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IMPROVED PERFLUOROALKYLETHER FLUID DEVELOPMENT

PHASE II REPORT
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FOREWORD

The Phase II report of this Small Business Innovation Research contract describes the work performed by Ultrasystems, Inc. during the period 1 March 1985 through 30 September 1987 under Contract NAS3-24632, "Improved Perfluoroalkylether Fluid Development". The investigations were carried out by S. R. Masuda, J. H. Nakahara, 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.

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1. SUMMARY

The objective of the Phase II Small Business Innovation contract was to optimize and scale up the linear perfluoroalkylether stabilization process and to provide test data regarding the fluids' thermal oxidative stability in the presence of metal alloys. Another objective was to develop guidelines regarding commercial and experimental fluids' thermal oxidative stability.

The stabilization process utilizing Fomblin Z-25 fluid was scaled up to 300 g of fluid and the modified fluid (MW, 7050; viscosity, 111 cSt at 40°C) was obtained in an overall yield of 71%. The fluid was stable at 316°C in oxygen in the presence of M-50 alloy for more than 24 hr but less than 40 hr; the amount of volatiles produced after 24 hr was 5.5 mg/g. In the presence of Ti(4Al,4Mn) alloy, under the above conditions, following an exposure of 24 hr, the amount of volatiles formed was 6.2 mg/g; 56 hr exposure yielded 13.9 mg/g. The commercial fluid at 288°C (in oxygen) in the presence of M-50 after 15 hr exposure decomposed extensively, 342 mg/g; in the presence of Ti(4Al,4Mn) alloy after only 8 hr at 288°C, the amount of volatiles was 191 mg/g.

Formulation of the commercial fluid with C_2PN_3 additive was not as effective as the processing; M-50 alloy, 316°C, 16 hr, 72 mg/g; Ti(4Al,4Mn) alloy, 316°C, 40 hr, 520.3 mg/g. The respective values for the P-3 additive were: M-50 alloy, 316°C,

40 hr, 9.5 mg/g; Ti(4Al,4Mn) alloy, 316°C, 40 hr, 113.7 mg/g. The modification of Fomblin Z-60 fluid was unsuccessful since the process, in this case, was accompanied by a decrease in molecular weight and viscosity giving essentially a stabilized Z-25 fluid.

Two grease formulations, based on Fomblin Z fluid, were evaluated under the program. The grease BR600-LB44 exhibited thermal oxidative stability comparable to that of the base fluid; the thermal oxidative stability of BR601-LB57 was lower. The greases were more resistant to M-50 alloy degradative action than the base fluid. Additives C_2PN_3 and P-3 were effective in arresting the degradation caused by Ti(4Al,4Mn) alloy.

All the perfluoroalkylether fluids studied were stable in nitrogen at 343°C. The thermal oxidative stability in the absence of metal alloys varied, with Aflunox exhibiting the best behavior. All the fluids were degraded in oxygen at 316°C during 24 hr exposure to Ti(4Al,4Mn) alloy with the exception of perfluoroalkylether-substituted triazine and the modified Z-25. The action of M-50 alloy was less detrimental. The presence of $-OCF_2O-$ linkages promoted the ease of decomposition.

2. INTRODUCTION

Aerospace systems require lubricants which can serve under oxidizing conditions in the presence of metals and metal alloys at extremes of temperatures. The linear perfluoroalkylethers presently employed in these applications [Ref 1] possess the required liquid ranges, but have been found to undergo degradation and cause corrosion [Ref 2-6]. Under the Phase I program [Ref 7], the feasibility of stabilizing the commercially available material by removal of weak sites, followed by linking of the acid fluoride terminated chains via monophospha-s-triazine ring arrangements, was established. The product obtained exhibited essentially identical molecular weight and viscosity at $40^{o}C$ as the original fluid; however, in oxygen at $300^{o}C$ in the presence of Ti(4Al,4Mn) alloy its stability was better by a factor of at least 2.6×10^{3}, based on volatiles formed than that of the untreated fluid. Specifically, during an 8 hr period under the above denoted conditions, the stabilized fluid produced 0.4 mg of volatiles per gram of fluid, whereas the unmodified fluid, upon such exposure, formed 1,061 mg/g; i.e., it was essentially completely unzipped. Phase II research was directed at the process optimization and scale up, as well as extension to fluids other than those studied under the Phase I program.

Inasmuch as a number of different types of perfluoroalkylethers are presently available both commercially and as research materials, another objective of the current work was to determine their thermal oxidative behavior, both alone and in the presence of metal alloys and to develop guidelines on relative stabilities. The ultimate aim was to provide data regarding the given fluids' applicability for service with respect to temperature, exposure duration, presence of oxygen, and the metals of construction. In conjunction with the above, degradation inhibitors were also evaluated and their efficiency was assessed as compared to modified fluids.

3. RESULTS AND DISCUSSION

The Phase II program, as mentioned in the preceding section, was directed at modification of commercially available perfluoroalkylether fluids and at assessing the thermal oxidative stabilities of commercial and experimental fluids. For clarity of presentation, the technical discussion was divided into sections addressing each of these topics.

3.1 Improved Perfluoroalkylether Synthesis

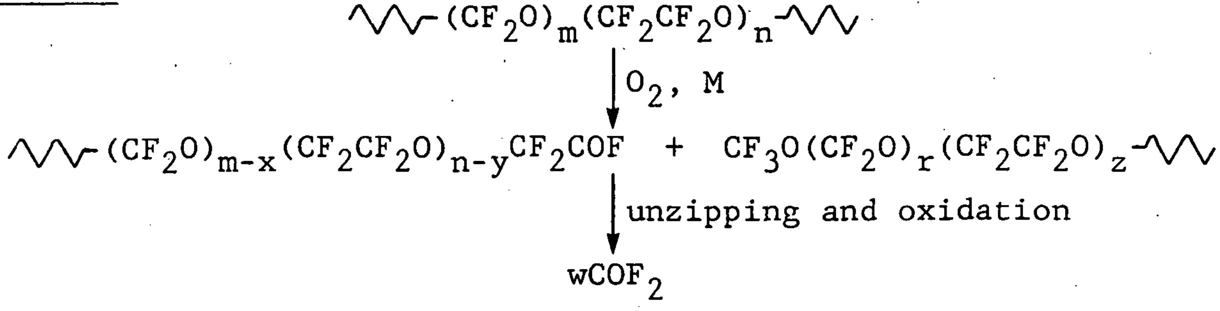
Under Phase I [Ref 7], a procedure was developed which led to the production of a fluid of vastly improved stability at elevated temperatures in oxidizing atmospheres in the presence of titanium alloys as compared to the as-received Fomblin Z-25 fluid. One of the objectives of the Phase II program was to determine whether this process provides fluid superior to the additive-fluid formulation and, if that is the case, to scale up the operations and to establish whether the procedure is applicable to different types of Fomblin Z fluids. For the current studies, large batches of Z-25 (low viscosity) and Z-60 (high viscosity) fluids were obtained from Montefluos. Their thermal oxidative stabilities and the influence of metals on the degradation differed somewhat from that of the previously investigated materials. These aspects will be discussed in detail in Section 3.2. It should be noted that the average molecular weights of the two new materials, Z25-P28 and Z60-P1, are not in line with their viscosities as compared to Z25-P21 and MLO-79-196. This is evident from the Table I compilation. The high viscosities of the new materials, in conjunction with their relatively low molecular weights, indicate the presence of low molecular weight constituents admixed with high molecular weight species.

3.1.1 Z-25 based fluid

Under Phase I, MLO-79-196, a fluid received in 1979 from Montefluos, was subjected to the stabilization process. A corresponding fluid, insofar as application and thus general properties are concerned, according to Montefluos, is Z25-P28. This material was received early in 1985. Yet, as mentioned above, its viscosity/molecular weight relationship, as well as its behavior in the presence of Ti(4Al,4Mn) alloy was found to differ somewhat from that of the other fluids tested. The increased thermal oxidative stability in the presence of Ti(4Al,4Mn) alloy (see Section 3.2) could be due to a number of factors, one being a lower molecular weight of the individual components which, in view of the high viscosity, does not seem likely. Another cause could be lower content of reactive $-CF_2O-$ linkages. In agreement with these findings, under the conditions (240°C) at which MLO-79-196 was "degraded" fairly extensively [Ref 7], Z25-P28 has undergone hardly any degradation, as evident from Table 2 data. To attain a comparable degree of degradation, heating at 266°C over a 5 hr period was required versus 5 hr at 240°C reported previously

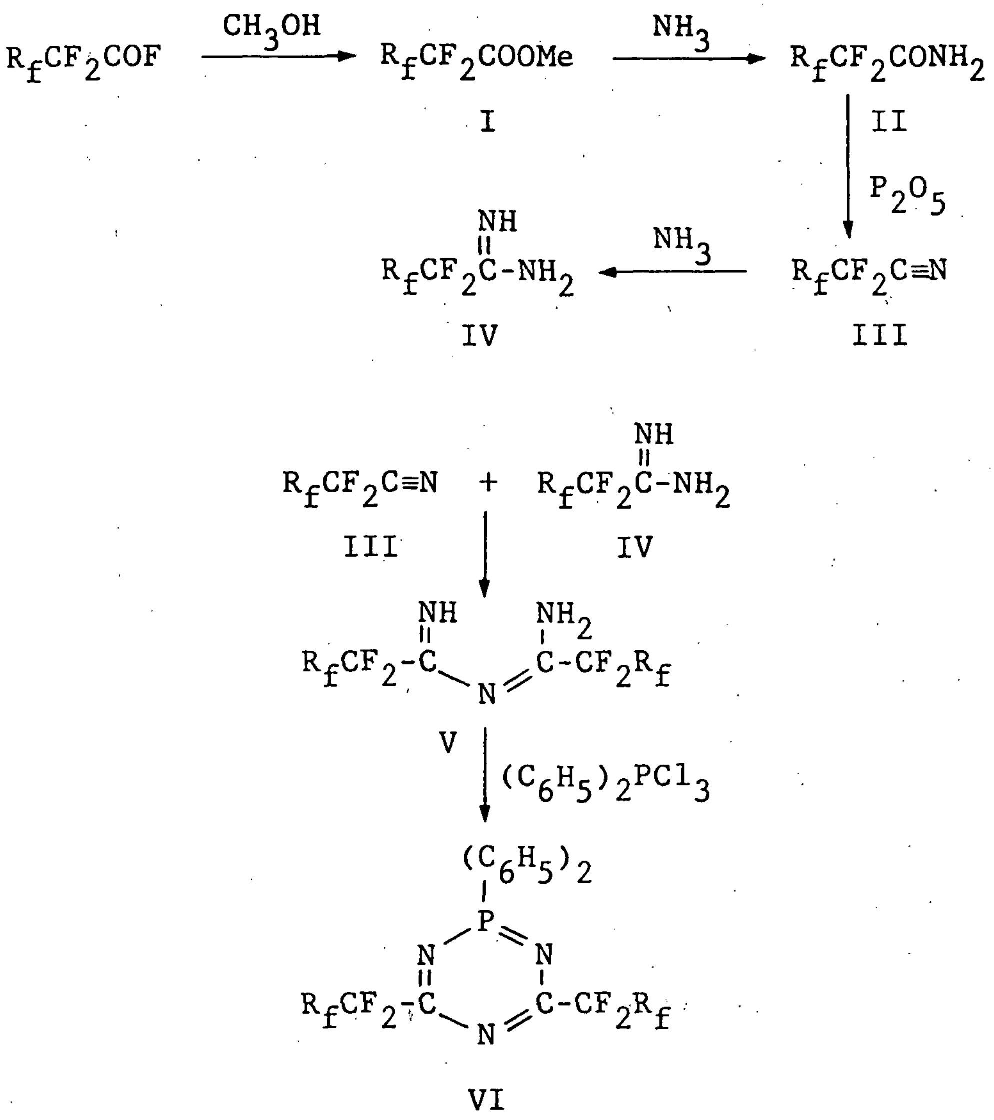
[Ref 7]. The degradation process is depicted in Scheme A:

SCHEME A



whereas the subsequent treatments followed the procedure established previously [Ref 7], according to Scheme B delineated below:

SCHEME B



As evident from the data given in Table 2, the methyl ester, Compound I, was obtained in a 77% yield, MW osmometry, 2600; MW functional, 3450; and MW based on viscosity, 3600 (using the graph developed under the Phase I program). It should be noted that the last two values correspond fairly closely to that obtained for the product in Test 16 [Ref 7]. This applies also to the yield. The discrepancy between the osmometric molecular weight and that based on viscosity is in agreement with the results obtained for the untreated fluid. The next series is summarized in Table 3.

As listed, the transformation of the methyl ester to the amide, Compound II, was quantitative. The subsequent dehydration with phosphorus pentoxide gave the desired nitrile, Compound III, in a 68% yield. The portion (18%) of relatively high volatility material was removed in vacuo at 200°C. The low volatility nitrile had a molecular weight of 6050 (osmometry).

From the nitrile, the corresponding amidine, Compound III, was obtained in a 91% yield; its number average molecular weight (6300) was in good agreement with that of its nitrile precursor. Based on the uptake of a volatile nitrile, $C_3F_7OCF(CF_3)CN$, the functional molecular weight was 30,200, indicating that 20% of the chains were terminated by the functional, namely the amidine, group. It should be pointed out that the molecular weight of 6300 corresponds closely to that of MLO-79-196 itself and its stabilized version using the same process as that utilized here. On the other hand, the molecular weight of the untreated Z25-P28 was 9800. The interaction of the nitrile, Compound III, with the amidine, Compound IV, gave the imidoylamidine, Compound V, in a quantitative yield. Up to that point, the overall yield starting with Z25-P28 fluid was 48%; unfortunately, due to the material taken out for all the characterizations, it amounted only to 3.2 g. The transformation of the imidoylamidine to the phospha-s-triazine, molecular weight 7000, was also quantitative. Unfortunately, great difficulty was experienced to free the product from excess of diphenyltrichlorophosphorane. A number of procedures were tried. Clear fluid could be only obtained by gravity filtration. The investigation of the various purification procedures resulted in a substantial material loss. Accordingly, not enough material was left over for viscosity determination. Testing of the modified fluid was carried out at 316°C. The results of the testing of this and other batches of the modified fluid are presented in Table 4. Although under Phase I [Ref 7] the upper test temperature of 300°C was employed, it was felt that for a fluid to be of use for the envisioned applications, it must withstand at least 316°C in oxygen in the presence of alloys for extended periods of times. The modified fluid, at least over the initial 16 hr period, was better by a factor of 9 than the C_2PN_3 formulated fluid (Section 2, Table 5). Thus, it is obvious that the treatment provides a more stable fluid than that resulting from simply adding phospha-s-triazine.

In view of the above encouraging data, the whole process was repeated using a five-fold scale up (Test 81, Tables 2 and 3). The overall yield of the modified fluid amounted to 64%. The molecular weight (6600) and the viscosity (104 cSt) were somewhat lower than the values found for the starting material, Z25-P28 (Table 1). On the other hand, the values corresponded fairly well to those recorded for MLO-79-196. The modified fluid was stable at 316°C in oxygen and in the presence of M-50 alloy for over 24 hr and in the presence of Ti(4Al,4Mn) alloy for at least 40 hr (see Table 4, Tests 2-6).

To provide an adequate supply of the modified fluid for NASA testing, a further scale up was carried out. As is evident from the data given in Table 2, difficulties were encountered in initiating the reaction using the relatively large mass of fluid. Initial temperature up to 319°C was required. It must be stressed that this is the outer glass surface temperature, not the liquid temperature. To prevent larger than necessary degradation extent, the process had to be interrupted and the quantity of volatiles collected and/or fluid depletion measured. Thus, in an actual uninterrupted process, the heating period will be expected to be significantly lower than the 14 hr employed here. The final weight loss was 7.5% and to ascertain that this was sufficient for weak link removal, a small portion, 20.4 g, of the fluid was employed as a pilot sample in Test 100A (Table 3). An overall yield of 58% was realized. This material was found to be completely stable for over 40 hr at 316°C in oxygen in the presence of M-50 and Ti(4Al,4Mn) alloys. Accordingly, the remainder of the fluid was subjected to the end-capping process (Test 100B, Table 3). The final product, 191.5 g, was obtained in an overall yield of 71%. The fluid was found to be stable for over 24 hr at 316°C in oxygen in the presence of M-50 alloy and for over 72 hr in the presence of Ti(4Al,4Mn) alloy under the above conditions. Both its viscosity, 111 cSt, and its molecular weight, 7000, were somewhat lower than the values recorded for Z25-P28 (148 cSt and 11000). Both were, however, higher than those found for MLO-79-196 (Table 1).

3.1.2 Z60-P1 based fluid

Stabilization studies similar to those performed on the Z25-P28 fluid were performed using the Z60-P1 fluid. In view of the absence of preliminary data, experimental conditions needed to be established. These are summarized in Table 2. Initial parameters selected paralleled those employed successfully in the case of Z25-P28 fluid. As apparent from Test 86, this resulted in a comparable weight loss; however, the viscosity was lower by a factor of 2 as compared to the Z25-P28 fluid, although initially it was higher by a factor of 2 (316 cSt at 40°C versus 154 cSt). Consequently, the operating temperature was dropped by ∿10°C. It must be noted that it is necessary to raise the temperature initially to ∿280°C to initiate the reaction. Following 5%

material loss (Test 87, Table 2), the viscosity dropped by ∿30%. The functional average molecular weight based on infrared spectral analysis of the methyl ester was 14600, whereas the molecular weight determined from viscosity relationship established under Phase I investigations was essentially identical, 15300. The reliability of the latter method is questionable due to a change in viscosity molecular weight relationships observed in the more recent samples of Fomblin Z fluids, as discussed earlier in this section.

Following the steps delineated in Scheme A, as evident from data for Test 87 listed in Table 3, the ester, Compound I, and the amide, Compound II, were obtained in essentially quantitative yields. The dehydration with phosphorus pentoxide to give the nitrile, Compound III, followed by distillation in vacuo (up to temperature of 208°C) resulted in a distillate which amounted to 3.2% by weight of the original sample. This material exhibited very strong nitrile absorption at 2265 cm^{-1}. The work-up of the residue afforded 45% yield of a fluid which exhibited a weak nitrile absorption. Using $C_7F_{15}CN$ as a standard, the infrared method gave the functional molecular weight of the product as 19400.

Difficulties were encountered in the synthesis of the amidine, Compound IV. Using the usual technique, i.e., treatment with liquid ammonia, resulted in the product still exhibiting the weak nitrile absorption. The lack of reaction was thought to be due to the very viscous nature of the reaction mixture at the low temperatures employed. However, the infrared spectrum remained the same following stirring in a closed system under 500 mm of ammonia over a 72 hr period. There was a remote chance that the weak band attributed to nitrile was due to some other entity and that amidine was formed. Based on this assumption, steps leading to Compounds V and VI were carried out resulting in an overall fluid yield of 37%. This fluid had a viscosity of 287 cSt at 40°C; no phospha-s-triazine absorption could be detected in the infrared spectrum. The material failed to survive exposure to M-50 alloy and oxygen at 316°C for 16 hr (Test 13, Table 4). Whether this failure is due to the lack of reaction of the potential nitrile links with ammonia as implied by infrared spectral analysis described above, or whether at the low, 5%, initial degradation some weak links remained, is not clear at present. It seemed more likely that the observed low stability was caused by lack of removal of the weak links. Accordingly, more drastic conditions, i.e., leading to a higher degradation extent, were employed. The pertinent data are given in Table 2, Test 96. The difficulty with thermal oxidative modification, as mentioned previously, is that initially a higher temperature needs to be utilized to initiate the process. The progress was monitored by the quantity of volatiles produced as illustrated by pressure measurements following warm-up to room temperature (after pumping down the noncondensibles).

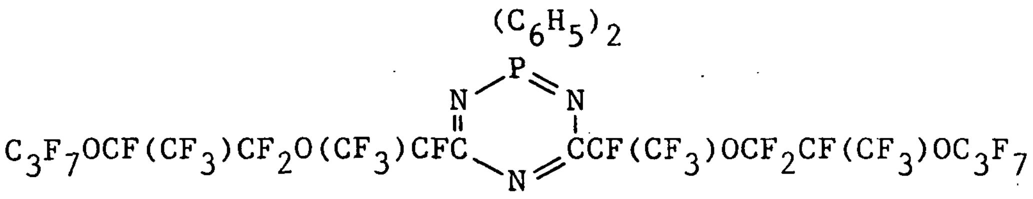
The methyl ester was obtained in an overall 83% yield and its transformation to the amide was accomplished in a quantitative yield. The synthesis of nitrile, Compound III, is a low recovery step, 49%, resulting in an overall yield up to this stage of 41%. The molecular weight of the nitrile was found to be 4100 which compares with 12000 of the starting material. From the nitrile, the corresponding amidine, Compound IV, was obtained in 82% yield. An interaction with a volatile, low molecular weight nitrile gave the functional molecular weight of 11800, indicating that approximately 1 in 3 chains are monofunctionally terminated. The formation of the imidoylamidine, Compound V, proceeded in a quantitative yield. The next step leading to phospha-s-triazine, Compound VI, gave the fluid in 70% yield (overall yield 24%; these data are summarized in Table 3). This fluid was yellow tinted, although it was clear. The average molecular weight was 5400 (Z60-P1, 12000) and the 40^{o}C viscosity was 126 cSt (Z60-P1, 316 cSt).

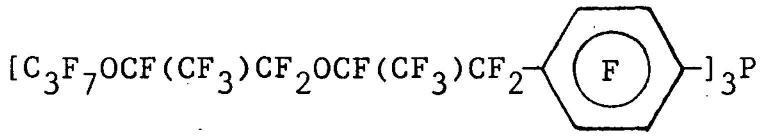
The final quantity of fluid available for evaluation was further diminished by filtration. The amount of fluid was just sufficient to determine its molecular weight, viscosity, and stability. The material failed to undergo degradation during 40 hr exposure to M-50 alloy in oxygen at 316^{o}C. Ti(4Al,4Mn) alloy under these conditions had no effect over 56 hr period. Unfortunately, although based on these evaluations the stabilization was successful, the viscosity and molecular weight are directly comparable to that of the modified Z25 fluid (MW, 6600;

viscosity at 40°C, 104 cSt). In view of the above, it has to be concluded that stabilization via weak link elimination could not be accomplished in the case of Z-60 fluid.

3.2 Evaluation of Thermal Oxidative Behavior of Linear Perfluoroalkylether Fluids, $CF_3(CF_2O)_x(CF_2CF_2O)_yCF_3$, Fomblin Z Series

The linear perfluoroalkylethers obtained by reaction of tetrafluoroethylene with oxygen under ultraviolet irradiation [Ref 1] possess extremely high viscosity index and thus are irreplaceable in applications where extremes of temperature are to be encountered. These properties prompted the modification investigations described in the preceding section. It should be pointed out that to determine the advantages of the modified fluid versus fluid formulated with appropriate additives and to develop guidelines for fluid assessment, systematic tests had to be conducted. These investigations, which are summarized in Table 5, required the evaluation of different fluid batches and types and the effect of additives and alloys on the degradation process. The two additives used were a phospha-s-triazine and a perfluoroalkylether substituted phosphine. The structural arrangements of both of these are depicted below:





The quantity of volatiles formed per gram of fluid following a 24 hr exposure at 288 and 316°C in an oxygen atmosphere was taken as a measure of thermal oxidative stability. In this evaluation were included four Z-25 fluids and one Z-60 material. The most extensive evaluations were carried out on Z25-P28 and Z60-P1 inasmuch as these were the fluids which were subjected to the modification process. Examining the data listed in Table 5, the thermal oxidative stability, as measured by exposure for 24 hr in oxygen at 288°C was found to be 12.2 (Test 1), 9.6 (Test 9), 1.4 (Test 22), 3.3 (Test 43), and 1.1 mg/g (Test 46) for MLO-79-196, Z25-P21, Z25-P28, Z25-P51, and Z60-P1 fluids, respectively. These results tend to imply that the last three fluids are inherently more thermal oxidatively stable than the earlier batches. Surprisingly enough, for the fluids where the 316°C thermal oxidative stability was determined, namely Z25-P21, Z25-P28, and Z25-P51, the degradation extent, 9.2 (Test 10), 1.7 (Test 23A), and 5.4 mg/g (Test 44A), respectively, was essentially identical to that recorded at 288°C. The behavior of the first three Z-25 fluids, MLO-79-196, Z25-P21, and Z25-P28, in the presence of M-50 at 288°C over 15 hr was found to be comparable, increasing from 293, 317, to 342 mg/g, respectively (Tests 2, 13, and 25). Based on this trend, one would expect Z60-P1 to produce even more volatiles, yet the material formed significantly less, 188 mg/g (Test 47), than any of the other fluids. If one assumes that the metal-initiated degradation proceeds via a chain scission followed by unzipping, then a higher molecular weight material should degrade more extensively than a low molecular weight material, assuming the same overall concentration of vulnerable sites. The results obtained would tend to indicate that the structural arrangement of Z60-P1 differs from that of Z25-P28, but this stipulation could not be verified.

The Ti(4Al,4Mn) alloy, in every instance, in the absence of additives, was found to be more detrimental than M-50 as determined from the quantity of volatiles formed. At 288°C over an 8 hr period for MLO-79-196, the value of 607 mg/g (Test 5), for Z25-P28 of 191 mg/g (Test 30), and for Z60-P1 of 751 mg/g (Test 52) is in agreement with the early work starting with poly(hexafluoropropylene oxide) fluids [Ref 8,10], followed by the unbranched materials studies [Ref 2-5]. These studies have shown that, at least in the absence of additives, the presence of Ti(4Al,4Mn) alloy is definitely more detrimental than that of M-50.

With respect to the action of the additives, the monophospha-s-triazine, C_2PN_3, and P-3 additive appeared to exert comparable inhibition in the presence of Ti(4Al,4Mn) alloy at 300°C over a period of 8 hr (Tests 7 and 8, MLO-76-96) and at 316°C over a period of 8 hr (Tests 20 and 21, Z25-P21). Yet, the behavior in the presence of M-50 was different. At 288°C, over a period of 24 hr, both additives acted the same (Tests 14 and 15, Z25-P21). This was also true at 316°C over an 8 hr period in the case of Z25-P21 (Tests 16 and 18); however, after 16 hr at 316°C, the extent of degradation in the presence of C_2PN_3 additive was higher by an order of magnitude as compared to the P-3 additive (Tests 17 and 19). The validity of these results is confirmed by the reproducibility of the experiments (compare Tests 26 and 28). As noted above, in the absence of additives, Ti(4Al,4Mn) alloy was shown to be more effective in promoting degradation than M-50. Yet, Z25-P28 in the presence of Ti(4Al,4Mn) alloy and the phospha-s-triazine and P-3 additives (Tests 32 and 40, respectively) survived 24 hr at 316°C with a minimum degradation. The 1.9 mg/g observed for Test 32 is lower by almost two orders of magnitude than the values recorded for Tests 26 and 27. It has to be remembered that the exposure time in Tests 26 and 27 was 16 hr versus 24 hr for Test 32. In the absence of an additive, even at 288°C, Ti(4Al,4Mn) alloy accelerates perfluoroalkylether degradation to a much higher degree than M-50. Thus, this behavior of the C_2PN_3 additive with respect to the two alloys is unexpected and unexplained.

Based on Test 29, the P-3 additive protected Z25-P28 at 316°C in the presence of M-50 alloy in oxygen up to 24 hr. Over a period of 16 hr (Tests 49 and 50), both P-3 and C_2PN_3 exerted comparable protection in the case of Z60-P1 (O_2, 316°C, M-50). It should be noted that the latter fluid was relatively more stable to M-50 than Z25-P28, by approximately a factor of 2 (compare Tests 25 and 47). However, it was less stable than Z25-P28 by a factor of approximately 3 (compare Tests 52 and 30) when used without additive with Ti(4Al,4Mn) alloy for 8 hr at 288°C in oxygen. Both of the additives provided essentially complete protection for Z60-P1 over a 24 hr period at 316°C in the presence of Ti(4Al,4Mn) alloy (Tests 55 and 56). Actually, this fluid was stabilized by the C_2PN_3 additive up to 72 hr under these conditions (Tests 57A through 57E).

These findings tend to indicate that M-50 and Ti(4Al,4Mn) promote degradation by different mechanisms and this is reflected in the effectiveness of a specific additive, which in turn implies that different additives inhibit the degradation by different mechanisms. Consequently, on the basis of the current data, it would appear that in an assessment of a given fluid's stability, more than one alloy will have to be investigated. The question arises whether it is best to use several alloys simultaneously to determine the overall stability or whether it might be advantageous to know which alloys are more or less detrimental to a specific fluid.

Earlier investigation of the action of Fomblin Z type fluids on M-50 alloy showed that chromium was preferentially attacked [Ref 3,9]. Similar findings resulted from investigation of poly(hexafluoropropene oxide) fluids [Ref 8,10]. It was of interest to determine whether cobalt also exhibits this behavior. Runs 42A, B, C, and D and 58A, B, C, and D were performed in the presence of cobalt metal using Z25-P28 and Z60-P1 fluids, respectively. It is obvious from the results of these tests that cobalt metal does not seem to promote degradation of Fomblin Z fluids. At 288°C, the quantity of volatiles produced in the presence of cobalt was almost identical to those formed by the fluids in the absence of metals, as evident from the comparison of Tests 22 and 46, respectively. The corresponding values at 316°C are not available. Inasmuch as the degree of degradation in the presence of cobalt at 316°C over 24 hr exposure (Tests 42C, D and 58C, D) was very low, 7.6 mg/g and 27 m/g/ for the Z25-P28 and Z60-P1 fluids, respectively, following 24 hr exposure, it is obvious that the metal does not promote fluids' degradation.

To compare the thermal stability with thermal oxidative stability, limited tests were carried out in nitrogen atmosphere at 343°C over a 24 hr period. The degree of degradation under these conditions, as measured by the volatiles produced, was 8.2 mg/g for Z25-P21 (Test 12), 0.6 mg/g for Z25-P28 (Test 24), and 1.2 mg/g for Z25-P51 (Test 45). In all these instances, the values corresponded closely to the numbers recorded in oxygen at

343^{o}C. These results confirm clearly the inherent oxidative stability of the perfluoroalkylether arrangements.

3.3 Investigation of Thermal Oxidative Behavior of Linear Perfluoroalkylether Based Greases

Two grease formulations, BR600-LB44 and BR601-LB57, received from Burmah Castrol Corporation, were evaluated under this program. It would appear from some of the results compiled in Table 6 that BR600-LB44 is definitely more thermal oxidatively stable than the BR601-LB57 material based on the extent of degradation (as measured by volatiles produced, 5.8 mg/g and 189 mg/g, respectively on exposure at 288^{o}C in oxygen for 24 hr, Tests 1 and 11). It should be noted that infrared spectra of the two greases were almost identical with the exception of the presence of weak CH-bands at 2920 and 2840 cm^{-1} in BR601-LB57. These are derived most likely from dioctadecylaminobentonate additive used in this grease (as understood from Burmah Castrol personnel). It is likely that the hydrocarbon entities gave rise to water observed among the degradation products. It is noteworthy that the same grease, BR601-LB57, when subjected to the above conditions but for 15 hr, has undergone minimal degradation (19.9 mg/g, Test 12A). However, an additional 24 hr treatment resulted in 501 mg/g (Test 12B). The involatile residue was dark and "dry"; its infrared spectrum showed the presence of R_fCOF and R_fCOOH moieties. Yet, if one compares the behavior at 316^{o}C over a 16 hr exposure to oxygen, the two formulations appear to be equivalent (Tests 2 and 13). Thus, it seems that the additive package present in both of the formulations is relatively unaffected by the increase in temperature of 28°C. Usually, one would expect doubling in the degradation rate for every 10°C increase in temperature. The presence of the phospha-s-triazine additive imparted greatly improved thermal oxidative stability to the BR601-LB57 grease, as shown by Test 16, where the extent of degradation following a 48 hr exposure at 288°C in oxygen atmosphere was relatively minimal. The effectiveness of P-3 additive under these conditions was definitely inferior; the quantity of volatiles produced in Test 17 was higher by a factor of six.

Both greases were unaffected by a 15 hr exposure in oxygen at 288°C to M-50 (Tests 3 and 18), which is contrary to the behavior of the "free" fluids. BR601-LB57 grease was found to be also stable over a 15 hr period to Ti(4Al,4Mn) alloy at 288°C in oxygen (Test 19), whereas the BR600-LB44 grease underwent an extensive degradation under these conditions. In the presence of the additives, even at 316°C, the degradative action of Ti(4Al,4Mn) was essentially arrested, at least for 16 hr (Tests 9 and 10).

It is obvious from the above results that an additive package or formulation has a tremendous influence on the material's behavior, which is to be expected. What is unexpected is the great dependence of the behavior on the nature of the alloy, length of exposure, and temperature, with the last two variables not being related in a linear fashion. It is thus apparent that any evaluation of a given formulation or formulations for broad based applications will be difficult. Consequently, several key tests need to be utilized to provide meaningful guidelines with respect to suitability for a specific end use.

3.4 Investigation of Thermal Oxidative Behavior of Miscellaneous Perfluoroalkylether Fluids and Model Compounds

To assess unequivocally the relative thermal oxidative stability of $-OCF_2O-$ versus $-OCF_2CF_2-$ arrangement, studies were carried out on pure compounds, $CF_3O(CF_2CF_2O)_4CF_3$ and $CF_3O(CF_2O)_4CF_3$. In view of the materials' low molecular weights (618 and 418, respectively) and the corresponding high volatility, both would be, at 288°C, in the gaseous phase. Consequently, a valid comparison with the other fluids is not possible. However, it is obvious from the data presented in Table 7 that the material containing the perfluoromethylene oxide units is less stable than the one containing perfluoroethylene oxide segments. The decomposition observed in Test 1 for the latter compound was most likely due to the presence of traces of hydrogen-containing species since the material recovered and then retested at more than four-fold higher pressure (same quantity, smaller tube) showed no degradation (Test 2) as determined by lack of formation of carbon dioxide and silicon tetrafluoride (compounds volatile at -78°C). Under parallel conditions, $CF_3O(CF_2O)_4CF_3$ liberated

18.0 mg/g (Test 4) of volatiles consisting of carbon dioxide and silicon tetrafluoride. The effect of pressure is clearly evident from comparison of Tests 3 and 4. Most likely had higher pressure been employed, the extent of degradation would have been more extensive. It should be noted that the degree of degradation was actually larger than implied by the -78°C volatiles inasmuch as the material collected in -78°C traps (7.2 mg) did exhibit an infrared spectrum different from that of the starting material. Carbon tetrafluoride appeared to be one of the constituents. The product separation was accomplished by fractionation through -47, -63, -78°C cooled traps into a -196°C cooled trap. The starting material was retained in the -47 and -63°C cooled traps.

The study of the nonvolatile fluids involved a variety of compositions, namely poly(hexafluoropropene oxide) (Krytox and Aflunox), a random polymer $-[CF(CF_3)CF_2O]_x[CF_2O]_y-$ (Fomblin Y), poly(hexafluoropropene oxide) $F(CF_2CF_2CF_2O)_xC_2F_5$ (Demnum), polydifluoromethylene $-(OCF_2)_x-$, F-dioxolane $-(CF_2CF_2OCF_2O)_x-$, F-trioxocane $-(CF_2CF_2OCF_2CF_2OCF_2O)_x-$, and perfluoroalkylether-substituted triazine $\{C_3F_7O[CF(CF_3)CF_2O]_4CF(CF_3)CN\}_3$. All the pertinent stability data are compiled in Table 8.

Evaluations performed on Krytox 143AC, batches obtained in 1971 (MLO-71-6) and 1976 (MLO-76-28), showed these materials to undergo a significant degree of degradation in oxygen atmosphere at 343°C over a 24 hr period. These values varied with the batches and were found to be 48.1 mg/g and 54.2 mg/g, respectively [Ref 8,10]. At 316°C, the extent of decomposition for MLO-71-6 was somewhat lower, 18.8 mg/g (under otherwise identical conditions); however, in nitrogen, even at 343°C, the quantity of volatiles produced was negligible (Test 3). PCR, Inc. recently made commercially available a fluid, Aflunox, believed to have an identical structural arrangement as Krytox 143. The quantity of volatiles given by this material corresponded to 1.0 mg/g (Test 9) indicating a stability 1.5 orders of magnitude better than the Krytox 143AC. It should be noted that the quantity of volatiles produced at 316°C was virtually unaffected by the presence of M-50 alloy (compare Tests 9 and 10), nor by exposure duration (compare Tests 10A and 10B). This was not true for Krytox MLO-71-6 and for a recent batch of Krytox 143AC, lot 124 (Tests 5 and 8A) where the extent of degradation under these conditions was relatively high. Yet, following the 24 hr treatment after volatiles removal with another 24 hr exposure (Tests 8A and 8B), showed fluid stabilization. This result agrees with postulations advanced earlier [Ref 8,10] regarding hydrogen terminated impurities and their removal. Both Krytox and Aflunox underwent degradation on exposure to Ti(4Al,4Mn) alloy at 316°C in oxygen (Tests 7 and 11), but the extent of degradation was higher in the case of Aflunox by a factor of 2. Very limited investigations were carried out on Fomblin Y, Y25-S20, fluid. Its thermal oxidative stability at 316°C appeared to be essentially identical to that of Krytox MLO-71-6 (compare Tests 1 and 12B).

The Demnum-S family of fluids, based on the molecular weight viscosity dependence, appear to lay between poly(hexafluoropropene oxide) derived materials and Fomblin Z type fluids. In view of the above, thermal oxidative stability tests were carried out on the representative members of the series. As evident from the results listed in Table 8, Demnum S-100 is significantly more stable in oxygen at elevated temperatures in the presence of both M-50 and Ti(4Al,4Mn) alloy than Fomblin Z (see Table 5). Its stability in the presence of M-50 corresponds closely to that of Aflunox (compare Tests 10A and 14A) and actually Krytox 143AC lot 124 after a 24 hr pretreatment (Test 8B). However, prolonged, 32 hr, exposure of Demnum S-100 to Ti(4Al,4Mn) alloy at 316°C in oxygen resulted in complete volatilization (Test 15B). It is noteworthy that the rate of degradation must increase suddenly since after 16 hr the mg/g value was 12.4 (Test 17), whereas after an additional 8 hr exposure (Test 16), the value became 670. The latter value was higher than the 243 mg/g recorded after 24 hr exposure for Aflunox (Test 11). Both of these values are high. On the other hand, pretreated Krytox was stable (4.5 mg/g) for 24 hr under these conditions (Test 44; Ref 10). These results tend to indicate that both Demnum S-100 and Aflunox contain certain weak links or impurities which are responsible for the observed action. The other Demnum fluids, namely Demnum S-200 and S-65, are definitely less stable than Demnum S-100, at least in the presence of Ti(4Al,4Mn) alloy, as evident by the high amounts of volatiles produced, 196 and 249 mg/g, respectively (Tests 19 and 21) during 16 hr exposure versus 12.4 mg/g for Demnum S-100 (Test 17). This action cannot be associated with molecular weight since Demnum S-65 is of lower molecular weight, whereas Demnum S-200 is of a higher molecular weight than Demnum S-100. In addition, Demnum S-65 exhibited also lowered stability in the presence of M-50 alloy (compare Tests 14B and 20B). The difference in the Demnum fluids behavior could very well be due to the actual batches and residual impurities.

The thermal oxidative stabilities of the perfluoroalkylethers wherein the $-OCF_2O-$ units were separated by one $-CF_2CF_2-$ entity (F-dioxolane) or by $-CF_2CF_2OCF_2CF_2-$ segment were essentially comparable, although it could be argued that the latter was more stable. This is based on 0.8 and 25.6 mg/g (Tests 25B, 25C) versus 3.1 and 59.3 mg/g (Tests 23B, 23C) measured at 316 and 343°C, respectively. On the other hand, F-polymethylene oxide exhibited a significantly lower stability as evidenced by the value of 23.4 mg/g after 24 hr exposure to oxygen at 288°C (Test 22). These findings support the postulations advanced earlier regarding the stability of $-OCF_2OCF_2O-$ arrangement [Ref 3,4,5]. It should be noted that all the perfluoroalkylether fluids investigated were thermally stable in inert atmosphere at 343°C (Tests 3, 13, 24, and 26).

The thermal oxidative stability of perfluoroalkylether-substituted triazines at 316°C in the presence of M-50 and

Ti(4Al,4Mn) alloys was better than that of the other fluids tested. This is in agreement with the inherent stability of the perfluoroalkylethers derived from hexafluoropropene oxide, as proven by the stability of the pretreated Krytox fluids and the stability associated with triazine ring itself.

4. EXPERIMENTAL DETAILS AND PROCEDURES

4.1 General

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 Corporation 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. All the viscosity measurements were performed at $100 \pm 0.02^{\circ}F$ using Cannon-Manning semimicroviscometers.

4.2 Materials

4.2.1 Fluids

Difluoromethylene oxide hexamer, $CF_3O(CF_2O)_4CF_3$, was obtained from DuPont (courtesy of Dr. P. R. Resnick);

F-tetraglyme, $CF_3O(CF_2CF_2O)_4CF_3$; F-dioxolane, $-(CF_2CF_2OCF_2O)_x-$; F-trioxocane, $-(CF_2CF_2OCF_2CF_2OCF_2)_x-$; and F-polymethylene oxide, $-(CF_2O)_x-$ were synthesized by Exfluor, Inc.; Krytox 143AC fluids are products of E. I. duPont de Nemours Co.; Aflunox is manufactured by PCR, Inc.; Demnum S-200, Demnum S-100, and Demnum S-65 are products of Daikin Industries; Fomblin Z and Fomblin Y family of fluids are manufactured by Montefluos.

4.2.2 Metal coupons

Ti(4Al,4Mn) and M-50 coupons 3/8" OD and 1/8" ID were obtained from Metaspec Company, San Antonio, Texas. Cobalt coupons 8 mm x 8 mm x 4 mm were obtained from NASA Lewis (courtesy of Mr. W. R. Jones, Jr.). Prior to testing, all the coupons 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.

4.3 Apparatus

4.3.1 Sealed tube test assembly

This was a modified, scaled-down version of the AFML Micro-O-C-Test arrangement [Ref 11]. It was described in detail previously [Ref 5]. 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 Figure 1); the extra gas reservoir was in the ambient environment.

In a typical experiment, the fluid was introduced into the degradation tube (see Figure 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 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 gas chromatography. The liquid nitrogen condensibles were fractionated through $-23^{\circ}C$, $-78^{\circ}C$, and a $-196^{\circ}C$ trap. The $-196^{\circ}C$ fractions were measured, weighed, and analyzed by infrared spectroscopy and mass spectrometry. The $-23^{\circ}C$ and $-78^{\circ}C$ 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.

4.3.2 Flow system utilized in the fluid stabilization process

For the fluid stabilization, the apparatus depicted in Figure 3 was employed. The Ti(4Al,4Mn) coupons used were the same as those utilized in the sealed tube assembly 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 $-78^{\circ}C$ and trap B to $-96^{\circ}C$, heating was commenced and continued for a specified 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 $-196^{\circ}C$, 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 $-196^{\circ}C$ cooled traps. All the fractions were measured and/or weighed and analyzed by infrared spectral analysis.

4.4 Fluid Transformations [Ref 7]

The weak link removal process was carried out according to Scheme A (see Section 3.1.2) following the conditions given in Table 2 and utilizing the apparatus described in Section 4.3.2

above. The acid fluoride end-groups present in the involatile residue were transformed into methyl ester (Compound I) moieties by reaction with dry methanol in an inert atmosphere enclosure. The subsequent steps were performed according to Scheme B and Table 3. The methyl ester was treated in ether with ammonia at $0^{o}C$. After removal of solvent and the excess ammonia, the product containing amide groups (Compound II) was then heated with phosphorus pentoxide for 5 hr at $220-240^{o}C$. From the reaction mixture, the more volatile portion was removed in vacuo at a bath temperature of $70-155^{o}C$. The involatile residue containing the nitrile (Compound III) was extracted with Freon-113 and half of the material left after solvent evaporation was subsequently transformed into the corresponding amidine (Compound IV) by reaction with liquid ammonia. A small portion of the amidine was reacted with a short chain nitrile, $C_3F_7OCF(CF_3)CN$, to determine the functional molecular weight (by nitrile consumption). Interaction of equal quantities of the nitrile (Compound III) with the corresponding amidine (Compound IV) at room temperature in the absence of solvent gave the imidoylamidine (Compound V). To the resultant imidoylamidine in Freon-113 and in the presence of triethylamine was then added diphenyltrichlorophosphorane (threefold excess) in benzene and the mixture was heated at $50^{o}C$ for 16 hr. After solvent evaporation (in vacuo), followed by washing with benzene and filtration, a fluid was obtained which exhibited absorption at 1575 cm^{-1}, characteristic of monophospha-s-triazine ring structure [Ref 12]. On this material, number average molecular weight, viscosity, and thermal oxidative stability in the presence of M-50 and Ti(4Al,4Mn) were determined.

5. REFERENCES

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TABLE 1
LISTING OF FOMBLIN Z FLUIDS STUDIED AND THEIR PROPERTIES

Fluid Ident.	Molecular weight (osmometry)	Viscosity cSt at 40°C
MLO-79-196	6400	80.85
FMZ-83-BJ	11000	148.0
Z25-P28	9770	153.9
Z60-P1	12000	316.2

TABLE 2

RESULTS OF EXPOSURE OF FOMBLIN Z FLUIDS TO ELEVATED TEMPERATURE UNDER OXYGEN FLOW IN THE PRESENCE OF Ti(4Al,4Mn) ALLOY

Test No.	Fluid		Temp °C	Time hr	-196°C volatiles	Con-densible volatiles	Involatile Fraction[a]				
									Molecular weight		Viscosity cSt at 40°C
	Type	Amt g			P^b mm	g	g	%	osm	IR	
74A	Z25-P28	20.51	240-250	1.75	-	0.32	20.19	98.4	-	∞	137.4
			250	2.5	-						
74B	Z25-P28	14.27	266	5.25	-	2.57	11.04	77.4	2600	3450	41.0
81	Z25-P28	101.46	260-270	7.0	-	8.03	85.70	84.5	4150[c]	3400	49.1
100	Z25-P28	300.16	285-278	1.0	-	-	-	-	-	-	-
			310-286	3.5	-	0.91	298.36	99.4	-	-	-
			319-285	4.0	-	1.24	-	-	-	-	-
			306-286	3.5	-	5.31	-	-	-	-	-
			297-285	2.0	-	5.25	277.69	92.5	4600[c]	6400	83.02
86	Z60-P1	20.55	260-270	3.25	-	3.49	14.60	71.0	-	-	24.1
87	Z60-P1	20.16	270-280	1.00	-	-	-	-	-	-	-
			254-247	2.00	-	-	-	-	-	-	-
			260-248	4.00	-	0.60	19.30	95.7	15300[c]	14600	209.
96	Z60-P1	20.49	255-280	3.5	-	n.d.	19.16	94.0	-	-	-
			255-270	1.0	315	-	-	-	-	-	-
			265-270	1.5	178	-	-	-	-	-	-
			260-265	1.5	396	2.36	17.03	83.1	3100	3950	67.1

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a) The molecular weights and viscosity measurements were performed on the methyl ester form of the involatile fraction; this is the functional molecular weight.
b) This is the pressure at room temperature in an ∿100 ml volume of condensible volatiles collected in the -196°C cooled traps.
c) The molecular weight in this case was determined from viscosity.

TABLE 3

MODIFICATION OF FOMBLIN Z FLUIDS, Z25-P28 AND Z60-P1; SUMMARY OF EXPERIMENTAL DATA[a]

		R_fCONH_2		R_fCN					$R_fC{=}NH(NH_2)$			$R_fCN(NH_2)C(NH)R_f$		Monophospha-s-triazine				
		Yield		Volatile Yield		Residue Yield			Yield			Yield		Yield				Viscosity cSt at 40°C
Fluid	Test No.	g	%[b]	g	%[b]	g	%[b]	MW (osm)[c]	g	%[b]	MW osm (func)	g	%[b]	g	%[b]	MW (osm)[c]	Product Ident	
Z25-P28	74B	7.9	100	1.4	18	5.3	68	6050	2.7	91	6300 (30200)	3.2	100 (48)	2.0	63 (30)	7000	$[\Phi_2PN][Z25\text{-}P28T\text{-}74CN]_2$	-
Z25-P28	81	75.6	99	14.0	19	58.5	78 (66)	5600	27.7	97	- (22600)	52.6	100 (53)	47.5	90 (64)	6600	$[\Phi_2PN][Z25\text{-}P28T\text{-}81CN]_2$	104
Z25-P28	100A	19.5	100	0.9	5	17.2	84 (78)	5250	8.4	93	- (19400)	14.9	100 (73)	11.7	79 (58)	7000	$[\Phi_2PN][Z25\text{-}P28T\text{-}100ACN]_2$	111
Z25-P28	100B	245.8	100	16.6	7	217.9	89 (82)	6700	108.0	98	- (26000)	212.7	100 (80)	191.5	90 (71)	7050	$[\Phi_2PN][Z25\text{-}P28T\text{-}100BCN]_2$	111
Z60-P1	87	16.4	100	0.5	3	9.1	55 (53)	-	4.7	92	-	7.2	79 (42)	6.0	87 (37)	-	$[\Phi_2PN][Z60\text{-}P1T\text{-}87CN]_2$	287
Z60-P1	96	13.9	99	1.6	12	6.7	49 (41)	4150	2.87	82	- (11800)	2.0	100 (34)	2.8	70 (24)	5400	$[\Phi_2PN][Z60\text{-}P1T\text{-}96CN]_2$	126

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a) The stepwise synthesis process is depicted in Scheme B; the details of the heat treatment are given in Table 2.
b) This corresponds to the yield of the product for the specific step only; the overall yield for the process up to that point is given in parentheses.
c) This is the number average molecular weight.

TABLE 4
THERMAL OXIDATIVE STABILITY EVALUATIONS AT 316°C OF MODIFIED PERFLUOROALKYLETHER FLUIDS IN THE PRESENCE OF METAL ALLOYS^a

Test No.	Material		Duration hr	Metal	Volatiles		Coupon weight change mg
	Identification	Amt g			mg	mg/g	
1A (75A)	[Φ_2PN][Z25-P28T-74CN]$_2$	0.79	16	M-50	7.5	9.5	-
1B^b(75B)	[Φ_2PN][Z25-P28T-74CN]$_2$	0.78	16	M-50	all volatilized		-
2 (84)	[Φ_2PN][Z25-P28T-81CN]$_2$	2.66	16	M-50	5.6	2.1	+0.1
3 (88)	[Φ_2PN][Z25-P28T-81CN]$_2$	1.58	16	M-50	4.1	2.6	-0.3
4A (102A)	[Φ_2PN][Z25-P28T-81CN]$_2$	1.58	24	M-50	8.9	5.6	-
4B^b(102B)	[Φ_2PN][Z25-P28T-81CN]$_2$	1.57	16	M-50	all volatilized		-23.7
5 (85)	[Φ_2PN][Z25-P28T-81CN]$_2$	3.08	16	Ti(4Al,4Mn)	13.7	4.4	-0.1
6 (92)	[Φ_2PN][Z25-P28T-81CN]$_2$	2.53	24	Ti(4Al,4Mn)	6.0	2.4	+0.1
7A (105A)	[Φ_2PN][Z25-P28T-100ACN]$_2$	1.59	16	M-50	4.0	2.5	-
7B^b(105B)	[Φ_2PN][Z25-P28T-100ACN]$_2$	1.59	24	M-50	2.2	1.4	+0.3
8A (106A)	[Φ_2PN][Z25-P28T-100ACN]$_2$	1.32	16	Ti(4Al,4Mn)	2.7	2.0	-
8B^b(106B)	[Φ_2PN][Z25-P28T-100ACN]$_2$	1.32	24	Ti(4Al,4Mn)	1.7	1.3	+0.1
9 (108)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.93	16	M-50	3.5	1.2	+4.2
10 (110)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.82	48	M-50	all volatilized		-17.5
11A (111A)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.32	24	M-50	12.7	5.5	-
11B^b(111B)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.32	16	M-50	all volatilized		-20.9
12A (113A)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.71	24	Ti(4Al,4Mn)	6.5	2.4	-
12B^b(113B)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.71	16	Ti(4Al,4Mn)	10.4	3.8	-
12C^b(113C)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.71	16	Ti(4Al,4Mn)	20.8	7.7	-
12D^b(113D)	[Φ_2PN][Z25-P28T-100BCN]$_2$	2.71	16	Ti(4Al,4Mn)	all volatilized		-0.2
13 (94)	[Φ_2PN][Z60-P1T-87CN]$_2$	1.43	16	M-50	all volatilized		-2.1
14A (101A)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.77	16	M-50	2.1	2.7	-
14B^b(101B)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.77	24	M-50	3.0	3.9	-0.1
15A (104A)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.32	16	Ti(4Al,4Mn)	1.5	4.7	-
15B^b(104B)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.32	8	Ti(4Al,4Mn)	0.5	1.6	-
15C^b(104C)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.32	16	Ti(4Al,4Mn)	2.7	8.4	-
15D^b(104D)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.32	16	Ti(4Al,4Mn)	1.7	5.4	-
15E^b(104E)	[Φ_2PN][Z60-P1T-96CN]$_2$	0.32	24	Ti(4Al,4Mn)	all volatilized		0.0

a) All the tests were performed in pure oxygen at 316°C; the values in parentheses next to the Test No. correspond to project reference.

b) Fluid used for this test was the residue from the preceding test after removal of the volatiles.

TABLE 5

THERMAL OXIDATIVE BEHAVIOR OF DIFFERENT BATCHES AND TYPES OF FOMBLIN Z FLUIDS AND THE EFFECT OF ADDITIVES AND ALLOYS ON THE DEGRADATION[a]

	Material						Volatiles		Coupon weight change
Test No.	Ident.	Amt g	Temp °C	Duration hr	Metal	Additive	mg	mg/g	mg
1[b](A)	MLO-79-196	3.15	288	24	none	none	38.4	12.2	n.a.
2 (27)	MLO-79-196	2.96	288	15	M-50	none	865.9	292.5	+0.5
3 (28)	MLO-79-196	3.10	288	24	M-50	C_2PN_3	11.2	3.6	+0.4
4 (22)	MLO-72-22	2.99	288	24	M-50	C_2PN_3	22.8	7.6	+1.5
5[b](B)	MLO-79-196	3.67	288	8	Ti(4Al,4Mn)	none	2229.	607.3	-
6[c](19)	MLO-79-196	2.12	300	8	Ti(4Al,4Mn)	none	2250.	1060.	-
7 (25)	MLO-79-196	3.04	300	8	Ti(4Al,4Mn)	C_2PN_3	4.0	1.3	-0.2
8 (24)	MLO-79-196	3.06	300	8	Ti(4Al,4Mn)	P-3	4.7	1.5	-0.2
9 (29)	Z25-P21	3.03	288	24	none	none	29.0	9.6	-
10 (128)	Z25-P21	3.52	316	24	none	none	32.5	9.2	-
11A(129A)	Z25-P21	3.06	316	24	none	none	29.1	9.5	-
11B[d](129B)	Z25-P21	3.06	343	24	none	none	62.8	20.5	-
12[e](132)	Z25-P21	3.12	343	24	none (N_2)	none	25.6	8.2	-
13 (26)	Z25-P21	3.23	288	15	M-50	none	1023.7	316.9	+0.9
14 (21)	Z25-P21	3.34	288	24	M-50	C_2PN_3	13.3	4.0	+1.6
15 (23)	Z25-P21	3.56	288	24	M-50	P-3	11.3	3.2	+1.0
16 (33)	Z25-P21	3.10	316	8	M-50	C_2PN_3	18.7	6.0	+0.6
17 (34)	Z25-P21	2.56	316	16	M-50	C_2PN_3	316.7	123.6	-5.1
18 (32)	Z25-P21	3.24	316	8	M-50	P-3	23.9	7.4	+1.8
19 (35)	Z25-P21	3.27	316	16	M-50	P-3	43.1	13.2	-1.3
20 (31)	Z25-P21	3.04	316	8	Ti(4Al,4Mn)	C_2PN_3	13.9	4.6	-0.2
21 (30)	Z25-P21	3.08	316	8	Ti(4Al,4Mn)	P-3	15.4	5.0	-0.1
22 (36)	Z25-P28	2.96	288	24	none	none	4.2	1.4	-
23A(127A)	Z25-P28	3.27	316	24	none	none	5.5	1.7	-
23B[d](127B)	Z25-P28	3.27	343	24	none	none	7.3	2.2	-
23C[d](127C)	Z25-P28	3.27	370	24	none	none	79.2	24.2	-
24[e](133)	Z25-P28	3.63	343	24	none (N_2)	none	2.3	0.6	-
25 (38)	Z25-P28	3.02	288	15	M-50	none	1033.3	342.2	+0.6
26 (40)	Z25-P28	3.17	316	16	M-50	C_2PN_3	227.8	71.9	-4.9
27 (53)	Z25-P28	3.24	316	16	M-50	C_2PN_3	277.1	83.0	-5.0
28 (41)	Z25-P28	2.93	316	16	M-50	P-3	7.4	2.5	+1.8
29 (48)	Z25-P28	3.04	316	24	M-50	P-3	21.4	7.0	-3.2
30 (52)	Z25-P28	3.13	288	8	Ti(4Al,4Mn)	None	597.0	191.0	0.0
31 (44)	Z25-P28	3.25	316	16	Ti(4Al,4Mn)	C_2PN_3	3.6	1.1	-0.2
32 (51)	Z25-P28	3.13	316	24	Ti(4Al,4Mn)	C_2PN_3	6.0	1.9	-0.1
33 (112)	Z25-P28	3.22	316	40	Ti(4Al,4Mn)	C_2PN_3[f]	1675.4	520.3	-0.3

TABLE 5 (Cont'd.)

THERMAL OXIDATIVE BEHAVIOR OF DIFFERENT BATCHES AND TYPES OF FOMBLIN Z FLUIDS AND THE EFFECT OF ADDITIVES AND ALLOYS ON THE DEGRADATION[a]

Test No.	Material Ident.	Material Amt g	Temp °C	Duration hr	Metal	Additive	Volatiles mg	Volatiles mg/g	Coupon weight change mg
40 (49)	Z25-P28	3.17	316	24	Ti(4Al,4Mn)	P-3	9.3	2.9	+0.1
41 (118)	Z25-P28	3.02	316	40	Ti(4Al,4Mn)	P-3	343.4	113.7	-0.4
42A(77A)	Z25-P28	3.06	288	8	Co	none	3.0	1.0	-
42B[d](77B)	Z25-P28	3.06	288	24	Co	none	4.0	1.3	-
42C[d](77C)	Z25-P28	3.05	316	8	Co	none	7.5	2.4	-
42D[d](77D)	Z25-P28	3.04	316	16	Co	none	15.8	5.2	-
43 (115)	Z25-P51	2.69	288	24	none	none	9.0	3.3	-
44A(130A)	Z25-P51	2.04	316	24	none	none	11.1	5.4	-
44B[d](130B)	Z25-P51	2.04	343	24	none	none	5.1	2.5	-
45[e](131)	Z25-P51	2.38	343	24	none (N_2)	none	2.8	1.2	-
46 (37)	Z60-P1	2.97	288	24	none	none	3.5	1.2	-
47 (39)	Z60-P1	3.09	288	15	M-50	none	581.2	188.1	-0.1
48 (43)	Z60-P1	3.04	316	16	M-50	C_2PN_3	20.2	6.6	+0.4
49 (59)	Z60-P1	3.37	316	16	M-50	C_2PN_3	5.2	1.5	+0.8
50 (42)	Z60-P1	2.84	316	16	M-50	P-3	7.2	2.5	+0.4
51 (47)	Z60-P1	3.13	288	15	Ti(4Al,4Mn)	none	all volatilized		-0.2
52 (50)	Z60-P1	3.07	288	8	Ti(4Al,4Mn)	none	2304.0[g]	751.0	-0.2
53 (54)	Z60-P1	2.76	316	24	Ti(4Al,4Mn)	P-3	3.0	1.1	-1.1
54 (121)	Z60-P1	2.89	316	40	Ti(4Al,4Mn)	P-3	191.9	66.4	-0.2
55 (55)	Z60-P1	3.23	316	24	Ti(4Al,4Mn)	C_2PN_3	2.9	0.9	-0.3
56 (103)	Z60-P1	2.99	316	24	Ti(4Al,4Mn)	C_2PN_3[f]	3.0	1.0	-
57A(117A)	Z60-P1	3.01	316	40	Ti(4Al,4Mn)	C_2PN_3[f]	2.7	0.9	-
57B[d](117B)	Z60-P1	3.01	316	8	Ti(4Al,4Mn)	C_2PN_3[f]	0.9	0.3	-
57C[d](117C)	Z60-P1	3.01	316	8	Ti(4Al,4Mn)	C_2PN_3[f]	0.7	0.2	-
57D[d](117D)	Z60-P1	3.01	316	8	Ti(4Al,4Mn)	C_2PN_3[f]	0.9	0.3	-
57E[d](117E)	Z60-P1	3.01	316	8	Ti(4Al,4Mn)	C_2PN_3[f]	2.0	0.7	-
57F[d](117F)	Z60-P1	3.01	316	8	Ti(4Al,4Mn)	C_2PN_3[f]	61.9	20.6	-0.6
58A(78A)	Z60-P1	3.04	288	8	Co	none	3.4	1.1	-
58B[d](78B)	Z60-P1	3.04	288	24	Co	none	12.1	4.0	-
58C[d](78C)	Z60-P1	3.02	316	8	Co	none	not determined		-
58D[d](78D)	Z60-P1	3.02	316	16	Co	none	82.0[h]	27.0[h]	-

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a) All the tests were performed in pure oxygen unless stated otherwise; the concentrations of the additives used were 1.0 weight percent; the values in parentheses next to the Test No. correspond to project reference.
b) This test was performed previously [Ref 5].
c) This test was performed previously [Ref 7].
d) Fluid used for this test was the residue from the preceding test after removal of the volatiles.
e) This test was performed in pure nitrogen.
f) The C_2PN_3 additive used was $[\phi_2PN][C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN]_2$. The C_2PN_3 additive used in other tests was $[\phi_2PN][C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$.
g) At the test temperature, no fluid was present in the tube.
h) The volatiles are from both Tests 78C and 78D.

TABLE 6

THERMAL OXIDATIVE BEHAVIOR OF FOMBLIN Z GREASES AND THE EFFECT OF ADDITIVES AND ALLOYS ON THE DEGRADATION[a]

Test No.	Material		Temp	Duration	Metal	Additive	Volatiles		Coupon weight change
	Ident.	Amt g	°C	hr			mg	mg/g	mg
1 (45)	BR600-LB44	1.02	288	24	none	none	5.9	5.8	-
2 (67)	BR600-LB44	1.04	316	16	none	none	13.5	13.0	-
3 (61)	BR600-LB44	0.97	288	15	M-50	none	5.3	5.5	+1.3
4 (56)	BR600-LB44	1.00	316	16	M-50	C_2PN_3[b]	9.4	9.4	+6.3
5 (60)	BR600-LB44	1.28	316	16	M-50	C_2PN_3	7.2	5.6	+6.7
6 (72)	BR600-LB44	1.03	288	15	Ti(4Al,4Mn)	none	259.7	252.1	+0.2
7 (68)	BR600-LB44	1.05	316	16	Ti(4Al,4Mn)	none	632.3	602.2	+0.9
8 (57)	BR600-LB44	1.04	316	16	Ti(4Al,4Mn)	C_2PN_3	76.0	73.1	+1.0
9 (64)	BR600-LB44	1.21	316	16	Ti(4Al,4Mn)	C_2PN_3	12.0	9.9	+0.5
10 (65)	BR600-LB44	1.26	316	16	Ti(4Al,4Mn)	P-3	18.7	14.8	+0.4
11 (46)	BR601-LB57	1.02	288	24	none	none	193.2	189.4	-
12A (66A)	BR601-LB57	1.14	288	15	none	none	22.7	19.9	-
12B[c](66B)	BR601-LB57	1.12	288	24	none	none	561.2	501.1	-
13 (69)	BR601-LB57	1.05	316	16	none	none	21.1	19.5	-
14 (58)	BR601-LB57	1.43	288	24	none	C_2PN_3	35.5	24.8	-
15 (63)	BR601-LB57	1.28	288	24	none	P-3	34.7	27.1	-
16 (70)	BR601-LB57	1.18	288	48	none	C_2PN_3	30.1	25.5	-
17 (71)	BR601-LB57	1.10	288	48	none	P-3	183.2	166.5	-
18 (62)	BR601-LB57	0.96	288	15	M-50	none	24.3	25.3	+1.2
19 (73)	BR601-LB57	1.02	288	15	Ti(4Al,4Mn)	none	21.7	21.3	0.0

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a) All the tests were performed in pure oxygen; the concentration of the additives used was 1.0 weight percent; the values in parentheses next to the Test No. correspond to project reference.
b) The C_2PN_3 additive used was $[\phi_2PN][C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$.
c) Grease for this test was the residue from the preceding test after removal of the volatiles.

TABLE 7

THERMAL OXIDATIVE DEGRADATION STUDIES OF PERFLUOROTETRAGLYME, $CF_3O(CF_2CF_2O)_4CF_3$, AND DIFLUOROMETHYLENE OXIDE HEXAMER, $CF_3O(CF_2O)_4CF_3$[a]

Test No.	Material				O_2	V tube	Temp	Time		Volatiles	
	Formula	$VP_{0°C}$	mg	mmol	mm	ml	°C	hr	coupon	mg	mg/g
1 (76)	$CF_3O(CF_2CF_2O)_4CF_3$	1.9	736.6	1.19	396	55.4	288	24	M-50	1.5	2.0
2 (82)	$CF_3O(CF_2CF_2O)_4CF_3$	1.9	704.3	1.13	204	13.0	288	24	M-50	0.0	0.0
3 (79)	$CF_3O(CF_2O)_4CF_3$	12.5	443.3	1.06	410	54.8	288	24	M-50	0.0	0.0
4[b](80)	$CF_3O(CF_2O)_4CF_3$	12.5	443.3	1.06	204	12.8	288	24	M-50	8.0	18.0

a) All the tests were performed in pure oxygen in sealed tubes; the values in parentheses next to the Test No. correspond to project reference.

b) Fluid used for this test was the residue from the preceding test.

TABLE 8

THERMAL OXIDATIVE BEHAVIOR, ALONE AND IN THE PRESENCE OF ALLOYS, OF MISCELLANEOUS PERFLUOROALKYLETHER FLUIDS^a

Test No.	Material		Temp	Duration	Metal	Volatiles		Coupon weight change
	Ident.	Amt g	°C	hr		mg	mg/g	mg
1 (Ref 8)	Krytox 143AC^b MLO-71-6	13.43	316	24	none	252.6	18.8	-
2 (Ref 8)	Krytox 143AC^b MLO-71-6	3.47	343	24	none	181.4	53.1	
3 (137)	Krytox 143AC^b MLO-71-6	3.00	343	24	none (N_2)	5.6	1.9	-
4 (Ref 8)	Krytox 143AC^b MLO-71-6	12.22	288	24	M-50	48.5	4.0	+0.2
5 (Ref 8)	Krytox 143AC^b MLO-71-6	12.13	316	24	M-50	576.7	47.5	+0.4
6 (Ref 8)	Krytox 143AC^b MLO-71-6	11.02	288	24	Ti(4Al,4Mn)	183.2	16.6	+0.2
7 (Ref 8)	Krytox 143AC^b MLO-71-6	11.40	316	24	Ti(4Al,4Mn)	1618.	142.0	-0.2
8A (116A)	Krytox 143AC^b Lot 124	2.78	316	24	M-50	100.4	36.1	-
8B^c(116B)	Krytox 143AC^b Lot 124	2.78	316	24	M-50	13.3	4.8	+3.3
9 (107)	AFLUNOX 2509^d Lot 10722	3.99	343	24	none	4.1	1.0	-
10A (109A)	AFLUNOX 2509^d Lot 10722	1.86	316	24	M-50	0.9	0.5	-
10B^c(109B)	AFLUNOX 2509^d Lot 10722	1.86	316	24	M-50	9.0	4.8	+0.3
11 (114)	AFLUNOX 2509^d Lot 10722	1.43	316	24	Ti(4Al,4Mn)	347.5	243.0	-0.4
12A (123A)	Y25-S20^e	3.19	288	24	none	9.3	2.9	-
12B^c(123B)	Y25-S20^e	3.19	316	24	none	59.1	18.5	-
13 (136)	Demnum S-100^f	3.05	343	24	none (N_2)	0.3	0.1	-
14A (83A)	Demnum S-100^f	3.12	316	16	M-50	11.4	3.6	+1.7
14B^c(83B)	Demnum S-100^f	2.66	316	24	M-50	5.6	2.1	-0.1
15A (89A)	Demnum S-100^f	3.14	316	8	Ti(4Al,4Mn)	1.9	0.6	-
15B^c(89B)	Demnum S-100^f	3.12	316	24	Ti(4Al,4Mn)	all volatilized		-0.1
16 (90)	Demnum S-100^f	3.11	316	24	Ti(4Al,4Mn)	2085.	670.0	+0.6
17 (95)	Demnum S-100^f	3.05	316	16	Ti(4Al,4Mn)	38.0	12.4	-
18A (98A)	Demnum S-200^f	3.07	316	16	M-50	2.0	0.6	-
18B^c(98B)	Demnum S-200^f	3.07	316	24	M-50	9.7	3.2	+1.3
19 (91)	Demnum S-200^f	2.99	316	16	Ti(4Al,4Mn)	587.0	196.0	-0.4
20A (97A)	Demnum S-65^f	3.17	316	16	M-50	10.7	3.4	-
20B^c(97B)	Demnum S-65^f	3.16	316	24	M-50	172.0	54.1	-3.9
21 (93)	Demnum S-65^f	2.97	316	16	Ti(4Al,4Mn)	738.0	249.0	-0.4

TABLE 8 (Cont'd.)

THERMAL OXIDATIVE BEHAVIOR, ALONE AND IN THE PRESENCE OF ALLOYS, OF MISCELLANEOUS PERFLUOROALKYLETHER FLUIDS[a]

	Material			Dura-		Volatiles		Coupon
Test No.	Ident.	Amt g	Temp °C	tion hr	Metal	mg	mg/g	weight change mg
22 (124)	F-Polymethylene Oxide	2.15	288	24	none	50.4	23.4	-
23A (125A)	F-Dioxolane[g]	2.17	288	24	none	0.9	0.4	-
23B[c] (125B)	F-Dioxolane[g]	2.17	316	24	none	6.8	3.1	-
23C[c] (125C)	F-Dioxolane[g]	2.17	343	24	none	128.7	59.3	-
24 (135)	F-Dioxolane[g]	2.03	343	24	none (N_2)	12.9	6.4	-
25A (126A)	F-Trioxocane[h]	2.14	288	24	none	0.6	0.3	-
25B[c] (126B)	F-Trioxocane[h]	2.14	316	24	none	1.7	0.8	-
25C[c] (126C)	F-Trioxocane[h]	2.14	343	24	none	54.9	25.6	-
26 (134)	F-Trioxocane[h]	2.06	343	24	none (N_2)	3.2	1.6	-
27 (119)	6,6,6(P)Triazine[i]	2.50	316	24	none	3.9	1.6	-
28A (120A)	6,6,6(P)Triazine[i]	2.50	316	16	M-50	1.9	0.8	-
28B[c] (120B)	6,6,6(P)Triazine[i]	2.50	316	24	M-50	2.0	0.8	-
28C[c] (120C)	6,6,6(P)Triazine[i]	2.50	316	16	M-50	2.6	1.0	-
29A (122A)	6,6,6(P)Triazine[i]	2.10	316	24	Ti(4Al,4Mn)	3.0	1.4	-
29B[c] (122B)	6,6,6(P)Triazine[i]	2.10	316	24	Ti(4Al,4Mn)	7.3	3.5	-
29C[c] (122C)	6,6,6(P)Triazine[i]	2.10	343	24	Ti(4Al,4Mn)	146.0	69.5	0.0

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a) All the tests, with the exception of Tests No. 3, 13, 24, and 26, were conducted in pure oxygen, the values in parentheses next to the Test No. correspond to project reference.

b) Product of E. I. duPont de Nemours and Co., general formula $C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$.

c) Fluid used for this test was the residue from the preceding test after removal of volatiles.

d) Product of PCR, Inc., general formula $C_3F_7[OCF(CF_3)CF_2]_xOC_2F_5$.

e) Product of Montedison Co., the general structure is believed to be $(OCF(CF_3)CF_2]_x[OCF_2)_y$.

f) Product of Daikin Industries, Ltd., general formula $F[CF_2CF_2CF_2O]_xC_2F_5$.

g) F-dioxolane, $(CF_2CF_2OCF_2O)_x$.

h) F-trioxocane, $(CF_2CF_2OCF_2CF_2OCF_2O)_x$.

i) 6,6,6(P)Triazine, $[C_3F_7O[CF(CF_3)CF_2O]_4CF(CF_3)CN]_3$.

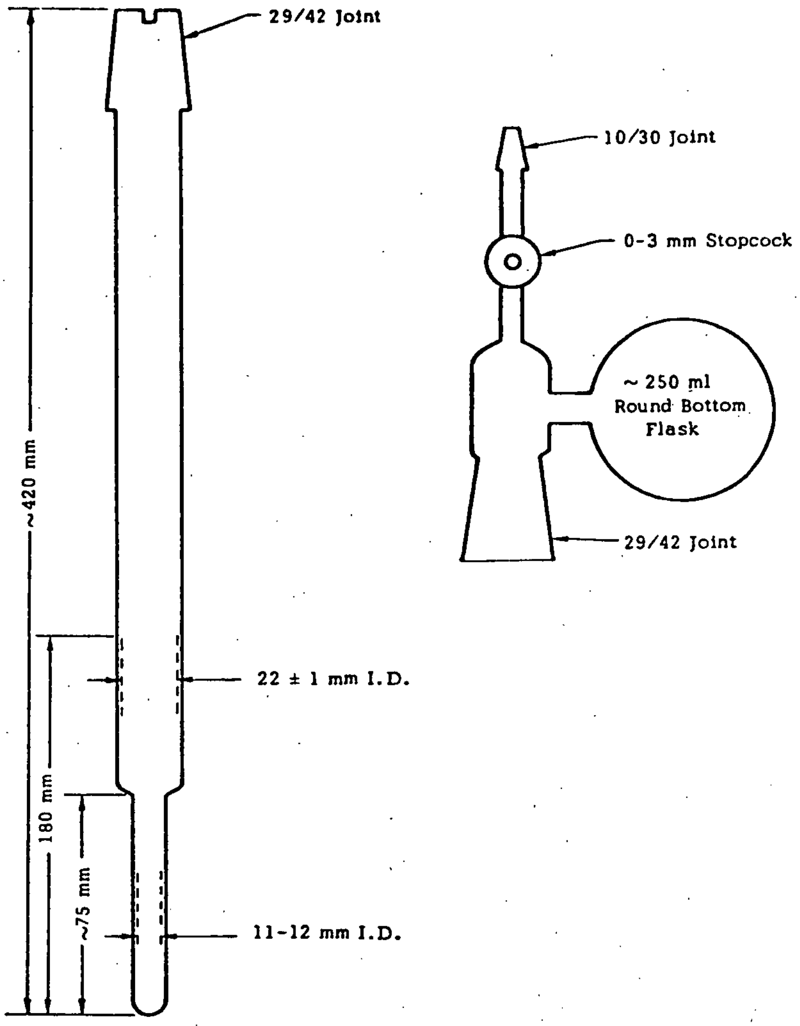

Figure 1: Decomposition tube and adapter

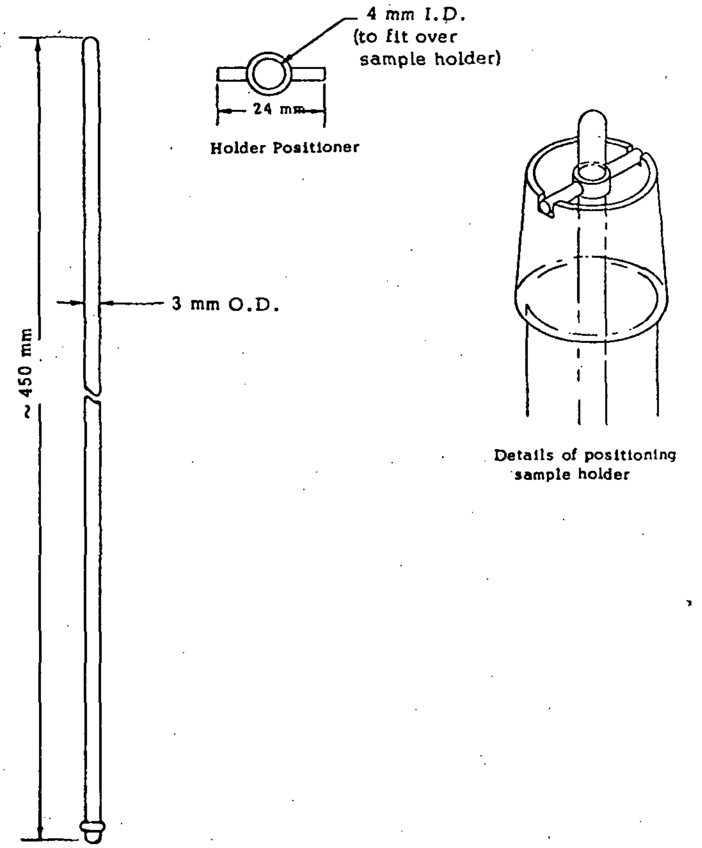

Figure 2: Metal specimen holder arrangement

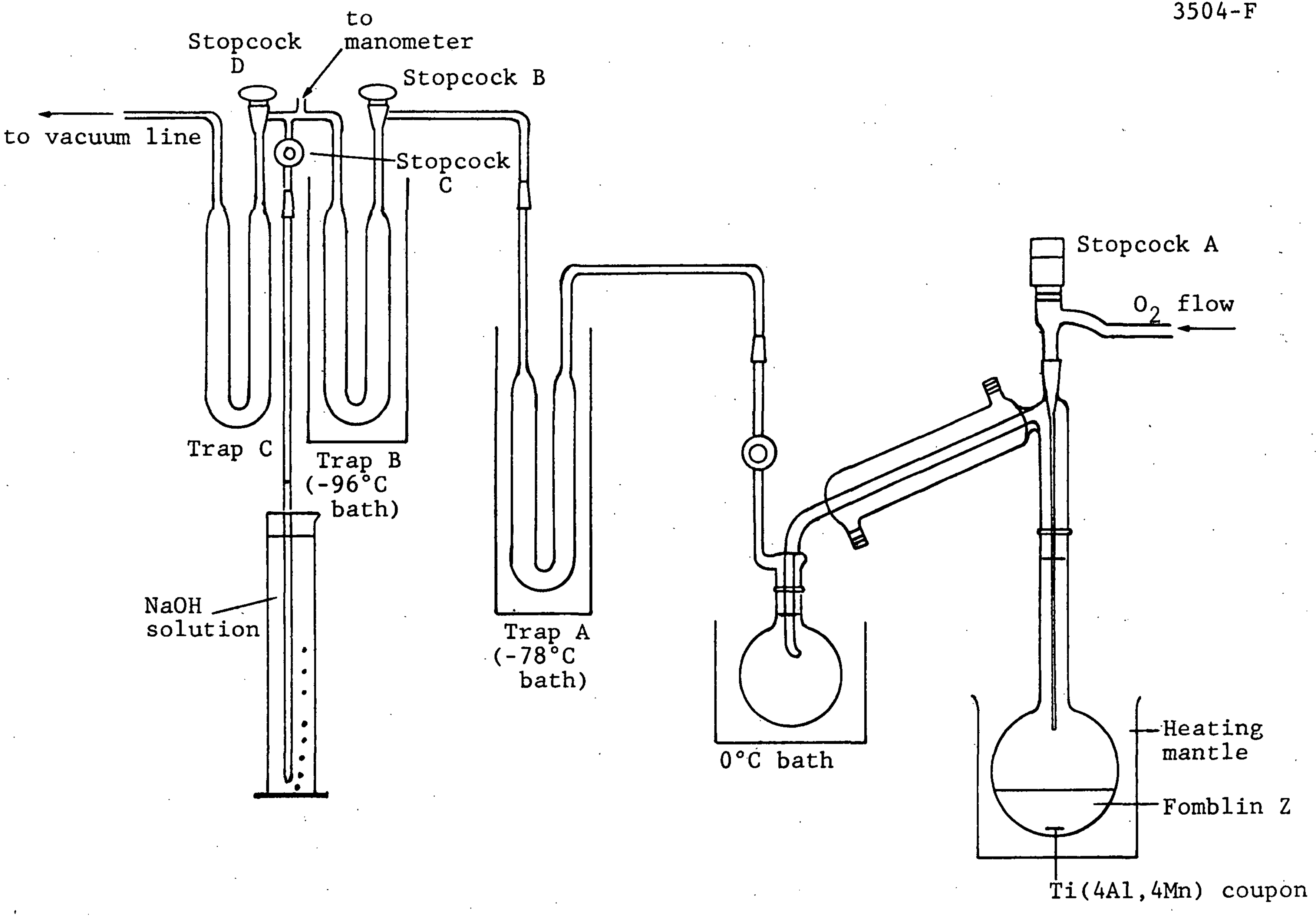

Figure 3: Schematic of apparatus used to prepare the stable fluid precursor

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16. Abstract

The objective of this program was to optimize and scale up the linear perfluoroalkylether stabilization process and to provide test data regarding the fluids' thermal oxidative stability in the presence of metal alloys.

The stabilization of Fomblin Z-25 was scaled up to 300 g of fluid. The modified fluid was stable at 316°C in oxygen in the presence of M-50 alloy for more than 24 hr but less than 40 hr; the amount of volatiles produced after 24 hr was 5.5 mg/g. In the presence of Ti(4Al,4Mn) alloy, under the above conditions, following an exposure of 24 hr, the amount of volatiles formed was 6.2 mg/g; 56 hr exposure yielded 13.9 mg/g. The commercial fluid at 288°C (in oxygen) in the presence of M-50 after 15 hr exposure decomposed extensively, 342 mg/g; in the presence of Ti(4Al,4Mn) alloy after only 8 hr at 288°C, the amount of volatiles was 191 mg/g. Formulation of the commercial fluid with C_2PN_3 additive was not as effective as the stabilization processing.

All the perfluoroalkylether fluids studied were stable in nitrogen at 343°C. The thermal oxidative stability in the absence of metal alloys varied, with Aflunox exhibiting the best behavior. All the fluids were degraded in oxygen at 316°C during 24 hr exposure to Ti(4Al,4Mn) alloy with the exception of a perfluoroalkylether-substituted triazine and the modified Z-25.

17. Key Words (Suggested by Author(s))
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