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**STUDY OF THE DEGRADATION OF TWO CANDIDATE
DIFFUSION-PUMP OILS, KRYTOX AND FOMBLIN**

Richard K. Pearson
James A. Happe
George W. Barton, Jr.

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FINAL REPORT

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OF TWO CANDIDATE DIFFUSION-PUMP OILS, KRYTOX AND FOMBLINRichard K. Pearson
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ABSTRACT

We have determined activation energies for decomposition of Fomblin HVAC 18/8 and Krytox 143AY oils (respectively 60.6 kcal/mole and 55.6 kcal/mole) in the temperature range of 325°-405°C in a monel vessel. At any temperature in this range, Fomblin decomposes 30 ± 10 times faster than Krytox. The estimated decomposition in 10 years at 250°C is 0.14% for Fomblin and 0.009% for Krytox.

With 304 stainless steel coupons present, the rate of Krytox decomposition is very nearly the same as the rate in the monel vessel. However, there is an initial inhibition of decomposition with steel present.

With aluminum coupons present, the activation energy for Krytox decreases to 23.7 kcal/mole or 33% in 10 years. This faster reaction stops abruptly after only 0.09% of the oil has decomposed. This effect was independent of the surface area of aluminum and the temperature. The recovered aluminum coupons are coated with a deposit of black material which contains graphitic carbon, CF_3COO —groups, and AlF_3 .

Although differences in the fluorine n.m.r. spectrum of different batches of Krytox are observed, there are no significant changes detected between aged and unaged oils of the same batch. HF does not react with Krytox at 405°C.

Krytox can be chromatographed in spite of its high average molecular weight (3600 amu). The chromatograph consists of an envelope of peaks from individual oligomers between 20 and 60 minutes retention time using a 50 meter Quadrex capillary column temperature-programmed to 280°C. In between each large peak in the envelope of peaks, a smaller peak about 10 to 20% of the area of the peaks on either side of it is present. In effect there is an envelope of smaller peaks under the envelope of larger peaks. GCMS showed that each smaller peak contained $\text{C}_2\text{F}_4\text{H}$ —groups while the larger peaks contained only C_2F_5 —groups. Hydrogen nmr on Krytox showed the $\text{C}_2\text{F}_4\text{H}$ —to be CF_3CHF —groups. These hydrogen containing groups possibly result from capping the oligomers of Krytox to stabilize them.

Chromatography of Fomblin gave a single broad envelope without resolved peaks. This behavior is consistent with a random copolymer.

INTRODUCTION

The Lawrence Livermore National Laboratory undertook this project at the request of the Oak Ridge K-25 staff. The goal was to investigate the stability of two perfluorinated polyethers, Fomblin* HVAC 18/8 and Krytox* 143 AY.

These oils are noted for their chemical and radiation stability. They were selected by K-25 as diffusion pump oils in the presence of HF and UF_6 at pump temperatures of 230 to 250°C and pressures of around 0.02 torr. After prolonged usage under these conditions, they observed a solids build-up of UO_2F_2 , UF_4 , and other substances. Some of the oil had disappeared and the remainder was a dark colloidal suspension which could not be centrifuged or filtered out.

As a result of these observations, LLNL was asked to study the oils. First, we were to characterize fresh and aged oils in order to be able to detect changes during the aging studies. We employed gas chromatography (GC), GC coupled to mass spectrometry (GC/MS), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), and emission spectroscopy. Solid residues on metal surfaces were examined by electron spectroscopy for chemical analysis (ESCA). Second, we were to conduct accelerated aging studies in order to estimate the service lifetime to be expected from the oils. These aging studies were to be conducted in the presence of actual diffusion pump materials such as iron, Monel, and aluminum, with their oxide coatings and with and without HF. It was decided to defer experiments in the presence of UF_6 until the methods were established and the equipment transferred to K-25. This way we could avoid the shipping problems associated with even small amounts of radioactivity. Monel was chosen as the reactor material because it is the most resistant of all common alloys to fluorine compounds.

*Fomblin is a tradename of Montedison and Krytox is a tradename of duPont.

Krytox 143 oils¹ are perfluoroalkylpolyethers with the general formula:

Fomblin oils^{2,3} differ by being copolymers of $\text{C}_3\text{F}_6\text{O}$ and CF_2O with a repeating structure of

with unspecified end groups and a molecular weight of about 2650.

The physical properties of these compounds have been investigated by Sianesi, et al.⁴ They reported that the molecules degraded by breaking the C-C bonds in the chain, after which they "unzipped" to form C_3F_6 , CF_3COF , and CF_2O in equimolar amounts. In the absence of water, these are discharged through the forepump. The physical properties of the undecomposed part were supposed to remain virtually unchanged.⁵

When we accelerated the aging by heating, no differences could be detected via nmr. The artificially aged material was thought to be less volatile but that could have resulted from the pumping on the samples that we did at 100°C to remove all volatile material from the oil.

EXPERIMENTAL

MATERIALS

Samples of new oils, both Krytox and Fomblin, were obtained both from K-25 and from the manufacturer. Samples of aged Fomblin were obtained from K-25. This Fomblin had been in service in a diffusion pump for up to 3250 hours, but there were no samples available of unused material from the same batch.

EQUIPMENT

The vacuum system in which decomposition studies were carried out is shown in Figure 1. Volumes of the various sections were calibrated by first evacuating the system and then expanding a known volume of gas into one section after another. The resulting pressure changes were simultaneously recorded. The various valved inlets permit the introduction of gases such as argon and hydrogen fluoride, and for the attachment of an infrared cell with AgCl windows. Three ion gauges are incorporated to monitor the high vacuum. The Baratron gauges are used to monitor pressure changes during decomposition experiments and to measure decomposition products.

The reaction vessel is shown in Figure 2. It also is made of Monel. It has a 2 3/4" flange and aluminum gasket at the top so that it can be cleaned and filled. It is 10" tall and has an inside diameter of 1 13/32". Thermocouples are placed so that the temperature is monitored 1 1/2" from the top in the cooling coil region, 6 1/2" from the top in the center of the cell, and 1/8" from the bottom in the liquid region.

The temperature of the decomposition cell is raised and maintained at the desired value by a surrounding oven, consisting of a cylindrical ceramic furnace. The inside diameter of the furnace is 3", the height 4", and it has a closed bottom. The cell is centered inside the furnace and separated from the bottom by an insulating spacer. It has a lid with two holes, one for the neck of the cell and the other for the thermocouple of the temperature controller. The temperature controller for the furnace itself is a Honeywell R7355 proportional controller precise to $\pm 0.1^\circ\text{C}$.

During a run the four thermocouples and the pressure are monitored and recorded at selected intervals. This is done using a Hewlett-Packard Model 3497A Data Acquisition/Control Unit driven by an HP-85 computer. Following the run, data are recalled from the magnetic cartridge and reduced on the same computer.

Infrared spectra were measured and identified using a Perkin-Elmer Model 457 Grating Spectrophotometer.

Gas chromatograms were run on a Hewlett-Packard Model 5880 Gas Chromatograph. The column was a Quadrex "007" bonded methylsilicone fused quartz capillary 50 meters long. Samples were injected in solution in trifluorotrichloroethane and eluted with helium. The injector temperature was 325°C. The initial oven temperature was 60°C rising at 4°C/min to a final temperature of 280°C. The total run time was 90 min.

Gas Chromatograph/Mass Spectrometer data were obtained on a Hewlett-Packard Model 5985 GCMS using a similar column and the same temperature schedule.

Gel permeation chromatography was done on a Waters Analytical Liquid Chromatograph 450/401.

The surface of one of the aluminum coupons used in the decomposition experiments was examined using a Hewlett-Packard Model 5950A ESCA spectrometer.

Nuclear magnetic spectra were taken using Fourier transform methods on a Nicolet Model FT-200 system operating at 200 MHz for protons and 188.2 MHz for fluorine. This spectrometer uses a superconducting magnet.

Thermogravimetric data were taken on a Perkin-Elmer Model TGS-2 system.

PROCEDURE

A typical experiment was conducted as follows:

The decomposition cell from the previous run containing vacuum over the liquid was isolated from the high vacuum system and filled with argon to atmospheric pressure. After closing the valve to the manifold the cell was removed, opened, and the oil removed. It was then thoroughly cleaned with trichlorotrifluoroethane (CCl_3CF_3), fitted with a new aluminum gasket, and resealed using 15 lb. torque. Ten ml of fresh oil were introduced through the 1/2" port in the cell top, the cell was refitted to the vacuum line, and evacuated. An initial conditioning run was carried out for each fresh batch of oil by introducing 400 torr of argon and allowing it to reflux at 405°C for about 16 hours. At the end of this overnight period the cell was allowed to cool, the decomposition gases were pumped out, and the cell was backfilled. If the experiment was to be carried out with metal coupons the argon pressure was brought to one atmosphere so that the cell could be removed from the line.

The desired weight of coupons was cleaned with trichloroethylene and absolute ethanol, and introduced through the cell top. The cell was reattached to the line and pumped overnight.

The run was started by filling the cell to 400 torr. of argon and valving it off. The furnace temperature was then raised to 25°C below the desired experimental temperature. It took about 15 minutes for the temperature to stabilize before the final increment of temperature was set on the controller. The data acquisition unit monitored the approach to temperature. When ready, the unit was switched to automatic data logging and the set of temperature and pressure points were logged at precise intervals for the balance of the run. Runs lasted between 16 hours and 7 days depending on the type of oil and decomposition conditions.

Pressure inside the cell was not allowed to exceed 760 torr. Temperature variations were $\pm 0.1^\circ\text{C}$ over periods of several hours and $\pm 1^\circ\text{C}$ over several days. The data logging program handled a maximum of 99 sets of temperature and pressure, so three or four sets were taken for each run. The timing interval could be changed as appropriate for each set. When enough points were generated to define a pressure-time table, the run was terminated by removing the furnace and cooling the cell with a stream of air. The results for a typical experiment are shown in Figure 3.

Product gases and argon were slowly pumped out of the cell through two liquid nitrogen traps in series. Pumping was first done at roughing pressure and finally at high vacuum. The control setting for the furnace was set to 100°C to warm the cell while pump-out continued.

In order to interpret the results of the decomposition experiments we have to know the stoichiometry of the products. As was reported by Sianesi, et al,⁴ the decomposition products of Fomblin are equimolar quantities of C_3F_6 , COF_2 , and CF_3COF . This was confirmed by the reaction product spectrum as shown in Figure 4 as compared to the spectra of the three product molecules, Figure 5. The IR spectrum of Krytox decomposition products (Fig. 4) is almost exactly the same, except for less COF_2 . We believe that COF_2 reacts to fluorinate the CF_3CFH - moiety, which we have shown to be present to a significant extent, consuming the COF_2 and removing it from the gaseous products. When aluminum coupons were placed in the reactor the COF_2 almost disappeared, apparently by reaction with the aluminum. Thus,

under these conditions, only two moles of gas are produced from the degradation of two polymer units rather than three. The calculation of the results with aluminum takes account of this factor.

The initial run with a fresh batch of oil usually exhibited a faster decomposition rate than subsequent runs. Since we are interested in long term stability, we have ignored all results from the initial runs.

Figure 6 is an Arrhenius plot of the data. Kinetic data are expected to follow the law

$$k = A \exp(-E_a/RT) = \text{rate of decomposition,}$$

where

E_a = activation energy,

R = gas constant, and

T = absolute temperature.

If we take the logarithm of both sides, we get

$$\log(k) = \log(A) - E_a/2.303RT$$

which is a straight line on the Arrhenius coordinates, $\log(k)$ vs. $1/T$.

Decomposition rates for Fomblin are given in Table 1. Moles of product were obtained from PVT measurements, assuming an average molecular weight of 110.7. The plots of pressure build-up versus time were all straight lines so it was not necessary to extract more than one reaction rate from the data even when aluminum coupons were present. The activation energy of 60.6 Kcal/mole was extracted by a least squares fit to the data. The two points taken with added aluminum coupons are also plotted, and do not differ significantly from the other points.

Decomposition rates for Krytox are given in Table 2. When aluminum coupons were present, there was an initial higher decomposition rate, which tailed off into the same long term rate as if the Al was not present. One run was made with stainless steel. In this experiment, decomposition was initially

inhibited, but later data returned to the usual rate. Figure 6, the Arrhenius plot, shows an activation energy of 55.6 Kcal/mole for Krytox.

These activation energies can be used to estimate the decomposition of the oils under the expected operating conditions of 250°C for 10 years. In terms of weight loss, we predict 0.009% for Krytox and 0.14% for Fomblin.

Although the initial rapid decomposition in the presence of aluminum lasts a very short time, we had to consider if it might become the dominant mode under pump conditions. We considered two possibilities, that there is an initial catalytic decomposition of Krytox that ceases when the surface of the aluminum is passivated, or, that there is a minor component of Krytox with a high decomposition rate which is quickly consumed. Two experiments lead us to the second choice. In the first, the amount of fast reaction was found to be independent of the amount of aluminum surface area exposed to the oil. 10.9 torr and 11.2 torr of products were produced in the cell by the fast reaction with 24.8 cm² and 99.1 cm² of Al present, respectively. In the second experiment, used Krytox from previous decomposition runs with aluminum was exposed to fresh aluminum, and there was no fast component to the decomposition curve (Figure 7). As a result of these experiments, we conclude that the assumption of a less stable minor component is the correct one. This less stable minor component may be the polymers containing the CF₃CHF- group. The reaction rate for the fast component is also plotted on Figure 6. It gives an activation energy of 23.7 Kcal/mole.

Hydrogen fluoride gas was added in some of the runs. Approximately 100 torr of HF was introduced into a 780 ml steel flask and allowed to stand overnight. The pressure decreased to a constant 88.5 torr and hydrogen was produced. The HF was frozen in liquid nitrogen and the H₂ pumped off. The bulb was then warmed and more HF added to bring the pressure to 105.9 torr, followed by argon to a total pressure of 801.3 torr. This stock gas is thus 13.1% HF. When it was expanded into the reaction cell the initial pressure was 493.9 torr. A decomposition run was then carried out at 645.5K for 67.4 hours. The decomposition gases were again measured by IR. No HF was consumed, and the decomposition rate was characteristic of Krytox in the absence of HF.

RECOVERY AND CLARIFICATION OF USED OIL

One question asked by K-25 was how to recover the discolored Fomblin oil recovered from clogged pumps. After filtering and centrifuging, the oils were still discolored. It was found that the color disappeared when ClF_3 was bubbled through it. NMR could see no significant change after this treatment. After a few weeks of standing, a brown filterable solid formed and floated on the surface of the initially darker oils. Emission spectroscopy and x-ray fluorescence showed this to be almost entirely sulfur, with trace amounts of the common impurities normally seen in samples. The complete emission spectroscopy report is included in Appendix I.

CAUTION

WHEN THE USED OILS CONTAINED SMALL QUANTITIES OF HYDROCARBONS, THE ClF_3 REACTION WAS ACCOMPANIED BY SMALL EXPLOSIONS OR FLASHES. PERFORMING THIS OPERATION ON LARGE BATCHES OF OIL COULD BE DANGEROUS, AND SAFETY PRECAUTIONS SHOULD BE CAREFULLY CONSIDERED BEFORE DOING SO.

DECOMPOSITION RATES

Decomposition rates were calculated by recognizing that for the slower component we were dealing with only a small fractional decomposition overall. Thus, we do not have to know the exact mechanism, but can treat it as a zero order reaction. Thus, the reaction rate is expressed as the weight of polymer unit

destroyed per unit time per 100g of sample. As reported by Sianesi, et al,⁴ this decomposes into the three molecules

The rate is calculated from the total number of moles of product gas recovered at the end of the reaction and the total duration of the run. Except when aluminum was present, an average gram molecular weight of 110.7 g/mole is applied (the average molecular weight of an equimole mixture of COF_2 , CF_3COF and C_3F_6).

Where aluminum coupons were present and little or no COF_2 could be detected in the gaseous infrared spectrum, we multiplied the moles of gas recovered by 3/2. This assumes that COF_2 had formed along with CF_3COF and C_3F_6 but that it had reacted with aluminum

The CO formed is non-condensable at liquid nitrogen temperatures and is removed along with argon when the decomposition gases are pumped through liquid nitrogen traps. When reactions with Al were run and pressure-time plots resolved into two curves, the Al portion of the pressure rise was multiplied by 3/2 and the Monel-vessel-slope-portion of the pressure rise was not.

CHARACTERIZATION OF THE OILS

Typical gas chromatograms for Krytox and Fomblin are shown in Figures 8 and 9. Since Fomblin is a random copolymer we expect the broad featureless spectrum we see. On the other hand, the oligomers of Krytox are resolved. In between each pair of large peaks is a smaller peak about

10% to 20% of the adjacent large peaks. GCMS showed that the small peaks contain C_2F_4H - groups, while the large peaks contain C_2F_5 - groups instead. See Appendix II for the complete GCMS results. Proton NMR on Krytox shows a doublet with a spin coupling constant of 53.1 Hz, indicating that this group is CF_3 -CHF- (Fig. 10). These hydrogen containing groups are reported⁶ to result from capping the oligomers to stabilize them. Proton NMR on Fomblin shows no significant hydrogen.

Samples of both oils were also analyzed by ^{19}F NMR. Typical spectra are shown in Figures 11, 12, and 13. Signals from CF- are found near -145 ppm and the CF_3 - and CF_2 - groups are found between -75 and to -90 ppm. Fomblin, but not Krytox, gives peaks in the low field region between -50 and -60 ppm. Samples of oil were compared by integrating various regions of the spectrum. One such comparison is shown in Table 3 for the two lots of Krytox of Figures 11 and 12. The principal difference is in the intensity of the singlet at -87.7 ppm. The triplet at -89.1 ppm is assigned to the CF_3 - group of the terminal C_2F_5 - group. By comparing the area under this triplet with the area in the CF- multiplet, we obtain a measure of the average polymer length, n.

$$n = \frac{3 \times \text{CF region area}}{CF_3 \text{ triplet area}}$$

For the two Krytox lots examined we found:

<u>Lot</u>	<u>n</u>	<u>Molecular Weight</u>
RKP 65-17-1	20.6	3750
RKP 65-4-3	19.95	3640

The ^{19}F spectrum of a fresh sample of Fomblin was compared with the spectrum of a sample which had had 3250 hours of service. Unfortunately, the lot

number of the used sample had not been recorded, so we do not know if they came from the same batch. The used sample showed a dark color which neither filtered or centrifuged out. Table 4 compares the two spectra. Although the same peaks are present in both spectra, the group intensities are very different. It is not possible to determine if the differences were caused by aging, existed in the original materials, or both. The observed difference was supported by gel permeation chromatography. Table 5 gives the molecular weight estimates. These are not accurate, because the column was calibrated with standards of polystyrene dissolved in toluene. No standards exist for fluoroethers dissolved in Freon 113.

A survey was made of Fomblin samples which had varying histories of use. Histories of the samples are given in Table 6 and the spectral data are given in Table 7 and Figure 14. Variations are seen which exceed experimental uncertainties, but again, no lot numbers were recorded, so the observations may just reflect differences in the initial materials.

Samples of oil which had been used in the accelerated aging tests were also examined by NMR, GC, and TGA. The ^{19}F NMR spectrum of Fomblin was unchanged. The spectrum of fresh Krytox differed from aged only in that the aged material had a decrease in a minor singlet at -85.3 ppm. The proton NMR showed a similar decrease in the signal from the protonated end groups. This suggests that the protonated molecules are less stable than the fully fluorinated ones.

TGA was used to compare fresh Krytox with a sample that had been used in the accelerated aging tests (Fig. 15 and 16). The fresh sample initially showed a more rapid weight loss, but this soon turned into the weight loss rate typical of aged samples. We ascribe this to the removal of lower molecular weight constituents by distillation during the extended heating and pumping of the aging tests.

Gas Chromatography shows a similar result. While the overall character of the spectra (Fig. 17) are similar, the aged oil shows a comparative reduction of the lower molecular weight components.

We conclude that the accelerated aging tests do not markedly change the composition of either Krytox or Fomblin. The gaseous products COF_2 , $\text{CF}_3\text{-COF}$, and C_3F_6 are the final products. We believe that the accelerated tests simulate the decomposition that is observed in real use under less adverse conditions. We cannot be totally sure of this because of the unfortunate lack of reference samples for the aged oils from K-25.

Several aluminum test plate surfaces which had been exposed to fluorinated polyethers at elevated temperatures (405°C) were analyzed by electron microprobe x-ray emission spectroscopy (EMP) and by x-ray photoelectron spectroscopy (XPS or ESCA) to characterize the dark colored surface layers that had resulted. The aluminum 2p line position was consistent with the presence of AlF_3 on the surface. The carbon 1s spectrum was consistent with graphitic carbon as well as indicative of $\text{CF}_3\text{C-}$ groups with indications of a possible $(\text{-CH}_2\text{-CF}_2\text{-})_n$ structure at a significantly reduced concentration. The oxygen 1s spectrum consisted of a complex structure of several partially resolved lines which were consistent with a $\text{CF}_3\text{C-}$ moiety. The fluorine 1s and fluorine Auger line positions and the Auger parameter information were clearly indicative of a $\text{CF}_3\text{C-}$ structure. The complete report on the analyses of aluminum test plate surfaces from Fomblin (JAH7-39-1) is given in Appendix III.

REFERENCES

1. Krytox Fluorinated Lubricants Technical Bulletin G-6. E. I. duPont de Nemours and Co. (Inc.) Petroleum Chemicals Division, Wilmington, DE, 19898, March 1, 1976.
2. Fomblin fluorinated lubricants Technical Bulletin G-6, E. I. duPont de Nemours & Co. (Inc.) Petroleum Chemicals Division Wilmington, DE, 19898, March 1, 1976.
3. A. Luches and M. R. Perrone, "Remarks on the use of Perfluoropolyether Fluids in Particle Accelerator Systems," J. Vac. Sci. Technol. Vol. 13, No. 5, 1976 p. 1097.
4. D. Sianesi, V. Zambeni, R. Fontanelli, and M. Binaghi, "Perfluoroethers: Their Physical Properties and Behavior at High and Low Temperature", Wear, 18 (1971), pp 85-100.
5. W. H. Gumprecht. 4th Intern. Fluorine Symp. Estes Park Colorado, July 1967.
6. Leo A. Wall, "Fluoropolymers," Wiley-Interscience a Division of John Wiley & Sons, Inc., New York-London-Sydney-Toronto, 1971, p. 245 .

Table 1. Thermal decomposition rate of Fomblin as a function of temperature and the effect of an aluminum surface (Al_2O_3).

Total Run Time (Min.)	$1/T$ $^{\circ}\text{K}^{-1}$	Decomp. Rate Wt. % $\times \text{sec}^{-1}$	$\text{Log}_{10}\text{Rate}$
358.5	1.5680×10^{-3}	16.6500×10^{-6}	-4.779
316.0	1.5730×10^{-3}	21.6670×10^{-6}	-4.6642
1348.0	1.6620×10^{-3}	1.3245×10^{-6}	-5.8779
219.0	1.5180×10^{-3}	67.9500×10^{-6}	-4.1678
2595.0	1.6560×10^{-3}	0.7663×10^{-6}	-6.1156
1027.0	1.5930×10^{-3}	3.8460×10^{-6}	-5.4150
1368.0	1.5974×10^{-3}	4.3183×10^{-6}	-5.3647*
325.0	1.5180×10^{-3}	42.3167×10^{-6}	-4.3735*

*24.8 cm^2 of aluminum surface area present as coupons.

Table 2. Thermal decomposition rate of Krytox as a function of temperature and the effect of aluminum (Al_2O_3)

Experiment Number	Duration of Experiment (min.)	Temperature		Decomposition Rate Wt. % x sec^{-1}	$\log_{10}$ Rate	Comment
		$^{\circ}\text{C}$	$^{\circ}\text{K}^{-1}$			
7-41	1177	404.4	1.4758×10^{-3}	9.62800×10^{-6}	-5.0164	
6-8	1300	418.0	1.4472×10^{-3}	12.12500×10^{-6}	-4.9163	
8-48	975	408.9	1.4661×10^{-3}	5.15300×10^{-6}	-5.2879	
9-50	10091	331.7	1.6532×10^{-3}	0.04638×10^{-6}	-7.3336	
10-53	5754	361.9	1.5746×10^{-3}	0.24430×10^{-6}	-6.6120	
11-55	300	374.5	1.5439×10^{-3}	9.39500×10^{-6}	-5.0271	24.8 cm^2 Al present, two rates resolved
	2900			0.67390×10^{-6}	-6.1714	
14-64	1139	326.6	1.6672×10^{-3}	2.00840×10^{-6}	-5.6972	27.7 cm^2 Al present, two rates resolved
	4779			0.03011×10^{-6}	-7.5213	
13-61	672	352.0	1.5994×10^{-3}	3.52900×10^{-6}	-5.4523	24.8 cm^2 Al present, two rates resolved
	4710			0.24687×10^{-6}	-6.6075	
17-73	922	351.6	1.6005×10^{-3}	0.59500×10^{-6}	-6.2255	24.8 cm^2 Al present, two rates estimated, oil reclaimed from Al decomp. runs
	6007			0.19910×10^{-6}	-6.7009	
18-77	5176	375.0	1.5427×10^{-3}	0.72610×10^{-6}	-6.1390	24.8 cm^2 (304) stainless steel
00-15	4041	372.3	1.5492×10^{-3}	1.77330×10^{-6}	-5.7512	HF added

Table 3. Integration of the ^{19}F spectra from two neat samples of Krytox liquids

Peak/Region (ppm)		Integral		Δ
		Lot 65-4-3	Lot 65-17-1	
-144 to -146	C-F Region	1666	1671	+0.3%
-130.2	Singlet	204	209	+2.0%
- 89.1	Triplet	251	243	-3.0%
- 87.7	Singlet	346	323	-6.6%
- 82.1	Singlet	235*	234*	0.4%
- 75 to -85	$\text{CF}_3\text{-C-CF}_2$	10000	9970	-0.3%

*These are peak heights rather than integrals.

Table 4. Integration of the ^{19}F spectra from neat samples of unused and used Fomblin liquids

Peak/Region (ppm)		Integral		Percent Change
		Fresh Fomblin	Used Fomblin	
-49.6	Broad peak	109	43	- 61%
-54.6	Doublet	223	144	- 35%
-55.7	Broad peak	70	42	- 40%
-56.4	Triplet	221	149	- 33%
-58.3	Broad peak	22	12	- 45%
-68 to -75	Multiplet	356	367	+ 3%
-78 to -84	$\text{O-C}(\text{CF}_3)\text{-CF}_2\text{-O}$	10000	10000	0%
-85 to -87	Multiplet	780	577	- 26%
-87.9	Singlet	8	38	+375%
-88.0	Singlet	42	71	+ 70%
-89.2	Triplet	31	57	+ 84%
-130.4	Singlet	57	68	+ 19%
-137 to -143	Broad Multiplet	97	95	- 2%
-143 to -148	CF region	2003	1953	- 2%

Table 5. Molecular weight estimates of Fomblin samples from gel permeation liquid chromatography measurements

Sample	M_n	M_w	M_z	MWD
Fomblin H 18/9 "New"	1173 $\pm$ 53	1771 $\pm$ 32	2144 $\pm$ 29	1.512 $\pm$ 0.042
Fomblin H 18/9 "Used"	1402 $\pm$ 89	2032 $\pm$ 27	2409 $\pm$ 20	1.453 $\pm$ 0.076

Conditions used for the analysis are:

Instrument: Waters ALC 450/401
 Columns: duPont SEC Bimodal KT-1166
 Eluant: Trichlorotrifluoroethane, Freon 113
 Flow rate: 1 ml/min
 Sample: 20 microliters of a 1% solution in Freon 113
 Detector: Differential refractive index, 32X

Table 6. Available Historical Information on Fomblin Samples Received from K-25 for NMR Analysis.

PIC	Run Hours	Gas Hours	Wt. of Extracted Lube Oil
S/N 115	2260	2010	.046
S/N 121	3832	0	0.698
S/N 124	4773	0	1.474
S/N 116	4523	0	1.483
S/N 119	329	0	1.134
S/N 125	4355	0	.926
S/N 118	5257	0	.869
 <u>P1A</u>			
S/N 109	~6200	~3400	0.873
PO 127-D	6369	4695	0.403
PO 105-D	6509	5224	.003
PO 109-D	5646	5071	0.191
0043D	69	0	0.000
0104A	7089	6821	0.293
0105B	6475	279	0.488
0101B	2249	1884	1.038

Table 7a. Repeat Measurements on Several Fomblin Samples
Showing Reproducibility of NMR Spectrum Integrations.

Peak Number	Sample 0043D				Sample L62131 #366601		Sample F107/1098 #366602		Sample 851502 #366604	
1	18	20	12	22	18	20	15	18	15	17
2	205	207	179	216	155	160	134	137	128	132
3	331	333	327	360	182	187	167	171	142	144
4	125	125	109	141	85	89	67	72	62	65
5	393	394	406	405	344	345	285	285	308	306
6	38	45	30	26	35	34	22	25	22	23
7	222	219	218	231	194	212	217	208	176	193
8	220	219	222	226	225	232	254	239	209	216
9	81	93	91	96	91	96	92	84	77	85
10	16826	16881	17634	17630	16728	16767	16823	16826	16929	16712
11	393	388	210	206	516	494	475	458	538	516
12	1043	1062	513	505	1092	1116	1095	1143	1063	1130
13	235	229	204	207	210	198	202	196	193	185
14	325	320	315	319	283	276	237	236	247	242
15	634	629	657	661	552	540	495	488	501	489
16	325	329	310	316	273	270	223	226	218	221
17	41	41	25	28	65	63	102	101	98	93
18	84	82	70	69	132	126	148	143	162	157
19	69	66	54	50	107	100	121	117	122	120
20	184	172	189	190	137	149	143	134	141	131
21	68	58	62	58	44	52	48	41	38	38
22	54	44	44	42	22	32	27	20	15	15
23	13	11	13	11	13	13	11	11	13	11
24	92	94	104	104	182	189	157	161	194	201
25	111	108	130	121	128	160	126	128	127	139
26	3493	3562	3535	3539	3430	3539	3420	3484	3470	3536
27	33	31	35	27	25	32	32	41	27	32
28	20	15	18	24	21	23	23	19	22	19
29	8	9	10	9	9	10	7	6	8	9

Table 7b. Comparison of Integrated ^{19}F NMR peak intensities for all "S/N" Fomblin Samples

Peak Number	S/N #109	S/N #115	S/N #116	S/N #118	S/N #119	S/N #121	S/N #124	S/N #125
1	14	15	25	24	18	5	18	16
2	140	190	241	238	209	2.1	227	222
3	201	333	372	373	351	3.0	384	365
4	61	109	139	138	135	1.4	143	140
5	288	407	404	405	392	4.02	413	406
6	19	34	27	27	31	1.3	28	31
7	241	230	227	220	213	2.25	217	214
8	289	251	226	220	213	2.6	220	217
9	103	116	94	92	94	1.5	99	97
10	17729	17616	17476	17562	17702	175.5	17613	17688
11	226	196	191	191	196	1.92	190	189
12	512	507	528	532	475	5.66	503	475
13	173	219	219	227	202	2.24	219	211
14	228	317	319	324	309	3.3	320	312
15	560	643	642	652	647	6.2	648	647
16	240	306	315	319	300	3.17	308	300
17	68	26	25	28	27	2.8	27	26
18	131	84	83	86	74	8.6	83	78
19	115	61	55	61	49	1	54	54
20	164	186	182	181	186	1.3	189	186
21	54	61	60	60	55	1.3	66	65
22	28	47	48	45	39	4.7	53	46
23	15	12	11	11	11	1.1	10	10
24	118	91	80	90	99	8.3	86	86
25	153	135	96	118	121	10.8	149	122
26	3470	3555	3478	3456	3501	3510	3555	3518
27	39	34	30	27	28	2.3	27	30
28	26	21	25	18	21	2.0	23	20
29	9	10	6	10	5	8	7	9

Table 7c. Comparison of Integrated ^{19}F NMR Peak Intensities
for all non "S/N" Designated Fomblin Samples.

Peak Number	Sample 0043D	Sample 105D	Sample 104A	Sample 101B
1	12	11	11	18
2	179	127	78	130
3	327	180	160	158
4	109	60	35	62
5	406	289	297	349
6	30	25	17	22
7	218	242	203	230
8	222	273	244	248
9	93	94	88	100
10	17634	17776	17802	17519
11	210	237	269	341
12	513	494	593	566
13	204	166	143	169
14	315	220	215	268
15	657	545	453	564
16	310	225	177	264
17	25	69	103	56
18	70	127	128	123
19	54	109	103	98
20	189	162	127	165
21	62	54	41	57
22	44	29	16	37
23	13	12	10	14
24	104	130	155	213
25	133	150	137	102
26	3535	3482	3470	3562
27	35	38	28	45
28	18	28	21	24
29	10	8	7	11

APPENDIX I -24-
SPECTROCHEMICAL ANALYSIS REPORT
LLL - LIVERMORE -- ANALYTICAL LABORATORY

Plate No.: 4022

Sample No.:

SS-2462

Submitted By:

D. P. Farson

Date Received:

4/12/82

Date Reported:

5/4/82

Analyst:

B. Armstrong

Sample Description:

#1) HVAC pure oil

#2) " after 3,249 hrs

#3) " " cleaning

Key: The elements listed are the only ones looked for. Values given are estimates; the majority of the values are expected to be within plus or minus a factor of two of the true value. For elements which are not detected (nd), the number cited is the concentration that must be present to confirm the element.

Analysis:

	#1)	#2)	#3)
Si	20 ppm by wt.	40 ppm by wt.	30 ppm by weight
U	nd < 4	4	± 4
Al	2	6	6
Fe	0.6	2	3
Ti	0.6	2	1
Ca	0.5	0.7	3
B	0.4	0.6	3
Ag	0.06	0.02	0.1
Pb*	0.06*	nd < 0.04	0.3*
Ni	0.06	0.1	0.1
Mg	0.04	0.06	0.7
Mn	nd < 0.04	0.06	nd < 0.04
Cu	0.02	0.1	0.2

The following elements were not detected:

< 4 Na

< 1 Nb, Sb, Zr

< 0.4 Ba, Pb, V, Zn

< 0.1 Bi, Cd, Sn

< 0.04 Co, Cr, Mo, Sr

* Possible contamination during sample preparation.

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APPENDIX II

26356

June 9, 1982

GC/MS of KRYTOX

GC/MS of fresh KRYTOX has been done with GC conditions identical to those used by J. Clarkson. The mass spectrometer scans only from 41 to 1000 amu, and is unable to observe the parent ion of the eluting species of the KRYTOX polymer mixture. The capillary column exits into a comparatively large chamber where the fragmentation takes place. The scan time and the ion chamber volume account for the lower resolution obtained in GC/MS as compared to GC with a FID detector. The total ion chromatogram appears to be a superposition of a major and a minor series of eluting species. The individual mass spectra of the major series of compounds are very similar as are those of the minor series. The two series differ most in the 147 mass (C_3F_5O), which is more intense in the minor series.

Some hydrogen containing mass fragments have been found in the GC/MS of fresh KRYTOX and the sample JAH-12-58 (Intermediate Volatiles of KRYTOX Decomposition). The mass fragments are: 433 ($C_8HF_{16}O_2$); 267 ($C_5HF_{10}O$); 151 (C_3HF_6); and 101 (C_2HF_4). The 433, 267 and 101 masses are correlated and relate to the minor series of GC peaks in the total ion chromatogram. The 151 mass ion chromatogram seems similar to the total ion chromatogram. The 267, 151 and 101 masses are also seen in the GC/MS of JAH-12-58 in greater intensity than in fresh KRYTOX, suggesting that the polymer specie containing hydrogen may be more susceptible to decomposition. The 267 and 101 masses are again correlated, with the 151 mass primarily in different decomposition products.

Russell Sanoorn
Analytical Section

KRYTOX MASS SPECTRA

<u>Mass</u>	<u>Assignment</u>
617	$C_4F_{23}O_3$
517	$C_9F_{19}O_3$
501	$C_9F_{19}O_2$
479	$C_9F_{17}O_3$
433	$C_8HF_{16}O_2$
401	$C_7F_{15}O_2$
379	$C_7F_{13}O_3$
351	$C_6F_{13}O_2$
335	$C_6F_{13}O$
313	$C_6F_{11}O_2$
297	$C_6F_{11}O$
285	$C_5F_{11}O$
267	$C_5HF_{10}O$
263	$C_5F_9O_2$
235	C_4F_9O
213	$C_4F_7O_2$
197	C_4F_7O
185	C_3F_7O
169	C_3F_7
151	C_3HF_6
150	C_3F_6
147	C_3F_5O
131	C_3F_5
119	C_2F_5
101	C_2HF_4
100	C_2F_4
97	C_2F_3O
85	CF_3O
69	CF_3

NAME KRYTON PRESS, 100 WINDY HILL, ARLING, 3 1/2 MI
NISC 3 12-54, 10 12-54, 12 12-54, 12 12-54, 12 12-54

SRB 1001

10 1/2

TI

15.10% (PECH) IN FREON-17, CAPILLARY, 1.0L
4-16-82, TO EV, 4 DEG MIN RAMP, CPN 38

FRN 7001

1F1.T01 SPESH1 IN FROTH-17, CAPILLARY, 2 UL
4-16-87, 70 EV, 4 DEG MIN RAMP, CEN 38

FRN T001

IRATO SPECIES IN FRESH-TRAPPLERS, 1.0.01
4-14-82, 70 E., 4 DEG MIN PAMP, LEN 88

7-88 1001

1P.TOT: (FRESH) IN FREON-TP, CAPILLARY, 3 UL
4-16-82, 70 EV, 4 DEG MIN RAMP, CPN 38

FRN 7001

12 TO 1 (F=ELH) IN FROST-IT VORILLAP, 1.0 L
400.00, TO EQ, 4 DEG MIN PAMP, CAN 39

1230 7001

PERTON (FRESH) IN FREON-113, CAPILLARY, 2.0 UL
4-18-82, 70 EV, 4 DEG/MIN FAMP, OFN 88

FRN 7001

10. TO: FREON IN FREON-TO CAPILLARY, 1.0 L
4-10-10, 10 EV, 4 DEC MIN FAMP, OFH 00

1231 7731

1.01701 (FRECH) IN FRECH-TF. CAPILLARY, 2 UL
3-16-68, TO EV, 4 DEG MIN RAMP, CRN 38

FRN 7001

NMR: 5.70 PRECH-10 PRECH-10, CAPILLARY 2.0 ML
 MISC: 4-1-60, 0.001, 4 DEG MIN. RAMP, 2000

FRN 7001

C_2F_3 68.7
 69.6

C_2F_3O 96.7
 97.6

C_2F_5 118.7
 119.6

C_3F_5O 146.7
 147.6

C_3F_7 168.7
 169.6

C_5F_{10} 284.7
 285.6

C_6F_{10} 334.7
 335.6

TI

NAME: A TON (FRECH) IN FREON-TP, CAPILLARY, 3.0L
 MISC: 4-16-ED, TO E, 4 DEG MIN FLOW, 0.01 IN

PRR 7901

NAME: PUTO (FRECH) IN FREON-TP, CAPILLARY, 1 UL
NISC 4-16-82, 70 EV, 4 DEG MIN PAIRF, CPM 35

FRM 7001

NAME: 2--13-EL-INT. VOLATILE, 1A TO: ISO... 1 UL
MISC: -- 10.1A C-5002, PAGE 8 BEG MIN: 0.00 13

FRW 6935

NAME JAW-10-55, INT. VOLATILES (EXTRACT DEC. 1, 55)
 RTSC 3-4-55, IN CHECKS, PAMP & REG MIN, CAN 15

FRN 1955

Interdepartmental letterhead

Mail Station L 311

Ext 2-6895

February 22, 1982

TO: R. Pearson

FROM: J. W. Fischer and D. D. McCoy

SUBJECT: The Analysis of Aluminum Test Plate Surfaces. (#B-194) JAH 7-17-1

We have examined several samples of aluminum plate to determine the composition and chemistry of the surface deposits present on these metallic platens. The samples, which had been exposed to fluorinated poly-ethers at elevated temperatures, were analyzed by electron microprobe x-ray emission spectroscopy (EMP) and by x-ray photoelectron spectroscopy (XPS or ESCA) to characterize the dark colored surface layers that had formed as a result of this treatment.

Initially, a sample with a relatively dark surface as well as one with minimal discoloration, were examined in the EMP, both before and after washing with Freon TF. No differences in elemental composition within the first 1 μm of the sample surfaces were noted. However, each of the samples contained relatively large quantities of fluorine with lesser amounts of carbon and oxygen. In addition, the fluorine and carbon signals from the lighter colored sample were significantly less intense than those of the dark sample; however, the situation was reversed for oxygen, where the lighter sample exhibited a substantially stronger signal. This relationship was apparent both before and after the Freon wash. These observations are consistent with the formation of deposits rich in fluorine and carbon on both of the samples, with the lighter sample possessing an apparently thinner layer thus permitting the detection of greater quantities of the oxygen that is present on all aluminum surfaces as Al_2O_3 .

The predominant effect observed as a result of the Freon TF wash was a reduction in the intensities of the carbon, fluorine, and oxygen signals. This was not an unexpected result, as quantities of the original oil that remained on the surfaces of the samples had been removed by the Freon TF, thus

University of California

Lawrence Livermore
National Laboratory

reducing the concentration of these elements on the aluminum surfaces. However, oxygen experienced the greatest reduction with significantly smaller changes noted in the carbon and fluorine signals. These results are consistent with the formation of residues containing greater concentrations of carbon and fluorine than did the original oil which was removed by the Freon. These excesses could exist as a carbonaceous residue and perhaps as fluorine bound to the aluminum.

A darkened platen, which had been washed in Freon TF, was then examined by ESCA. The surface of this sample was initially analyzed under low resolution conditions to determine its elemental composition. This was followed by the generation of high resolution spectra of the fluorine Auger transitions and the F 1s line, the O 1s lines, the C 1s lines and the Al 2p line. The results of the initial multi-element analysis were not unexpected. Fluorine, carbon, and oxygen were the major elements noted with small quantities of sodium, nitrogen, calcium, and chlorine also detected. An aluminum signal was also found, but at a relatively low intensity as the aluminum surface was rather well covered by the dark material rich in fluorine and carbon.

Examination and analysis of the high resolution spectra yielded chemical state information on the major elements of interest. The aluminum 2p line position was consistent with the presence of AlF_3 on the sample surface. The carbon 1s spectrum was rather complex; the various line positions were indicative of substantial graphitic carbon, and as well, there was strong evidence of $\text{CF}_3\text{-C(=O)-}$ groups with indications of a possible $(-\text{CH}_2\text{-CF}_2-)_n$ structure at a significantly reduced concentration. The oxygen 1s spectrum consisted of a complex structure of several partially resolved lines. Although it was difficult to make definitive assignments to the various lines, the structure observed was not inconsistent with a $\text{CF}_3\text{-C(=O)-}$ moiety. The fluorine 1s and fluorine Auger line positions and the Auger parameter information their combination generated, were clearly indicative and characteristic of a $\text{CF}_3\text{-C(=O)-}$ structure.

The EMP and ESCA data thus indicate the presence of a layer of residual material formed as a result of the high temperature degradation of the fluorinated poly-ether oil. This process apparently generated a residue with

a carbonaceous component as well as trifluoroacetate species as previously described. In addition, the surface of the aluminum was apparently fluorinated, forming aluminum fluoride during the generation of the residue. As well, the carbonaceous component probably resulted in the black coloration observed on the surfaces of most of the aluminum test plates.

James Tischer

Figure 1. Monel line for K-25 diffusion pump oil studies.

Figure 2. Monel reactor for K-25 diffusion pump oil decomposition studies.

Figure 3. Run 11-55 pressure vs. scan number and temperature vs. scan number. (Interval between scans is 15.00 min.)

Figure 4. Infrared spectrum of decomposition gases of Fomblin (top) and Krytox (bottom). 7.0 cm cell.

THE INFRARED SPECTRA OF FLUOROCARBONS

Figure 5. The infrared spectra of individual decomposition product molecules.

Figure 7. Comparison of two Krytox decomposition runs with 24.8 cm^2 of aluminum at 352°C . Top experiment (JAH 17-73) with Krytox reclaimed from aluminum runs; Bottom experiment (JAH 13-61) with fresh conditioned Krytox.

Figure 8. Chromatogram of aged Krytox oil (JAH13-61) from a 50 meter Quadrex 007 column.

Figure 9. Chromatogram of fresh Fomblin oil from a 50 meter Quadrex 007 column.

Figure 10. Proton NMR spectrum of aged Krytox (JAH-12-49) run at 200 Mhz on a 25% solution in 1,1,2-trichlorotrifluoroethane. Shifts in ppm vs. tetramethylsilane.

Figure 11. Fluorine-19 NMR spectrum of fresh Krytox 143AY Lot 2 run neat at 188.233 MHz. Chemical shift scale in ppm vs. CFCl_3 .

Figure 12. Fluorine-19 NMR spectrum of fresh Krytox 143AY Lot 12A run neat at 188.233 MHz. Chemical shift scale in ppm vs. CFCl_3 .

Figure 13. Fluorine-19 NMR spectrum of fresh Fomblin run neat at 188.233 MHz.
Chemical shift scale in ppm vs. CFCl_3 .

Figure 14. Numbering of peaks used to compare the ^{19}F NMR spectra of Fomblin oils. The triplet defined as 0.0 Hz has a chemical shift of 89.116 ppm vs. a CFC_3 reference.

Figure 15. Thermogravimetric measurements on fresh Krytox and on Krytox after use in accelerated aging studies.

Derivative: .2 MG per Minute per Inch

Figure 16. Thermogravimetric measurements on fresh Krytox and on Krytox after use in accelerated aging studies - derivative presentation.

FLAME IONIZATION DETECTOR RESPONSE

Figure 17. Comparison of gas chromatograms of fresh Krytox and of two different samples of Krytox after use in accelerated aging studies.