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Phospha-s-Triazines and Related Compositions of Improved Hydrolytic and Thermal Stability

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PHOSPHA-S-TRIAZINES AND RELATED COMPOSITIONS OF IMPROVED HYDROLYTIC AND THERMAL STABILITY

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SBIR PHASE II DRAFT FINAL REPORT

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FOREWORD

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1. SUMMARY

The objectives of the Phase II Small Business Innovation Contract were to develop novel degradation inhibitors for perfluoropolyalkylether fluids, to compare the action of representative additives (including those synthesized under the program and to provide data base for the selection of optimum fluid/alloy/additive systems for specific applications.

Under the Phase II Program four novel additives, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$, $[C_3F_7O(CF(CF_3)CF_2O)_2C(CF_3)_2CN][(C_6H_5)_2PN]_2$, u-$[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ and $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$, were prepared. Thermal stabilities of these compounds, the monophospha-s-triazine, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$, synthesized under Phase I and the phosphate ester, $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]_2P(O)OC_6H_5$, were determined. The monophospha-s-triazine was partially stable over 24 h at 343°C (81% starting material recovery); no decomposition was observed at 316°C. Diphospha-s-triazines were completely decomposed at 300°C; at 285°C the starting material recovery was 25%. The 1,3-diphosphatetraazacyclooctatetraene was the least stable of the heterocyclics, at 285°C only 2% of the starting material survived the 24 h exposure. The two phosphate esters, $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]_2P(O)OC_6H_5$ and $C_3F_7(OCF(CF_3)CF_2)_6C_6H_4OP(O)(OC_6H_5)_2$ showed approximately 10% decomposition at 316°C; at 343°C the starting material recovery was below 50%. None of the above compounds was found to undergo hydrolysis at 100°C.

All the materials were effective in arresting the degradation of perfluoropolyalkylether fluids in the presence of metal alloys at elevated temperature, >300°C, in oxidizing atmospheres.

The action of alloys: 440C steel, M-50 steel, Pyrowear 675, Cronidur 30, Ti(4Al,4Mn) and Ti(6Al,4V); the effect of additives: monophospha-s-triazine, diphospha-s-triazines, 1,3-diphosphatetraazacyclooctatetraene, phosphate esters, $(R_fC_6H_4O)_2P(O)OC_6H_5$, $R_fC_6H_4OP(O)(OC_6H_5)_2$, phosphate/diester rust inhibiting mixtures, and phosphine $[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4]_3P$ were evaluated in Krytox 143AC, Krytox 16256 and Fomblin Z25. Two batches of Fomblin Z25 were tested, P28 and P151. The degradation promoting action of the different ferrous alloys in Krytox 16256 was comparable; the behavior of Ti(6Al,4V) alloy did not differ significantly , whereas Ti(4Al,4Mn) alloy was by far most detrimental. However, in Fomblin Z both the titanium alloys were equally detrimental. The assessment of complete inhibition was denoted as $\leq$0.5 mg/g volatile production. The overall rating of additives was phosphates > phosphate/diester mixture > phosphine $\geq$ phospha-s-triazines. Krytox 16256 was less responsive to the additive inhibition than Krytox 143AC. The same applied to P28 versus P151 batches of Fomblin Z25. Phosphate esters were fully effective over 24 h exposure at 330°C in the systems: Krytox 16256/440C, Krytox 16256/Ti(4Al,4Mn), Krytox 16256/Ti(6Al,4V), Fomblin Z25/440C, Fomblin Z25/Ti(4Al,4Mn) and Fomblin Z25/Ti(6Al,4V). In general the phosphine, PH-3, was less effective with ferrous alloys than the phosphates and phospha-s-triazines and also less effective in the Fomblin Z25/Ti(4Al,4Mn). Metal surface treatments tested failed to inhibit fluids' degradation; metal washing protocols involving water enhanced fluids' degradation.

2. INTRODUCTION

Perfluoropolyalkylethers as represented by commercial fluids namely Krytox, Aflunox, Demnum, Fomblin Z and the new experimental compositions [Ref. 1-4] represent a family of materials of high viscosity index and an exceptional thermal and oxidative stability. A number of investigations were carried out to assess the thermal oxidative stability of these materials both in the absence and presence of metals, metal oxides and metal halides [Ref. 5-18]. These studies have shown that all these materials in the presence of metals undergo degradations and cause metal corrosions, in particular at elevated temperatures and in oxidizing atmospheres. Corrosion and fluid degradation were observed also at "bulk" ambient temperatures under boundary lubrication situations [Ref. 5, 13, 15]. It is believed that under these conditions high temperatures are reached at the molecular level leading to thermodynamically favored fluoride formation. The metal fluorides in turn promote scissions of the perfluoroalkylether chains, as originally postulated by Gumprecht [Ref. 1], and later substantiated by Carré [Ref. 13] and others [Ref. 15].

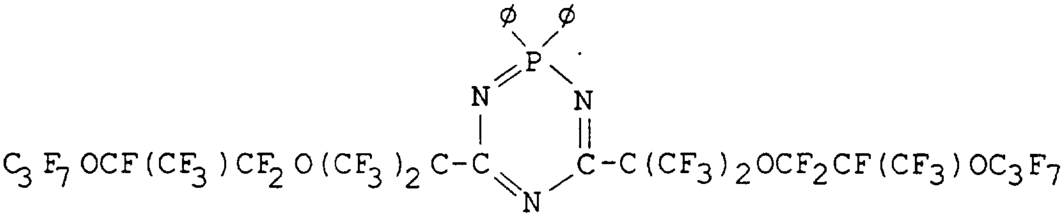
Two families of materials, phosphines and phosphorus-containing heterocyclics such as phospha-s-triazines and diphosphatetraazacyclooctatetraenes, were identified as effective inhibitors of the degradation process [Ref. 19-23]. The initially synthesized phospha-s-triazines exhibited hydrolytic instability due to the presence of $-OCF(CF_3)$ linkage adjacent to the ring. Replacement of this group by $OC(CF_3)_2$ moiety in monophospha-s-triazines, accomplished under Phase I program [Ref. 24], alleviated this shortcoming without diminishing the corrosion and degradation arresting action. A part of Phase II research was devoted to extending the concept of a "hindered carbon" ring attachment to other phosphorus-containing heterocyclics. A large effort was directed at determining the action of different metal alloys on perfluoropolyalkylethers of interest to NASA and at evaluating the degradation and corrosion inhibiting behavior of additives synthesized under the subject program as well, as that of phosphines and other novel additives. The ultimate objective was to provide a spectrum of additives and to develop a reliable data compilation to allow the selection of an optimum fluid/alloy/additive system for a specific application.

3. RESULTS AND DISCUSSION

Phase II efforts were directed at synthesis and characterization of novel perfluoropolyalkylether fluids degradation inhibitors and their and other additives evaluations. For the ease of presentation the technical discussion was divided into these two main sections.

3.1 Synthesis

Under Phase I program the synthesis of the monophospha-s-triazine (I) was successfully accomplished [Ref. 24, 25].



I

The material was found to be hydrolytically stable and to arrest the degradation of poly(hexafluoropropene oxide) fluid (Krytox 143AC) at elevated temperature (316°C) in the presence of Ti(4Al,4Mn) alloy. At that time I was not characterized by mass spectrometry. This analysis was carried out under the current program. The presence of a high intensity molecular ion at m/e 1253 confirmed the structure whereas, the parent ion at m/e 225, $[(C_6H_5)_2PN_2C]^+$, showed clearly that the fragmentation path is fully consistent with that of the monophospha-s-triazines having

$-(CF_2)_n$ and $-OCF(CF_3)$ groups adjacent to the ring carbon [Ref. 26]. The material was soluble in commercial perfluoropolyalkylether fluids, namely Krytox 143AC, Krytox 16256 and Fomblin Z25 down to -40°C. The relevant data are listed in Table 1.

Compound I did undergo significant degradation at 343°C *in vacuo* over a 24 h period (see Table 2) as shown by the volatiles production which, amounted to 14% of the original sample, and the recovery of 81% of the starting material. At 316°C, under otherwise identical conditions, the starting material recovery was essentially quantitative >96%. The volatiles production was minimal, 0.6%. In both tests the three main constituents were the nitrile, $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$, the corresponding hydrogen-terminated analogue, $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$, and benzene in a relative ratio of ~13:1:3.4 (based on the GC areas, not corrected for the specific detector responses). Very small quantities of breakdown products such as $C_3F_7OCF(CF_3)CN$, $C_3F_7OCF(CF_3)CF_2H$, $CF_3CF_2C_6H_5$ and $CF_3CF_2CF_2C_6H_5$ were also observed. Surprisingly, the product distribution was similar at 343°C and 316°C.

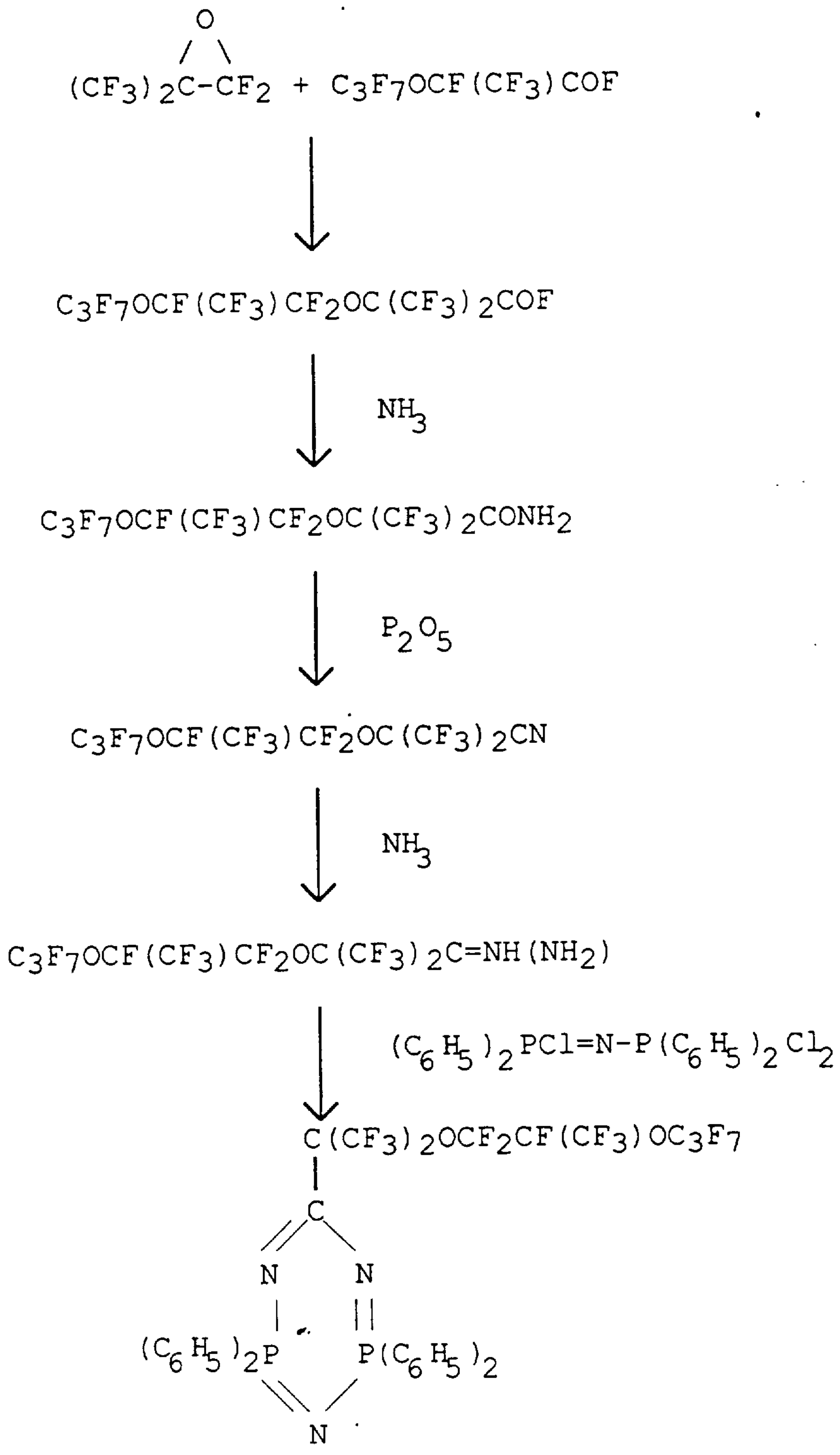
3.1.1 Diphospha-s-triazines

Diphospha-s-triazines $[C_3F_7O(CF(CF_3)CF_2O)_xCF(CF_3)CN][(C_6H_5)_2PN]_2$ [Ref. 27], although effective in arresting perfluoropolyalkylether fluid degradation, are, however, also susceptible to hydrolysis. The replacement of the $CF(CF_3)$ ring attachment by a $C(CF_3)_2$ moiety would be expected to alleviate this shortcoming, whereas the presence of the two phosphorus ring atoms should enhance any lubricating action.

The reaction sequence utilized for the preparation of Compound II is presented in Scheme I. The steps up to the nitrile, $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$, were successfully developed under Phase I [Ref. 24, 25]. After the conditions were optimized the novel amidine, $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$, was formed readily and was isolated in a 62% yield. Its reaction with imido-tetraphenyl-diphosphinic acid trichloride gave the diphospha-s-triazine, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II), in 84.5% yield. The infrared characteristics and mass spectral breakdown pattern, in particular the parent peak at m/e 424, which portrays the loss of the perfluoroalkylether substituent, are fully consistent with those observed for the $R_fOCF(CF_3)$ substituted diphospha-s-triazines [Ref. 27]. As expected, in view of the $(CF_3)_2C$ ring attachment, Compound II was hydrolytically stable.

The diphospha-s-triazine, II, was insoluble at room temperature in the perfluoropolyalkylether fluids (see Table 1). Yet, was effective in arresting fluid's degradation at elevated temperatures in oxidizing atmospheres in the presence of metal alloys. These investigations will be discussed in Section 3.2. The material showed drastically lower thermal stability than the monophospha-s-triazine, I. No starting material remained after exposure at 300°C, however, at 285°C 25% of the starting material

SCHEME I


(CF3)2C-CF2 + C3F7OCF(CF3)COF
C3F7OCF(CF3)CF2OC(CF3)2COF
NH3
C3F7OCF(CF3)CF2OC(CF3)2CONH2
P2O5
C3F7OCF(CF3)CF2OC(CF3)2CN
NH3
C3F7OCF(CF3)CF2OC(CF3)2C=NH(NH2)
(C6H5)2PCl=N-P(C6H5)2Cl2
C(CF3)2OCF2CF(CF3)OC3F7
C
N
N
(C6H5)2P
P(C6H5)2
N

II

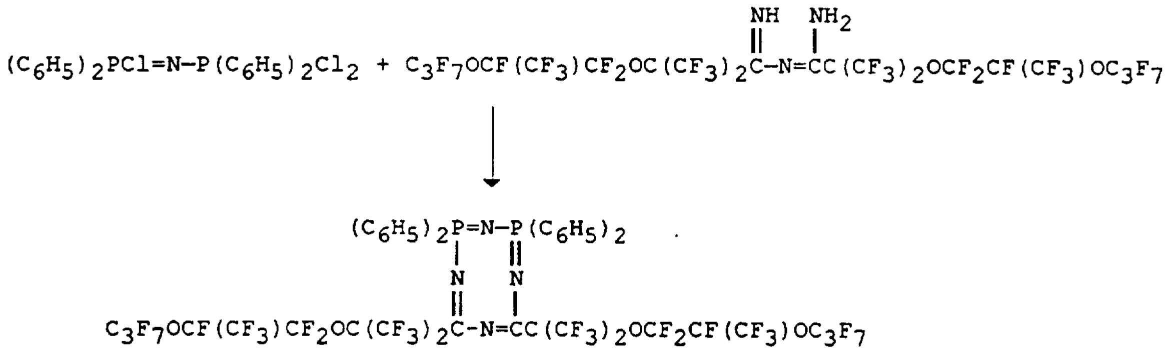
was recovered, as shown by the data given in Table 2. The corresponding diphospha-s-triazine wherein the carbon substituent was $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ survived the 24 h 316°C heat treatment unchanged [Ref. 28]. The low stability of II is totally unexpected. The nitrile, $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$, was not detected among the volatiles. At 285°C the major product was $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$ admixed with $C_3F_7OCF(CF_3)CN$, $C_3F_7OCF(CF_3)CF_2H$ in the ratio of 8:0.5:0.5. In the test performed at 343°C benzene, $C_2F_5C_6H_5$ and $C_3F_7C_6H_5$ were also observed among the volatiles. The absence of the nitrile, $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$, in the degradation of II, indicates that the mechanism responsible for the decomposition does not involve dissociation. The latter process appears to be operative in the previously synthesized phospha-s-triazines, both mono and diphospha [Ref. 28] as well as Compound I. On the basis of the mass spectral breakdown pattern, discussed above, one would expect $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$, II, to exhibit similar degradation characteristics, at least, insofar as the nature of the products liberated is concerned as $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN][(C_6H_5)_2PN]_2$. Thus, the observed results are unexpected.

One way to increase the solubility of a diphospha-s-triazine in perfluoropolyalkylether fluids is to increase the length of the perfluoroalkylether chain. Accordingly, in the telomerization step (see Scheme I) instead of $C_3F_7OCF(CF_3)COF$ the longer chain acid fluoride, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$, was utilized to give $C_3F_7O[CF(CF_3)CF_2O]_2C(CF_3)_2COF$ in a 41% yield. The subsequent reaction steps were identical to those employed in the synthesis of II. The diphospha-s-triazine, $[C_3F_7O(CF(CF_3)CF_2O)_2C(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III), was obtained in an 86% yield. It exhibited somewhat better solubility in the perfluoropolyalkylether fluids than II, as evident from Table 1; however, it still required elevated temperatures to achieve solution. Compound III, in agreement with the data obtained for II, was unstable at 316°C; after 24 h exposure no starting material was recovered. A spectrum of products was found: $C_3F_7OCF(CF_3)CF_2H$, $C_3F_7OCF(CF_3)CN$, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$, $C_3F_7[OCF(CF_3)CF_2]_2H$, $C_3F_7[OCF(CF_3)CF_2]_2C(CF_3)_2H$, C_6H_6, $CF_3CF_2C_6H_5$ and $C_3F_7C_6H_5$ in the relative ratio of 1:1:2.5:2.5:0.7:0.5:0.1:0.3:0.2. Again no nitrile $C_3F_7[OCF(CF_3)CF_2]_2C(CF_3)_2CN$ was observed. In direct analogy with II, diphospha-s-triazine III functioned effectively as a corrosion and degradation inhibitor in perfluoropolyalkylether fluids in the presence of alloys at elevated temperatures in oxidizing atmospheres.

3.1.2 Diphosphatetraazacyclooctatetraenes

A diphosphatetraazacyclooctatetraene ring arrangement contains two phosphorus atoms and two carbon atoms in addition to the four nitrogens. Thus, insofar as the potential lubricity characteristics are concerned a diphosphatetraazacyclooctatetraene would be expected to be better than a monophospha-s-triazine system. The higher ratio of the perfluoroalkylether chains, compared to diphospha-s-triazines, should provide for increased solubility in perfluoropolyalkylether fluids.

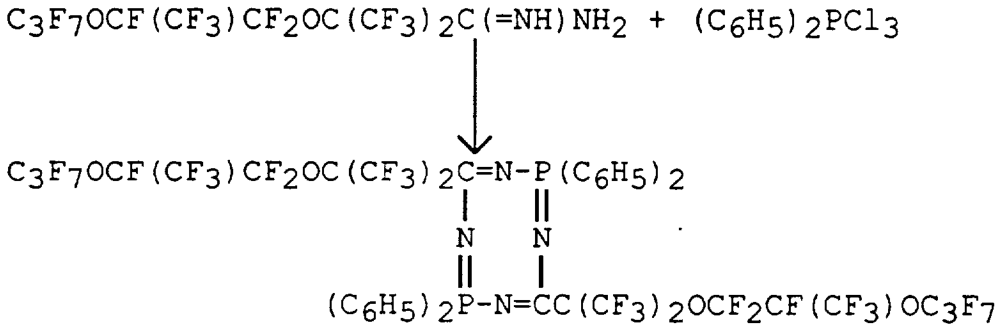
The unsymmetrical 1,3-diphosphatetraazacyclooctatetraene, IV, was the first representative of the system. It was synthesized using the procedure developed earlier [Ref. 29] e.g.



The infrared spectral characteristics, specifically the absorptions at 1610, 1580 and 1540 cm^{-1} were consistent with those observed for the previously prepared compounds [Ref. 29]. The mass spectral breakdown pattern also parallels that of $R_f(CF_2)_n$- and $R_fOCF(CF_3)$-substituted 1,3-diphosphatetraazacycloocta-tetraenes. Of particular significance are the M - R_f (m/e 951) and the M - R_f - R_fCN ions (m/e 424) which are typical of this arrangement. These results show clearly that the $O(CF_3)_2C$ ring attachment does not affect the electronic configuration of the ring system.

The octatetraene IV was hydrolytically stable. It was less stable thermally than the corresponding diphospha-s-triazines, as evident from the data given in Table 2. At 300°C no starting material was recovered; even at 285°C the recovery amounted only to 2%. The thermal stability of the $R_fOC(CF_3)_2$-substituted 1,3-diphosphatetraazacyclooctatetraene was significatly lower than that of the corresponding $R_fOCF(CF_3)$-substituted analogue, wherein at 316°C 13% of the starting material was recovered [Ref. 30]. In the volatiles, both at 300°C and 285°C, the nitrile $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ accounted for 50% of the products, $C_3F_7OCF(CF_3)H$, $C_3F_7OCF(CF_3)CN$ and $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$ comprised the rest. The relative ratio was 5:2:0.7:2, respectively. Approximately 2% of monophospha-s-triazine, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$, was detected in the involatile residue. The formation of the monophospha-s-triazine on thermal decomposition of 1,3-diphosphatetraazacyclooctatetraene is in agreement with earlier studies [Ref. 30]. However, formation of the nitrile is unexpected. It is of interest that the nitrile $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ and the hydrogen terminated compound $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$, were the major components of the volatiles produced on exposure of IV in Krytox 16256 in the presence of 440C steel at 316°C over 24 h in oxygen (Test 102, Table 3).

Several attempts, varying reagents ratios, solvents and temperatures, were made to prepare the 1,5-diphosphatetraazacyclooctatetraene s-$[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$, the symmetrical isomer of IV, by the reaction of the amidine with trichlorodiphenylphosphorane, e.g.:



$$C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2 + (C_6H_5)_2PCl_3 \longrightarrow$$

$$\begin{array}{rcccl} C_3F_7OCF(CF_3)CF_2OC(CF_3)_2 & C & {=}N{-} & P & (C_6H_5)_2 \\ & | & & \| & \\ & N & & N & \\ & \| & & | & \\ (C_6H_5)_2 & P & {-}N{=} & C & C(CF_3)_2OCF_2CF(CF_3)OC_3F_7 \end{array}$$

A spectrum of products was obtained in each instance. The majority of the compounds were not identified. At best, based on GC data, the desired material amounted only to 9% of the products mixture. Its mass spectrum matched that of the $R_fOCF(CF_3)$-substituted analogue. Of particular importance is the high intensity peak at m/e 225, $[CNP(C_6H_5)_2N]^+$ ion, which is characteristic of the symmetrical octatetraene and monophospha-s-triazine arrangements [Ref. 29]. It is noteworthy that the thermal stability of the symmetrical octatetraene s-$[C_3F_7OCF(CF_3)CN]_2[(C_6H_5)_2PN]_2$, was significantly lower than that of the unsymmetrical isomer [Ref. 30]. In view of the observed much lower thermal stability of the $R_fOC(CF_3)_2$-substituted materials versus $R_fOCF(CF_3)$-substituted analogues, the latter's thermal stability must be very low. It is likely that the inherent stability of the final product affects the ease of its formation or the behavior of its precursor.

3.1.3 Phosphate

Under the Air Force Program [Ref. 31] phosphates and phosphonates, substituted on the phenyl rings by perfluoroalkylether chains, were identified as very effective inhibitors of perfluoropolyalkylether fluid thermal oxidative degradation. The only investigated perfluoroalkylether substituents were $C_3F_7[OCF(CF_3)CF_2]_x-$, wherein x=2 and 3. It was necessary for two of the phenoxy groups to be perfluoroalkylether substituted to render the additive soluble in perfluoropolyalkylether fluids. Compounds having only one phenoxy group substituted by a perfluoroalkylether moiety, $R_fC_6H_4OP(O)(OC_6H_5)_2$, were however more hydrolytically stable than $(R_fC_6H_4O)_2P(O)OC_6H_5$. Furthermore, there were indications that the former were also more effective in arresting fluids' degradations. In view of these findings under NASA Phase II program synthesis of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ was pursued. The reaction sequence utilized is depicted in Scheme II.

No pure ester $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)CO_2CH_3$ was available. The only starting material which could be procured was a mixture of $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)COF$ and $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)H$. Having the hydrogen terminated compound caused some problems in achieving better yields of the intermediates. On the other hand, no efforts were expanded to optimize the yields, inasmuch as the main goal was to determine

SCHEME II

$$\begin{tikzcd}
C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)CO_2CH_3 \arrow[d, "BrC_6H_4Br/n\text{-}C_4H_9Li"] \\
C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)COC_6H_4Br \arrow[d, "SF_4"] \\
C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br \arrow[d, "\begin{array}{c} n\text{-}C_4H_9Li/(CH_3O)_3B \\ CH_3CO_2H/H_2O_2 \end{array}"] \\
C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH \arrow[d, "ClP(O)(OC_6H_5)_2/(C_2H_5)_3N"] \\
C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2
\end{tikzcd}$$

the properties of the final product $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V).

As expected the phosphate V exhibited much better hydrolytic stability than the phosphate esters $(R_fC_6H_4O)_2P(O)OC_6H_5$ [Ref. 31]. This was proven by on essentially quantitative starting material recovery following exposure to water at 100°C versus <70% recovery for the series $(R_fC_6H_4O)_2P(O)OC_6H_5$ [Ref. 31]. Compound V was stable at 316°C over 24 h period as shown by the absence of volatiles formation and 91% starting material recovery. The data are summarized in Table 2. At 343°C, under otherwise identical conditions, the starting material recovery was reduced to 45%. The thermal stability of V appears to be somewhat better than that of Additive C, $[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4O]_2P(O)OC_6H_5$, synthesized under the Air Force program [Ref. 31], wherein at 316 and 343°C the starting material recovery was 88 and 30%, respectively. Insofar as the perfluoropolyalkylether fluid degradation inhibiting action is concerned (see Section 3.2.4), Compound V seems more effective than the Additive C. Unfortunately, as can be seen from the listing in Table 1, its solubility in perfluoropolyalkylether fluids is marginal. Apparently, longer chains than the heptamer are required.

3.2 Perfluoropolyalkylether Fluid evaluations

3.2.1 Fluid Characterization

The investigations were limited to three commercial fluids namely Krytox series 143AC (MLO 71-6) and 16256, $C_3F_7O(CF(CF_3)CF_2O)_xC_2F_5$, and Fomblin Z25, $-(CF_2O)_x(CF_2CF_2O)_y-$. Of the latter material, two batches were tested, P28 and P151. All the fluids were characterized by ^1H and ^{19}F NMR spectroscopy.

The ^1H NMR of Krytox 16256 shows the presence of CF_3CFHO- by the typical doublet (actually doublet of quartets) at 5.6 and 5.8 ppm. Due to the fluid's high molecular weight and the low intensities of the end groups, the molecular weight and the end group ratio ($CF_3CF_2CF_2O:CF_3CF_2O$) were difficult to determine from the ^{19}F NMR spectrum. Compared to Krytox 143AC (MLO 71-6), Krytox 16256 appears to have a higher hydrogen content. The ^{19}F NMR spectrum is essentially identical with that of Krytox 143AC (MLO 71-6) [Ref. 32]. Based on the method of synthesis, i.e. telomerization of hexafluoropropene oxide, the only difference between the two fluids should be the number average molecular weight, which was determined by osmometry.

The ^1H NMR spectra of the two batches of Fomblin Z25 fluid confirmed the absence of hydrogen. Based on the ^{19}F NMR data the ratio of CF_2CF_2O to CF_2O in the P28 batch is 0.68:1.00, whereas in the P151 batch it is 0.74:1.00. These values indicate that the relative proportion of adjacent CF_2O units i.e. segments $-O(CF_2O)_x-$ wherein x>1 is higher in P28 than in P151 which should be reflected by a lower thermal oxidative stability in the presence of metals [Ref. 5]. Experimental data, as will become evident from the results discussed in the later portions of this report, are conflicting. In the absence of degradation inhibitors the extent of degradation was actually lower in the case of the P28 material. Yet, the degradation arresting action of additives was definitely more pronounced in P151, both in relative and absolute values. These results indicate more subtle factors to be involved. Namely, there is a good probability that there are other structural differences present not identified by ^{19}F NMR. These effects are not molecular weight related since the molecular weights of the two batches are virtually identical, 9750 versus 9700.

The two Krytox fluids differed widely in their molecular weights. Krytox 143AC was the low molecular weight material, 5500, whereas the molecular weight of Krytox 16256 was almost twice as high, 9900. Thus one would expect the effect of metals to be more drastic, with respect to the degradation extent, in the latter case. This stipulation assumes initiation followed by unzipping [Ref. 6]. It must be stressed as mentioned above, that the presence of the terminal hydrogen in both of the poly(hexafluoropropene oxide) fluids represents the weak link and consequently lowers the degradation onset inherent to this structural arrangement [Ref.33].

3.2.2 Metal Alloys

Six metal alloys were studied: M-50 steel, 440C steel, Pyrowear 675 [Ref. 34], Cronidur 30 [Ref. 35], Ti(4Al,4Mn) and Ti(6Al,4V) alloys. In addition very limited investigations were carried out using TiC coated 440C steel as well as 440C treated with silane derivatives. Also tested were two ceramics, silicon nitride and zirconia.

M-50 steel, 440C steel, Ti(4Al,4Mn) and Ti(6Al,4V) alloys were in the form of coupons of 1.67 cm^2 surface area. Pyrowear 675 and Cronidur 30 were in the form of balls 9.58 and 1.50 cm^2 surface area, respectively. Thus assuming the surface area to be proportional to the degradation catalyzing action one would expect Pyrowear 675 to promote more extensive degradation than the other steels; provided the inherent catalytic action is the same.

Due to the general phasing out of Freon solvents, the effect of using water wash instead of Freon-113 in the final cleaning of a 440C coupon was investigated. Exposure of a 440C coupon (washed with water and dried under vacuum, 0.001 mm Hg at room temperature for ~72 h) in Fomblin Z25-P151 in oxygen at 316°C for 8 h resulted in 527 mg/g of volatiles. This quantity is larger than that produced using a coupon washed with Freon-113 and dried under nitrogen stream, 475 mg/g (Table 3A, Test 44). Exposure of a coupon soaked in water for 1 h, dried under vacuum at room temperature for 0.5 h and stored under nitrogen for 16 h, resulted in 673 mg/g of volatiles and an unusually high coupon weight loss, -5.7 mg/cm^2. For a direct comparison, a 440C coupon was soaked in Freon-113 for 1 h and dried under a nitrogen stream. Heat treatment in Fomblin Z25-P151 of this coupon gave 417 mg/g of volatiles. This value corresponds to 62% of volatiles generated using the water soaked coupon. Based on these data it is obvious that there is a definite increase in fluid degradation when a coupon is treated with water. The magnitude of the effect appears to depend on the length of time of the water exposure and the extent of drying.

3.2.3 Additives

A series of additives were evaluated. The three phospha-s-triazines $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II), $[C_3F_7(OCF(CF_3)CF_2)_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III), the 1,3-diphosphatetraazacyclooctatetraene (IV) and the phosphate $C_3F_7[OCFC(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V) were synthesized under the current program and were discussed in Section 3.1. All five materials, in contrast to the earlier prepared mono- and diphospha-s-triazines and the $(R_fC_6H_4O)_2P(O)OC_6H_5$ phosphates were hydrolytically stable. The phosphine, $[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4]_3P$ (PH-3) first described by Tamborski, Snyder and Christian [Ref. 20] was resynthesized for NASA. The phosphates $C_3F_7(OCF(CF_3)CF_2)_2C_6H_4OP(O)(OC_6H_5)_2$ (A), $[C_3F_7(OCF(CF_3)CF_2)_4C_6H_4O]_2P(O)OC_6H_5$ (B), $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]_2P(O)OC_6H_5$ (C), and the mixtures of 61%

of C and 39% $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]P(O)(OC_6H_5)OH$ (D-1), 81% of C and 19% $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]P(O)(OC_6H_5)OH$ (D-2), 78% of C and 22% of $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]P(O)(OC_6H_5)OH$ (D-4) were developed under Air Force contract [Ref. 31]. Inasmuch as the phosphates and the related compositions were found to inhibit very effectively the degradation of Krytox 143AC and Demnum S-100 in the presence of M-50, under the Air Force program, their evaluation in Krytox 16256 in the presence of 440C steel and related alloys was strongly warranted. Furthermore, since the mixtures D-1, D-2 and D-4 were found to act also as rust inhibitors, investigation of their performance in the materials of interest to NASA, in particular since long storage periods are anticipated, was mandatory.

3.2.4 Fluid Stability Investigations

The major thrust of this undertaking was centered on Krytox 16256/440C steel system in view of NASA requirements. The work involving Krytox 143AC was conducted to provide information on different molecular weight materials, whereas Fomblin Z25 was investigated to assess the effect of additives and metals on the least stable perfluoropolyalkylether fluid [Ref. 5]. Also, depending on the specific applications, NASA does employ a variety of perfluoropolyalkylether fluids due to the different performance requirements. All the tests carried under the subject contract are summarized in a chronological order in Table

3A and are grouped in Tables 3B-3D by fluid, coupon and additive, respectively.

The effect of the different alloys on the thermal oxidative degradation of Krytox 16256 is presented in Figure 1. It is clearly apparent that the action of Ti(4Al,4Mn) is the most detrimental, whereas the Ti(6Al,4V) action is comparable to that of the steel alloys. At 316°C the quantity of volatiles produced in the presence of Ti(4Al,4Mn) was found to be higher by a factor of 8 compared to 440C and by factor of 4 compared to Cronidur 30 and Pyrowear 675. It is surprising that the last two alloys affected essentially the same degree of degradation since their respective surface areas differ by a factor of 6. At 330°C the extent of fluid degradation in the presence of 440C steel, as compared to the quantity produced at 316°C, was in a reasonably good agreement with the doubling of reaction rate for every 10°C temperature rise. Having two 440C steel coupons resulted in a 1.7 fold increase in volatiles, which indicates at least in this case, that the rate of degradation is almost directly proportional to the surface area. Doubling the exposure time, from 24 to 48 h, increased the volatiles production from 61 to 212 mg/g. This finding clearly confirms that the process is autocatalytic.

The increase in the degradation extent for Pyrowear 675 and Cronidur 30 with temperature was minimal. Cleaning of the metal, whether just wiped with Freon-113 or whether cleaned by ultrasound in Freon-113 had no significant effect upon the metal's action on the fluid.

No data are available for the M-50 action on Krytox 16256 at 316°C, however at 343°C, 440C steel was significantly more detrimental; almost by a factor of 3. Again, the quantity of volatiles produced agreed with the reaction rate/temperature relationship.

The effectiveness of the different additives in arresting Krytox 16256 degradation in the presence of 440C steel is displayed in Figure 2. The most effective additives are the phosphates C, B and V; 0.2 mg/g of volatiles formed at 330°C. Based on our previous studies [Ref. 33], a value of ≤ 0.5 mg/g represents essentially an absence of degradation. Lengthening of the exposure of C to 48 h resulted in a drastic increase of the volatiles formed to 4.3 mg/g. This was associated with 4.6 mg/cm^2 weight loss of the coupon, which indicates severe corrosion. The corresponding value for the first 24 h was 0.06 mg/cm^2. However a duplicate 48 h test resulted only in 0.5 mg/g of volatiles and 0.06 mg/cm^2 coupon weight loss. Similar behavior was observed with Additive V. The first 48 h test at 330°C resulted in volatile production of 36 mg/g. Yet, a duplicate test afforded only 0.4 mg/g of volatiles. These results indicate that both additives have time limited effectiveness at 330°C and 48 h appears to be the limit.

None of the phospha-s-triazines nor the 1.3-diphosphatetraazacyclooctatetraene (IV), with the possible exception of I (0.7 mg/g), exhibited an acceptable performance even at 316°C. On the other hand, comparison of the 330°C results showed I and possibly IV to be definitely more effective than PH-3. It is noteworthy that the rust inhibiting mixtures, D-1 and D-2, exhibited degradation inhibition comparable to that of the phosphates A, B, C and V. The relative effectiveness of phosphate A at 343°C is surprising. Phosphate A differs from phosphates B and C in having only one of the phenoxy groups substituted by a perfluoroalkylether chain, namely $R_fC_6H_4OP(O)(OC_6H_5)_2$. The consequently lowered content of the perfluoroalkylether units resulted in A being insoluble at room temperature in Krytox 16256. To alleviate this shortcoming synthesis of A analogues, having longer perfluoroalkylether chain namely Compound V was carried out.

It is evident from the Figure 3 data that compounds C, I, II and III were fully effective in the presence of Ti(4Al,4Mn) at 316°C in arresting Krytox 16256 degradation. Yet, in the absence of an additive this alloy was much more detrimental than 440C steel, as mentioned earlier. At 330°C additives A, C and V were fully effective in the presence of Ti(4Al,4Mn) alloy. This is based on volatiles production of $\leq$ 0.5 mg/g. The action of C at this temperature over 24 h is limited since in a duplicate test the volatiles amounted to ~9 mg/g. On the other hand V was effective over 48 h. Considering the extent of degradation in the absence of an additive, PH-3 and I did arrest to some degree the degradation of Krytox 16256 even up to 343°C. All the additives tested were efective in the presence of Ti(6Al,4V).

The relative effectiveness of representative additives, namely the rust and degradation inhibiting mixture D of $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]_2P(O)OC_6H_5$ and $[C_3F_7(OCF(CF_3)CF_2)_3C_6H_4O]P(O)(OC_6H_5)OH$, the hindered monophospha-s-triazine I, the phosphine PH-3 and the phosphate V in arresting the degradation of Krytox 16256 in the presence of the three steel alloys, 440C, Pyrowear 675 and Cronidur 30 is illustrated in Figure 4. It is of interest that in each instance, with the possible exception of Pyrowear 675, the order of effectiveness is essentially the same, V>mixtureD>I>PH-3. In the case of 440C steel the differences are sharp; in the case of Cronidur 30 negligible. However, in all the examples with the possible exception of 440C steel, the mixture D performed as well as compound V within the acceptance limits.

Figure 5 compilation illustrates the differences in thermal oxidative behavior between Krytox 143AC and Krytox 16256 in the presence of different metals (M-50, Ti(4Al,4Mn) and 440C) and additives (monophospha-s-triazine and phosphine, PH-3). Invariably, the additives were more effective in Krytox 143AC than Krytox 16256 as measured by the volatiles production. Yet, there is virtually no difference between Krytox 143AC and Krytox 16256 in the degradation extent at 343°C promoted by 440C steel in the absence of additives.

As discussed earlier Fomblin Z25 is much more susceptible to thermal oxidative degradation in the presence of metal alloys than poly(hexafluoropropene oxides) represented by the Krytox family of fluids. This is clearly evident from the data depicted in Figure 6, specifically by the 8 h exposure at 316°C, of the P151 fluid batch to 440C steel. The extent of degradation under these conditions was of the order of 50%. Yet, in this fluid batch all the additives tested (A, B, C, D-2, D-4, I, II, III, V and PH-3) were fully effective at 316°C over 24 h period, with an exception of monophospha-s-triazine I and a possible exception of diphospha-s-triazine III (0.9 mg/g). The phosphate C exhibited acceptable inhibition even at 330°C; V was unexpectedly less effective (1.4 mg/g). Based on the comparisons given in Figure 7 the Fomblin Z25-P28 batch is definitively less susceptible to the additive action than the P151 material. This is shown by the action of M-50, 440C and Ti(4Al,4Mn) alloys and the additives I, PH-3 and the phosphate A. It should be noted that in the absence of an additive the extent of degradation of the batch P151 at 288°C over 8 h in the presence of Ti(4Al,4Mn) is higher by a factor of 2 compared to batch P28.

The additives, C, D-2 and PH-3, in particular the first two, were fully effective in arresting the degradation of Fomblin Z25 batch P151 at 316°C in oxygen in the presence of Ti(4Al,4Mn) alloy (see Figure 8). The hindered phospha-s-triazines, Compounds II and III were only marginally inferior in performance (0.9-1.0 mg/g). The data for I (1.9 mg/g) is definitely higher.

Additives V and C were also fully effective in Fomblin Z25 at 330°C over 24 h, both in the presence of Ti(4Al,4Mn) and Ti(6Al,4V) alloys.

As illustrated in Figure 9 neither the phosphines nor phospha-s-triazines provided acceptable degradation arresting action, based on $\geq$0.5 mg/g limit, for Fomblin Z25-P28 in the presence of M-50 at 316°C even over the shortened 16 h exposure. PH-3 exhibited the best performance, 1.1 mg/g of volatiles. The phospha-s-triazines were relatively ineffective decreasing the volatiles production only to 108-142 mg/g. However, at 300°C the monophospha-s-triazine, I, was essentially fully effective (0.7 mg/g). It must be emphasized that in the absence of an additive over only 8 h period, at 316°C, Fomblin Z25-P28 produced 337 mg/g of volatiles; the value for the P151 batch was higher, 482 mg/g. It is of interest that although M-50 does not promote the fluid's degradation to as high a degree as Ti(4Al,4Mn), the latter is significantly more receptive to inhibition by additives.

Ceramics such as Si_3N_4 and zirconia had a significantly lesser effect on Fomblin Z25 degradation than the metal alloys. The data depicted in Figure 10 illustrate these aspects. Si_3N_4 (88 mg/g, 24 h), based on the duration of the exposure has less of a detrimental influence than zirconia (90 mg/g, 8 h).. Apparently, the origin of a given ceramic affects its action on the fluid, inasmuch as Si_3N_4 obtained from CERBEC promoted the production of only 5.5 mg/g [Ref. 36] under the conditions used for the NASA supplied Si_3N_4. In the absence of a metal or ceramic, Fomblin Z25-P151 under otherwise identical conditions (316°, O_2, 24 h), undergoes a minimal degradation, 3.4 mg/g [Ref. 36].

Different treatments of 440C steel such as TiC coating, exposure to hexamethyldisilazane and 3-aminopropyltriethoxysilane, contrary to observations reported by others [Ref. 37], failed to decrease the extent of fluid's degradation. Actually, the results using Fomblin Z25-P151 are virtually identical for all the steels tested. This includes the new alloys Cronidur 30 and Pyrowear 675 as well as the treated 440C steel. Both of the titanium alloys, Ti(4Al,4Mn) and Ti(6Al,4V) were found to cause almost complete fluid degradation even at 288°C over just 8 h.

To summarize, as noted above, the action of the different steels on Krytox 16256 was found to be virtually identical at 316°C, in oxygen over a 24 h period, insofar as the volatiles production is concerned. The Ti(4Al,4Mn) alloy promoted the degradation to a much higher degree. Protective surface treatments on 440C steel coupons had no effect on its degradation promoting action; however, water exposure had a definite detrimental effect.

Phosphates V and C were found to be fully effective at 330°C in the Krytox 16256/440C system and this seems to apply also to the new alloys, Pyrowear 675 and Cronidur 30 and both titanium alloys. Phospha-s-triazines were marginal at 316°C, but phosphines appeared to be even less effective. In the Krytox

16256/Ti(4Al,4Mn) and Ti(6Al,4V) systems at 316°C phosphates, phospha-s-triazines arrested essentially completely the fluid's degradation; at 330°C only the phosphates A, C and V exhibited an acceptable performance.

Studies have shown Krytox 143AC (MLO 71-6) to be definitely more responsive to additive action than Krytox 16256. Whether the factor responsible for this behavior is the molecular weight or an absence of a labile structural arrangement in the early batch, cannot be ascertained from the data on hand. The latter possibility offers a more plausible explanation. Phosphate C was fully effective in arresting the degradation of Fomblin Z25/440C system at 330°C; phosphate V was marginal. Both C and V were fully effective in the Fomblin Z25/Ti(4Al,4Mn) and Fomblin Z25/Ti(6Al,4V) system at 330°C. Large differences in responsiveness to additives were noted between the batches. Specifically an earlier Fomblin Z25 batch was less susceptible to additives' action. Based on the investigations performed the overall rating of additives effectiveness in arresting perfluoropolyalkylether fluids' degradation, at elevated temperatures in oxygen in the presence of metals over a 24 h exposure, is phosphates > phosphate rust inhibiting mixtures > phosphines $\geq$ phospha-s-triazines.

4. EXPERIMENTAL

General

Operations involving moisture or air sensitive materials were carried out either in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass or *in vacuo*.

All the melting points are uncorrected and were determined in evacuated, sealed capillaries, unless otherwise stated. Infrared spectra (IR) were recorded using Perkin-Elmer Corp. Model 1330 infrared spectrophotometer. Molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Gas chromatography (GC) was performed by employing either a 10 ft x 1/8 in stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb GAW or a 3 ft x 1/8 in stainless steel column packed with 3% Dexsil 300 on 100/120 mesh Chromosorb WAW using a programming rate of 8°C/min. The mass spectrometric analyses were obtained with 21-491B double focusing mass spectrometer attached to Varian Aerograph Model 2700 gas chromatograph equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. The ^1H and ^{19}F NMR spectra were recorded at 200 MHz on Varian VRX 200. The spectra were obtained using 40% concentration in mixed solvents of $CFCl_3$ and C_6F_6 with an acetone-D_6 capillary lock. All proton shifts are relative to TMS at 0 ppm; all fluorine shifts are relative to $CFCl_3$ at 0 ppm. Vacuum line techniques were utilized where applicable. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of Imido-tetraphenyl-diphosphine Acid Trichloride, $(C_6H_5)_2PCl{=}N{-}P(C_6H_5)_2Cl_2$ [Ref. 38]

In an inert atmosphere enclosure, into a 500 mL 3-neck round bottom flask were introduced chlorodiphenylphosphine (99.7 g, 0.45 mol), ammonium chloride (18.2 g, 0.34 mol) and 1,1,2,2-tetrachloroethane (220 mL). The flask was then equipped with a reflux condenser and chlorine gas (39 g, 0.55 mol) diluted with nitrogen was bubbled through the stirred solution at ambient temperature over a period of 2 h. Subsequently, the reaction mixture was heated in an oil bath; chlorine (12.0 g, 0.169 mol) addition continued for 2 more h at 100-125°C. After stirring for additional 0.5 h at 125°C, the hot solution was filtered (using a filter stick assembly) into an evacuated flask. From the clear filtrate, solvent was removed *in vacuo* at 60-70°C, followed by pumping at 75°C for 5 h. The resultant product was repeatedly washed with hot, dry benzene (6 x 130 mL) in an inert atmosphere enclosure until the decanted solution was clear at room temperature. After drying, a white, powdery solid imido-tetraphenyl-diphosphinic acid trichloride (65.3 g, 59.3% yield) was obtained. The infrared spectrum, given in Figure 11, is identical with that of an authentic spectrum. From the benzene washings, 23.4 g of $(C_6H_5)_2PCl_3$ byproduct was recovered.

Preparation of octafluoroisobutylene epoxide [Ref. 24]

In a typical reaction hexafluoropropylene oxide (20.00 g, 120 mmol) and hexafluoroacetone (19.82 g, 119 mmol) were measured by volume using a calibrated vacuum system and condensed into a 125 mL stainless steel Parr bomb at -196°C. The bomb was then heated in a tall, sand filled, heating mantle at 260°C (sand temperature) for 17 h. Subsequently, the bomb was cooled to room temperature, attached to a vacuum system and the volatiles transferred to an ampule were fractionated through traps cooled to -96, and -196°C. The -196°C fraction was refractionated as above and the crude epoxide collected in the -96°C cooled trap. Final purification was performed by fractionation through a -78, -96 and -196°C cooled traps. The pure epoxide (8.5 g, 33% yield), which condensed in the -96°C trap, had vapor pressure of 4.5 mm Hg at -78°C.

Purification of $C_3F_7OCF(CF_3)COF$

In an inert atmosphere enclosure, ~50 g of $C_3F_7OCF(CF_3)COF$ (as received from PCR Inc.) was transferred to a 100 mL round bottom flask equipped with a magnetic stirrer (1 in) and Teflon-glass stopcock adapter. After degassing at -196°C, the acid fluoride was fractionated from the warming flask through traps cooled at -78 and -196°C. A small quantity of cloudy, tinted liquid was left in the warming flask. The pure acid fluoride ($VP_{0°C}$ = 71 mm Hg) was collected in the -78°C trap. Another 50 g portion of the acid fluoride was purified in the same manner. Overall, 93 g of pure $C_3F_7OCF(CF_3)COF$ was obtained separated from 3.7 g of the less volatile impurity.

Preparation of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2COF$

Typically, in an inert atmosphere enclosure cesium fluoride (1.50 g, 9.87 mmol, dried in vacuo at 195°C for 8 h) and tetraglyme (3.0 g, $CH_3(OCH_2CH_2)_4OCH_3$ distilled over $LiAlH_4$) were weighed into a 25 mL round bottom flask (cleaned consecutively with 20% KOH in ethanol, methanol and Freon-113) equipped with a 1 in magnetic stirring bar and Teflon-glass stopcock adapter. Following evacuation (<0.001 mm Hg) at room temperature, $C_3F_7OCF(CF_3)COF$ (8.16 g, 24.57 mmol) was condensed into the flask at -196°C. The resultant mixture was stirred at room temperature for 2 h, and then at -20°C for 20 min. The first portion (~25%) of octafluoroisobutylene epoxide (4.79 g, 22.15 mmol) was condensed at -20°C with vigorous stirring; the rest of the epoxide was condensed at -196°C and the solution stirred at -15 to -20°C for 20 h. Subsequently, the volatiles (9.06 g) were removed *in vacuo* (initially at room temperature, then at 40°C), and fractionated through traps cooled to 0, -23, -47, and -196°C, giving 5.47 g of the product in the -23°C trap and a small amount in the -47°C trap. Refractionation of the -47°C fraction through -23, -47, -196°C cooled traps gave an additional 0.74 g in the

-23°C trap. The -47°C fraction thus obtained was fractionated again to give 0.13 g of product. The combined -23°C fractions amounted to 6.34 g (52.2% yield, $VP_{0°C}$ = 3 mm Hg) of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2COF$. The -196°C fractions were combined and refractionated using traps cooled to -78 and -196°C. In the -78°C trap was obtained 2.12 g of an unidentified acid fluoride. Neither of the starting materials was recovered. Three preparations were performed to give 17.5 g of the desired acid fluoride.

Preparation of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CONH_2$

$C_3F_7OCF(CF_3)CF_2OC(CF_3)_2COF$ (9.41 g, 17.17 mmol) and NH_3 (40.0 mmol) were condensed *in vacuo* at -196°C into an ampule (65 mL) fitted with a Teflon-glass stopcock adapter. The reaction mixture was warmed to -78°C for 10 min, -47°C for 10 min, then held at -23°C for 4 h, and at -78°C overnight. The volatiles were fractionated through traps cooled to -23, -47, -78, and -196°C. The unreacted NH_3 (4.7 mmol) was recovered in the -196°C trap. In the -23 and -47°C traps was collected the byproduct $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$ (69 mg). The residue (9.17 g), remaining in the ampule, was treated with Freon-113 (15 mL) and filtered in an inert atmosphere enclosure. Evaporation of solvent from the filtrate resulted in 7.8 g (83.4% yield) of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CONH_2$. Two preparations were conducted to give 14.1 g of the amide.

Preparation of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$

In an inert atmosphere enclosure into a 100 mL round bottom flask containing $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CONH_2$ (11.56 g, 21.21 mmol) was added P_2O_5 (37 g, 262 mmol). The flask was then equipped with a short distillation bridge and a receiver flask cooled in ice. The mixture was heated at 197-210°C under nitrogen bypass until distillation stopped. After cooling to room temperature, the whole set-up was attached to the vacuum system and the reaction flask was heated again at 190°C for 1 h. The volatiles collected in a -196°C cooled trap were fractionated through traps held at -47 and -196°C. The -47°C fraction contained the nitrile (9.7 g, $VP_{0°C}$, 3.5 mm Hg). A small quantity of the starting amide was recovered in the receiver; it was treated with fresh P_2O_5 at 213-232°C to give an additional 0.5 g of nitrile. The combined nitrile was refractionated through traps cooled to 0, -23, -47, and -78°C to give pure $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ (10.0 g, 89.4% yield, $VP_{0°C}$, 3 mm Hg) collected in the -23°C trap.

Preparation of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$

$C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ was prepared by treatment of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ with liquid ammonia. To identify optimum conditions five preparations were performed and are summarized in Table 4. Tests were carried out in the absence of solvent and employing varying proportions of solvent. The yield was improved by the presence of Freon-113, and it was further optimized by increasing the ratio of solvent : ammonia to 2 : 1. In the early tests the major impurity was the imidoylamidine. Reaction No. 5 is described below.

Into a 100 mL ampule, equipped with a 1 in stirring bar, were condensed in vacuo Freon-113 (35 mL), NH_3 (15 mL) and $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ (5.89 g, 11.18 mmol). The sealed ampule was stirred vigorously at -20°C for 0.5 h, at 0°C for 1 h, and at room temperature for 17 h. Subsequently, it was opened to the vacuum system; Freon and unreacted ammonia were distilled through a trap cooled to -23°C into an ampule cooled to -196°C. The light yellow semi-solid remaining in the reaction ampule was dissolved in Freon-113 (10 mL) in an inert atmosphere enclosure and filtered. A light yellow gel-like product (5.73 g, 85% GC purity) was obtained. This material was combined with the crude product (0.94g, 79% GC purity) of reaction No. 4 and purified by distillation at 50-65°C (bath temperature) *in vacuo* (0.001 mm Hg) to give 4.47 g (62% yield, GC purity >98%) of white solid $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$, MP 42-44°C. The infrared spectrum is given in Figure 12 and the mass spectrum in Table 5.

Preparation of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II)

Under nitrogen bypass to a stirred suspension of imidotetraphenyl-diphosphinic acid trichloride (2.25 g, 4.58 mmol) in acetonitrile (25 mL) was added at 50°C over 50 min a solution of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ (2.50 g, 4.60 mmol) and triethylamine (1.9 g, 18.3 mmol) in Freon-113 (20 mL). This was followed by heating at 50°C for 90 h. After filtration and solvent removal the yellow-brown solid (4.4 g) was treated with hot benzene (20 mL) and filtered. The residue (4.0 g), obtained on the evaporation of the filtrate, was treated with Freon-113 (10 mL) and passed through an alumina column (neutral, 10 g, 1.5 cm x 12 cm). Elution with Freon-113 (60 mL) resulted in a slightly tinted gel which crystallized on standing at room temperature to give 3.6 g (84.5% yield) of white solid (MP 69-70°C, GC purity 98%). The molecular weight determined by osmometry was 950 (Calcd MW, 925.51). The infrared spectrum is given in Figure 13, the mass spectrum in Table 6.

Evaluation of Hydrolytic Stability of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$

A mixture of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (211.3 mg) and water (5 mL) was stirred at 100°C in air for 24 h. After cooling, the solution was extracted with ether (10, 10, 5 mL) and the combined ether extracts were dried over anhydrous $MgSO_4$. Solvent removal, followed by pumping *in vacuo* at 55°C for 5 h, gave 205 mg of gel (which solidified upon standing). Quantitative GC analysis, using $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ internal standard, showed the recovered material to be pure $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$. The recovery was 97%.

Purification of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$

In an inert atmosphere enclosure, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ (~25g) was transferred to a 50 mL round bottom flask equipped with a magnetic stirrer (1 in) and Teflon-glass stopcock adapter. After degassing at -196°C, the acid fluoride was fractionated from the warming flask through traps cooled at -23, -47, -78 and -196°C. A small quantity (1.27 g) of cloudy liquid remained in the flask; the pure acid fluoride ($VP_{25°C}$, 17 mm Hg) was collected in the -23°C cooled trap.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2COF$

In an inert atmosphere enclosure cesium fluoride (0.58 g, 3.02 mmol, dried in vacuo at 195°C for 8 h) and tetraglyme (1.2 g, $CH_3(OCH_2CH_2)_4OCH_3$ distilled over $LiAlH_4$) were weighed into a 25 mL round bottom flask (cleaned consecutively with 20% KOH in ethanol, methanol, and Freon-113) equipped with a 1 in stirring bar and Teflon-glass stopcock adapter. The mixture was evacuated (<0.001 mm Hg) at room temperature, followed by condensation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ (4.79 g, 9.62 mmol) at -196°C. The resultant mixture was stirred at room temperature for 1.5 h. Octafluoroisobutylene epoxide (2.08 g, 9.62 mmol) was condensed in at -20°C into the vigorously stirred solution; the last traces of the epoxide were condensed in at -196°C. Subsequently, the mixture was stirred at -15 to -20°C for 18 h. After reaction, the volatiles (4.86 g) were removed *in vacuo* (at room temperature, then at 50°C), and fractionated through traps cooled to 0, -23, -78, and -196°C, giving the major portion (2.81 g) of the product in the 0°C trap together with a small quantity in the -23°C trap. The -23°C fraction was refractionated through 0, -23, -78, and -196°C cooled traps. The 0°C fractions were combined and refractionated through traps cooled to 0, -23, and -78°C. In the 0°C trap was collected $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2COF$ (2.81 g, 41% yield). The room temperature vapor pressure was below 0.5 mm Hg. The infrared spectrum of the acid fluoride is given in Figure 14; the mass spectrum of the corresponding ester, $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CO_2CH_3$, is presented in Table 7.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CONH_2$

$C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2COF$ (8.11 g, 11.36 mmol) and NH_3 (26.9 mmol) were condensed in vacuo at -196°C into an ampule (65 mL) fitted with a Teflon-glass stopcock adapter. The reaction mixture was warmed to -78°C for 10 min, -47°C for 1.5 h, then held at -23°C for 3 h, and -78°C overnight. The volatiles, removed *in vacuo* at room temperature, were fractionated through traps cooled to 0, -23, -47, and -196°C. Unreacted NH_3 (3.0 mmol) was recovered in the -196°C trap. In the -23 and -47°C traps was collected the byproduct $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2H$ (50 mg) identified by its infrared and mass spectra given in Figure 15 and Table 8. The residue in the ampule was treated with Freon-113 (15 mL) and filtered in an inert atmosphere enclosure. The product (6.8 g) isolated from the filtrate was stirred *in* *vacuo* at room temperature for 4 h, to remove the last traces of the hydrogen terminated compound. The residue consisted of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CONH_2$ (6.58 g, 81.4% yield). This compound was found to decompose at the GC injector temperature of 250°C, but was stable at 150°C (GC purity 95%). The infrared spectrum is given in Figure 16; the mass spectrum in Table 9.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN$

A mixture of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CONH_2$ (6.58 g, 9.25 mmol) and P_2O_5 (19 g, 135 mmol) was heated at 212-234°C under nitrogen bypass using a short distillation bridge and a receiver flask cooled at 0°C until no more distillate was observed. After cooling to room temperature, the apparatus was attached to the vacuum system and the residual product was distilled at 60°C (with the receiver in Dry Ice). The product was transferred under vacuum (using continuous pumping) into a trap cooled to -196°C to give 5.42 g (84.7% yield) $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN$ (GC purity 99%). The vapor pressure at room temperature was below 0.5 mm Hg. The infrared spectrum is given in Figure 17, the mass spectrum in Table 10.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(=NH)NH_2$

Into a 100 mL ampule , equipped with a 1 in magnetic stirring bar, were condensed <u>in vacuo</u> $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN$ (5.22 g, 7.53 mmol), Freon-113 (35 mL), and NH_3 (15 mL). The sealed ampule was stirred vigorously at 0°C for 0.5 h, then at room temperature for 17 h. After removal of the volatiles in vacuo the residue was dissolved in Freon-113 (10 mL) (in an inert atmosphere enclosure and filtered to give, after solvent removal, a light yellow liquid (5.10 g, 85% GC purity). Distillation resulted in 3.44 g (64.3% yield) of colorless amidine, $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(=NH)NH_2$, (BP 57-60°C/0.001 mm Hg, 98% GC purity). The infrared spectrum is given in Figure 18, the mass spectrum in Table 11.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III)

Under nitrogen bypass to a stirred suspension of imidotetraphenyl-diphosphinic acid trichloride (2.24 g, 4.56 mmol) in acetonitrile (25 mL) at 50°C was added over 1.5 h a solution of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(=NH)NH_2$ (3.22 g, 4.53 mmol) and triethylamine (1.94 g, 19.2 mmol) in Freon-113 (20 mL) followed by stirring at 50°C for 20 h. After cooling, the solution was filtered in an inert atmosphere enclosure. Solvent removal gave 4.9 g of a clear, viscous, yellow liquid which solidified on standing. The crude product was dissolved in Freon-113 (2 mL) and filtered through a neutral alumina column (12g, 1.5 cm x 11.5 cm). The light yellow solid (4.5 g, yield 86%, MP 70-74°C, GC purity 98.0%) recovered from the Freon-113 eluent was heated *in vacuo* at 105°C for 1.5 h followed by recrystallization from hexanes to give III 2.92 g (55.8% yield, MP 74-76°C, GC purity 98.5%). Additional quantity of III was isolated from the mother liquors: 0.89 g (17.0% yield) MP 64-71°C, GC purity 87.6%. The infrared spectrum of III is given in Figure 19; the mass spectrum in Table 12.

Evaluation of Hydrolytic Stability of $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$

A mixture of $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (205.9 mg) and water (5 mL) was stirred at 100°C in air for 24 h. After cooling, the solution was extracted with ether (10, 10, 5 mL) and the combined ether extracts were dried over anhydrous $MgSO_4$. Solvent removal, followed by pumping *in vacuo* at 50°C for 5 h, gave 204.7 mg of white solid. Quantitative GC analysis, using $(C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ internal standard, showed the recovered material to consist of 92.5% of $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$. The recovery was 92.0%.

Preparation of $R_fC(=NH)N=C(NH_2)R_f$, $R_f = C_3F_7OCF(CF_3)CF_2OC(CF_3)_2$

Into a 14 mL ampule (O.D. = 24 mm), equipped with a 1 in stirring bar, were condensed in vacuo the nitrile $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ (3.87 g, 7.34 mmol) and ammonia (7.64 mmol). The ampule was sealed and heated for 72 h at 50°C. After opening to the vacuum system the volatiles were fractionated through traps held at 0, -23, -45 and -196°C. The unreacted ammonia (2.42 mmol) was recovered in the -196°C trap; in the -45°C cooled trap 90 mg of the byproduct $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$. The light brown liquid, remaining in the ampule, was dissolved in Freon-113 and filtered in an inert atmosphere enclosure. Solvent removal resulted in a clear, yellow liquid (3.73 g) which based on GC analysis consisted of 62% of $R_fC(=NH)N=C(NH_2)R_f$ and 29% of $R_fC(=NH)NH_2$. The mixture (3.60 g) was thus stirred with nitrile (3.53 g, 6.70 mmol) at 45°C for 65 h in an ampule fitted with a Teflon-glass stopcock adapter. After reaction the volatiles were removed at 35°C *in vacuo*, and fractionated through traps held at -23, -45 and -196°C. In the -23 and -45°C traps the excess of nitrile (2.56 g, 4.86 mmol) was recovered. The involatile material (4.40 g) contained 90% of the imidoylamidine and 0.4% of the corresponding amidine. Two distillations under reduced pressure gave 3.78 g (75% yield) of the imidoylamidine (BP 67-70°C/0.001 mm Hg). The mass spectrum is given in Table 13.

Preparation of 1,3-Diphosphatetraazacyclooctatetraene, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ (IV)

Under nitrogen bypass to a stirred suspension of imidotetraphenyl-diphosphinic acid trichloride (1.61 g, 3.28 mmol) in acetonitrile (15 mL) at 50°C was added over 3 h a solution of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)N=C(NH_2)OC(CF_3)_2CF_2CF(CF_3)OC_3F_7$ (3.78 g, 3.53 mmol) and triethylamine (1.5 g, 10.6 mmol) in Freon-113 (35 mL). The resulting mixture was heated at 50°C for 90 h. After cooling, the solution was filtered in an inert atmosphere enclosure. Solvent removal gave 5.06 g of a sticky solid which was purified by filtration through a column of neutral alumina (12 g, 1.5 cm x 11.5 cm) using Freon-113 (50 mL). The obtained yellow solid (4.5 g) was recrystallized from hexanes to give 3.17 g (62% yield) white crystals MP 100-102°C, GC purity >99%. The product was characterized by infrared and mass spectra given in Figure 20 and Table 14, respectively.

Hydrolytic Stability Evaluation of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ (IV)

In a 50 mL round bottom flask equipped with a 1 in magnetic stirrer and a reflux condenser, a mixture of water (5 mL) and Compound IV (201.8 mg) was stirred vigorously for 24 h at 100°C. After cooling, the solution was extracted with ether (2 x 10 mL, 5 mL). The combined organic layers were dried over anhydrous magnesium sulfate. Solvent removal followed by pumping at 55°C for 2.5 h gave 201.4 mg of white solid. Quantitative GC analysis, using $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ as an internal standard, showed the presence of 96.6% of Compound IV corresponding to 96.4% recovery.

Attempted Preparations of 1,5-Diphosphatetraazacyclooctatetraene, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$; Interaction of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ and $(C_6H_5)_2PCl_3$

Three reactions were performed varying reactants ratios and solvents. The experiments are summrized in Table 15.

(a) In benzene/Freon-113 using ratio 1:1

Under nitrogen bypass to a stirred suspension of $(C_6H_5)_2PCl_3$ (0.22 g, 0.76 mmol) in benzene (5 mL) at room temperature was added over 45 min a solution of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ (0.40 g, 0.74 mmol) and triethylamine (0.31 g, 3.07 mmol) in Freon-113 (5 mL). The resulting mixture was allowed to stir at room temperature for an additional 30 min, then at 50°C for 92 h. After cooling, the solution was filtered in an inert atmosphere enclosure to separate triethylamine hydrochloride (0.3 g, 100% yield). The filtrate, after solvent removal, gave 0.63 g of a viscous yellow liquid. GC analysis showed the sample to be a mixture containing 9% of the desired octatetraene and 6% diphospha-s-triazine $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$. The mass spectrum of the octatetraene is given in Table 16.

(b) In benzene/Freon-113 using ratio of 1:2

Under nitrogen bypass to a stirred suspension of diphenyltrichlorophosphorane $(C_6H_5)_2PCl_3$ (1.07 g, 3.67 mmol) in benzene (10 mL) at 50°C was added over 2.25 h a solution of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ (0.97 g, 1.78 mmol) and tiethylamine (0.60 g, 5.94 mmol) in Freon-113 (10 mL). The resulting mixture was heated at 50°C for 67 h. After cooling, the solvents were removed *in vacuo*. Following addition of Freon-113 (20 mL) the solution was filtered in an inert atmosphere enclosure to separate triethylamine hydrochloride and the unreacted $(C_6H_5)_2PCl_3$ (total weight 1.06 g). Solvent was removed from the filtrate *in vacuo* initially at room temperature then at

50°C to give 1.49 g of viscous yellow liquid. GC analysis showed the sample to consist of a spectrum of products containing, among other unidentified compounds, 9% of the desired octatetraene and 12% of diphospha-s-triazine $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$.

(c) In acetonitrile/Freon-113 using a reagent ratio 1:2

Under nitrogen bypass to a stirred solution of $(C_6H_5)_2PCl_3$ (0.46 g, 1.58 mmol) in acetonitrile (5 mL) at 70°C was added over 1 h a solution $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ (0.43 g, 0.79 mmol) and tiethylamine (0.32 g, 3.17 mmol) in Freon-113 (5 mL). The reaction mixture was stirred at this temperature for 92 h. After cooling, the solution was filtered in an inert atmosphere enclosure; 0.29 g (88% yield) of triethylamine hydrochloride was obtained. The residue following solvent evaporation, was taken up in Freon-113 (10 mL) and refiltered to remove 0.30 g of unreacted $(C_6H_5)_2PCl_3$ admixed with a trace of the hydrochloride. Solvent was evaporated from the filtrate and the residue was heated at 55°C *in vacuo* for 3 h to give 0.56 g of a yellow liquid. GC analysis showed a complex mixture containing only 2% of the desired octatetraene, and 16.5% of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$.

Esterification of Poly(hexafluoropropene oxide) Acid Fluoride Mixture

Under nitrogen atmosphere to stirred mixture of sodium fluoride (16 g, 0.38 mol, dried *in vacuo* for 6 h at 190°C) and the acid fluorides (500 g, 0.20 mol; equivalent weight 2480 determined by quantitative infrared spectral analysis using tetramer methyl ester, MW 676.15 as standard) cooled in an ice/water bath was added over 25 min methanol (16 g, 0.38 mol; dried and distilled over magnesium methoxide). After warming to room temperature the mixture was stirred for additional 2 h. Following filtration of the solid (20 g) the filtrate was distilled *in vacuo* BP 50-75°C/0.001 mm Hg, to give 482 g of material which consisted of 33% $C_3F_7O[CF(CF_3)CF_2O]_5CF(CF_3)CO_2CH_3$, 5% $C_3F_7O[CF(CF_3)CF_2O]_4CF(CF_3)CO_2CH_3$, and 54% $C_3F_7O[CF(CF_3)CF_2O]_5CF(CF_3)H$. The respective mass spectra are compiled in Tables 17-19.

Preparation of $C_3F_7O[CF(CF_3)CF_2O]_5CF(CF_3)COC_6H_4Br$

Under nitrogen bypass, into a 1 L 3-neck round bottom flask equipped with a mechanical stirrer containing 1,4-dibromobenzene (25.28 g, 0.107 mol) and freshly distilled ether (200 mL) at -10°C, was added n-butyllithium (46.5 mL, 2.5M in hexanes, 0.116 mol) over a period of 1.5 h. After stirring for an additional 0.5 h at -10°C, the solution was cooled to -77°C and the methyl ester $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)CO_2CH_3$ (240 g, 0.1 mol, based on equivalent weight of 2480) mixed with ether (20 mL) was added over a period of 2.5 h. This was followed by stirring at -77°C for 45 min. Subsequently, hydrochloric acid (2N, 175 mL) was added over 1 h at -77°C. The mixture was then allowed to warm to room temperature and stirred overnight. The organic layer was separated, combined with the etheral extract (75 mL) of the aqueous layer, washed with water (4 x 75 mL) and dried over anhydrous magnesium sulfate. Solvent evaporation resulted in the presence of some suspended precipitate, which was filtered to give 242 g of a crude liquid product. Most of the H-terminated material was distilled out, BP 65-75°C/0.001 mm Hg. Final distillation was performed using a 5 in Vigreux column to give 27.7 g (22% yield; based on the calculated quantity of the heptamer and hexamer methyl esters present in the starting material) of $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)COC_6H_4Br$. The mass spectra are given in Tables 20 and 21, respectively and the infrared spectrum is given in Figure 21.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br$

Into a Parr bomb (125 mL) cooled in Dry Ice containing Freon-113 (20 mL) and $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)C(O)C_6H_4Br$ (39.00 g, 30.0 mmol) was added, under nitrogen flow, anhydrous hydrogen fluoride (~ 5 mL). The bomb was closed and maintained at -78°C. Subsequently, sulfur tetrafluoride (16.5 g, 153 mmol) was condensed in. After warming to room temperature, the bomb was agitated, using a shaker assembly, at 100-112°C (sand bath temperature) for 18 h. At the end of the heating period, after cooling to room temperature, the excess sulfur tetrafluoride was vented. Subsequently, Freon-113 (25 mL) was added to the reactor and the mixture was poured onto ice-water (100 mL). The reactor was rinsed with an additional quantity of Freon-113 (25 mL). The organic layer and the Freon-113 rinsing solution were combined and washed with a saturated sodium bicarbonate solution (6 x 50 mL) then with water (3 x 50 mL) and dried over anhydrous $MgSO_4$. Solvent removal resulted in 37.0 g of a viscous product admixed with a suspended solid which was removed by filtration, to give 36.4 g of a clear, dark-yellow liquid. The crude material was distilled in vacuo to give 32.6 g of a clear, colorless liquid, $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br$, BP 119-123°C/0.001 mm Hg, GC purity 97%. GC/MS analysis verified the structure and identified as major impurities $C_3F_7[OCF(CF_3)CF_2]_5C_6H_4Br$ (0.6%) and $C_4F_9[OCF(CF_3)CF_2]_5C_6H_4Br$ (0.9%). The mass spectra are presented in Tables 22-24 and the infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br$ is given in Figure 22.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$

Under nitrogen atmosphere, into a stirred solution of freshly distilled ether (40 mL) and n-butyllithium (5 mL, 2.5 M in hexanes, 12.5 mmol) at -15°C was added $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br$ (11.85 g, 8.95 mmol) admixed with ether (5 mL), over a period of 35 min. After stirring for an additional 1.5 h at -15°C, the cold solution (two layers) was added over a 15 min period (via a double-tip needle) to a stirred solution of trimethyl borate (4.8 g, 46 mmol) in ether (40 mL) held at -15°C. After an additional 1.75 h, acetic acid (2.9 g, 47 mmol) was added and the solution was stirred for another 1 h. To the above solution, at -15°C, was then introduced hydrogen peroxide (30%, 7.0 mL) in H_2O (7.0 mL). The reaction mixture was subsequently stirred at room temperature overnight. This was followed by the addition of water (50 mL). The organic layer was washed with ferrous sulfate solution (15 g $FeSO_4.7H_2O$, 6 mL concentrated hydrochloric acid, 15 mL H_2O), water (5 x 20 mL), and dried over anhydrous $MgSO_4$.

After solvent removal the dark crude product (9.9 g) was first purified by silica gel column chromatography (80 g, 2.5 cm x 34.5 cm, packed in 5% ether/hexanes). Elution using ether/hexanes 5% (215 mL), 10% (200 mL), 20% (100 mL) and 50% (400 mL) resulted in 1.0 g mainly of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_5$ in the 5% eluent (the first yellow band), and 8.0 g of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$ (86% purity, GC) from the 50% eluent (the second yellow band). The latter portion was distilled to give 6.3 g (56% yield) of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$, BP 113-120°C/0.001 mm Hg, GC purity 98%. The mass spectrum is given in Table 25 and the infrared spectrum in Figure 23. The mass spectrum of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Cl$ is given in Table 26; this material was formed when Freon-113 was added to the reaction mixture to solubilize the bromide.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$ (3.05 g, 2.42 mmol) and $(C_6H_5O)_2P(O)Cl$ (0.65 g, 2.42 mmol) in Freon-113 (6.5 mL) was added, via an addition funnel, triethylamine (0.75 g, 7.41 mmol) in benzene (6.5 mL) over a period of 15 min. After stirring for an additional 30 min, the addition funnel was replaced with a reflux condenser. The assembly was removed from the inert atmosphere enclosure and the solution was heated at 60°C under nitrogen bypass for 24 h. After cooling, the reaction mixture was filtered and the white solid rinsed with Freon-113 (10 mL) to give 0.36 g (109% yield) of triethylamine hydrochloride. Solvent removal from the filtrate gave a yellow liquid (3.61 g).

The crude material was mixed with 10% ether/hexanes (2 mL) and passed through a silica gel column (40g, 17 cm x 2.5 cm, packed in 10% ether/hexanes). The column was eluted with 10% (260 mL) and 20% (300 mL) ether/hexanes. No phosphate was present in the first 260 mL; the following 215 mL contained 3.46 g of a clear colorless liquid. Further purification by removal of the remaining impurities by sublimation onto a cold finger initially at 85-90°C for 1 h, then at 90-95°C for 5 h gave 3.19 g (87% yield) of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (GC purity > 99%), MW, 1550 (Calcd, 1490). The infrared spectrum is presented in Figure 24, the mass spectrum in Table 27.

Hydrolytic Stability Evaluation of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V)

In a 50 mL round bottom flask equipped with a 1 in magnetic stirrer and a reflux condenser, a mixture of water (5 mL) and Compound V (233.5 mg) was stirred vigorously for 24 h at 100°C. After cooling, the solution was extracted with ether (2 x

10 mL, 5 mL). The combined organic layers were dried over anhydrous magnesium sulfate. Solvent removal followed by pumping at 55°C for 2.5 h gave 229.0 mg of liquid. Quantitative GC analysis, using $C_2F_5C_6H_4OP(O)(C_6H_5)_2$ as an internal standard, showed the presence of 99% of Compound V corresponding to 97.2% recovery.

Characterization of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$

The mass spectrum of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ was not obtained under Phase I [Ref. 24], consequently it was determined under the current program and is given in Table 28.

Pyrolyses

The tests were performed in 18-20 mL ampules. The samples were weighed in and then the ampules were evacuated using the vacuum line assembly and sealed. Following heating, the ampules were cooled to -196°C, opened to the vacuum system and the -196°C noncondensibles, if any, separated and analyzed by infrared spectroscopy. Subsequently, the contents were warmed to room temperature and the volatiles collected in the calibrated portion of the vacuum line. If the quantities were larger than 0.2 mmol, the condensibles were fractionated through -78°C into -196°C cooled traps. The fractions were analyzed by quantitative infrared spectroscopy and/or mass spectrometry. The starting material remaining in the involatile portion was quantified either by quantitative GC, using an internal standard, or by quantitative infrared spectroscopy using a matched cell technique. The tests are summarized in Table 2. The degradation products were quantified by GC and identified by mass spectroscopy; the relevant spectra are presented in Tables 29-34.

Perfluoropolyalkylether Fluids Characterization Data

Four commercial fluids were investigated, Krytox 143AC (MLO 71-6), Fomblin Z25 lots P28 and P151, and Krytox 16256 lot 5.

Krytox 143AC: MW, 5500; viscosity at 100°C, 27.3 cSt; ^1H and ^{19}F NMR spectra have been reported [Ref. 32].

Fomblin Z25-P28: MW, 9750; viscosity at 100°C, 47.2 cSt; ^{19}F NMR is given in Figure 25; peak assignments are listed in Table 35.

Fomblin Z25-P151: MW, 9700; viscosity at 100°C, 42.6 cSt; ^1H and ^{19}F NMR spectra are given in Figures 26 and 27, respectively. The ^{19}F peak assignments are listed in Table 36.

Krytox 16256 lot 5: MW, 9900; viscosity at 100°C, 64.1 cSt; ^1H and ^{19}F NMR spectra are given in Figures 28 and 29, respectively. The ^{19}F peak assignments are listed in Table 37.

Alloys and Ceramics

The alloys: M-50 steel, 440C steel, Ti(4Al, 4Mn) and Ti(6Al,4V) were purchased from Metaspec Co., San Antonio, Texas, in the form 3/8 in OD and 1/8 in ID, 0.04 in thick, metal coupons with a total surface area of 1.67 cm^2.

Cronidur 30 was received from FAG Bearings Corp., Trumbull, Connecticut in the form of 0.25 in balls; surface area 1.50 cm^2.

Pyrowear 675 was received from MRC Bearings, Falconer, New York in the form of 11/16 in balls; surface area 9.58 cm^2.

Silicon nitride and zirconia were received from NASA Lewis Research Center in the form of 3/8 in balls and were tested without further preparation.

Fluid Stability Evaluation, Apparatus and Alloy Specimen Pretreatment

The apparatus used in the evaluation of the alloy action on a given fluid was previously fully described together with the procedures followed [Ref. 14]. Preparation protocols for the alloy coupons were also reported earlier [Ref. 14] and will not be reiterated here.

The alloy balls Cronidur 30 and Pyrowear 675 were initially polished, prior to testing, according to the standard procedure [Ref. 14]. Based on the test results, Freon-113 wash alone was later implemented. Ultrasonic cleaning using Freon-113 was found to give the most reproducible data and this process was ultimately adopted for the alloy balls.

Surface Treatments of 440C Coupon

a) 3-aminopropyltriethoxysilane

In an attempt to deactivate the metal surface, the silane treatment described by Morales [Ref. 37] was followed. A polished 440C coupon was soaked for 1 min in a solution of 3-aminopropyltriethoxysilane (1 mL) in methanol (20 mL). It was subsequently placed on an aluminum foil on a hot plate for 1 min. A thermometer wrapped inside the aluminum foil read a temperature of 224°C. Thus treated 440C coupon was tested in Fomblin Z25-P151 for 8 h at 316°C under an oxygen atmosphere (Test 65).

b) hexamethyldisilazane

In an inert atmosphere enclosure a solution of hexamethyldisilazane (0.25 mL) in benzene (5 mL) was prepared. A polished 440C coupon was soaked in the solution for 0.5 h followed by rinsing with benzene (4 x 1 mL). It was then quickly placed in the degradation tube and dried under vacuum (<0.001 mm Hg) for 2 h at room temperature. The apparatus was opened and Fomblin Z25-P151 (3.68 g) was added while maintaining a nitrogen flow into the tube. Subsequently, the apparatus was evacuated, filled with oxygen (402 mm Hg) and heated at 316°C for 8 h (Test 61).

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TABLE 1

SUMMARY OF PROPERTY DATA FOR THE ADDITIVES DEVELOPED

Compound[a]		Yield %	MP °C	BP °C	MW		Solubility(°C)[b,c]		
					Calc	Found	K-143AC	K-16256	FZ25-P151
$[R_fOC(CF_3)_2CN]_2[\Phi_2PN]$	I	89		134[d]	1253	1200	<-40	<-40	<-40
$[R_fOC(CF_3)_2CN]_2[\Phi_2PN]_2$	II	73	69-70		925	950	135	152	135
$[R_f'OC(CF_3)_2CN]_2[\Phi_2PN]_2$	III	86	70-74		1091	1150	113	125	110
u-$[R_fOC(CF_3)_2CN]_2[\Phi_2PN]_2$	IV	62	100-102		1452	1400	81	92	87
$R_f''C_6H_4OP(O)(OC_6H_5)_2$	V	87	n.a.[e]	n.d.[f]	1490	1550	25	35	46

a) $R_f = C_3F_7OCF(CF_3)CF_2$; $R_f' = C_3F_7[OCF(CF_3)CF_2]_2$; $R_f'' = C_3F_7[OCF(CF_3)CF_2]_6$; $\Phi = C_6H_5$

b) Solubility was determined on 1% by wt solutions of the additives in a perfluoropolyalkylether fluid (1.2-1.4 g) using a tube (5 cm x 1 cm) heated in an oil bath. The temperature, when solution cleared, was recorded on the inside thermometer. For the low temperature solubility the bath was cooled and the temperature recorded when the solution turned hazy. The low temperature tests were conducted under nitrogen atmosphere to avoid water condensation.

c) K-143AC = Krytox 143AC; K-16256 = Krytox 16256; FZ25-P151 = Fomblin Z25-P151.

d) This is the bath temperature; distillation was performed at 0.001 mm Hg.

e) The material was a liquid.

f) Not determined.

TABLE 2

SUMMARY OF SELECTED ADDITIVES PYROLYSIS DATA[a]

Compound[b]		Quantity		Temp	Residue[c]		Volatiles[e], mg		
		mg	mmol	°C	mg	%S.M. Recov[d]	Total	-78°C	-196°C
$[R_fCN]_2[(C_6H_5)_2PN]$,	I	255.0	0.204	343	229.2	81	37.4	18.0	19.4
$[R_fCN]_2[(C_6H_5)_2PN]$,	I	223.8	0.179	316	218.3	96	1.4		
$[R_fCN][(C_6H_5)_2PN]_2$,	II	261.0	0.282	343	143.0	<1	137.5	48.6	88.9
$[R_fCN][(C_6H_5)_2PN]_2$,	II	205.9	0.222	300	129.5	<1	93.7	45.9	47.8
$[R_fCN][(C_6H_5)_2PN]_2$,	II	214.6	0.232	316	122.0	<1	103.0	43.0	60.0
$[R_fCN][(C_6H_5)_2PN]_2$,	II	212.7	0.230	285	163.7	25	46.1	30.3	15.8
$[R_f'CN][(C_6H_5)_2PN]_2$,	III	252.9	0.232	316	100.5	<1	159.4	78.4	81.0
$[R_fCN]_2[(C_6H_5)_2PN]_2$,	IV	198.8	0.137	285	105.7	2	114.8	49.8	65.0
$[R_fCN]_2[(C_6H_5)_2PN]_2$,	IV	202.1	0.139	300	95.5	<1	136.1	56.9	79.2
$R_f''C_6H_4OP(O)(OC_6H_5)_2$	V	197.1	0.132	300	197.0	93	none		
$R_f''C_6H_4OP(O)(OC_6H_5)_2$	V	203.8	0.137	343	191.6	45	0.5		
$R_f''C_6H_4OP(O)(OC_6H_5)_2$	V	209.2	0.140	316	207.9	91	none		
$(R_f'''C_6H_4O)_2P(O)OC_6H_5$	C	199.2	0.120	300	197.9	90	none		
$(R_f'''C_6H_4O)_2P(O)OC_6H_5$	C	204.0	0.123	316	198.2	88	0.7		
$(R_f'''C_6H_4O)_2P(O)OC_6H_5$	C	212.0	0.128	343	204.7	30	0.6		

a) All of the pyrolyses were performed in evacuated ampules over 24 h.
b) $R_f = C_3F_7OCF(CF_3)CF_2OC(CF_3)_2$, $R_f' = C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2$, $R_f'' = C_3F_7[OCF(CF_3)CF_2]_6$, $R_f''' = C_3F_7[OCF(CF_3)CF_2]_3$.
c) This material was involatile at room temperature.
d) The percent of starting material recovered is with respect to the quantity of starting material used.
e) Volatiles were separated into materials condensable at -78 and -196°C.

TABLE 3A

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm²
i[b]	Fomblin Z25-P151	3.02	M-50	O_2	none	-	316	8	-	1454	481.5	+0.30
ii[b]	Fomblin Z25-P151	3.17	M-50	O_2	PH-3[c]	1.0	316	16	42.3	1.1	0.4	+0.06
1	Krytox 143AC	2.90	Ti(4Al,4Mn)	O_2	I[d]	1.0	343	24	27.8[e]	7.0	2.4	-0.12
2	Fomblin Z25-P28	3.01	M-50	O_2	I[d]	1.0	316	24	33.4[f]	398.5	132.4	-5.3
3	Fomblin Z25-P28	2.85	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	45.3	20.5	7.2	+0.06
4	Krytox 143AC	2.87	M-50	O_2	I[d]	1.0	316	24	27.9	0.5	0.17	0.0
5	Krytox 143AC	3.11	M-50	O_2	I[d]	1.0	343	24	27.3	16.5	5.3	-5.6
6	Fomblin Z25-P28	3.07	M-50	O_2	I[d]	1.0	316	16	29.3	435.2	141.8	-2.2
7	Fomblin Z25-P28	3.14	M-50	O_2	I[d]	1.0	300	24	46.4	7.4	2.4	+0.54
8	Krytox 143AC	2.93	Ti(4Al,4Mn)	O_2	I[d]	1.0	350	24	27.4	11.1	3.8	-0.42
9	Fomblin Z25-P28	3.35	M-50	O_2	C_2PN_3[g]	1.0	316	16	33.2	361.6	107.9	-3.3
10	Fomblin Z25-P28	3.09	M-50	O_2	none	-	316	8	11.3	1042	337.1	+0.12
11	Fomblin Z25-P28	2.99	M-50	O_2	P-3[h]	1.0	316	16	45.7	12.5	4.2	-1.2
12	Krytox 143AC	3.00	M-50	O_2	P-3[h]	1.0	343	24	28.6	172.6	57.5	+0.42
13	Krytox 143AC	2.82	M-50	O_2	PH-3[c]	1.0	343	24	28.3	9.4	3.3	+4.3

TABLE 3A (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
14	Fomblin Z25-P28	3.27	M-50	O_2	PH-3[c]	1.0	316	16	46.7	4.7	1.4	+2.4
15	Fomblin Z25-P28	3.15	Ti(4Al,4Mn)	O_2	PH-3[c]	1.0	316	24	46.7	5.4	1.7	-0.06
16	Krytox 143AC[i]	3.02	M-50	O_2	I[d]	1.0	350	24	33.6	18.8	6.2	-14.5
17	Krytox 16256	3.09	M-50	O_2	none	-	343	24	-	173.3	56.1	+0.54
18	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	none	-	316	24	46.5	478.4	156.8	-0.36
19	Krytox 143AC	3.17	440C	O_2	none	-	343	24	26.7	494.1	155.9	-4.8
20	Fomblin Z25-P28	3.01	440C	O_2	none	-	316	8	-	1602	532.2	-1.2
21	Krytox 16256	3.03	440C	O_2	none	-	343	24	55.3	494.1	163.1	-6.4
22	Krytox 16256	3.06	M-50	O_2	I[d]	1.0	343	24	-	139.5	45.6	+1.1
23	Krytox 16256	2.91	440C	O_2	I[d]	1.0	343	24	-	123.1	42.3	0.0
24	Krytox 16256	3.01	M-50	O_2	PH-3[c]	1.0	343	24	-	230.6	76.6	-4.8
25	Krytox 143AC	2.89	M-50	O_2	PH-3[j]	1.0	343	24	28.4	11.7	4.0	+1.4
26	Krytox 16256	3.02	440C	O_2	none	-	330	24	-	155.7	51.6	-2.3
27	Krytox 16256	3.00	440C	O_2	I[d]	1.0	330	24	-	5.2	1.7	-0.06
28	Krytox 16256	3.02	440C	O_2	PH-3[c]	1.0	330	24	-	22.8	7.5	+0.18

TABLE 3A (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
29	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	I^d	1.0	343	24	-	419.5	137.5	-0.42
30	Krytox 16256	3.01	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	343	24	-	420.4	139.7	-0.60
31	Krytox 16256	2.98	440C	O_2	A^k	1.0	343	24	-	13.2	4.4	-0.06
32	Fomblin Z25-P28	3.01	440C	O_2	I^d	1.0	316	24	37.9	138.5	46.0	-1.1
33	Fomblin Z25-P28	3.04	440C	O_2	PH-3^c	1.0	316	24	47.0	4.8	1.6	+0.30
34	Fomblin Z25-P28	2.95	440C	O_2	A^k	1.0	316	24	46.5	9.2	3.1	-0.60
35	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	I^d	1.0	330	24	64.8	138.4	47.7	+0.12
36	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	330	24	-	3.7	1.3	-0.12
37	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	A^k	1.0	330	24	-	0.5	0.2	0.0
38	Krytox 16256	2.93	440C	O_2	I^d	1.0	316	24	-	2.0	0.7	+0.06
39	Krytox 16256	2.91	440C	O_2	A^k	1.0	330	24	-	71.2	24.5	+0.06
40	Krytox 16256	3.04	440C	O_2	A^k	1.0	330	24	-	0.8	0.3	-0.06
41	Fomblin Z25-P28	3.07	440C	O_2	I^d	1.0	300	24	46.4	2.2	0.7	+0.06
42	Fomblin Z25-P28	3.03	440C	O_2	A^k	1.0	300	24	46.3	0.6	0.2	-0.06
43	Fomblin Z25-P28	3.26	440C	O_2	PH-3^c	1.0	300	24	46.7	2.5	0.8	+0.18

TABLE 3A (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
44	Fomblin Z25-P151	3.09	440C	O_2	none	-	316	8	-	1466	474.6	-0.24
45	Fomblin Z25-P151	3.10	Ti(4Al,4Mn)	O_2	none	-	288	8	-	3094	997.9	-0.18
45A	Fomblin Z25-P28	3.04	Ti(4Al,4Mn)	O_2	none	-	288	8	-	1264	415.8	-0.06
46	Fomblin Z25-P151	3.01	Ti(4Al,4Mn)	O_2	PH-3[c]	1.0	316	24	42.7	1.6	0.5	-0.18
47	Fomblin Z25-P151	3.08	440C	O_2	PH-3[c]	1.0	316	24	42.3	1.5	0.5	+0.18
48	Fomblin Z25-P151	3.06	440C	O_2	A[k]	1.0	316	24	42.7	0.5	0.2	+0.06
49	Krytox 16256	3.01	440C	O_2	B[l]	1.0	330	24	-	0.6	0.2	+0.06
53	Krytox 16256	3.42	440C	O_2	II[m]	1.0	316	24	-	5.4	1.6	0.0
54	Fomblin Z25-P151	3.25	440C	O_2	II[m]	1.0	316	24	42.6	1.7	0.5	+0.18
55	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	II[m]	1.0	316	24	42.7	3.1	1.0	+0.12
56	Krytox 16256	3.19	Ti(4Al,4Mn)	O_2	II[m]	1.0	316	24	-	2.1	0.7	-0.06
57	Krytox 16256	3.10	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	-	1.0	0.4	+0.12
58	Fomblin Z25-P151	3.14	440C	O_2	B[l]	1.0	316	24	42.6	0.0	0.0	+0.06
59	Fomblin Z25-P151	3.20	440C	O_2	C[n]	1.0	316	24	42.8	0.0	0.0	+0.12
60	Fomblin Z25-P151	3.06	TiC/440C[o]	O_2	none	-	316	8	-	1347	440.2	-0.79

TABLE 3A (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
61	Fomblin Z25-P151	3.68	440C^p	O_2	none	-	316	8	-	1451	394.3	+0.36
62	Fomblin Z25-P151	3.04	Si_3N_4	O_2	none	-	316	24	30.4	267.6	88.0	+1.72
63	Fomblin Z25-P151	3.00	Zirconia	O_2	none	-	316	8	29.0	270.8	90.3	-0.07
64	Fomblin Z25-P151	3.07	440C	O_2	C^n	1.0	330	24	42.3	1.6	0.5	-0.36
65	Fomblin Z25-P151	3.10	440C^q	O_2	none	-	316	8	-	1436	463.3	+0.12
66	Fomblin Z25-P151	3.04	Ti(4Al,4Mn)	O_2	C^n	1.0	316	24	42.4	0.0	0.0	0.0
67	Krytox 16256	2.93	440C	O_2	C^n	1.0	330	24	-	0.6	0.2	+0.06
68	Krytox 16256	2.82	Ti(4Al,4Mn)	O_2	C^n	1.0	330	24	-	25.0	8.9	+0.06
69	Krytox 16256	2.90	440C	O_2	D-1^r	1.0	316	24	-	0.2	0.1	+0.12
70	Krytox 16256	2.85	440C	O_2	III^s	1.0	316	24	-	7.9	2.8	0.0
71	Fomblin Z25-P151	3.28	440C	O_2	III^s	1.0	316	24	42.9	2.8	0.9	-0.24
72	Krytox 16256	3.21	Ti(4Al,4Mn)	O_2	III^s	1.0	316	24	-	2.5	0.8	+0.18
73	Fomblin Z25-P151	3.25	Ti(4Al,4Mn)	O_2	III^s	1.0	316	24	42.8	3.0	0.9	0.0
74	Krytox 16256	2.88	Ti(4Al,4Mn)	O_2	C^n	1.0	316	24	-	0.6	0.2	0.0
75	Krytox 16256	2.82	440C	O_2	C^n	1.0	343	24	-	108.8	38.6	+0.48

TABLE 3A (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^{a}
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^{2}
76	Krytox 16256	2.81	440C	O_2	C^{n}	1.0	330	48	-	12.0	4.3	-4.60
77	Krytox 16256	2.86	440C	O_2	D-2^{r}	1.0	330	24	-	1.4	0.5	+0.12
78	Fomblin Z25-P151	2.97	440C	O_2	D-2^{r}	1.0	316	24	42.5	0.7	0.2	+0.06
79	Fomblin Z25-P151	2.92	Ti(4Al,4Mn)	O_2	D-2^{r}	1.0	316	24	42.4	0.1	0.03	0.0
80	Krytox 16256	3.03	440C	O_2	none	-	316	24	-	60.7	20.0	+0.18
81^{t}	Fomblin Z25-P151	3.54	Pyrowear675	O_2	none	-	316	8	-	1634	461.6	+0.21
82^{u}	Fomblin Z25-P151	3.51	Pyrowear675	O_2	none	-	316	8	-	1670	475.9	+0.17
83	Krytox 16256	3.48	Pyrowear675	O_2	none	-	316	24	-	145.4	41.8	+0.18
84	Krytox 16256	2.97	Cronidur 30	O_2	none	-	316	24	-	125.6	42.3	+0.13
85	Fomblin Z25-P151	3.00	Cronidur 30	O_2	none	-	316	8	39.2	35.0	11.7	+0.07
86	Krytox 16256	3.44	Pyrowear675	O_2	none	-	330	24	65.7	157.6	45.8	+0.29
87	Krytox 16256	3.50	Cronidur 30	O_2	none	-	330	24	65.5	204.1	58.3	-4.47
88	Fomblin Z25-P151	3.07	Cronidur 30	O_2	none	-	316	8	-	1429	465.5	+3.60
89	Krytox 16256	3.18	Pyrowear675	O_2	I^{d}	1.0	330	24	-	4.7	1.5	+0.04
90	Krytox 16256	2.97	Cronidur 30	O_2	I^{d}	1.0	330	24	-	1.8	0.6	+0.07

TABLE 3A (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
91	Krytox 16256	2.84	Pyrowear675	O_2	D-4[r]	1.0	330	24	64.0	1.9	0.7	+0.16
92	Krytox 16256	2.90	Cronidur 30	O_2	D-4[r]	1.0	330	24	-	1.4	0.5	+0.07
93	Krytox 16256	2.91	Cronidur 30	O_2	PH-3[c]	1.0	330	24	-	3.0	1.0	0.0
94	Krytox 16256	3.02	Pyrowear675	O_2	PH-3[c]	1.0	330	24	-	2.8	0.9	+0.07
95	Krytox 16256	3.16	2 x 440C	O_2	none	-	330	24	61.8	328.3	103.9	-2.00[v]
96	Fomblin Z25-P151	3.12	Pyrowear675	O_2	D-4[r]	1.0	316	24	42.7	1.0	0.3	+0.05
97	Fomblin Z25-P151	3.00	Cronidur 30	O_2	D-4[r]	1.0	316	24	42.6	0.9	0.3	+0.27
98	Krytox 16256	3.32	440C	O_2	IV[w]	1.0	330	24	-	18.0	5.4	+0.60
99	Krytox 16256	3.21	Pyrowear675	O_2	none	-	330	24	-	172.7	53.8	+0.27
99A[x]	Krytox 16256	3.01	Pyrowear675	O_2	none	-	330	24	-	137.0	45.5	+0.06
100	Krytox 16256	3.27	Ti(6Al,4V)	O_2	none	-	316	24	62.8	163.1	49.9	+0.24
101	Krytox 16256	3.15	440C	O_2	none	-	330	24	-	191.1	60.7	-3.11
102	Krytox 16256	3.06	440C	O_2	IV[w]	1.0	316	24	-	4.8	1.6	+0.18
103	Krytox 16256	2.99	Ti(4Al,4Mn)	O_2	none	-	316	24	-	509.4	170.4	-0.24
104	Fomblin Z25-P151	3.05	Ti(6Al,4V)	O_2	none	-	288	8	-	3030	993.3	0.0

TABLE 3A (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
105	Fomblin Z25-P151	3.08	Ti(6Al,4V)	O_2	C^n	1.0	316	24	42.7	0.4	0.1	0.0
106	Krytox 16256	2.93	440C	O_2	V^y	1.0	330	24	-	0.5	0.2	+0.06
107	Fomblin Z25-P151	2.97	440C	O_2	I^d	1.0	316	24	41.7	10.1	3.4	0.0
108	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	I^d	1.0	316	24	42.5	5.9	1.9	+0.06
109	Fomblin Z25-P151	3.01	440C	O_2	V^y	1.0	316	24	42.7	0.6	0.2	-0.06
110	Krytox 16256	2.93	Ti(4Al,4Mn)	O_2	V^y	1.0	330	24	-	0.9	0.3	0.0
111	Fomblin Z25-P151	3.11	440C	O_2	V^y	1.0	330	24	42.3	4.3	1.4	-0.60
112	Krytox 16256	2.84	440C	O_2	C^n	1.0	330	48	-	1.3	0.5	+0.06
113	Fomblin Z25-P151	3.11	Ti(4Al,4Mn)	O_2	V^y	1.0	316	24	42.7	0.6	0.2	0.0
114	Krytox 16256	3.07	440C	O_2	none	-	330	48	-	653.4	212.8	-6.63
115	Krytox 16256	2.96	440C	O_2	V^y	1.0	330	48	-	106.1	35.8	0.0
116	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	V^y	1.0	330	48	-	1.7	0.6	-6.63
117	Fomblin Z25-P151	3.15	Ti(4Al,4Mn)	O_2	C^n	1.0	330	24	42.7	0.8	0.2	0.0
118	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	C^n	1.0	330	24	42.7	0.8	0.2	-0.06
119	Krytox 16256	2.89	Ti(6Al,4V)	O_2	C^n	1.0	330	24	-	0.8	0.3	+0.12

TABLE 3A (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
120	Krytox 16256	2.99	Ti(6Al,4V)	O_2	V^{Y}	1.0	330	24	65.1	1.0	0.3	0.0
121	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	C^{n}	1.0	330	24	64.7	1.4	0.5	0.0
122^{x}	Krytox 16256	2.98	Cronidur 30	O_2	V^{Y}	1.0	330	24	-	1.4	0.5	+0.06
123	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	V^{Y}	1.0	330	24	42.6	0.5	0.2	0.0
124	Krytox 16256	3.00	440C	O_2	V^{Y}	1.0	330	48	-	1.2	0.4	+0.18
125	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	V^{Y}	1.0	330	24	42.8	0.6	0.2	0.0
126	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	PH-3^{c}	1.0	330	24	42.5	9.8	3.1	-0.24
127	Krytox 16256	3.03	Pyrowear675	O_2	V^{Y}	1.0	330	24	-	1.8	0.6	+0.07

a) Coupon weight change.
b) [Ref. 31]
c) PH-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$
d) Additive I, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$
e) The viscosity of Krytox 143AC (MLO 71-6) fluid alone is 27.3 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Krytox 143AC (MLO 71-6), prior to heat treatment was 26.7 cSt at 100°C. The viscosity of Krytox 16256 (lot 5) fluid alone is 64.1 cSt at 100°C.
f) The viscosity of Fomblin Z25-P28 fluid alone is 47.2 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Fomblin Z25-P28, prior to heat treatment was 46.4 cSt at 100°C. The viscosity of Fomblin Z25-P151 fluid alone is 42.6 cSt at 100°C.
g) $C_2PN_3 = [C_3F_7(OCF(CF_3)CF_2)_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$
h) P-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6F_4]_3P$

TABLE 3A (concluded)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

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i) Fluorinated Krytox 143AC (MLO 91-21).
j) Residue after hydrolysis of PH-3 in water at 100°C for 24 h.
k) $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ [Ref. 31].
l) $(C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
m) Additive II, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
n) $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
o) 1/4 in 440C ball coated with TiC.
p) This 440C coupon was treated with hexamethyldisilazane before testing.
q) This 440C coupon was treated with 3-aminopropyltriethoxy silane in methanol and dried on a hot plate at 224°C before testing.
r) D-1: 61% $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C) and ~39% $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OC_6H_5)OH$; D-2: 81% C; D-4: 78% C [Ref. 31].
s) Additive III, $[C_3F_7(OCF(CF_3)CF_2)_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
t) In this test the Pyrowear 675 ball was rinsed with Freon-113 and used without polishing.
u) In this test the Pyrowear 675 ball was polished with 500A paper before rinsing with Freon-113.
v) This is the average value for weight loss of the two 440C coupons used; top coupon weight loss 3.1 mg/cm^2, bottom coupon 0.90 mg/cm^2. The two coupons were separated by a 4 mm glass spacer.
w) Additive IV, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$
x) In this test the metal bearing was first wiped with Freon-113 soaked tissue, then cleaned ultrasonically for 5 min in Freon-113 and dried in a stream of nitrogen (extra dry grade).
y) Additive V, $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$

TABLE 3B

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
20	Fomblin Z25-P28	3.01	440C	O_2	none	-	316	8	-	1602	532.2	-1.2
32	Fomblin Z25-P28	3.01	440C	O_2	I[d]	1.0	316	24	37.9	138.5	46.0	-1.1
34	Fomblin Z25-P28	2.95	440C	O_2	A[k]	1.0	316	24	46.5	9.2	3.1	-0.60
33	Fomblin Z25-P28	3.04	440C	O_2	PH-3[c]	1.0	316	24	47.0	4.8	1.6	+0.30
41	Fomblin Z25-P28	3.07	440C	O_2	I[d]	1.0	300	24	46.4	2.2	0.7	+0.06
42	Fomblin Z25-P28	3.03	440C	O_2	A[k]	1.0	300	24	46.3	0.6	0.2	-0.06
43	Fomblin Z25-P28	3.26	440C	O_2	PH-3[c]	1.0	300	24	46.7	2.5	0.8	+0.18
10	Fomblin Z25-P28	3.09	M-50	O_2	none	-	316	8	11.3	1042	337.1	+0.12
6	Fomblin Z25-P28	3.07	M-50	O_2	I[d]	1.0	316	16	29.3	435.2	141.8	-2.2
2	Fomblin Z25-P28	3.01	M-50	O_2	I[d]	1.0	316	24	33.4[f]	398.5	132.4	-5.3
9	Fomblin Z25-P28	3.35	M-50	O_2	C_2PN_3[g]	1.0	316	16	33.2	361.6	107.9	-3.3
11	Fomblin Z25-P28	2.99	M-50	O_2	P-3[h]	1.0	316	16	45.7	12.5	4.2	-1.2
7	Fomblin Z25-P28	3.14	M-50	O_2	I[d]	1.0	300	24	46.4	7.4	2.4	+0.54
14	Fomblin Z25-P28	3.27	M-50	O_2	PH-3[c]	1.0	316	16	46.7	4.7	1.4	+2.4
45A	Fomblin Z25-P28	3.04	Ti(4Al,4Mn)	O_2	none	-	288	8	-	1264	415.8	-0.06

TABLE 3B (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
3	Fomblin Z25-P28	2.85	Ti(4Al,4Mn)	O_2	I^d	1.0	316	24	45.3	20.5	7.2	+0.06
15	Fomblin Z25-P28	3.15	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	316	24	46.7	5.4	1.7	-0.06
44	Fomblin Z25-P151	3.09	440C	O_2	none	-	316	8	-	1466	474.6	-0.24
107	Fomblin Z25-P151	2.97	440C	O_2	I^d	1.0	316	24	41.7	10.1	3.4	0.0
54	Fomblin Z25-P151	3.25	440C	O_2	II^m	1.0	316	24	42.6	1.7	0.5	+0.18
71	Fomblin Z25-P151	3.28	440C	O_2	III^s	1.0	316	24	42.9	2.8	0.9	-0.24
111	Fomblin Z25-P151	3.11	440C	O_2	V^y	1.0	330	24	42.3	4.3	1.4	-0.60
109	Fomblin Z25-P151	3.01	440C	O_2	V^y	1.0	316	24	42.7	0.6	0.2	-0.06
47	Fomblin Z25-P151	3.08	440C	O_2	PH-3^c	1.0	316	24	42.3	1.5	0.5	+0.18
48	Fomblin Z25-P151	3.06	440C	O_2	A^k	1.0	316	24	42.7	0.5	0.2	+0.06
58	Fomblin Z25-P151	3.14	440C	O_2	B^l	1.0	316	24	42.6	0.0	0.0	+0.06
59	Fomblin Z25-P151	3.20	440C	O_2	C^n	1.0	316	24	42.8	0.0	0.0	+0.12
64	Fomblin Z25-P151	3.07	440C	O_2	C^n	1.0	330	24	42.3	1.6	0.5	-0.36
78	Fomblin Z25-P151	2.97	440C	O_2	D-2^r	1.0	316	24	42.5	0.7	0.2	+0.06
61	Fomblin Z25-P151	3.68	440C^p	O_2	none	-	316	8	-	1451	394.3	+0.36

TABLE 3B (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
65	Fomblin Z25-P151	3.10	440C[q]	O_2	none	-	316	8	-	1436	463.3	+0.12
60	Fomblin Z25-P151	3.06	TiC/440C[o]	O_2	none	-	316	8	-	1347	440.2	-0.79
i[b]	Fomblin Z25-P151	3.02	M-50	O_2	none	-	316	8	-	1454	481.5	+0.30
ii[b]	Fomblin Z25-P151	3.17	M-50	O_2	PH-3[c]	1.0	316	16	42.3	1.1	0.4	+0.06
81[t]	Fomblin Z25-P151	3.54	Pyrowear675	O_2	none	-	316	8	-	1634	461.6	+0.21
82[u]	Fomblin Z25-P151	3.51	Pyrowear675	O_2	none	-	316	8	-	1670	475.9	+0.17
96	Fomblin Z25-P151	3.12	Pyrowear675	O_2	D-4[r]	1.0	316	24	42.7	1.0	0.3	+0.05
85	Fomblin Z25-P151	3.00	Cronidur 30	O_2	none	-	316	8	39.2	35.0	11.7	+0.07
88	Fomblin Z25-P151	3.07	Cronidur 30	O_2	none	-	316	8	-	1429	465.5	+3.60
97	Fomblin Z25-P151	3.00	Cronidur 30	O_2	D-4[r]	1.0	316	24	42.6	0.9	0.3	+0.27
45	Fomblin Z25-P151	3.10	Ti(4Al,4Mn)	O_2	none	-	288	8	-	3094	997.9	-0.18
108	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	42.5	5.9	1.9	+0.06
55	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	II[m]	1.0	316	24	42.7	3.1	1.0	+0.12
73	Fomblin Z25-P151	3.25	Ti(4Al,4Mn)	O_2	III[s]	1.0	316	24	42.8	3.0	0.9	0.0
123	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	V[y]	1.0	330	24	42.6	0.5	0.2	0.0

TABLE 3B (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
113	Fomblin Z25-P151	3.11	Ti(4Al,4Mn)	O_2	V^y	1.0	316	24	42.7	0.6	0.2	0.0
126	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	330	24	42.5	9.8	3.1	-0.24
46	Fomblin Z25-P151	3.01	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	316	24	42.7	1.6	0.5	-0.18
117	Fomblin Z25-P151	3.15	Ti(4Al,4Mn)	O_2	C^n	1.0	330	24	42.7	0.8	0.2	0.0
66	Fomblin Z25-P151	3.04	Ti(4Al,4Mn)	O_2	C^n	1.0	316	24	42.4	0.0	0.0	0.0
79	Fomblin Z25-P151	2.92	Ti(4Al,4Mn)	O_2	D-2^r	1.0	316	24	42.4	0.1	0.03	0.0
104	Fomblin Z25-P151	3.05	Ti(6Al,4V)	O_2	none	-	288	8	-	3030	993.3	0.0
125	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	V^y	1.0	330	24	42.8	0.6	0.2	0.0
118	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	C^n	1.0	330	24	42.7	0.8	0.2	-0.06
105	Fomblin Z25-P151	3.08	Ti(6Al,4V)	O_2	C^n	1.0	316	24	42.7	0.4	0.1	0.0
62	Fomblin Z25-P151	3.04	Si_3N_4	O_2	none	-	316	24	30.4	267.6	88.0	+1.72
63	Fomblin Z25-P151	3.00	Zirconia	O_2	none	-	316	8	29.0	270.8	90.3	-0.07
19	Krytox 143AC	3.17	440C	O_2	none	-	343	24	26.7	494.1	155.9	-4.8
12	Krytox 143AC	3.00	M-50	O_2	P-3^h	1.0	343	24	28.6	172.6	57.5	+0.42
5	Krytox 143AC	3.11	M-50	O_2	I^d	1.0	343	24	27.3	16.5	5.3	-5.6

TABLE 3B (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
25	Krytox 143AC	2.89	M-50	O$_2$	PH-3^j	1.0	343	24	28.4	11.7	4.0	+1.4
13	Krytox 143AC	2.82	M-50	O$_2$	PH-3^c	1.0	343	24	28.3	9.4	3.3	+4.3
4	Krytox 143AC	2.87	M-50	O$_2$	I^d	1.0	316	24	27.9	0.5	0.17	0.0
8	Krytox 143AC	2.93	Ti(4Al,4Mn)	O$_2$	I^d	1.0	350	24	27.4	11.1	3.8	-0.42
1	Krytox 143AC	2.90	Ti(4Al,4Mn)	O$_2$	I^d	1.0	343	24	27.8^e	7.0	2.4	-0.12
16	Krytox 143AC^i	3.02	M-50	O$_2$	I^d	1.0	350	24	33.6	18.8	6.2	-14.5
21	Krytox 16256	3.03	440C	O$_2$	none	-	343	24	55.3	494.1	163.1	-6.4
114	Krytox 16256	3.07	440C	O$_2$	none	-	330	48	-	653.4	212.8	-6.63
26	Krytox 16256	3.02	440C	O$_2$	none	-	330	24	-	155.7	51.6	-2.3
101	Krytox 16256	3.15	440C	O$_2$	none	-	330	24	-	191.1	60.7	-3.11
95	Krytox 16256	3.16	2 x 440C	O$_2$	none	-	330	24	61.8	328.3	103.9	-2.00^v
80	Krytox 16256	3.03	440C	O$_2$	none	-	316	24	-	60.7	20.0	+0.18
28	Krytox 16256	3.02	440C	O$_2$	PH-3^c	1.0	330	24	-	22.8	7.5	+0.18
39	Krytox 16256	2.91	440C	O$_2$	A^k	1.0	330	24	-	71.2	24.5	+0.06
40	Krytox 16256	3.04	440C	O$_2$	A^k	1.0	330	24	-	0.8	0.3	-0.06

TABLE 3B (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis (100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
31	Krytox 16256	2.98	440C	O_2	A[k]	1.0	343	24	-	13.2	4.4	-0.06
49	Krytox 16256	3.01	440C	O_2	B[l]	1.0	330	24	-	0.6	0.2	+0.06
75	Krytox 16256	2.82	440C	O_2	C[n]	1.0	343	24	-	108.8	38.6	+0.48
76	Krytox 16256	2.81	440C	O_2	C[n]	1.0	330	48	-	12.0	4.3	-4.60
112	Krytox 16256	2.84	440C	O_2	C[n]	1.0	330	48	-	1.3	0.5	+0.06
67	Krytox 16256	2.93	440C	O_2	C[n]	1.0	330	24	-	0.6	0.2	+0.06
69	Krytox 16256	2.90	440C	O_2	D-1[r]	1.0	316	24	-	0.2	0.1	+0.12
77	Krytox 16256	2.86	440C	O_2	D-2[r]	1.0	330	24	-	1.4	0.5	+0.12
23	Krytox 16256	2.91	440C	O_2	I[d]	1.0	343	24	-	123.1	42.3	0.0
27	Krytox 16256	3.00	440C	O_2	I[d]	1.0	330	24	-	5.2	1.7	-0.06
38	Krytox 16256	2.93	440C	O_2	I[d]	1.0	316	24	-	2.0	0.7	+0.06
53	Krytox 16256	3.42	440C	O_2	II[m]	1.0	316	24	-	5.4	1.6	0.0
70	Krytox 16256	2.85	440C	O_2	III[s]	1.0	316	24	-	7.9	2.8	0.0
98	Krytox 16256	3.32	440C	O_2	IV[w]	1.0	330	24	-	18.0	5.4	+0.60
102	Krytox 16256	3.06	440C	O_2	IV[w]	1.0	316	24	-	4.8	1.6	+0.18

TABLE 3B (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test No.	Fluid		Coupon	Atm	Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
	Type	g	Type		Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
106	Krytox 16256	2.93	440C	O_2	V[y]	1.0	330	24	-	0.5	0.2	+0.06
115	Krytox 16256	2.96	440C	O_2	V[y]	1.0	330	48	-	106.1	35.8	0.0
124	Krytox 16256	3.00	440C	O_2	V[y]	1.0	330	48	-	1.2	0.4	+0.18
17	Krytox 16256	3.09	M-50	O_2	none	-	343	24	-	173.3	56.1	+0.54
24	Krytox 16256	3.01	M-50	O_2	PH-3[c]	1.0	343	24	-	230.6	76.6	-4.8
22	Krytox 16256	3.06	M-50	O_2	I[d]	1.0	343	24	-	139.5	45.6	+1.1
86	Krytox 16256	3.44	Pyrowear675	O_2	none	-	330	24	65.7	157.6	45.8	+0.29
99	Krytox 16256	3.21	Pyrowear675	O_2	none	-	330	24	-	172.7	53.8	+0.27
99A[x]	Krytox 16256	3.01	Pyrowear675	O_2	none	-	330	24	-	137.0	45.5	+0.06
83	Krytox 16256	3.48	Pyrowear675	O_2	none	-	316	24	-	145.4	41.8	+0.18
91	Krytox 16256	2.84	Pyrowear675	O_2	D-4[r]	1.0	330	24	64.0	1.9	0.7	+0.16
89	Krytox 16256	3.18	Pyrowear675	O_2	I[d]	1.0	330	24	-	4.7	1.5	+0.04
127	Krytox 16256	3.03	Pyrowear675	O_2	V[y]	1.0	330	24	-	1.8	0.6	+0.07
94	Krytox 16256	3.02	Pyrowear675	O_2	PH-3[c]	1.0	330	24	-	2.8	0.9	+0.07
87	Krytox 16256	3.50	Cronidur 30	O_2	none	-	330	24	65.5	204.1	58.3	-4.47

TABLE 3B (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
84	Krytox 16256	2.97	Cronidur 30	O_2	none	-	316	24	-	125.6	42.3	+0.13
92	Krytox 16256	2.90	Cronidur 30	O_2	D-4[r]	1.0	330	24	-	1.4	0.5	+0.07
90	Krytox 16256	2.97	Cronidur 30	O_2	I[d]	1.0	330	24	-	1.8	0.6	+0.07
122[x]	Krytox 16256	2.98	Cronidur 30	O_2	V[y]	1.0	330	24	-	1.4	0.5	+0.06
93	Krytox 16256	2.91	Cronidur 30	O_2	PH-3[c]	1.0	330	24	-	3.0	1.0	0.0
18	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	none	-	316	24	46.5	478.4	156.8	-0.36
103	Krytox 16256	2.99	Ti(4Al,4Mn)	O_2	none	-	316	24	-	509.4	170.4	-0.24
30	Krytox 16256	3.01	Ti(4Al,4Mn)	O_2	PH-3[c]	1.0	343	24	-	420.4	139.7	-0.60
29	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	I[d]	1.0	343	24	-	419.5	137.5	-0.42
35	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	I[d]	1.0	330	24	64.8	138.4	47.7	+0.12
57	Krytox 16256	3.10	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	-	1.0	0.4	+0.12
56	Krytox 16256	3.19	Ti(4Al,4Mn)	O_2	II[m]	1.0	316	24	-	2.1	0.7	-0.06
72	Krytox 16256	3.21	Ti(4Al,4Mn)	O_2	III[s]	1.0	316	24	-	2.5	0.8	+0.18
110	Krytox 16256	2.93	Ti(4Al,4Mn)	O_2	V[y]	1.0	330	24	-	0.9	0.3	0.0
116	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	V[y]	1.0	330	48	-	1.7	0.6	-6.63

TABLE 3B (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

Test No.	Fluid Type	Fluid g	Coupon Type	Atm	Additive Type	Additive %	Temp °C	Time h	Vis(100°C) cSt	Products mg	Products mg/g	Coupon^{a} mg/cm^{2}
36	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	PH-3^{c}	1.0	330	24	-	3.7	1.3	-0.12
37	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	A^{k}	1.0	330	24	-	0.5	0.2	0.0
68	Krytox 16256	2.82	Ti(4Al,4Mn)	O_2	C^{n}	1.0	330	24	-	25.0	8.9	+0.06
121	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	C^{n}	1.0	330	24	64.7	1.4	0.5	0.0
74	Krytox 16256	2.88	Ti(4Al,4Mn)	O_2	C^{n}	1.0	316	24	-	0.6	0.2	0.0
100	Krytox 16256	3.27	Ti(6Al,4V)	O_2	none	-	316	24	62.8	163.1	49.9	+0.24
119	Krytox 16256	2.89	Ti(6Al,4V)	O_2	C^{n}	1.0	330	24	-	0.8	0.3	+0.12
120	Krytox 16256	2.99	Ti(6Al,4V)	O_2	V^{y}	1.0	330	24	65.1	1.0	0.3	0.0

a) Coupon weight change.
b) [Ref. 31]
c) PH-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$
d) Additive I, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$
e) The viscosity of Krytox 143AC (MLO 71-6) fluid alone is 27.3 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Krytox 143AC (MLO 71-6), prior to heat treatment was 26.7 cSt at 100°C. The viscosity of Krytox 16256 (lot 5) fluid alone is 64.1 cSt at 100°C.
f) The viscosity of Fomblin Z25-P28 fluid alone is 47.2 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Fomblin Z25-P28, prior to heat treatment was 46.4 cSt at 100°C. The viscosity of Fomblin Z25-P151 fluid alone is 42.6 cSt at 100°C.
g) $C_2PN_3 = [C_3F_7(OCF(CF_3)CF_2)_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$

TABLE 3B (concluded)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Fluid)

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h) P-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6F_4]_3P$
i) Fluorinated Krytox 143AC (MLO 91-21).
j) Residue after hydrolysis of PH-3 in water at 100°C for 24 h.
k) $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ [Ref. 31].
l) $(C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
m) Additive II, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
n) $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
o) 1/4 in 440C ball coated with TiC.
p) This 440C coupon was treated with hexamethyldisilazane before testing.
q) This 440C coupon was treated with 3-aminopropyltriethoxy silane in methanol and dried on a hot plate at 224°C before testing.
r) D-1: 61% $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C) and ~39% $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OC_6H_5)OH$; D-2: 81% C; D-4: 78% C [Ref. 31].
s) Additive III, $[C_3F_7(OCF(CF_3)CF_2)_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
t) In this test the Pyrowear 675 ball was rinsed with Freon-113 and used without polishing.
u) In this test the Pyrowear 675 ball was polished with 500A paper before rinsing with Freon-113.
v) This is the average value for weight loss of the two 440C coupons used; top coupon weight loss 3.1 mg/cm^2, bottom coupon 0.90 mg/cm^2. The two coupons were separated by a 4 mm glass spacer.
w) Additive IV, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$
x) In this test the metal bearing was first wiped with Freon-113 soaked tissue, then cleaned ultrasonically for 5 min in Freon-113 and dried in a stream of nitrogen (extra dry grade).
y) Additive V, $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$

TABLE 3C

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
20	Fomblin Z25-P28	3.01	440C	O_2	none	-	316	8	-	1602	532.2	-1.2
32	Fomblin Z25-P28	3.01	440C	O_2	I^d	1.0	316	24	37.9	138.5	46.0	-1.1
34	Fomblin Z25-P28	2.95	440C	O_2	A^k	1.0	316	24	46.5	9.2	3.1	-0.60
33	Fomblin Z25-P28	3.04	440C	O_2	PH-3^c	1.0	316	24	47.0	4.8	1.6	+0.30
41	Fomblin Z25-P28	3.07	440C	O_2	I^d	1.0	300	24	46.4	2.2	0.7	+0.06
42	Fomblin Z25-P28	3.03	440C	O_2	A^k	1.0	300	24	46.3	0.6	0.2	-0.06
43	Fomblin Z25-P28	3.26	440C	O_2	PH-3^c	1.0	300	24	46.7	2.5	0.8	+0.18
44	Fomblin Z25-P151	3.09	440C	O_2	none	-	316	8	-	1466	474.6	-0.24
107	Fomblin Z25-P151	2.97	440C	O_2	I^d	1.0	316	24	41.7	10.1	3.4	0.0
54	Fomblin Z25-P151	3.25	440C	O_2	II^m	1.0	316	24	42.6	1.7	0.5	+0.18
71	Fomblin Z25-P151	3.28	440C	O_2	III^s	1.0	316	24	42.9	2.8	0.9	-0.24
111	Fomblin Z25-P151	3.11	440C	O_2	V^y	1.0	330	24	42.3	4.3	1.4	-0.60
109	Fomblin Z25-P151	3.01	440C	O_2	V^y	1.0	316	24	42.7	0.6	0.2	-0.06
47	Fomblin Z25-P151	3.08	440C	O_2	PH-3^c	1.0	316	24	42.3	1.5	0.5	+0.18
48	Fomblin Z25-P151	3.06	440C	O_2	A^k	1.0	316	24	42.7	0.5	0.2	+0.06

TABLE 3C (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
58	Fomblin Z25-P151	3.14	440C	O_2	B^l	1.0	316	24	42.6	0.0	0.0	+0.06
59	Fomblin Z25-P151	3.20	440C	O_2	C^n	1.0	316	24	42.8	0.0	0.0	+0.12
64	Fomblin Z25-P151	3.07	440C	O_2	C^n	1.0	330	24	42.3	1.6	0.5	-0.36
78	Fomblin Z25-P151	2.97	440C	O_2	D-2^r	1.0	316	24	42.5	0.7	0.2	+0.06
19	Krytox 143AC	3.17	440C	O_2	none	-	343	24	26.7	494.1	155.9	-4.8
21	Krytox 16256	3.03	440C	O_2	none	-	343	24	55.3	494.1	163.1	-6.4
114	Krytox 16256	3.07	440C	O_2	none	-	330	48	-	653.4	212.8	-6.63
26	Krytox 16256	3.02	440C	O_2	none	-	330	24	-	155.7	51.6	-2.3
101	Krytox 16256	3.15	440C	O_2	none	-	330	24	-	191.1	60.7	-3.11
95	Krytox 16256	3.16	2 x 440C	O_2	none	-	330	24	61.8	328.3	103.9	-2.00^v
80	Krytox 16256	3.03	440C	O_2	none	-	316	24	-	60.7	20.0	+0.18
28	Krytox 16256	3.02	440C	O_2	PH-3^c	1.0	330	24	-	22.8	7.5	+0.18
23	Krytox 16256	2.91	440C	O_2	I^d	1.0	343	24	-	123.1	42.3	0.0
27	Krytox 16256	3.00	440C	O_2	I^d	1.0	330	24	-	5.2	1.7	-0.06
38	Krytox 16256	2.93	440C	O_2	I^d	1.0	316	24	-	2.0	0.7	+0.06

TABLE 3C (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
53	Krytox 16256	3.42	440C	O_2	II^m	1.0	316	24	-	5.4	1.6	0.0
70	Krytox 16256	2.85	440C	O_2	III^s	1.0	316	24	-	7.9	2.8	0.0
98	Krytox 16256	3.32	440C	O_2	IV^w	1.0	330	24	-	18.0	5.4	+0.60
102	Krytox 16256	3.06	440C	O_2	IV^w	1.0	316	24	-	4.8	1.6	+0.18
106	Krytox 16256	2.93	440C	O_2	V^y	1.0	330	24	-	0.5	0.2	+0.06
115	Krytox 16256	2.96	440C	O_2	V^y	1.0	330	48	-	106.1	35.8	0.0
124	Krytox 16256	3.00	440C	O_2	V^y	1.0	330	48	-	1.2	0.4	+0.18
39	Krytox 16256	2.91	440C	O_2	A^k	1.0	330	24	-	71.2	24.5	+0.06
40	Krytox 16256	3.04	440C	O_2	A^k	1.0	330	24	-	0.8	0.3	-0.06
31	Krytox 16256	2.98	440C	O_2	A^k	1.0	343	24	-	13.2	4.4	-0.06
49	Krytox 16256	3.01	440C	O_2	B^l	1.0	330	24	-	0.6	0.2	+0.06
75	Krytox 16256	2.82	440C	O_2	C^n	1.0	343	24	-	108.8	38.6	+0.48
76	Krytox 16256	2.81	440C	O_2	C^n	1.0	330	48	-	12.0	4.3	-4.60
112	Krytox 16256	2.84	440C	O_2	C^n	1.0	330	48	-	1.3	0.5	+0.06
67	Krytox 16256	2.93	440C	O_2	C^n	1.0	330	24	-	0.6	0.2	+0.06

TABLE 3C (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
69	Krytox 16256	2.90	440C	O_2	D-1[r]	1.0	316	24	-	0.2	0.1	+0.12
77	Krytox 16256	2.86	440C	O_2	D-2[r]	1.0	330	24	-	1.4	0.5	+0.12
61	Fomblin Z25-P151	3.68	440C[p]	O_2	none	-	316	8	-	1451	394.3	+0.36
65	Fomblin Z25-P151	3.10	440C[q]	O_2	none	-	316	8	-	1436	463.3	+0.12
60	Fomblin Z25-P151	3.06	TiC/440C[o]	O_2	none	-	316	8	-	1347	440.2	-0.79
7	Fomblin Z25-P28	3.14	M-50	O_2	I[d]	1.0	300	24	46.4	7.4	2.4	+0.54
10	Fomblin Z25-P28	3.09	M-50	O_2	none	-	316	8	11.3	1042	337.1	+0.12
6	Fomblin Z25-P28	3.07	M-50	O_2	I[d]	1.0	316	16	29.3	435.2	141.8	-2.2
2	Fomblin Z25-P28	3.01	M-50	O_2	I[d]	1.0	316	24	33.4[f]	398.5	132.4	-5.3
9	Fomblin Z25-P28	3.35	M-50	O_2	C_2PN_3[g]	1.0	316	16	33.2	361.6	107.9	-3.3
11	Fomblin Z25-P28	2.99	M-50	O_2	P-3[h]	1.0	316	16	45.7	12.5	4.2	-1.2
14	Fomblin Z25-P28	3.27	M-50	O_2	PH-3[c]	1.0	316	16	46.7	4.7	1.4	+2.4
i[b]	Fomblin Z25-P151	3.02	M-50	O_2	none	-	316	8	-	1454	481.5	+0.30
ii[b]	Fomblin Z25-P151	3.17	M-50	O_2	PH-3[c]	1.0	316	16	42.3	1.1	0.4	+0.06
12	Krytox 143AC	3.00	M-50	O_2	P-3[h]	1.0	343	24	28.6	172.6	57.5	+0.42

TABLE 3C (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS

(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
5	Krytox 143AC	3.11	M-50	O_2	I[d]	1.0	343	24	27.3	16.5	5.3	-5.6
25	Krytox 143AC	2.89	M-50	O_2	PH-3[j]	1.0	343	24	28.4	11.7	4.0	+1.4
13	Krytox 143AC	2.82	M-50	O_2	PH-3[c]	1.0	343	24	28.3	9.4	3.3	+4.3
4	Krytox 143AC	2.87	M-50	O_2	I[d]	1.0	316	24	27.9	0.5	0.17	0.0
16	Krytox 143AC[i]	3.02	M-50	O_2	I[d]	1.0	350	24	33.6	18.8	6.2	-14.5
24	Krytox 16256	3.01	M-50	O_2	PH-3[c]	1.0	343	24	-	230.6	76.6	-4.8
17	Krytox 16256	3.09	M-50	O_2	none	-	343	24	-	173.3	56.1	+0.54
22	Krytox 16256	3.06	M-50	O_2	I[d]	1.0	343	24	-	139.5	45.6	+1.1
81[t]	Fomblin Z25-P151	3.54	Pyrowear675	O_2	none	-	316	8	-	1634	461.6	+0.21
82[u]	Fomblin Z25-P151	3.51	Pyrowear675	O_2	none	-	316	8	-	1670	475.9	+0.17
96	Fomblin Z25-P151	3.12	Pyrowear675	O_2	D-4[r]	1.0	316	24	42.7	1.0	0.3	+0.05
86	Krytox 16256	3.44	Pyrowear675	O_2	none	-	330	24	65.7	157.6	45.8	+0.29
99	Krytox 16256	3.21	Pyrowear675	O_2	none	-	330	24	-	172.7	53.8	+0.27
99A[x]	Krytox 16256	3.01	Pyrowear675	O_2	none	-	330	24	-	137.0	45.5	+0.06
83	Krytox 16256	3.48	Pyrowear675	O_2	none	-	316	24	-	145.4	41.8	+0.18

TABLE 3C (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
89	Krytox 16256	3.18	Pyrowear675	O$_2$	I^d	1.0	330	24	-	4.7	1.5	+0.04
127	Krytox 16256	3.03	Pyrowear675	O$_2$	V^y	1.0	330	24	-	1.8	0.6	+0.07
94	Krytox 16256	3.02	Pyrowear675	O$_2$	PH-3^c	1.0	330	24	-	2.8	0.9	+0.07
91	Krytox 16256	2.84	Pyrowear675	O$_2$	D-4^r	1.0	330	24	64.0	1.9	0.7	+0.16
85	Fomblin Z25-P151	3.00	Cronidur 30	O$_2$	none	-	316	8	39.2	35.0	11.7	+0.07
88	Fomblin Z25-P151	3.07	Cronidur 30	O$_2$	none	-	316	8	-	1429	465.5	+3.60
97	Fomblin Z25-P151	3.00	Cronidur 30	O$_2$	D-4^r	1.0	316	24	42.6	0.9	0.3	+0.27
87	Krytox 16256	3.50	Cronidur 30	O$_2$	none	-	330	24	65.5	204.1	58.3	-4.47
84	Krytox 16256	2.97	Cronidur 30	O$_2$	none	-	316	24	-	125.6	42.3	+0.13
92	Krytox 16256	2.90	Cronidur 30	O$_2$	D-4^r	1.0	330	24	-	1.4	0.5	+0.07
90	Krytox 16256	2.97	Cronidur 30	O$_2$	I^d	1.0	330	24	-	1.8	0.6	+0.07
122^x	Krytox 16256	2.98	Cronidur 30	O$_2$	V^y	1.0	330	24	-	1.4	0.5	+0.06
93	Krytox 16256	2.91	Cronidur 30	O$_2$	PH-3^c	1.0	330	24	-	3.0	1.0	0.0
45A	Fomblin Z25-P28	3.04	Ti(4Al,4Mn)	O$_2$	none	-	288	8	-	1264	415.8	-0.06
3	Fomblin Z25-P28	2.85	Ti(4Al,4Mn)	O$_2$	I^d	1.0	316	24	45.3	20.5	7.2	+0.06

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TABLE 3C (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
15	Fomblin Z25-P28	3.15	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	316	24	46.7	5.4	1.7	-0.06
45	Fomblin Z25-P151	3.10	Ti(4Al,4Mn)	O_2	none	-	288	8	-	3094	997.9	-0.18
108	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	I^d	1.0	316	24	42.5	5.9	1.9	+0.06
55	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	II^m	1.0	316	24	42.7	3.1	1.0	+0.12
73	Fomblin Z25-P151	3.25	Ti(4Al,4Mn)	O_2	III^s	1.0	316	24	42.8	3.0	0.9	0.0
123	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	V^y	1.0	330	24	42.6	0.5	0.2	0.0
113	Fomblin Z25-P151	3.11	Ti(4Al,4Mn)	O_2	V^y	1.0	316	24	42.7	0.6	0.2	0.0
126	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	330	24	42.5	9.8	3.1	-0.24
46	Fomblin Z25-P151	3.01	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	316	24	42.7	1.6	0.5	-0.18
117	Fomblin Z25-P151	3.15	Ti(4Al,4Mn)	O_2	C^n	1.0	330	24	42.7	0.8	0.2	0.0
66	Fomblin Z25-P151	3.04	Ti(4Al,4Mn)	O_2	C^n	1.0	316	24	42.4	0.0	0.0	0.0
79	Fomblin Z25-P151	2.92	Ti(4Al,4Mn)	O_2	D-2^r	1.0	316	24	42.4	0.1	0.03	0.0
8	Krytox 143AC	2.93	Ti(4Al,4Mn)	O_2	I^d	1.0	350	24	27.4	11.1	3.8	-0.42
1	Krytox 143AC	2.90	Ti(4Al,4Mn)	O_2	I^d	1.0	343	24	27.8^e	7.0	2.4	-0.12
18	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	none	-	316	24	46.5	478.4	156.8	-0.36

TABLE 3C (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS[a]
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
103	Krytox 16256	2.99	Ti(4Al,4Mn)	O_2	none	-	316	24	-	509.4	170.4	-0.24
57	Krytox 16256	3.10	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	-	1.0	0.4	+0.12
56	Krytox 16256	3.19	Ti(4Al,4Mn)	O_2	II[m]	1.0	316	24	-	2.1	0.7	-0.06
72	Krytox 16256	3.21	Ti(4Al,4Mn)	O_2	III[s]	1.0	316	24	-	2.5	0.8	+0.18
110	Krytox 16256	2.93	Ti(4Al,4Mn)	O_2	V[y]	1.0	330	24	-	0.9	0.3	0.0
30	Krytox 16256	3.01	Ti(4Al,4Mn)	O_2	PH-3[c]	1.0	343	24	-	420.4	139.7	-0.60
29	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	I[d]	1.0	343	24	-	419.5	137.5	-0.42
35	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	I[d]	1.0	330	24	64.8	138.4	47.7	+0.12
116	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	V[y]	1.0	330	48	-	1.7	0.6	-6.63
36	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	PH-3[c]	1.0	330	24	-	3.7	1.3	-0.12
37	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	A[k]	1.0	330	24	-	0.5	0.2	0.0
68	Krytox 16256	2.82	Ti(4Al,4Mn)	O_2	C[n]	1.0	330	24	-	25.0	8.9	+0.06
121	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	C[n]	1.0	330	24	64.7	1.4	0.5	0.0
74	Krytox 16256	2.88	Ti(4Al,4Mn)	O_2	C[n]	1.0	316	24	-	0.6	0.2	0.0
104	Fomblin Z25-P151	3.05	Ti(6Al,4V)	O_2	none	-	288	8	-	3030	993.3	0.0

TABLE 3C (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS[a]
(Grouped By Coupon)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
125	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	v^y	1.0	330	24	42.8	0.6	0.2	0.0
118	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	c^n	1.0	330	24	42.7	0.8	0.2	-0.06
105	Fomblin Z25-P151	3.08	Ti(6Al,4V)	O_2	c^n	1.0	316	24	42.7	0.4	0.1	0.0
100	Krytox 16256	3.27	Ti(6Al,4V)	O_2	none	-	316	24	62.8	163.1	49.9	+0.24
120	Krytox 16256	2.99	Ti(6Al,4V)	O_2	v^y	1.0	330	24	65.1	1.0	0.3	0.0
119	Krytox 16256	2.89	Ti(6Al,4V)	O_2	c^n	1.0	330	24	-	0.8	0.3	+0.12
62	Fomblin Z25-P151	3.04	Si_3N_4	O_2	none	-	316	24	30.4	267.6	88.0	+1.72
63	Fomblin Z25-P151	3.00	Zirconia	O_2	none	-	316	8	29.0	270.8	90.3	-0.07

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a) Coupon weight change.
b) [Ref. 31]
c) PH-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$
d) Additive I, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$
e) The viscosity of Krytox 143AC (MLO 71-6) fluid alone is 27.3 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Krytox 143AC (MLO 71-6), prior to heat treatment was 26.7 cSt at 100°C. The viscosity of Krytox 16256 (lot 5) fluid alone is 64.1 cSt at 100°C.
f) The viscosity of Fomblin Z25-P28 fluid alone is 47.2 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Fomblin Z25-P28, prior to heat treatment was 46.4 cSt at 100°C. The viscosity of Fomblin Z25-P151 fluid alone is 42.6 cSt at 100°C.
g) C_2PN_3 = $[C_3F_7(OCF(CF_3)CF_2)_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$

TABLE 3C (concluded)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS[a]
(Grouped By Coupon)

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h) P-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6F_4]_3P$
i) Fluorinated Krytox 143AC (MLO 91-21).
j) Residue after hydrolysis of PH-3 in water at 100°C for 24 h.
k) $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ [Ref. 31].
l) $(C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
m) Additive II, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
n) $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
o) 1/4 in 440C ball coated with TiC.
p) This 440C coupon was treated with hexamethyldisilazane before testing.
q) This 440C coupon was treated with 3-aminopropyltriethoxy silane in methanol and dried on a hot plate at 224°C before testing.
r) D-1: 61% $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C) and ~39% $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OC_6H_5)OH$; D-2: 81% C; D-4: 78% C [Ref. 31].
s) Additive III, $[C_3F_7(OCF(CF_3)CF_2)_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
t) In this test the Pyrowear 675 ball was rinsed with Freon-113 and used without polishing.
u) In this test the Pyrowear 675 ball was polished with 500A paper before rinsing with Freon-113.
v) This is the average value for weight loss of the two 440C coupons used; top coupon weight loss 3.1 mg/cm^2, bottom coupon 0.90 mg/cm^2. The two coupons were separated by a 4 mm glass spacer.
w) Additive IV, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$
x) In this test the metal bearing was first wiped with Freon-113 soaked tissue, then cleaned ultrasonically for 5 min in Freon-113 and dried in a stream of nitrogen (extra dry grade).
y) Additive V, $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$

TABLE 3D

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
20	Fomblin Z25-P28	3.01	440C	O_2	none	-	316	8	-	1602	532.2	-1.2
10	Fomblin Z25-P28	3.09	M-50	O_2	none	-	316	8	11.3	1042	337.1	+0.12
45A	Fomblin Z25-P28	3.04	Ti(4Al,4Mn)	O_2	none	-	288	8	-	1264	415.8	-0.06
44	Fomblin Z25-P151	3.09	440C	O_2	none	-	316	8	-	1466	474.6	-0.24
61	Fomblin Z25-P151	3.68	440C[p]	O_2	none	-	316	8	-	1451	394.3	+0.36
65	Fomblin Z25-P151	3.10	440C[q]	O_2	none	-	316	8	-	1436	463.3	+0.12
60	Fomblin Z25-P151	3.06	TiC/440C[o]	O_2	none	-	316	8	-	1347	440.2	-0.79
i[b]	Fomblin Z25-P151	3.02	M-50	O_2	none	-	316	8	-	1454	481.5	+0.30
81[t]	Fomblin Z25-P151	3.54	Pyrowear675	O_2	none	-	316	8	-	1634	461.6	+0.21
82[u]	Fomblin Z25-P151	3.51	Pyrowear675	O_2	none	-	316	8	-	1670	475.9	+0.17
85	Fomblin Z25-P151	3.00	Cronidur 30	O_2	none	-	316	8	39.2	35.0	11.7	+0.07
88	Fomblin Z25-P151	3.07	Cronidur 30	O_2	none	-	316	8	-	1429	465.5	+3.60
45	Fomblin Z25-P151	3.10	Ti(4Al,4Mn)	O_2	none	-	288	8	-	3094	997.9	-0.18
104	Fomblin Z25-P151	3.05	Ti(6Al,4V)	O_2	none	-	288	8	-	3030	993.3	0.0
62	Fomblin Z25-P151	3.04	Si_3N_4	O_2	none	-	316	24	30.4	267.6	88.0	+1.72

TABLE 3D (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
63	Fomblin Z25-P151	3.00	Zirconia	O_2	none	-	316	8	29.0	270.8	90.3	-0.07
19	Krytox 143AC	3.17	440C	O_2	none	-	343	24	26.7	494.1	155.9	-4.8
21	Krytox 16256	3.03	440C	O_2	none	-	343	24	55.3	494.1	163.1	-6.4
114	Krytox 16256	3.07	440C	O_2	none	-	330	48	-	653.4	212.8	-6.63
26	Krytox 16256	3.02	440C	O_2	none	-	330	24	-	155.7	51.6	-2.3
101	Krytox 16256	3.15	440C	O_2	none	-	330	24	-	191.1	60.7	-3.11
95	Krytox 16256	3.16	2 x 440C	O_2	none	-	330	24	61.8	328.3	103.9	-2.00^v
80	Krytox 16256	3.03	440C	O_2	none	-	316	24	-	60.7	20.0	+0.18
17	Krytox 16256	3.09	M-50	O_2	none	-	343	24	-	173.3	56.1	+0.54
86	Krytox 16256	3.44	Pyrowear675	O_2	none	-	330	24	65.7	157.6	45.8	+0.29
99	Krytox 16256	3.21	Pyrowear675	O_2	none	-	330	24	-	172.7	53.8	+0.27
99A^x	Krytox 16256	3.01	Pyrowear675	O_2	none	-	330	24	-	137.0	45.5	+0.06
83	Krytox 16256	3.48	Pyrowear675	O_2	none	-	316	24	-	145.4	41.8	+0.18
87	Krytox 16256	3.50	Cronidur 30	O_2	none	-	330	24	65.5	204.1	58.3	-4.47
84	Krytox 16256	2.97	Cronidur 30	O_2	none	-	316	24	-	125.6	42.3	+0.13

TABLE 3D (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
18	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	none	-	316	24	46.5	478.4	156.8	-0.36
103	Krytox 16256	2.99	Ti(4Al,4Mn)	O_2	none	-	316	24	-	509.4	170.4	-0.24
100	Krytox 16256	3.27	Ti(6Al,4V)	O_2	none	-	316	24	62.8	163.1	49.9	+0.24
34	Fomblin Z25-P28	2.95	440C	O_2	A^k	1.0	316	24	46.5	9.2	3.1	-0.60
42	Fomblin Z25-P28	3.03	440C	O_2	A^k	1.0	300	24	46.3	0.6	0.2	-0.06
48	Fomblin Z25-P151	3.06	440C	O_2	A^k	1.0	316	24	42.7	0.5	0.2	+0.06
39	Krytox 16256	2.91	440C	O_2	A^k	1.0	330	24	-	71.2	24.5	+0.06
40	Krytox 16256	3.04	440C	O_2	A^k	1.0	330	24	-	0.8	0.3	-0.06
31	Krytox 16256	2.98	440C	O_2	A^k	1.0	343	24	-	13.2	4.4	-0.06
37	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	A^k	1.0	330	24	-	0.5	0.2	0.0
58	Fomblin Z25-P151	3.14	440C	O_2	B^l	1.0	316	24	42.6	0.0	0.0	+0.06
49	Krytox 16256	3.01	440C	O_2	B^l	1.0	330	24	-	0.6	0.2	+0.06
59	Fomblin Z25-P151	3.20	440C	O_2	C^n	1.0	316	24	42.8	0.0	0.0	+0.12
64	Fomblin Z25-P151	3.07	440C	O_2	C^n	1.0	330	24	42.3	1.6	0.5	-0.36
117	Fomblin Z25-P151	3.15	Ti(4Al,4Mn)	O_2	C^n	1.0	330	24	42.7	0.8	0.2	0.0

TABLE 3D (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
66	Fomblin Z25-P151	3.04	Ti(4Al,4Mn)	O_2	C[n]	1.0	316	24	42.4	0.0	0.0	0.0
118	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	C[n]	1.0	330	24	42.7	0.8	0.2	-0.06
105	Fomblin Z25-P151	3.08	Ti(6Al,4V)	O_2	C[n]	1.0	316	24	42.7	0.4	0.1	0.0
75	Krytox 16256	2.82	440C	O_2	C[n]	1.0	343	24	-	108.8	38.6	+0.48
76	Krytox 16256	2.81	440C	O_2	C[n]	1.0	330	48	-	12.0	4.3	-4.60
112	Krytox 16256	2.84	440C	O_2	C[n]	1.0	330	48	-	1.3	0.5	+0.06
67	Krytox 16256	2.93	440C	O_2	C[n]	1.0	330	24	-	0.6	0.2	+0.06
68	Krytox 16256	2.82	Ti(4Al,4Mn)	O_2	C[n]	1.0	330	24	-	25.0	8.9	+0.06
121	Krytox 16256	2.95	Ti(4Al,4Mn)	O_2	C[n]	1.0	330	24	64.7	1.4	0.5	0.0
74	Krytox 16256	2.88	Ti(4Al,4Mn)	O_2	C[n]	1.0	316	24	-	0.6	0.2	0.0
119	Krytox 16256	2.89	Ti(6Al,4V)	O_2	C[n]	1.0	330	24	-	0.8	0.3	+0.12
69	Krytox 16256	2.90	440C	O_2	D-1[r]	1.0	316	24	-	0.2	0.1	+0.12
77	Krytox 16256	2.86	440C	O_2	D-2[r]	1.0	330	24	-	1.4	0.5	+0.12
78	Fomblin Z25-P151	2.97	440C	O_2	D-2[r]	1.0	316	24	42.5	0.7	0.2	+0.06
79	Fomblin Z25-P151	2.92	Ti(4Al,4Mn)	O_2	D-2[r]	1.0	316	24	42.4	0.1	0.03	0.0

TABLE 3D (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
96	Fomblin Z25-P151	3.12	Pyrowear675	O_2	D-4[r]	1.0	316	24	42.7	1.0	0.3	+0.05
91	Krytox 16256	2.84	Pyrowear675	O_2	D-4[r]	1.0	330	24	64.0	1.9	0.7	+0.16
97	Fomblin Z25-P151	3.00	Cronidur 30	O_2	D-4[r]	1.0	316	24	42.6	0.9	0.3	+0.27
92	Krytox 16256	2.90	Cronidur 30	O_2	D-4[r]	1.0	330	24	-	1.4	0.5	+0.07
9	Fomblin Z25-P28	3.35	M-50	O_2	C_2PN_3[g]	1.0	316	16	33.2	361.6	107.9	-3.3
32	Fomblin Z25-P28	3.01	440C	O_2	I[d]	1.0	316	24	37.9	138.5	46.0	-1.1
41	Fomblin Z25-P28	3.07	440C	O_2	I[d]	1.0	300	24	46.4	2.2	0.7	+0.06
6	Fomblin Z25-P28	3.07	M-50	O_2	I[d]	1.0	316	16	29.3	435.2	141.8	-2.2
2	Fomblin Z25-P28	3.01	M-50	O_2	I[d]	1.0	316	24	33.4[f]	398.5	132.4	-5.3
7	Fomblin Z25-P28	3.14	M-50	O_2	I[d]	1.0	300	24	46.4	7.4	2.4	+0.54
3	Fomblin Z25-P28	2.85	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	45.3	20.5	7.2	+0.06
107	Fomblin Z25-P151	2.97	440C	O_2	I[d]	1.0	316	24	41.7	10.1	3.4	0.0
108	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	42.5	5.9	1.9	+0.06
5	Krytox 143AC	3.11	M-50	O_2	I[d]	1.0	343	24	27.3	16.5	5.3	-5.6
4	Krytox 143AC	2.87	M-50	O_2	I[d]	1.0	316	24	27.9	0.5	0.17	0.0

TABLE 3D (continued)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
8	Krytox 143AC	2.93	Ti(4Al,4Mn)	O_2	I[d]	1.0	350	24	27.4	11.1	3.8	-0.42
1	Krytox 143AC	2.90	Ti(4Al,4Mn)	O_2	I[d]	1.0	343	24	27.8[e]	7.0	2.4	-0.12
16	Krytox 143AC[i]	3.02	M-50	O_2	I[d]	1.0	350	24	33.6	18.8	6.2	-14.5
23	Krytox 16256	2.91	440C	O_2	I[d]	1.0	343	24	-	123.1	42.3	0.0
27	Krytox 16256	3.00	440C	O_2	I[d]	1.0	330	24	-	5.2	1.7	-0.06
38	Krytox 16256	2.93	440C	O_2	I[d]	1.0	316	24	-	2.0	0.7	+0.06
22	Krytox 16256	3.06	M-50	O_2	I[d]	1.0	343	24	-	139.5	45.6	+1.1
89	Krytox 16256	3.18	Pyrowear675	O_2	I[d]	1.0	330	24	-	4.7	1.5	+0.04
90	Krytox 16256	2.97	Cronidur 30	O_2	I[d]	1.0	330	24	-	1.8	0.6	+0.07
29	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	I[d]	1.0	343	24	-	419.5	137.5	-0.42
35	Krytox 16256	2.90	Ti(4Al,4Mn)	O_2	I[d]	1.0	330	24	64.8	138.4	47.7	+0.12
57	Krytox 16256	3.10	Ti(4Al,4Mn)	O_2	I[d]	1.0	316	24	-	1.0	0.4	+0.12
54	Fomblin Z25-P151	3.25	440C	O_2	II[m]	1.0	316	24	42.6	1.7	0.5	+0.18
55	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	II[m]	1.0	316	24	42.7	3.1	1.0	+0.12
53	Krytox 16256	3.42	440C	O_2	II[m]	1.0	316	24	-	5.4	1.6	0.0

TABLE 3D (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
56	Krytox 16256	3.19	Ti(4Al,4Mn)	O_2	II^m	1.0	316	24	-	2.1	0.7	-0.06
71	Fomblin Z25-P151	3.28	440C	O_2	III^s	1.0	316	24	42.9	2.8	0.9	-0.24
70	Krytox 16256	2.85	440C	O_2	III^s	1.0	316	24	-	7.9	2.8	0.0
73	Fomblin Z25-P151	3.25	Ti(4Al,4Mn)	O_2	III^s	1.0	316	24	42.8	3.0	0.9	0.0
72	Krytox 16256	3.21	Ti(4Al,4Mn)	O_2	III^s	1.0	316	24	-	2.5	0.8	+0.18
98	Krytox 16256	3.32	440C	O_2	IV^w	1.0	330	24	-	18.0	5.4	+0.60
102	Krytox 16256	3.06	440C	O_2	IV^w	1.0	316	24	-	4.8	1.6	+0.18
111	Fomblin Z25-P151	3.11	440C	O_2	V^y	1.0	330	24	42.3	4.3	1.4	-0.60
109	Fomblin Z25-P151	3.01	440C	O_2	V^y	1.0	316	24	42.7	0.6	0.2	-0.06
123	Fomblin Z25-P151	3.08	Ti(4Al,4Mn)	O_2	V^y	1.0	330	24	42.6	0.5	0.2	0.0
113	Fomblin Z25-P151	3.11	Ti(4Al,4Mn)	O_2	V^y	1.0	316	24	42.7	0.6	0.2	0.0
125	Fomblin Z25-P151	3.10	Ti(6Al,4V)	O_2	V^y	1.0	330	24	42.8	0.6	0.2	0.0
106	Krytox 16256	2.93	440C	O_2	V^y	1.0	330	24	-	0.5	0.2	+0.06
115	Krytox 16256	2.96	440C	O_2	V^y	1.0	330	48	-	106.1	35.8	0.0
124	Krytox 16256	3.00	440C	O_2	V^y	1.0	330	48	-	1.2	0.4	+0.18

TABLE 3D (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS^a
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon^a
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
127	Krytox 16256	3.03	Pyrowear675	O_2	V^y	1.0	330	24	-	1.8	0.6	+0.07
122^x	Krytox 16256	2.98	Cronidur 30	O_2	V^y	1.0	330	24	-	1.4	0.5	+0.06
110	Krytox 16256	2.93	Ti(4Al,4Mn)	O_2	V^y	1.0	330	24	-	0.9	0.3	0.0
116	Krytox 16256	3.05	Ti(4Al,4Mn)	O_2	V^y	1.0	330	48	-	1.7	0.6	-6.63
120	Krytox 16256	2.99	Ti(6Al,4V)	O_2	V^y	1.0	330	24	65.1	1.0	0.3	0.0
11	Fomblin Z25-P28	2.99	M-50	O_2	P-3^h	1.0	316	16	45.7	12.5	4.2	-1.2
12	Krytox 143AC	3.00	M-50	O_2	P-3^h	1.0	343	24	28.6	172.6	57.5	+0.42
33	Fomblin Z25-P28	3.04	440C	O_2	PH-3^c	1.0	316	24	47.0	4.8	1.6	+0.30
43	Fomblin Z25-P28	3.26	440C	O_2	PH-3^c	1.0	300	24	46.7	2.5	0.8	+0.18
14	Fomblin Z25-P28	3.27	M-50	O_2	PH-3^c	1.0	316	16	46.7	4.7	1.4	+2.4
15	Fomblin Z25-P28	3.15	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	316	24	46.7	5.4	1.7	-0.06
47	Fomblin Z25-P151	3.08	440C	O_2	PH-3^c	1.0	316	24	42.3	1.5	0.5	+0.18
ii^b	Fomblin Z25-P151	3.17	M-50	O_2	PH-3^c	1.0	316	16	42.3	1.1	0.4	+0.06
126	Fomblin Z25-P151	3.12	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	330	24	42.5	9.8	3.1	-0.24
46	Fomblin Z25-P151	3.01	Ti(4Al,4Mn)	O_2	PH-3^c	1.0	316	24	42.7	1.6	0.5	-0.18

TABLE 3D (continued)

EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS[a]
(Grouped by Additive)

Test	Fluid		Coupon		Additive		Temp	Time	Vis(100°C)	Products		Coupon[a]
No.	Type	g	Type	Atm	Type	%	°C	h	cSt	mg	mg/g	mg/cm^2
13	Krytox 143AC	2.82	M-50	O_2	PH-3[c]	1.0	343	24	28.3	9.4	3.3	+4.3
25	Krytox 143AC	2.89	M-50	O_2	PH-3[j]	1.0	343	24	28.4	11.7	4.0	+1.4
28	Krytox 16256	3.02	440C	O_2	PH-3[c]	1.0	330	24	-	22.8	7.5	+0.18
24	Krytox 16256	3.01	M-50	O_2	PH-3[c]	1.0	343	24	-	230.6	76.6	-4.8
30	Krytox 16256	3.01	Ti(4Al, 4Mn)	O_2	PH-3[c]	1.0	343	24	-	420.4	139.7	-0.60
36	Krytox 16256	2.90	Ti(4Al, 4Mn)	O_2	PH-3[c]	1.0	330	24	-	3.7	1.3	-0.12
94	Krytox 16256	3.02	Pyrowear675	O_2	PH-3[c]	1.0	330	24	-	2.8	0.9	+0.07
93	Krytox 16256	2.91	Cronidur 30	O_2	PH-3[c]	1.0	330	24	-	3.0	1.0	0.0

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a) Coupon weight change.

b) [Ref. 31]

c) PH-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$

d) Additive I, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$

e) The viscosity of Krytox 143AC (MLO 71-6) fluid alone is 27.3 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Krytox 143AC (MLO 71-6), prior to heat treatment was 26.7 cSt at 100°C. The viscosity of Krytox 16256 (lot 5) fluid alone is 64.1 cSt at 100°C.

f) The viscosity of Fomblin Z25-P28 fluid alone is 47.2 cSt at 100°C; the viscosity of 1% by wt solution of the additive I in Fomblin Z25-P28, prior to heat treatment was 46.4 cSt at 100°C. The viscosity of Fomblin Z25-P151 fluid alone is 42.6 cSt at 100°C.

g) $C_2PN_3 = [C_3F_7(OCF(CF_3)CF_2)_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$

TABLE 3D (concluded)

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EFFECTS OF ADDITIVES ON DEGRADATION OF PERFLUOROALKYLETHER FLUIDS[a]
(Grouped by Additive)

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h) P-3 = $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6F_4]_3P$
i) Fluorinated Krytox 143AC (MLO 91-21).
j) Residue after hydrolysis of PH-3 in water at 100°C for 24 h.
k) $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ [Ref. 31].
l) $(C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
m) Additive II, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
n) $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ [Ref. 31].
o) 1/4 in 440C ball coated with TiC.
p) This 440C coupon was treated with hexamethyldisilazane before testing.
q) This 440C coupon was treated with 3-aminopropyltriethoxy silane in methanol and dried on a hot plate at 224°C before testing.
r) D-1: 61% $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C) and ~39% $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OC_6H_5)OH$; D-2: 81% C; D-4: 78% C [Ref. 31].
s) Additive III, $[C_3F_7(OCF(CF_3)CF_2)_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$
t) In this test the Pyrowear 675 ball was rinsed with Freon-113 and used without polishing.
u) In this test the Pyrowear 675 ball was polished with 500A paper before rinsing with Freon-113.
v) This is the average value for weight loss of the two 440C coupons used; top coupon weight loss 3.1 mg/cm^2, bottom coupon 0.90 mg/cm^2. The two coupons were separated by a 4 mm glass spacer.
w) Additive IV, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$
x) In this test the metal bearing was first wiped with Freon-113 soaked tissue, then cleaned ultrasonically for 5 min in Freon-113 and dried in a stream of nitrogen (extra dry grade).
y) Additive V, $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$

TABLE 4

SUMMARY OF REACTIONS OF $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN$ WITH NH_3[a]

Rxn	R_fCN[b]		NH_3	Freon-113	Ampule	Reaction Condition		Product	
No.	g	mmol	mL	mL	mL	Temp (°C)	Time (h)	Wt (g)	purity (%)[c]
1	0.90	1.71	3	0	15	-30 0 RT	1 4 17	0.77	48 (40)[d]
2	1.13	2.14	3	2	15	-20 0 RT	1 3 17	1.08	70 (64)[d]
3	1.19	2.26	6	2	40	-20 0 RT	1 3 17	1.09	65 (58)[d]
4	1.09	2.07	6	6	40	-20 0 RT	1 3 17	0.94	79 (66)[d]
5	5.89	11.18	15	35	100	-20 0 RT	0.5 1 17	5.73	85 (81)[d]

a) All the reactions were performed in liquid ammonia in evacuated sealed ampules.
b) $R_f = C_3F_7OCF(CF_3)CF_2OC(CF_3)_2$
c) This is the area percent of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ in the crude product as determined by gas chromatography.
d) Yield.

TABLE 5

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C{=}NH(NH_2)$ (MW 544)

m/e	%	m/e	%	m/e	%	m/e	%
31	14.5	100	24.6	177	6.0	342	14.0
42	14.6	116	6.2	190	3.5	359	5.5
43	100.0	119	25.6	192	19.0	405	8.8
44	14.7	128	3.4	193	18.7	408	5.8
46	4.9	131	5.9	194	4.3	425	10.0
47	13.4	138	3.8	197	3.0	455	3.8
50	11.4	145	8.5	217	12.8	458	7.3
51	11.7	147	18.5	221	4.5	475	6.4
54	3.0	150	14.2	239	10.7	483	3.0
66	41.8	151	14.9	242	19.1	505	7.0
67	3.2	153	6.9	259	13.1	508	7.8
69	68.5	157	3.2	285	9.5	525	19.2
70	7.3	158	4.8	289	13.7	526	5.1
78	5.9	166	9.5	290	4.5	527	4.5
81	4.0	169	54.0	317	9.9	544	12.3M^+
93	4.4	170	7.8	332	13.3	545	9.6
96	9.6	173	12.8	335	6.3		
97	23.4	176	25.5	339	5.3		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

544 - $[M]^+$

525 - $[M - F]^+$

425 - $[M - C_2F_5]^+$

342 - $[C_3F_6OC(CF_3)_2CN]^+$

332 - $[C_3F_7OCF(CF_3)COF]^+$

259 - $[CF_2OC(CF_3)_2C(NH)NH_2]^+$

242 - $[CF_2OC(CF_3)_2CN]^+$

176 - $[C(CF_3)_2CN]^+$

43 - $[C(NH)NH_2]^+$

TABLE 6

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (MW 925)

m/e	%	m/e	%	m/e	%	m/e	%
69	4.0	199	5.2	423	3.2	640	4.7
108	2.1	200	3.2	424	100.0	641	2.1
122	3.0	212	4.1	425	41.2	740	2.9
151	3.6	225	2.6	426	8.7	809	2.8
153	2.4	262	2.3	458	3.2	856	2.0
160	2.5	268	2.2	483	2.2	906	11.7
169	5.1	270	2.3	554	8.7	907	5.2
183	3.6	297	2.1	555	9.8	924	20.7
185	4.0	306	7.5	556	3.6	925	47.8 M+
192	2.4	317	3.5	574	7.9	926	26.2
198	2.1	422	2.0	575	5.1	927	8.6

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

925 - M^+

906 - $[M - F]^+$

809 - $[M - C_2F_5]^+$

740 - $[M - C_3F_7O]^+$

m/e

640 - $[M - C_3F_7OCF(CF_3)]^+$

574 - $[M - C_3F_7OCF(CF_3)CF_2O]^+$

424 - $[M - C_3F_7OCF(CF_3)CF_2OC(CF_3)_2]^+$

398 - $[M - C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]^+$

TABLE 7

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(O)OCH_3$ (MW 726)

m/e	%	m/e	%	m/e	%	m/e	%
31	31.8	93	6.4	179	11.2	336	7.1
33	7.9	97	38.8	181	44.1	347	13.0
34	3.0	100	54.6	182	5.8	348	3.1
43	4.3	101	5.0	197	7.7	373	9.2
44	9.9	109	5.0	199	3.8	375	70.0
45	3.5	112	5.2	209	67.9	376	26.2
47	18.2	113	3.7	210	11.5	377	6.3
50	17.3	119	47.6	211	3.0	435	3.1
51	4.1	120	4.4	213	3.4	441	7.8
58	4.4	128	7.2	219	3.0	501	23.5
59	100.0	131	53.4	225	6.9	502	5.8
60	34.0	132	8.2	231	3.4	541	23.1
61	10.8	147	61.1	247	6.3	542	5.9
62	3.7	148	8.9	263	3.6	607	5.3
65	4.4	150	66.2	266	3.4	648	4.4
66	9.7	151	10.8	275	51.5	657	12.5
69	74.2	159	28.2	276	9.6	658	3.8
70	9.1	160	3.2	285	7.2	679	3.4
71	4.3	162	3.4	297	12.2	707	18.8
78	11.9	169	77.5	313	7.1	708	6.2
81	71.4	170	15.9	316	5.0		
82	11.8	178	21.4	335	40.1		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e
707 - $[M - F]^+$

657 - $[M - CF_3]^+$

541 - $[[CF(CF_3)CF_2O]_2C(CF_3)_2CO_2CH_3]^+$

375 - $[CF(CF_3)CF_2OC(CF_3)_2CO_2CH_3]^+$

275 - $[CF_2OC(CF_3)_2CO_2CH_3]^+$

m/e
209 - $[C(CF_3)_2CO_2CH_3]^+$

169 - $[C_3F_7]^+$

81 - $[C_2F_3]^+$

59 - $[CO_2CH_3]^+$

TABLE 8

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2H$ (MW 668)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	34.7	97	39.8	151	89.6	267	42.3	435	11.8
32	10.8	98	3.1	152	26.1	268	5.9	483	39.4
47	24.2	100	53.8	156	3.0	275	3.1	484	8.0
50	25.7	101	13.1	169	98.6	279	3.1	501	6.2
51	36.3	105	5.5	170	32.4	285	9.3	514	6.1
63	10.5	106	3.8	181	6.4	295	10.7	533	5.4
66	9.6	112	3.8	200	3.3	298	3.6	549	12.1
69	100.0	113	18.3	207	3.0	313	4.5	550	3.0
70	17.1	119	61.1	208	3.7	317	88.9	580	4.9
71	7.1	120	5.9	209	9.0	318	32.4	583	13.5
72	49.2	128	5.4	216	3.2	319	5.9	584	3.5
75	3.5	129	10.6	217	76.0	335	53.7	599	13.6
78	11.8	131	33.9	218	18.7	336	12.2	600	3.2
79	7.3	132	11.6	219	20.1	367	15.0	649	13.0
81	11.0	147	52.6	235	3.0	383	48.0	650	3.0
82	14.2	148	7.4	245	6.5	384	9.5		
93	6.9	150	46.2	263	11.7	433	10.3		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e
649 - $[M - F]^+$

483 - $[[CF(CF_3)CF_2O]_2C(CF_3)_2H]^+$

383 - $[CF_2OCF(CF_3)CF_2OC(CF_3)_2H]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

m/e
317 - $[CF(CF_3)CF_2OC(CF_3)_2H]^+$

217 - $[CF_2OC(CF_3)_2H]^+$

169 - $[C_3F_7]^+$

151 - $[C(CF_3)_2H]^+$

TABLE 9

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(O)NH_2$ (MW 711)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	20.5	96	15.8	170	18.6	297	27.1	501	6.1
42	4.8	97	38.5	176	4.4	298	6.7	526	29.2
43	23.0	100	54.5	177	4.0	310	8.7	527	7.6
44	100.0	101	8.6	178	5.8	313	5.5	529	3.5
45	17.5	112	5.6	194	57.4	316	4.8	549	12.3
46	6.8	113	10.6	195	10.1	317	79.4	530	4.0
47	14.3	116	11.3	210	6.4	318	18.8	592	17.3
50	15.0	119	62.0	217	78.8	319	3.2	593	4.2
51	26.7	120	4.0	218	13.1	320	9.0	599	12.8
63	3.9	128	6.9	219	3.2	335	60.8	629	4.8
65	6.5	129	6.0	235	3.4	336	8.1	242	14.8
66	27.3	131	19.1	245	4.2	359	3.2	643	4.4
69	77.9	132	6.0	247	4.2	360	65.7	648	6.0
70	14.4	146	14.5	260	45.9	361	16.4	649	9.6
71	5.0	147	61.1	261	6.9	362	3.0	692	29.7
72	11.8	148	5.5	262	4.3	363	8.3	693	9.4
73	3.8	150	51.0	263	3.9	383	37.9	712	15.1
78	13.1	151	78.6	267	19.6	384	7.6	713	4.1
79	3.3	152	14.9	275	3.1	426	4.9		
81	8.9	159	9.4	285	7.0	463	4.3		
82	7.9	166	9.1	291	10.5	483	24.3		
93	5.8	169	89.6	295	6.9	484	6.2		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

712 - $[M + 1]^+$

692 - $[M - F]^+$

526 - $[(CF(CF_3)CF_2O)_2C(CF_3)_2CONH_2]^+$

360 - $[OCF(CF_3)CF_2OC(CF_3)_2CONH_2]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

m/e

317 - $[CF(CF_3)CF_2OC(CF_3)_2H]^+$

217 - $[CF_2OC(CF_3)_2H]^+$

194 - $[C(CF_3)_2CONH_2]^+$

151 - $[C(CF_3)_2H]^+$

44 - $[CONH_2]^+$

TABLE 10

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN$ (MW 693)

m/e	%	m/e	%	m/e	%	m/e	%
31	30.6	107	9.4	217	4.7	392	7.8
47	22.5	119	64.0	219	7.0	408	44.3
50	21.5	120	5.0	235	3.6	409	9.0
54	11.9	128	5.1	242	72.1	458	6.2
63	3.1	131	19.5	243	14.5	501	3.9
66	10.5	138	3.4	276	4.2	508	36.3
69	100.0	147	64.3	285	9.2	509	8.7
70	18.0	148	9.6	288	3.3	574	15.9
76	6.7	150	56.9	292	5.8	575	3.8
78	14.8	151	10.3	297	5.3	605	3.7
81	8.9	157	9.6	313	4.0	608	4.3
88	8.8	164	10.0	314	4.1	624	14.2
92	9.2	169	97.9	317	6.9	625	3.8
93	4.6	170	23.1	335	60.5	674	14.2
97	57.3	176	78.8	336	10.1	675	3.6
98	4.2	177	13.6	342	66.4	693	16.0 M^+
100	59.2	192	64.0	343	16.5	694	4.5
101	4.6	193	8.8	345	4.7		
104	4.7	197	3.0	364	5.4		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e
693 - M^+

674 - $[M - F]^+$

508 - $[[CF(CF_3)CF_2O]_2C(CF_3)_2CN]^+$

408 - $[CF_2OCF(CF_3)CF_2OC(CF_3)_2CN]^+$

m/e
342 - $[CF(CF_3)CF_2OC(CF_3)_2CN]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

242 - $[CF_2OC(CF_3)_2CN]^+$

176 - $[C(CF_3)_2CN]^+$

TABLE 11

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(=NH)NH_2$ (MW 710)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	24.3	100	51.2	174	6.3	292	5.6	498	9.3
42	32.4	101	5.3	176	50.8	297	8.6	508	16.3
43	100.0	116	11.1	177	12.1	309	10.8	571	8.7
44	28.2	119	48.5	190	5.2	313	6.5	574	8.2
46	8.6	128	6.4	192	32.1	317	37.1	591	24.8
47	20.2	131	14.0	193	33.0	318	5.5	592	6.8
48	4.0	138	6.2	194	7.8	332	6.0	621	6.2
50	18.8	146	12.3	197	5.6	335	39.4	624	7.4
51	18.2	147	47.7	213	5.2	336	7.1	641	9.2
66	57.6	148	6.4	217	27.3	339	10.8	671	10.2
67	6.7	150	51.0	221	8.7	342	43.0	674	7.0
69	82.2	151	43.2	239	13.1	343	7.3	691	43.9
70	12.5	153	13.7	242	35.6	359	12.1	692	11.8
78	11.9	157	6.6	243	5.2	383	12.4	693	9.5
81	9.2	158	9.0	259	28.5	405	20.2	710	13.7 M^+
91	5.9	166	16.4	267	7.7	408	17.3	711	21.5
93	8.7	169	75.2	285	7.9	425	29.7	712	6.7
96	12.6	170	15.2	289	21.8	426	7.4		
97	42.3	173	18.7	290	10.3	483	7.4		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

710 - M^+

691 - $[M - F]^+$

425 - $[M - C_3F_7OCF(CF_3)]^+$

342 - $[CF(CF_3)CF_2OC(CF_3)_2CN]^+$

m/e

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

193 - $[C(CF_3)_2C(=NH)NH_2]^+$

176 - $[C(CF_3)_2CN]^+$

43 - $[C(=NH)NH_2]^+$

TABLE 12

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][NP(C_6H_5)_2]_2$ (MW 1091)

m/e	%	m/e	%	m/e	%	m/e	%
31	5.2	152	5.2	268	3.2	426	13.4
47	4.7	153	2.1	270	3.2	427	2.8
50	5.2	154	2.0	275	2.4	442	3.7
51	4.2	160	10.9	276	2.2	516	2.0
69	21.8	165	2.4	296	2.6	554	11.7
77	8.5	169	20.1	306	9.7	555	12.9
78	3.6	170	2.8	307	2.4	556	5.3
96	2.3	183	15.2	312	2.5	574	14.3
97	6.4	184	4.1	316	2.3	575	10.5
100	7.2	185	5.8	326	2.0	576	3.6
107	3.3	191	3.6	333	2.4	640	4.9
108	4.0	198	6.1	335	4.1	740	8.4
119	10.2	199	11.1	397	2.8	741	3.5
122	8.4	200	6.5	420	2.9	806	6.5
127	2.5	201	2.8	421	2.3	807	2.5
131	3.8	211	5.4	422	8.6	906	2.4
147	3.9	212	3.7	423	7.0	972	11.4
150	6.8	225	4.7	424	100.0	973	5.1
151	4.2	262	3.1	425	38.6	1022	3.7

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e
1022 - $[M - CF_3]^+$

972 - $[M - C_2F_5]^+$

574 - $[M - C_3F_7[OCF(CF_3)CF_2]_2O]^+$

424 - $[M - C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2]^+$

m/e
199 - $[NP(C_6H_5)_2]^+$

183 - $[P(C_6H_4)_2]^+$

169 - $[C_3F_7]^+$

TABLE 13

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)N=C(NH_2)C(CF_3)_2OCF_2CF(CF_3)OC_3F_7$ (MW 1071)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	10.1	93	3.2	170	3.5	285	5.6	570	100.0
42	6.2	96	3.4	173	4.0	289	3.0	571	24.0
43	25.4	97	18.5	176	9.3	314	9.1	572	5.3
44	3.9	100	18.0	177	5.6	317	3.1	693	4.6
47	10.7	119	18.1	181	3.0	332	4.2	718	4.0
50	9.9	131	6.7	191	5.8	335	4.4	720	6.5
51	5.0	138	4.9	192	6.3	338	3.7	786	6.9
53	3.2	141	4.0	193	20.7	339	4.6	886	3.1
66	9.0	147	17.0	200	3.5	342	4.7	952	10.1
68	18.0	150	14.9	217	4.8	359	7.2	1001	11.1
69	73.0	151	7.7	219	8.7	364	3.1	1002	3.0
70	4.6	157	3.1	239	12.0	505	9.5	1052	22.9
78	4.2	158	7.5	242	6.0	525	20.4	1053	7.4
81	3.4	166	11.9	259	9.2	526	4.1		
91	5.2	169	39.5	284	3.0	550	3.0		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1052 - $[M - F]^+$

1001 - $[M - CF_3H]^+$

952 - $[M - C_2F_5]^+$

570 - $[M - C_3F_7OCF(CF_3)CF_2OC(CF_3)_2]^+$

525 - $[M - F - C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]^+$

193 - $[OC(CF_3)_2CNH]^+$ or $[C(CF_3)_2C(NH_2)NH]^+$

TABLE 14

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF 1,3-DIPHOSPHATETRAAZACYCLOOCTATETRAENE $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ (MW 1452)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	6.5	119	10.5	184	2.4	212	7.2	426	3.6
47	4.2	122	4.1	185	4.6	223	2.0	442	2.7
50	4.4	131	2.8	191	7.0	225	4.2	574	2.9
51	2.1	147	2.9	192	5.5	262	2.4	581	5.1
69	23.1	150	4.1	198	3.6	270	2.4	582	2.0
77	5.8	152	4.0	199	10.2	306	6.9	601	4.0
78	3.1	160	6.2	200	3.8	422	3.1	941	8.3
97	4.7	162	3.1	201	11.5	423	3.2	951	100.0
100	6.9	169	10.7	202	3.2	424	32.2	952	13.9
108	3.0	183	7.9	211	7.8	425	12.6	969	3.1

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

951 - $[M - C_3F_7OCF(CF_3)CF_2OC(CF_3)_2]^+$

581 - $[CF_2OCF(CF_3)CF_2OC(CF_3)_2P(C_6H_5)_2N]^+$

574 - $[(C_6H_5)_2PNP(C_6H_5)_2NC(CF_3)_2NC]^+$

424 - $[(C_6H_5)_2PNP(C_6H_5)_2NCN]^+$

199 - $[(C_6H_5)_2PN]^+$

169 - $[C_3F_7]^+$

TABLE 15

SUMMARY OF INTERACTIONS OF $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$ and $(C_6H_5)_2PCl_3$

	$R_fC(=NH)NH_2$[a]		$(C_6H_5)_2PCl_3$		$(C_2H_5)_3N$		Solvents[b]	Rxn Cond		Products						
								Temp	Time	wt	GC Area%[c]					
	g	mmol	g	mmol	g	mmol	(mL)	°C	h	g	I[d]	II[d]	III[d]	VI[e]	V[f]	VI[d]
1.	0.97	1.78	1.07	3.67	0.60	5.94	C_6H_6(10) F-113(10)	50	67	1.49	56	12	0.6	9	12	1
2.	0.43	0.79	0.46	1.58	0.32	3.17	CH_3CN(5) F-113(5)	70	92	0.56	30	29	0	2	17	6
3.	0.40	0.74	0.22	0.76	0.31	3.07	C_6H_6(5) F-113(5)	50	92	0.63	46	0	10	9	6	26

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a) $R_f = C_3F_7OCF(CF_3)CF_2OC(CF_3)_2$
b) F-113 : Freon-113
c) GC Area% not corrected for different detector responses.
d) not identified.
e) desired product, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$
f) diphospha-s-triazine, $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$

TABLE 16

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF 1,5-DIPHOSPHATETRAAZACYCLOOCTATETRAENE $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ (MW 1452)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	11.7	100	12.3	169	25.5	219	2.8	425	10.5
32	11.6	107	4.4	170	2.2	223	6.7	426	2.2
47	11.4	108	4.5	180	4.3	224	3.9	581	6.7
50	8.7	119	24.4	183	19.8	225	43.5	582	2.6
51	5.7	122	4.1	184	3.8	226	11.1	601	7.9
69	63.8	127	5.1	185	15.5	230	2.7	602	3.1
73	2.6	131	3.0	186	2.0	267	2.6	951	100.0
77	15.2	147	5.0	198	2.7	285	2.2	952	48.3
78	3.6	150	5.7	199	2.5	300	3.4	953	11.9
81	2.0	152	2.4	201	2.3	306	3.2		
96	2.3	154	3.4	202	3.1	422	2.4		
97	8.0	165	4.0	204	2.5	424	40.8		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

951 - $[M - C_3F_7OCF(CF_3)CF_2OC(CF_3)_2]^+$

424 - $[(C_6H_5)_2PNCNP(C_6H_5)_2N]^+$

225 - $[CNP(C_6H_5)_2N]^+$

169 - $[C_3F_7]^+$

TABLE 17

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)CO_2CH_3$ (MW 1174)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	19.2	70	4.9	148	6.4	297	15.6	501	12.9
33	4.6	78	6.2	150	60.0	313	10.7	557	6.4
43	4.6	81	39.1	151	8.4	316	6.5	657	21.9
44	5.5	82	3.3	159	64.8	323	4.2	658	5.7
45	13.8	97	32.9	160	10.2	325	68.2	667	3.3
47	15.5	100	41.2	169	87.9	326	16.0	723	6.9
50	13.1	101	4.1	170	14.0	327	3.4	823	11.4
58	7.0	109	9.6	181	19.1	335	42.8	889	7.2
59	100.0	119	49.7	199	7.2	336	8.0	989	6.8
60	13.0	120	3.6	225	24.8	347	7.6	992	11.4
61	4.0	128	12.5	226	3.5	391	8.3	993	3.1
65	4.4	131	70.6	247	5.9	479	3.2	999	5.9
66	7.2	132	9.6	263	5.1	491	35.6	1055	4.8
69	79.4	147	62.4	285	9.9	492	8.5		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1055 - $[M - C_2F_5]^+$

999 - $[C_3F_7[OCF(CF_3)CF_2]_5]^+$

989 - $[M - C_3F_7O]^+$

823 - $[(CF(CF_3)CF_2O)_4CF(CF_3)CO_2CH_3]^+$

657 - $[(CF(CF_3)CF_2O)_3CF(CF_3)CO_2CH_3]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

325 - $[CF(CF_3)CF_2OCF(CF_3)CO_2CH_3]^+$

159 - $[CF(CF_3)CO_2CH_3]^+$

59 - $[CO_2CH_3]^+$

TABLE 18

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_4OCF(CF_3)CO_2CH_3$ (MW 1008)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
15	30.5	69	66.0	150	49.8	297	11.9	557	4.2
29	4.0	70	3.3	151	4.0	313	4.6	657	14.2
30	2.3	78	3.9	159	51.2	316	4.0	658	3.0
31	10.5	81	25.8	160	5.6	325	69.2	723	4.6
33	3.2	97	18.3	169	91.2	326	10.5	823	4.2
43	2.9	100	21.3	170	10.7	327	2.2	826	5.0
44	3.2	109	5.3	181	12.5	335	23.1	833	3.5
47	10.8	119	24.8	199	5.9	336	4.4	889	2.7
50	8.0	128	8.8	225	16.7	347	5.1	939	12.1
59	100.0	131	66.7	226	2.0	391	4.8	940	3.4
60	9.5	132	5.6	247	3.3	491	21.4	989	12.1
61	2.6	147	43.3	263	3.0	492	5.1	990	3.6
66	4.2	148	3.7	285	4.1	501	7.0		

Peaks having intensities lower than 2% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

m/e

989 - $[M - F]^+$

939 - $[M - CF_3]^+$

657 - $[(CF(CF_3)CF_2O)_3CF(CF_3)CO_2CH_3]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

325 - $[CF(CF_3)CF_2OCF(CF_3)CO_2CH_3]^+$

159 - $[CF(CF_3)CO_2CH_3]^+$

59 - $[CO_2CH_3]^+$

TABLE 19

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_5OCFH(CF_3)$ (MW 1116)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
28	8.6	82	6.0	159	4.0	268	10.4	463	14.1
29	6.6	93	3.1	167	48.6	275	5.3	464	3.2
31	16.7	97	73.2	168	7.1	285	38.7	479	5.2
47	17.7	98	8.7	169	100.0	286	5.8	499	11.9
50	15.3	100	47.9	170	22.5	297	9.1	501	22.6
51	19.8	101	76.5	181	6.5	313	28.9	502	5.6
59	7.4	102	8.0	185	6.2	314	4.8	599	4.9
62	3.0	109	4.4	197	13.2	316	3.9	645	3.9
64	6.0	119	66.2	213	6.2	325	4.0	665	10.5
65	5.7	120	6.5	217	7.0	333	22.2	667	8.0
66	9.1	128	8.5	219	3.8	334	5.2	811	4.0
69	89.1	131	51.0	225	3.7	335	55.9	831	7.7
70	7.0	132	5.5	235	7.0	336	13.3	833	11.2
78	8.8	147	88.9	245	6.3	363	5.4	977	3.6
79	15.6	148	13.0	247	5.4	413	10.7	997	6.4
80	3.3	150	50.1	263	4.4	433	21.8	999	10.8
81	23.2	151	7.5	267	61.6	434	4.1	1000	3.1

Peaks having intensities lower than 3% of the base peak and lower than m/e 28 are not reported.

Significant Ions in Support of Structure and Composition

m/e

999 - $[M - OCFHCF_3]^+$

501 - $[C_3F_7(OCF(CF_3)CF_2)_2]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

333 - $[(OCF(CF_3)CF_2)_2OCFHCF_3]^+$

267 - $[CF(CF_3)CF_2OCFHCF_3]^+$

167 - $[CF_2OCFHCF_3]^+$

101 - $[CFHCF_3]^+$

TABLE 20

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_5OCF(CF_3)C(O)C_6H_4Br$ (MW 1298)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
31	9.4	97	13.0	158	4.2	256	3.0	515	4.3
47	11.0	100	18.4	169	70.4	257	17.9	517	4.1
50	24.6	104	17.1	170	6.2	283	5.3	615	8.6
51	4.6	105	6.3	176	5.5	285	8.5	617	8.9
66	5.1	119	19.9	183	95.1	313	5.4	681	4.0
69	64.2	123	5.0	184	18.6	335	19.6	683	4.3
74	5.9	128	3.4	185	100.0	349	5.2	781	6.3
75	19.6	131	10.3	186	20.9	351	5.2	783	6.2
76	23.6	147	22.1	195	3.0	413	3.2	847	5.2
77	4.3	150	24.2	202	3.9	449	18.1	849	4.7
78	3.6	151	3.9	204	8.0	450	4.4	947	4.5
81	6.1	155	23.6	205	6.6	451	16.8	949	3.9
82	3.3	156	4.9	207	5.5	452	4.0	1013	5.6
95	3.9	157	21.9	255	17.8	501	4.8	1015	5.6

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

947 - $[(CF(CF_3)CF_2O)_4CF(CF_3)C(O)C_6H_4Br]^+$

781 - $[(CF(CF_3)CF_2O)_3CF(CF_3)C(O)C_6H_4Br]^+$

615 - $[(CF(CF_3)CF_2O)_2CF(CF_3)C(O)C_6H_4Br]^+$

449 - $[CF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

283 - $[CF(CF_3)C(O)C_6H_4Br]^+$

183 - $[C(O)C_6H_4Br]^+$

155 - $[C_6H_4Br]^+$

TABLE 21

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_4OCF(CF_3)C(O)C_6H_4Br$ (MW 1132)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
20	6.4	81	4.7	155	26.6	207	7.9	452	2.8
31	14.1	82	2.4	156	4.6	233	13.1	515	2.0
47	14.9	97	12.5	157	27.2	235	13.6	517	2.0
50	21.7	100	21.4	158	2.0	255	15.8	615	8.4
51	3.6	101	2.5	169	68.5	257	13.6	617	7.5
66	5.7	104	14.9	170	4.6	283	5.2	681	2.6
69	70.1	105	3.7	176	2.5	285	6.1	683	2.7
70	2.3	119	24.0	182	2.0	313	2.5	781	3.9
74	6.0	123	2.8	183	100.0	335	13.2	783	3.0
75	21.0	126	4.3	184	20.8	349	4.2	847	2.5
76	23.4	131	9.1	185	96.6	351	4.6	849	2.8
77	3.1	147	23.7	186	16.9	449	13.0	1015	2.0
79	2.0	150	21.2	204	6.3	450	2.5	1063	4.1
80	3.0	151	5.5	205	9.1	451	14.8	1065	4.5

Peaks having intensities lower than 2% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1063 - $[M - CF_3]^+$

781 - $[(CF(CF_3)CF_2O)_3CF(CF_3)C(O)C_6H_4Br]^+$

615 - $[(CF(CF_3)CF_2O)_2CF(CF_3)C(O)C_6H_4Br]^+$

449 - $[CF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

283 - $[CF(CF_3)C(O)C_6H_4Br]^+$

183 - $[C(O)C_6H_4Br]^+$

155 - $[C_6H_4Br]^+$

TABLE 22

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br$ (MW 1320)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
47	16.6	126	45.6	208	31.0	304	12.2	474	7.7
50	23.4	127	15.1	223	10.8	305	72.2	501	14.2
51	5.7	128	6.6	224	6.3	306	15.6	637	6.7
66	8.2	131	16.1	225	13.1	307	67.8	639	7.9
69	81.8	145	18.5	226	21.4	308	16.1	667	5.9
70	5.2	147	60.5	227	7.8	313	10.6	703	17.7
74	6.1	148	5.6	235	5.4	335	51.5	705	13.7
75	13.6	150	45.9	236	6.7	336	7.1	803	6.1
76	9.7	151	5.3	238	6.3	371	5.1	851	5.2
78	5.6	157	12.2	245	15.8	372	6.3	869	17.6
79	5.6	169	99.6	255	23.5	373	6.9	871	12.5
80	5.9	170	16.5	256	5.9	401	6.6	872	5.0
81	12.0	176	11.0	257	23.8	403	6.4	969	6.5
82	5.4	195	16.3	258	5.1	405	5.3	971	6.2
97	21.3	204	10.4	275	5.2	453	5.6	1015	6.4
100	32.6	205	100.0	285	19.8	471	23.8	1017	6.2
107	8.6	206	32.2	287	12.3	472	7.7	1035	12.8
119	43.9	207	96.6	302	10.4	473	24.2	1037	13.4
125	19.7								

Peaks having intensities lower than 5% of the base peak and lower than m/e 47 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1035 - $[M - C_3F_7OCF(CF_3)]^+$

969 - $[M - F(CF(CF_3)CF_2O)_2]^+$

703 - $[CF_2[OCF(CF_3)CF_2]_3C_6H_4Br]^+$

471 - $[CF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Br]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

305 - $[CF(CF_3)CF_2C_6H_4Br]^+$

m/e

205 - $[CF_2C_6H_4Br]^+$

169 - $[C_3F_7]^+$

126 - $[CF_2C_6H_4]^+$

TABLE 23

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_5C_6H_4Br$ (MW 1154)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
20	2.7	107	3.7	208	16.7	305	33.5	501	5.3
28	3.2	119	19.0	223	3.4	306	9.2	637	3.5
31	7.8	125	7.6	224	2.4	307	35.9	639	3.9
47	6.6	126	22.7	225	5.3	308	7.7	703	10.1
50	8.9	131	6.5	226	10.2	313	2.6	704	2.3
51	2.6	145	8.8	235	2.4	335	20.0	705	7.9
66	4.1	147	25.2	236	3.2	336	2.8	706	2.7
69	48.1	150	15.6	238	2.6	371	2.2	803	2.7
70	2.2	157	4.6	245	8.0	372	3.4	805	2.0
74	2.3	169	66.7	255	13.1	373	3.1	849	2.5
75	6.7	170	5.7	256	2.3	401	2.8	851	2.3
76	4.4	176	5.0	257	12.6	403	3.1	869	9.0
78	2.2	195	6.6	285	7.5	453	2.2	870	2.3
80	2.4	204	4.0	286	2.0	471	17.0	871	7.2
81	4.3	205	100.0	287	6.6	472	4.0	872	2.1
82	2.9	206	20.9	302	4.3	473	16.2	1035	4.7
97	10.6	207	99.8	304	5.6	474	3.4	1037	4.4
100	15.1								

Peaks having intensities lower than 2% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1035 - $[M - C_2F_5]^+$

869 - $[M - C_3F_7OCF(CF_3)]^+$

703 - $[CF_2[OCF(CF_3)CF_2]_3C_6H_4Br]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

305 - $[CF(CF_3)CF_2C_6H_4Br]^+$

m/e

205 - $[CF_2C_6H_4Br]^+$

169 - $[C_3F_7]^+$

126 - $[CF_2C_6H_4]^+$

TABLE 24

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_4F_9[OCF(CF_3)CF_2]_5C_6H_4Br$ (MW 1204)

m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
20	3.6	125	7.1	206	17.6	289	3.6	474	3.9
28	6.5	126	20.3	207	95.7	302	4.5	501	2.7
31	7.1	127	5.9	208	16.4	304	5.2	551	2.1
47	7.5	128	2.4	219	24.9	305	34.3	637	4.3
50	10.2	131	14.7	220	2.3	306	9.1	639	3.7
51	2.6	145	9.7	223	3.2	307	30.7	703	7.0
66	4.8	147	24.5	224	2.5	308	9.0	704	2.0
69	53.6	150	18.2	225	5.7	313	3.2	705	8.2
70	2.8	157	5.4	226	11.1	335	11.5	805	2.0
74	2.6	169	60.8	227	2.8	371	2.2	849	2.7
75	6.7	170	5.7	235	2.2	372	3.0	851	2.3
76	4.8	176	4.5	236	2.6	373	3.7	869	7.6
78	2.0	181	2.5	238	3.1	385	14.1	870	2.2
80	2.7	187	18.5	245	7.6	401	2.8	871	8.3
81	5.1	188	2.7	255	11.3	403	2.9	872	2.0
82	2.8	189	15.9	256	2.1	451	3.1	969	3.3
97	10.3	190	2.2	257	12.2	453	2.2	971	3.5
100	14.0	195	7.2	285	9.4	471	16.7	1017	2.3
107	4.8	197	8.9	286	2.9	472	4.4	1035	3.7
108	3.0	204	3.5	287	8.0	473	16.6	1037	2.9
119	17.5	205	100.0	288	2.1				

Peaks having intensities lower than 2% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1035 - $[M - C_3F_7]^+$

869 - $[M - C_4F_9OCF(CF_3)]^+$

703 - $[CF_2[OCF(CF_3)CF_2]_3C_6H_4Br]^+$

471 - $[CF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Br]^+$

385 - $[C_4F_9OCF(CF_3)CF_2]^+$

m/e

305 - $[CF(CF_3)CF_2C_6H_4Br]^+$

219 - $[C_4F_9]^+$

205 - $[CF_2C_6H_4Br]^+$

126 - $[CF_2C_6H_4]^+$

TABLE 25

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$ (MW 1258)

m/e	%	m/e	%	m/e	%	m/e	%
31	25.4	101	5.0	163	3.2	245	5.4
32	10.2	111	4.3	169	94.1	263	3.2
39	3.9	113	3.2	170	10.1	285	9.0
44	4.1	114	7.3	173	4.2	309	3.8
47	27.7	119	51.2	174	5.7	313	22.5
50	24.3	120	3.6	181	3.6	335	26.3
51	5.5	121	11.0	185	3.3	336	3.1
62	3.1	123	4.9	192	4.6	339	3.3
64	3.4	125	3.8	193	12.3	379	4.2
65	3.3	128	5.2	194	3.3	409	6.6
66	14.9	131	14.7	195	5.5	479	3.4
69	100.0	142	6.7	213	7.8	501	6.3
70	5.3	143	87.8	214	14.3	621	7.8
75	5.9	144	16.2	223	23.6	641	4.9
78	7.6	145	19.5	224	12.7	787	7.0
81	7.3	147	35.6	225	3.1	807	3.1
93	5.1	148	4.1	235	3.9	953	9.4
95	5.6	150	34.9	242	7.4		
97	29.8	151	9.7	243	22.9		
100	30.4	161	7.8	244	4.5		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

953 - $[M - C_3F_7OCF(CF_3) - HF]^+$

807 - $[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)]^+$

641 - $[CF_2(OCF(CF_3)CF_2)_3C_6H_4OH]^+$

409 - $[CF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH]^+$

335 - $[C_3F_7OCF(CF_3)CF_2]^+$

243 - $[CF(CF_3)CF_2C_6H_4OH]^+$

143 - $[CF_2C_6H_4OH]^+$

69 - $[CF_3]^+$

TABLE 26

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Cl$ (MW 1276)

m/e	%	m/e	%	m/e	%	m/e	%
31	6.2	125	3.7	169	51.1	263	28.8
47	7.0	126	7.8	170	5.0	264	3.3
50	7.3	131	5.3	195	3.0	335	16.8
66	3.6	145	4.4	211	11.3	427	16.0
69	42.3	147	24.5	213	5.7	428	3.5
75	5.7	150	14.7	241	7.1	429	7.6
97	8.0	161	100.0	245	3.5	501	4.3
100	12.2	162	19.3	258	3.7	659	5.3
111	3.9	163	44.4	261	39.6	825	4.4
119	14.8	164	8.0	262	9.1	991	3.6

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

991 - $[M - C_3F_7OCF(CF_3)]^+$

825 - $[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)]^+$

659 - $[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)]^+$

427 - $[CF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Cl]^+$

261 - $[CF(CF_3)CF_2C_6H_4Cl]^+$

161 - $[CF_2C_6H_4Cl]^+$

TABLE 27

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (MW 1490)

m/e	%	m/e	%	m/e	%	m/e	%
20	18.2	96	17.0	168	11.2	252	16.0
28	23.4	97	26.7	169	91.2	255	8.3
31	31.2	100	31.9	170	18.5	281	6.5
38	7.5	107	7.3	178	7.8	285	8.6
39	22.5	112	6.5	181	8.8	297	7.7
47	34.0	114	9.3	187	43.3	301	15.2
50	30.9	119	45.1	188	17.6	313	19.3
51	23.7	126	10.0	189	11.0	335	22.2
62	6.1	127	11.5	203	9.0	373	8.0
63	12.1	128	8.7	205	11.4	374	6.2
64	7.6	131	19.0	213	8.8	375	91.0
65	29.1	139	9.7	215	16.1	376	31.3
66	24.1	140	17.0	217	8.9	377	10.5
67	5.0	141	8.5	218	5.6	393	9.7
69	100.0	142	10.3	219	15.8	475	14.5
70	7.8	143	26.8	223	6.0	476	7.2
74	5.4	144	6.8	227	7.7	501	5.9
75	9.6	145	20.2	232	8.6	541	10.1
76	10.8	147	36.0	233	15.8	641	6.7
77	61.0	150	42.3	234	5.1	707	18.0
78	18.7	151	11.9	237	11.3	708	6.6
81	10.4	152	10.5	245	7.0	873	22.6
92	5.0	153	8.1	249	6.8	874	9.0
93	21.2	154	8.5	250	5.3	1038	28.4
94	31.5	156	7.4	251	6.5	1039	10.8
95	9.0						

Peaks having intensities lower than 5% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

m/e

1039 - $[CF_2[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2]^+$
873 - $[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)]^+$
707 - $[CF_2[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2]^+$
541 - $[CF_2OCF(CF_3)CF_2C_6H_4OP(O)(OC_6H_5)_2]^+$
475 - $[CF(CF_3)CF_2C_6H_4OP(O)(OC_6H_5)_2]^+$
375 - $[CF_2C_6H_4OP(O)(OC_6H_5)_2]^+$
233 - $[P(O)(OC_6H_5)_2]^+$

TABLE 28

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK

$[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (MW 1253)

m/e	%	m/e	%	m/e	%	m/e	%
31	14.8	107	6.8	180	5.8	227	3.5
47	12.2	108	6.7	183	11.6	230	2.2
50	15.9	119	16.0	184	3.1	242	2.3
51	8.4	122	4.7	185	8.0	243	3.6
66	3.3	127	7.4	198	2.8	325	7.2
69	48.5	128	2.1	201	2.5	375	5.7
70	2.3	131	3.4	202	2.3	541	3.7
77	15.6	147	6.8	203	3.0	883	2.1
78	5.5	150	7.9	204	6.2	968	8.0
81	2.6	152	3.4	211	3.6	969	2.3
92	2.6	154	4.2	219	2.2	1134	4.3
93	2.4	165	5.8	223	8.7	1234	10.1
96	2.9	169	25.3	224	5.5	1235	3.6
97	9.6	170	2.4	225	100.0	1253	11.7M^+
100	16.9	176	3.5	226	27.5	1254	2.5

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure Nd Composition

m/e

1253 - M^+

1234 - $[M - F]^+$

1134 - $[M - C_2F_5]^+$

968 - $[M - C_3F_7OCF(CF_3)]^+$

541 - $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN_2]^+$

225 - $[(C_6H_5)_2PNCN]^+$

169 - $[C_3F_7]^+$

TABLE 29

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2H$ (MW 502)

m/e	%	m/e	%	m/e	%	m/e	%
31	70.2	98	8.6	167	6.5	275	10.0
32	26.9	100	95.0	169	100.0	279	2.7
44	9.2	101	30.3	170	48.2	285	45.2
48	3.2	105	24.6	171	2.7	286	5.9
50	55.0	106	3.2	179	6.3	295	41.6
51	79.7	109	4.4	181	5.5	296	7.3
52	4.3	112	10.8	195	2.0	297	11.2
62	9.6	113	61.7	197	12.4	298	11.5
63	24.9	114	6.3	193	2.6	299	2.2
64	5.7	116	2.1	204	2.0	313	12.6
65	2.5	119	82.5	208	70.8	314	3.0
66	13.0	120	9.5	216	8.1	315	13.5
67	5.5	128	10.5	217	89.5	317	77.6
69	94.1	129	31.7	218	44.6	318	49.0
70	36.4	130	2.8	219	10.3	319	9.7
71	4.3	131	46.0	225	3.7	335	70.0
72	56.2	132	40.5	229	4.4	336	14.7
74	4.4	133	5.5	231	2.0	337	2.5
75	4.9	145	2.0	232	2.9	383	53.3
78	25.1	147	78.7	235	2.1	384	10.0
79	19.4	148	14.7	245	39.3	414	15.1
81	23.1	149	3.7	246	5.9	415	2.9
82	53.1	150	70.3	247	5.4	433	60.8
83	3.9	151	91.7	248	6.8	434	15.3
85	3.7	152	54.1	262	5.2	435	3.7
91	2.3	153	2.9	263	5.8	463	5.7
93	13.1	159	4.4	266	8.0	483	97.5
94	3.4	163	3.0	267	62.9	484	38.8
97	68.6	166	4.3	268	11.7	485	10.5

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

483 - $[M - F]^+$
433 - $[M - CF_3]^+$
383 - $[M - C_2F_5]^+$
335 - $[C_3F_7OCF(CF_3)CF_2]^+$

m/e

317 - $[CF(CF_3)CF_2OC(CF_3)_2H]^+$
267 - $[M - C_3F_7OCF_2]^+$
217 - $[CF_2OC(CF_3)_2H]^+$
151 - $[C(CF_3)_2H]^+$

TABLE 30

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2H$ (MW 336)

m/e	%	m/e	%	m/e	%	m/e	%
31	27.0	78	3.4	130	3.2	218	2.0
32	6.2	79	6.4	131	17.7	219	13.3
44	3.0	81	9.1	132	4.0	231	8.8
47	13.8	82	29.7	142	3.9	235	17.0
50	16.4	83	2.0	147	9.1	236	2.2
51	61.9	93	7.3	150	15.4	242	7.2
52	2.2	97	13.8	151	93.6	243	3.4
54	2.2	100	34.2	152	17.6	267	7.3
60	14.7	101	17.5	159	2.4	269	2.0
62	4.7	107	2.9	163	4.3	281	2.0
63	3.7	112	2.9	169	93.9	285	12.9
66	5.6	113	15.3	170	17.4	293	2.4
67	2.5	119	42.4	176	5.9	301	2.6
69	100.0	120	3.0	181	8.8	317	11.4
70	14.5	126	29.9	192	6.2	347	2.6
75	2.8	127	2.9	213	4.4	367	4.0
76	13.1	129	33.7	217	15.1		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

317 - $[M - F]^+$

285 - $[C_3F_7OCF(CF_3)]^+$

235 - $[C_3F_7OCF_2]^+$

m/e

169 - $[C_3F_7]^+$

151 - $[CF(CF_3)CF_2H]^+$

51 - $[CF_2H]^+$

TABLE 31

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CN$ (MW 311)

m/e	%	m/e	%	m/e	%	m/e	%
31	72.5	76	38.6	107	15.1	169	79.7
32	3.4	77	10.7	114	3.3	170	12.9
33	4.6	78	13.0	119	59.3	176	3.6
45	5.0	79	2.4	120	5.3	181	3.6
47	32.7	81	10.5	123	2.1	192	30.8
50	36.7	82	2.3	126	100.0	193	4.1
51	16.7	88	4.3	127	22.3	214	4.4
54	29.7	93	4.3	131	7.8	217	4.9
55	2.5	95	2.9	142	35.6	219	2.4
57	18.0	97	60.8	143	3.4	231	2.1
62	3.5	98	4.7	145	2.0	242	19.9
66	9.2	100	51.4	147	13.5	243	2.8
69	93.0	101	36.8	150	9.1	264	3.9
70	17.9	102	2.2	151	2.4	285	5.9
73	4.2	104	8.4	167	9.1	292	2.0

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

292 - $[M - F]^+$

242 - $[M - CF_3]^+$

192 - $[M - C_2F_5]^+$

m/e

169 - $[C_3F_7]^+$

142 - $[M - C_3F_7]^+$

126 - $[CF(CF_3)CN]^+$

TABLE 32

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $CF_3CF_2C_6H_5$ (MW 196)

m/e	%	m/e	%	m/e	%	m/e	%
31	2.9	63	3.8	95	2.1	127	100.0
38	2.4	69	2.9	99	2.9	128	16.7
39	4.4	74	3.2	101	4.2	145	7.5
50	3.3	75	8.9	105	2.7	177	9.1
51	15.8	76	2.3	107	5.9	196	43.7M^+
57	3.1	77	29.0	125	5.9	197	6.9
62	2.3	81	2.4	126	4.7		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

196 - $[M]^+$
177 - $[M - F]^+$

m/e

127 - $[CF_2C_6H_5]^+$
77 - $[C_6H_5]^+$

TABLE 33

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $CF_3CF_2CF_2C_6H_5$ (MW 246)

m/e	%	m/e	%	m/e	%	m/e	%
31	5.0	69	7.1	100	2.8	128	16.3
38	2.6	74	3.6	101	3.6	145	5.3
39	5.9	75	7.7	107	5.3	158	3.8
50	11.4	76	3.2	108	2.3	207	3.7
51	19.8	77	33.5	119	2.4	227	7.4
57	2.6	78	3.2	125	4.2	246	28.0M^+
62	2.0	81	2.5	126	5.7	247	5.6
63	3.6	99	2.0	127	100.0		

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

246 - $[M]^+$
227 - $[M - F]^+$

m/e

127 - $[CF_2C_6H_5]^+$
77 - $[C_6H_5]^+$

TABLE 34

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2H$ (MW 502)

m/e	%	m/e	%	m/e	%	m/e	%
31	15.2	82	19.3	147	26.5	218	3.3
32	4.5	93	3.2	150	14.8	245	3.2
47	10.1	97	13.4	151	<u>100.0</u>	267	4.1
50	12.1	100	36.6	152	17.6	285	5.2
51	31.5	101	28.9	167	9.1	317	14.2
60	3.4	113	8.4	169	81.6	333	2.4
63	3.4	119	43.0	170	14.8	335	51.5
66	3.5	120	3.2	176	6.0	336	9.1
69	81.8	126	8.9	181	3.6	383	8.4
70	9.0	129	23.7	192	3.5	483	3.4
78	4.9	131	11.0	213	5.3		
81	7.5	132	3.8	217	27.5		

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

<u>m/e</u>

483 - $[M - F]^+$

335 - $C_3F_7OCF(CF_3)CF_2^+$

317 - $[M - C_3F_7O]^+$

<u>m/e</u>

217 - $CF_2OCF(CF_3)CF_2H^+$

151 - $CF(CF_3)CF_2H^+$

51 - CF_2H^+

TABLE 35

^{19}F NMR CHEMICAL SHIFT ASSIGNMENT OF FOMBLIN Z25-P28

(ppm)	Rel. Int.	Assignment
-50.0	2.65	$-OCF_2CF_2OC\underline{F}_2OCF_2CF_2O-$
-51.6	7.15	$-OCF_2CF_2OC\underline{F}_2(OCF_2)_xOC\underline{F}_2OCF_2CF_2O-$
-53.3	5.0	$-OCF_2CF_2OCF_2(OC\underline{F}_2)_xOCF_2OCF_2CF_2O-$
-54.2	0.1	$C\underline{F}_3OCF_2CF_2O-$
-56.0	0.2	$C\underline{F}_3OCF_2O-$
-81.6	0.64	?
-83.3	1.0	$-OC\underline{F}_2CF_2CF_2C\underline{F}_2O-$ + ?
-86.8	7.7	$-OCF_2OCF_2C\underline{F}_2(OC\underline{F}_2C\underline{F}_2)_yOC\underline{F}_2CF_2OCF_2O-$
-88.5	12.35	$-OCF_2OC\underline{F}_2CF_2(OCF_2CF_2)_yOCF_2C\underline{F}_2OCF_2O-$ $-OCF_2OC\underline{F}_2C\underline{F}_2OCF_2O-$
-123.8	0.65	$-OCF_2C\underline{F}_2C\underline{F}_2CF_2O-$
-127.5	0.45	?

Ratio of $-OCF_2CF_2O-$: $-OCF_2O-$ = 0.68 : 1

TABLE 36

^{19}F NMR CHEMICAL SHIFT ASSIGNMENT OF FOMBLIN Z25-P151

(ppm)	Rel. Int.	Assignment
-50.0	2.8	$-OCF_2CF_2OC\underline{F}_2OCF_2CF_2O-$
-51.7	7.1	$-OCF_2CF_2OC\underline{F}_2(OCF_2)_xOC\underline{F}_2OCF_2CF_2O-$
-53.4	4.5	$-OCF_2CF_2OCF_2(OC\underline{F}_2)_xOCF_2OCF_2CF_2O-$
-54.3	0.1	$C\underline{F}_3OCF_2CF_2O-$
-56.0	0.15	$C\underline{F}_3OCF_2O-$
-81.7	0.25	?
-83.5	0.42	$-OC\underline{F}_2CF_2CF_2C\underline{F}_2O-$ + ?
-87.0	8.05	$-OCF_2OCF_2C\underline{F}_2(OC\underline{F}_2C\underline{F}_2)_yOC\underline{F}_2CF_2OCF_2O-$
-88.7	13.4	$-OCF_2OC\underline{F}_2CF_2(OCF_2CF_2)_yOCF_2C\underline{F}_2OCF_2O-$ $-OCF_2OC\underline{F}_2C\underline{F}_2OCF_2O-$
-123.9	0.34	$-OCF_2C\underline{F}_2C\underline{F}_2CF_2O-$
-127.7	0.19	?

Ratio of $-OCF_2CF_2O-$: $-OCF_2O-$ = 0.74 : 1

TABLE 37

^{19}F NMR CHEMICAL SHIFT ASSIGNMENT OF KRYTOX 16256

(ppm)	Rel. Int.	Assignment
-76.9 (v. weak) -77.2 (shoulder) -78.1 (major) -78.8 (v. weak)	8.9	$-OC\underline{F}_2CF(C\underline{F}_3)O-$
-80.0	0.1 (?)	$C\underline{F}_3CF_2CF_2O-$
-81.1	<0.1	$CF_3CF_2C\underline{F}_2O-$
-85.6	<0.1	$C\underline{F}_3CF_2O-$
-86.7	<0.1	$CF_3C\underline{F}_2O-$
-87.6	<0.1	?
-128.0	<0.1	$CF_3C\underline{F}_2CF_2O-$
-142.4	1.7	$-OCF_2C\underline{F}(CF_3)O-$

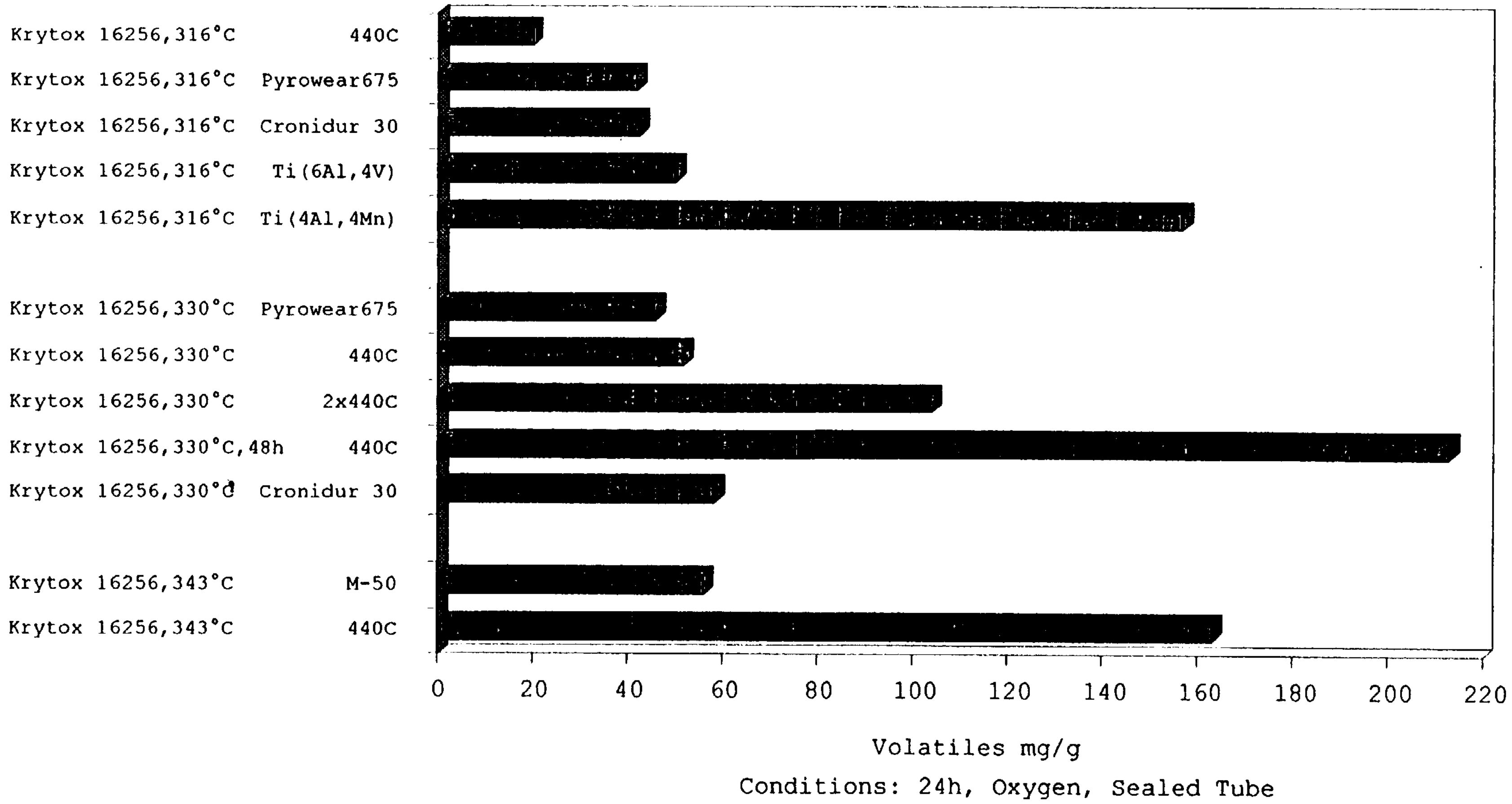


Figure 1. Comparison of the effects of different metals and temperatures on the thermal oxidative stability of Krytox 16256.

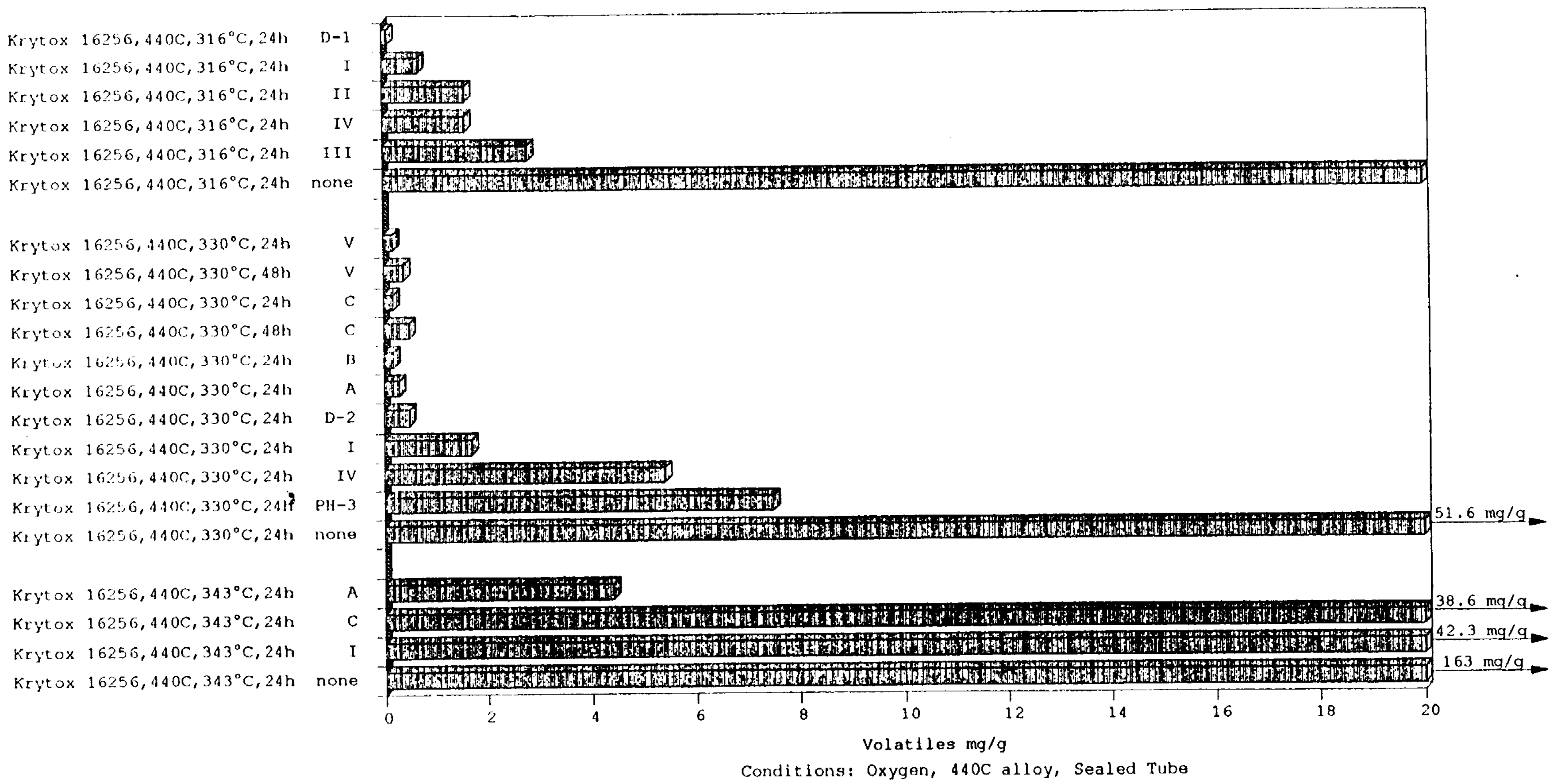


Figure 2. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II), $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III), $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ (IV), $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (A), $(C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O)_2P(O)OC_6H_5$ (B), $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C), D-1 and D-2 in arresting Krytox 16256 thermal oxidative degradation in the presence of 440C alloy.

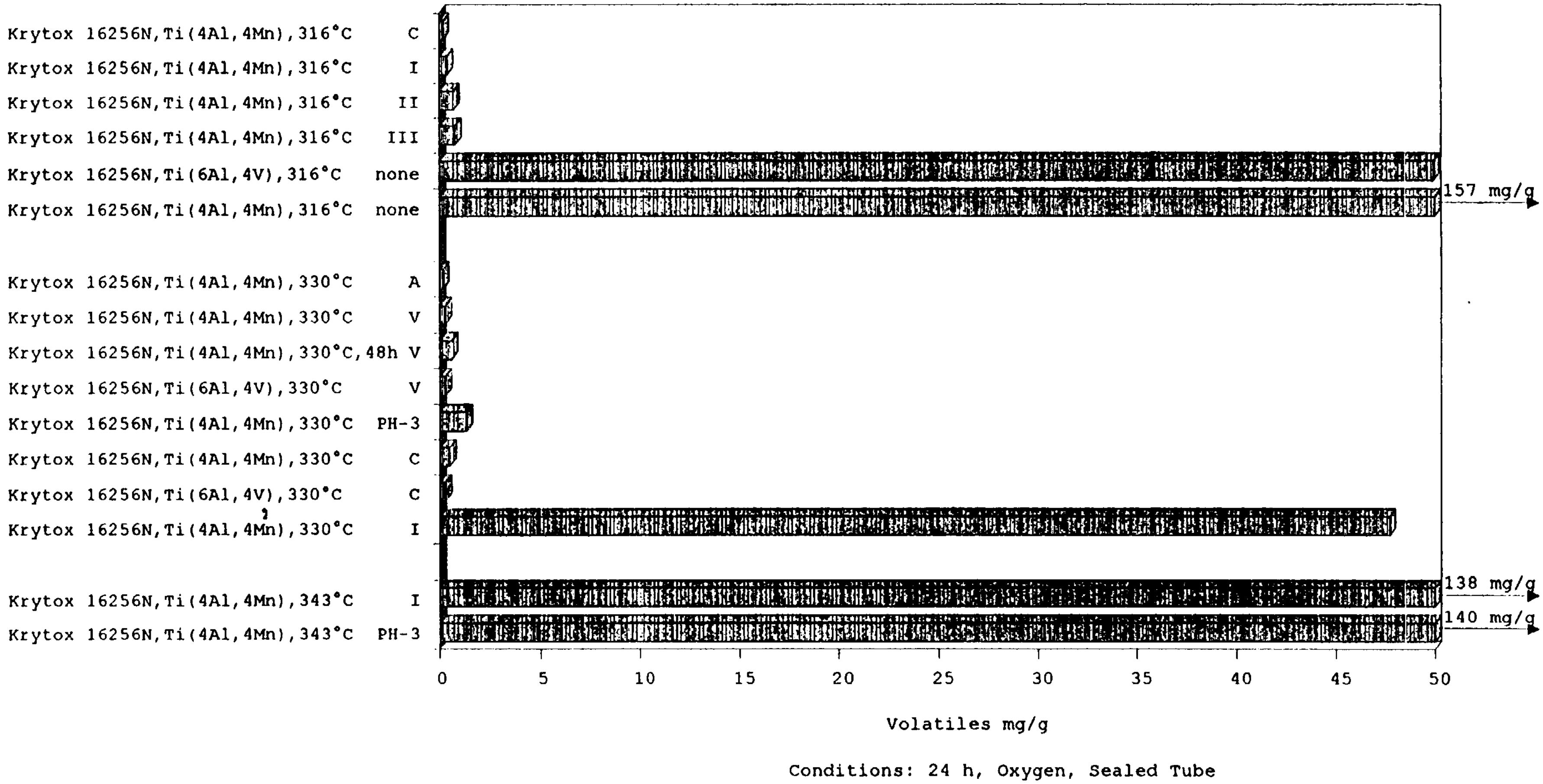
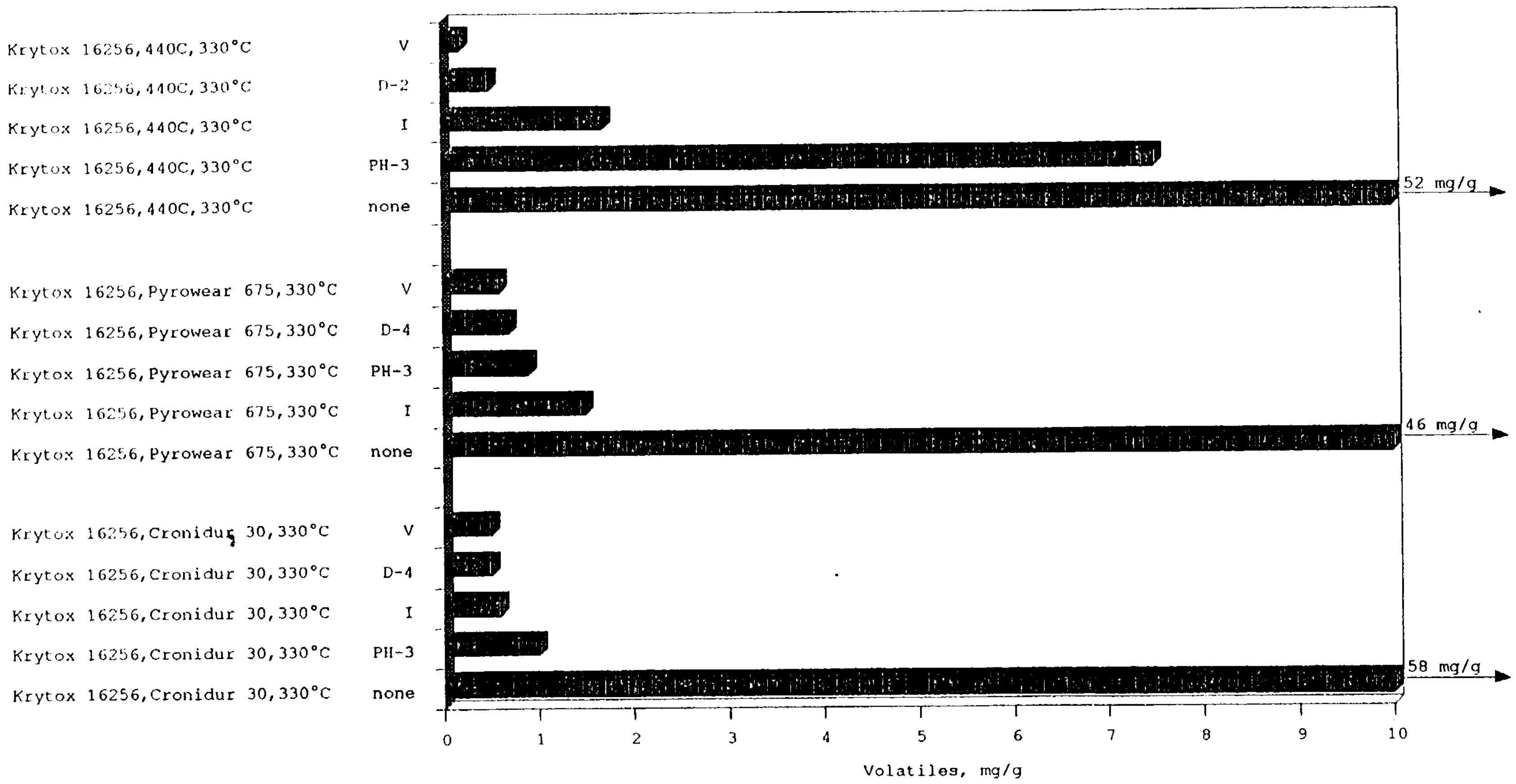
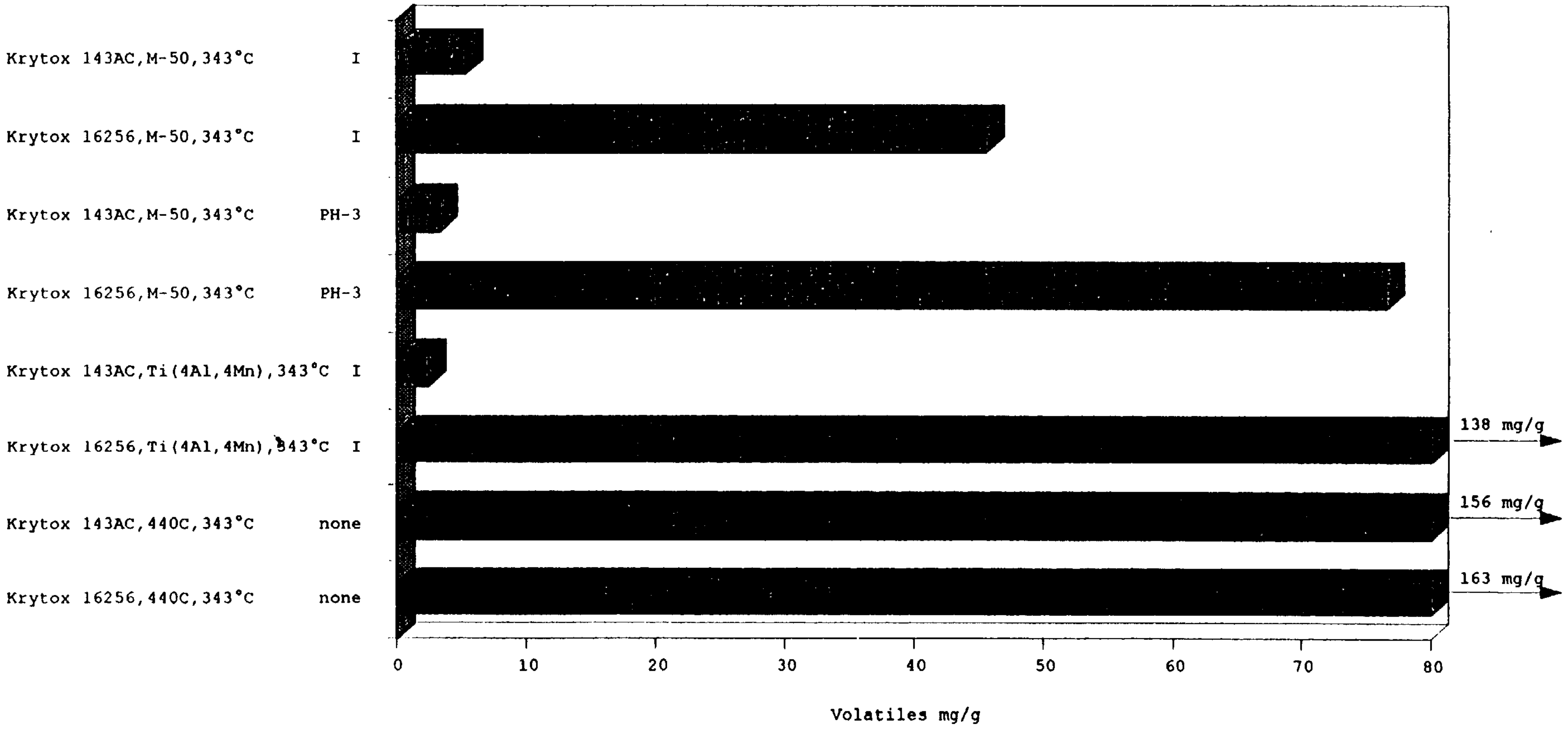


Figure 3. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II), $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III), $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (A), and $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C), in arresting Krytox 16256 thermal oxidative degradation in the presence of titanium alloys.



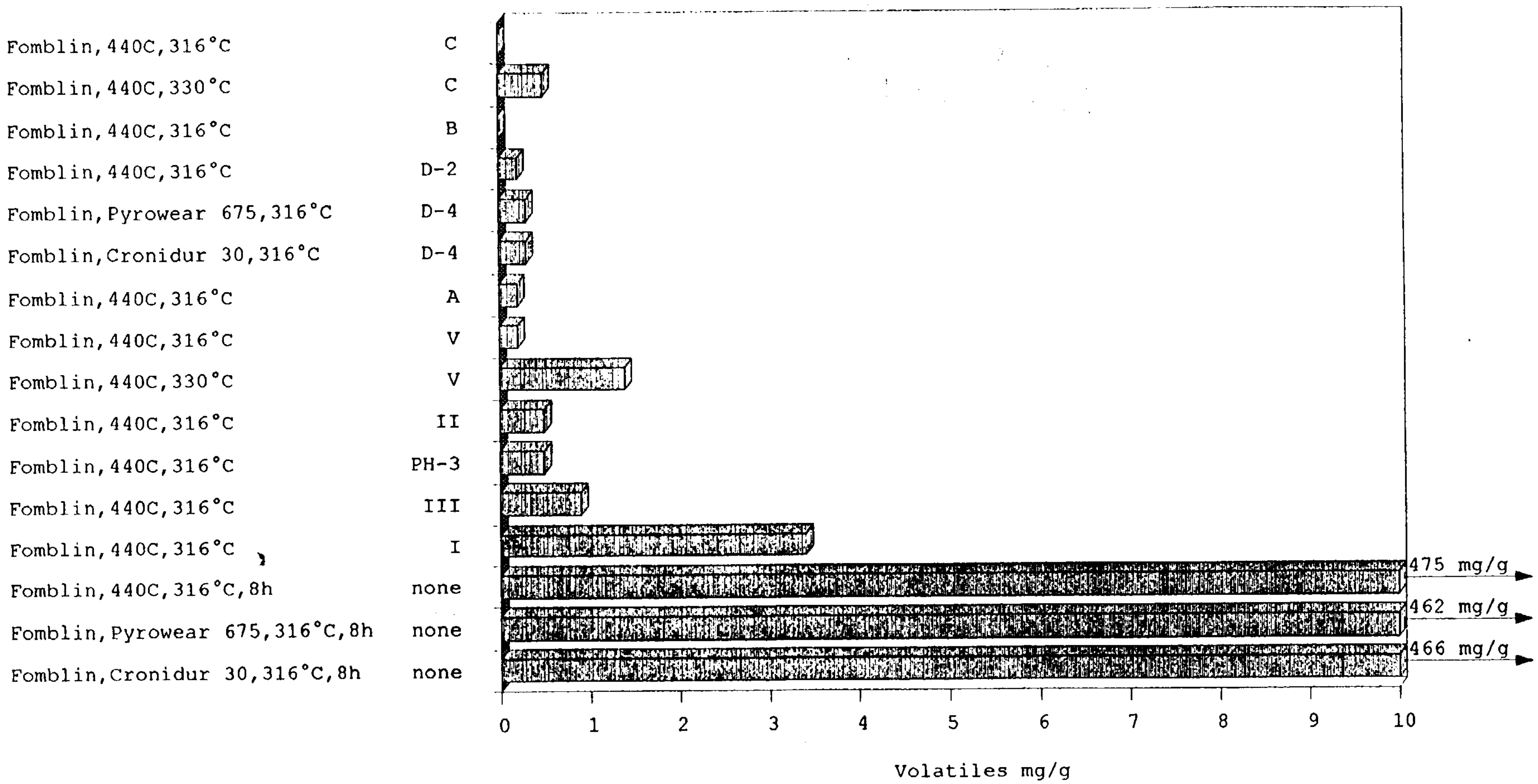
Conditions: 330°C, 24 h, Oxygen, Sealed Tube

Figure 4. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), D-2 and D-4 in arresting Krytox 16256 thermal oxidative degradation in the presence of ferrous alloys at 330°C.



Conditions: 343°C, 24 h, Oxygen, Sealed Tube

Figure 5. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I) and $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), in arresting Krytox 16256 and Krytox 143AC thermal oxidative degradation in the presence of different alloys at 343°C.



Conditions: 24h, Oxygen, Sealed Tube

Figure 6. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II), $[C_3F_7O[CF(CF_3)CF_2O]_2C(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III), $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (A), $(C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O)_2P(O)OC_6H_5$ (B), $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C), D-2 and D-4 in arresting Fomblin Z25-P151 thermal oxidative degradation in the presence of ferrous alloys.

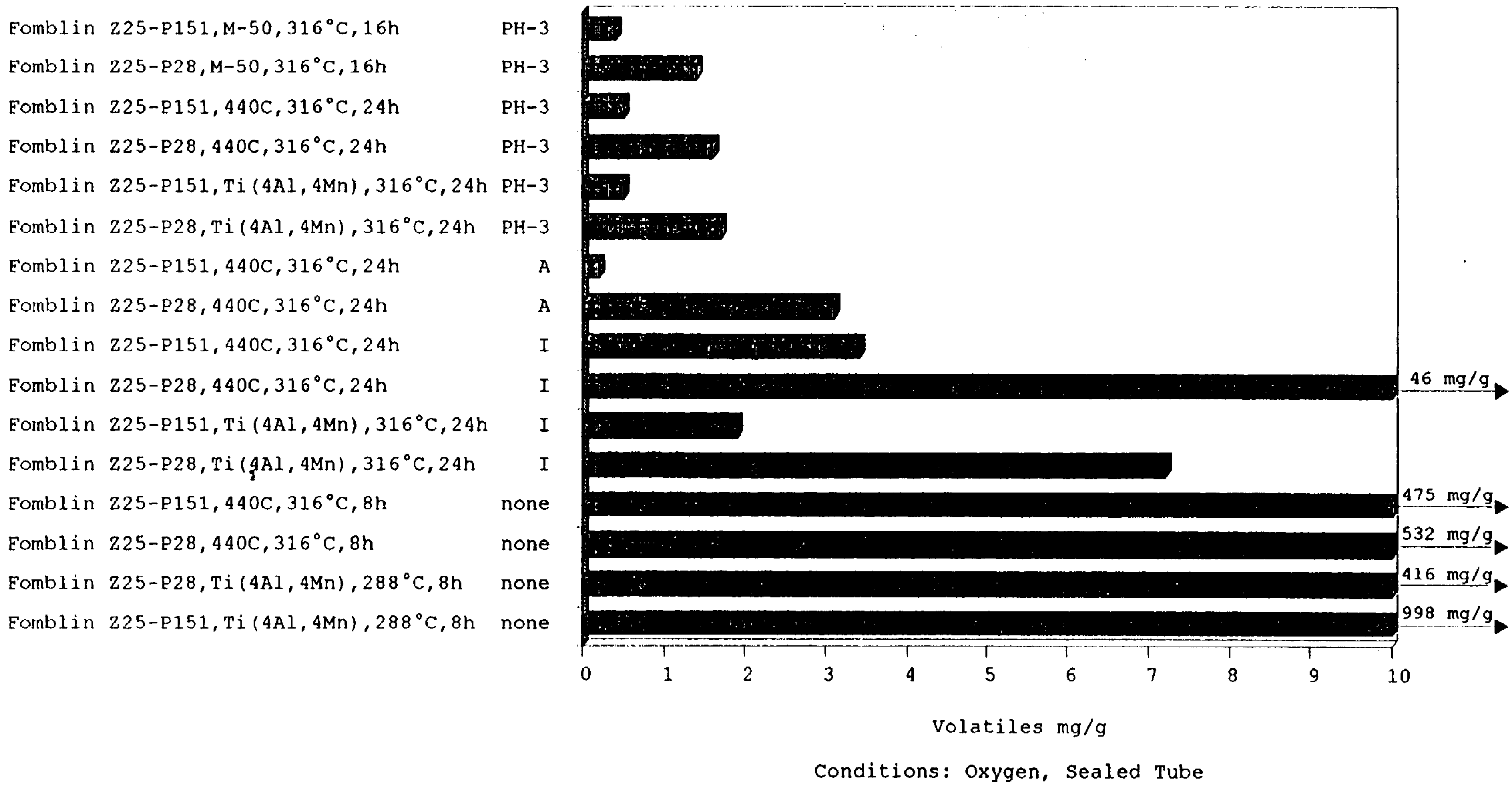
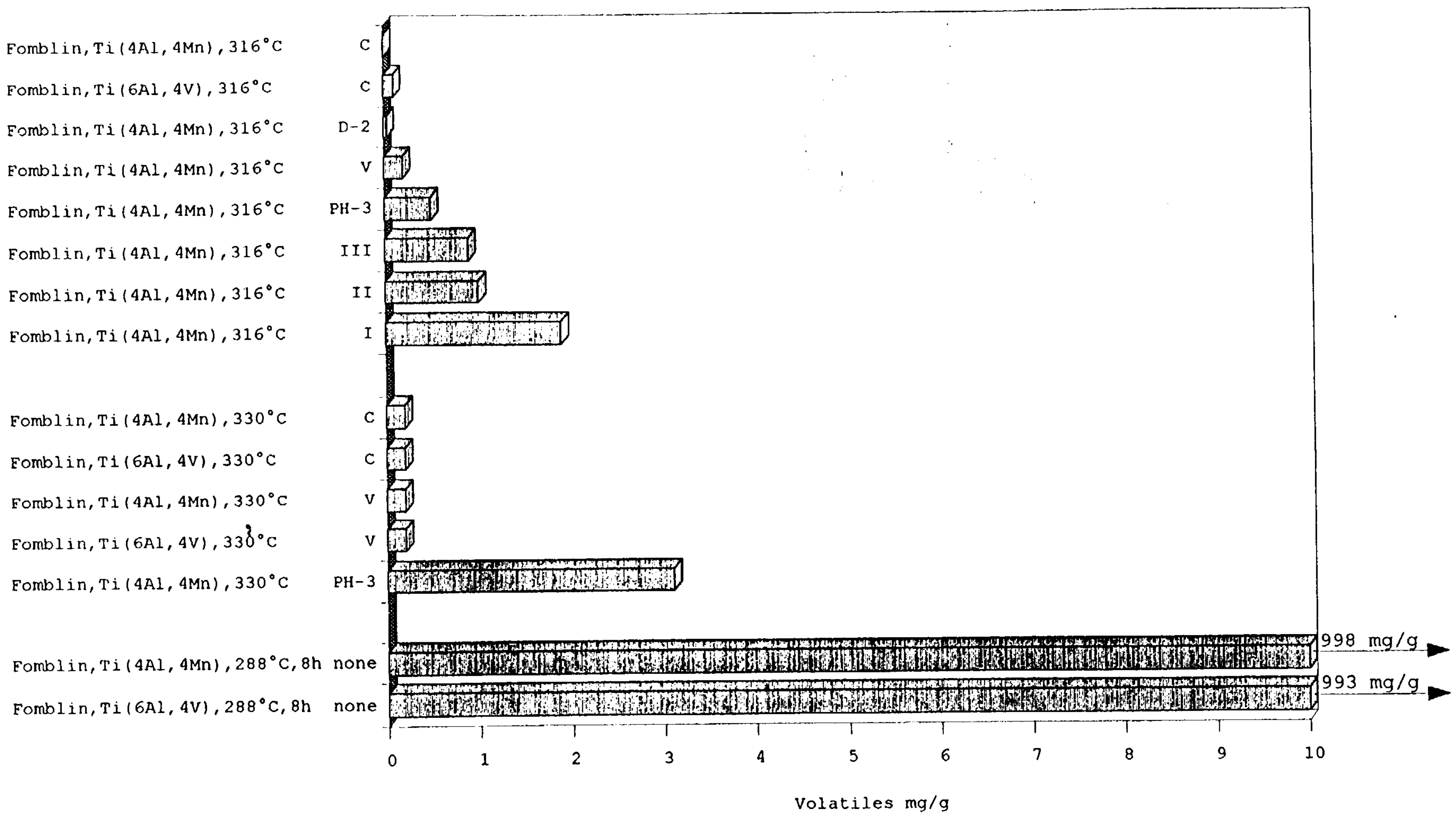
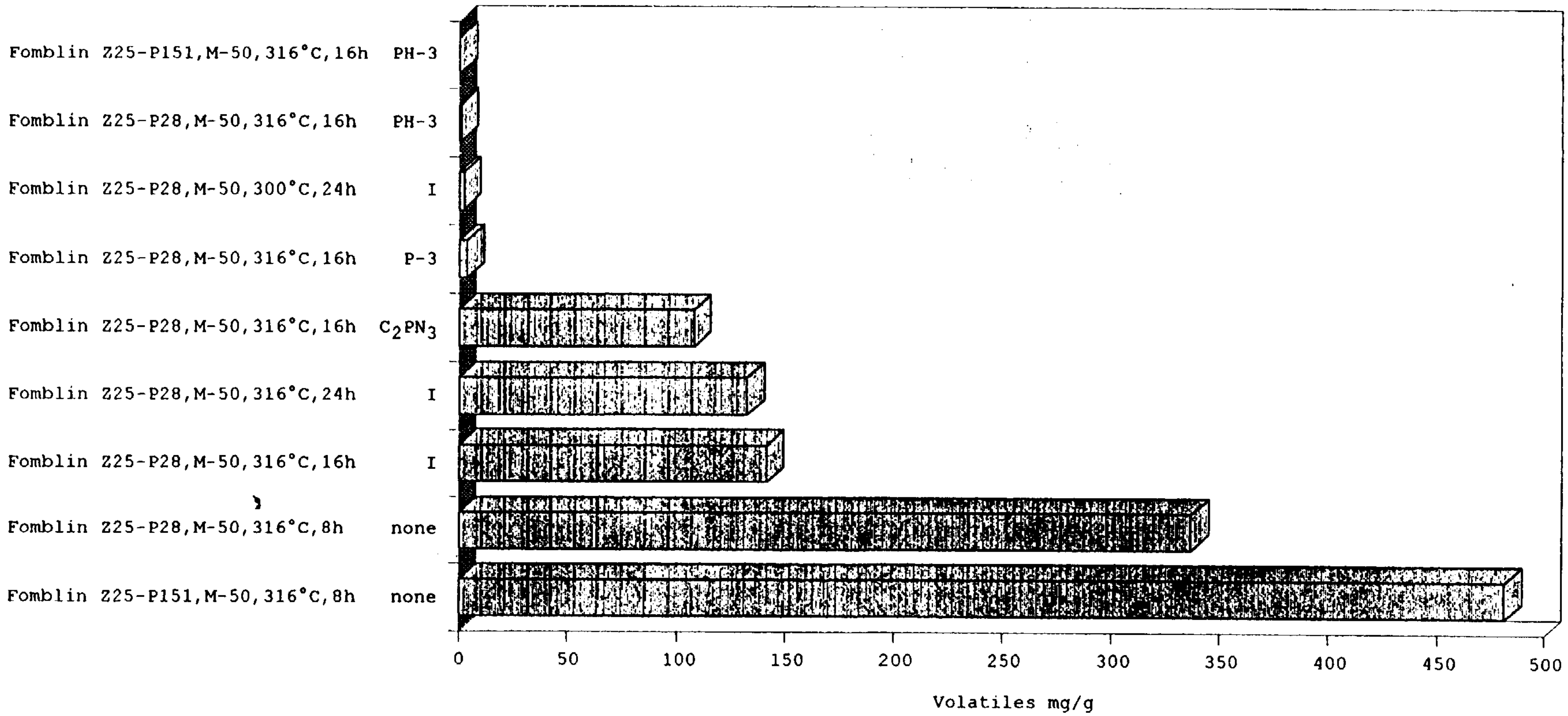


Figure 7. Comparison of effectiveness of additives $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (A), and $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), in arresting thermal oxidative degradation of the two batches of Fomblin Z25 in the presence of different alloys.



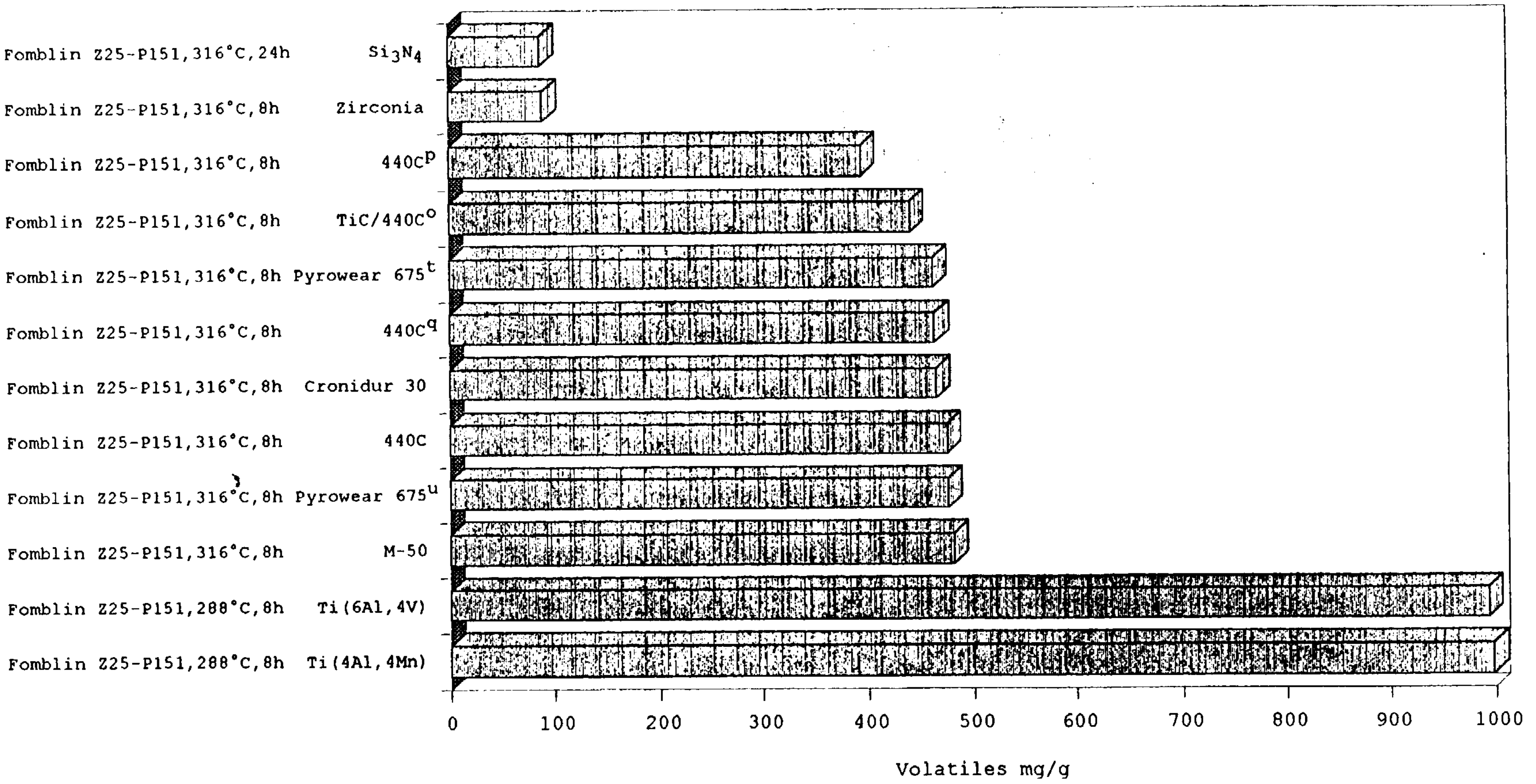
Conditions: 24h, Oxygen, Sealed Tube

Figure 8. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$ (II), $[C_3F_7O[CF(CF_3)CF_2O]_2C(CF_3)_2CN][(C_6H_5)_2PN]_2$ (III), $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (V), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)OC_6H_5$ (C), and D-2 in arresting Fomblin Z25-P151 thermal oxidative degradation in the presence of titanium alloys.



Conditions: Oxygen, M-50 Alloy, Sealed Tube

Figure 9. Comparison of effectiveness of the additives $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]$ (I), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4]_3P$ (PH-3), $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6F_4]_3P$ (P-3), and $[C_3F_7(OCF(CF_3)CF_2)_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$ (C_2PN_3) in arresting Fomblin Z25 thermal oxidative degradation in the presence of M-50 alloy.



Conditions: 316°C, Oxygen, Sealed tube

Figure 10. Comparison of the effects of different metals, metal treatment and ceramics on the thermal oxidative stability of Fomblin Z25-P151 (440C^p is a 440C coupon treated with hexamethyldisilazane, 440C^q is a 440C coupon treated with 3-aminopropyltriethoxy silane, TiC/440C^o is a TiC coated 440C ball, Pyrowear 675^t is as received ball and Pyrowear 675^u is repolished).

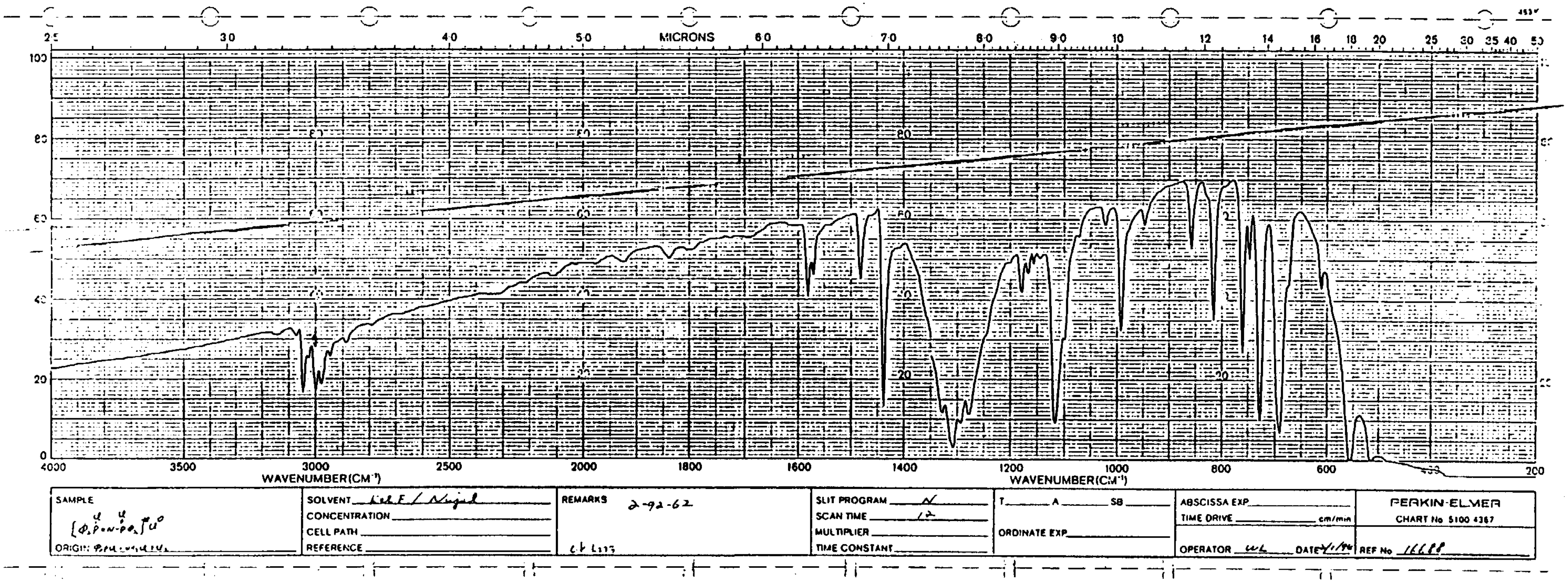


Figure 11. Infrared spectrum of $(C_6H_5)_2PCl{=}N{-}P(C_6H_5)_2Cl_2$.

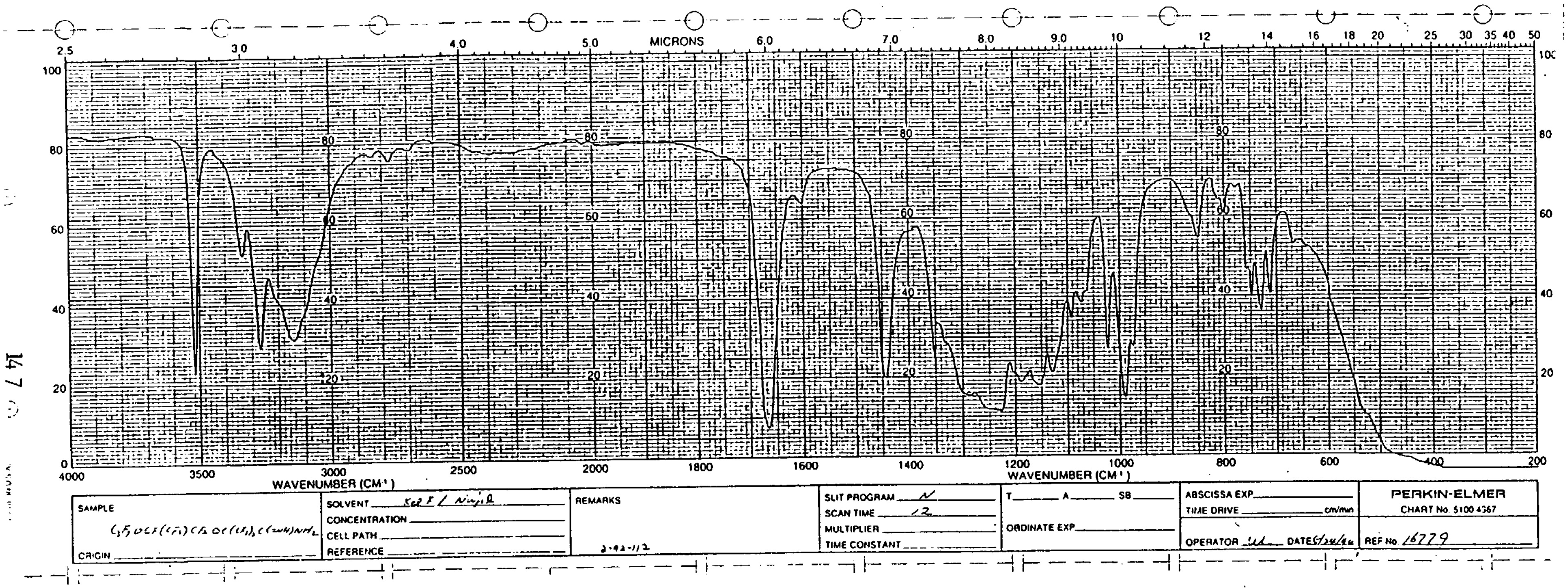


Figure 12. Infrared spectrum of $C_3F_7OCF(CF_3)CF_2OC(CF_3)_2C(=NH)NH_2$.

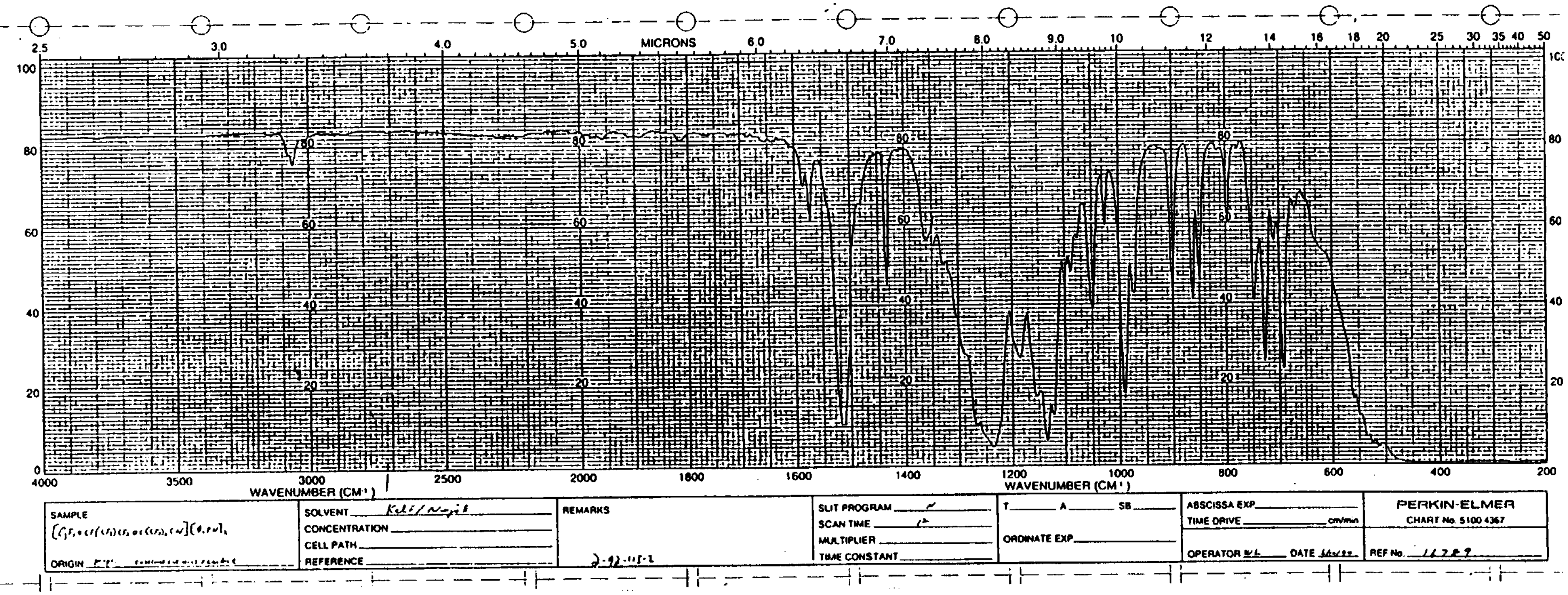


Figure 13. Infrared spectrum of $[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$.

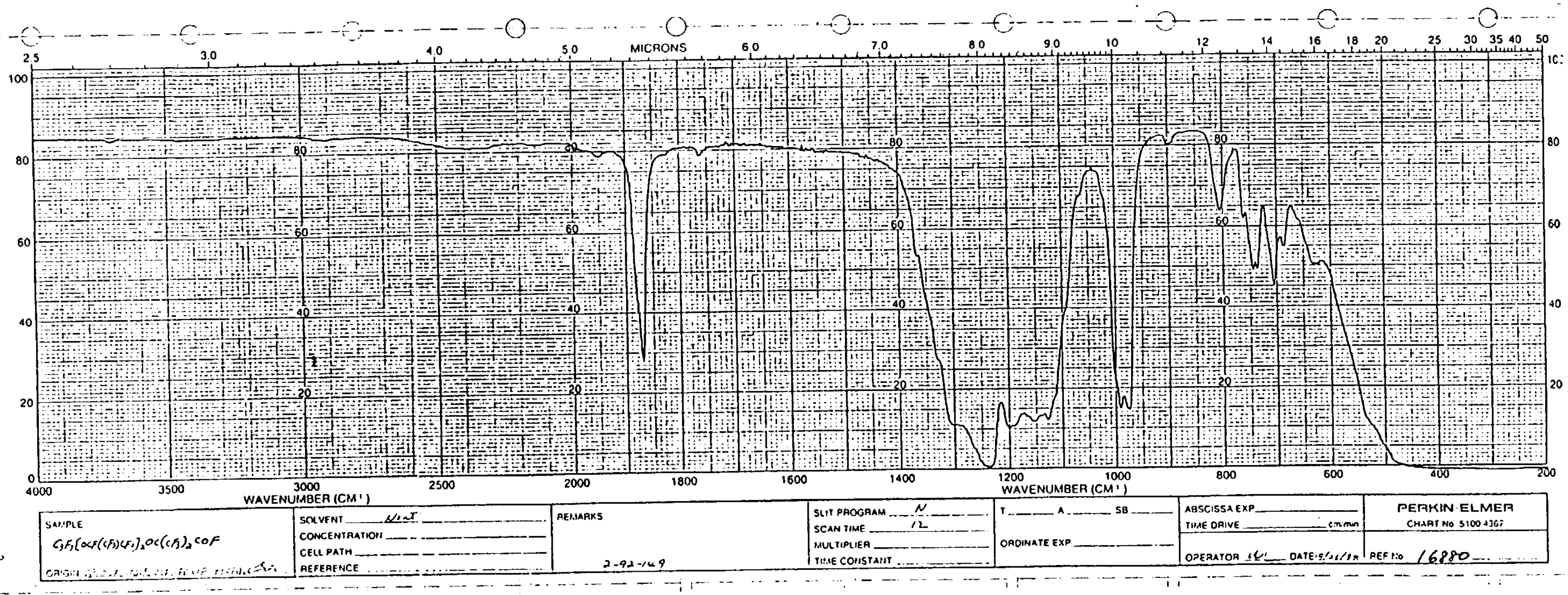


Figure 14. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2COF$.

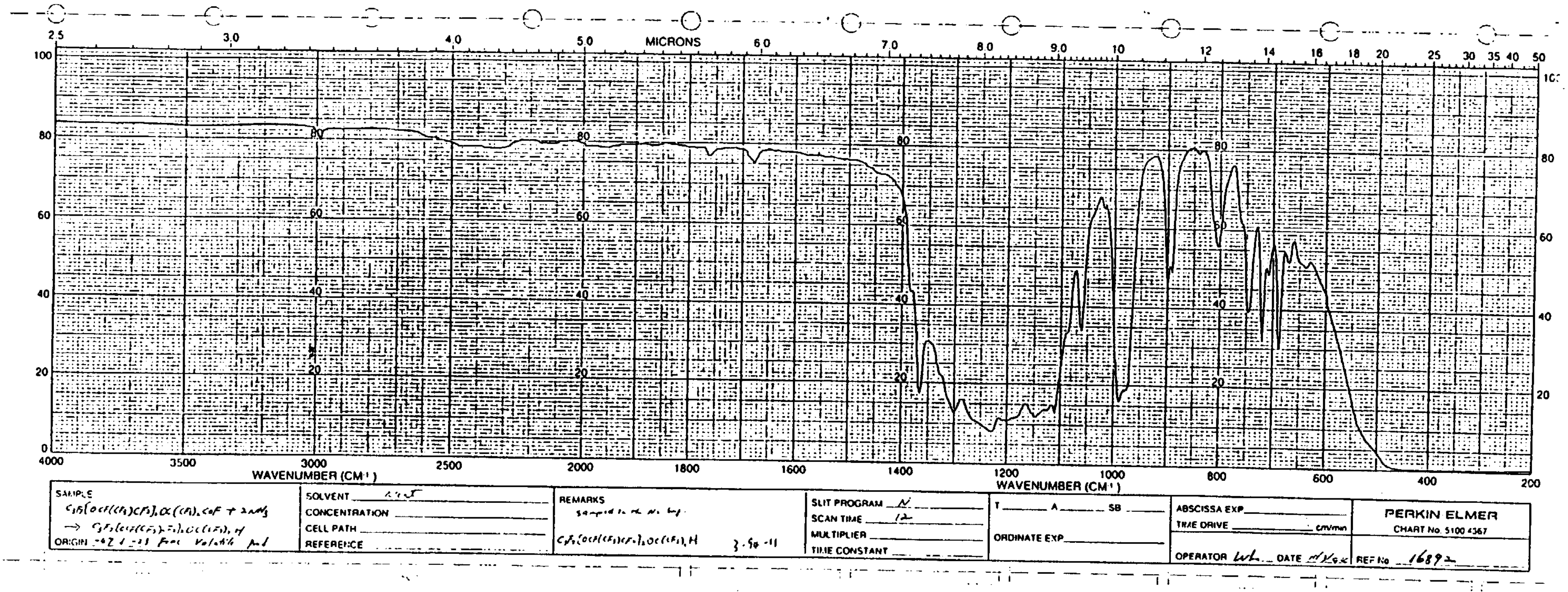


Figure 15. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2H$.

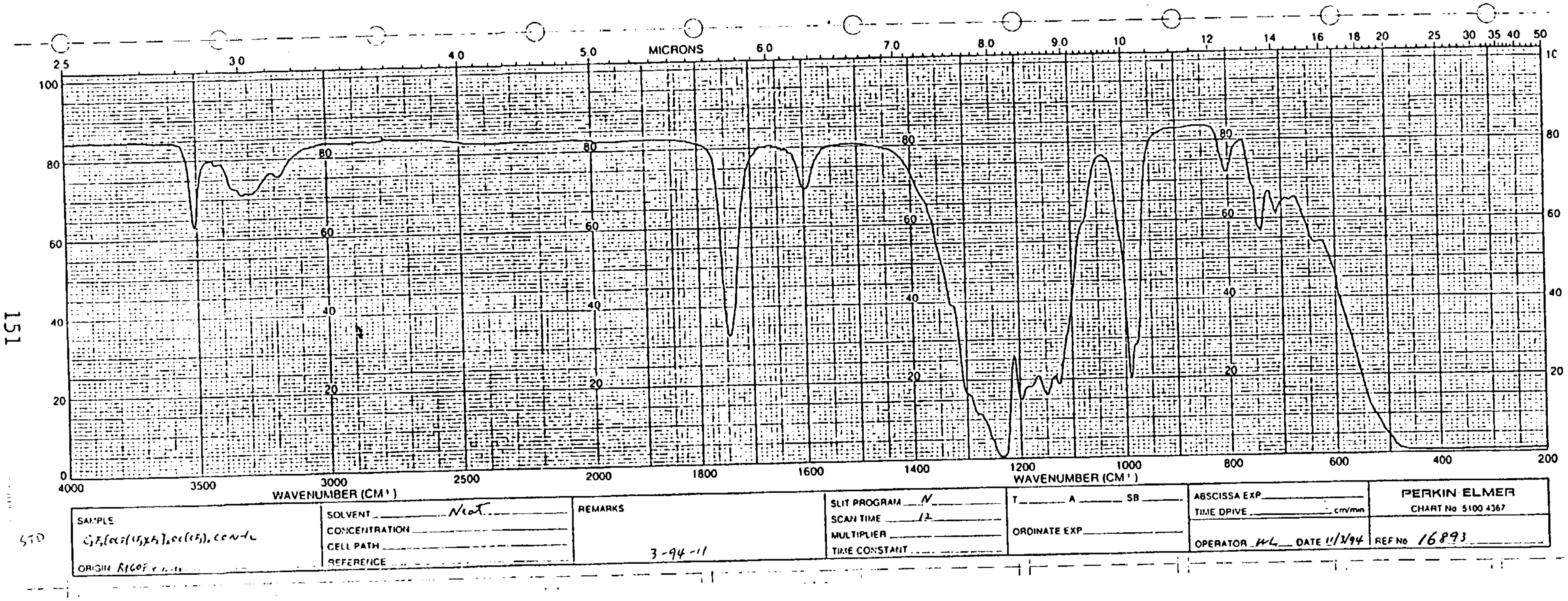


Figure 16. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CONH_2$.

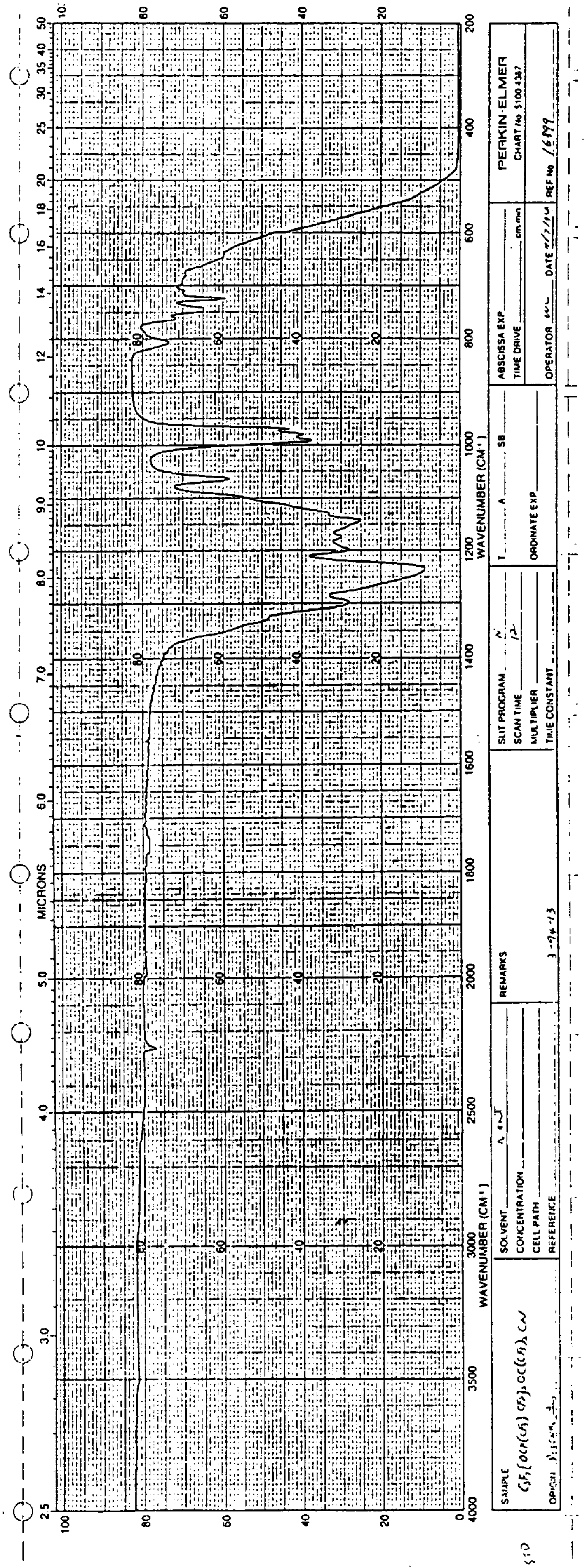


Figure 17. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN$.

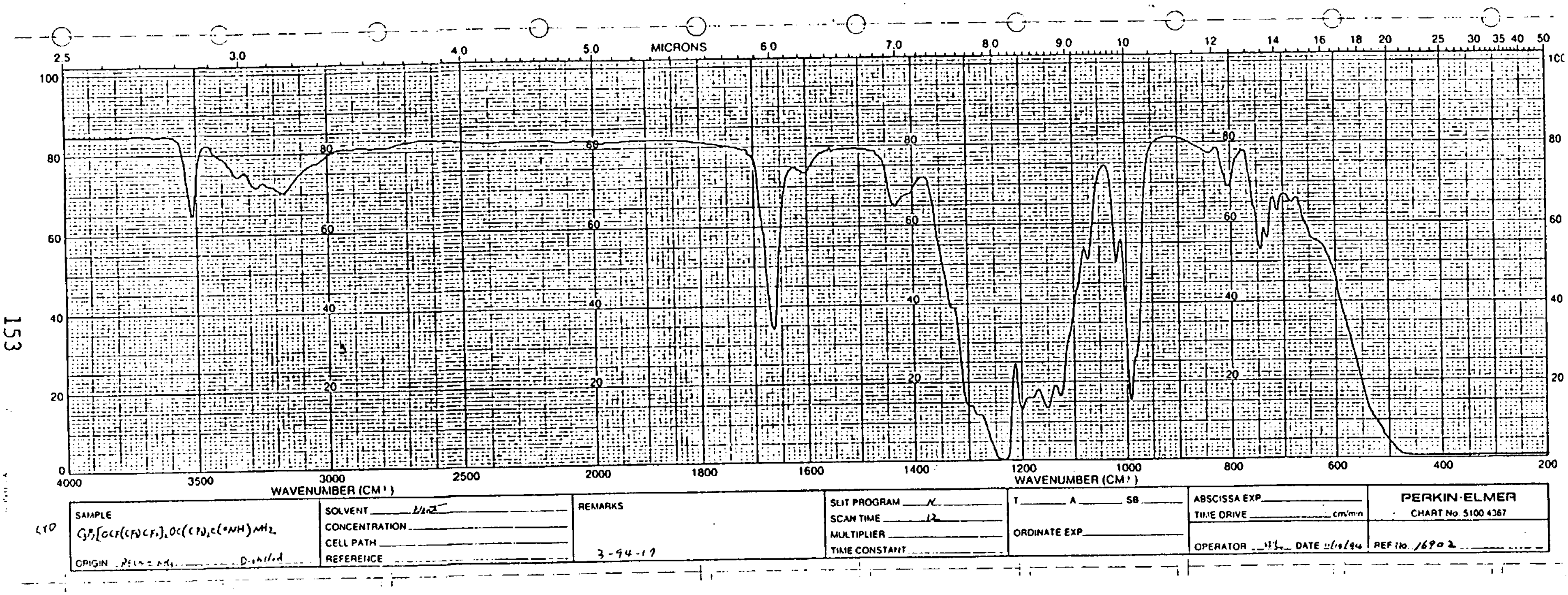
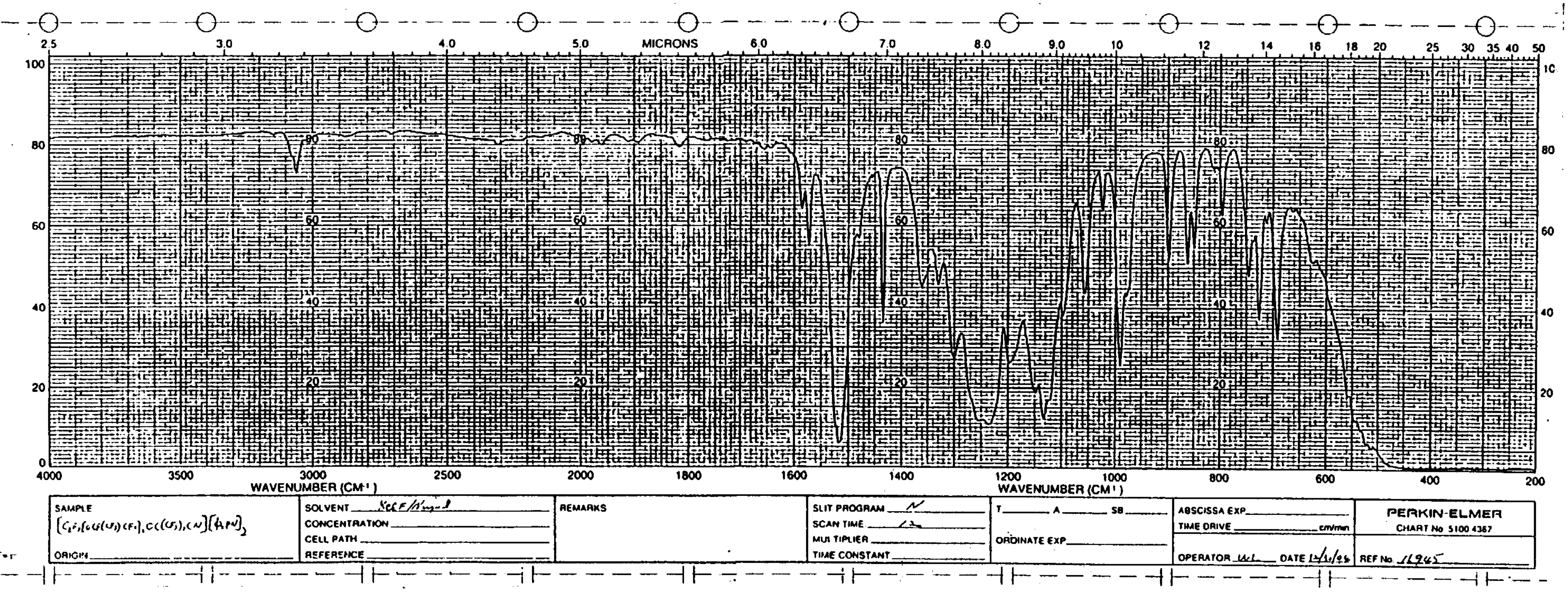


Figure 18. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2C(=NH)NH_2$.



SAMPLE $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][\phi_2PN]_2$

ORIGIN

SOLVENT NaCl/Nujol

CONCENTRATION

CELL PATH

REFERENCE

REMARKS

SLIT PROGRAM N

SCAN TIME 12

MULTIPLIER

TIME CONSTANT

T A SB

ORDINATE EXP

ABSCISSA EXP

TIME DRIVE cm/min

OPERATOR W.L. DATE 12/1/94

REF No. 11945

Figure 19. Infrared spectrum of $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN][(C_6H_5)_2PN]_2$.

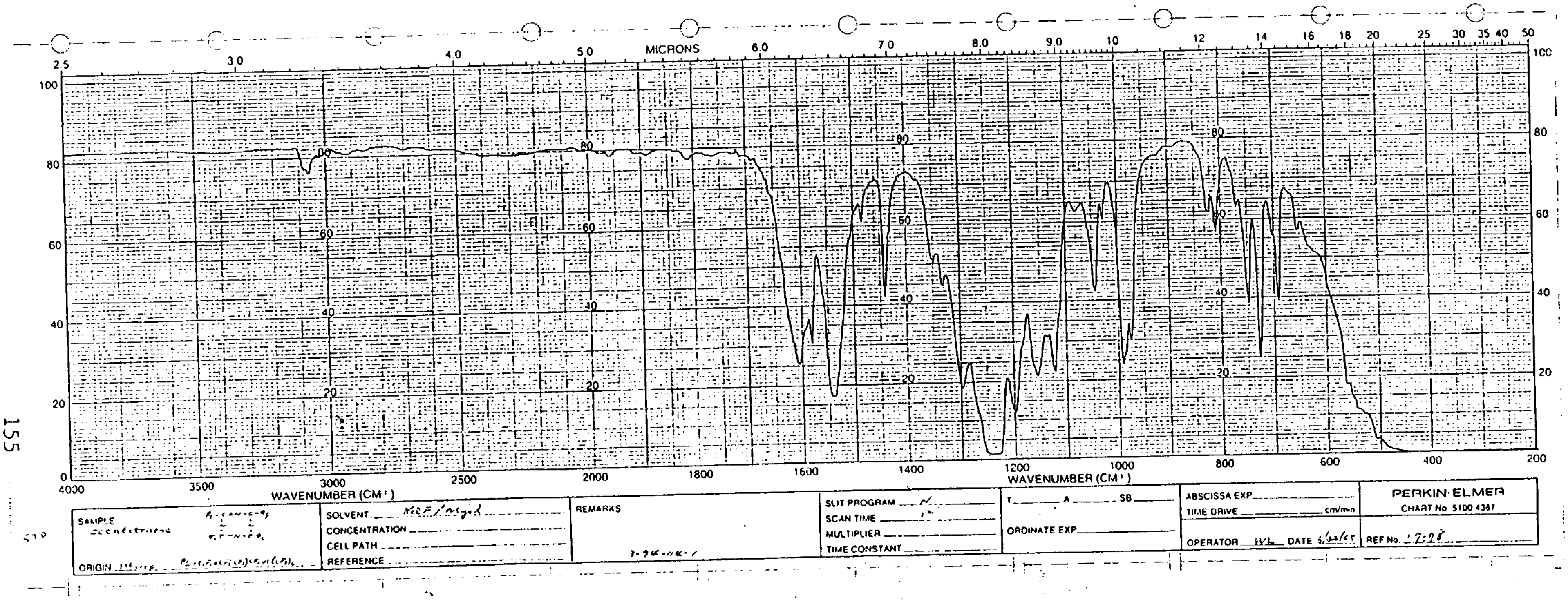


Figure 20. Infrared spectrum of $[C_3F_7[OCF(CF_3)CF_2]_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$.

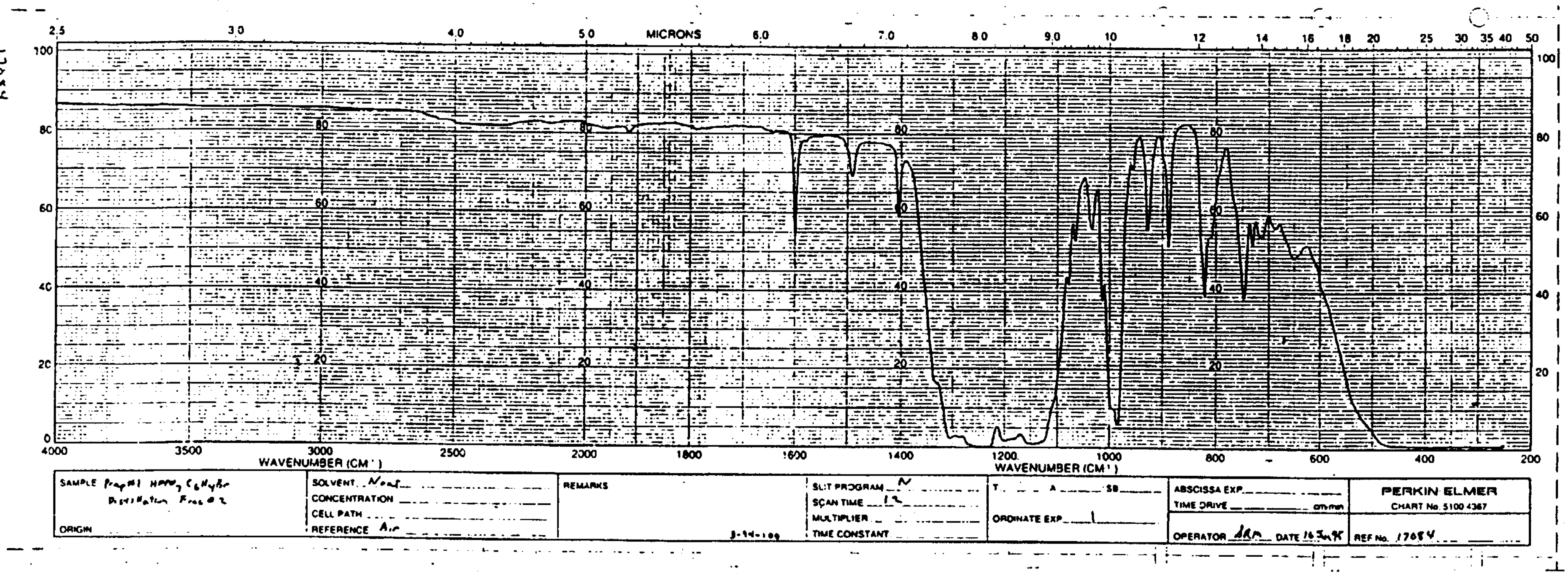
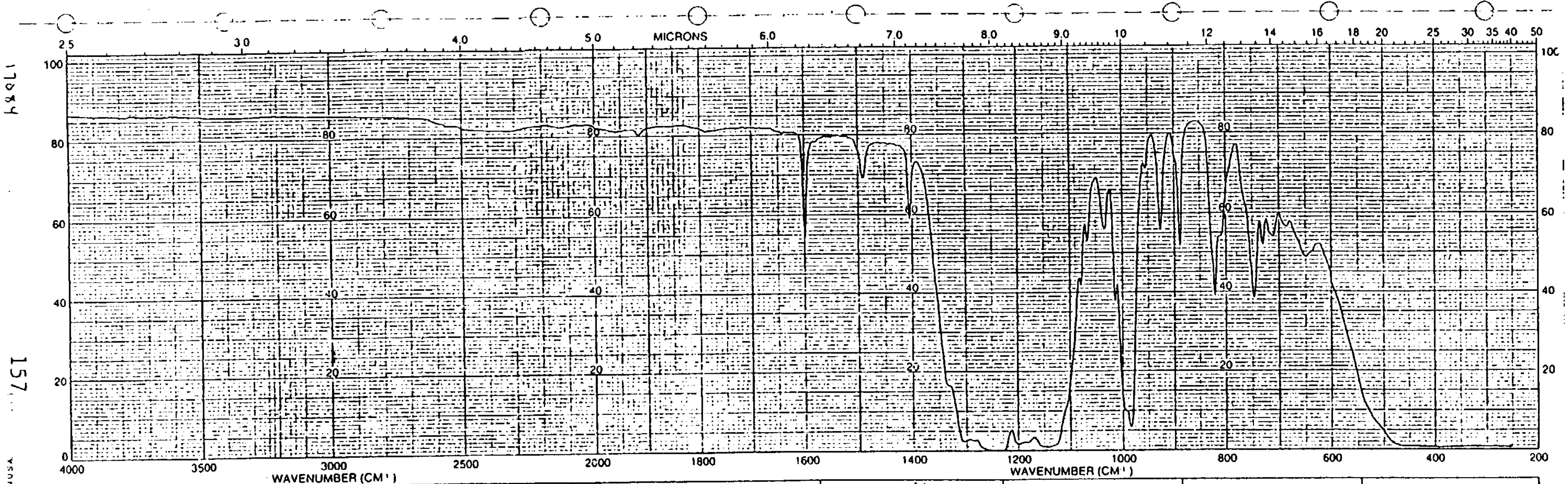


Figure 21. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_5CF(CF_3)C(O)C_6H_4Br$.



SAMPLE Prep#1 HFPO$_7$ C_6H_4Br
Distillation Frac #2
ORIGIN
SOLVENT Neat
CONCENTRATION
CELL PATH
REFERENCE Air
REMARKS
SLIT PROGRAM N
SCAN TIME 12
MULTIPLIER
TIME CONSTANT
T A SB
ORDINATE EXP 1
ABSCISSA EXP
TIME DRIVE cm/min
OPERATOR dRm DATE 16 Ju 95
PERKIN-ELMER
CHART No. 5100 4367
REF No 17084

17084

Figure 22. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4Br$.

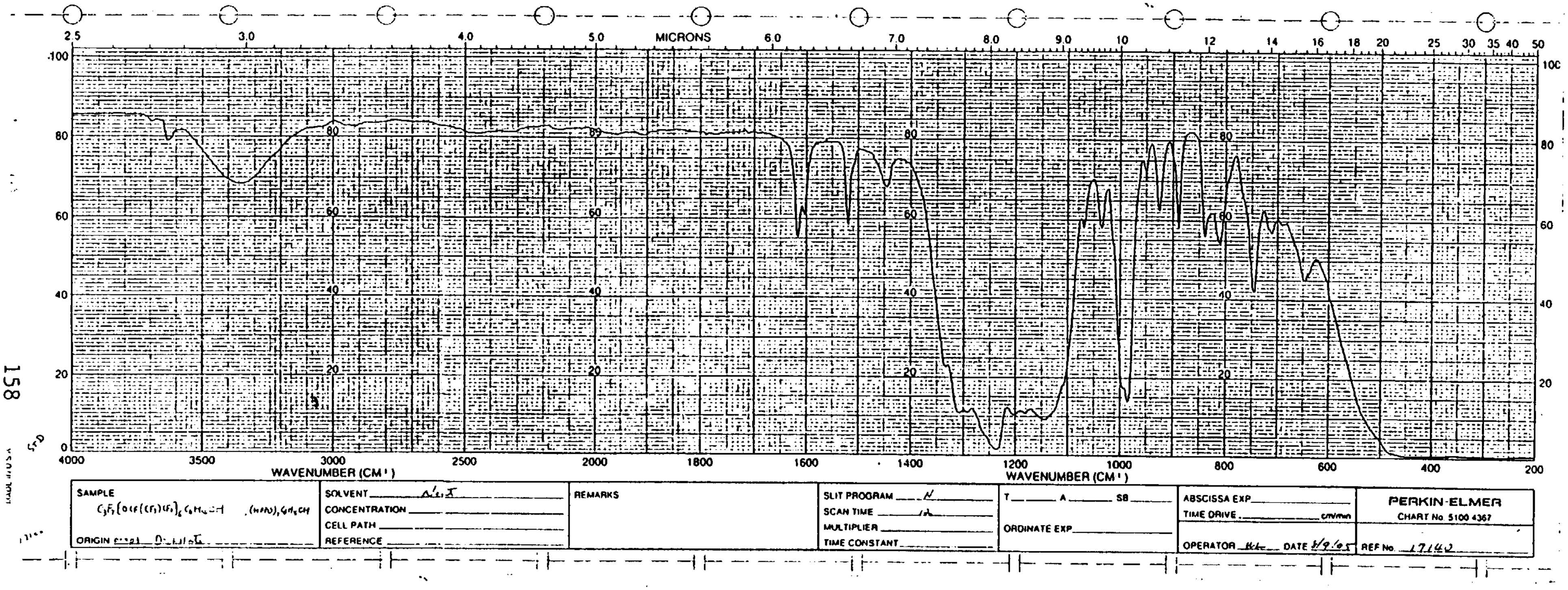


Figure 23. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$.

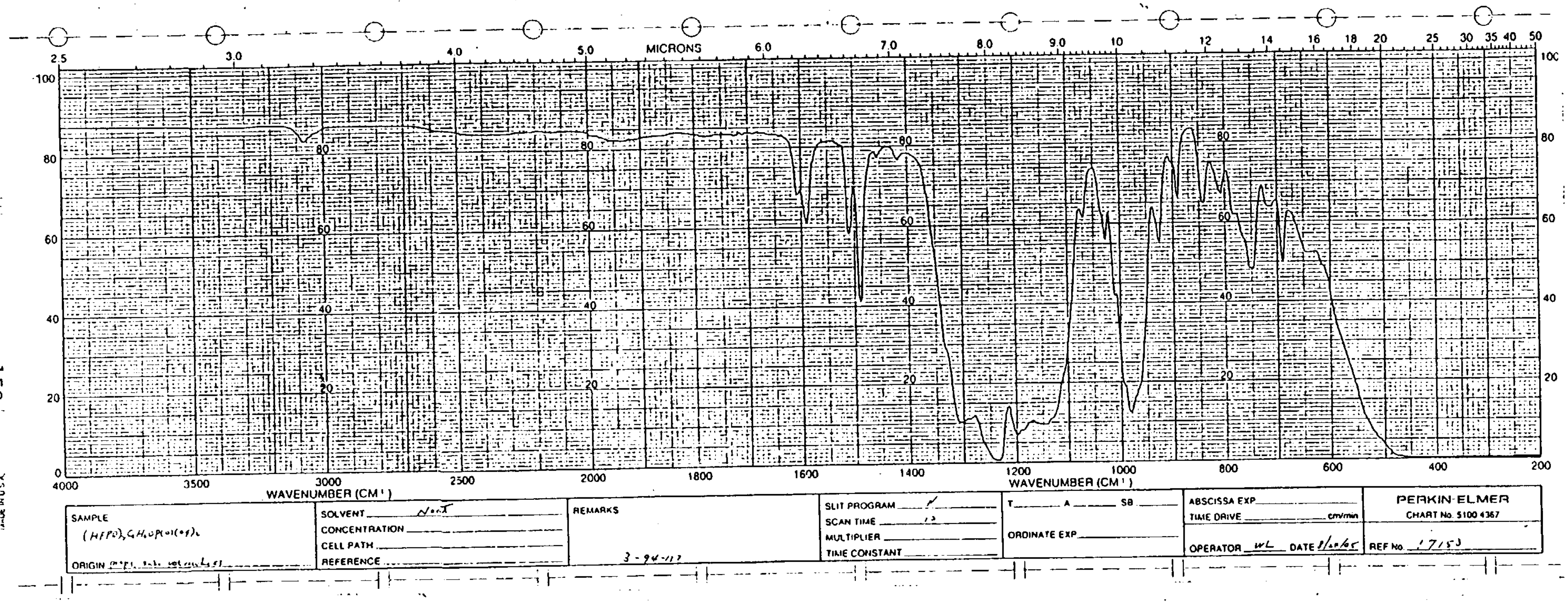


Figure 24. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$.

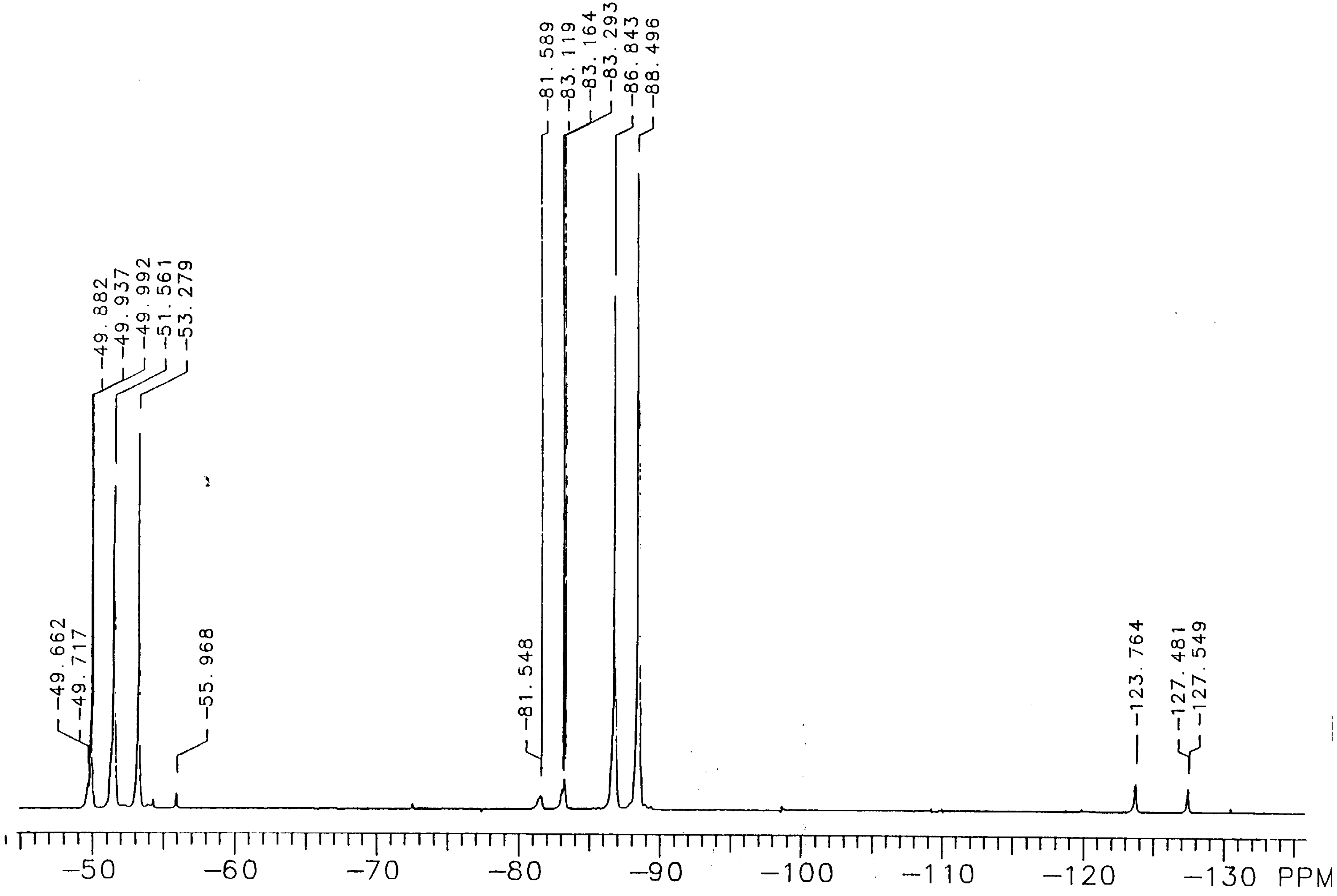


Figure 25. Fluorine NMR spectrum of Fomblin Z25-P28.

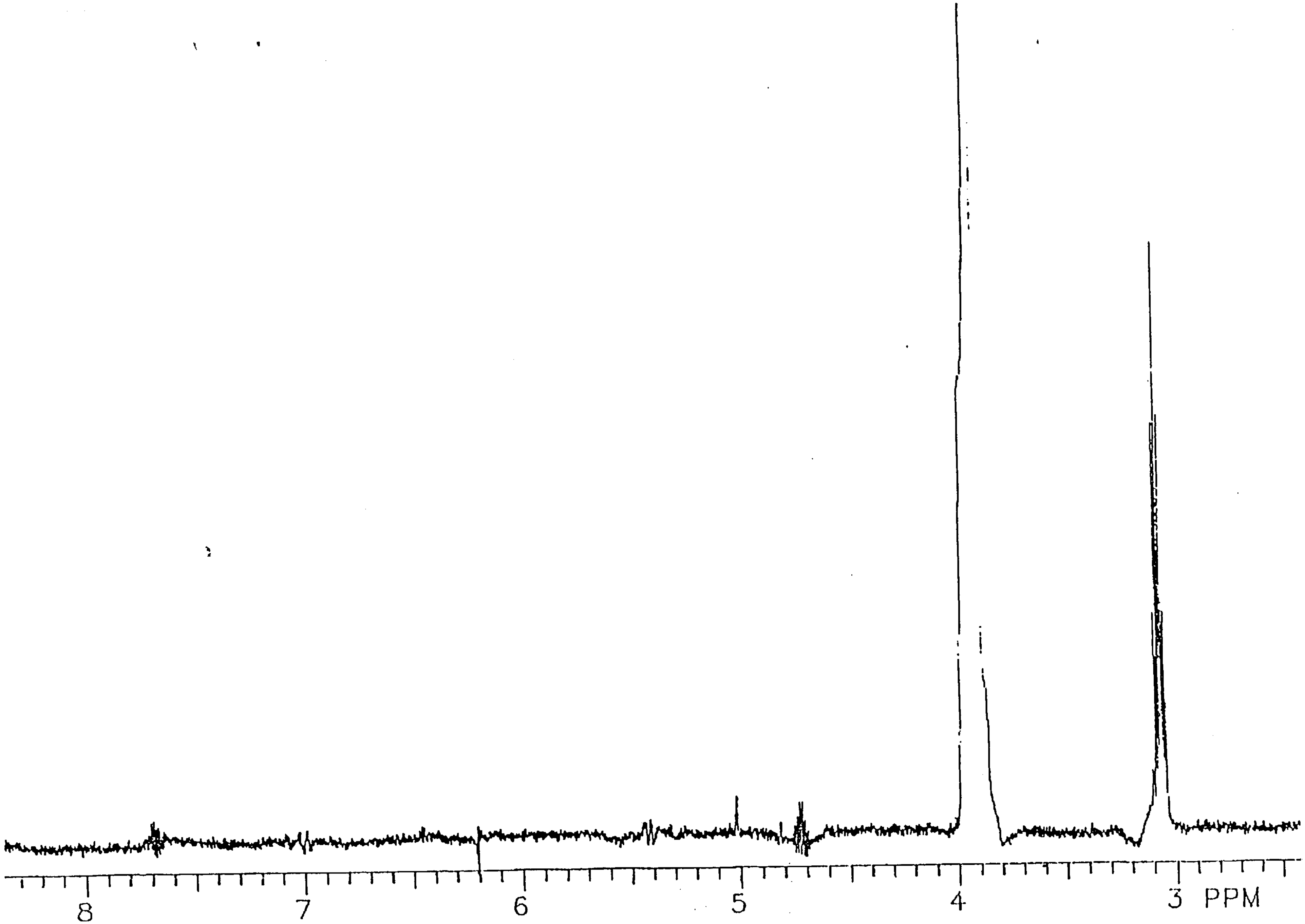


Figure 26. Proton NMR spectrum of Fomblin Z25-P151 (1000 scans).

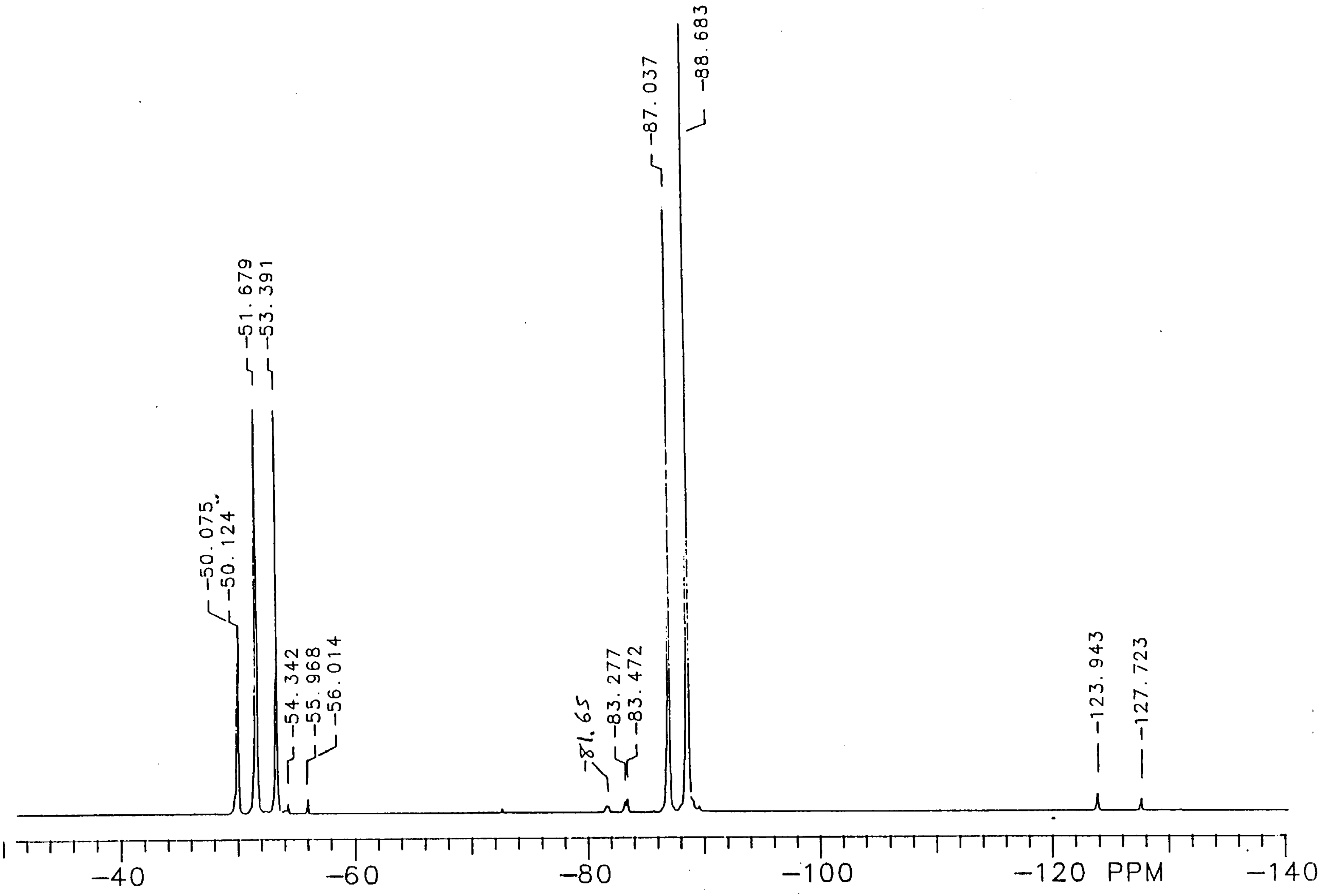


Figure 27. Fluorine NMR spectrum of Fomblin Z25-P151.

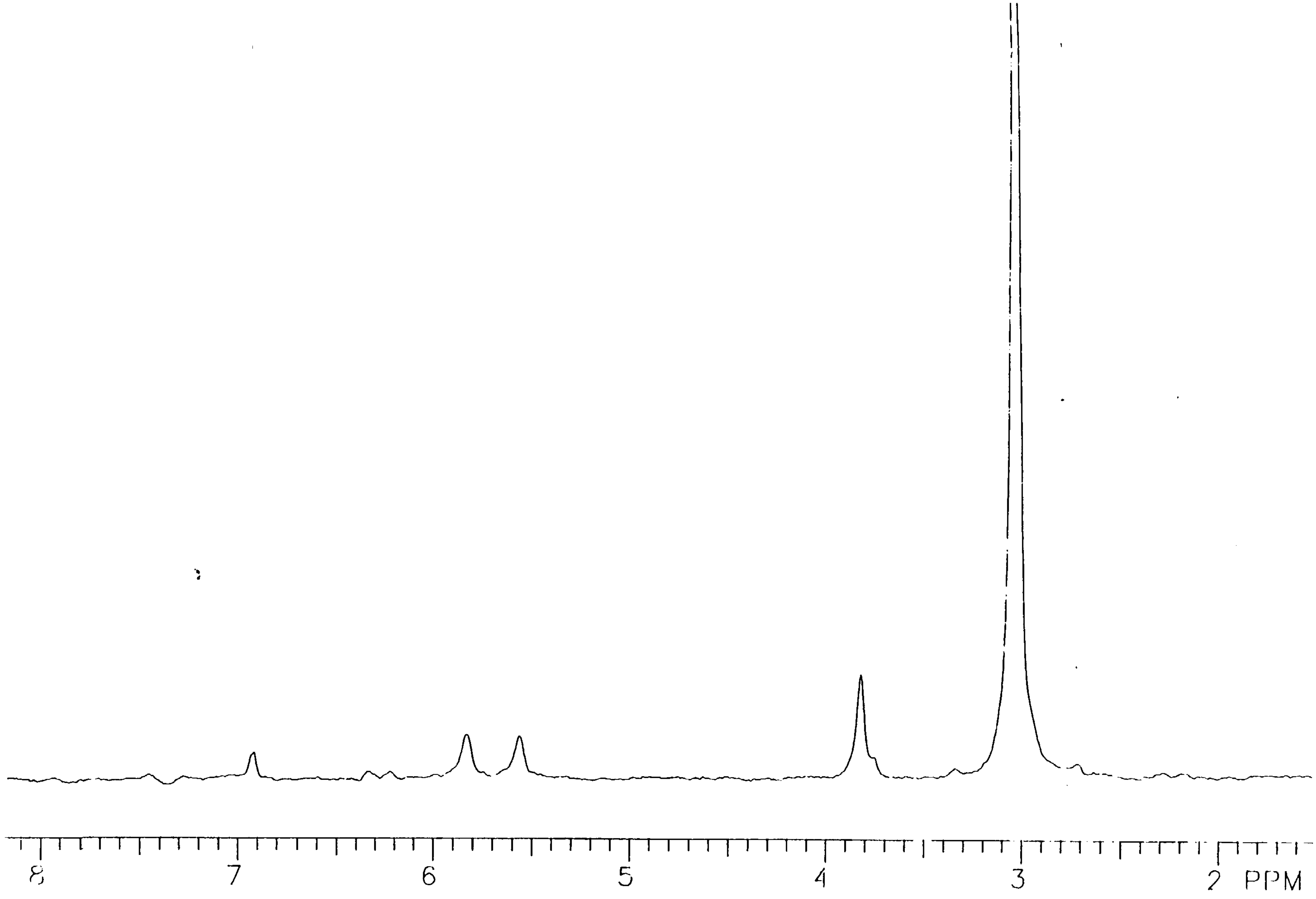


Figure 28. Proton NMR spectrum of Krytox 16256 (702 scans).

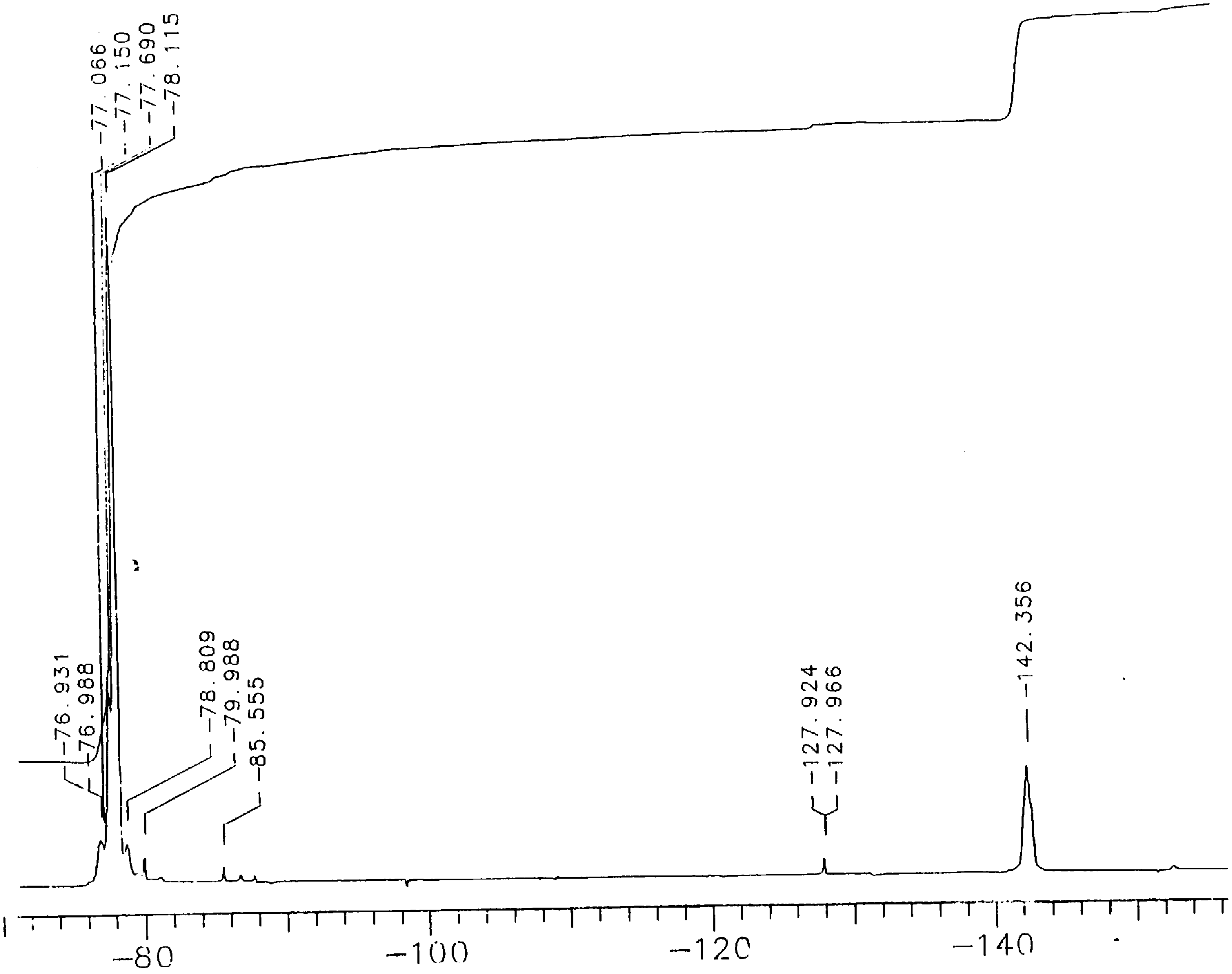


Figure 29. Fluorine NMR spectrum of Krytox 16256.

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13. ABSTRACT ***(Maximum 200 words)***

The objective of the Program was to synthesize novel degradation inhibitors for perfluoropolyalkylether fluids and to evaluate their performance as well as that of other available inhibitors. Four novel additives:
$[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]\ [(C_6H_5)_2PN]_2$,
$[C_3F_7O(CF(CF_3)CF_2O)_2C(CF_3)_2CN]\ [(C_6H_5)_2PN]_2$,
u-$[C_3F_7OCF(CF_3)CF_2OC(CF_3)_2CN]_2[(C_6H_5)_2PN]_2$ and
$C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)\ (OC_6H_5)_2$ were prepared, characterized and their thermal stabilities established. The alloys studied were: 440C steel, M-50 steel, Pyrowear 675, Cronidur 30, Ti (4Al, 4Mn), and Ti (6Al, 4V). The additives and metals were evaluated in two different lots of Fomblin Z25, in Krytox 143AC and in Krytox 16256. Phosphate esters were found to be fully effective in arresting perfluoropolyalkylether fluid's degradation at temperatures up to 300 °C over 24 h in the presence of alloys in oxygen. The overall rating of additives was: phosphates>phosphate/diester mixture>phosphine≥phospha-s-triazines.

14. SUBJECT TERMS
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