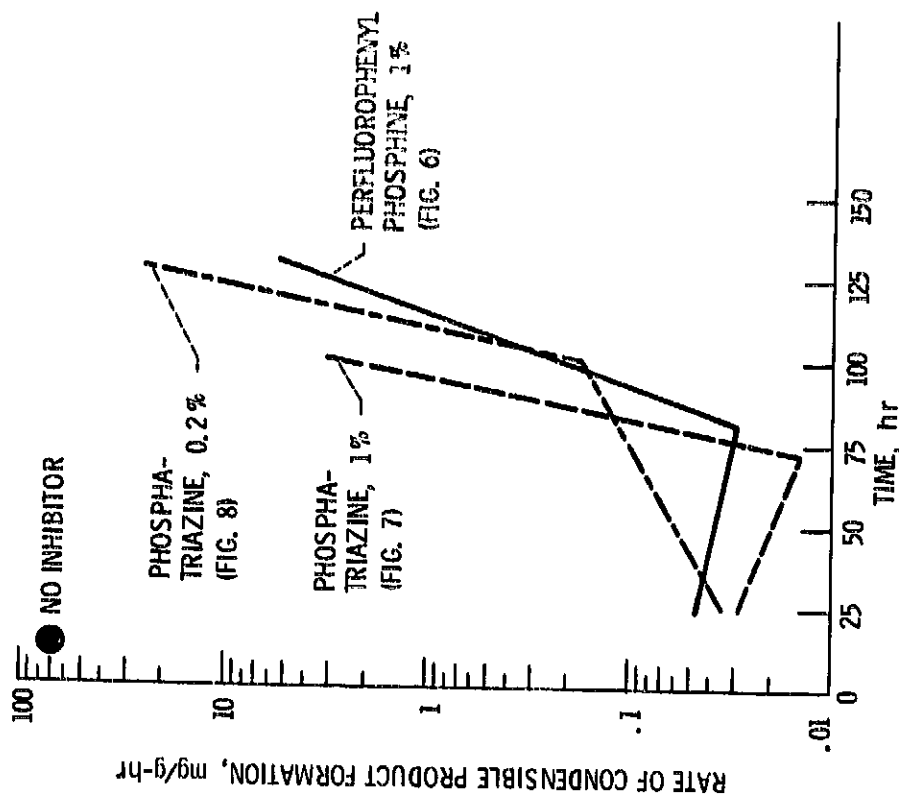


Figure 9. - Effect of inhibitors on degradation of unbranched perfluoroalkylether, 288°C, O₂, Ti (4A1, 4Mn).

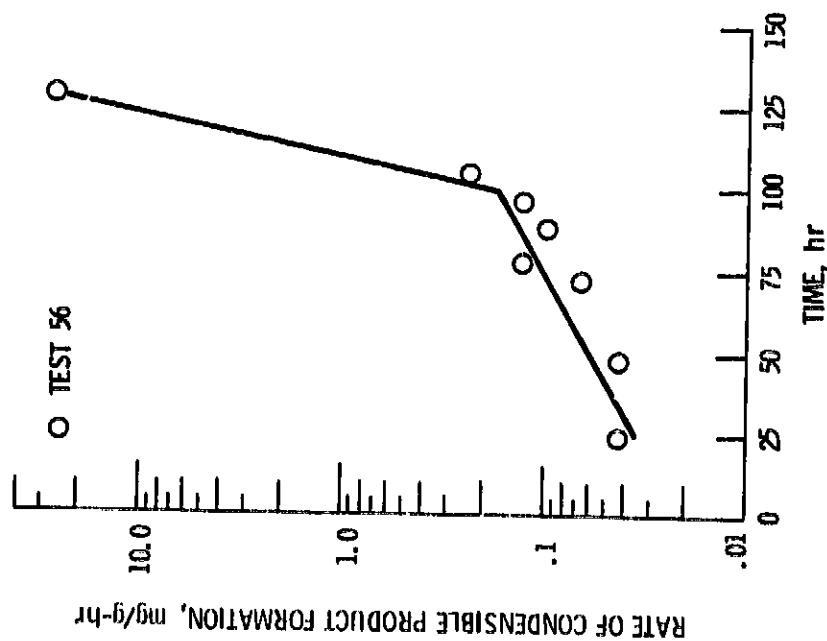


Figure 8. - Effect of inhibitor (phosphazine) on degradation of unbranched perfluoroalkylether, 288°C, O₂, concentration 0.2% wt, Ti (4A1, 4Mn) alloy.

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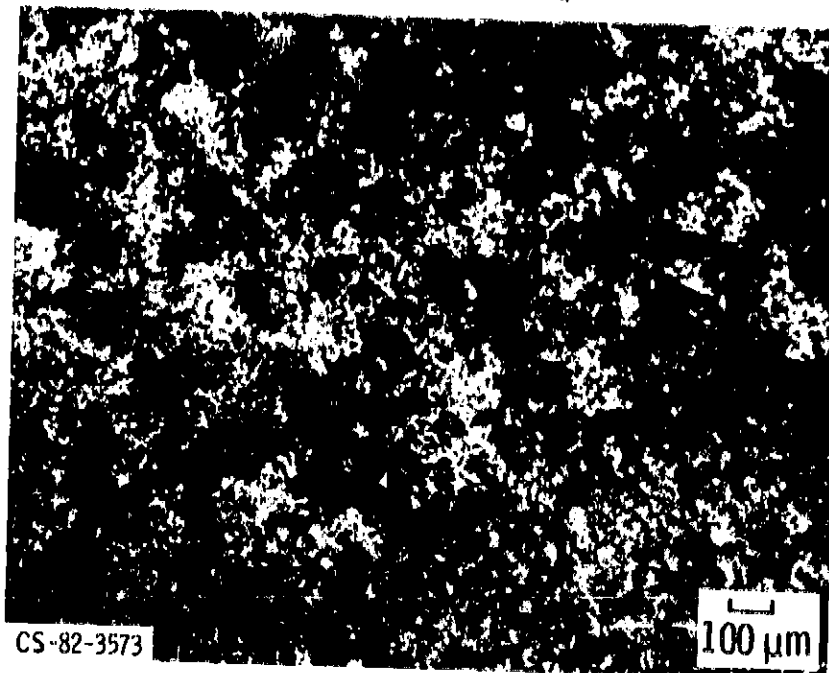


Figure 10. - SEM of M-50 metal from test 38 (unbranched perfluoroalkyl-ether, 288^o C, O₂, no inhibitor), (ref. 11).

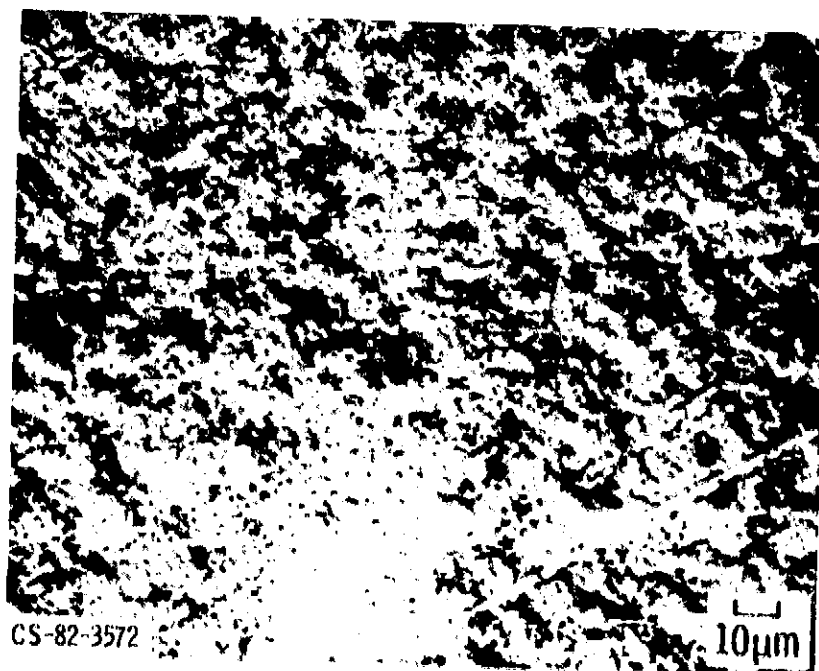
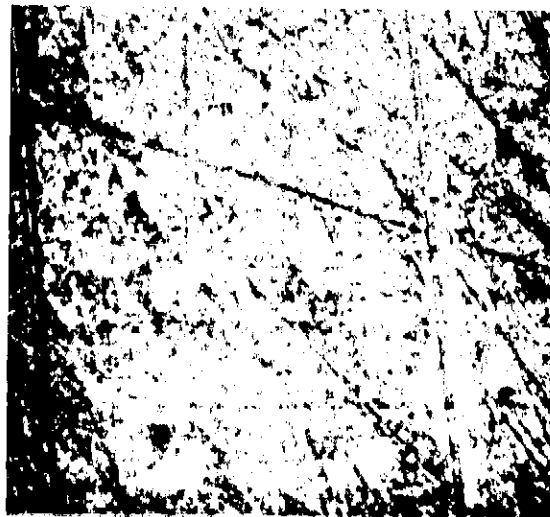
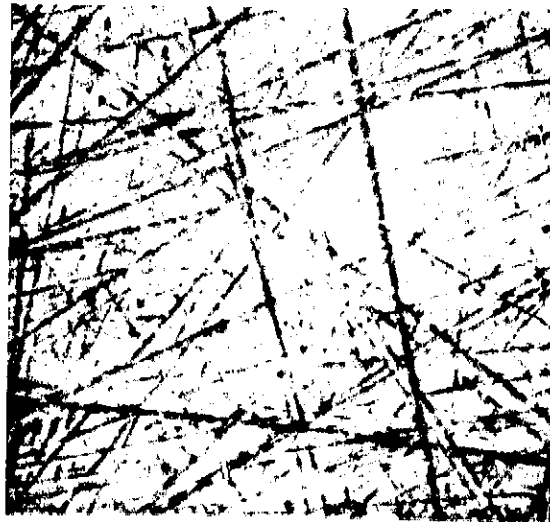


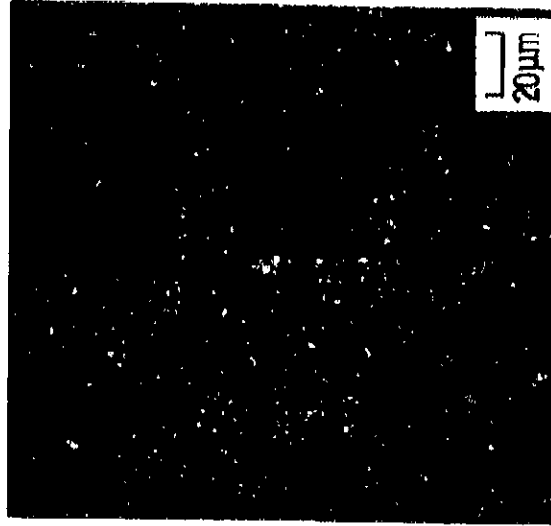
Figure 11. - SEM of M-50 metal from test 37 (unbranched perfluoroalkyl-ether, 288^o C, O₂, perfluorophenyl phosphine inhibitor), (ref. 11).



PHOSPHA-TRIAZINE



UNUSED



PERFLUOROPHENYL PHOSPHINE

Figure 12. - Photomicrographs of M-50 metal surfaces (unbranched perfluoroalkylether, 288° C, C₂), (ref. 11). CS-83-0537

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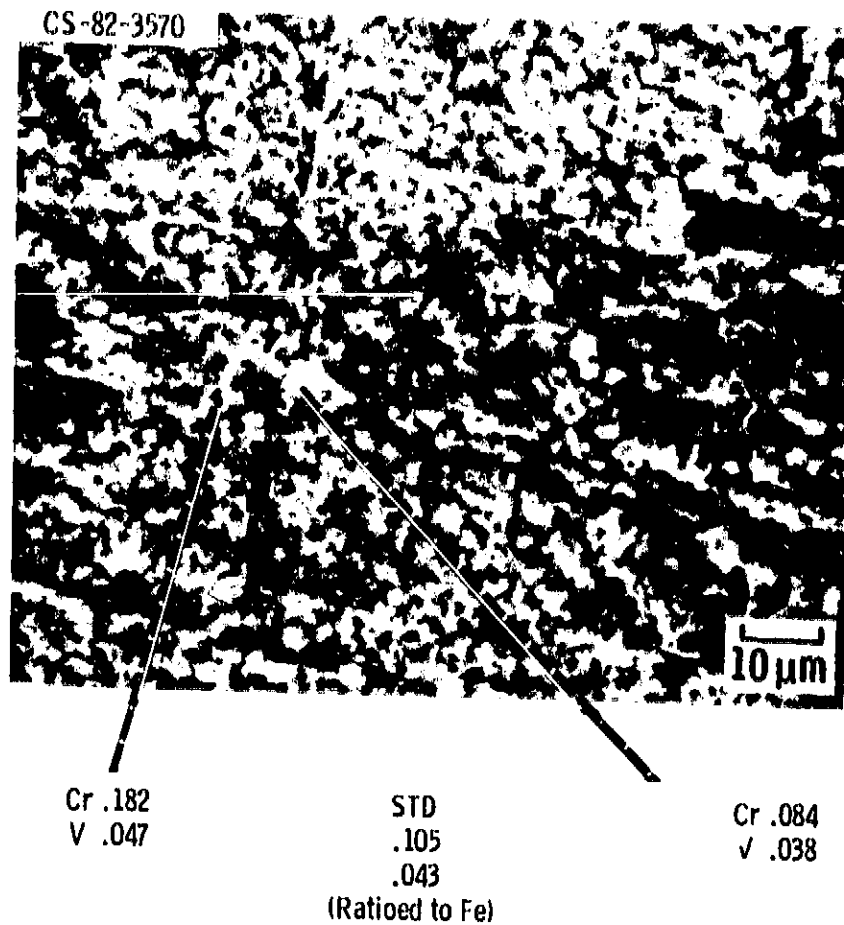


Figure 13. - SEM of M-50 metal from test 37 (unbranched perfluoroalkyl-
ether, 288^o C, O₂, P-3 inhibitor), (ref. 11).

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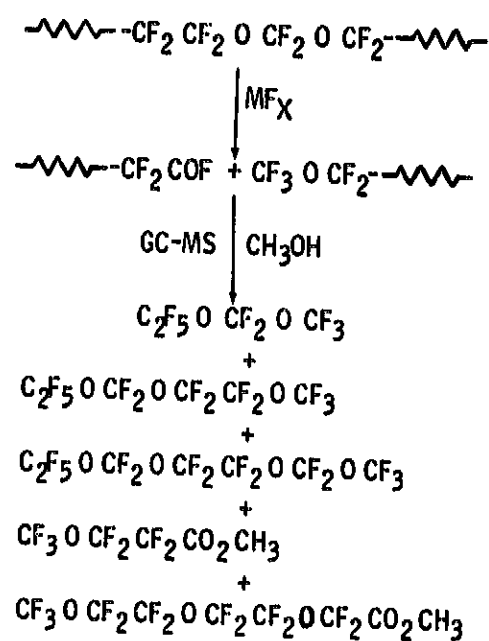


Figure 14. - Degradation of an unbranched
perfluoroalkylether in the presence of
TI (4A ℓ , 4Mn) at 288 $^\circ$ C in O $_2$.