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NASA Technical Memorandum 106659

Thermal-Oxidative Pretreatment and Evaluation of Poly(Hexafluoropropene Oxide) Fluids

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Prepared for the
Tribology Conference
cosponsored by the Society of Tribologists and Lubrication Engineers
and the American Society of Mechanical Engineers
Lahaina, Hawaii, October 16–19, 1994

(NASA-TM-106659) THERMAL-OXIDATIVE PRETREATMENT AND EVALUATION OF POLY (HEXAFLUOROPROPENE OXIDE) FLUIDS (NASA. Lewis Research Center) 20 p

N94-37300

Unclas

G3/27 0017064

National Aeronautics and
Space Administration

THERMAL-OXIDATIVE PRETREATMENT AND EVALUATION OF POLY(HEXAFLUOROPROPENE OXIDE) FLUIDS

by

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ABSTRACT

Two commercial poly(hexafluoropropene oxide) fluids were thermally pretreated at 343 °C in pure oxygen. IR and NMR spectra indicate that this pretreatment was effective in removing hydrogen end-capped impurities. Decrease in the quantity of volatile material produced during thermal oxidative decomposition and increase in the thermal decomposition temperature indicated improvement in the stability of the fluids. However, this pretreatment failed to render the fluids completely stable in oxidizing atmospheres at 316 °C in the presence of metal alloys.

INTRODUCTION

Perfluoropolyalkylethers (PFPAE) represent a class of liquid lubricants which have been used for space applications for over 30 years (1), (2). In addition, these fluids are promising candidates for high temperature aeronautical applications (3) - (5). One member of this class based on poly(hexafluoropropene oxide)(HFPO) has been commercially available for many years (6).

Poly(HFPO) fluids have been studied extensively. These studies include: thermal stability (7), oxidative stability (8), stability in the presence of Lewis acids (9) - (13), viscoelastic behavior (14), elastohydrodynamic behavior (15), pressure-viscosity characteristics (16), time-of-flight secondary ion mass spectroscopy (17), (18), electron beam (19) and x-ray damage (20), surface migration (21), and conformation (22) and tribochemical degradation (12), (23), (24).

Thermal stability, in the absence of catalytic surfaces and oxygen, for poly(HFPO) fluids has been shown to range from 356 to 376 °C depending on molecular weight (7). Although these stabilities are similar to other members of the PFPAE class, they certainly do not represent the ultimate stability of the poly(HFPO) polymers. For example, Gumprecht (25) has reported thermal stabilities for very pure research grade HFPO polymers of 410 °C using an isoteniscope. This 30 to 50 °C difference has usually been attributed to the presence of small amounts (ppm) of thermally labile impurities. These impurities may take the form of hydrogen end-capped chains, peroxides, carbonyl groups, or other arrangements not represented by the usual HFPO structure.

Of all of these impurities, hydrogen end-capped chains ($-OCHFCF_3$) are most prevalent. This group is easily detected by Fourier Transform Infrared Spectroscopy (FT-IR) (18), proton Nuclear Magnetic Resonance (NMR) (26), and Time-Off-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) (18). Typically, commercial poly(HFPO) fluids contain from 1 to 5 ppm by weight of hydrogen. Although this appears to be a rather small amount, it does represent approximately 1 to 3 percent of the chains, depending on molecular weight.

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Stabilization of poly(HFPO) fluids by removing these hydrogen end-capped chains appeared to be a viable procedure. These chains can be removed by exhaustive fluorination or by simply treating the fluid at high temperature with oxygen (8). However, this earlier work (8) did not address the structural changes taking place during pretreatment and only involved one batch of fluid (MLO–71–6).

Therefore, the objective of this study was to thermally pretreat two new batches of poly(HFPO) fluids in oxygen in order to determine if pretreatment results in more stable fluids in the presence of catalytic surfaces for currently produced materials. In addition, proton NMR, F^{19} NMR, and FT-IR were used to determine structural changes. Improvement in stability was determined by measuring the volatiles produced during thermal-oxidative degradation, and confirmed by measuring the thermal decomposition temperature (T_d) with a tensimeter (7).

EXPERIMENTAL

Fluids

Two commercial poly(HFPO) fluids, 143AC (Batch 53538-29-2) and 143AB (Batch 42420-13), were tested. Henceforth, these fluids will be referred to as AC and AB. The fluids had essentially an identical chemical structure but differed in molecular weight and viscosity (Table 1, Footnote 2).

Thermal-Oxidative Pretreatment

Fluids (~28 to 31 g samples) were stabilized by heating in oxygen at 343°C for the time periods shown in Table 1 (Tests 3, 4, 8, and 9). Duplicate pretreatments of the fluids were performed in order to assure adequate oxygen supply and to demonstrate test repeatability (e.g. Tests 3 and 4). The pretreatment was conducted in two steps (a and b) with data obtained after each step. Data are reported in Table I.

Thermal-Oxidative Degradation Apparatus and Procedure

Success of the pretreatment was evaluated by conducting thermal-oxidative degradation tests with Ti(4Al, 4Mn) alloy in oxygen at 316 °C for 24 hr and comparing the results to those obtained for the untreated fluids.

The thermal-oxidative degradation apparatus appears in Fig. 1. In a typical experiment the fluid was introduced into the degradation tube which was then evacuated and filled at a known temperature with oxygen. Since the apparatus was calibrated and the fluid volume measured, the quantity of oxygen introduced was exactly known. The degradation tube was then inserted into a box furnace for a specified time; throughout this exposure the temperature was continuously recorded. After removal from the furnace the tube was allowed to cool to room temperature, attached to the high-vacuum line, and opened. The liquid-nitrogen condensibles, which were volatile at room temperature, were collected and weighed. The fluid residue itself was weighed and, in some cases, subjected to viscosity determinations. The results are summarized in Table 1.

Metal catalysts were in the form of disks, 9.5 mm o.d., 3.2 mm i.d., and 0.94 to 1.27 mm thick. Prior to testing, the metal disks were polished using finishing paper followed by open-coated silicon carbide paper grades 400 and 500A. Subsequently, the disks were washed in trichlorotrifluoroethane (TCF), dried, weighed, and suspended in the test apparatus. For more details on this test procedure, refer to Ref. 8.

Thermal Stability Apparatus and Procedure

Recently, a thermal stability apparatus (computerized tensimeter) was used to compare stabilities of a variety of PFPAE fluids (7). This device is particularly sensitive to low impurity levels. Therefore, thermal decomposition temperatures (T_d) were determined for the fluids after treatment and compared to those of the untreated fluids in order to determine the extent of improvement in thermal stability due to removal of impurities.

The tensimeter measures isothermal rates of pressure rise (during a 144 second time interval) from which thermal decomposition temperatures (T_d) (in the absence of oxygen and catalytic surfaces) are determined. Test repeatability is ±2 °C. T_d is defined as the temperature at which log dP/dt equals 0.3. A schematic representation of this device is shown in Fig. 2. The device consists of a sample cell assembly, an oven, a temperature programmer, temperature and pressure measuring components, and a data acquisition system. A detailed description of this apparatus and procedure appears in Ref. 7. A typical example of the determination of T_d of a poly(HFPO) fluid appears in Fig. 3.

Analysis

Proton Nuclear Magnetic Resonance (200 mHz) (NMR) spectra were obtained on 40 percent solutions of the fluids in TCF. All chemical shifts are relative to TMS (tetramethylsilane) at 0 ppm. ^{19}F NMR spectra

(188 mHz) were obtained on 40 percent solutions of the fluids in C_6F_6. Chemical shifts are reported relative to fluorotrichloromethane at 0 ppm. Transmission FT-IR spectra were obtained on neat samples in a 1 mm cell. The lower limit of detectability of carbon-hydrogen species is 1 ppm.

RESULTS AND DISCUSSION

AC Fluid

The AC fluid, as received, was unstable as indicated by the relatively large amount of volatile material produced in the presence of Ti(4Al, 4Mn) alloy in oxygen at 316 °C in 24 hr (231 mg/g, Test 1), and the relatively low thermal decomposition temperature (369 °C) compared to 410 °C observed for highly purified HFPO polymers by Gumprecht using an identical technique. Therefore, duplicate samples of AC fluid were treated at 343 °C with oxygen in an attempt to improve the stability (Tests 3 and 4). The "pretreatment" was conducted in two steps of 192 hr (a) and 96 hr (b), resulting in a total treatment time of 288 hr. The yield of volatile material after the first step was 43.6 mg/g (Test 3a.) It should be noted that volatiles were not measured for test 4a after the 192 hr treatment. However, the weight loss data for the duplicate samples (Tests 3a and 4a) corresponded closely, demonstrating good repeatability. The low volatile production, 2 mg/g, following the 96 hr treatment (Test 3b and 4b), indicated completeness of the operation. The stability of the fluid was then determined.

Exposure of the fluid to Ti(4Al, 4Mn) alloy at 316 °C (Test 5) resulted in production of 134 mg/g of volatile material, a reduction of 42 percent compared to 230 mg/g for the untreated fluid (Test 1). This improvement in stability is also confirmed by the accompanying increase in T_d from 369 to 382 °C. However, production of 134 mg/g of volatile material in Test 5 is surprisingly high when compared to MLO-71-6, a well studied poly(HFPO) fluid which, after a similar pretreatment, was stable at 316 °C (4.5 mg/g) in the presence of titanium alloy and oxygen (8). In addition, the T_d of 382 °C is still well below the 410 °C observed by Gumprecht. Why is the treated fluid not more stable?

At this stage, two potential explanations can be advanced: either the hydrogen terminated chains were not completely removed or some other unusual and unstable structural arrangement was present in this fluid which was not present in the MLO-71-6 fluid. IR and NMR spectra may help to distinguish between these two possibilities.

The ^{1}H NMR spectrum of the AC fluid as received is shown in Fig. 4 (274 scans). The presence of hydrogen is evident by the doublet centered at 5.85 ppm. Following the treatment with oxygen at 343 °C for 288 hr, no peaks in the 5.7 to 6.0 ppm region were observed after 752 scans (Fig. 5). A similar loss of C-H absorption bands was observed in the 3000 cm^{-1} region of the infrared spectra (Fig. 6). Based on this data, the treatment was effective in the removal of hydrogen (or rather the removal of the hydrogen terminated chains) to less than the 1 ppm limit of detectability. It should be noted that, based on the infrared absorption in other specific group regions before and after treatment, no chemical change in the fluid itself occurred due to the treatment. This is further supported by the lack of change in the viscosity data (Test 3b).

Figures 7 and 8 present ^{19}F NMR spectra of the AC fluid as received, and after treatment, respectively. These were compared to the ^{19}F spectrum of MLO-71-6 (Fig. 9). The main difference between the AC fluid, both as received and treated, and MLO-71-6 is the small, yet distinctive peak at -76.6 ppm. Based on ^{19}F NMR spectral study of experimental PFPAE fluids, this peak may be due to a linkage of the general structure $-O\underline{CF}_2CF(CF_2OR_f)OCF(CF_3)CF_2-$. Specifically, the resonance at -76.6 ppm is due to the underlined CF_2 adjacent to the CF having the $-CF_2OR_f$ side chain. It should be mentioned that Kasai et al. (9) assigned a -77.0 ppm resonance to $FCO-\underline{CF}_2-O-$ and a signal at -76.5 ppm to CF_3CO_2H (27).

However, the signal at -76.6 ppm in the spectra of the AC fluids cannot be due to fluorines on a carbon adjacent to a carbonyl group because of the absence of carbonyl absorption bands in the 1600-1800 cm^{-1} region of the infrared spectrum (Fig. 10). This conclusion is supported by the absence of resonances in the ^{19}F NMR spectra at -12.7, 13.0 and 23.0 ppm due to the fluorine attached to the carbonyl carbon. (The other complex resonances in these fluids, centered around -78 ppm, are due to $-OCF(\underline{CF}_3)-$ and $-CF_2-O$ groupings (28).

Therefore, the IR and NMR spectra indicate that the residual instability in the treated AC fluid is not due to the presence of traces of hydrogen end-capped chains, but may be due to the presence of chains containing groups, such as $-OCF_2CF(CF_2OR_f)OCF(CF_3)CF_2-$, which are not represented by the basic poly(HFPO) structural formula.

AB Fluid

The AB fluid was treated and analyzed similarly. The fluid, as received, was even less stable than the AC fluid as indicated by the larger amount of volatile materials produced (277 mg/g) when exposed to the titanium alloy in the presence of oxygen at 316 °C for 24 hr (Test 2) and by the lower T_d (354 °C). Treatment of duplicate samples of the AB fluid in two steps at 343 °C with oxygen over 353 hr, using the same procedure as that employed for the AC fluid, gave similar weight losses, demonstrating good repeatability (Tests 8a and 9a). In the first 257 hr, 40.5 mg/g were obtained (Test 8a); in the subsequent 96 hr, only 2.0 mg/g were collected (Test 8b, 9b), indicating completeness of the pretreatment.

Following the 353 hr treatment, the stability of the fluid in the presence of a catalytic surface was determined. The volatiles produced in the presence of the titanium alloy amounted to 55 mg/g (Test 10), a reduction of 80 percent compared to the untreated fluid (Test 2). A sharp increase in the T_d from 352 to 383 °C confirms this improvement in thermal-oxidative stability. However, a significant degree of instability still remains. Again, the IR and NMR spectra are informative.

The ^{1}H NMR spectrum of the fluid as received (Fig. 11), shows the typical doublet centered at 5.85 ppm due to the presence of the hydrogen-terminated chains. The absence of protons in the treated fluid is shown by the ^{1}H NMR spectrum presented in Fig. 12 (800 scans). Loss of C-H absorption is also observed in the 3000 cm^{-1} region of the IR spectra. The ^{19}F NMR spectrum of the AB fluid (Fig. 13) is essentially identical to that of AC fluid. However, here the resonance at -76.6 ppm is just barely visible as a shoulder. The assumption that this resonance may be due to the impurity causing the fluid's instability is supported by formation of a significantly smaller quantity of volatile products (a measure of the degradation extent) in the AB fluid (Test 10) compared to the AC fluid (Test 5) for treated materials. Again, IR and NMR spectra indicated that the residual instability is not due to the presence of hydrogen-end capped impurities.

CONCLUSIONS AND SUMMARY

Thermal oxidative treatments of poly(HFPO) fluids AC and AB were effective in removal of the proton-containing impurities. The treatment, however, failed to render the fluids stable in oxidizing atmospheres and elevated temperatures (316 °C) in the presence of a titanium alloy, although the degree of degradation was reduced.

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Table 1

THERMAL OXIDATIVE TREATMENT OF POLY (HFPO) FLUIDS[1]

Test number	Fluid type	Quantity, g	Temperature °C	Time, hr	Metal coupon	Weight loss		Volatiles		Viscosity[2]
						g	mg/g	mg	mg/g	100 °C, cSt
1	AC	4.99	316	24	Ti(4Al,4Mn)	0.99	198.4	1154.4	230.5	[3]N.D.
2	AB	5.15	316	24	Ti(4Al,4Mn)	1.28	248.5	1425.0	276.7	N.D.
3a	AC	28.13	343	192	NONE	1.03	36.6	1227.4	43.6	N.D.
4a	AC	28.05	343	192	NONE	1.17	41.7	N.D.	N.D.	N.D.
3b	AC	27.10	343	96	NONE	0.12	4.4	58.5	2.2	23.16
4b	AC	26.88	343	96	NONE	0.09	3.3	63.2	2.4	N.D.
5	AC	3.07	316	24	Ti(4Al,4Mn)	0.31	101.0	412.7	134.4	N.D.
3c	AC	19.11	316	72	M-50	0.30	15.7	366.9	19.2	22.82
4c	AC	26.84	316	72	M-50	0.12	4.5	115.4	4.3	N.D.
6	AC	1.84	316	24	Ti(4Al,4Mn)	0.22	119.6	291.5	158.4	N.D.
7	AC	1.87	316	24	Ti(4Al,4Mn)	0.31	165.8	347.8	186.0	N.D.
8a	AB	29.81	343	257	NONE	1.08	36.2	1207.9	40.5	N.D.
9a	AB	31.11	343	257	NONE	1.02	32.8	N.D.	N.D.	8.92
8b	AB	28.73	343	96	NONE	0.10	3.5	57.3	2.0	N.D.
9b	AB	30.09	343	96	NONE	0.09	3.0	69.5	2.3	N.D.
10	AB	2.03	316	24	Ti(4Al,4Mn)	0.12	59.1	111.1	54.7	N.D.

[1] All tests were performed in an atmosphere of pure oxygen (approximately 5.3×10^4 Pa) at the denoted temperature and period of time.

[2] Viscosity at 100 °C after test. Viscosity of AC (Batch 53538-29-2) as received was 22.60 cSt at 100 °C. Viscosity of AB (Batch 42420-13) as received was 8.86 cSt at 100 °C.

[3] N.D. = Not Done.

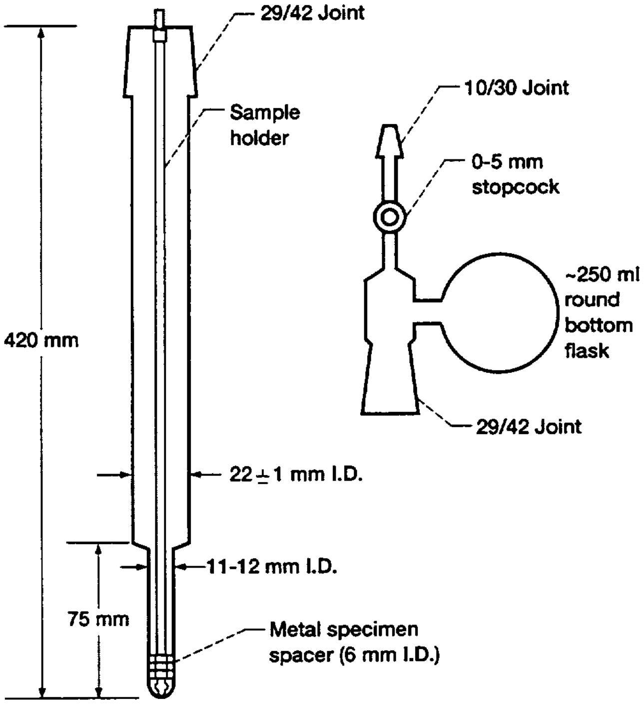


Figure 1.—Thermal-oxdative degradation apparatus.

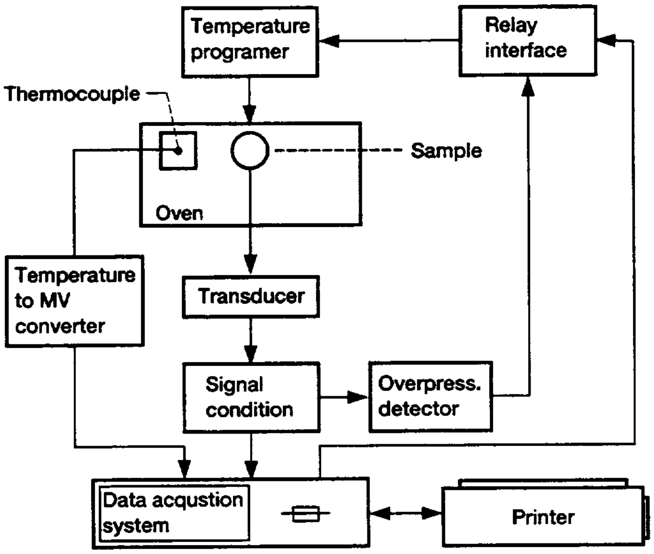
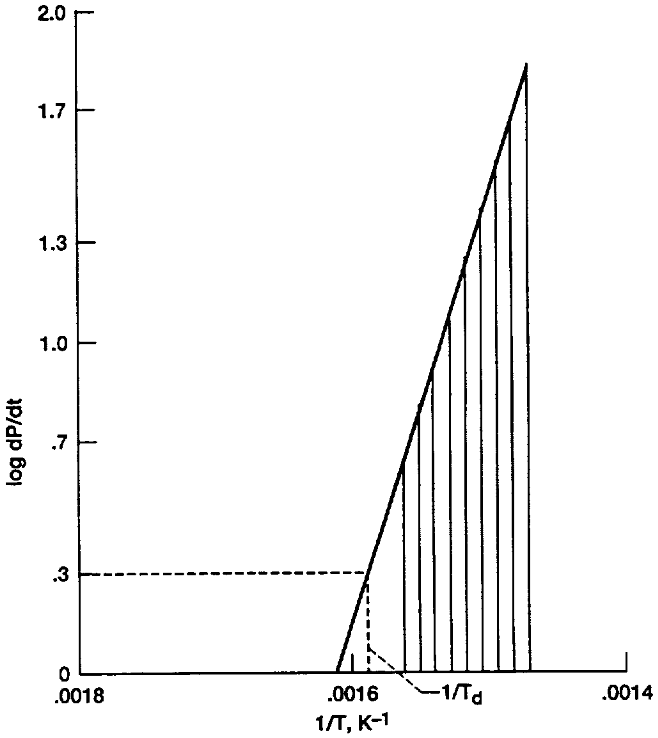


Figure 2.—Schematic diagram of thermal stability apparatus (tensimeter).



Number	Temperature, °C	dP/dt	log, dP/dt
1	365.0	4.338	0.6373
2	370.2	6.074	.7834
3	375.1	7.809	.8926
4	380.3	12.14	1.0845
5	385.1	15.61	1.1936
6	390.4	25.16	1.4007
7	395.5	34.70	1.5404
8	400.3	48.59	1.6865
9	405.5	72.02	1.8574

T_d = 355.7 °C

Figure 3.—Determination of T_d for a poly(HFPO) fluid.

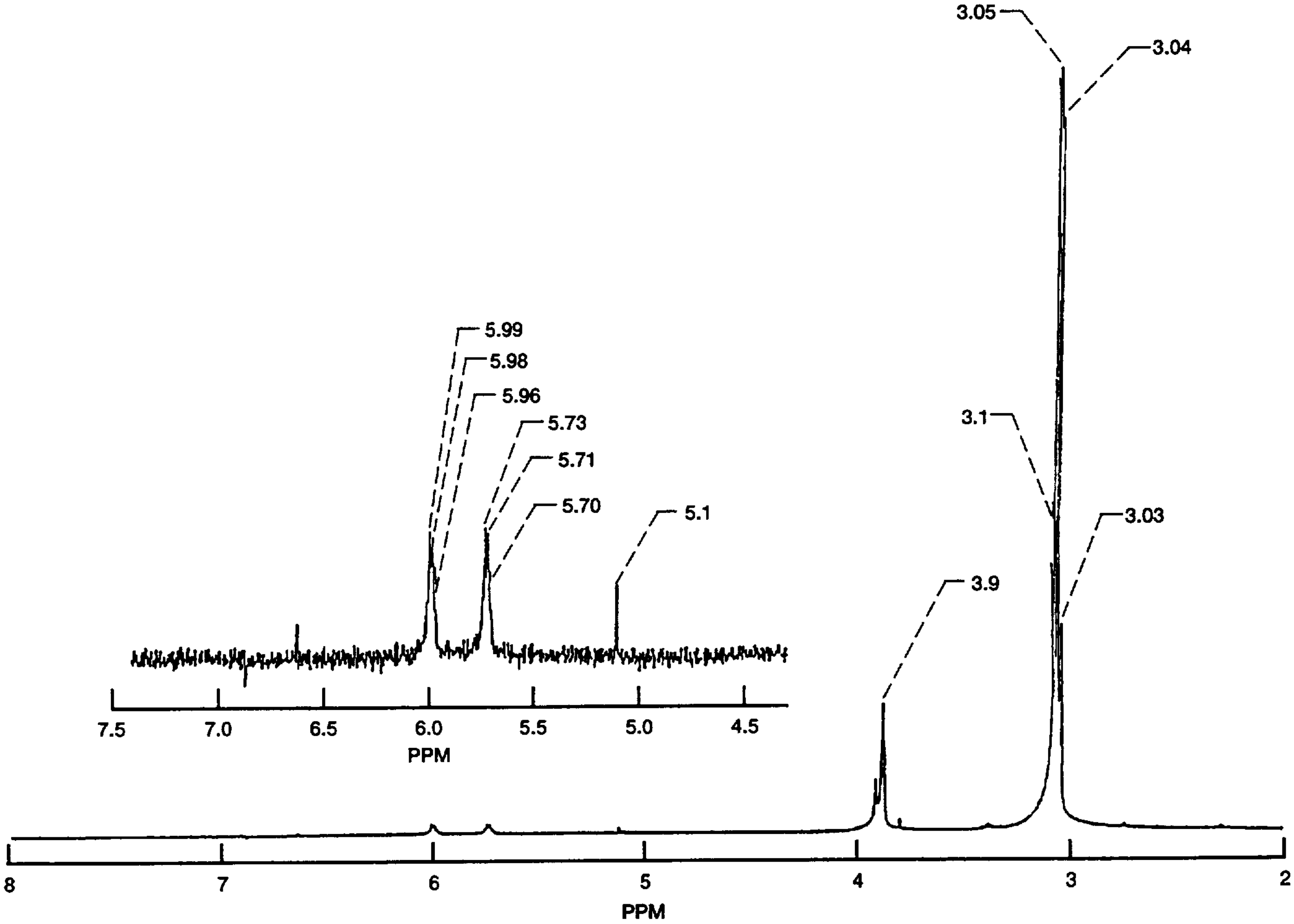


Figure 4.—^{1}H NMR of AC fluid (as received).

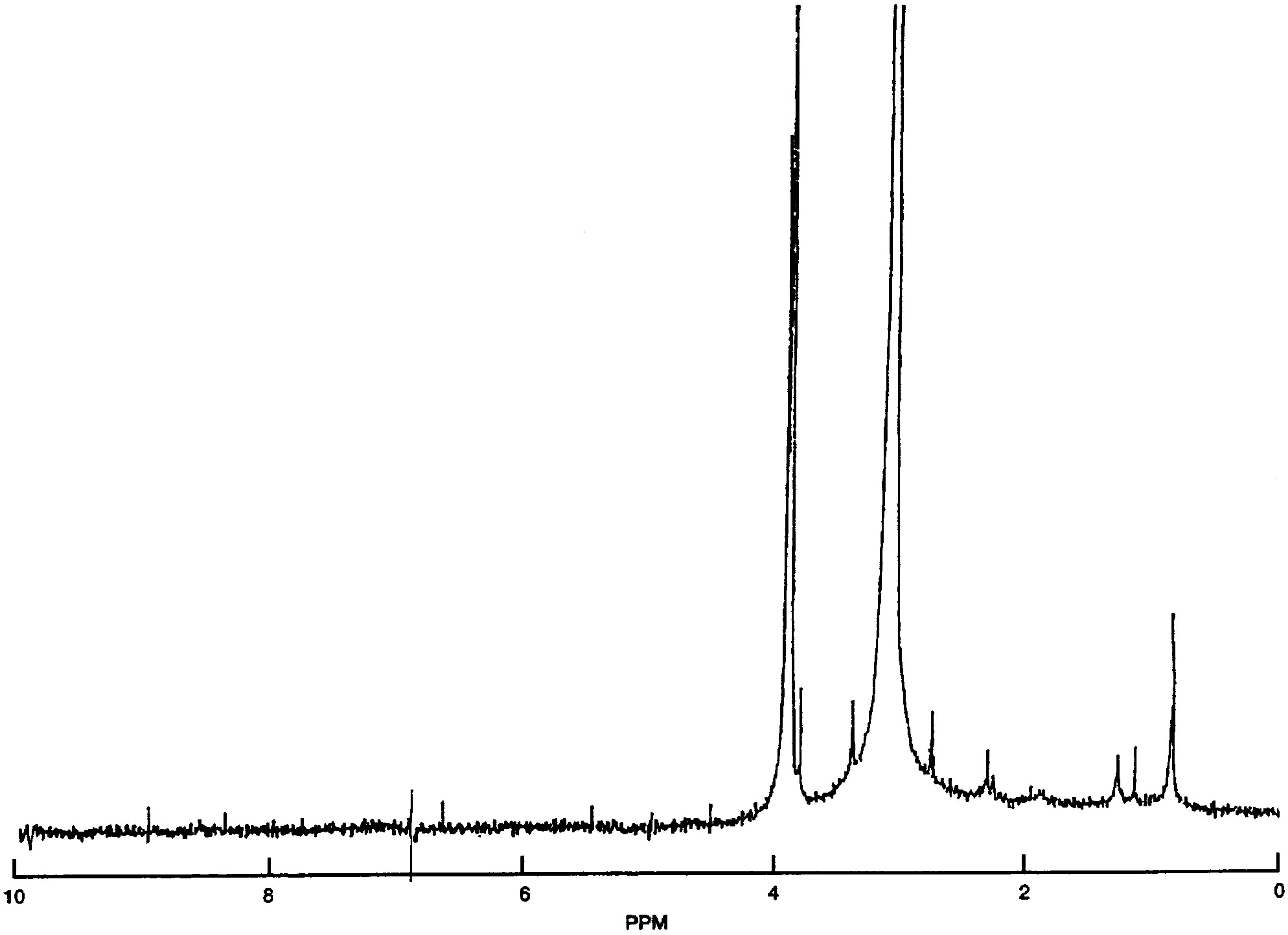


Figure 5.—^{1}H NMR of AC fluid treated in 0_2 for 288 hrs at 343 °C.

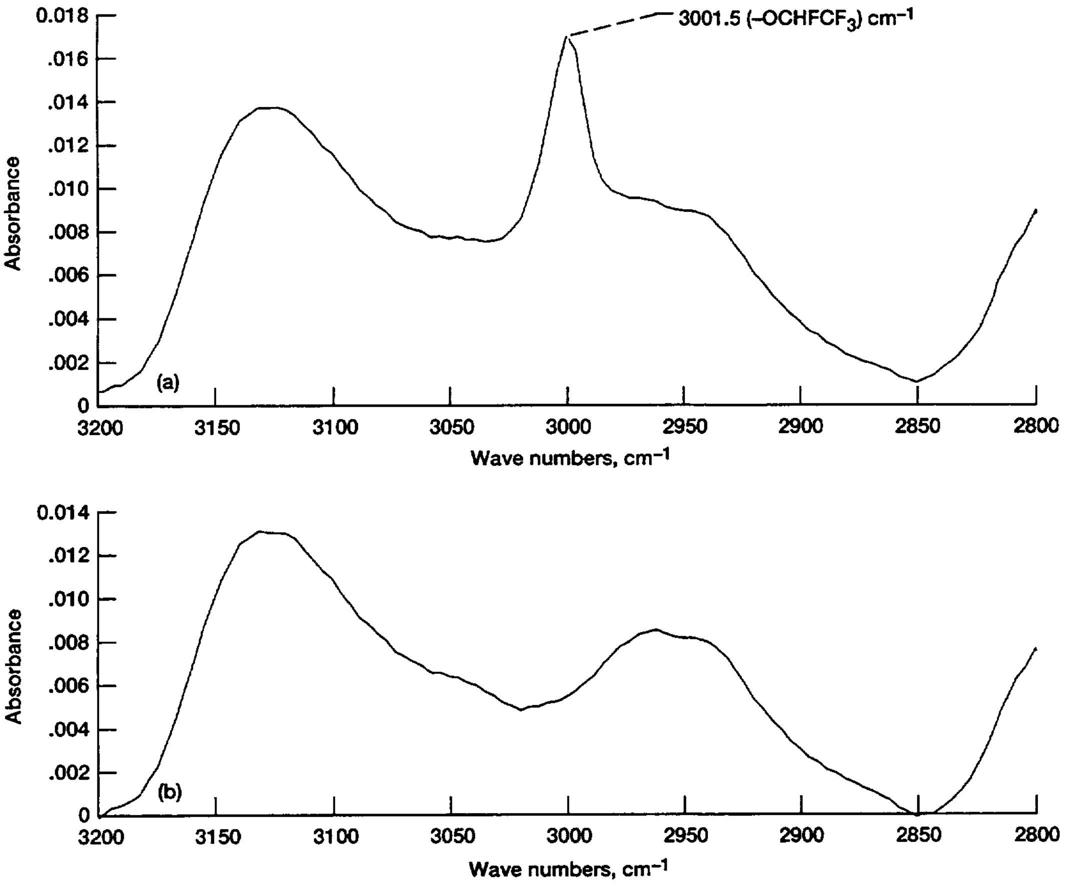


Figure 6.—Infrared spectra of AC fluid. (a) As received. (b) After pretreatment.

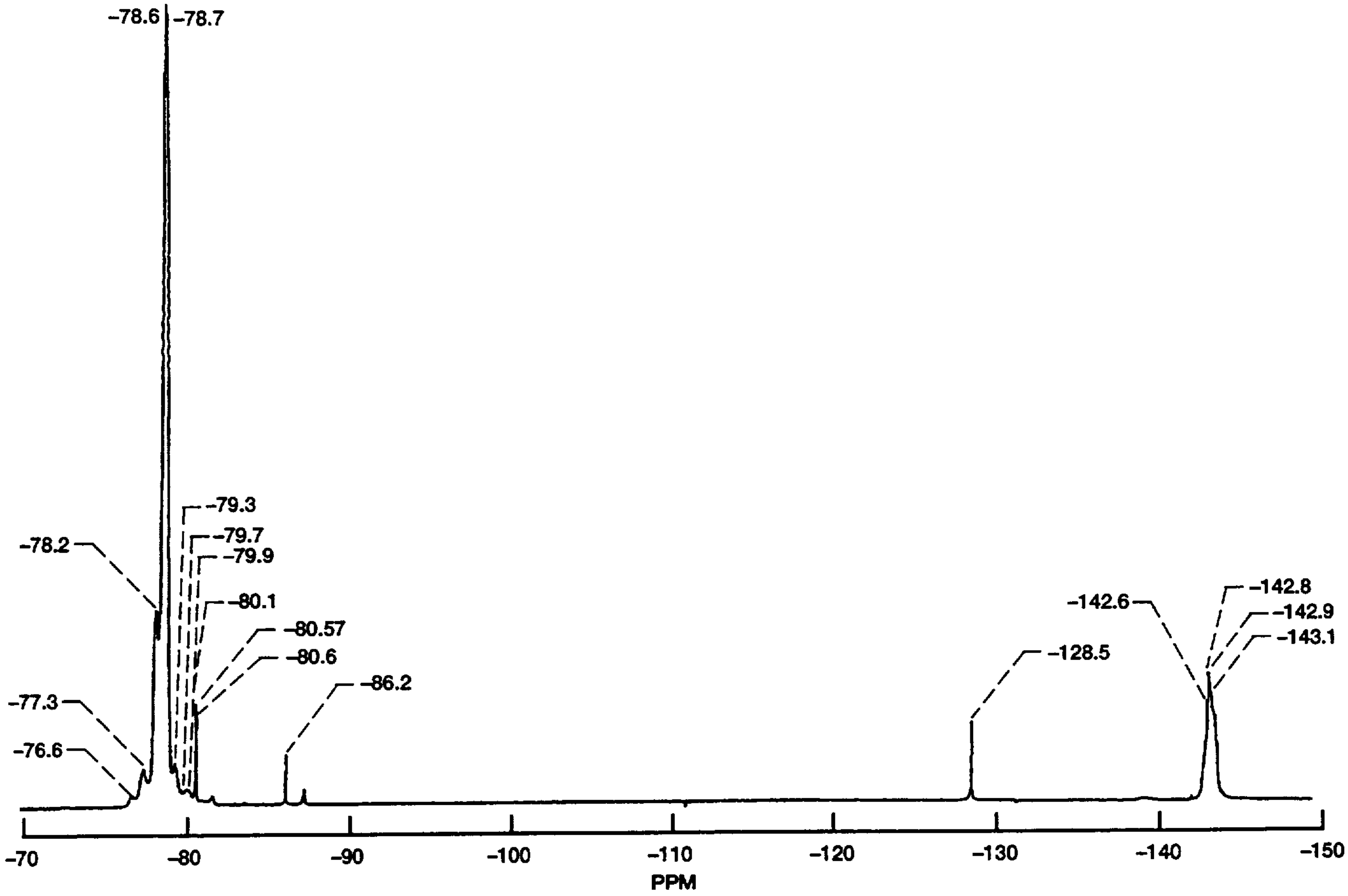


Figure 7.—^{19}F NMR of AC fluid (as received).

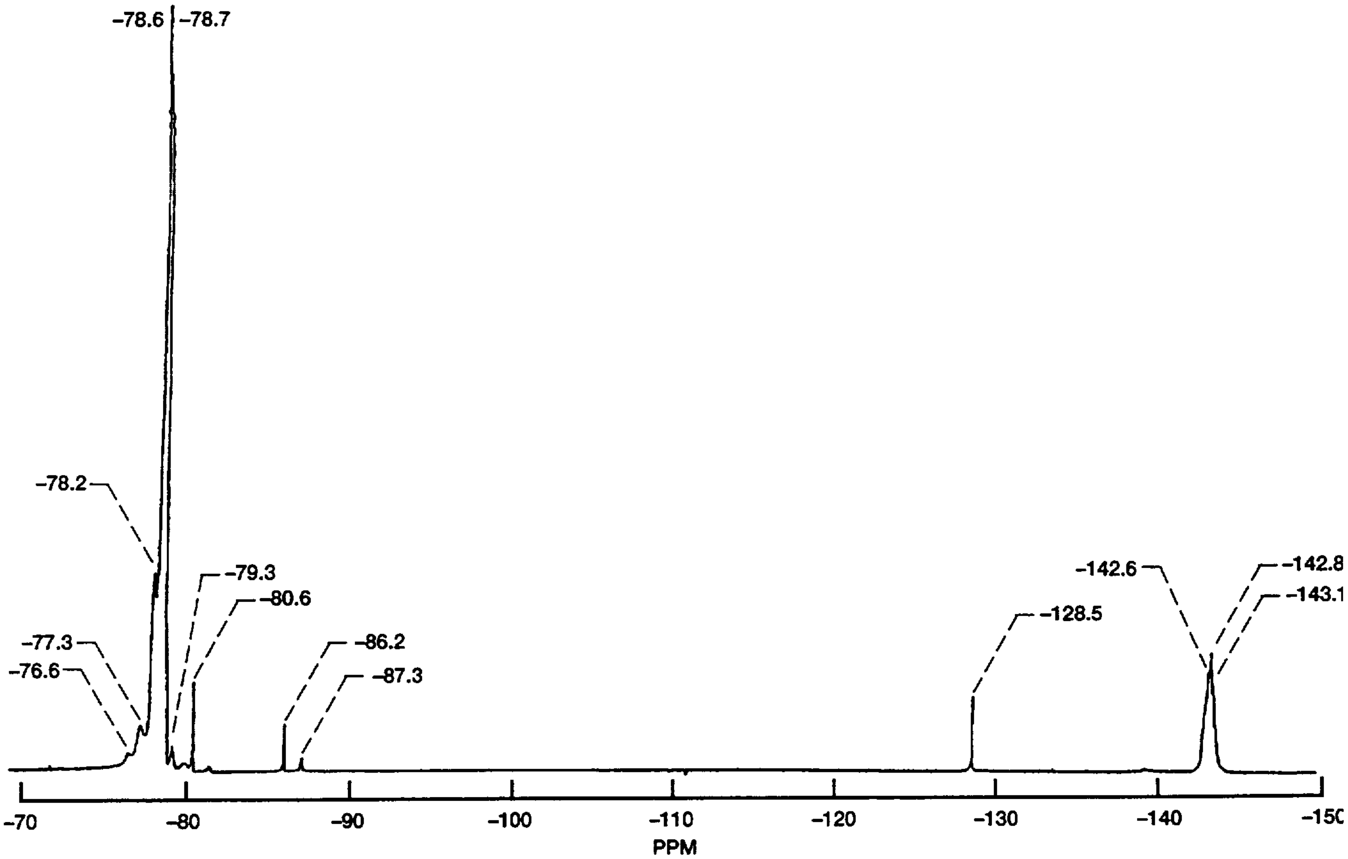


Figure 8.—^{19}F NMR of AC fluid treated in 0_2 for 288 hrs at 343 °C.

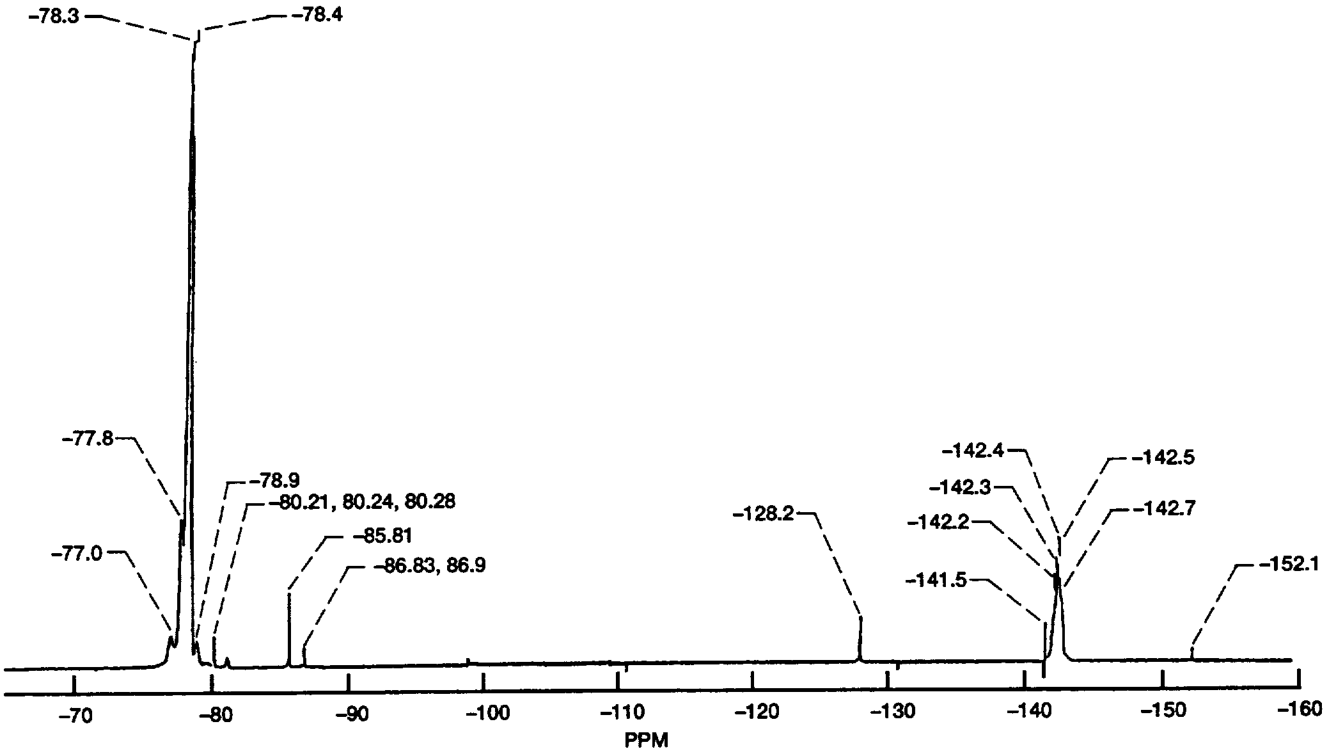


Figure 9.—^{19}F NMR of MLO-71-6 fluid as received (ref. 8).

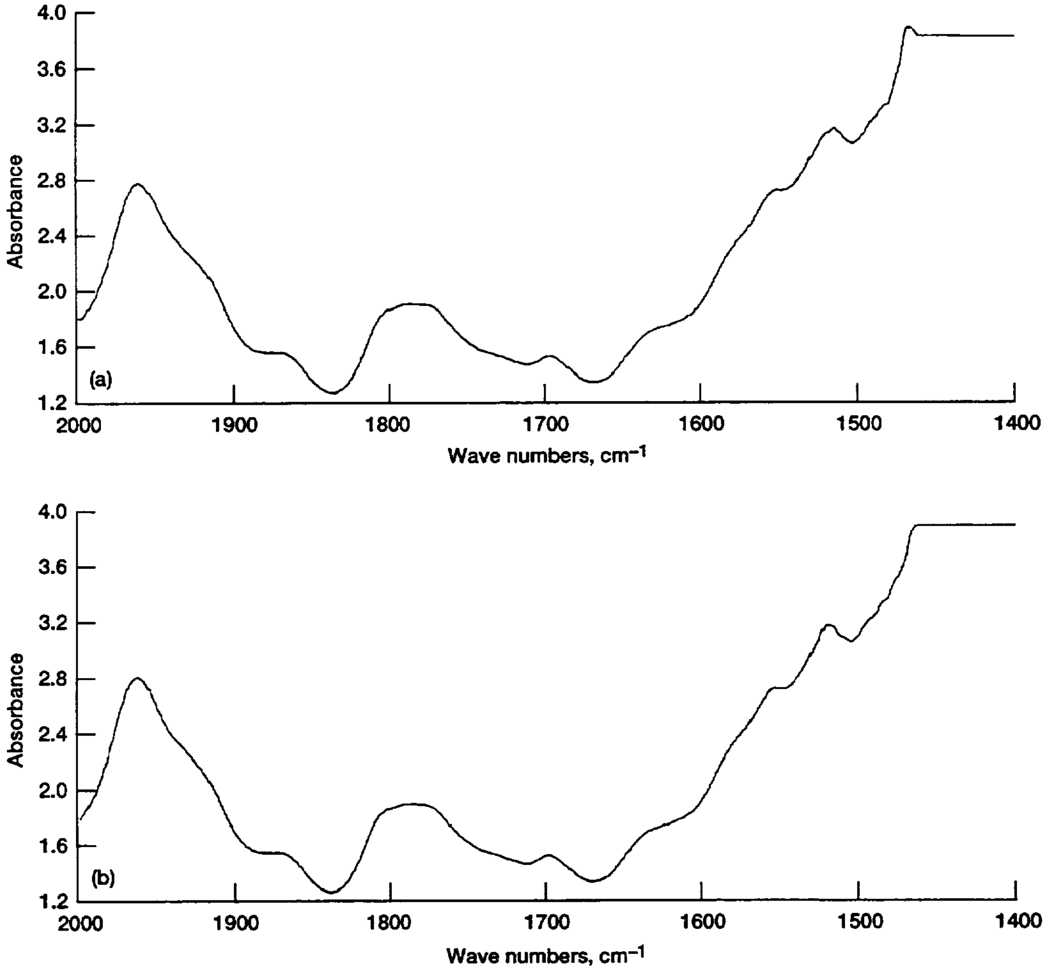


Figure 10.—Infrared spectra of AC fluid showing similarity of carbonyl region. (a) As received. (b) After pretreatment.

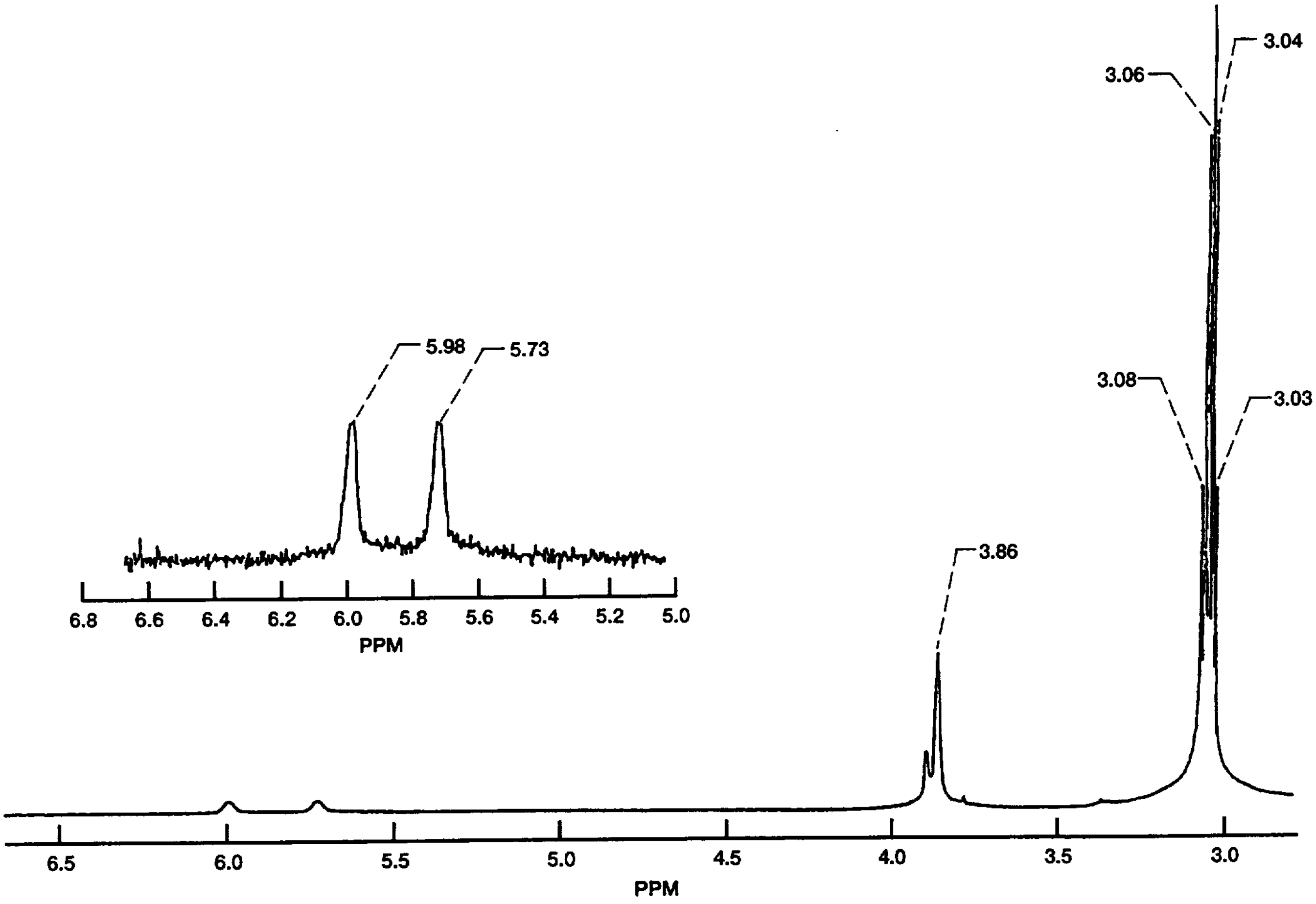


Figure 11.—^{1}H NMR of AB fluid (as received).

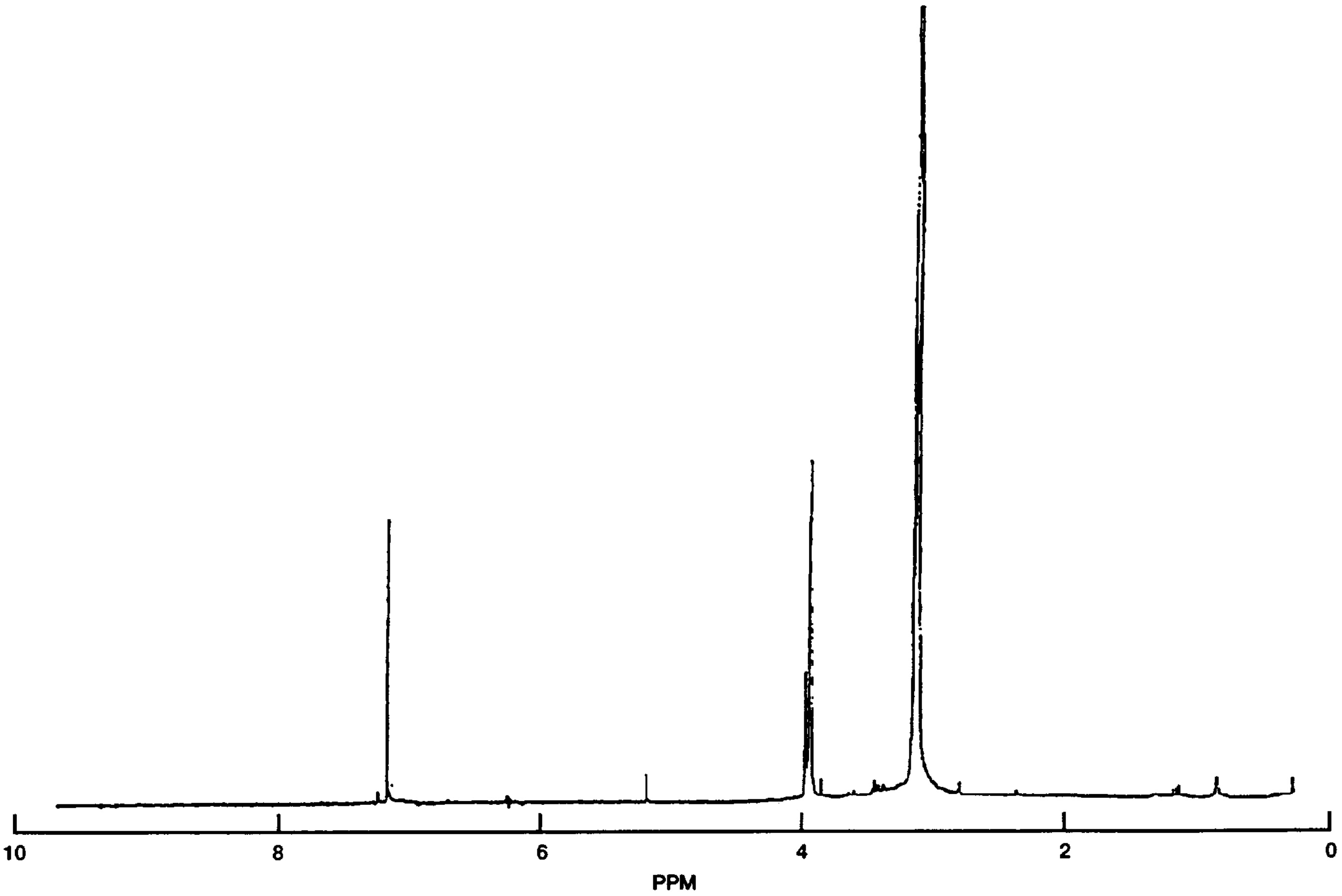


Figure 12.—^{1}H NMR of AB fluid treated in 0_2 for 353 hrs at 343 °C.

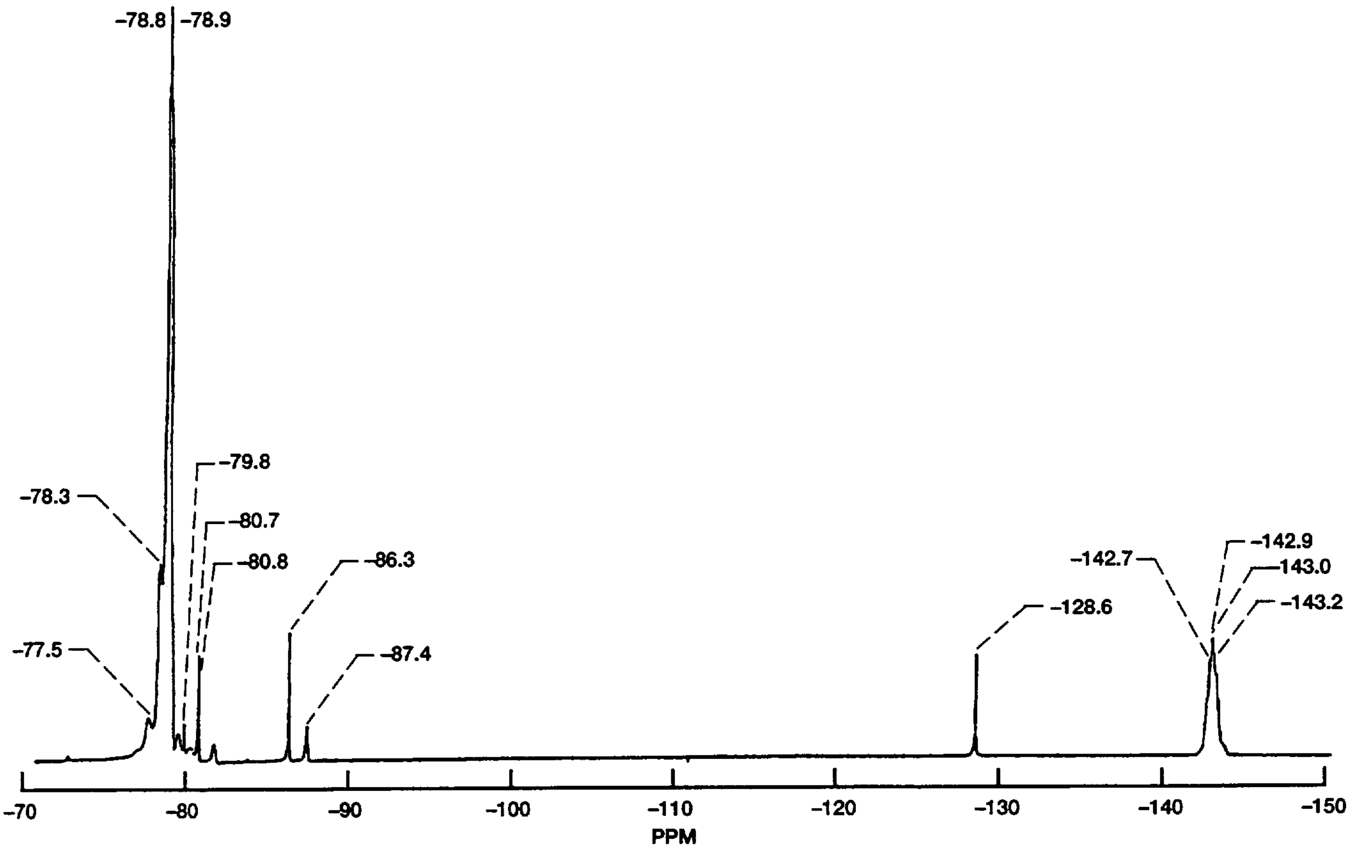


Figure 13.—^{19}F NMR of AB fluid (as received).

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. AGENCY USE ONLY (*Leave blank*)	**2. REPORT DATE** July 1994	**3. REPORT TYPE AND DATES COVERED** Technical Memorandum

4. TITLE AND SUBTITLE

Thermal-Oxidative Pretreatment and Evaluation of Poly(Hexafluoropropene Oxide) Fluids

5. FUNDING NUMBERS

WU-233-02-0D

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E-8974

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM-106659

11. SUPPLEMENTARY NOTES

Prepared for the Tribology Conference cosponsored by the Society of Tribologists and Lubrication Engineers and the American Society of Mechanical Engineers, Lahaina, Hawaii, October 16-19, 1994. K.J.L. Paciorek, S.R. Masuda, and W-H. Lin, Technolube Products Co., 3365 E. Slauson Ave., Vernon, California 90058; W.R. Jones, Jr., NASA Lewis Research Center; and L.S. Helmick, Cedarville College, Cedarville, Ohio 45314, and Summer Faculty Fellow at Lewis Research Center. Responsible person, W.R. Jones, Jr., organization code 5140, (216) 433-6051.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 27

12b. DISTRIBUTION CODE

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

Two commercial poly(hexafluoropropene oxide) fluids were thermally pretreated at 343°C in pure oxygen. IR and NMR spectra indicate that this pretreatment was effective in removing hydrogen end-capped impurities. Decrease in the quantity of volatile material produced during thermal oxidative decomposition and increase in the thermal decomposition temperature indicated improvement in the stability of the fluids. However, this pretreatment failed to render the fluids completely stable in oxidizing atmospheres at 316°C in the presence of metal alloys.

14. SUBJECT TERMS

Lubricants; Perfluoropolyethers

15. NUMBER OF PAGES

20

16. PRICE CODE

A03

17. SECURITY CLASSIFICATION OF REPORT Unclassified	**18. SECURITY CLASSIFICATION OF THIS PAGE** Unclassified	**19. SECURITY CLASSIFICATION OF ABSTRACT** Unclassified	**20. LIMITATION OF ABSTRACT**

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102