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THERMAL OXIDATIVE DEGRADATION REACTIONS OF PERFLUOROALKYLETHERS

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16. Abstract

The objective of this contract was to investigate the mechanisms operative in thermal and thermal oxidative degradation of Fomblin Z and hexafluoropropene oxide derived fluids and the effect of alloys and additives upon these processes.

The nature of arrangements responsible for the inherent thermal oxidative instability of the Fomblin Z fluids has not been established. It was determined that this behavior was not associated with hydrogen end-groups or peroxy linkages. The degradation rate of these fluids at elevated temperatures in oxidizing atmospheres was found to be dependent on the surface/volume ratio. Once a limiting ratio was reached, a steady rate appeared to be attained. Based on elemental analysis and oxygen consumption data, $-CF_2OCF_2CF_2O-$, not $-CF_2CF_2O-$, is one of the major arrangements present. The action of the M-50 and Ti(4 Al, 4 Mn) alloys was found to be much more drastic in the case of Fomblin Z fluids than that observed for the hexafluoropropene oxide derived materials. The effectiveness of antioxidation/anticorrosion additives, P-3 and phospha-s-triazine, in the presence of metal alloys was very limited at 316°C; at 288°C the additives arrested almost completely the fluid degradation. The phospha-s-triazine appeared to be at least twice as effective as the P-3 compound; it also protected the coupon better. The Ti(4 Al, 4 Mn) alloy degraded the fluid mainly by chain scission processes; this took place to a much lesser degree with M-50.

The presence of a certain proportion of hydrogen-terminated chains in Krytox MLO-71-6 fluid was verified by NMR spectroscopy. These were eliminated on exposure of the fluid to oxygen at 343°C. In oxygen at 316°C, aluminum metal did not seem to promote chain scissions; a steady but low rate of degradation was observed for pure titanium metal.

17. Key Words (Suggested by Author(s)) Perfluoroalkylethers, Degradation mechanisms, Fomblin Z, Krytox, Corrosion and Effect of Metal Alloys, Additives, Inhibitors	18. Distribution Statement

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FOREWORD

This annual report describes the work performed by Ultrasystems, Inc, during the period 6 November 1981 through 30 June 1983 under Contract NAS3-22517, "Thermal Oxidative Degradation Reactions of Perfluoroalkylethers". The investigations were carried out by D. H. Harris, M. E. Smythe, R. H. Kratzer, and K. L. Paciorek, project manager, at the Chemicals and Materials Research Department, Irvine, California. The contract was administered by the NASA Lewis Research Center with Mr. William R. Jones, Jr. as the project manager.

We would like to acknowledge the cooperation and assistance of Mr. C. E. Snyder of the Air Force Wright Aeronautical Laboratories, Fluids, Lubricants, and Elastomers Branch. We also would like to express our indebtedness to Dr. Paul R. Resnick of E. I. DuPont de Nemours and Company for providing a model perfluoroalkylether.

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1. SUMMARY

Investigations of the thermal oxidative degradations of unbranched (Fomblin Z) and hexafluoropropene oxide derived (Krytox 143AC) fluids in the presence of pure metals and metal alloys, as well as evaluation of the effect of additives are reported. Both the P-3 (perfluoroalkylether-substituted perfluorophenylphosphine) and the monophospha-s-triazine additives at 1% by weight concentration prevented the decomposition of Fomblin Z fluid for over three days in oxygen at 288°C. The degradation inhibiting action persisted even at 0.1% concentration in the case of the monophospha-s-triazine. In the absence of the additives, essentially complete degradation occurred within 8 hr.

Limited data indicated better protection of M-50 surface by the monophospha-s-triazine than P-3 inhibitor. Based on the nature of products formed in the degradations catalyzed by metals, the same bond scission mechanisms appear to be operative in both types of fluids. Krytox 143AC fluids, in which the hydrogen-terminated chain impurity was present, exhibited an initial high rate of degradation when exposed to 316°C and oxygen in the presence of pure metals or metal alloys. Depending on the metal, the rates passed either through a minimum followed by an increase or they kept diminishing. The only exception was Ti(4Al, 4Mn) alloy where no rate decrease was observed even at 288°C. The effectiveness of metals and metal alloys in enhancing fluids' degradation followed the same order in the branched and unbranched materials, the difference being the temperature at which the decomposition occurred. The unbranched, Fomblin Z, fluids exhibit significantly lower thermal oxidative stability than the hexafluoropropene oxide derived materials.

2. INTRODUCTION

Advanced aircraft and re-entry vehicles will require nonflammable hydraulic fluids and lubricants functioning at elevated temperatures and in oxidizing atmospheres. Perfluoroalkylethers are excellent candidates for these applications. Products obtained by telomerization of hexafluoropropene oxide [ref. 1,2] are oxidatively more stable [ref. 3] than the unbranched materials [ref. 4-8], yet the latter fluids exhibit better viscosity-temperature characteristics [ref. 9]. The thermal oxidative degradation of both types of perfluoroalkylethers is adversely affected by metals [ref. 1-3,6-11], however, the presence of inhibitors can arrest the degradation almost completely [ref. 3,6-11]. The maximum temperature at which the inhibitors functioned was higher for the hexafluoropropene oxide derived materials.

Certain aspects relating to the instabilities of the two types of materials were addressed previously [ref. 3, 6-8, 11]. The current study was directed largely at determining the effectiveness of the inhibitors with respect to concentration and exposure duration, as well as the evaluation and the influence of different metals and alloys upon degradation.

3. RESULTS AND DISCUSSION

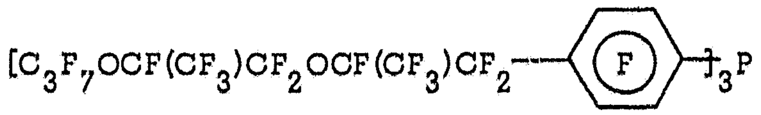
The present study was a continuation of the work described in the first report generated under this contract [ref. 6]. Two classes of perfluoroalkylethers were investigated, namely the branched products formed by telomerization of hexafluoropropene oxide [ref. 1,2] and the "unbranched" fluids prepared from tetrafluoroethylene and oxygen under ultraviolet radiation [ref. 4,5].

Two different batches of Fomblin Z fluid were obtained from the U.S. Air Force, AFWAL-MLBT. The bulk of work performed under the first phase of this program utilized the batch MLO-72-22, which was shown to be somewhat more oxidatively stable than the sample received later by the Air Force, MLO-79-196. The evaluations of the effectiveness of the inhibitors were carried out using the first batch of the fluid; other investigations had to be conducted with the batch MLO-79-196 due to the depletion of MLO-72-22 material.

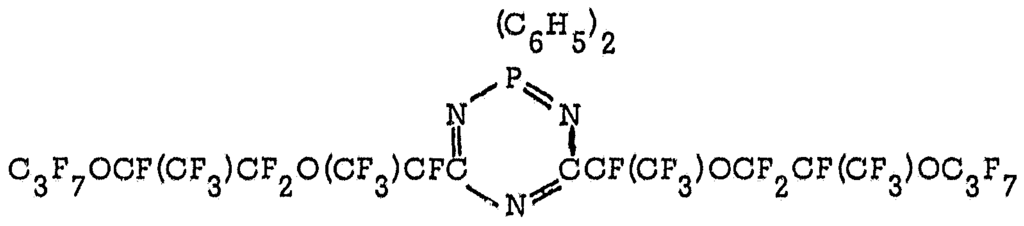
For the poly(hexafluoropropene oxide) studies, the same batch MLO-71-6 of Krytox 143AC as that utilized in the past [ref. 3,6] was employed.

3.1 Inhibitor Action on Unbranched Perfluoroalkylethers

Earlier work [ref. 6] indicated that the Ti(4Al, 4Mn) alloy leads to maximum degradation of perfluoroalkylethers. This was verified by the current investigations to be discussed in the later portions of this report. Based on the above, Ti(4Al, 4Mn) alloy was selected for the inhibitors' evaluation tests summarized in Table I. The two inhibitors studied were a phospha-s-triazine [ref. 12] and a perfluoroalkylether-substituted perfluorophenylphosphine. The structural arrangements of the two compounds are presented below:



P-3



Monophospha-s-triazine

The tests performed are summarized in Table I.

The fluid utilized in these experiments was pretreated at 343°C in oxygen for 24 hr. To illustrate fluid behavior in the absence of metal and inhibitor and the effect of metal alone and in the presence of the inhibitor on the fluid degradation, Tests 40, 41, and 42, respectively, were included in this tabulation, although the actual runs were conducted under the previous phase of the program [ref. 6]. The degradation arresting action of the inhibitors as measured by volatiles production, although significant in the absence of metal (compare Runs 40 and 61), was really drastic in the presence of the Ti(4Al, 4Mn) alloy (compare Test 41 with Tests 42 and 54A).

To evaluate the duration of the inhibitors' protection at 288°C, tests 46, 55, and 54 were conducted. To assess the concentration of inhibitor required to arrest fluid degradation, the 56 series of tests was carried out. The results of these tests are presented graphically in Figure 1. Both of the inhibitors, P-3 and C_2PN_3, seem to exhibit essentially the same behavior insofar as duration of protection is concerned. The low concentration, 0.2% (test series 56), of phospha-s-triazine appears to arrest the degradation for an equivalent period of time compared to the higher concentration, 1% (test series 54), however, the degree of protection seems lowered as determined by the rate of degradation product formation. It should be noted that a number of individual runs within this series were carried out for 8 hr intervals. Since it requires certain time lapse to heat the fluid to temperature, after insertion in the oven, it is possible that the onset of "catastrophic" decomposition would occur sooner had the material been heated without interruption for the 104 hr period.

It is noteworthy that the phospha-s-triazine at 1% concentration in Fomblin Z fluid seemed to provide better surface protection than the P-3 inhibitor for a M-50 metal coupon in oxygen at 288°C, at least over a 24 hr period, as evidenced by the surface appearance (Figure 2). The surface, in the absence of any inhibitor, was drastically corroded as shown in Figure 3. In a lightly corroded specimen, the overall surface alloying metal content remained unchanged as can be seen from Table II, however, the "deposits" were enriched in chromium and vanadium with the metals depleted in the light areas (Figure 4). Thus, in highly corroded specimens where flaking did take place, loss of these metals would be expected to occur. This agrees with the SIMS analysis of M-50 metal exposed to Krytox fluid in oxidizing atmospheres at elevated temperatures, where depletion of chromium and vanadium was observed 1000 Å below the surface [ref. 11].

3.2 Effect of Different Metals on the Degradation Rate of Unbranched Perfluoroalkylethers

Studies performed on Krytox fluids [ref. 6] indicated that pure metals catalyzed degradation less than the alloys in which these metals were present. Furthermore, the action of the pure metals was not self catalyzing which was shown to be the case with, e.g., Ti(4Al, 4Mn) alloy. To determine whether this behavior applied also to Fomblin Z fluids, tests summarized in Table III were conducted. Since the batch MLO-72-22 was no longer available, fluid batch MLO-79-196 was utilized. This material appeared to be rendered thermo-oxidatively unstable by pretreatment at 343°C in oxygen (Tests 63 and 71) as shown by the high rate of volatile production of the recovered fluid compared to the as received material (compare Tests 64 with 72A and 72B). This result is not due to an inadvertent impurity introduction since the repeat pretreatment, Run 71, afforded parallel data. It can be thus speculated that using the relatively large quantity of material results in an incomplete oxidation and formation of chains terminated by reactive groups which break down on subsequent exposures. Indications of similar behavior were noted for the batch MLO-72-22, where the mg/g value at 316°C for the pre-treated fluid was higher than that recorded during pretreatment at 343°C [ref. 6]. This effect is, however, much more pronounced in the case of batch MLO-79-196. The "activated" material exhibited highly accelerated degradation in the presence of metals, Runs 66, 69, and 70. Accordingly, the evaluation studies were performed using the as received fluid, with Runs 72A and B serving as the base data. It is apparent from the compilation given in Table III and from the bar graphs presented in Figure 5 that each of the metals enhanced degradation, with Ti(4Al, 4Mn) alloy having the greatest influence. The latter material could be tested only for an 8 hr period since during that time the major portion of the fluid was degraded. With pure titanium metal, the degradation rate increased on prolonged exposure, whereas the opposite trend was observed for aluminum. These results are in line with the data obtained for hexafluoropropene oxide derived fluids (Krytox 143AC fluids) [ref. 6].

3.3 Fomblin Z Degradation Product Investigation

Degradation of Fomblin Z fluids, in particular in the presence of Ti(4Al, 4Mn) alloy, yielded a large portion of volatile yet relatively high molecular weight products [ref. 6-8]. These, e.g., in Run 73, amounted to 51% of the volatiles formed. In the absence of metals, the volatiles consisted of COF_2, SiF_4, and CO_2, showing the predominance of unzipping [ref. 6-8]. Based on infrared spectral analysis, acyl fluoride terminated chains were present in the "high" molecular weight products. In agreement with the mechanism advanced by Gumprecht [ref. 2] for metal fluoride assisted chain scissions in perfluoroalkyl ethers, both acyl fluoride and trifluoromethyl terminated chains would be expected to result. The ready transformation of acyl fluorides into methyl esters and the suitability of the latter derivatives for mass spectral analysis has been shown in the investigation of other perfluoroalkylethers [ref. 13].

The combined gas chromatography-mass spectrometry (GC-MS) of the esterified -78°C fraction of the condensible volatiles from the run conducted in the presence of Ti(4Al, 4Mn) alloy (Test 73) afforded a spectrum of products as shown by the trace given in Figure 6. Only a few of these could be identified, e.g., $C_2F_5OCF_2OCF_3$ (retention time 9.9 min), $C_2F_5OCF_2OCF_2CF_2OCF_3$ (rt. time 16 min), $CF_3OCF_2CF_2CO_2CH_3$ (rt. time 17.6 min), $C_2F_5OCF_2OCF_2CF_2OCF_2OCF_3$ (rt. time 21.1 min), and $CF_3OCF_2CF_2OCF_2CF_2OCF_2CO_2CH_3$ (rt. time 22.9 min).

The difficulty in structure and molecular weight assignment lies in the absence of molecular and M-19 ions in many of the compounds associated with an extensive breakdown into small, non-characteristic fragments. The mass spectrum of the model perfluoroalkylether $CF_3O-[CF_2O]_4CF_3$ (MW, 418) presented in Table IV emphasizes this problem. For illustration, in Tables V and VI are presented the mass spectral breakdown patterns of a perfluoroalkyl group and a representative ester terminated materials as enumerated above.

3.4 Investigation of the Effect of Pure Metals and Metal Alloys Upon the Degradation of Krytox 143AC Fluid

Under Phase I of the subject program study, the action of pure metals on Krytox 143AC was initiated. The results obtained indicated that heating a fluid, pretreated in oxygen at 343°C, (to remove the hydrogen-terminated chains) with pure titanium metal at 316°C in oxygen gave a steady degradation rate of ~ 10 mg/g/24 hr. To see whether a larger metal surface area will promote the degradation in test series 48, summarized in Table VII, three titanium coupons were employed. The rate of degradation over the first 24 hr was only ~ 1 mg/g and on subsequent exposure it reached 9 mg/g. These experiments were repeated with fresh fluid and coupons, test series 57; identical results were obtained for the first 48 hr. Extending the exposure for additional 24 hr resulted in the rate increase to ~ 20 mg/g/24 hr. These data do not correlate well with the one coupon studies, since it indicates acceleration in degradation with time. On the other hand, the degradation rate over the 72 hr period, Test 57A-C, is ~ 9.8 mg/g/24 hr which is the same as that found previously [ref. 6]. One aspect is certain, pretreatment of Krytox fluid does not arrest completely degradation by titanium at 316°C. Consequently, it is tempting to speculate that at this temperature bond scission does take place.

Studies performed previously in oxygen at 316°C using non-pretreated Krytox revealed that with pure metals the degradation rate over the initial 24 hr period was substantially higher than over the subsequent 24 hr [ref. 3,6,11]. Similar behavior was noted for the Ti(6Al, 4V) and Ti(8Mn) alloys. Both of these alloys, however, on prolonged exposure, caused acceleration in the degradation rate. This data is given in Table VII and expressed graphically in Figure 7. To facilitate comparison, in Figure 7 are also included results of the studies reported earlier [ref. 3,6,11]. The fast initial rate is due to the reaction of the hydrogen-terminated chains; the subsequent rate increase must be due to chain scission process which is autocatalytic. This has been observed to occur with M-50 alloy at 343°C, but not at 316°C where after the first 24 hr the rate over the next 192 hr dropped to 0.07 mg/g/hr and is too low to be included in Figure 7 [ref. 3,11]. Of all the metals tested, Ti(4Al, 4Mn) alloy accelerated the fluid degradation the most. Even at 288°C, a continuous rate increase was observed as shown in Figure 8 [ref. 3,11]. Apparently, all three elements (Ti, Al, and Mn) must be present in an alloy to exhibit this action, inasmuch as Ti(8Mn) and Ti(6Al, 4V) were much less detrimental to Krytox fluid than Ti(4Al, 4Mn) alloy. These results also emphasize that temperatures at which a perfluoroalkylether is stable in the presence of metal depends very strongly on the alloy. Having stability data on related alloys and pure metals does not permit one to predict the materials' behavior in the environment wherein an alloy composed of the tested elements or groups of elements is present.

If one compares the behavior of Fomblin Z fluids with that of Krytox 143AC, the difference in the effect of metals on the thermal oxidative stability is only one of degree, i.e., Fomblin Z materials degrade at lower temperatures and at higher rates than the hexafluoropropene oxide derived fluids. Yet, the direction of action is the same for the two series of materials which indicates that the mechanisms involved are the same. The more detrimental action of metals on Fomblin Z fluids as compared to Krytox 143AC implies that the bonding present in the former is more susceptible to metal or metal fluoride attack. It is tempting to speculate that the $-OCF_2O-$ arrangement present in Fomblin Z somehow promotes this process, but since no investigations were performed on pure poly(tetrafluoroethylene oxide), the hindering action of the pendant trifluoromethyl group in Krytox fluid cannot be discounted.

4. EXPERIMENTAL DETAILS AND PROCEDURES

The perfluoroalkylether fluids employed in this study, namely Krytox 143AC fluid batch MLO-71-6 (product of E. I. DuPont de Nemours and Co.), and the Fomblin Z fluids, MLO-72-22 and MLO-79-129 (products of Montedison), and P-3 additive were obtained through the courtesy of Mr. C. E. Snyder, Air Force Wright Aeronautical Laboratories.

The degradation apparatus was a modified, scaled-down version of the AFML Micro-O-C-Test arrangement [ref. 14]. It was described in detail previously [ref. 6,11]. The schematics given in Figures 9 and 10 show the reaction tube configuration and the rod assembly for holding the metal coupon specimens. The metal coupons were 3/8" OD and 1/8" ID. These were obtained from Metaspec Company, San Antonio, Texas. For heating of sample tubes in a vertical position, a modified Lindberg Heavy-Duty box furnace, Type 51232 (see Figure 11) 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 Figure 9), the extra gas reservoir was in the ambient environment.

In a typical experiment, the fluid was introduced into the degradation tube (see Figure 9) 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 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 mass spectrometry. The liquid nitrogen condensibles were fractionated through -78°C into a -196°C trap. The -196°C fractions were measured, weighed and analyzed by infrared spectroscopy and mass spectrometry. The -78°C fractions were weighed, analyzed by infrared spectroscopy, and esterified prior to subjecting to GC-MS. The fluid residue itself was weighed and subjected to infrared spectral analysis; in selected instances, molecular weight and NMR determinations were performed.

The metal coupons prior to testing 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, weighed, and suspended in the test apparatus (see Figure 10). After the completion of a given experiment, the metal coupons were washed with Freon 113, dried inside an inert atmosphere chamber, then weighed and visually inspected. The used coupons were subsequently sealed in Mylar envelopes.

GC-MS analyses were performed employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2740 gas chromatograph and a DuPont 21-094 data acquisition and processing system.

5. CONCLUSIONS

Summarized below are conclusions reached.

1. Degradation inhibitors perfluoroalkylether perfluorophenyl phosphine (P-3) and a monophospha-s-triazine at 1% per weight concentration almost completely arrested the degradation of Fomblin Z in the presence of Ti(4Al, 4Mn) alloy in oxygen at 288°C for more than 75 hr. At concentrations lower by a factor of 5, the monophospha-s-triazine was found to exhibit comparable effectiveness.

2. The monophospha-s-triazine offered better surface protection to an M-50 alloy on exposure to Fomblin Z at 288°C in oxygen for 24 hr than was the case with the P-3 additive.

3. Titanium and aluminum were found to accelerate the degradation of Fomblin Z fluid to a significantly lower degree than Ti(4Al, 4Mn) alloy.

4. Pretreatment at 343°C in oxygen of certain batches of Fomblin Z fluid was detrimental to the materials' thermo-oxidative stability at 288°C.

5. Products formed on degradation of Fomblin Z fluid, in the presence of metals, indicated that the operative mechanisms are the same as in poly(hexafluoropropene oxide).

6. Evaluation of the effect of different metals and alloys on Krytox fluids revealed that no prediction can be made as to the degree of influence of a given alloy upon fluid's degradation based on the behavior of the alloy's constituent metals both in pure form or in combination.

7. The catalytic action of metals and alloys on the degradation of hexafluoropropene oxide derived fluids (Krytox 143AC) and Fomblin Z fluids followed the same direction but it required significantly less drastic conditions to decompose Fomblin Z.

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TABLE I

EVALUATION OF THE EFFECTIVENESS OF ADDITIVES IN ARRESTING DEGRADATION OF FOMBLIN Z FLUID IN THE PRESENCE OF Ti(4Al, 4Mn) ALLOY IN OXYGEN AT 288°C

Test No.[a]	Amt Used, g	Duration hr	Ti(4Al, 4Mn) coupon	Additive	Condensible Products		Oxygen Consumed				CO Produced	
					mg	mg/g[b]	mg	mg/g[c]	mg/mg[d]	%[e]	mg	mg/mg[f]
40	3.74	24	No	None	92.0	24.60	n.d.[g]	n.d.	n.d.	n.d.	n.d.	n.d.
61	2.82	24	No	1% C_2PN_3[h]	2.4	0.85	0.88	0.81	0.37	0.78	0.05	0.02
41	3.84	8	Yes	None	2235.0	582.03	51.06	13.31	0.02	17.2	4.09	0.00
42	3.67	24	Yes	1% P-3[i]	4.1	1.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
46A	3.60	72	Yes	1% P-3	8.4	2.33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
46B	3.58	48	Yes	1% P-3	867.5	242.32	27.82	7.77	0.03	25.3	0.96	0.00
55A	4.94	86	Yes	1% P-3	10.9	2.21	3.05	0.62	0.28	2.8	0.83	0.08
55B	4.92	16	Yes	1% P-3	8.8	1.79	1.19	0.24	0.14	1.1	0.19	0.02
55C	4.91	8	Yes	1% P-3	7.6	1.55	1.53	0.31	0.20	1.4	0.21	0.03
55D	4.90	16	Yes	1% P-3	134.5	27.45	2.24	0.46	0.02	2.0	3.04	0.02
54A	3.81	24	Yes	1% C_2PN_3	2.6	0.68	0.26	0.07	0.10	0.2	0.08	0.04
54B	3.81	48	Yes	1% C_2PN_3	2.5	0.66	0.55	0.14	0.22	0.5	0.13	0.05
54C	3.80	28	Yes	1% C_2PN_3	359.0	94.23	1.94	0.51	0.01	1.8	3.46	0.01
56A	4.03	24	Yes	0.2% C_2PN_3	4.1	1.02	1.41	0.35	0.34	1.3	0.10	0.03
56B	4.02	24	Yes	0.2% C_2PN_3	4.2	1.04	1.33	0.33	0.32	1.2	0.16	0.04
56C	4.02	24	Yes	0.2% C_2PN_3	6.4	1.59	1.13	0.28	0.18	1.0	0.23	0.04
56D	4.01	8	Yes	0.2% C_2PN_3	4.0	1.00	1.22	0.30	0.30	1.1	0.28	0.07
56E	4.01	8	Yes	0.2% C_2PN_3	3.1	0.77	1.75	0.44	0.56	1.6	0.11	0.04
56F	4.01	8	Yes	0.2% C_2PN_3	4.3	1.07	1.48	0.37	0.34	1.3	0.28	0.06
56G	4.00	8	Yes	0.2% C_2PN_3	7.6	1.91	0.75	0.19	0.10	0.7	0.24	0.03
56H	4.00	24	Yes	0.2% C_2PN_3	2608.5	652.13	23.23	5.81	0.01	21.2	8.18	n.d.

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a) The fluid used was batch MLO-72-22 which was 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.

b) Products in mg per g of fluid employed.

c) Oxygen consumed in mg per g of fluid employed.

d) Oxygen consumed in mg per mg of products formed.

e) Percent of oxygen available.

f) Mg of carbon monoxide formed per mg of products liberated.

g) Not determined.

h) 1-diphenylphospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-2,4,6-triazine.

i) MLO-80-279.

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TABLE II

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

	Inhibitor	Cr	V
Unused M-50		.105	.043
Test 36	Monophospha-*s*-triazine	.103	.045
Test 37	Perfluorophenyl phosphine	.104	.044
Test 38	None	.102	.045

TABLE III

EFFECT OF METALS ON THE DEGRADATION OF FOMBLIN Z FLUID IN OXYGEN

Test	Atm	Temp	Duration		Condensible Products		Oxygen Consumed				CO Produced	
No.[a]	Used,g	°C	hr	Metal	mg	mg/g[b]	mg	mg/g[c]	mg/mg[d]	%[e]	mg	mg/mg[f]
63	30.17	343	24	none	290.6	9.26	3.04	0.10	0.01	3.04	5.09	0.02
71	30.00	343	24	none	303.2	10.10	8.82	0.29	0.03	3.13	1.15	0.00
64[g]	3.20	288	24	none	265.0	82.81	4.73	1.48	0.02	4.32	0.13	0.00
66[g]	3.76	288	8	Ti(4Al,4Mn)	?[h]	?	?	?	?	?	?	?
69[g]	3.54	288	8	Ti	1365.3	385.68	18.07	5.10	0.01	12.57	0.39	0.00
70[g]	3.64	288	8	Al	879.7	241.67	13.66	3.75	0.02	12.62	0.49	0.00
72A	3.15	288	24	none	38.4	12.19	2.39	0.76	0.06	2.12	0.18	0.00
72B	3.10	288	24	none	33.4	10.77	2.23	0.72	0.07	1.98	0.19	0.01
73	3.67	288	8	Ti(4Al,4Mn)	2228.7	607.28	46.57	12.69	0.02	16.11	6.25	0.00
74A	3.56	288	8	Ti	159.7	44.86	2.71	0.76	0.02	0.94	0.50	0.00
74B	3.42	288	16	Ti	1620.5	473.84	59.70	17.46	0.04	20.93	0.38	0.00
75A	3.50	288	8	Al	344.5	98.43	9.58	2.74	0.03	3.27	0.45	0.00
75B	3.15	288	8	Al	199.6	63.16	7.73	2.45	0.04	2.67	0.27	0.01
75C	2.93	288	24	Al	290.6	99.18	9.38	3.20	0.03	3.21	0.32	0.00

a) The fluid used was batch MLO-79-196, as received. 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.
b) Products in mg per g of fluid employed.
c) Oxygen consumed in mg per g of fluid employed.
d) Oxygen consumed in mg per mg of products formed.
e) Percent of oxygen available.
f) Mg of carbon monoxide formed per mg of products liberated.
g) These tests utilized the residue from Run No. 63.
h) In this test, all the fluid was degraded and a portion of the products leaked out.

TABLE IV

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $CF_3OCF_2OCF_2OCF_2OCF_2OCF_3$ (MW, 418)[a]

m/e		m/e		m/e	
28	17.7	49	19.3	90	3.6
31	8.8	65	21.3	135	100.0
32	5.9	68	79.2	136	14.1
46	31.7	69	7.2	201	10.0

a) Peaks having intensities less than 2% of the base peak are not reported.

TABLE V

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_2F_5OCF_2OCF_2CF_2OCF_2OCF_3$ (MW, 452)[a]

m/e		m/e		m/e	
28	13.4	81	5.8	136	9.3
31	26.5	97	42.9	147	3.0
47	30.4	100	56.8	163	29.2
50	33.0	101	4.6	169	8.6
59	12.0	109	5.1	185	65.5
66	13.1	116	4.1	186	9.3
69	89.6	119	100.0	197	4.3
70	18.3	120	38.6	213	31.8
75	28.8	131	3.1	251	23.0
78	10.6	135	75.7	301	9.4

a) Peaks having intensities less than 3% of the base peak are not reported.

TABLE VI

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $CF_3OCF_2CF_2OCF_2CF_2OCF_2CO_2Me$ (MW, 426)[a]

m/e		m/e		m/e	
28	22.3	67	3.4	127	7.0
29	29.8	69	74.3	131	18.4
30	14.3	70	8.0	135	33.7
31	37.3	75	9.7	147	3.3
32	3.3	78	30.2	149	9.9
33	10.4	80	8.0	163	5.6
43	5.1	81	53.0	166	3.1
44	9.5	82	3.0	169	4.5
45	16.2	97	20.8	175	4.8
47	35.5	99	15.4	178	5.7
50	39.2	100	51.7	185	34.6
51	8.3	101	[illegible] 7	197	3.1
59	100.0	109	76.9	213	3.1
60	23.6	110	10.4	225	27.5
61	7.3	116	4.0	251	10.1
65	50.1	119	78.6	291	5.5
66	12.6	120	16.4	325	7.9

a) Peaks having intensities less than 3% of the base peak are not reported.

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TABLE VII

EFFECT OF METALS ON THE DEGRADATION OF KRYTOX FLUID

IN OXYGEN AT 316°C OVER A 24 HR PERIOD

Test No.[a]	Amt Used,g	Metal	Condensible Products		Oxygen Consumed				CO Produced	
			mg	mg/g[b]	mg	mg/g[c]	mg/mg[d]	%[e]	mg	mg/mg
48A	4.53	3 Ti[g]	4.2	0.93	1.51	0.33	0.36	1.4	0.17	0.04
48B	4.53	3 Ti[g]	40.3	8.88	6.05	1.34	0.15	5.5	0.71	0.02
57A	6.93	3 Ti[h]	6.3	0.91	2.19	0.32	0.35	2.1	0.50	0.08
57B	6.92	3 Ti[h]	59.1	8.54	8.04	1.16	0.14	7.4	1.45	0.02
57C	6.86	3 Ti[h]	137.0	15.97	17.84	2.60	0.13	17.0	0.98	0.01
59A	4.68	Ti(6Al, 4V)	242.1	51.72	27.89	5.96	0.12	25.4	2.14	0.01
59B	4.48	Ti(6Al, 4V)	134.3	29.98	11.89	2.65	0.09	10.9	1.75	0.01
59C	4.35	Ti(6Al, 4V)	918.6	211.18	97.86	22.50	0.11	85.7	1.51	0.00
60A	4.98	Ti(8Mn)	294.6	59.2	34.14	6.85	0.12	31.3	0.90	0.00
60B	4.77	Ti(8Mn)	151.0	31.7	18.93	3.97	0.12	17.3	0.54	0.00
60C	4.66	Ti(8Mn)	189.2	40.60	22.84	4.90	0.12	20.94	0.52	0.00
62A	4.79	Ti(4Al, 4Mn)	758.7	158.4	75.07	15.7	0.10	68.2	0.05	0.00

a) The fluids used in the test series 48 and 57 were pretreated at 343°C in oxygen for 194 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.

b) Products in mg per g of fluid employed.

c) Oxygen consumed in mg per g of fluid employed.

d) Oxygen consumed in mg per mg of products formed.

e) Percent of oxygen available.

f) Mg of carbon monoxide formed per mg of products liberated.

g) Three Ti coupons were used stacked one on top of the other.

h) Three Ti coupons were used separated by 6 mm glass spacers.

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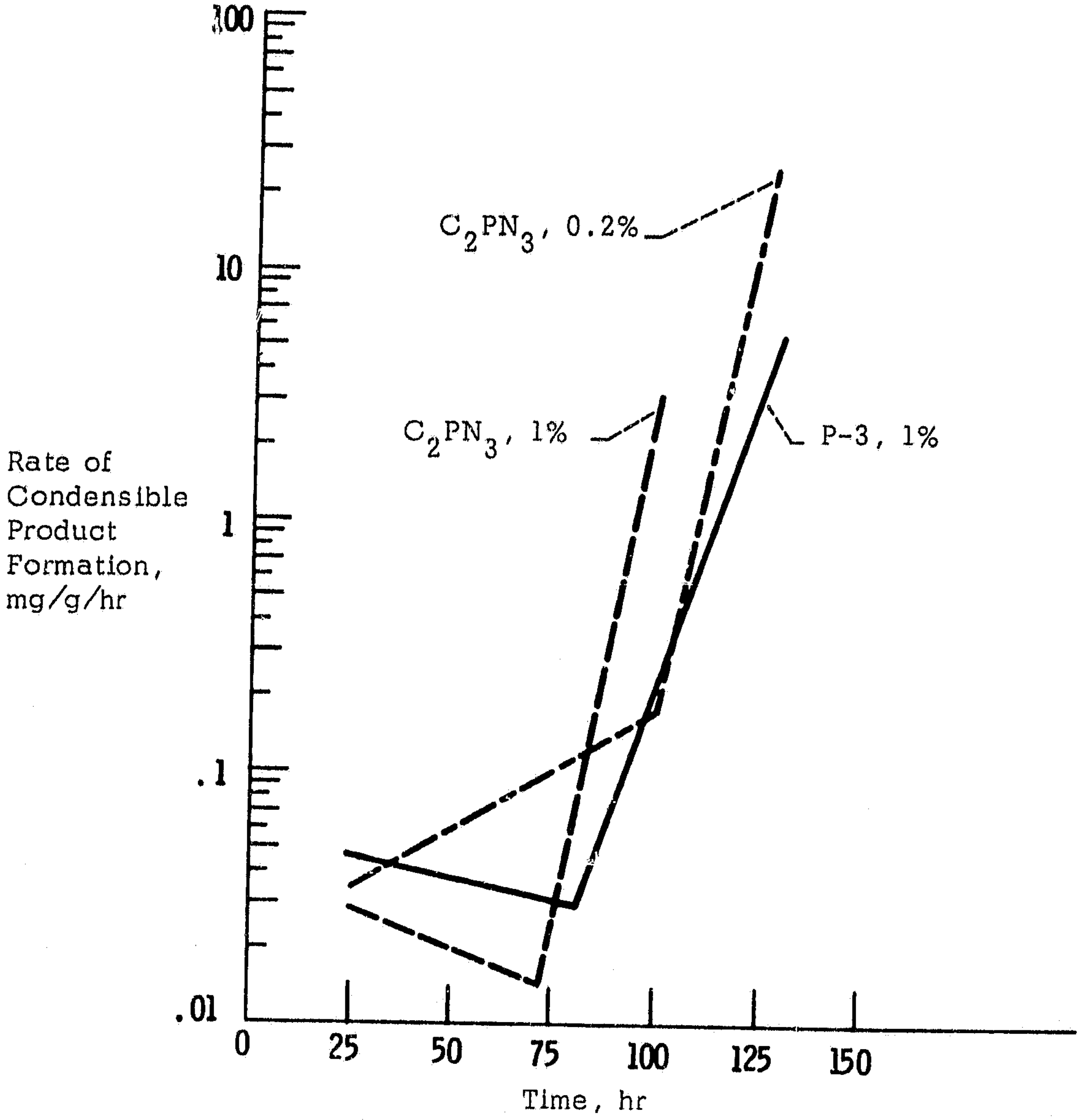
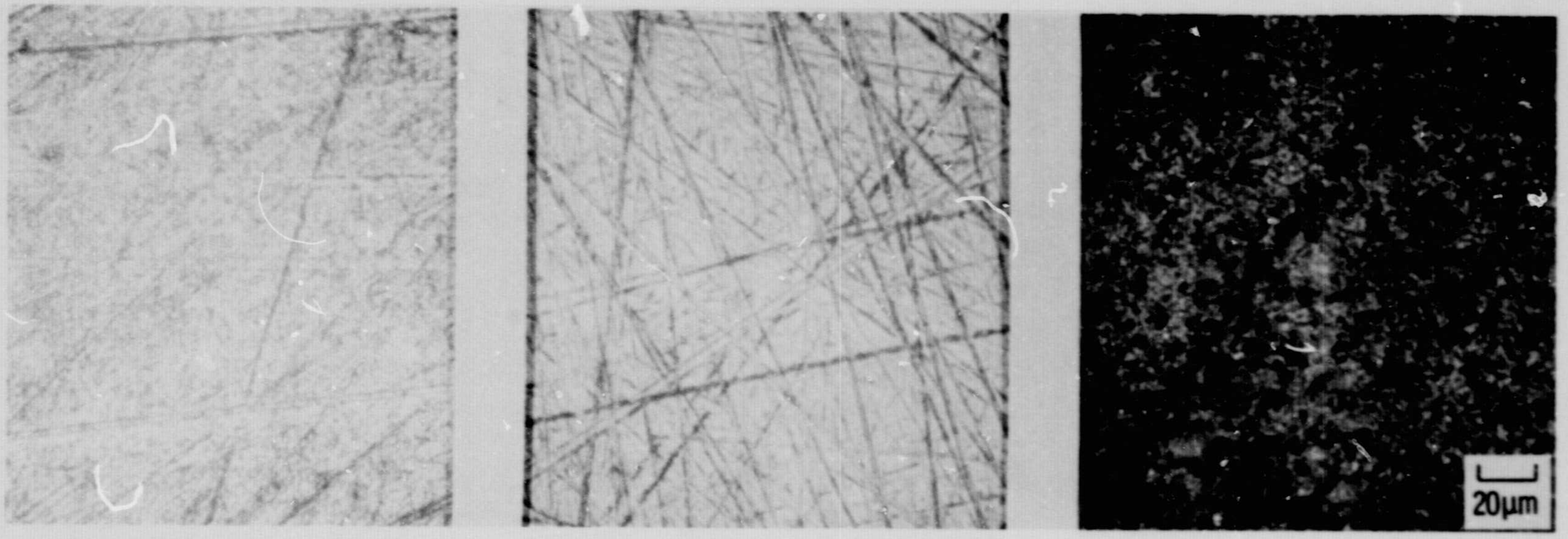


Figure 1: Effectiveness of inhibitors on Fomblin Z degradation in oxygen at 288°C as a function of time



Treated in the presence of C_2PN_3 inhibitor in Fomblin Z at 288°C in O_2 for 24 hr

Unused polished coupon

Treated in the presence of P-3 inhibitor in Fomblin Z at 288°C in O_2 for 24 hr

Figure 2: Photomicrographs of M-50 coupons

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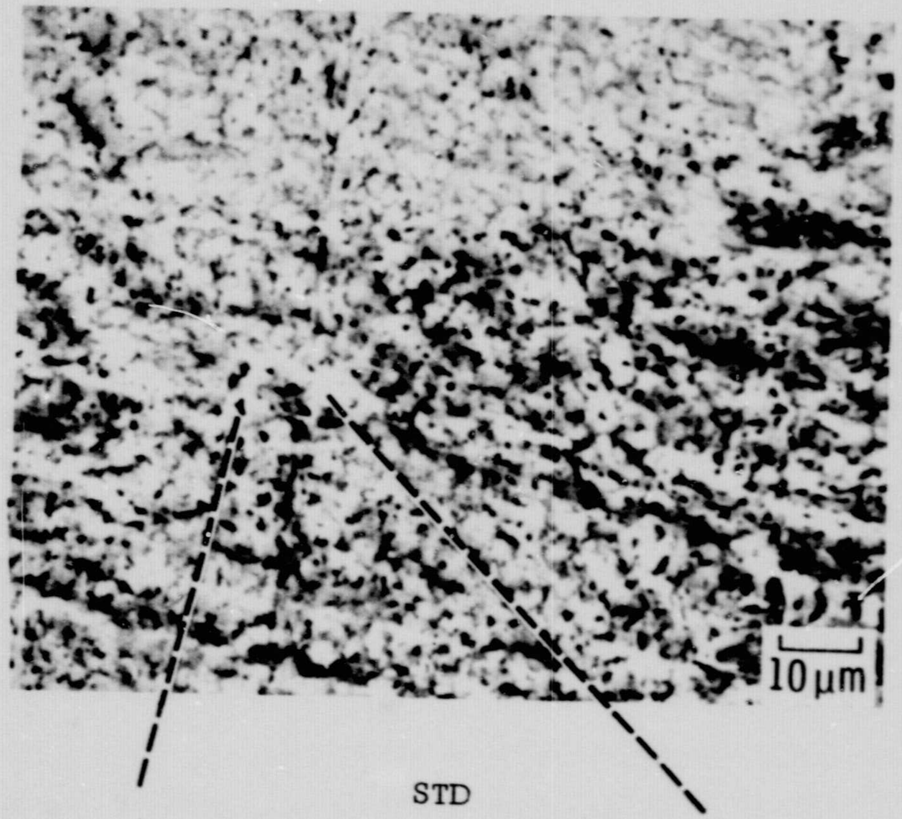
Figure 3: SEM of M-50 coupon after exposure for 24 hr to Fomblin Z at 288^{O}C in oxygen



		STD		
Cr	.182	.105	Cr	.084
V	.047	.043	V	.038

(Ratioed to Fe)

Figure 4: SEM of M-50 coupon after exposure for 24 hr to Fomblin Z at 288°C in oxygen in the presence of P-3 inhibitor

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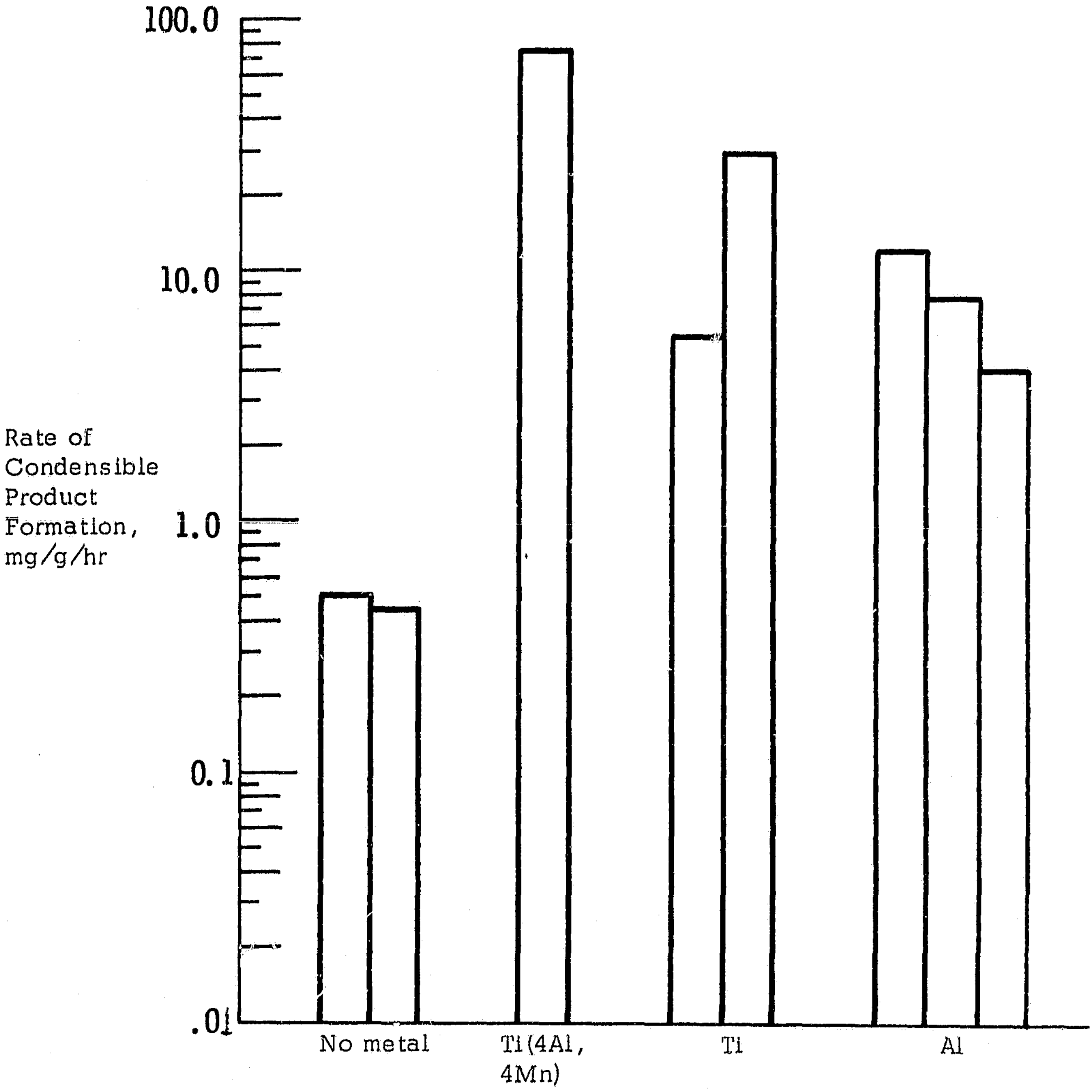

Figure 5: Effect of metals on the degradation of Fomblin Z fluid in oxygen at 288°C

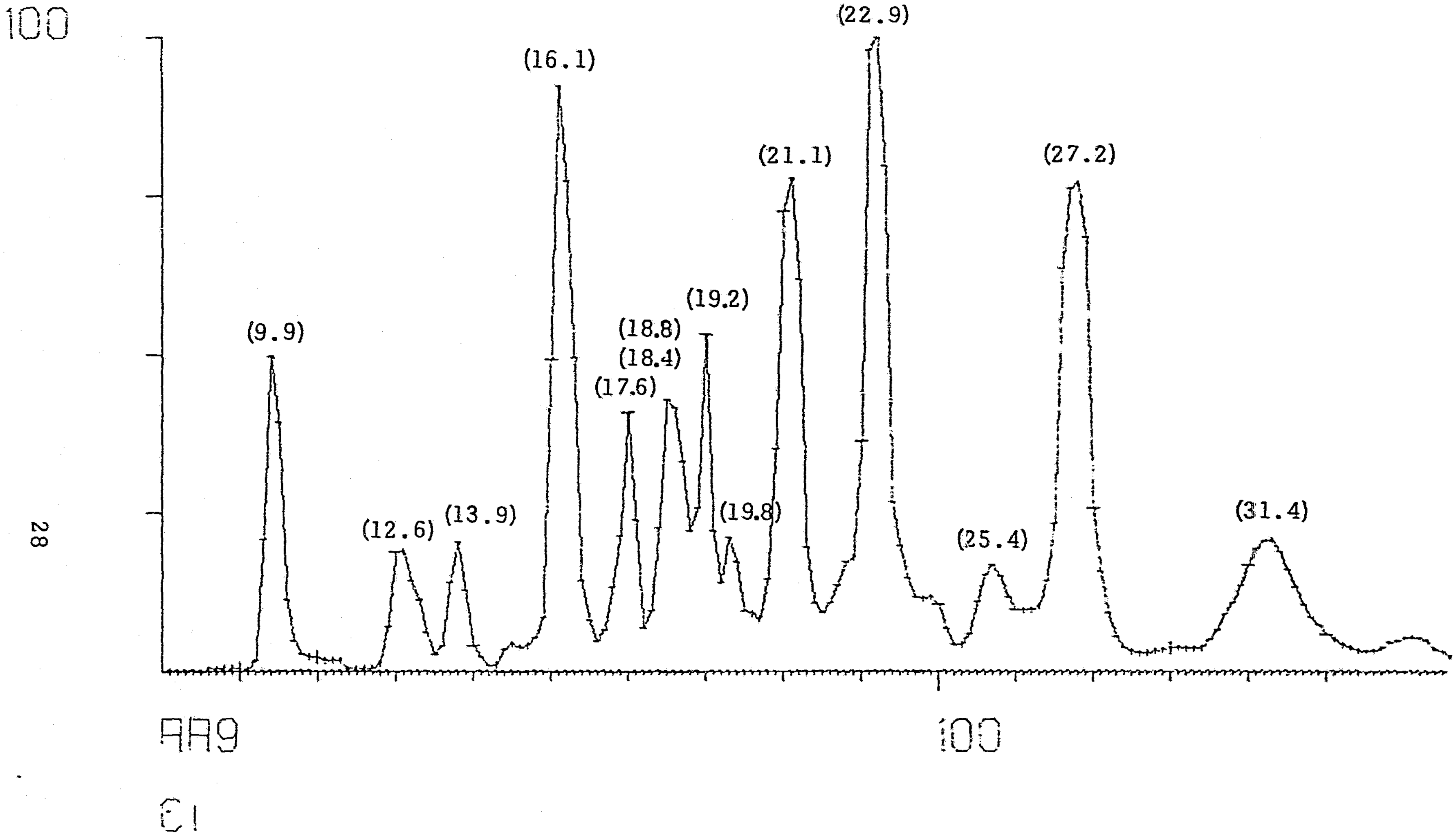

Figure 6: GC-MS trace of condensible volatiles formed, $-78^{\circ}C$ fraction, on exposure of Fomblin Z to O_2 and Ti(4Al, 4Mn) alloy at $288^{\circ}C$ for 8 hr (Conditions: 8' x 1/8" Porapak Q column programmed, $40-220^{\circ}C$ at $8^{\circ}C/min$, He flow 35 ml/min)

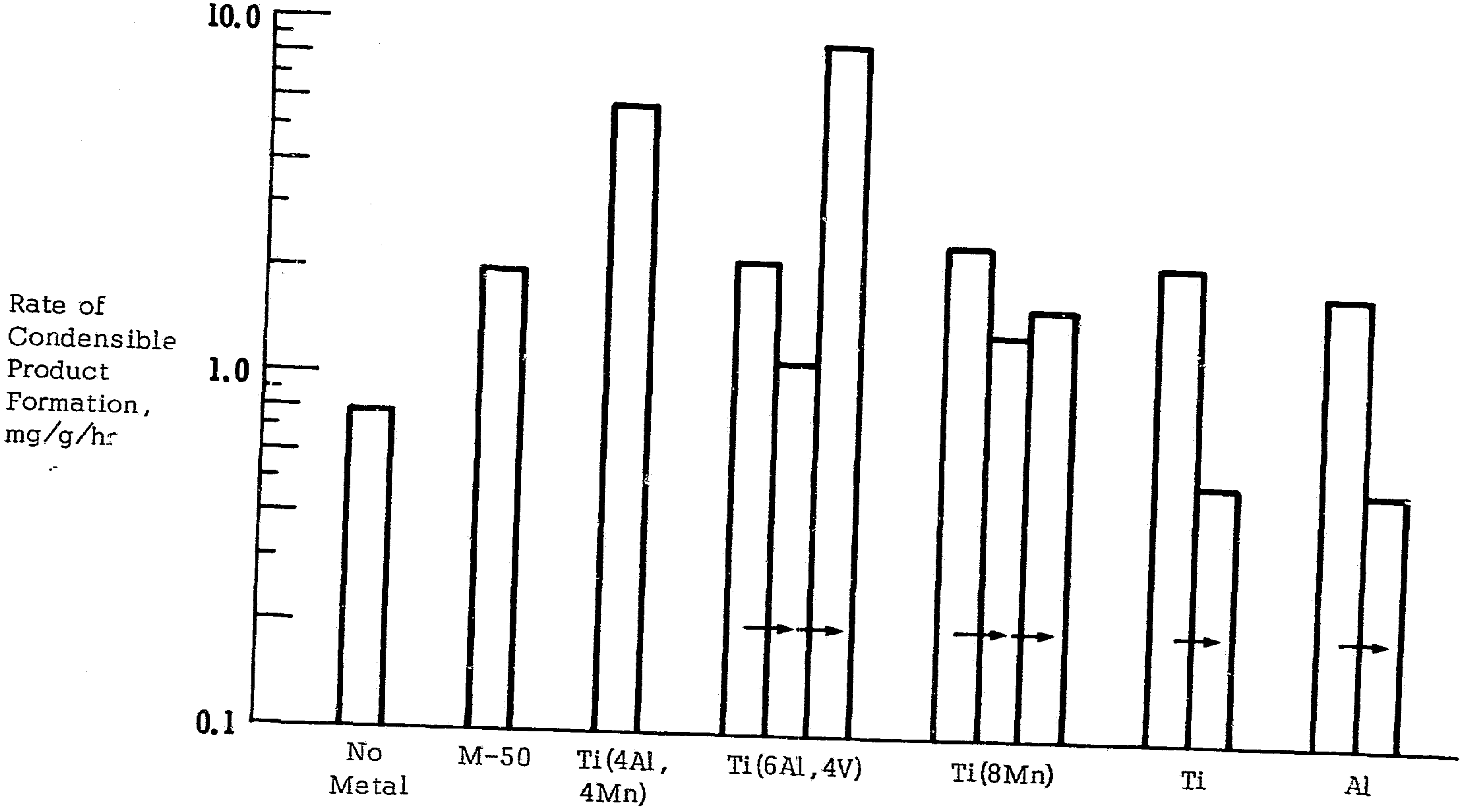

Figure 7: Effect of metals on the degradation of Krytox fluid in oxygen at 316°C over 24 hr

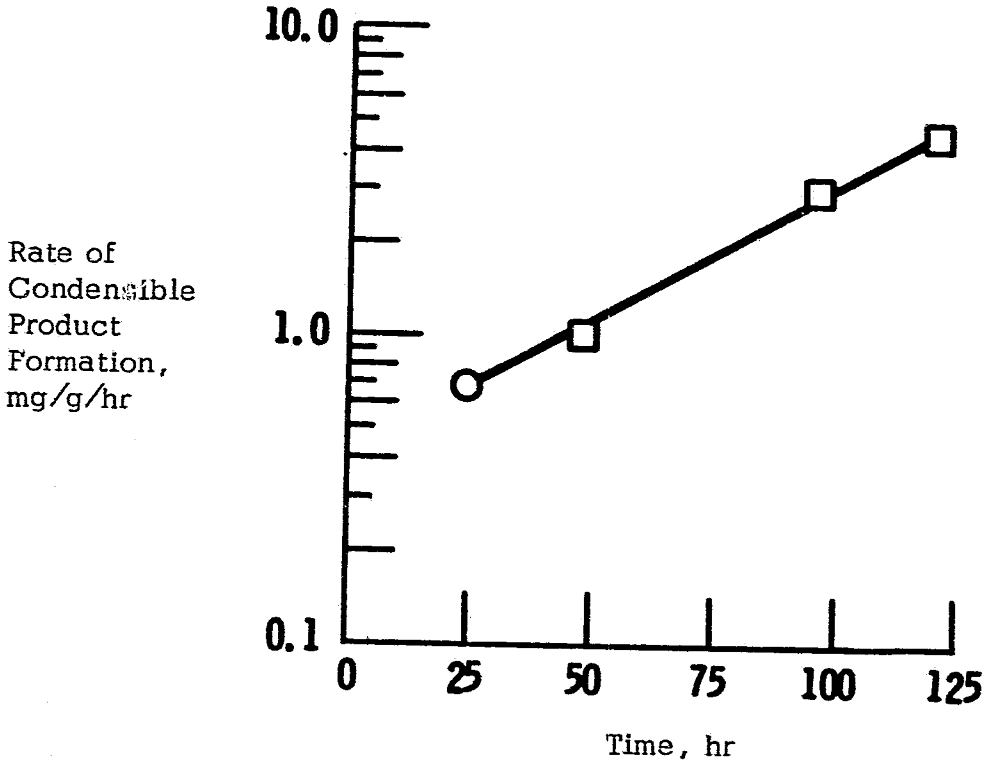

Figure 8: Effect of Ti(4Al,4Mn) on the degradation of Krytox fluid in oxygen at 288°C

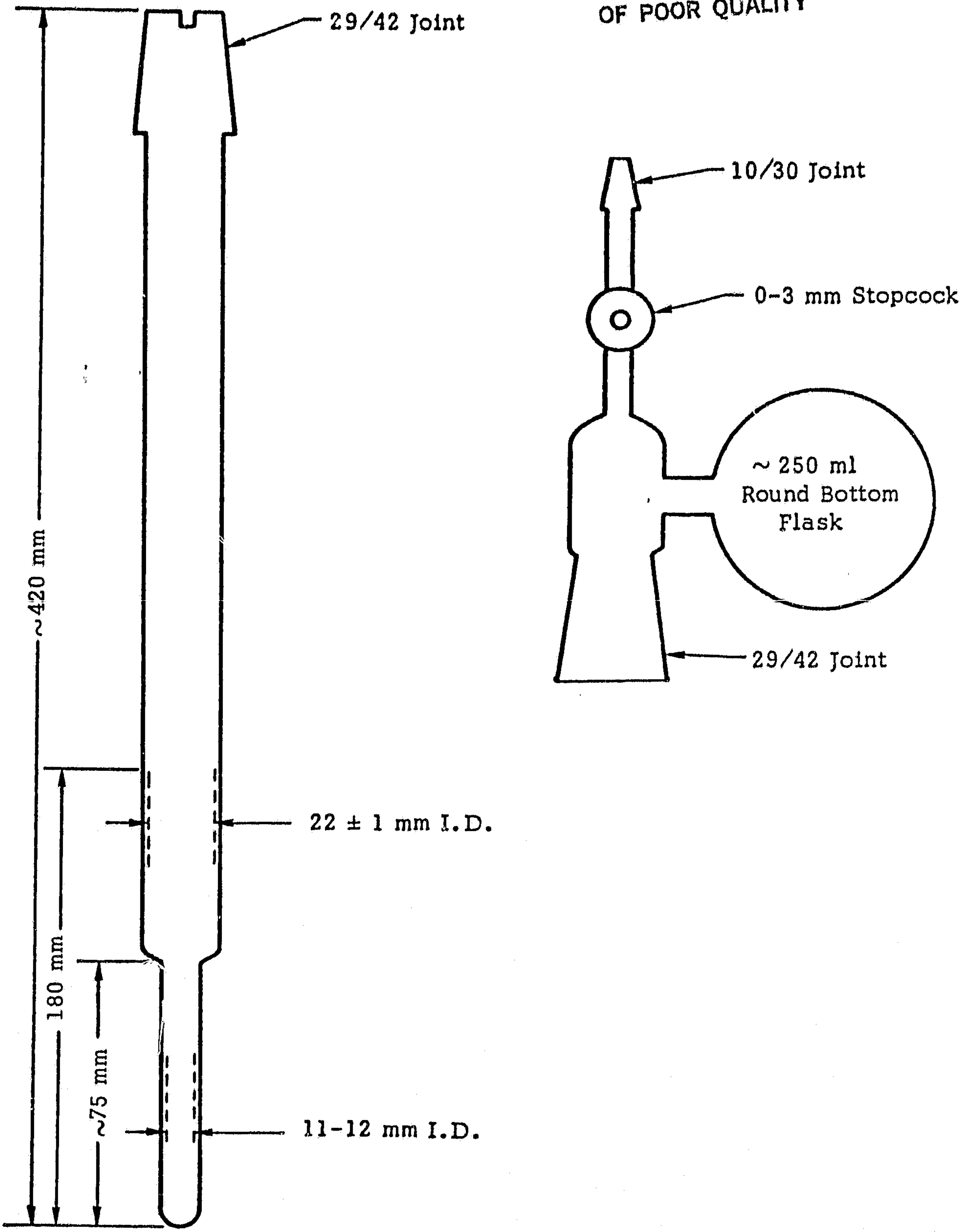

Figure 9 : Decomposition tube and adapter

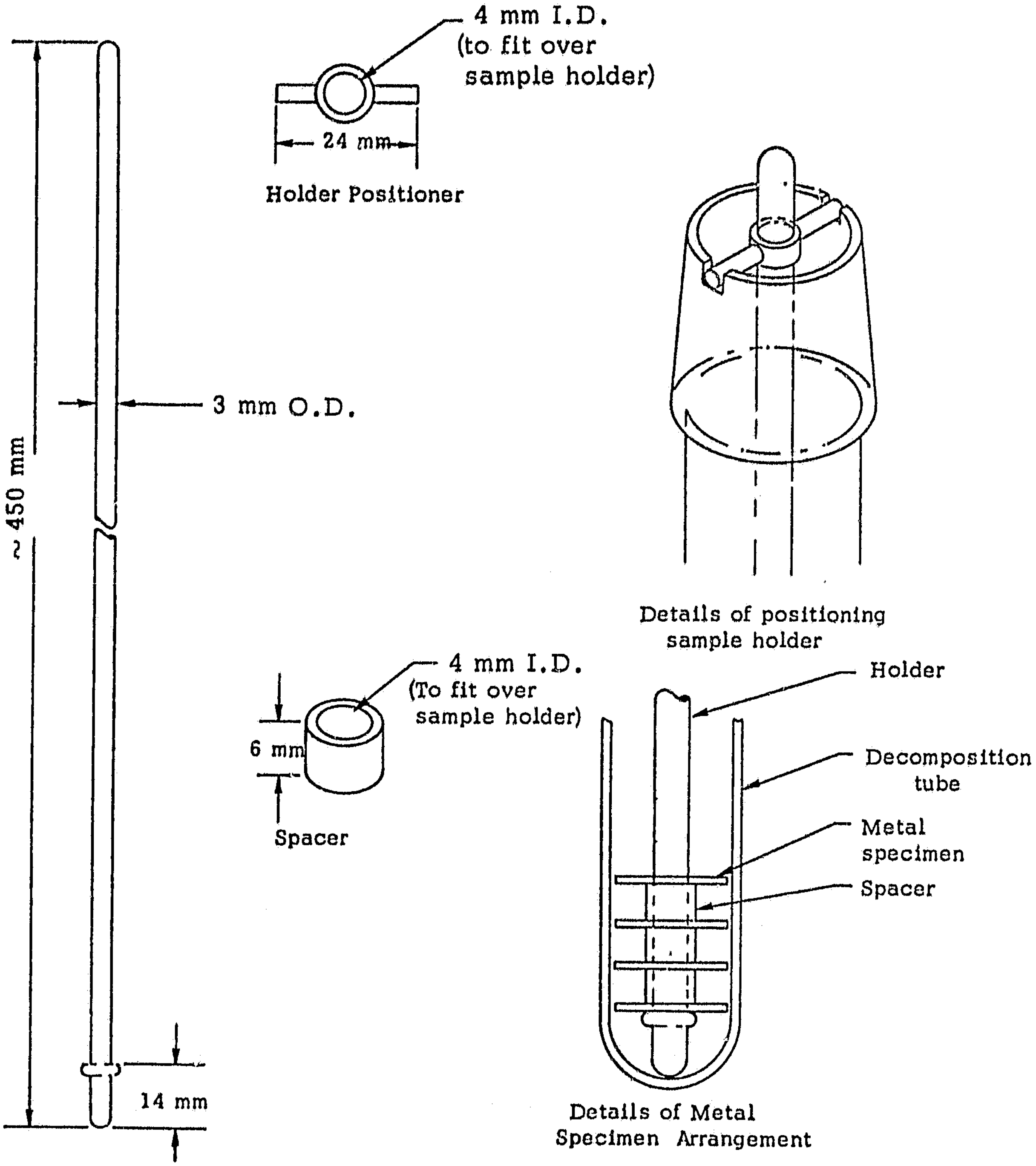

Figure 10: Metal specimen holder arrangement

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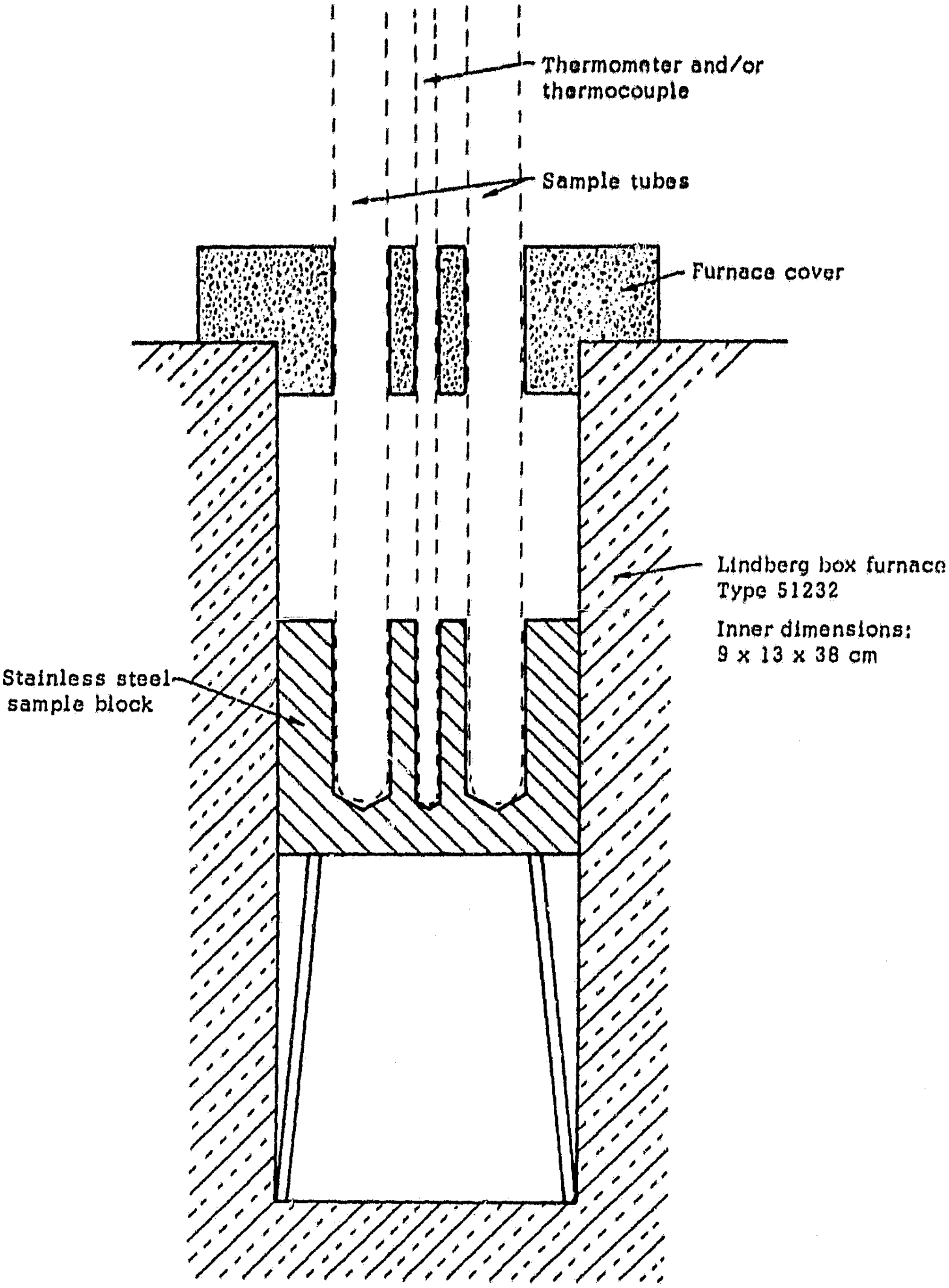

Figure 11: Box furnace arrangement