

# Thermal Oxidative Studies of Poly(hexafluoropropene Oxide) Fluids

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## Synopsis

Elucidation of mechanisms operative in thermal oxidative degradation of hexafluoropropene oxide derived polyethers and the effect of metals on these processes are reported. Thermal oxidative instability of a commercial fluid, at moderate temperatures (550°F), was found to be due to the presence of ~3% of thermooxidatively unstable chains believed to be hydrogen terminated; treatment at 650°F in oxygen volatilized these chains by unzipping. The resultant fluid was unaffected by oxygen at 650°F and by M-50 and Ti(4Al, 4Mn) alloys at 600°F in oxidizing atmospheres. M-50 alloy catalyzed the degradation of the hydrogen-terminated chains below and at 600°F, but after completion of this process did not affect the remainder of the fluid at these temperatures. At 650°F a chain scission process promoted by the metals constituting the alloy, or their oxides or fluorides, came into play. Ti(4Al, 4Mn) alloy in the presence of  $\text{CF}_3\text{COF}$  and  $\text{COF}_2$  species, formed via decomposition of the hydrogen-terminated chains, degraded poly(hexafluoropropene oxide) fluids at 550°F by chain scissions.

## INTRODUCTION

Poly(hexafluoropropene oxides) of the general formula  $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{-CF}_2]_x\text{OCF}(\text{CF}_3)\text{X}$  (X is F), as represented by the Krytox family of fluids, possess remarkable thermal stability associated with low pour points and low vapor pressures. These properties render these compositions attractive candidates for high-performance hydraulic fluids, oils, and greases. However, their oxidative stability is limited to approximately 550°F, and above this temperature these materials are incompatible with ferrous and titanium alloys. This degradation could be arrested to a degree by addition of phosphines and related compounds.<sup>1-5</sup> It has been claimed that the fluorine-endcapped materials have an incipient decomposition temperature slightly above 410°C (770°F) and that the presence of oxygen does not accelerate the degradation process.<sup>6,7</sup> The latter data applied to well-characterized materials wherein the endgroup denoted by X in the above formula was definitely a fluorine atom.

In the absence of information concerning the mechanisms of the reactions these fluids undergo with oxygen and metals, it is difficult, if not impossible, to devise improvements which would prevent these undesirable processes from occurring.

Thus, the objective of this study was to elucidate first the mechanisms involved in the oxidative degradation of poly(hexafluoropropene oxide) fluids at temperatures up to 650°F and then to establish the effects that ferrous alloys and titanium alloys have on the degradation mode of these materials.

### EXPERIMENTAL

The sample decomposition tubes and the metal specimen holders were constructed essentially in the same manner as those used in the AFML Micro-O-C test<sup>2,3</sup> with the exception that the tubes were closed via a 29/42 ground joint adapter with a 0-5 mm Teflon stopcock and 10/30 ground joint for ready attaching of the system to the high-vacuum line. To provide a sufficient supply of oxygen for any oxidation process, these adapters were furthermore equipped with a ~250-ml reservoir. For reproducible centering of the metal specimen holder, a positioner was constructed which held the rod of the specimen holder in the center of the 29/42 ground joint as shown in Figure 1.

To reduce the volume of fluid required for the test, the diameter of the bottom portion of the tube was reduced to 11-12 mm and the metal coupon's size was scaled down from the 3/4 in. O.D., 1/4 in. I.D. used in the above referenced test to 3/8 in. O.D., 1/8 in. I.D. This allowed the use of as little as 6-8 cm<sup>3</sup> of fluid per actual run. For heating of sample tubes in a vertical position, which was necessary in all experiments involving metal specimens, a modified Lindberg heavy-duty box furnace Type 51232 was employed.

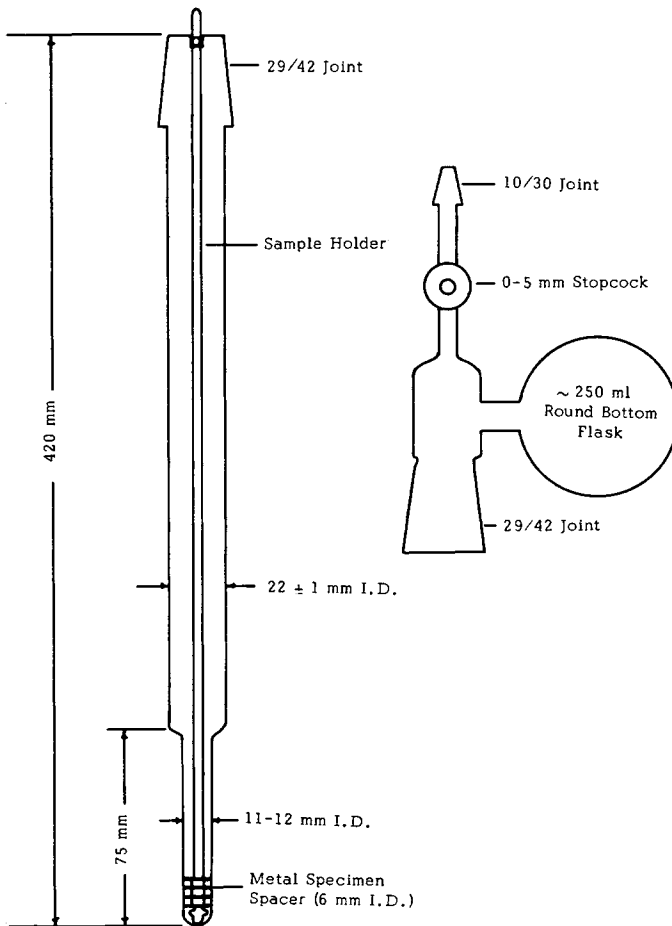


Fig. 1. Decomposition tube arrangement.

In a typical experiment the fluid was introduced into the degradation tube which was then evacuated and filled to a known pressure at a known temperature with a selected gas (air, N<sub>2</sub>, or O<sub>2</sub>). Inasmuch as the apparatus was calibrated and the fluid volume measured, the quantity of gas thus introduced was exactly known. The degradation tube was then inserted into the preheated box furnace and kept there for a specified period of time; throughout this exposure the temperature was continuously recorded. After removal from the furnace the tube was allowed to cool to room temperature, attached to the high-vacuum line, and opened. The liquid-nitrogen noncondensibles were collected quantitatively, measured, and analyzed by mass spectrometry. The liquid-nitrogen condensibles, which were volatile at room temperature, were measured, weighed, and analyzed by infrared spectroscopy, mass spectrometry, and GC-MS. The fluid residue itself was weighed and subjected to infrared spectral analysis, differential scanning calorimetry (DSC), molecular weight measurement, and viscosity determinations. The tests performed are summarized in Tables I through III whereas the product compilations are given in Tables IV through VI.

In view of possible and actually expected variations in different fluid batches the majority of tests performed utilized a specific batch of poly(hexafluoropropene oxide) fluid, namely, Krytox MLO-71-6, with limited work conducted on other batches to supplement and confirm conclusions reached. The molecular weight of this fluid was found to be 5500 using a Hewlett-Packard osmometer Model 302. The primary standard used was *tris*-perfluoro-*n*-heptyl-*s*-triazine; measurements were conducted in hexafluorobenzene. In all the determinations of the treated fluid, the original Krytox MLO-71-6 sample was used as the standard.

Prior to testing the metal coupons were polished using first Norton No-Fil Durite finishing paper Type 4 220A, followed by open-coat silicon carbide papers Grades 400A and 500A. Subsequently the coupons were washed in Freon 113, dried, weighed, and suspended in the test apparatus. After the completion of a given experiment, the metal coupons were weighed after washing with Freon 113 and drying inside an inert atmosphere chamber.

Oxygen consumption, when applicable, and volatiles production were the primary and quantitative criteria of the degradation extent. The changes in viscosity and molecular weight of the residual fluid together with the metal corrosion characteristics, i.e., appearance and weight loss or gain, provided additional but mainly qualitative data.

## RESULTS AND DISCUSSION

### Mechanistic Considerations of Volatiles Production

Gumprecht et al.<sup>6,7</sup> have shown that the thermal decomposition of poly(hexafluoropropene oxide), C<sub>3</sub>F<sub>7</sub>[OCF(CF<sub>3</sub>)CF<sub>2</sub>]<sub>x</sub>OCF(CF<sub>3</sub>)F, produces in vacuo as the main products CF<sub>3</sub>CF=CF<sub>2</sub>, CF<sub>3</sub>COF, and COF<sub>2</sub>. Examining Tables IV and V, it is apparent that the major products were SiF<sub>4</sub> and CO<sub>2</sub> together with some BF<sub>3</sub>. No hexafluoropropene was detected under oxidizing conditions, although it was one of the main products observed in the tests conducted in nitrogen atmospheres as shown by run 11 (see Tables I and IV). This instability of fluorinated olefins in the presence of oxygen has been established by studies

TABLE I  
Experimental Data for Thermal Degradation Studies of Poly(hexafluoropropene Oxide) Fluids<sup>a</sup>

Test no. <sup>b</sup>	Starting material used, g	Temp., °F	Duration, hr	Viscosity <sup>c</sup> change, %	MW <sup>d</sup>	Oxygen consumed		Total products mg	Fluid consumed, mg	O/C <sub>3</sub> F <sub>8</sub> O ratio, atm/mole
						mg	% <sup>e</sup>			
1	10.43	Air	24	-0.38	5500	1.7	32	13.7	1.3	—
2	11.82	Air	24	—	5500	1.2	22	12.3	1.0	—
3	11.33	N <sub>2</sub>	24	—	5500	—	—	0.7	0.1	—
4	11.87	N <sub>2</sub>	216	—	5500	—	—	11.5	1.0	—
5	12.05	Air	216	+0.80	5500	11.9	100	130.6	10.8	—
6	18.59	Air	24	+0.89	5500	11.6	100	159.3	8.6	—
7	20.76	Air	24	+0.60	5500	51.0	84	338.3	16.3	—
8	3.55	Air	24	+3.70	5600	17.0	27	152.3	42.9	—
9	3.42	O <sub>2</sub>	24	+5.47	5600	17.9	6.1	181.4	53.1	—
10	3.28	O <sub>2</sub>	216	+6.01	5600	24.8	8.4	238.0	72.6	—
11	10.26	N <sub>2</sub>	216	+1.02	5500	—	—	64.7	6.3	—
15	28.96	O <sub>2</sub>	208	+2.39	—	n.d.	—	2141	73.9	—
19	16.74	O <sub>2</sub>	24	+1.62	5500	90.0	31.3	805.7	48.1	1.67
22	12.44	O <sub>2</sub>	120	+2.63	5500	88.9	30.8	780	62.6	2.25
23 <sup>a</sup>	13.49	O <sub>2</sub>	24	+1.86	5000	77.5	26.8	731.1	54.2	1.68
34A	13.43	O <sub>2</sub>	24	—	—	21.4	7.5	252.6	18.8	—
34B	13.26	O <sub>2</sub>	192	+2.51	5200	40.8	14.4	381.1	28.7	—

<sup>a</sup> In test no. 23 Krytox MLO-76-28 was used. In all other tests Krytox MLO-71-6 was employed.

<sup>b</sup> Test nos. 1-5 were performed in 50-ml sealed ampoules totally enclosed in the furnace; test no. 6 was conducted in a 90-ml sealed ampoule; the remainder of the tests were performed in 438-ml apparatus in which only the liquid portion of the sample was at the denoted temperature.

<sup>c</sup> All the measurements were conducted at  $100 \pm 0.02^\circ\text{F}$  using Cannon-Manning semimicroviscometers; if differences between untreated fluids and a given sample were less than 0.35%, these are not listed.

<sup>d</sup> The molecular weight of untreated Krytox MLO-71-6 was found to be 5500; that of Krytox MLO-76-28 was found to be 4800.

<sup>e</sup> Percent of the oxygen available.

<sup>f</sup> Oxygen consumed in mg/g of fluid employed.

<sup>g</sup> Products formed in mg/g of fluid employed.

TABLE II  
Experimental Data for Thermal Degradation Studies of Poly(hexafluoropropene Oxide) Fluids in the Presence of M-50 Alloy<sup>a,b</sup>

Test no.	Fluid used, g	Temp., °F	Duration, hr	Viscosity change, <sup>c</sup> %	MW <sup>d</sup>	Oxygen consumed		Total products	Fluid consumed, mg	O/C <sub>3</sub> F <sub>6</sub> O ratio, atm/mole	Coupon weight gain/loss, mg/cm <sup>2</sup> h
						mg	% <sup>e</sup>				
12	12.22	550	24	—	5500	9.0	3.1	48.5	—	—	+ 0.18
13	12.13	600	24	—	5600	70.8	24.6	576.7	340	2.16	+ 0.42
14	12.33	650	24	+ 1.52	5500	82.5	28.9	798.3	560	1.53	+ 0.42
16 <sup>i</sup>	12.01	650	24	+ 1.90	5600	27.3	9.6	184.9	—	—	+ 5.0
17	12.96	650	216	+14.93	6900	283.0	100	2623.5	1580	1.86	- 6.3
18	12.80	650	216	—	6500	—	—	47.7	—	—	+ 0.6
21	12.90	600	216	+ 2.98	5500	94.9	33.3	774.9	490	2.01	+ 3.0
24 <sup>a</sup>	12.81	650	24	+ 1.26	5000	108.5	37.1	1021.0	690	1.63	+ 0.67
28A <sup>j</sup>	12.93	650	48	n.d.	—	118.6	42.1	1050.4	—	—	n.d.
28B	12.19	650	48	n.d.	—	130.3	45.2	1143.5	—	—	n.d.
28C	11.39	650	48	n.d.	—	242.9	83.5	2180.0	—	—	n.d.
28D	9.86	650	24	n.d.	—	117.0	40.4	997.2	—	—	n.d.
28E	9.16	650	24	- 8.13	5000	97.8	34.0	891.8	—	—	-22.7
35 <sup>i</sup>	9.37	600	24	+ 3.20	5600	~2.0	0.7	2.2	—	—	+ 0.30

<sup>a</sup> In test no. 24 Krytox MLO-76-28 was used; in all the other tests Krytox MLO-71-6 was employed.

<sup>b</sup> In these tests only the liquid portion of the sample was at the denoted temperature; the apparatus used was equipped with a finger-like projection, the volume of the apparatus minus fluid (ca. 12 g) was 416 ml.

<sup>c</sup> All the measurements were conducted at  $100 \pm 0.02^\circ\text{F}$  using Cannon-Manning semimicroviscometers; if differences between untreated fluids and a given sample were less than 0.35%, these were not listed.

<sup>d</sup> The molecular weight of the untreated Krytox MLO-71-6 was found to be 5500; that of Krytox MLO-76-28 was found to be 4800.

<sup>e</sup> Percent of the oxygen available.

<sup>f</sup> Oxygen consumed in mg/g of fluid employed.

<sup>g</sup> Products formed in mg/g of fluid employed.

<sup>h</sup> The area of the coupon (both sides, including the area of the rims) is 1.6459 cm<sup>2</sup>.

<sup>i</sup> The Krytox fluid, MLO-71-6, used in this test was pretreated at 650°F (see test no. 15).

<sup>j</sup> Tests 28A-28D were performed stepwise, removing the condensibles and replenishing oxygen at times specified. The weight of fluid employed in tests 28B-28E was calculated using the expression:  $0.701 \times \text{weight of products formed} = \text{fluid weight loss}$ .

TABLE III  
Experimental Data for Thermal Degradation Studies of Poly(hexafluoropropene Oxide) Fluid in the Presence of Ti(4Al, 4Mn) Alloy<sup>a,b</sup>

Test no.	Fluid used, g	Atm	Temp., °F	Period, hr	Viscosity change, %	MW <sup>d</sup>	Oxygen consumed		Total products		Coupon weight gain/loss, mg/cm <sup>2</sup> h	
							mg	% <sup>e</sup>	mg/gf	mg		mg/g <sup>e</sup>
36	11.40	O <sub>2</sub>	600	24	-21.6	4900	174.0	60.6	15.3	1617.9	142	-0.17
37	11.02	O <sub>2</sub>	550	24	—	5400	18.8	6.5	1.71	183.2	16.6	+0.17
39A <sup>i</sup>	12.91	O <sub>2</sub>	550	48	n.d.	n.d.	66.3	23.1	5.14	622.6	48.2	n.d.
39B	12.53	O <sub>2</sub>	550	48	n.d.	n.d.	182.7	63.5	14.6	1824.4	146	n.d.
39C	11.15	O <sub>2</sub>	550	24	-44.8	4200	122.6	42.0	11.0	1236.9	111	-0.68
43 <sup>j</sup>	12.23	O <sub>2</sub>	550	24	+1.73	5500	2.4	0.8	0.20	2.9	0.2	0
44 <sup>j</sup>	10.80	O <sub>2</sub>	605	24	+0.38	5500	5.5	1.9	0.51	48.4	4.5	+0.17

<sup>a</sup> The fluid used was Krytox MLO-71-6.

<sup>b</sup> In these tests only the liquid portion of the sample was at the denoted temperature; the apparatus used was equipped with a finger-like projection, the volume of the apparatus minus the Krytox (ca. 12 g) was 416 ml.

<sup>c</sup> All the measurements were conducted at 100 ± 0.02°F using Cannon-Manning semimicroviscometers; if differences between untreated fluids and a given sample were less than 0.35%, these were not listed.

<sup>d</sup> The molecular weight of the untreated Krytox MLO-71-6 was found to be 5500.

<sup>e</sup> Percent of the oxygen available.

<sup>f</sup> Oxygen consumed in mg/g of fluid employed.

<sup>g</sup> Products formed in mg/g of fluid employed.

<sup>h</sup> The area of the coupon (both sides, including the area of the rims) is 1.7735 cm<sup>2</sup>.

<sup>i</sup> Tests 39A-39C were performed by removing the condensibles and replenishing oxygen at time specified. The weight of fluid employed in tests 39B and 39C was calculated using the expression: 0.723 X weight products formed = fluid weight loss.

<sup>j</sup> These tests were performed using Krytox MLO-71-6 which was pretreated in oxygen at 650°F for 168 hr.

TABLE IV  
Volatile Products Obtained on Thermal Degradation of Poly(hexafluoropropene Oxide) Fluids<sup>a</sup>

Test no.	CO		SiF <sub>4</sub>		CO <sub>2</sub>		BF <sub>3</sub>		COF <sub>2</sub>		CF <sub>3</sub> COF		C <sub>2</sub> F <sub>6</sub>		Others <sup>c</sup>	
	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>
1	0.5	3.7	6.95	50.8	5.88	43.0	—	—	0.03	0.2	0.32	2.3	—	—	—	—
2	0.3	2.4	4.65	37.7	4.63	37.6	—	—	0.18	1.5	2.56	20.8	—	—	0.01	0.08
3	0.1	11.8	0.01	1.5	0.18	26.5	—	—	—	—	—	—	0.41	60.3	—	—
4	1.1	9.4	3.49	30.2	3.61	31.3	—	—	?	?	0.21	1.8	2.67	23.1	0.47	4.07
5	10.5	8.0	48.4	37.1	56.1	43.0	13.6	10.4	?	?	6.19	3.9	1.5	1.1	0.47	0.36
6	14.3	9.0	64.9	40.7	55.4	34.8	12.3	7.7	?	?	57.2	16.9	4.8	3.0	0.25	0.16
7	19.3	5.7	127.1	37.6	113.2	33.5	14.1	4.2	3.27	1.0	—	—	—	—	—	—
8	9.4	6.2	77.1	50.6	48.8	32.0	14.8	9.7	1.38	0.9	0.81	0.5	—	—	—	—
9	3.8	2.1	83.3	45.9	77.7	42.8	15.9	8.8	0.27	0.1	0.65	0.4	—	—	—	—
10	0.6	0.2	122.7	51.6	97.1	40.8	17.6	7.4	—	—	—	—	—	—	—	—
11	4.8	7.4	22.7	33.5	15.6	24.1	0.33	0.5	?	?	1.05	1.6	18.1	28.0	2.4	3.7
19	1.0	0.1	366.1	45.4	226.3	28.1	72.5	9.0	26.9	3.3	117.7	13.9	—	—	1.2	0.1
22	1.2	0.2	415.3	53.3	293.8	37.7	65.3	8.4	—	—	3.3	0.4	—	—	—	—
23 <sup>a</sup>	3.1	0.5	312.2	42.7	257.6	35.2	71.6	9.8	8.0	1.1	79.2	10.8	—	—	—	—
34A	1.5	0.6	68.7	27.2	44.3	17.5	10.9	4.3	27.5	10.9	92.9	36.8	—	—	6.8	2.7
34B	3.6	0.9	221.7	58.2	127.9	33.6	26.6	7.0	0.3	0.1	1.0	0.3	—	—	—	—

<sup>a</sup> In test no. 23 Krytox MLO-76-28 was used; in all other tests Krytox MLO-76-6 was employed.

<sup>b</sup> Weight percent of total products.

<sup>c</sup> These were mainly olefins and hydrogen terminated C<sub>2</sub> to C<sub>7</sub> fluorinated species.

TABLE V  
 Volatile Products Obtained on Thermal Degradation of Poly(hexafluoropropene Oxide) Fluids in the Presence of M-50 Metal<sup>a</sup>

Test no.	CO		SiF <sub>4</sub>		CO <sub>2</sub>		BF <sub>3</sub>		COF <sub>2</sub>		CF <sub>3</sub> COF		C <sub>2</sub> F <sub>6</sub>		CF <sub>4</sub>		C <sub>3</sub> F <sub>6</sub>		Others		
	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	
12	1.19	2.4	13.6	28.0	16.0	33.0	—	—	2.9	5.9	14.9	30.7	—	—	—	—	—	—	—	—	
13	1.31	0.2	242.5	42.1	199.6	34.6	34.3	6.0	20.7	3.6	75.9	13.2	—	—	—	—	—	—	3.0	0.4	
14	5.12	0.6	370.0	46.3	284.1	35.6	84.6	10.6	5.7	0.7	46.8	5.9	—	—	—	—	—	—	2.0	0.2	
16	3.26	1.8	100.2	54.2	50.7	27.4	18.0	9.7	2.5	1.4	1.3	0.7	8.8	4.8	0.1	0.05	—	—	—	—	
17	26.8	1.0	1464.4	55.8	853.6	32.5	158.6	6.0	—	—	—	—	115.8	4.4	0.3	0.01	—	—	4.0	0.2	
18	3.86	8.1	14.7	30.8	10.6	22.2	1.1	2.3	—	—	?	?	—	—	—	—	15.0	31.4	2.4	5.0	
20	4.53	0.5	477.2	57.8	237.3	28.7	63.9	7.7	5.8	0.7	27.6	3.3	9.5	1.2	—	—	—	—	0.3	0.04	
21	4.15	0.5	423.7	54.6	283.0	36.5	57.7	7.4	2.2	0.3	—	—	4.1	0.5	0.1	0.01	—	—	—	—	
24	4.9	0.5	588.0	57.6	331.8	32.5	69.8	6.8	5.6	0.5	20.9	2.0	—	—	—	—	—	—	—	—	
28A	4.6	0.4	550.9	52.4	377.8	36.0	91.9	8.7	1.9	0.2	7.9	0.8	14.9	1.4	0.5	0.05	—	—	—	—	
28B	4.1	0.4	474.8	41.5	463.0	40.5	129.2	11.3	4.8	0.4	12.4	1.1	53.9	4.7	1.5	0.13	—	—	—	—	
28C	16.5	0.8	1011.2	46.4	766.8	35.2	247.9	11.4	9.3	0.4	5.2	0.2	119.3	5.5	3.8	0.17	—	—	—	—	
28D	9.2	0.9	387.9	38.9	415.6	41.7	129.6	13.0	3.2	0.3	8.3	0.8	39.0	3.9	4.5	0.45	—	—	—	—	
28E	11.0	1.2	426.6	47.8	287.9	32.3	117.9	13.2	1.6	0.2	5.1	0.6	36.5	4.1	5.2	0.58	—	—	0.1	3.0	
35	?	?	?	?	2.1	95.5	?	?	?	?	?	?	?	?	?	?	?	?	?	0.1	4.5

<sup>a</sup> In test no. 26 Krytox MLO-76-28 was used; in all the other tests Krytox MLO-71-6 was employed.

<sup>b</sup> Weight percent of total products.



TABLE VI  
 Volatile Products Obtained on Thermal Degradation of Poly(hexafluoropropene Oxide) Fluid in the Presence of Ti(4Al, 4Mn) Alloy<sup>a</sup>

Test no.	CO		SiF <sub>4</sub>		CO <sub>2</sub>		BF <sub>3</sub>		COF <sub>2</sub>		CF <sub>3</sub> COF		C <sub>2</sub> F <sub>6</sub>		CF <sub>4</sub>		Others <sup>d</sup>	
	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>	mg	% <sup>b</sup>
36	T <sup>c</sup>	—	817.1	50.5	413.8	25.6	203.9	12.6	86.7	5.4	63.8	3.9	13.0	0.8	19.6	1.2	—	—
37	—	—	69.1	37.7	55.5	30.3	15.8	8.6	19.1	10.4	21.8	11.9	0.7	0.4	1.2	0.7	—	—
39A	—	—	227.1	36.5	182.1	29.2	52.4	8.4	36.8	5.9	25.5	4.1	78.8	12.7	5.2	0.8	14.7	2.4
39B	—	—	686.8	37.6	589.0	32.3	145.3	8.0	66.1	3.6	44.3	2.4	217.0	11.9	45.4	2.5	30.5	1.7
39C	—	—	370.5	30.0	370.0	29.9	99.3	8.0	78.1	6.3	50.2	4.1	173.1	14.0	31.3	2.5	64.4	5.2
42	—	—	0.3	18.8	0.9	56.4	—	—	—	—	—	—	—	—	—	—	—	—
44	1.5	3.1	14.5	30.0	12.8	26.4	0.2	0.4	3.9	8.1	5.6	11.6	5.7	11.8	0.9	1.9	3.3	6.8
46	0.6	T	830.3	39.0	510.2	24.0	207.5	9.8	98.4	4.6	128.7	6.0	299.5	14.1	36.8	1.7	15.3	0.7

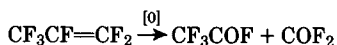
<sup>a</sup> The fluid employed was Krytox MLO-71-6.

<sup>b</sup> Weight percent of total products.

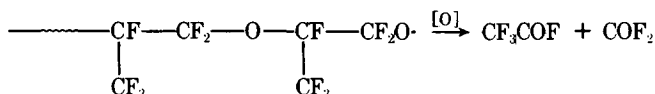
<sup>c</sup> Trace.

<sup>d</sup> These were relatively involatile materials which were collected in the -78°C fraction; these consisted of C<sub>3</sub>F<sub>7</sub>[OCF(CF<sub>3</sub>)CF<sub>2</sub>]<sub>x</sub>OC<sub>2</sub>F<sub>5</sub>.

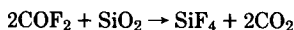
conducted on Teflon where in oxygen no tetrafluoroethylene was observed.<sup>8</sup> The following process could be responsible for hexafluoropropene consumption:



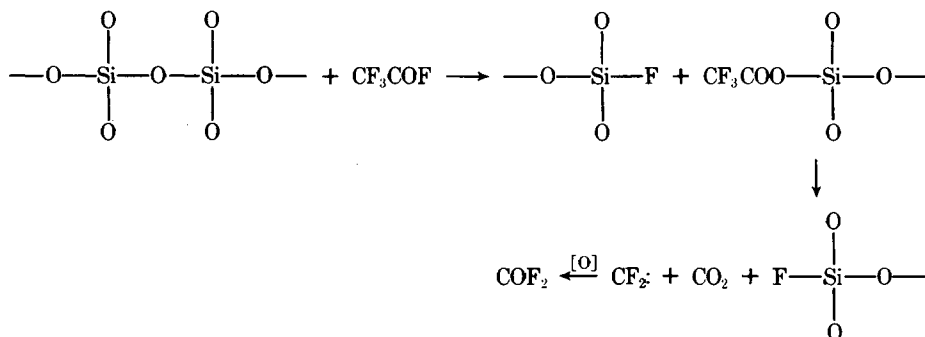
although it is more likely that in the presence of oxygen the polymer radical unzips directly into  $\text{CF}_3\text{COF}$  and  $\text{COF}_2$ , i.e.,



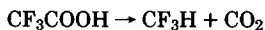
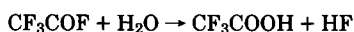
The production of  $\text{CO}_2$  and  $\text{SiF}_4$  is due to the reaction of the primary products, such as  $\text{COF}_2$ , with the glass surface:



Regarding the fate of  $\text{CF}_3\text{COF}$ , several possibilities exist. Under the existing conditions,  $\text{COF}_2$  might be predominantly formed or the originally liberated  $\text{CF}_3\text{COF}$  degrades further via salt-type pyrolysis found to be operative in the case of, e.g., the sodium salt of trifluoroacetic acid:<sup>9</sup>



Another possible path involves hydrolysis followed by degradation:



Since in all the tests only small quantities of  $\text{CF}_3\text{H}$  were found, this process is either relatively unimportant or, more likely,  $\text{CF}_3\text{H}$  once formed is oxidized further. The production of volatile hydrogen-containing fluorocarbons is to be expected inasmuch as these types of products were also encountered in the degradation of perfluoroalkylether substituted heterocycles.<sup>10,11</sup> Regarding  $\text{BF}_3$ , this compound is formed in a reaction analogous to that responsible for  $\text{SiF}_4$  production.

Based on the above equations, to degrade poly(hexafluoropropene oxide) to  $\text{CO}_2$  and  $\text{SiF}_4$  requires two atoms or one molecule of oxygen per repeating unit of the polymer. Consequently, the ratio of oxygen consumed per "mole" of hexafluoropropene oxide lost should be equal to 2. In the experiments where this ratio was measured (see Tables I and II), it varied from 1.5 to 2.2. If one considers the difficulty of weighing back accurately the remaining fluid, the agreement with the theoretical value is not as bad as would appear from the observed deviations.

### Degradation Studies in the Absence of Metal

Examining the data contained in Table I, several points become apparent: (a) In the absence of oxygen (air), even at 650°F, the extent of degradation as determined by volatiles produced is very low (see test no. 11). (b) In the presence of oxygen (air), the reaction at 540–610°F is relatively limited, at least during the first 24-hr period, as indicated by the oxygen consumed and volatiles produced (tests 2 and 34A). (c) At 650°F the final extent of degradation is more or less reached within the first 24 hr (compare tests 9 and 10); no significant additional consumption of oxygen and volatiles production is observed during the following 192 hr. (d) The rate or rather extent of reaction is not greatly affected by using pure oxygen instead of air (compare tests 8 and 9) as long as the oxygen partial pressure is kept above a certain minimum (compare tests 1 and 34A), i.e., not more than 30% oxygen depletion in air is reached. (A consequence of this finding was that all further experiments were performed in pure oxygen which permitted the use of a relatively small apparatus). (e) The reaction rate is practically independent of the ratio of exposed liquid surface to liquid volume (compare tests 9 and 19). (f) Different batches of Krytox reached different extents of degradation under identical conditions (compare tests 19 and 23). (g) The fluid recovered after all the tests listed exhibited the same infrared spectral characteristics as the starting material. The changes in molecular weight and viscosity were experimentally not significant.

Based on the findings cited above it can be deduced that up to 650°F (the highest temperature employed in this study), Krytox is oxidatively stable. The limited degradation observed at 650°F must be due to an oxidative instability of some weak links or endgroups present in the fluid. The oxidation of these endgroups or at least the initial steps of this reaction must take place in the liquid phase and must therefore be caused by dissolved oxygen. The fact that neither the oxygen partial pressure in the gas phase (to a degree) nor the liquid surface-to-volume ratio do significantly affect the extent of reaction in turn indicates that, at least over the time periods employed, the fluid must contain sufficient oxygen to produce "complete" reaction of these endgroups and that, again within the time intervals studied, consumed dissolved oxygen must be replenished from the gas phase at a rate sufficient to maintain that oxygen concentration.

Inasmuch as the nature of the residual fluid was virtually the same as that of the starting materials (molecular weight, viscosity, infrared spectral characteristics) and a specific constant degree of decomposition (as measured by oxygen consumed and volatiles formed) was reached reproducibly with a given fluid batch, it must be deduced that a certain number of chains had to be hydrogen terminated. These would be oxidatively relatively unstable and, once attacked, would proceed to unzip. In this way only a limited number of volatiles would be formed, which was found to be the case (see Table IV), and once all the "weak" chains were consumed or "burned off," a stable fluid would result. Based on the fluid consumed on prolonged exposure to oxygen at 650°F, the hydrogen-terminated chains account for ca. 3.3% of Krytox MLO-71-6. The support of the theory that the weak links or rather endgroups are indeed hydrogen atoms has been provided by collaborative investigations with Air Force Materials Laboratory personnel. The results of this work will be published elsewhere.

### Degradation Studies in the Presence of M-50 Alloy

The extent of degradation of Krytox MLO-71-6 in the presence of M-50 ball-bearing alloy coupons in a nonoxidizing atmosphere, e.g., nitrogen, was found to be negligible even at 650°F (see Table II, test 18). It is apparent that degradation in oxygen at 550°F is also not very extensive (compare tests 12 and 18), yet increases by a factor of  $\sim 10$  when the temperature is raised to 600°F (see test 13). The difference between the 600° and 650°F 24-hr treatments in oxygen (tests 13 and 14) is surprisingly small, and the values measured are fairly close to those found at 650°F in oxygen on prolonged heating in the absence of the alloy (compare with tests 10 or 22, Table I). No really significantly increased degree of degradation was noted on heating the fluid in the presence of the M-50 coupon at 600°F in oxygen for 216 hr as compared to a 24-hr period (see tests 13 and 21). This finding would then imply that at 600°F the metal is merely accelerating the rate of the oxidative degradation so that the extent reached at 600°F approaches or equals that found at 650°F under identical conditions but in the absence of metal. It again supports the stipulations advanced in the preceding section that this process must be due to some weak links, most likely hydrogen endgroups.

The actual proof of the above theory is the stability of the fluid pretreated at 650°F in oxygen (see test 15, Table I) to M-50 coupon at 600°F in oxygen (see test 35, Table II) as shown by the minimal amounts of oxygen consumed and volatiles evolved in addition to the unchanged appearance of the metal coupon itself.

At 650°F in the presence of M-50 and oxygen the reaction of the "weak links" is supplemented and then exceeded by another process, the rate of which increases with time. This is shown by the test series 28 (see Table II). Each of these tests was conducted for the period of time recorded in Table II. At the end of each period the volatiles were removed, separated into liquid-nitrogen condensibles and noncondensibles, measured, and analyzed. Subsequently, fresh oxygen was introduced and the residual fluid was heated for the next designated period. The quantity of fluid given in test 28A was weighed in, and all the other quantities were calculated based on test 14 using the expression

$$\text{fluid weight loss (in g)} = 0.56 \times \frac{\text{total products}}{0.7983} = 0.701 \times \text{total products}$$

Test 28E was the last of the series, and at its conclusion the tube was opened to the atmosphere, the coupon and fluid were weighed, and the latter was subjected to the usual analyses. The results of this test series are better illustrated by the graph given in Figure 2 wherein "corrections" for the "weak link process" have been incorporated, tests 14-19 or test 16 (wherein pretreated fluid was employed) being thus given as the first data point. The cause for the rate decrease after 168 hr is unknown; on the other hand, it may be due to the metal or rather metal salts produced either in the form of the flaked-off "rust" or as the coating on the coupon. The coupon during the total exposure lost 9.3% of its original weight, consequently the bulk of metal was not consumed. It should be stressed that, although viscosity was decreased by 8% (in all the other instances it was increased), no difference could be noted in the residual fluid neither by molecular weight measurement nor by infrared spectral analysis. One can thus deduce that the rate increase observed with time of exposure is not caused by

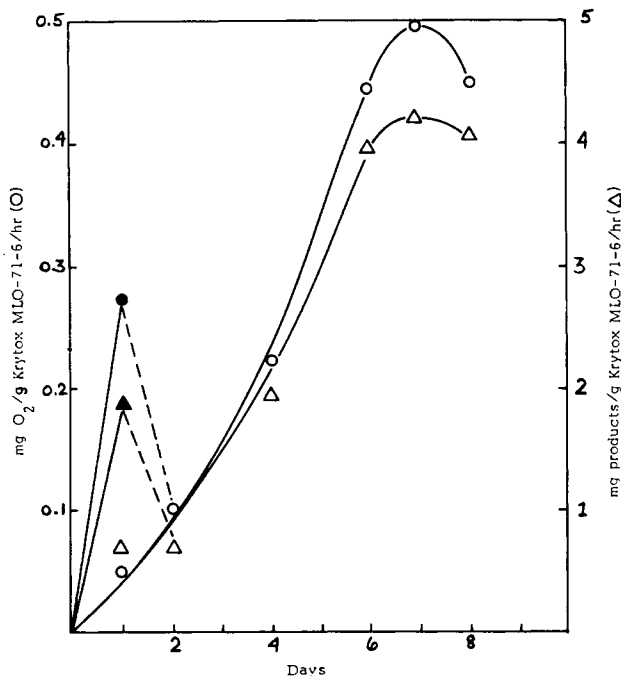


Fig. 2. Rate of oxygen uptake and product evolution as a function of successive exposures of Krytox MLO-71-6 to oxygen at 650°F in the presence of M-50 coupon. (●,▲) Run No. 14.

a change in the fluid but is due to production of active sites or species by the metal which promote scissions to occur, these being then followed by unzipping.

### Degradation Studies in the Presence of Ti(4Al, 4Mn) Alloy

The investigations conducted utilizing Ti(4Al, 4Mn) alloy in Krytox MLO-71-6 fluid are summarized in Table III, and the type and quantities of the volatiles liberated are given in Table VI. Comparing the results of these tests with the corresponding experiments performed in the presence of M-50 coupons, it is apparent that the degradation, as indicated by oxygen consumed and volatiles produced, is significantly accelerated by the presence of the titanium alloy. Actually the 24-hr exposure at 600°F is more severe for the fluid than 48 hr at 650°F in the presence of M-50 (compare test 36, Table III, with test 28A, Table II).

In view of the findings generated in the investigations of the M-50 alloy, it was expected (see Table II, tests 13 and 21) that possibly at 550°F the titanium alloy merely accelerates the degradation due to the "active" endgroups (as was found to take place with M-50 at 600°F). However, this does not appear to be the case with the Ti(4Al, 4Mn) alloy, which is evident from tests 37 and 39A-39C (see Table III) and even more so from the graphic presentation in Figure 3. A similar action was observed with M-50 at 650°F (see Fig. 2); however, the operative mechanisms must be different. This is shown by the different types of products formed, namely, the absence of carbon monoxide and hydrogen-terminated fluorocarbons as well as the production of materials of the general formula  $C_3F_7[OCF(CF_3)CF_2]_xOC_2F_5$  and  $C_2F_6$  (see Table VI). The reduction in mo-

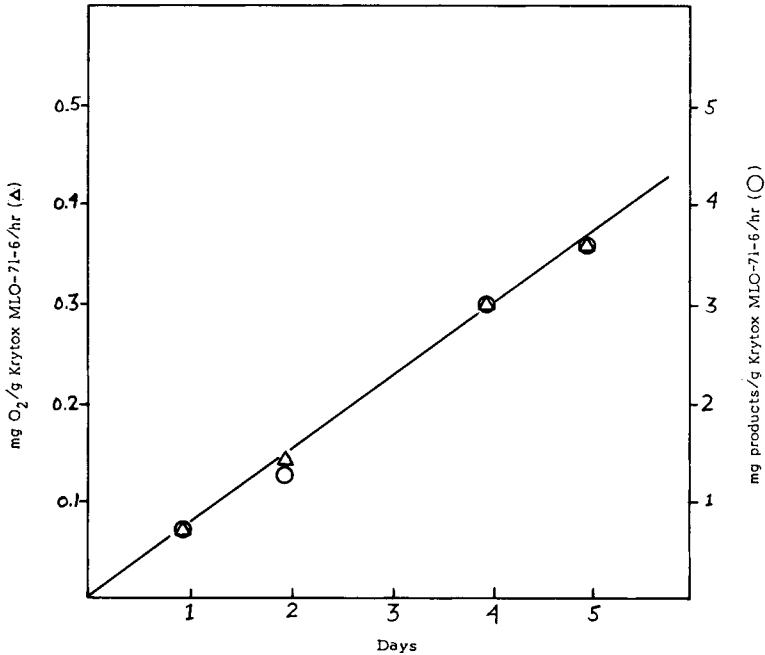
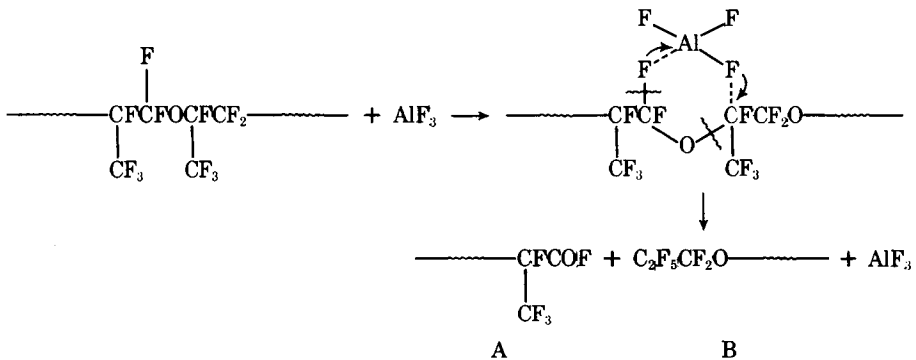


Fig. 3. Rate of oxygen uptake and product evolution as a function of successive exposures of Krytox MLO-71-6 to oxygen at 550°F in the presence of Ti(4Al, 4 Mn) coupon.

lecular weight of the residual fluid and the drastic decrease of viscosity in conjunction with the production of the compounds of the type just mentioned would tend to show that chain scissions by a fluorinating agent, e.g.,  $\text{AlF}_3$ , do take place. This stipulation is in agreement with the work of Gumprecht<sup>7</sup> who indicated that the attack by  $\text{AlF}_3$  leads to chain scissions and formation of  $\text{C}_2\text{F}_5$ -terminated materials via the mechanism depicted below:



Of the two fragments A can degrade further without assistance from  $\text{AlF}_3$ , whereas B is a lower molecular weight "Krytox" telomer.

Inasmuch as no degradation was observed in the presence of Ti(4Al, 4Mn) alloy in an inert atmosphere even at 600°F (test 45, Table III), it has to be assumed that at that stage  $\text{AlF}_3$  is absent and the three metal constituents of the alloy are inactive. On the other hand, it has been shown that even in the absence of metal, Krytox MLO-71-6 undergoes thermal oxidative degradation at temperatures

as low as 550°F (test 2, Table I). Consequently, at this temperature  $\text{AlF}_3$  is conceivably formed via reaction of, e.g.,  $\text{Al}_2\text{O}_3$  (formed by surface oxidation of the alloy) with the fluid's oxidation products  $\text{COF}_2$  and  $\text{CF}_3\text{COF}$ , most likely via the path delineated for  $\text{SiF}_4$  production. This type of a process would also explain the rate increase with time (see Fig. 3) since the concentration of  $\text{AlF}_3$  would increase as degradation would proceed. The postulation regarding  $\text{AlF}_3$  formation and its action is strongly supported by test 43 (Table III) wherein pretreated fluid (i.e., fluid free of the weak endgroups) was employed and where the extent of degradation as measured by volatiles produced, oxygen consumed, and as judged by coupon appearance changes was negligible as compared to test 37, in which the as-received Krytox MLO-71-6 was used. Similar results were obtained in experiment 44, which was conducted in the vicinity of 600°F. Thus, it would seem safe to postulate that at least up to 600°F oxides of the metals present in the Ti(4Al, 4Mn) alloy do not degrade hexafluoropropylene oxide-derived telomers, provided these are terminated by a perfluoroalkyl moiety, i.e., compositions of the type  $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_x\text{OR}_f$  ( $\text{R}_f = \text{C}_n\text{F}_{2n+1}$ ).

This investigation was supported by the U.S. Air Force Materials Laboratory under Contract No. F33615-75-C-5201. The authors are indebted to C. E. Snyder and Dr. C. Tamborski for helpful discussions and suggestions.

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Received January 29, 1979