N72-14940

DRA

FUNDAMENTAL IGNITION STUDY FOR MATERIAL FIRE SAFETY IMPROVEMENT

K. L. PACIOREK, R. H. KRATZER, AND J. KAUFMAN

CASE FILE
COPY

FINAL REPORT, PART II
CONTRACT NASW-1921

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER
MOFFETT FIELD, CALIFORNIA 94035

JUNE 1971

DYNAMIC SCIENCE
A Division of Marshall Industries
2400 Michelson Drive, Irvine, California 92664 (714) 833-2670

FUNDAMENTAL IGNITION STUDY FOR MATERIAL FIRE SAFETY IMPROVEMENT

K. L. Paciorek, R. H. Kratzer, and J. Kaufman

Final Report, Part II
Contract NASW-1921

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Ames Research Center
Moffett Field, California 94035

June 1971

DYNAMIC SCIENCE
A Division of Marshall Industries
2400 Michelson Drive
Irvine, California 92664

FOREWORD

This Final Report describes the work performed at Dynamic Science, a Division of Marshall Industries, under NASA Contract NASW-1921 during the period July 15, 1970 to May 15, 1971. The investigations were performed by K. L. Paciorek, R. H. Kratzer, and J. Kaufman. The work was administered by the Chemical Research Projects Office, NASA-Ames Research Center, Moffett Field, California, with Dr. Domenick Cagliostro furnishing technical guidance.

SUMMARY

The aim of the present study was to determine the autoignition behavior of a number of polymeric compositions in oxidizing media as well as the nature and relative concentration of the volatiles produced during the various stages of oxidative decomposition culminating in combustion. The materials investigated were Teflon, Fluorel KF-2140 raw gum and its compounded versions Refset and Ladicote, 45B3 intumescent paint and Ames isocyanurate foam. The majority of the tests were conducted using a stagnation burner arrangement which provided a laminar gas flow and allowed the sample block and gas temperatures to be varied independently. This apparatus, together with a sampling probe attachment, was constructed during the first portion of this work and is fully described in Part I of the present report.

The oxidizing atmospheres were essentially air and oxygen, athough in the case of the Fluorel family of materials, due to partial blockage of the gas inlet system, some tests were performed unintentionally in enriched air (not oxygen). The 45B3 paint was not amenable to sampling in a dynamic system, due to its highly intumescent nature. Consequently, selected experiments were conducted using a sealed tube technique both in air and oxygen media.

Preliminary Teflon investigations were carried out under the first portion of this program. Based on the completed work, it is obvious that insofar as autoignition is concerned this is the most nonflammable organic material tested. The nature of volatiles formed in oxygen and air is different. In oxygen the predominant process is the oxidation of tetrafluoroethylene initially to COF_2 which during combustion disproportionates largely into CO_2 and CF_4. The concentration of free tetrafluoroethylene under these conditions is negligibly low. In air relatively large concentrations of tetrafluoroethylene were observed together with a spectrum of rearrangement derived fluorocarbons in addition to the expected oxidation products. Prior to ignition the air medium allows a considerable buildup of toxic species. The autoignition temperature in air is considerably higher than in oxygen (575° versus $510^\circ C$).

Fluorel KF 2140 raw gum was found to autoignite in oxygen at the equitemperature of 400°C; yet in air the autoignition occurred only above 630°C. Prior to ignition and during combustion fluorinated species, e.g., hydrogen fluoride (analyzed as SiF_4), CHF_3, CH_2CF_2, possibly $CF_3CF{=}CF_2$ and other not identified fluorinated hydrocarbons were formed in addition to CO and CO_2. Refset, a composition of Fluorel containing magnesium salt and other undisclosed ingredients, was found to autoignite in oxygen at ca 380°C. No autoignition took place in air, although the material glowed. Both in oxygen and air residue remained (48 and 57%, respectively). Hydrogen fluoride was observed only during combustion, indicating the presence of an internal absorber. The hydrogen fluoride formed on combustion is believed to originate from the gaseous fluorinated hydrocarbons, CHF_3 and CH_2CF_2. Relatively large quantities of CO were detected prior to ignition; there is no explanation for this finding. Fluorel consitutes only 20% of Ladicote II, the remainder being a wide assortment of ingredients. The autoignition equitemperature in oxygen was found to be in the vicinity of 455°C, in air ignition was sporadic and irreproducible. Thus no ignition curve could be obtained. Hydrogen fluoride was detected only on combustion.

The 45B3 paint autoignited in oxygen at ca 365°C, in air at ca 495°C. The combustion in oxygen was virtually complete, whereas in air the sample burned only briefly and the residue amounted to 30-40%. Due to the intumescent nature no sampling tests could be conducted in the burner. Sealed tube reactions were performed at 200, 300, 400° and 500°C in oxygen and air. No apparent reaction took place at 200°C; at the higher temperatures the following gaseous species were identified: SO_2, CO, CO_2, HCN, COS and CS_2. The presence of solid and liquid products was also noted.

In oxygen the autoignition equitemperature for the Ames isocyanurate foam was found to be ca 350°C, whereas no ignition could be initiated in air up to ca 600°C, the sample merely glowed. Combustion in oxygen left no residue, whereas after the glow disappearance in air ca 16% of residue remained. The only gaseous products detected on sampling were CO and CO_2 together with small quantities of aromatic and possibly cyanurate linkages containing species. Other compounds formed appeared to be nonvolatile at room temperature.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

INTRODUCTION

The technological advances as exemplified among others by space travel, larger and faster flying commercial aircraft and high-rise buildings bring into focus the problems associated with the flammability of non-metallic materials and the toxicity of their decomposition and combustion products.

Under normal circumstances, such as exist, e.g., in a one story building, the dangers created by the decomposition and combustion of flammable materials are minimized by the ease of egress. However, in enclosed environments represented by these mentioned above, an escape is virtually impossible even when a hazardous condition has been detected. It is therefore very important to know under which conditions a given material will start to be a hazard both in regard to toxicity and flammability. This understanding will then allow to eliminate (or improve) candidate materials of construction which are known to be inadequate for the specific application.

The studies discussed in the present report involved the investigation of the ignition behavior of a number of compositions, namely Teflon, the Fluorel family of materials, i.e., Fluorel KF-2140 raw gum, Refset, Ladicote, 45B3 intumescent paint, and the Ames isocyanurate foam in air and oxygen media utilizing the stagnation burner arrangement. The nature and relative concentrations of volatiles evolved prior to ignition, on ignition, and during combustion were determined and based on this the operative mechanisms were postulated. To supplement the investigation performed under dynamic conditions limited tests were conducted in sealed tubes.

RESULTS AND DISCUSSION

The studies of the pyrolysis, oxidation, and ignition behavior of selected polymeric materials were commenced under the first portion of this program (Ref. 1). The initial effort was centered largely on the development of suitable test equipment and selection of appropriate diagnostic tools as well as a delineation of a broad theoretical treatment adaptable to a variety of flammability aspects. Due to time limitation only two materials were investigated, namely Delrin and Teflon; the latter not completely.

The current study is a direct continuation of the work begun under the first program. The apparatus and experimental procedure described in the first part of this report (Ref. 1) cover amply the overall details of instrumentation and analysis. The specific modifications of the normal experimental procedure employed during this program, which were necessitated by the particular properties of some of the materials investigated, will be described when discussing these individual compositions.

TEFLON INVESTIGATIONS

Teflon studies were initiated under the first portion of this program. To summarize briefly the previous work the ignition curve in oxygen was determined and the equitemperature (that point on the ignition curve at which the gas and heating block temperatures are equal) was found to be ca 510°C. In conjunction with the preliminary tests in air, it was found that the off-gassing characteristics, e.g., evolution of toxic components, are more dangerous in air than in oxygen. This is due to the significantly higher autoignition temperatures in air which resulted in turn in the production (prior to ignition) of relatively high quantities of COF_2. In oxygen this effect is minimized since once combustion occurs the disproportionation of COF_2 to CO_2 and CF_4 takes place.

During the current investigations of Teflon the ignition behavior in air was determined and the results are summarized in Table I and expressed graphically in Figure 1. The equitemperature under these conditions appears to be 575°C. To obtain a better understanding of the processes occurring prior to ignition, at ignition, and during combustion of Teflon special

TABLE I. SUMMARY OF EXPERIMENTS CONDUCTED ON TEFLON IN AIR ATMOSPHERE[a]

Run No.	Pellet Diam. In[b]	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec[c]	Burn Time Sec[d]	Remarks
535	1/2	609	590	85	10	Not true ignition; complete evaporation in 128 sec.
536	1/2	616	595	100	-	Difficult to observe
537	1/2	620	601	60	30	Seems true ignition
538	1	625	611	60	75	---
539	1	630	618	70	60	---
540	1	634	621	63	67	---
541	1	567	618	85	55	---
542	1	574	618	110	40	---
543	1	581	621	118	59	---
544	1	590	620	114	51	Sampling run
545	1	592	619	117	52	Sampling run
553	1	630	590	95	51	---
554	1	613	591	93	62	---
555	1	607	584	137	48	---
556	1	599	575	150	70	---
557	1	530	520	n.i.[e]	n.a.[f]	Pellet removed after 10 min.
558	1	522	540	n.i.	n.a.	Complete evaporation in 10 min.
559	1	536	559	n.i.	n.a.	Complete evaporation in 9 min.
560	1	569	587	128	63	---
561	1	588	576	140	63	---
562	1	592	563	n.i.	n.a.	Complete evaporation in 7 min. 20 sec.
563	1	562	566	n.i.	n.a.	Complete evaporation in 7 min. 30 sec.
564	1	546	580	?	?	Ignition at 235 sec; 25 sec burning; complete evaporation additional 85 sec; total time 345 sec.

TABLE I. (Continued)

Run No.	Pellet Diam. In[b]	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec[c]	Burn Time Sec[d]	Remarks
565	1	544	586	190	55	---
566	1	509	584	n.i.	n.a.	Complete evaporation in 7 min 25 sec.
567	1	478	606	225	41	---
856	1/2	560	579	88	17	---
857	1/2	522	588	71	21	---
858	1/2	513	579	n.i.	n.a.	Complete evaporation in 4 min 30 sec.
859	1/2	487	609	75	53	---
860	1/2	490	598	100	40	---
861	1/2	481	583	n.i.	n.a.	Complete evaporation in 4 min.
862	1/2	485	592	n.i.	n.a.	Complete evaporation in 3 min 45 sec.

[a] All temperatures were recorded just prior to Teflon insertion.

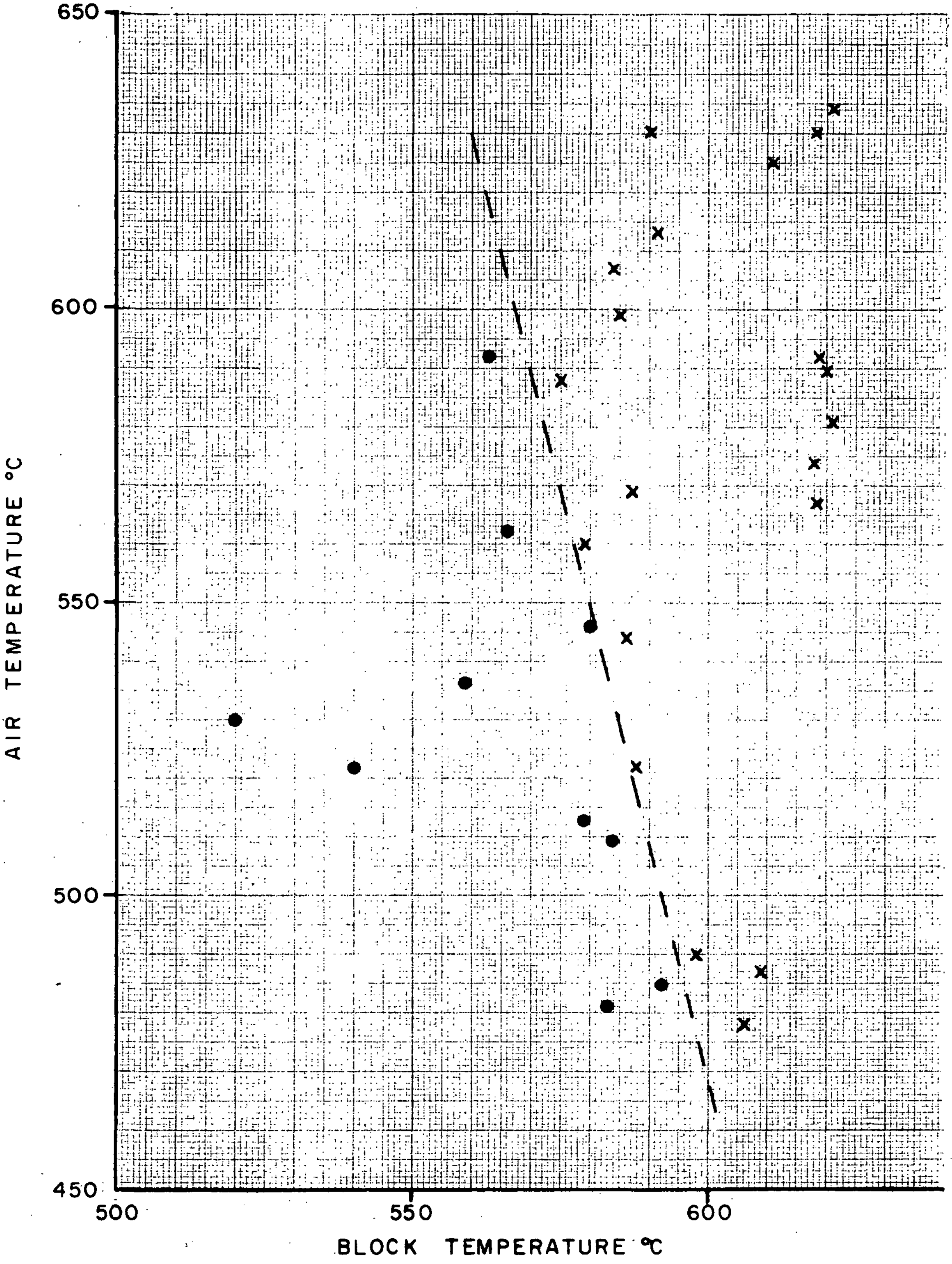
[b] All the pellets were 0.05" thick.

[c] Time measured from the insertion of the Teflon pellet.

[d] Time from ignition onset to conclusion of burning.

[e] No ignition.

[f] Not applicable.



X = IGNITION

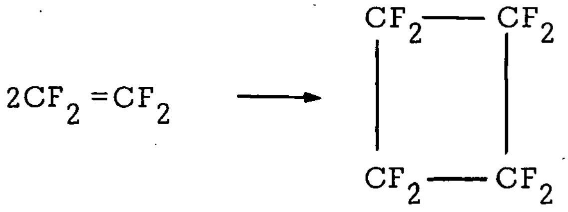
• = NO IGNITION

Figure 1. Effect of Polymer Heating Block and Air Temperatures Upon Teflon Ignition.

emphasis was placed on the determination of the nature and the relative ratios of the volatiles produced. The sampling schedules and experimental details of these tests are given in Table II, whereas the mass spectral results are summarized in Table III.

Examining Table III, it is apparent that only traces of tetrafluoroethylene were detected in the oxygen runs (552, 574) both prior to ignition and during combustion. One explanation for this finding is that at the temperatures employed (gas and heating block) the relative concentration of tetrafluoroethylene, as compared to that of oxygen, is very low resulting in an essentially quantitative reaction. In the case of air, the experiments were usually performed at higher temperatures (necessary to effect ignition). At these temperatures the rate of production of tetrafluoroethylene prior to ignition is significantly higher than in the oxygen tests and this, in conjunction with the diluting effect of nitrogen, results in fairly high tetrafluoroethylene concentrations. Accordingly the tetrafluoroethylene which failed to react with oxygen is free to undergo other reactions resulting in the formation of C_3F_8, C_2F_6, C_3F_6, C_4F_8, etc. These deductions are supported by the argon test (run 576).

On the basis of the extended work performed to date on the pyrolytic behavior of polytetrafluoroethylene (Refs. 2-14), it is safe to assume that the decomposition in vacuo and in inert media proceeds via the production of tetrafluoroethylene. In a closed system the initially formed tetrafluoroethylene mainly dimerizes into tetrafluorocyclobutane.



(1)

In the presence of an inert gas a portion of the initially formed tetrafluoroethylene (note the rate of decomposition is identical in vacuo and in the presence of an inert gas) interacts with the production of fluorinated species such as those listed above, e.g., c-C_4F_8, C_3F_8, C_2F_6, etc. (Refs.7,9).

TABLE II. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN THE TEFLON RUNS[a]

Run No.[b]	Sample No.	Sampling Time Sec[c,d]	Ignition Delay Sec[c]	Total Time Min:Sec[e]	Gas Temp. °C	Block Temp. °C	Gas
544	1	110-115	114	2:45	590	620	Air
544	2	120-125	114	2:45	590	620	Air
544	3	130-135	114	2:45	590	620	Air
545	1	100-105	107	2:49	592	619	Air
545	2	110-115	107	2:49	592	619	Air
545	3	120-125	107	2:49	592	619	Air
552	2	115-120	136	2:55	546	527	O_2
552	3	137-142	136	2:55	546	527	O_2
574	-	300-305	n.a.[f]	20:10	506	500	O_2
575	-	300-305	n.a.	7:25	578	558	Air
576	-	300-305	n.a.	16:45	592	559	Ar

[a] All temperatures were recorded just prior to Teflon insertion.

[b] All the pellets used in these tests were 1" diameter.

[c] Times are measured from insertion of Teflon pellet.

[d] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[e] Time from insertion of Teflon pellet to conclusion of burning or to complete evaporation if no ignition took place.

[f] Not applicable, since no ignition took place.

TABLE III. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING TEFLON HEAT TREATMENTS IN OXYGEN, AIR, AND ARGON ATMOSPHERES[a]

Run No.	Total %	Air %	O_2 %	CO_2 %	N_2 %	Ar %	SiF_4 %	C_3F_8 %	C_3F_6 %	c-C_4F_8 %	C_2F_6 %	C_2F_4 %	CF_4 %	COF_2 %
552-2	101.39	b	55.58	0.73	44.12	0.52	0.25	-	-	0.04	0.04	0.01	0.04	0.07
552-3[c]	99.74	b	42.49	18.81	17.10	0.18	2.95	-	0.12	-	0.14	-	16.89	1.06
574	101.06	b	64.53	0.25	35.72	0.41	0.07	-	-	0.02	-	0.01	0.03	0.02
544-1[c]	101.60	42.50	d	6.05	31.83[e]	0.30	2.05	0.12	2.32	0.86	3.14	4.02	4.51	3.90
544-2	100.00	10.13	d	11.21	44.06[e]	0.43	5.27	0.15	3.43	0.50	5.30	3.49	14.90	1.13
544-3	91.25[f]	11.09	d	6.30	46.08[e]	0.44	2.30	0.15	2.33	0.36	4.92	2.34	11.20	3.74
545-1	101.07	87.21	d	3.19	5.33[e]	0.08	1.12	-	0.84	0.64	0.14	2.10	0.40	0.02
545-2[c]	99.84	33.32	d	10.94	37.07[e]	0.37	3.66	0.12	1.54	0.39	3.52	2.39	5.72	0.70
545-3	95.12[f]	12.09	d	9.86	46.10[e]	0.45	3.14	0.16	2.83	0.43	4.77	3.59	9.60	2.05
575	98.96	83.95	d	2.36	8.89[e]	0.12	0.69	0.04	0.36	0.16	0.05	0.09	0.71	1.54
576	98.10	33.31	d	0.32	1.81[e]	61.92	0.02	0.06	0.09	0.13	0.03	0.41	-	-

[a] All the analyses are given in mole percent.

[b] These runs were conducted under oxygen flow, however, due to partially blocked sintered disc through which the gas enters, the oxygen flow was reduced resulting in air inflow. The presence of air is shown by the nitrogen content. Accordingly, air in 552-2 = 56.50%, in 552-3 = 21.90% and in 574 = 45.74%.

[c] This is the sample where ignition occurred.

[d] The oxygen present is expressed as air of which it constitutes 20.936%.

[e] This is the nitrogen in excess of that present in air, this value is proportional to oxygen depletion; the same applies to argon.

[f] The missing percent to 100% appears to be CO, in view of the left over output at m/e = 12 and m/e = 28.

These reactions take place also in air concurrently with oxidation as shown by the data given in Table III. It is not clear whether oxidation of polytetrafluoroethylene is primarily a gas reaction or whether a solid-gas interaction also plays a part. There is a definite increase in the pyrolysis rate in air and even more so in oxygen as was shown by a number of investigators (Refs. 4,14,15) and by our own studies. Mathias and Miller (Ref. 16), for their electric discharge treatment of Teflon, showed that oxidation does occur in the gas phase via reaction of C_2F_4 with oxygen, e.g.,

$$C_2F_4 + O \longrightarrow (C_2F_4O) \longrightarrow COF_2 + CF_2 \quad \text{or} \qquad (2)$$

$$C_2F_4{}^* + O_2 \longrightarrow 2COF_2 \qquad (3)$$

where $C_2F_4{}^*$ is an electronically excited species. Accordingly, it is not an unreasonable assumption that also under the thermal conditions existing in our system the oxidation process is a gas phase reaction of the evolved tetrafluoroethylene with oxygen. In the presence of air this simple picture is complicated by the secondary reactions of tetrafluoroethylene giving rise to other fluorinated species and their oxidation products. The latter materials, such as e.g., CF_3COF, we were unable to detect in our work; however, this does not mean that these were not formed.

In the majority of our experiments we have isolated SiF_4. As explained previously (Ref. 1) this material is derived from hydrolysis of COF_2 followed by reaction of the formed hydrogen fluoride with the silica of the ampoule.

$$2COF_2 + 2H_2O \longrightarrow 2CO_2 + 4HF \qquad (4)$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \qquad (5)$$

Thus one can express all the SiF_4 as COF_2 since, as shown above, the former must be derived from the hydrolysis of COF_2.

In such a conversion every molecule of SiF_4 is equivalent to two molecules of COF_2, together with a loss of two molecules of CO_2; in agreement with the reverse of reactions 4 and 5. We also know that part of the CF_4 must originate from COF_2 disproportionation, since the oxidation of tetrafluoroethylene is believed to proceed via COF_2.

$$2COF_2 \longrightarrow CO_2 + CF_4 \qquad (6)$$

Using the data obtained previously (Ref. 1, run 462, in the oxygen series) and expressing all the SiF_4 as COF_2, in conjunction with correction of the carbon dioxide value, one obtains the graph given in Figure 2. The data agree very well with the postulation that all the CF_4, in the oxygen experiment (prior to COF_2 hydrolysis with atmospheric moisture), is derived from COF_2 disproportionation. The absence of other fluorinated species furthermore supports the deduction that under these conditions C_2F_4 once formed reacts quantitatively with oxygen giving COF_2 without undergoing any rearrangements. In the presence of air the picture becomes much more complicated which is apparent from the graphical presentation of the run 545 in Figure 3. The point worth noting is that here CF_4 is produced not only via COF_2 disproportionation but also by other processes, since its relative concentration is higher by a factor of three than that of the corrected value for CO_2. The high content of CF_4, if one considers the rearrangement of C_2F_4 is not surprising. Similar results were found in the case of C_2F_4 discharge treatment where CF_4 was found to be one of the main products (Ref. 17).

To summarize briefly, the temperature at which autoignition occurs is governed by the fuel (in the case of Teflon tetrafluoroethylene), and oxygen concentrations. The rate of production of tetrafluoroethylene is temperature dependent. The oxidative reaction, i.e., COF_2 formation which takes place prior to ignition, is of much greater importance in air than in oxygen atmosphere since in the latter ignition occurs at lower temperatures, i.e., at lower C_2F_4 concentrations. During combustion COF_2 is also formed but it disproportionates largely into CF_4 and CO_2. In air another effect becomes pronounced, namely the rearrangement of C_2F_4 into other fluorinated species, one of these being the highly toxic perfluoroisobutene. The present study was too limited in time to allow a truly detailed investigation. On the other hand, several significant aspects become apparent as the result of this work.

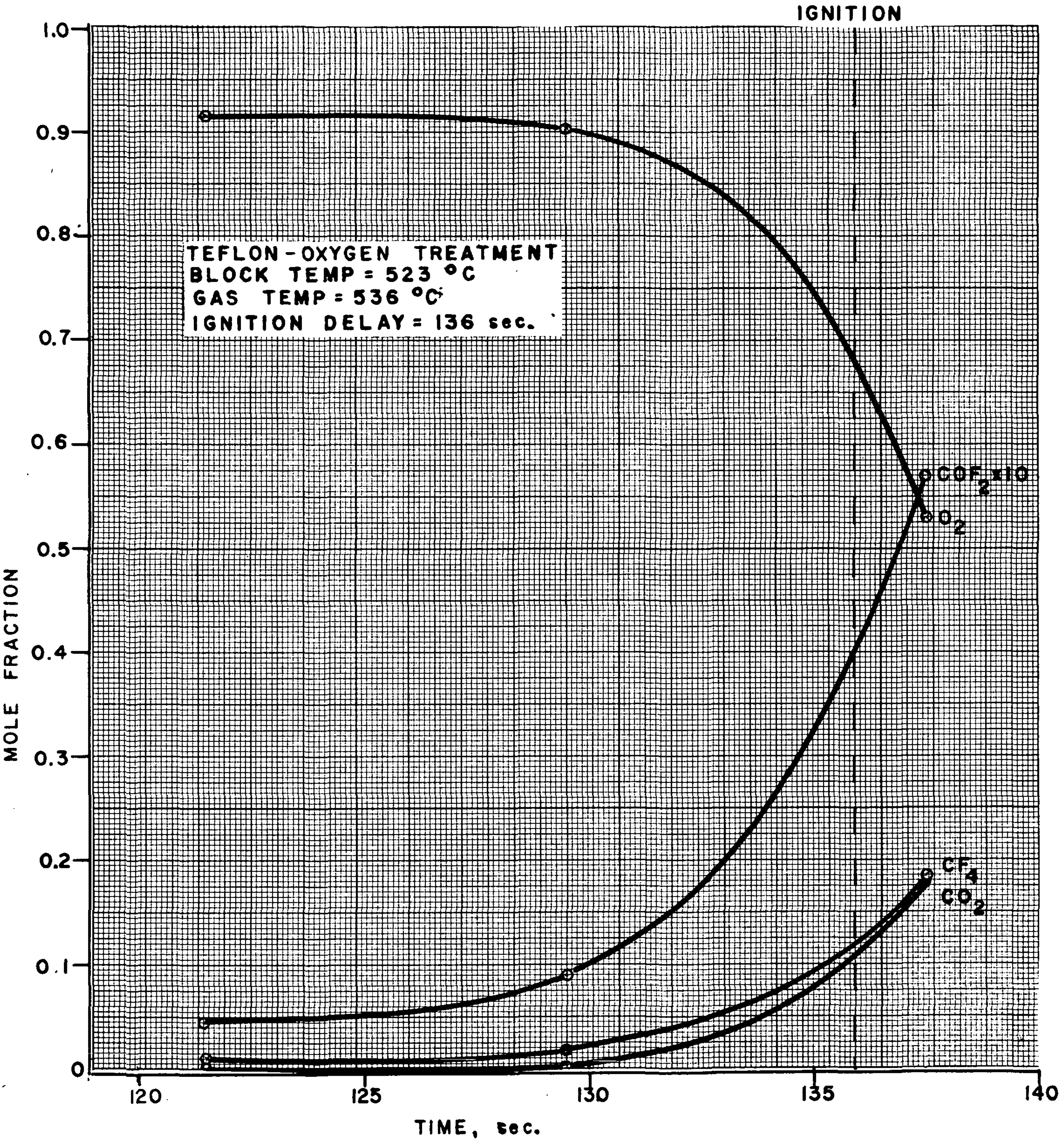


Figure 2. Relative Species Concentration as a Function of Heat Treatment Duration in a Teflon-Oxygen Test

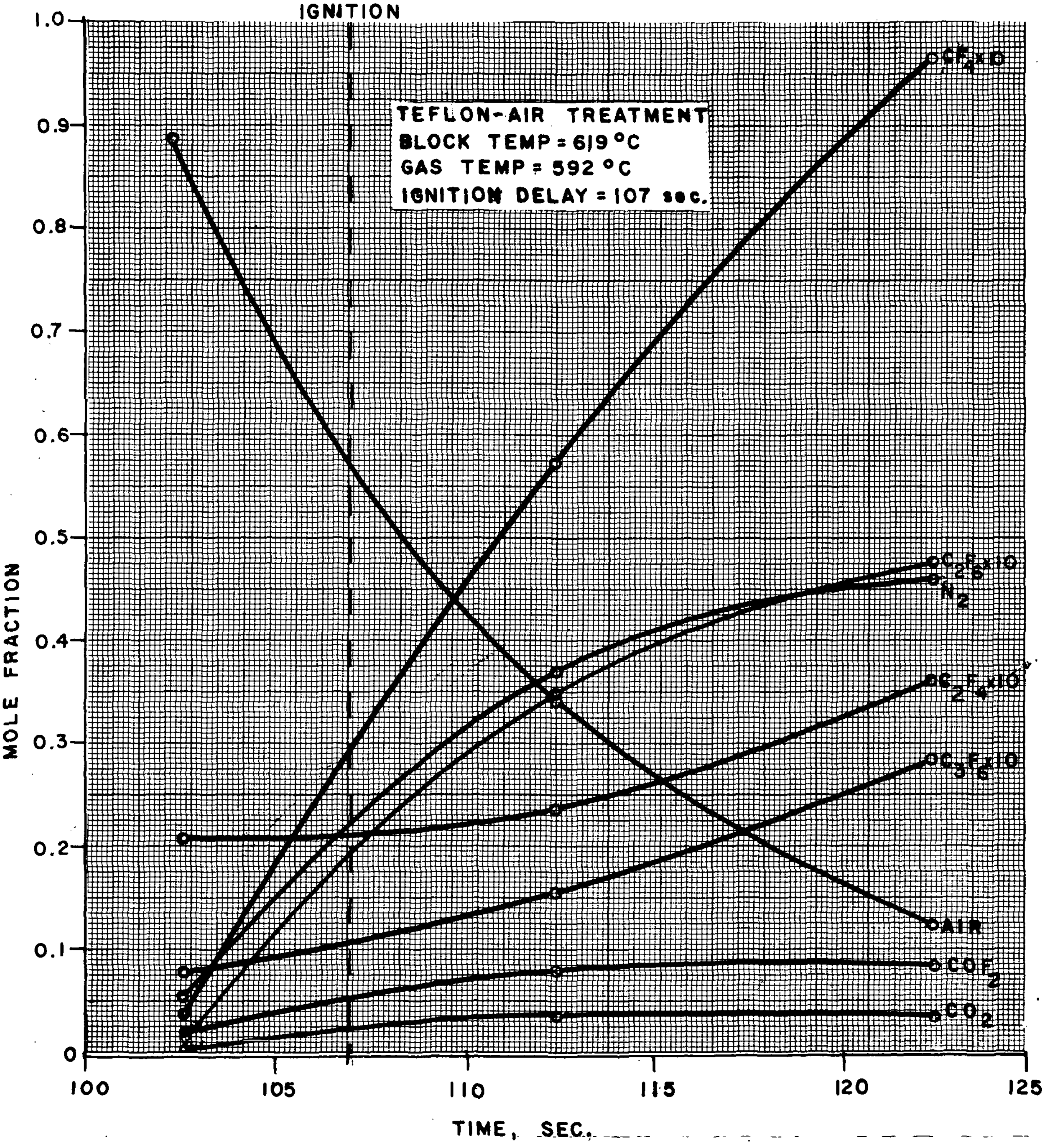


Figure 3. Relative Species Concentration as a Function of Heat Treatment Duration in a Teflon-Air Test

FLUOREL, REFSET AND LADICOTE INVESTIGATIONS

The three materials were grouped together inasmuch as Fluorel, i.e., the vinylidene fluoride-hexafluoropropene copolymer, is a major ingredient of the compounded versions as represented by Refset and Ladicote. Thus the data obtained using the raw gum denote the behavior of untreated polymer, which is significantly altered by the addition of suitable agents as is shown by Refset and Ladicote investigations.

The vinylidene fluoride-hexafluoropropene copolymers represented by the Vitons (E. I. duPont de Nemours and Company), and Fluorels (Minnesota Mining and Manufacturing Company) comprise a series of materials wherein the range of vinylidene fluoride varies from 85 to 50%. In most of the commercially available products vinylidene fluoride usually accounts for more than 50%, giving segments of polyvinylidene fluoride. Regarding the preferential structural arrangement of the monomer units, the work of Ferguson (Ref. 18) is probably most reliable. There has been a relatively limited investigation performed on the stability of the raw gums, their ease of oxidation, and type of products formed in different media. The Russians have done some work in this field (Refs. 19,20) and limited studies were performed by others (Refs. 21,22,23,24); however, these dealt mainly with problems associated with curing. The various facets of the latter aspects have been reviewed fairly recently (Ref. 25). Based on the above referenced data it is clear that the uncured rubber is definitely more stable than the cured elastomer in vacuum and in oxidizing atmospheres. The Russian work seems to indicate that the main volatile products of Viton A decomposition are $CF_2=CH_2$, CF_3H and HF. The lack of $CF_3CF=CF_2$ isolation is somewhat surprising.

Fluorel Raw Gum Studies

The current work was performed using Fluorel KF-2140 raw gum. Based on the elemental analysis (H,2.1%; C, 32.52%; F, 65.79%) this material consists of 80 mole percent $CH_2=CF_2$ and 20 mole percent of $CF_3CF=CF_2$. The composition given is not accurate since it is an average value calculated from the analytical results for C and F. On a weight basis the content of vinylidene fluoride is 61% based on fluorine and 63% based on carbon, but calculated from the hydrogen content the figure becomes 67%. Inasmuch as the hydrogen content is low (2.1%) it is expected to give a relatively inaccurate value, consequently the composition is based on the average value from C and F.

For the actual experiments Fluorel pellets 1/2 and 1 inch diameter; thickness, 0.075 inch; weight, 452.7 ± 9.6 mg, and 1853 ± 42 mg, were employed. The pellets were cut out from sheets 0.075 inch thick, press molded at 1200 pounds/inch^2 and heated to 300°F. To avoid the use of solvents the molds were opened, after overnight cooling to room temperature, by freezing in Dry Ice.

The ignition studies performed on Fluorel in oxygen are summarized in Table IV.

Fluorel was found not to burn as cleanly as Teflon and in almost every instance the formation of black smoke was noted. It is unknown whether it was the carbon produced or reaction with other ingredients formed; in any case the sintered disc through which the gas enters the burner chamber became partially blocked. This resulted in reduced flow of oxygen, which happened to be the medium under investigation, and in an inflow of air. Accordingly, frequent sintered disc changes were necessitated. In the ignition curve (Figure 4) the "reliable" points obtained using the freshly changed discs are enclosed in triangles. Based on this curve the autoignition equitemperature appears to be <u>ca</u> 400°C, which is significantly lower than the value found for Teflon (<u>ca</u> 510°C). If one considers, however, that ignition is governed by the gaseous fuel-oxidizer ratio, this finding is to be expected since below 450°C Teflon thermal decomposition is negligible, thus no fuel is released.

The tests conducted on Fluorel in air are rather surprising (see Table V) inasmuch as ignition occurred only above 600°C (meaning that both heating block and air had to be raised to this temperature) which is significantly higher than the limits found for Teflon (<u>ca</u> 575°C) under analogous conditions. There are several plausible explanations for this apparent behavior anomaly. In Teflon, even during the latter stages of decomposition one still deals with more or less the same gaseous species due to the unzipping characteristic

TABLE IV. SUMMARY OF EXPERIMENTS CONDUCTED ON FLUOREL KF 2140 IN OXYGEN[a,b,c]

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Remarks[f]
577	210	226	n.i.[g]	n.a.[h]	Pellet removed after 10 min; no change in weight
578	263	265	n.i.	n.a.	Pellet removed after 10 min
579	298	307	n.i.	n.a.	Pellet removed after 10 min
580	336	346	n.i.	n.a.	Pellet removed after 10 min
581	371	385	n.i.	n.a.	Evaporation in 18 min, 30 sec
582	417	420	103	42	---
583	425	405	136	21	---
585	410	404	185	7	Incomplete combustion; residue evaporated in 10 min
586	388	419	130	32	---
587	382	408	n.i.	n.a.	Evaporation in 17 min, 20 sec
588	331	421	175	38	---
589	345	412	n.i.	n.a.	Evaporation in 16 min
590	375	407	n.i.	n.a.	Evaporation in 18 min
591	366	418	183	36	---
592	431	402	165	25	---
593	452	386	143	13	Incomplete combustion; black residue evaporated in 13 min
594	460	377	n.i.	n.a.	Pellet removed after 23 min
595	465	409	83	49	---
596	473	427	72	38	---
597	532	411	65	45	---
598	525	391	83	30	---
599	519	371	117	18	Incomplete combustion; black residue evaporated in 15 min
600	201	405	n.i.	n.a.	Evaporation in 33 min
601	231	418	n.i.	n.a.	Evaporation in 21 min
602	245	437	n.i.	n.a.	Evaporation in 18 min

TABLE IV. (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Remarks[f]
603	252	452	n.i.	n.a.	Evaporation in 10 min
605	250	480	74	24	---
606	245	493	63	17	---
608	292	483	57	29	---
611	261	491	55	28	---
612	263	499	50	28	---
613	294	478	111	16	---
615	201	471	n.i.	n.a.	Evaporation in 7 min
617	207	499	39	34	---
618	210	488	55	31	---
619	203	461	n.i.	n.a.	Sampling run; evaporation in 5 min; N_2 = 44%
620	362	406	n.i.	n.a.	Sampling run; evaporation in 14 min; N_2 = 52%
621	354	219	n.i.	n.a.	Sampling run; pellet removed after 6 min; residue, 99.73%; N_2 = 43%
622	214	501	42	32	---
623	215	501	45	30	---
624	217	505	34	34	Sampling run; N_2 = 55%
625	425	426	110	32	---
626	425	425	113	49	---
627	424	425	150	41	Sampling run; N_2 = 43%
628	432	426	111	41	---
629	434	429	105	39	---
630	434	430	91	36	---
631	427	426	108	33	---
632	434	430	104	38	Sampling run; N_2 = 42%
633	208	491	59	30	This run was performed after the porous disc was replaced; N_2 = 4%

TABLE IV. (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Remarks[f]
634	214	474	175	12	---
635	210	468	160	12	---
636	212	460	n.i.	n.a.	Evaporation in 6 min
637	240	460	205	14	---
638	245	453	n.i.	n.a.	Evaporation in 6 min
639	285	452	n.i.	n.a.	Evaporation in 5 min, 30 sec
640	294	467	112	17	---
641	329	462	126	16	---
642	333	450	169	13	---
643	343	441	152	21	Great amount of black residue
644	348	426	n.i.	n.a.	Evaporation in 8 min
645	368	440	130	22	---
646	368	431	157	26	---
647	371	415	171	29	---
648	373	406	n.i.	n.a.	Evaporation in 11 min
649	399	402	174	26	---
650	413	393	n.i.	n.a.	Evaporation in 12 min
651	432	407	132	18	---
652	427	392	n.i.	n.a.	Evaporation in 18 min; great amount of black residue
653	459	402	115	19	---
654	457	392	n.i.	n.a.	Evaporation in 19 min, 30 sec
655	487	405	105	26	---
656	490	389	110	25	---
657	485	382	130	16	Incomplete combustion; black residue evaporated in 25 min

TABLE IV. (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Remarks[f]
658	522	376	110	18	Incomplete combustion; black residue evaporated in 21 min
659	537	394	91	23	---
660	250	459	n.i.	n.a.	Evaporation in 7 min
662	263	483	69	27	---
663	304	480	67	25	---
665	348	422	n.i.	n.a.	Evaporation in 12 min; N_2 = 4%
666	350	431	148	27	---
667	462	383	158	16	Incomplete combustion; N_2 = 2.4%; black residue evaporated in 35 min
668	473	412	138	72	Smoke at 70 sec
669	473	414	116	69	Smoke at 80 sec
670	476	416	147	70	Smoke at 75 sec; sampling run; N_2 = 5%
686	473	451	91	44	Disc changed before run 686; smoke at 20 sec
687	474	450	93	40	Smoke at 25 sec
688	474	451	75	45	Heavy smoke at 48 sec
689	474	451	82	38	Sampling run; smoke at 30 sec; N_2 = 5.5%

[a] Since Fluorel produces carbon the sintered disc through which the oxygen enters the burner chamber becomes partially blocked, resulting in lower oxygen flow and inflow of air from the open sides. The net result is that the experiments are not performed in oxygen, but in oxygen enriched air, i.e., the lowest oxygen content was found to be 41% (in air it is 21%).

[b] All temperatures were recorded just prior to Fluorel insertion.

[c] All the pellets were 0.075" thick; the runs 577-667 were performed using 1/2" diameter pellets, whereas for the tests 668-689 the 1" pellets were employed.

TABLE IV. (Continued)

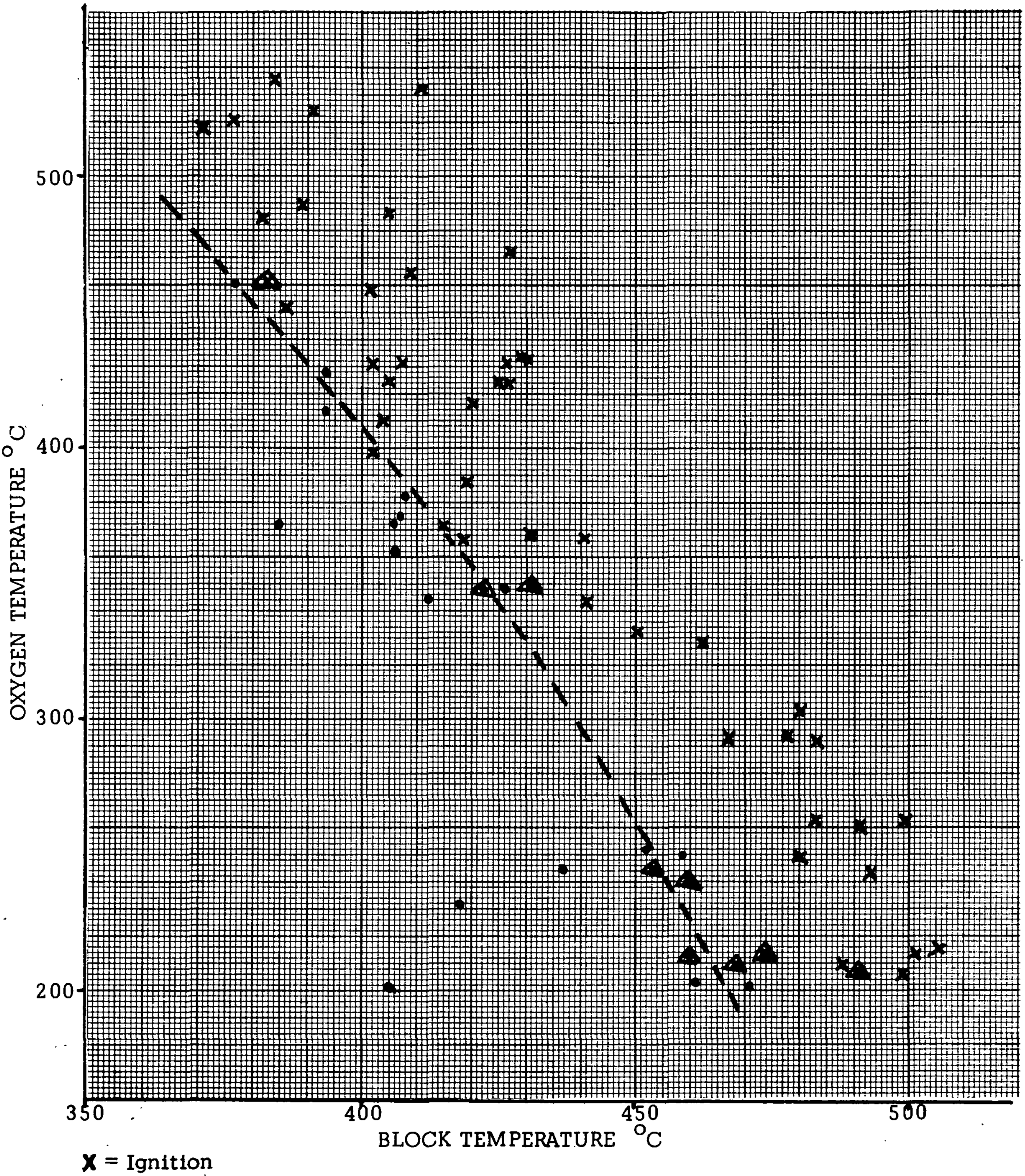
[d] Time measured from the insertion of the Fluorel pellet.

[e] Time from ignition onset to conclusion of burning.

[f] By evaporation it is meant when hardly any smoke was observed; but in each instance some residue, carbon?, remained which had to be physically removed. The time of evaporation in the case of incomplete combustion is measured from the insertion of the Fluorel pellet.

[g] No ignition.

[h] Not applicable.



X = Ignition
● = No ignition

FIGURE 4. EFFECT OF POLYMER HEATING BLOCK AND OXYGEN TEMPERATURE UPON FLUOREL KF 2140 IGNITION

TABLE V. SUMMARY OF EXPERIMENTS CONDUCTED ON FLUOREL KF 2140 IN AIR AND ARGON ATMOSPHERES[a,b]

Run No.[c]	Pellet Diam. in[d]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[e]	Burn Time Sec[f]	Remarks[g]
671	1/2	305	427	n.i.[h]	n.a.[i]	Evaporation in 21 min; smoke at 2 min
672	1/2	322	504	n.i.	n.a.	Evaporation in 3 min; smoke at 25 sec; heavy smoke at 1 min
673	1/2	336	521	n.i.	n.a.	Evaporation in 1 min, 45 sec; smoke at 15 sec; heavy smoke at 45 sec
674	1/2	343	552	n.i.	n.a.	Evaporation in 1 min, 40 sec; smoke at 8 sec; heavy smoke at 20 sec
675	1/2	417	572	n.i.	n.a.	Evaporation in 1 min, 45 sec; smoke at 10 sec; heavy smoke at 25 sec
676	1/2	476	598	n.i.	n.a.	Evaporation in 1 min, 10 sec; smoke at 15 sec; heavy smoke at 25 sec
677	1/2	525	595	n.i.	n.a.	Evaporation in 1 min, 15 sec; smoke at 15 sec; heavy smoke at 23 sec
678	1/2	592	604	n.i.	n.a.	Evaporation in 1 min, 5 sec; smoke at 12 sec; heavy smoke at 20 sec; disc was changed prior to run 679
679	1/2	466	453	n.i.	n.a.	Sampling run; smoke at 45 sec; heavy smoke at 90 sec; evaporation in 4 min, 30 sec
680	1/2	509	501	n.i.	n.a.	Sampling run, evaporation in 1 min, 55 sec; smoke at 22 sec; heavy smoke at 45 sec
681	1/2	527	551	n.i.	n.a.	Evaporation in 1 min, 15 sec; smoke at 10 sec; heavy smoke at 23 sec

TABLE V. (Continued)

Run No.[c]	Pellet Diam. in[d]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[e]	Burn Time Sec[f]	Remarks[g]
682	1/2	616	596	n.i.	n.a.	Evaporation in 1 min; smoke at 5 sec; heavy smoke at 35 sec
683	1/2	655	638	30	10	Smoke at 8 sec; heavy smoke at 25 sec
684	1	667	644	35	15	Smoke at 8 sec; heavy smoke at 25 sec
685	1	677	644	45	15	Sampling run; smoke at 15 sec
693	1/2	681	644	25	13	Heavy smoke at 15 sec
694	1	691	649	43	11	Heavy smoke at 25 sec
695	1	705	649	38	12	Heavy smoke at 17 sec; sampling run
701	1/2	639	614	28	11	Smoke at 15 sec
702	1/2	637	606	n.i.	n.a.	Evaporation in 50 sec; smoke at 20 sec; heavy smoke at 35 sec
690[c]	1/2	690	645	n.i.	n.a.	Evaporation in 1 min; smoke at 10 sec; heavy smoke at 30 sec
691[c]	1/2	681	645	n.i.	n.a.	Evaporation in 1 min; very heavy smoke at 35 sec
692[c]	1	688	641	n.i.	n.a.	Sampling run; evaporation in 1 min, 45 sec; smoke at 10 sec; very heavy smoke at 35 sec; sampling 40-45 sec

[a] The sintered disc through which the air enters the burner chamber becomes partially blocked resulting in lower air flow. The decrease in flow is best found by passing oxygen through the disc and determining nitrogen in the burner atmosphere. Depending on the N_2 value the sintered disc was then changed, if necessary.

[b] All temperatures were recorded prior to Fluorel insertion.

TABLE V. (Continued)

[c] The runs 671-695, 701 and 702 were performed in air atmosphere, whereas the runs 690-692 were conducted in argon.

[d] All the pellets were 0.075" thick.

[e] Time measured from insertion of the Fluorel pellet.

[f] Time from ignition onset to conclusion of burning.

[g] Evaporation means when no more smoke was observed (timed from insertion of Fluorel pellet). After each run the heating block was cleaned to remove the left over residue.

[h] No ignition.

[i] Not applicable.

of polytetrafluoroethylene. This is not the case with Fluorel, where in view of its structural arrangement on thermal decomposition a variety of processes occur releasing a number of volatiles and leaving behind a char derived by aromatization of the unsaturated linkages (Ref. 26). Furthermore, the presence of hydrogen fluoride, in analogy with the other halogen halides, would be expected to exert a flame retardant action. Accordingly in air to effect ignition one requires a truly high temperature to reach the critical conditions.

To elucidate the processes taking place and the nature of the evolved products, sampling runs were performed in oxygen, air, and argon. The experimental details of these tests are given in Tables VI and VIII whereas the mass spectral results are presented in Tables VII and IX, respectively. Examining Table VII it is obvious that the experiments 619-632 were conducted not in oxygen but in oxygen enriched air; in addition, since 1/2" pellets were used the concentration of the evolved species was relatively low. This is in particular apparent in the absence of combustion. However, once combustion occurred large quantities of CO_2 and hydrogen fluoride (analyzed as SiF_4) were given off (runs 624-1, 624-2, 632). It should be explained that the hydrogen fluoride, in all the experiments, was analyzed as SiF_4, which it formed on reaction with the glass ampoule silica (see Eq. (5), page 9). Consequently, the hydrogen fluoride concentration in all instances was four times as high as that of SiF_4, since four HF molecules are required to form one of SiF_4.

The tests conducted in almost pure oxygen (Table VII, runs 670 and 689) illustrate this point much better. As noted in Table IV, at 75 sec in run 670, smoke could be observed and at the sampling times 105-118 sec (prior to ignition, Table VI) it became fairly dense, yet the analyses (Table VII) fail to show significant quantities of the fluorinated or oxidation species. The same applies to the ignition or truly preignition sample (689-1). The infrared spectrum (Figure 5) of this particular sample exhibited only a relatively weak absorption at 9.65μ , 9.70μ showing just the presence of SiF_4. The very strong band centered at 14.95μ , according to Heicklen (Ref. 27), is due to sodium fluoride formed by the interaction of active fluorine species with the infrared cell sodium chloride windows. The combustion samples, on the other hand, 689-2 and 670-3, contained a number of compounds. This is most

TABLE VI. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN THE FLUOREL KF 2140 OXYGEN RUNS[a,b]

Run No.	Pellet Size In	Sampling Time min:sec[c,d]	Ignition Delay min:sec[c]	Total Time min:sec[e]	Gas Temp. °C	Block Temp. °C
619	1/2	2:00-2:05	n.i.[f]	5:00	203	461
620	1/2	4:00-4:05	n.i.	n.d.[h]	362	406
621	1/2	5:00-5:05	n.i.	n.a.[g]	354	219
624-1	1/2	0:32-0:37	0:34	1:08	217	505
624-2	1/2	0:40-0:45	0:34	1:08	217	505
627	1/2	1:50-1:55	2:30	3:11	424	425
632	1/2	1:40-1:45	1:44	2:22	434	430
670-1[i]	1	1:45-1:50	2:27	3:00	474	415
670-2	1	1:53-1:58	2:27	3:00	474	415
670-3	1	2:30-2:35	2:27	3:00	474	415
689-1	1	1:17-1:22	1:22	2:00	474	451
689-2	1	1:25-1:30	1:22	2:00	474	451

[a] Due to partial blockage of the sintered disc, some experiments were conducted in _ca_ 50% O_2-N_2 mixture.

[b] All temperatures were recorded just prior to Fluorel insertion.

[c] Times are measured from insertion of Fluorel pellet.

[d] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[e] Time from insertion of Fluorel pellet to conclusion of burning or complete evaporation.

[f] No ignition.

[g] Not applicable, as pellet removed before it evaporated.

[h] Not determined.

[i] In this particular run the hood was switched on after sampling and this action blew off the flame.

TABLE VII. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING FLUOREL KF 2140-OXYGEN TREATMENT[a,b,c]

Run No.	Total %	N_2 %	O_2 %	Ar %	CO %	CO_2 %	SiF_4 %	CF_4 %	CHF_3 %	CH_2CF_2 %
619	99.19	43.39	54.86	0.53	n.d.[f]	0.35	0.06	-	n.d.	n.d.
620	99.82	51.19	47.79	0.61	n.d.	0.17	0.06	-	n.d.	n.d.
621	99.60	42.48	56.54	0.51	n.d.	0.02	0.05	-	n.d.	n.d.
624-1[d]	99.37	54.34	42.04	0.67	n.d.	2.10	0.22	-	n.d.	n.d.
624-2[d]	99.71	53.10	37.50	0.64	n.d.	7.43	1.04	-	n.d.	n.d.
627	99.83	41.68	57.53	0.49	n.d.	0.02	0.11	-	n.d.	n.d.
632[d]	99.20	40.74	51.62	0.50	n.d.	5.52	0.82	-	n.d.	n.d.
670-1	100.81	5.66	94.90	0.09	-	-	0.13	-	-	0.03
670-2	99.50	6.00	92.04	0.10	0.76	0.39	0.17	-	-	0.04
670-3[d]	100.21	4.93	48.53	0.13	16.64	21.10	6.98	1.50 ?	0.18	0.22
689-1	100.69	9.59	90.01	0.05	0.21	0.50	0.29	-	0.17	0.08
689-2[d]	99.86	5.38	5.15	0.10	23[e]	39[e]	15.98	?	7.02	4.23

[a] All analyses are given in mole percent.

[b] Runs 619-632 were conducted using 1/2" diameter pellets, whereas in the runs 670-689 the 1" diameter pellets were employed.

[c] Runs 619-632, as can be seen from the nitrogen content, were conducted in oxygen enriched air, not oxygen. This was due to the blocking of the oxygen inlet sintered disc, which in turn allowed air inflow.

[d] These samples were taken during combustion.

[e] These are only approximate values due to interference from other species.

[f] Not determined.

TABLE VIII. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN FLUOREL KF 2140-AIR AND ARGON RUNS[a]

Run No.	Sampling Time Sec[b,c]	Ignition Delay Sec[b]	Total Time Sec[d]	Gas Temp. °C	Block Temp. °C	Gas
679	145-150	n.i.[e]	270	466	453	Air
680	85-90	n.i.	115	509	501	Air
681	50-55	n.i.	75	527	551	Air
685-2	28-33	45	60	677	644	Air
685-3	47-52	45	60	677	644	Air
695-1	23-28	38	50	705	649	Air
695-2	31-36	38	50	705	649	Air
695-3	39-44	38	50	705	649	Air
692	40-45	n.i.	105	688	641	Argon

[a] All temperatures were recorded just prior to Fluorel insertion.

[b] Times are measured from insertion of Fluorel pellet.

[c] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[d] Time from insertion of Fluorel pellet to conclusion of burning or complete evaporation.

[e] No ignition.

TABLE IX. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING FLUOREL KF 2140-AIR AND ARGON TREATMENTS[a]

Run No.[b]	Total %	Air %	N_2 %[d]	Ar %[d]	CO %	CO_2 %	SiF_4 %	CF_4 %[c]	CHF_3 %	CH_2CF_2 %
679	100.70	96.83	3.10	0.03	-	0.39	0.25	?	0.08	0.02
680	99.66	91.31	5.61	0.07	0.75	1.09	0.29	?	0.37	0.17
681	100.33	91.05	6.56	0.08	0.73	1.15	0.43	?	0.21	0.12
685-2	99.50	89.02	6.08	0.08	0.83	1.86	0.55	?	0.62	0.46
685-3[e]	95.40	50.84	27.17	0.44	3.64	8.16	2.25	?	1.85	1.05
695-1	100.65	74.94	15.42	0.18	1.57	3.96	1.93	?	0.85	1.80
695-2	99.33	71.43	16.39	0.20	1.70	4.35	2.31	?	1.05	1.90
695-3[e]	101.37	36.71	37.07	0.45	8.11	8.11	4.89	?	2.75	3.28
692	99.49	0.23	0.09	93.72	0.38	0.74	1.42	?	0.89	2.02

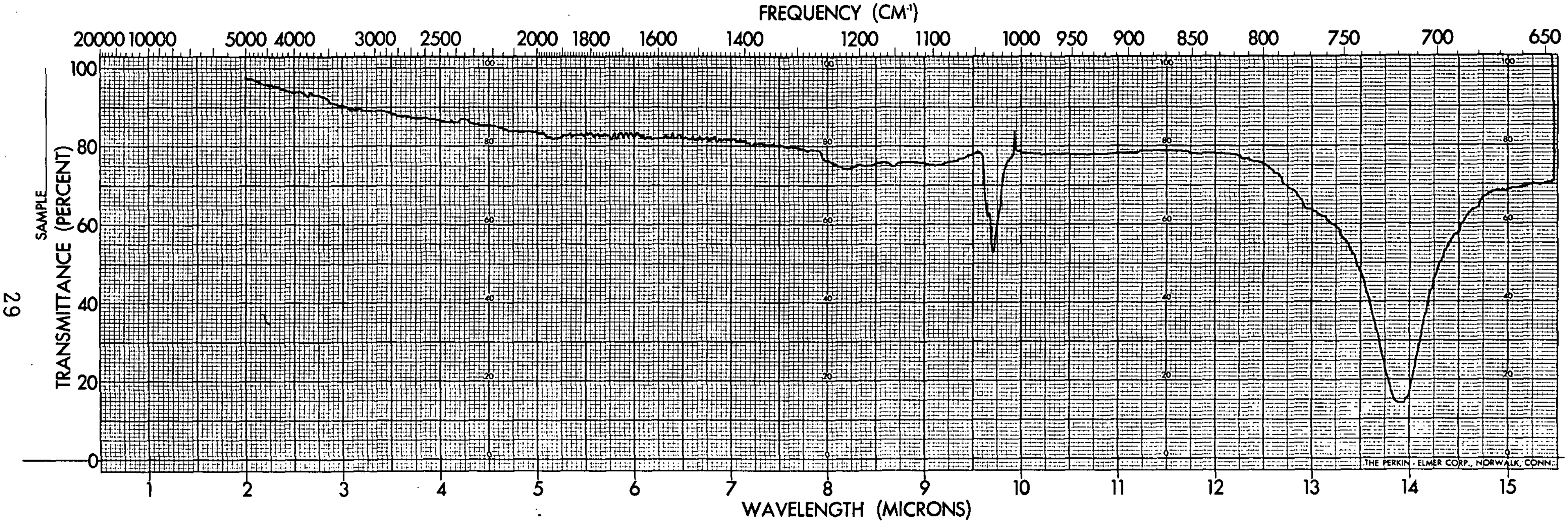
[a] All the analyses are given in mole percent.

[b] All the tests except the run 692, which was performed in argon, were conducted in air.

[c] Although there are intensities left over at m/e=69 in a number of runs, these cannot be legitimately assumed to be CF_4 derived since any fluorinated species produce this peak.

[d] This is the nitrogen in excess of that present in air, this value is proportional to oxygen depletion; the same applies to argon.

[e] This sample was taken during combustion.



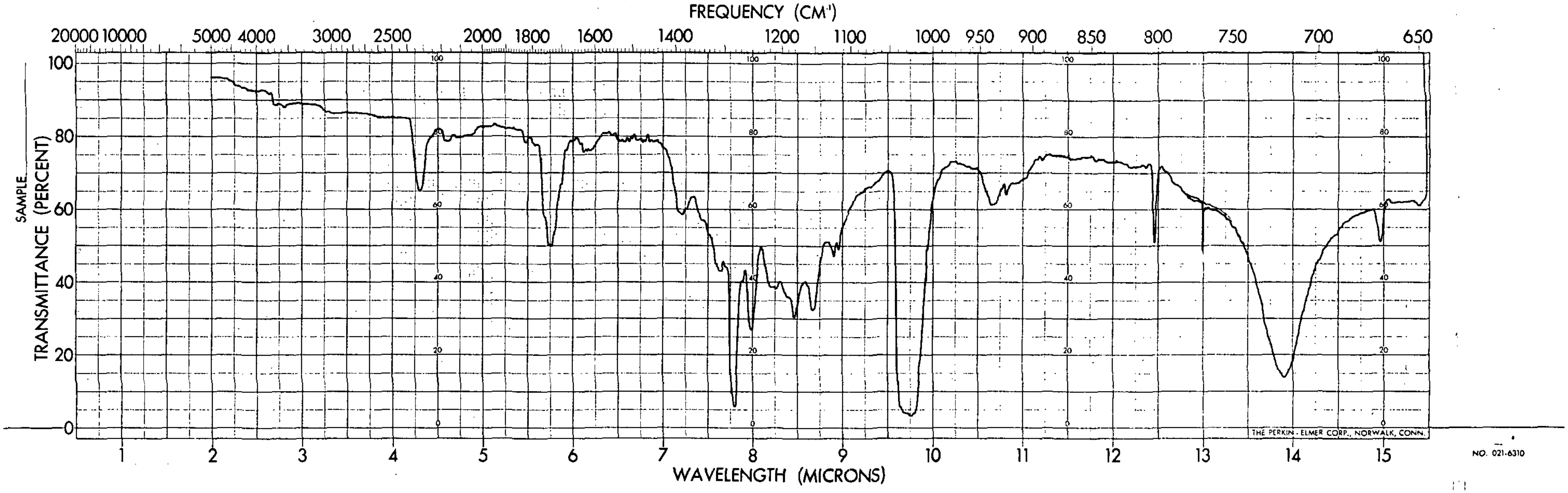
10 cm cell

P = 56.2 mm

Figure 5. Infrared Spectrum of Gaseous Products Fluorel-Oxygen Treatment Preignition Sample 689-1

evident in Sample 689-2 where oxygen was depleted to 5.38% and high contents of SiF_4, CHF_3, and CH_2CF_2 were noted (see Table VII). Figure 6 represents the infrared gas spectrum of this sample. The identified peaks of the spectrum are in good agreement with the mass spectral data. The peaks have been assigned as follows: CO_2, 4.3μ, 13.90μ, 14.98μ; CO, 4.61μ, 4.74μ; $CF_2=CH_2$, 5.77μ, 7.78μ, 10.66μ, 10.82μ, 12.46μ; CHF_3, 7.25μ, 8.30μ, 8.67μ; and SiF_4, 9.65μ, 9.70μ. It should be pointed out that the only assignment here which could be in error is that for CHF_3 and unfortunately the same is true for the mass spectral results for this compound. In the mass spectrum this material's concentration is based on m/e = 51 (CF_2H) and a number of other species can also give rise to this peak. Only trace of COF_2 was detected in these samples as indicated by abundances at m/e = 47, 66. No absorption in the vicinity of 5.12μ characteristic of COF_2, was observed in the infrared spectra. This is not surprising since any COF_2 formed from oxidation of a $-CF_2-$ entity would be expected to be hydrolyzed into CO_2 and SiF_4, by the water formed in the oxidation of CH groups.

The sampling schedules for the Fluorel-air tests are given in Table VIII and the analytical results are presented in Table IX. Examining Table IX it is apparent that in the absence of ignition a certain degree of oxidation took place as shown by the presence of CO and CO_2; however, the extent of decomposition was found to be very low as indicated by the concentration of fluorinated moieties. This is surprising in particular if one considers that sampling was performed during the heavy smoking and the ampoules appeared full of smoke after sampling. On standing, however, the smoke disappeared which would indicate a number of things: the presence of water from oxidation of CH containing moieties, repolymerization, heavy molecular weight species or reaction of HF with the ampoule walls to form SiF_4. As noted previously every SiF_4 molecule corresponds to four HF molecules. Examining Table IX it is obvious that the increase in the oxidation products and fluorinated materials does not follow significantly the increase in the temperature of the heating block and air (runs 679, 680, 681). This is not readily explainable. On the other hand the trend of increase in the decomposition and oxidation products with preignition, ignition and combustion is almost perfectly illustrated in samples 685-2 and 685-3, 695-1, 695-2, and 695-3 (see Tables VIII and IX). These data for run 695 are graphically expressed in Figure 7.



10 cm cell

P = 51.5 mm

Figure 6. Infrared Spectrum of Gaseous Products Fluorel-Oxygen Treatment Combustion Sample 689-2

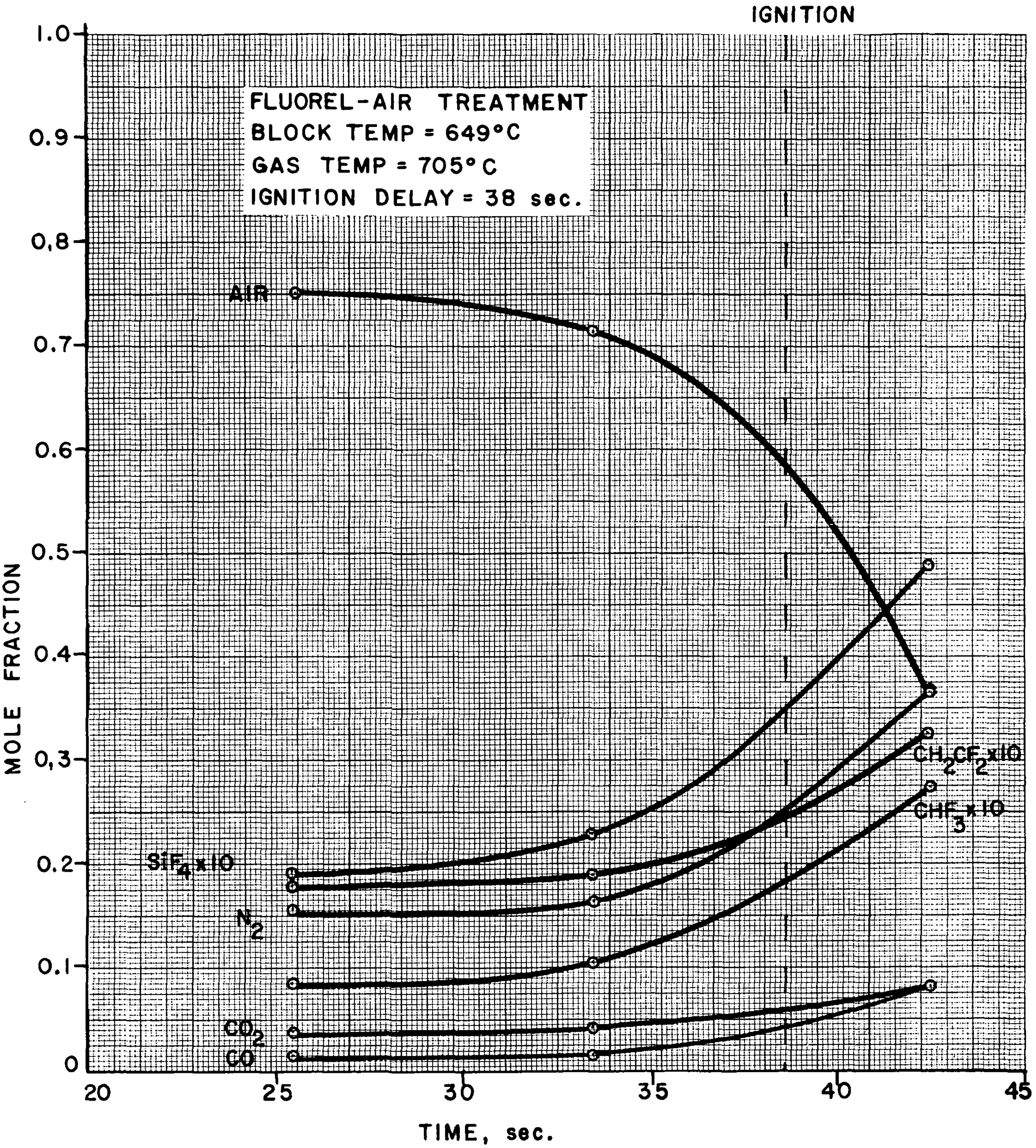


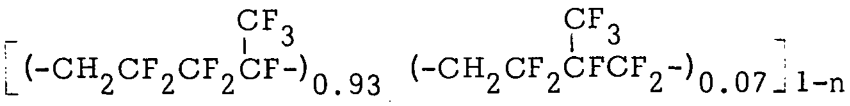
Figure 7. Relative Species Concentration as a Function of Heat Treatment Duration in a Fluorel-Air Test

The good agreement between the mass spectral results and infrared can be seen by comparing the spectrum of the volatiles in samples 685-2 and 685-3 (Figures 8 and 9, respectively).

To see whether the material composition and evaporation rate changes significantly in an inert atmosphere, a limited number of experiments was conducted in argon (see Tables VIII and IX). Surprisingly enough, both the rate of evaporation in argon (as compared to the time from Fluorel insertion to completion of burning at corresponding temperature in air), and the concentration of fluorinated species, together with the overall mass spectral breakdown pattern, were found to be very similar (compare runs 692 and 695). This is further supported by the similarity of the infrared spectra (see Figure 10). The only truly significant difference between this spectrum and the others obtained in oxidizing media (neglecting the relative bonds' intensity) is the very low concentration of CO_2 (4.3μ, 13.90μ, 14.98μ). Actually, there should be no CO_2 produced and based on the mass spectral data the air inflow in this particular experiment was negligible. Consequently it has to be deduced that the CO_2 is derived from an impurity present in the polymer.

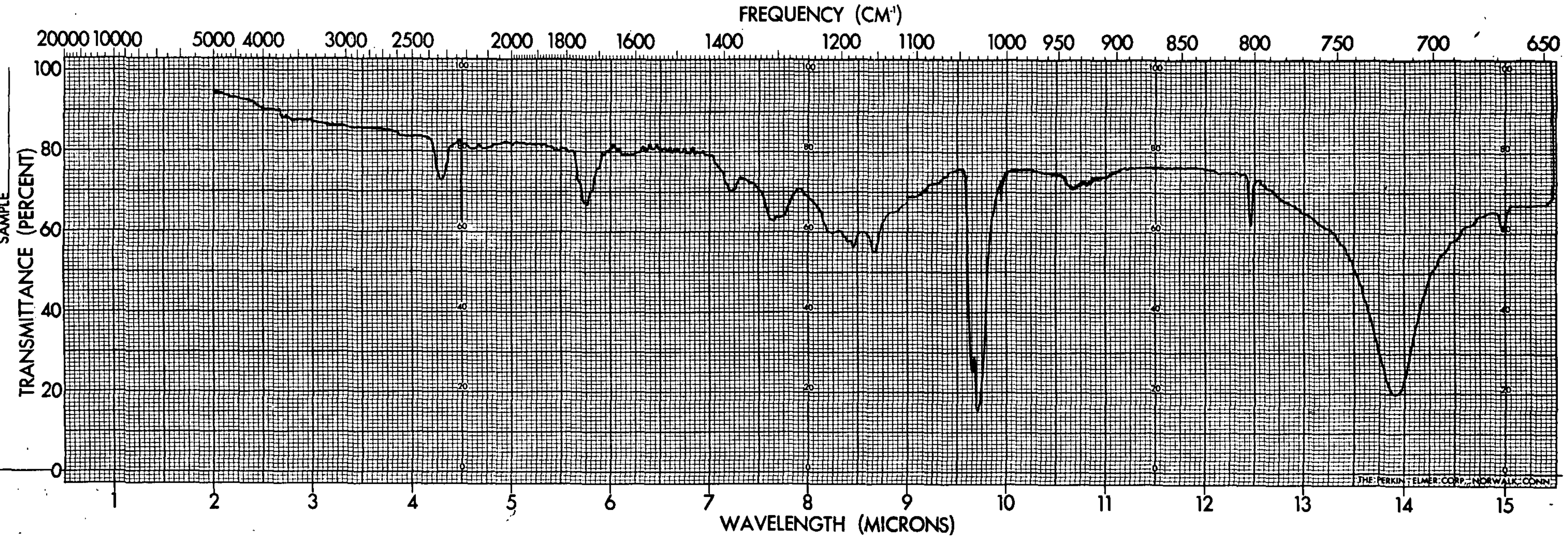
It is obvious from the study of the infrared spectra, that not all the bands have been identified, consequently other species, in addition to CHF_3, $CF_2=CH_2$ and possibly $CF_3CF=CF_2$ must also be present. The mass spectral patterns of the volatiles likewise indicate the presence of other moieties. We have observed a number of peaks with significant abundances which we could not include in our results since we do not know the sensitivities for the compounds most likely responsible for these peaks. On the other hand, all these materials appear to account for less than one percent of the total gaseous components. This is based on both the abundances and on our found total sum of the species. As of interest we attempted to deduce the nature of these unidentified materials.

Ferguson (Ref. 18) put forward the following structural arrangements for the $CF_2=CH_2$ and $CF_3CF=CF_2$ family of copolymers:



$$\left[(-CH_2CF_2CF_2\overset{CF_3}{\overset{|}{C}}F-)_{0.93}\ (-CH_2CF_2\overset{CF_3}{\overset{|}{C}}FCF_2-)_{0.07}\right]_{1-n}$$

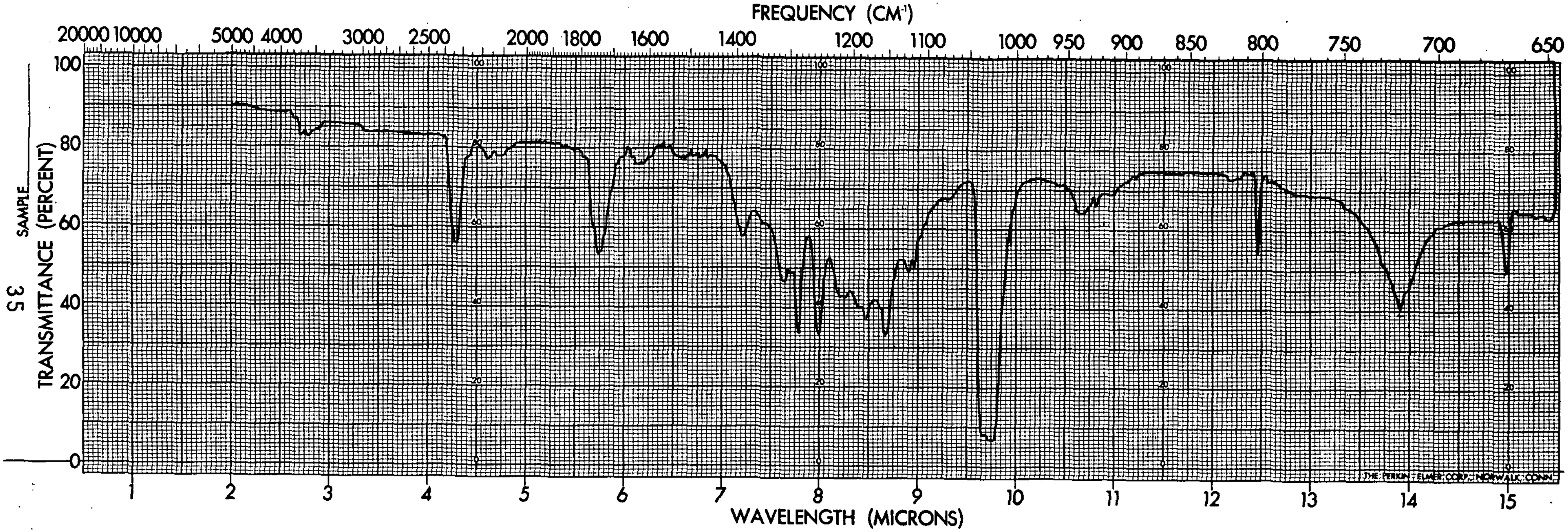
$$\left[(-CH_2CF_2CH_2CF_2-)_{0.95}\ (-CH_2CF_2CF_2CH_2)_{0.05}\right]_{n/2}$$



10 cm cell

P = 182.5 mm

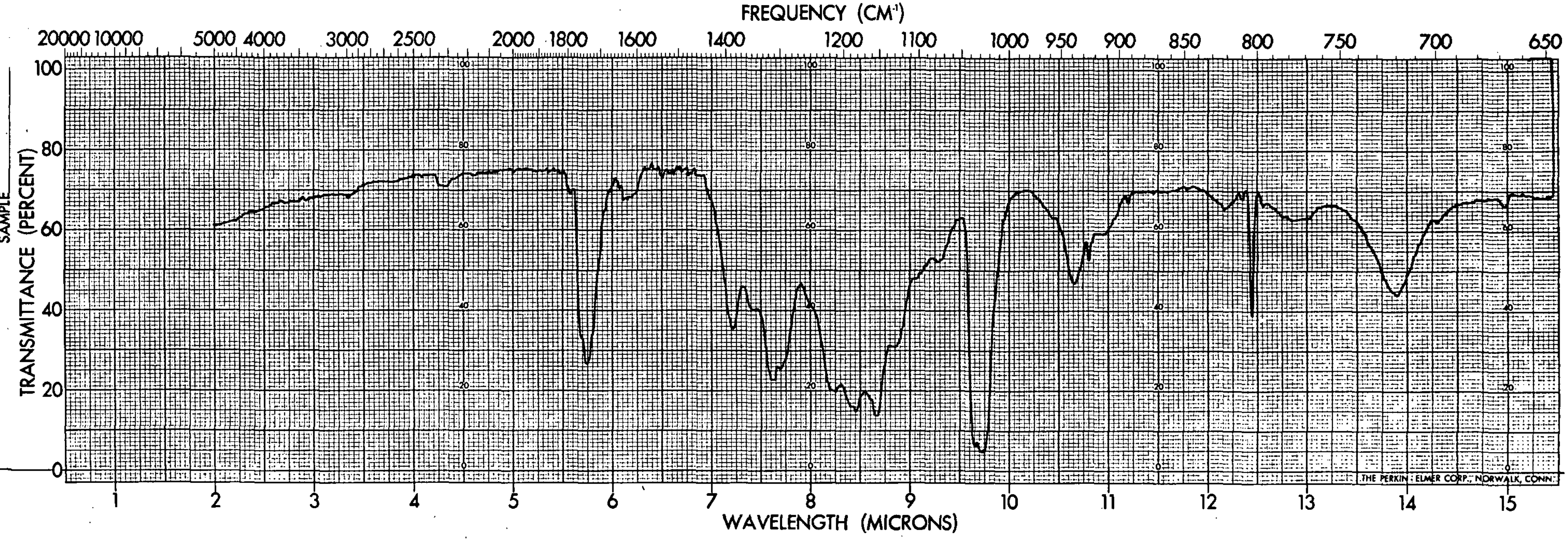
Figure 8. Infrared Spectrum of Gaseous Products Fluorel-Air Treatment Preignition Sample 685-2



10 cm cell

P = 163.5 mm

Figure 9. Infrared Spectrum of Gaseous Products Fluorel-Air Treatment Combustion Sample 685-3



10 cm cell

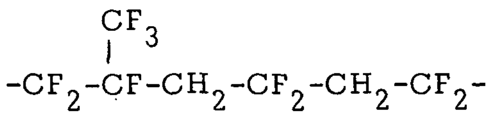
P = 218.7

Figure 10. Infrared Spectrum of Gaseous Products Fluorel-Argon Treatment Sample 692-1

where n is a function of mole fraction of vinylidene fluoride. These data are derived from NMR spectroscopy and are in agreement with experimental telomerization studies performed by Hazeldine in his early work.

An arrangement such as, e.g., $-CH_2CF_2CF_2\overset{\overset{\displaystyle CF_3}{|}}{C}F-CH_2CF_2-$ should give among others a $\overset{\overset{\displaystyle CF_3}{|}}{C}F=CH_2$ fragment. Such a material would be expected to have the following series of peaks: m/e = 114 ($C_3F_4H_2$), 113 (C_3F_4H), 112 (C_3F_4); 95 ($C_3F_3H_2$), 94 (C_3F_3H), 93 (C_3F_3); 76 ($C_3F_2H_2$), 75 (C_3F_2H), 74 (C_3F_2). The three series of peaks were observed in our spectra indicating the presence of such a compound. Since the sensitivities are unknown the percentages could not be calculated.

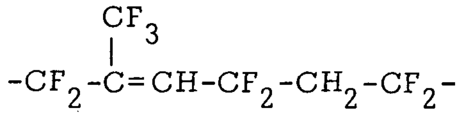
Other intensities of unidentified origin were observed at m/e 150, 131. These would point to the presence of $CF_3CF=CF_2$. The absorptions in the infrared at 7.2μ would tend to support this deduction. Unfortunately, none of these absorptions is really typical for $CF_3CF=CF_2$ and the characteristic band for this compound at 13.1μ is of relatively low intensity. Consequently its absence in our spectra does not necessarily mean the complete absence of $CF_3CF=CF_2$ in gaseous mixture. As discussed earlier $CF_3CF=CF_2$ comprises only 20 mole percent of Fluorel, which could explain partly lack of detection of this material by the Russians (Refs. 19,20). It is obvious that $CH_2=CF_2$ is obtained from the $CH_2=CF_2$ component of Fluorel; less obvious is the origin of CHF_3. However, the Russian work (Ref. 19) has shown that this material is derived from $CH_2=CF_2$. The predominant structural arrangement for vinylidene fluoride-perfluoropropene copolymers



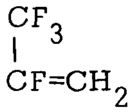
$$-CF_2-\overset{\overset{\displaystyle CF_3}{|}}{C}F-CH_2-CF_2-CH_2-CF_2-$$

places the tertiary fluorine in a position adjacent to the methylene group. This fluorine was deduced to be the one most readily eliminated as HF during amine treatment (Refs. 28,29,30). Whether the initial hydrogen fluoride elimination in the thermal dehydrohalogenation, operative prior to ignition, involves primarily the tertiary fluorine atom is unknown.

However, the lack of detection of significant quantities of perfluoropropene in the gaseous atmosphere prior to ignition and in particular in the argon experiment, would tend to indicate that this particular elimination is favored. The resulting arrangement shown below would not be likely to liberate on



$$-CF_2-\overset{\overset{\displaystyle CF_3}{|}}{C}=CH-CF_2-CH_2-CF_2-$$

decomposition either perfluoropropene or the arrangement  $\overset{\overset{\displaystyle CF_3}{|}}{C}F=CH_2$ postulated as one of the potential products of Fluorel degradation. It is clear that due to insufficient analytical data, any deductions as to the nature of unidentified products are highly speculative and more work is needed to arrive at firm conclusions.

Refset Studies

Refset is a trade name for compounded Fluorel gum, the nature of the other additives is supposedly a trade secret. On the other hand, based on literature--in particular, a summary of "Toxicity of Spacecraft Elastomers" (a report?)--it would appear that magnesium (most likely originally in the form of its oxide) is one of the main constituents. This would be in agreement with the known curing system for Fluorel elastomers. The presence of magnesium salt would also explain the low content of SiF_4 in the gaseous samples (see Tables XII and XV), in view of the reaction of the produced hydrogen fluoride with magnesium oxide, i.e.,

$$2HF + MgO \rightarrow MgF_2 + H_2O \qquad (7)$$

The Refset pellets or wafers employed in this work were cut out from cured sheets of Refset L-3203-6 supplied by Raybestos Manhattan.

The sheets used for the cutting out of wafers varied in thickness from 0.064 to 0.085" giving the average thickness of 0.075 ± 0.007". The weight of the 1/2" wafers varied from 435 to 563 mg (average 511 ± 37 mg), whereas the weight of the 1" wafers varied from 1.871 to 2.059g (average 1.940 ± 0.056g).

There are basically three different versions of this particular Refset available:

a) uncured L-3203-6 which is in chunks and contains the same ingredients as the cured materials but has not been subjected to the press cure,

b) cured L-3203-6 the same material as above but subjected to press cure,

c) uncured L-3203-6, without the cure activator.

To conduct the ignition studies of Refset, due to the residue, a removable platinum inlay framed in a stainless steel ring was fabricated. The platinum sheet was only 0.01" thick and it fitted closely to the surface of the heating block thus assuring good heat transfer and accurate temperature measurement. The actual ignition experiments were performed using the 1/2 inch pellets, whereas in the sampling tests the 1 inch wafers were employed. The oxygen tests are summarized in Table X, whereas the ignition data are plotted in Figure 11. Before proceeding with the discussion of the ignition results, the description of the actual ignition and combustion seems in order. The onset of ignition was usually preceded by heavy smoke, quite often also by a surface glow (duration ~ 1 sec). The actual ignition was accompanied by an audible pop and the initial flame was bright yellow (fuel rich?). The yellow flame subsided after 15-30 sec and then only a small blue flame remained which finally deteriorated into a glow. Consequently, what is denoted as the burn time is the period from the ignition onset to the glow disappearance. The residue left after the combustion resembled in appearance grey cigarette ashes and amounted to 47.6 ± 0.6% of the original sample.

Examining Figure 11 it is obvious that the ignition onset is dependent both on the gas and heating block temperatures. The equitemperature for Refset was found to be just above 380°C, whereas in the case of Fluorel this temperature was slightly above 400°C. Comparison of the graph of ignition data of uncured Fluorel gum (Figure 4) with that of Refset (Figure 11) indicates that the former is somewhat less flammable. There are two possible

TABLE X. SUMMARY OF EXPERIMENTS CONDUCTED ON REFSET IN OXYGEN ATMOSPHERE[a]

Run No.	Pellet Diam. In	Gas Temp. °C	Block Temp. °C	Ignition Delay Min:Sec[b]	Burn Time Sec[c]	Remarks
703	1/2	322	361	n.i.[d]	n.a.[e]	Pellet removed after 10 min; residue 85.17%.
704	1/2	396	436	2:30	48	Smoke at 2 min 16 sec; residue 46.05%.
705	1/2	406	444	3:04	51	Smoke at 2 min 40 sec; residue 46.67%.
708	1/2	228	439	7:22	58	Smoke at 7 min 5 sec; red glow 7 min 15 sec; 7 min 45 sec flame out; residue 48.71%.
709	1/2	228	431	n.i.	n.a.	Pellet removed after 10 min; residue 84.30%.
710	1/2	327	429	5:35	60	Smoke at 5 min 20 sec; residue 47.75%.
711	1/2	329	419	9:35	85	Smoke at 9 min 20 sec; residue 47.64%.
712	1/2	333	411	9:50	67	Smoke at 9 min 40 sec.
713	1/2	410	415	5:52	53	Smoke at 5 min 40 sec; residue 46.87%.
714	1/2	411	404	4:48	64	Smoke at 4 min 35 sec; residue 47.02%
715	1/2	410	397	6:07	55	Smoke at 5 min 55 sec.
716	1/2	410	385	7:20	56	Smoke at 7 min 10 sec; residue 47.60%.
717	1/2	408	367	n.i.	n.a.	Pellet removed after 10 min; residue 79.07%
718	1/2	404	375	10:08	61	Smoke at 10 min; ignited just before removal of pellet.
719	1/2	455	377	7:25	61	Smoke at 7 min 18 sec.
720	1/2	452	369	8:03	66	Smoke at 8 min; N_2 = 48%; porous disc changed.
721	1/2	455	363	9:42	58	Smoke at 9 min 38 sec; N_2 = 4%.
722	1/2	455	355	n.i.	n.a.	Pellet removed after 10 min; residue 79.51%.
723	1/2	499	338	n.i.	n.a.	Pellet removed after 10 min; residue 78.87%.
724	1/2	501	343	6:28	47	Smoke at 6 min 22 sec.
725	1/2	488	348	6:29	52	Smoke at 6 min 25 sec.
726	1/2	357	408	4:53	49	Smoke at 4 min 30 sec.

TABLE X. (Continued)

Run No.	Pellet Diam. In	Gas Temp. °C	Block Temp. °C	Ignition Delay Min:Sec[b]	Burn Time Sec [c]	Remarks
727	1/2	364	380	n.i.	n.a.	Pellet removed after 10 min.
728	1/2	366	386	6:52	67	Smoke at 6 min 47 sec.
729	1/2	502	485	1:51	68	Smoke at 1 min 21 sec.
730	1/2	502	483	1:54	70	Smoke at 1 min 20 sec.
731	1	499	480	2:48	132	Light smoke at 1 min 45 sec; heavy smoke at 1 min 52 sec; residue 47.68%.
732	1	491	471	2:45	119	Sampling run; light smoke at 2 min; residue 48.09%; N_2 = 23%; porus disc changed.
733	1/2	331	394	n.i.	n.a.	Pellet removed after 10 min; residue 76.17%.
735	1/2	245	404	n.i.	n.a.	Pellet removed after 10 min; residue 79.73%.
736	1/2	245	415	n.i.	n.a.	Pellet removed after 10 min; residue 75.66%.
737	1/2	245	431	8:38	62	Smoke at 8 min 30 sec.
738	1	387	398	7:02	86	Smoke at 6 min 52 sec; residue 47.95%.
739	1	399	403	8:09	106	Sampling run; smoke at 7 min 58 sec; residue 49.67%.
740	1	410	360	n.i.	n.a.	Sampling run; no smoke; residue 86.66% in 8 min 30 sec; N_2= 49%; porous disc changed.
741	1/2	277	419	6:33	47	Smoke at 6 min 20 sec.
742	1/2	270	406	n.i.	n.a.	Pellet removed after 10 min; residue 78.59%.
743	1/2	299	403	n.i.	n.a.	Pellet removed after 10 min; residue 82.02%.
744	1/2	299	414	10	-	Pellet ignited as it was being removed at 10 min.
745	1/2	298	421	8:43	58	Smoke at 8 min 38 sec
746	1/2	301	432	7:06	67	Smoke at 7 min 52 sec.

---

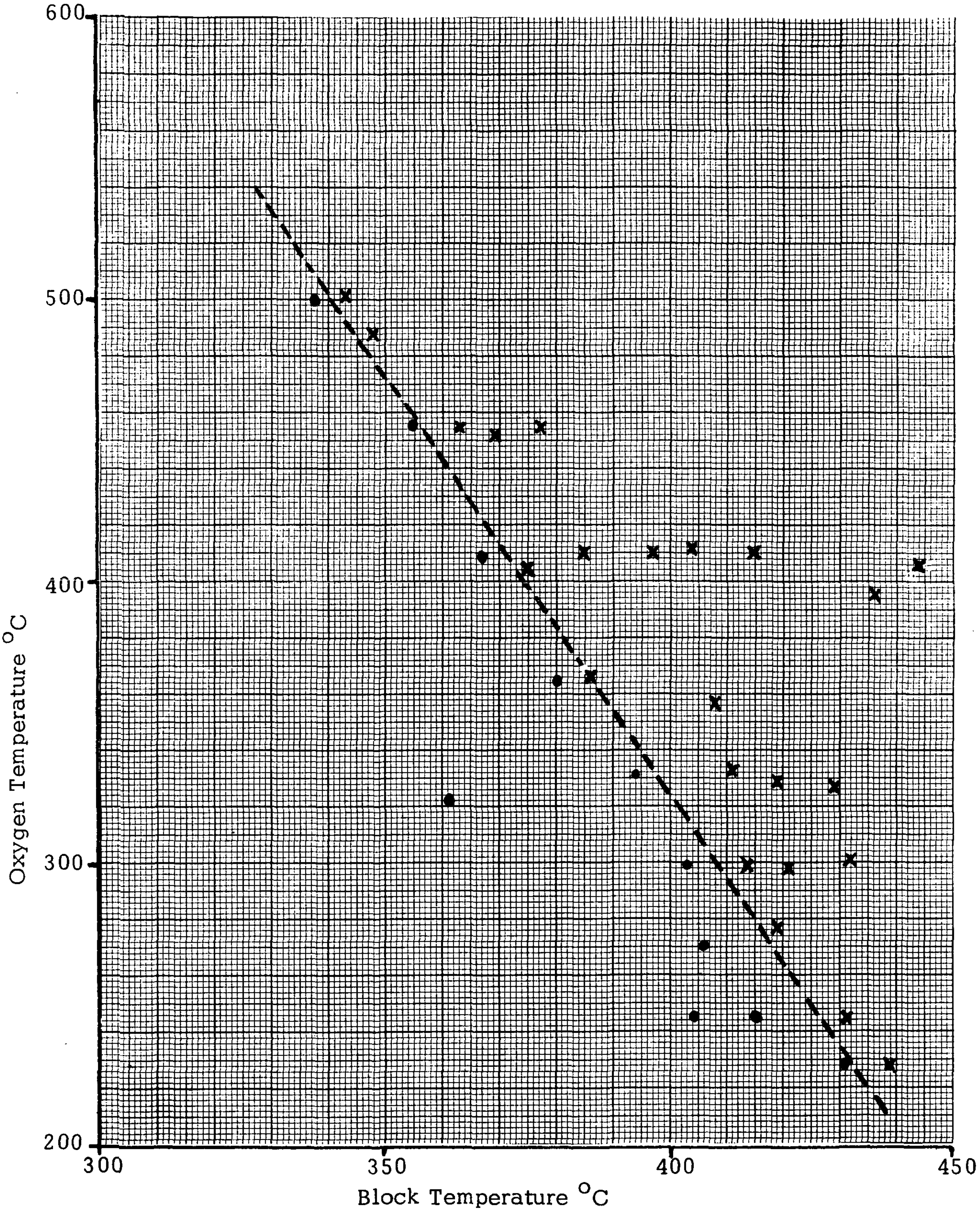
[a] All the temperatures were recorded just prior to Refset insertion.

[b] Time measured from the insertion of Refset pellet.

[c] Time from ignition onset to conclusion of burning.

[d] No ignition.

[e] Not applicable.



X = ignition
o = no ignition

Figure 11. Effect of Polymer Heating Block and Oxygen Temperatures Upon Refset Ignition.

explanations for this observation: (1) the hydrogen fluoride liberated into the gas phase, in the case of uncured Fluorel gum, acts as fire suppressant. In the case of Refset hydrogen fluoride is absorbed by formation of magnesium fluoride, (2) the presence of the curing agents and the actual curing process resulted in partial degradation of the polymer. Consequently, at the temperatures involved in the ignition studies, the thermal degradation proceeds more readily than is the case with the raw gum, resulting in the evolution of sufficient amounts of combustibles to trigger ignition. The latter explanation is supported partially by the decreased thermal stability of cured vinylidene fluoride-perfluoropropene copolymers (Refs. 22,25), as compared to the uncured material. Most likely, however, both factors, 1 and 2, are responsible for the lower ignition onset temperature of Refset.

It is noteworthy that the ignition delays in the Refset series were much longer, at comparable temperatures, than those noted in Fluorel work. There is no ready explanation for this observation. In all the Refset tests when no ignition was noted up to 10 min the sample was removed. Consequently, with the exception of the run 718 (when ignition took place at 10 min, 8 sec), if no ignition occurred up to 10 min, an absence of ignition was recorded.

In Table XI the sampling schedules and pertinent details are summarized, whereas in Table XII the actual analytical data are presented. In examining Table XII one aspect can be immediately noted, namely the nitrogen content of all the samples is very high, showing that again the sintered disc in the oxygen inlet was partially blocked resulting in the inflow of the air from the open sides of the burner. Thus, for practical purposes, the tests were actually performed in oxygen enriched air. Accordingly, the ignition limits in pure oxygen must be still lower than those shown in Figure 11. It is clear from Table XII (run 740) that at 360^{o}C (block temperature) the decomposition of Refset does not proceed at an appreciable rate. This assumption is in an agreement with the recovery of 87% of the Refset sample. The gas sample, 732-1, was collected just prior to ignition and at this stage (under the specific conditions of gas and block temperatures) CO and CO_2 appear to be formed in relatively large and surprisingly equal concentrations. Only traces of SiF_4 were found, however, the fluorinated hydrocarbons

TABLE XI. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN REFSET - OXYGEN RUNS[a]

Run No.	Sampling Time min:sec[b,c]	Ignition Delay min:sec[b]	Total Time min:sec[d]	Gas Temp. °C	Block Temp. °C
732-1	2:35-2:40	2:45	4:44	491	471
732-2	2:44-2:49	2:45	4:44	491	471
732-3	2:52-2:57	2:45	4:44	491	471
739-1	0:43-0:48	8:09	9:55	399	403
739-2	3:30-3:35	8:09	9:55	399	403
739-3	8:00-8:05	8:09	9:55	399	403
740-1	0:43-0:48	n.i.[e]	n.a.[f]	410	360
740-3	8:00-8:05	n.i.	n.a.	410	360

[a] All temperatures were recorded just prior to Refset insertion.

[b] Times are measured from insertion of Refset pellet.

[c] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[d] Time from insertion of Refset pellet to conclusion of burning.

[e] No ignition.

[f] Not applicable as pellet removed after 8 min, 30 sec.

TABLE XII. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING REFSET - OXYGEN TREATMENT[a]

Run No.[b]	Total %	O_2 %	Ar %	N_2 %	CO_2 %	CO %	SiF_4 %	CH_2CF_2 %	CHF_3 %
732-1	100.50	61.46	0.24	17.31	10.42	10.33	0.03	0.40	0.31
732-2[c]	100.10	44.11	0.33	21.86	32.34	0.95	0.49	-	0.02
732-3	100.92	47.55	0.38	23.36	27.30	1.83	0.50	-	-
739-1	100.63	70.64	0.57	28.74	0.30	0.34	-	-	0.04
739-2	100.36	70.88	0.57	28.79	0.12	-	-	-	-
739-3	99.86	56.10	0.32	29.69	5.35	7.24	0.13	0.56	0.47
740-1	100.76	53.07	0.54	47.15	-	-	-	-	-
740-3	100.74	51.90	0.55	48.29	-	-	-	-	-

[a] All the analyses are given in mole percent.

[b] All these tests were performed using 1 inch pellets.

[c] At ignition.

seemed to be evolved in significant quantities. The virtual absence of hydrogen fluoride (SiF_4) is most likely due to the presence of the magnesium salt, which acts as an absorber for the hydrogen fluoride evolved on thermal dehydrohalogenation of the Fluorel constituent of Refset. On combustion relatively large concentrations of hydrogen fluoride (ca 2.00%) were reached (Table XII, samples 732-2 and 732-3). It is thus tempting to postulate that hydrogen fluoride, in the case of Refset, does indeed originate from the combustion in the gas phase of the evolved fluorinated hydrocarbons. Under these conditions the magnesium salt, being within the solid residue, would be of no help in hydrogen fluoride capture.

It is interesting that on ignition and during combustion mainly CO_2 was detected. Based on samples 739-1 and 739-2 it would appear that much prior to the ignition hardly any oxidation takes place and very little volatiles are evolved. Yet close to ignition, sample 739-3, again fairly high CO_2 and CO concentration was observed. Actually in this particular instance the CO content was somewhat higher than the CO_2 concentration. The run 732 is expressed graphically in Figure 12. It should be pointed out that the fluorinated hydrocarbons are not included since these have been observed only in the preignition sample. The decrease in CO_2 concentration with concomitant increase in the relative oxygen concentration in the latter stages of combustion is to be expected due to fuel exhaustion.

Parallel tests to those performed in oxygen were conducted in air atmospheres, however, in air no ignition, i.e., no flame, was observed, although the material did definitely glow. As can be seen from Table XIII depending on the temperature the onset of glow can be delayed for as much as 12 min (run 764). At block and gas temperatures of $\approx 390^{\circ}C$ no glow could be produced at all (run 765). This is in good agreement with the results obtained in oxygen, from which it can be deduced that below $\approx 380^{\circ}C$ the rate of decomposition is apparently too low to allow glow to occur. It should be pointed out that the absence of glow in run 765 is not due to an insufficient observation time, but to depletion of the combustible, volatile matter originally present in the sample. This can be proven by comparing the weight of the residue after pyrolysis of sample 765 (59.32%) which is in agreement with the average residue weights ($57.3 \pm 2.2\%$) of all the Refset-air tests, where glow did take place.

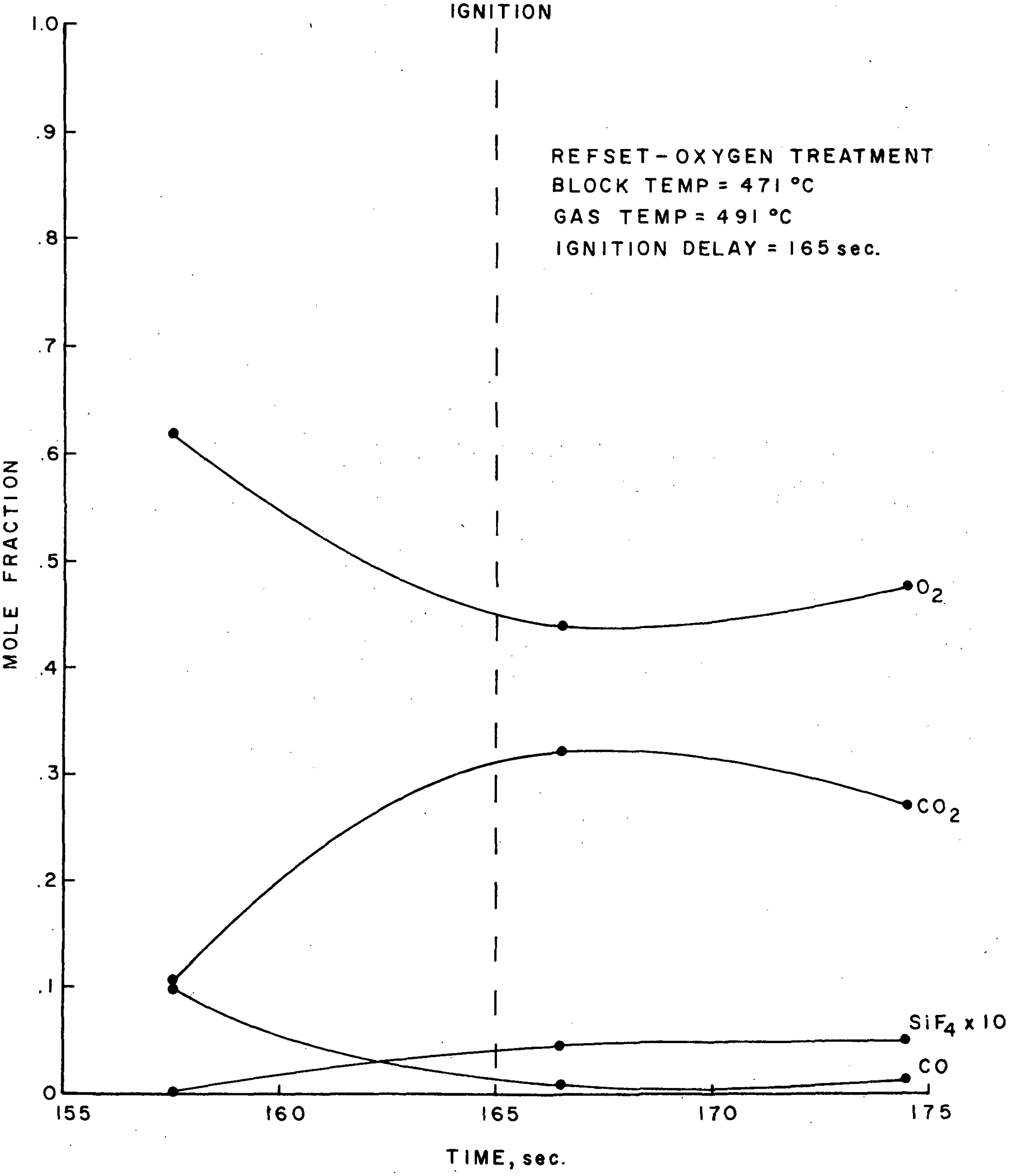


Figure 12. Relative Species Concentration as a Function of Heat Treatment Duration in a Refset-Oxygen Test

TABLE XIII. SUMMARY OF EXPERIMENTS CONDUCTED ON REFSET IN AIR ATMOSPHERE[a]

Run No.	Pellet Diam. In	Gas Temp. °C	Block Temp. °C	Glow Delay Min:Sec[b]	Glow Time Sec[c]	Remarks
747	1/2	508	520	1:35	21	Smoke at 1 min 20 sec, heavy smoke at 1 min 30 sec, no smoke at 1 min 56 sec; 57.46% residue
748	1/2	515	527	1:33	12	Smoke at 1 min 11 sec, heavy smoke at 1 min 15 sec, no smoke at 1 min 45 sec, 52.39% residue
749	1	508	513	2:07	28	Smoke at 1 min 42 sec, heavy smoke at 1 min 47 sec, no smoke at 2 min 30 sec; 56.66% residue
750	1	509	508	2:05	31	Sampling run; smoke at 1 min 49 sec, heavy smoke at 1 min 55 sec, no smoke at 2 min 40 sec
751	1/2	562	570	1:10	22	Smoke at 40 sec, heavy smoke at 55 sec, no smoke at 1 min 32 sec; 50.77% residue
752	1/2	611	614	1:05	20	Smoke at 55 sec, no smoke at 1 min 5 sec; 55.04% residue
753	1/2	530	555	1:12	13	Smoke at 1 min, heavy smoke at 1 min 12 sec, no smoke at 1 min 25 sec; 56.45% residue
754	1/2	464	513	2:30	20	Smoke at 2 min 30 sec, no smoke at 2 min 50 sec; 55.09% residue
755	1/2	441	481	2:37	18	Smoke at 2 min 20 sec, heavy smoke at 2 min 37 sec, no smoke at 3 min; 57.32% residue
756	1/2	425	465	2:53	16	Smoke at 2 min 38 sec, heavy smoke at 2 min 44 sec, no smoke 3 min 9 sec; 59.29% residue
757	1/2	403	444	4:00	27	Smoke at 4 min, no smoke at 4 min 30 sec; 59.37% residue
758	1/2	389	426	5:27	15	Smoke at 5 min 20 sec, heavy smoke at 5 min 27 sec, no smoke at 5 min 45 sec, 58.76% residue
759	1/2	385	408	9:45	13	Smoke at 9 min 41 sec, heavy smoke at 9 min 45 sec, no smoke at 9 min 58 sec; 58.76% residue
760	1	396	428	6:15	35	Smoke at 4 min 40 sec, heavy smoke at 6 min 10 sec, no smoke at 6 min 50 sec; 61.02% residue
761	1	399	430	6:30	45	Sampling run; smoke at 5 min 40 sec, heavy smoke at 5 min 50 sec, no smoke at 7 min 15 sec; 59.94% residue
762	1	399	429	7:45	50	Smoke at 7 min 30 sec, heavy smoke at 7 min 35 sec, no smoke at 8 min 35 sec

TABLE XIII. (Continued)

Run No.	Pellet Diam. In	Gas Temp. °C	Block Temp. °C	Glow Delay Min:Sec[b]	Glow Time Sec[c]	Remarks
763	1/2	385	406	5:40	38	Smoke at 5 min 35 sec, heavy smoke at 5 min 40 sec, no smoke at 6 min 18 sec; 58.41% residue
764	1/2	385	398	12:05	15	Smoke at 12 min 3 sec, heavy smoke at 12 min 5 sec, no smoke at 12 min 20 sec, 58.03% residue
765	1/2	385	395	n.g.[d]	n.g.	Smoke at 10 min 15 sec 59.32% residue

[a] All the temperatures were recorded just prior to Refset insertion.

[b] Time measured from the insertion of Refset pellet.

[c] Time from glow onset to glow disappearance.

[d] No glow.

Inspection of Tables XIV and XV shows that the amounts of CO and CO_2 formed increase with the time the specimens are exposed to temperature. When sampling was performed early after inserting of the pellet (far from the onset of glow) the CO_2 and CO concentrations were low (see samples 761-1, 761-2). During actual glow, however, from the same specimen (sample 761-3) a significant (six fold) increase in CO and CO_2 production was noted. Furthermore, it can be seen that considerable oxidation occurs just prior to the onset of glow as evidenced by the CO and CO_2 levels in samples 750-1 and 750-2. The quantities of SiF_4 produced in all these tests were truly negligible being of the order of 0.01-0.02 mole percent. This would then indicate that any hydrogen fluoride produced reacted with the magnesium salt present in the material. Since the glow occurred within the material (as opposed to e.g., a combustion zone above a polymer surface) this would be expected. The production of significant amounts of fluorinated hydrocarbon species in, e.g., run 750 (Table XV) shows that if true combustion was established hydrogen fluoride would be produced in the gas phase. Reexamining the Refset-oxygen tests (Table XII), run 732) one can see that during combustion hydrogen fluoride (analyzed as SiF_4) was formed. It is noteworthy that in this particular run the gas sample taken just prior to ignition (sample 732-1) contained fluorinated hydrocarbons. It would thus appear as postulated previously that the detected hydrogen fluoride, in the case of Refset, does indeed originate from the combustion in the gas phase of the evolved fluorinated hydrocarbons.

The change of species concentration with the duration of heat treatment and the occurrance of the glow is depicted graphically in Figure 13. The appearance of this graph emphasizes the lack of accelerated oxidation on glow onset which is contrary to the behavior noted on ignition (see Figure 12).

The residue left after Refset combustion in oxygen amounted to 47.6 ± 0.6% of the original material. In the air experiments the values were much more scattered and the average higher, 57.3 ± 2.2%. The appearance of the two residues was also very different. The residue left after combustion in oxygen was similar to cigarette ashes whereas the

TABLE XIV. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN REFSET - AIR RUNS[a]

Run No.	Sampling Time Min: Sec[b,c]	Glow Delay Min :Sec[b]	Total Time Min:Sec[d]	Gas Temp. °C	Block Temp. °C
750-1	1:52-1:57	2:05	2:36	509	508
750-2	2:00-2:05	2:05	2:36	509	508
750-3	2:08-2:13	2:05	2:36	509	508
761-1	5:45-5:50	6:50	7:15	399	430
761-2	6:00-6:05	6:50	7:15	399	430
761-3	6:55-7:00	6:50	7:15	399	430

[a] All temperatures were recorded just prior to Refset insertion.

[b] Times are measured from insertion of Refset pellet.

[c] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[d] Time from insertion of Refset pellet to glow disappearance.

TABLE XV. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING REFSET - AIR TREATMENT[a]

Run No.[b]	Total %	Air %	N_2 %	Ar %	CO_2 %	CO %	CH_2CF_2 %	CHF_3 %	SiF_4 %
750-1	100.46	96.02	0.84	0.01	1.44	1.50	0.29	0.35	0.01
750-2	100.69	92.75	1.99	0.03	2.60	2.57	0.31	0.43	0.01
750-3[c]	99.66	88.46	4.58	0.07	2.85	3.00	0.27	0.42	0.01
761-1	99.32	97.67	0.97	0.01	0.35	0.26	0.01	0.03	0.02
761-2	99.96	98.87	0.30	0.01	0.31	0.38	0.04	0.05	Trace
761-3[c]	99.63	88.64	6.81	0.08	1.91	1.95	0.08	0.13	0.03

[a] All the analyses are given in mole percent.

[b] All these tests were performed using 1 inch pellets.

[c] Sample taken during glow.

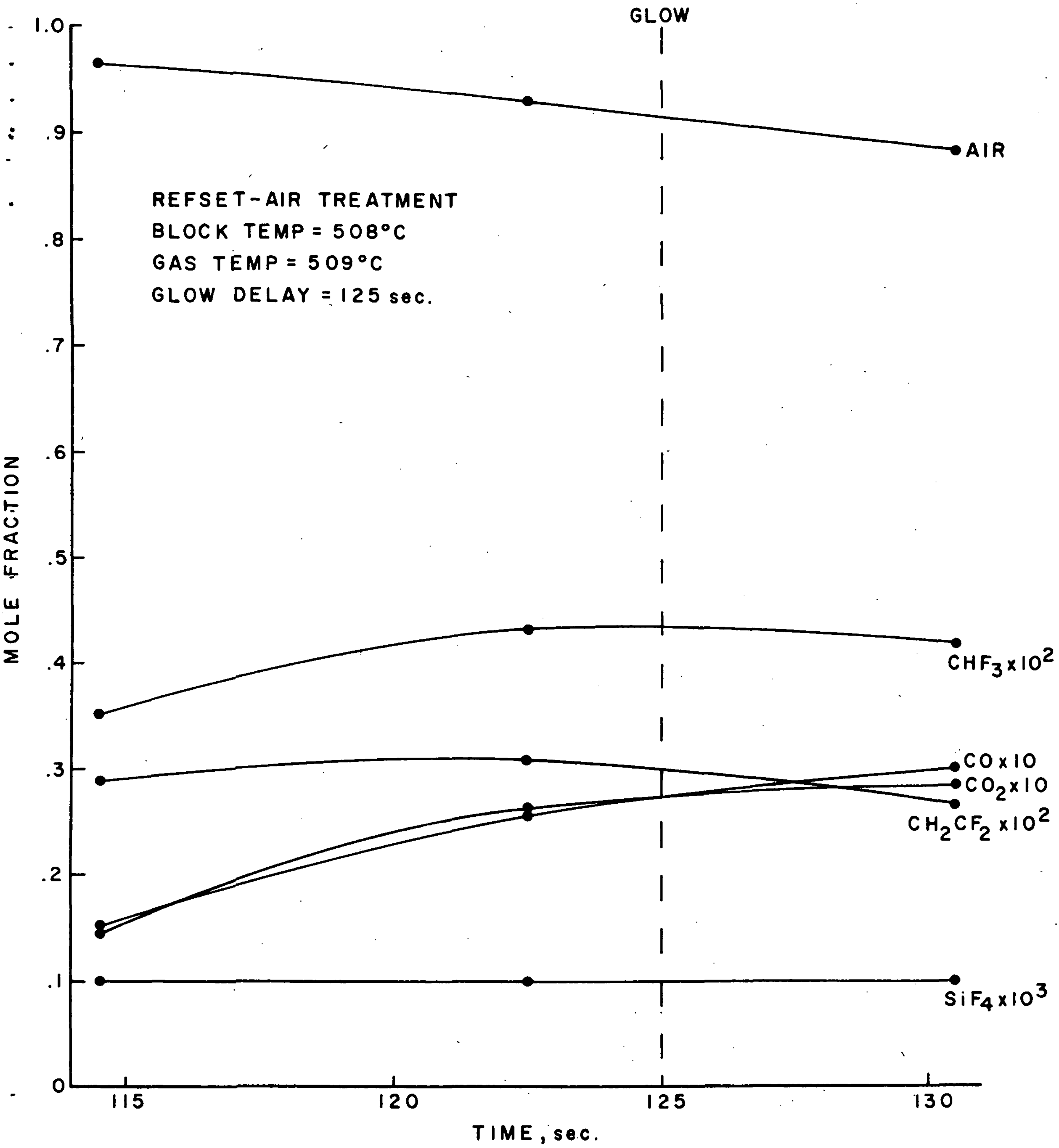


Figure 13. Relative Species Concentration as a Function of Heat Treatment Duration in a Refset-Air Test

residue left after the material glowed in air looked like coke. The appearance together with the approximately 20% higher residue weight would indicate that some carbon stayed behind. The infrared spectra of the two kinds of residues failed to provide any insight. The two infrared spectra were almost identical. The only absorption which could be identified was that of water; most likely present in the form of a hydrated inorganic salt. No infrared spectrum could be taken of the Refset sample prior to heat treatment since the material, a cured elastomer, did not lend itself to the usual sample preparation techniques. Inasmuch as no definite information is available as to the other constituents of Refset, besides Fluorel, any discussion of the nature of the residue left after the heat treatment of Refset at elevated temperatures in oxidizing media would be a pure speculation.

Ladicote Studies

The Ladicote used in this work was "Ladicote Fire-Retardant Coating Type II" obtained from the Los Angeles Division of North American-Rockwell Corporation in the form of blue paint. Two procedures were used to cast pellets from this material:

(a) Aluminum foil forms approximately 1/2" diameter and 1/2" high were coated with a very light film of silicone high vacuum grease (which acted as a release agent), and then the paint was poured into these forms to a height of approximately 0.2". These forms were then allowed to stand at room temperature for 12 hours followed by 5 hours at 55-60°C in an air circulating oven.

(b) In another variation the paint was poured into a Petri dish, which had been very lightly coated with a thin film of silicone grease. Subsequently the material was treated in the same manner as in procedure (a). From the solid plate thus obtained pellets were cut using cork borers. Two sizes of pellets were thus prepared, 1/2 and 0.85" diameter. The thickness varied from 0.08 to 0.12".

Procedure (b) was found to give more uniform pellets than procedure (a) and thus the majority of specimens were cast by this method.

In Table XVI are summarized the Ladicote oxygen runs, whereas in Figure 14 the ignition curve for Ladicote is presented.

TABLE XVI. SUMMARY OF EXPERIMENTS CONDUCTED ON LADICOTE IN OXYGEN ATMOSPHERE[a]

Run No.	Pellet Diam. In[b]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[c]	Burn Time Sec[d]	Remarks
766	1/2	425	471	52	23	Smoke at 20 sec, heavy smoke at 40 sec; 51.01% residue
767	1/2	429	464	42	18	Smoke at 21 sec, heavy smoke at 30 sec; 50.49% residue
768	1/2	389	438	n.i.[e]	n.a.[f]	Smoke at 19 sec, heavy smoke & glow at 70 sec; no glow at 1 min 30 sec; 51.75% residue
769	1/2	399	450	n.i.	n.a.	Smoke at 20 sec, heavy smoke at 43 sec; glow from 1 min 27 sec to 1 min 55 sec; 52.39% residue
770	1/2	228	480	n.i.	n.a.	Smoke at 21 sec, heavy smoke at 2 min 5 sec; glow from 2 min 15 sec to 2 min 25 sec; 50.83% residue
771	1/2	219	501	n.i.	n.a.	Smoke at 15 sec, heavy smoke at 50 sec; glow from 55 sec to 1 min; 52.55% residue
773	1/2	224	518	n.i.	n.a.	Smoke at 7 sec, heavy smoke at 30 sec; 52.78% residue
774	1/2	232	517	n.i.	n.a.	Smoke at 12 sec, heavy smoke at 30 sec; glow from 57 sec to 1 min; 52.51% residue
775	1/2	238	529	26	24	Smoke at 8 sec, heavy smoke at 23 sec; no smoke at 1 min 10 sec; 50.91% residue
776	1/2	326	513	26	34	Smoke at 8 sec, heavy smoke at 22 sec; no smoke at 1 min; 50.90% residue
777	1/2	329	497	31	24	Smoke at 10 sec, heavy smoke at 30 sec; no smoke at 55 sec; 49.49% residue
778	1/2	322	470	n.i.	n.a.	Smoke at 9 sec, heavy smoke at 25 sec; glow from 35 sec to 1 min; 51.76% residue
779	1/2	322	483	n.i.	n.a.	Smoke at 10 sec, heavy smoke at 28 sec, glow from 43 sec to 50 sec; 52.21% residue
780	1/2	322	490	n.i.	n.a.	Smoke at 10 sec, heavy smoke at 25 sec, glow from 40 sec to 58 sec; 53.23% residue
781	1/2	368	488	22	10	Smoke at 10 sec, heavy smoke at 20 sec; no smoke at 35 sec; 50.61% residue
782	1/2	369	480	n.i.	n.a.	Smoke at 12 sec, heavy smoke at 32 sec; glow from 45 to 50 sec 52.52% residue
783	1/2	404	471	n.i.	n.a.	Smoke at 9 sec, heavy smoke at 19 sec, glow from 35 sec to 40 sec; 51.85% residue

TABLE XVI. (Continued)

Run No.	Pellet Diam. In[b]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[c]	Burn Time Sec[d]	Remarks
784	1/2	424	493	23	15	Smoke at 10 sec, heavy smoke at 20 sec; no smoke at 38 sec; 50.55% residue
785	1/2	422	486	58	8	Smoke at 10 sec, heavy smoke at 25 sec; no smoke at 1 min 6 sec; 51.58% residue
786	1/2	418	476	n.i.	n.a.	Smoke at 11 sec, heavy smoke at 23 sec; glow from 47 sec to 55 sec; 52.51% residue
787	1/2	460	466	56	9	Smoke at 15 sec, heavy smoke at 35 sec; no smoke at 1 min 15 sec; 50.91% residue
788	1/2	459	451	n.i.	n.a.	Smoke at 12 sec, heavy smoke at 30 sec; glow from 54 sec to 1 min; 52.19% residue
789	1/2	459	461	65	22	Smoke at 15 sec, heavy smoke at 30 sec; no smoke at 1 min 27 sec; 51.82% residue
790	1/2	509	471	29	21	Smoke at 15 sec, heavy smoke at 26 sec; no smoke at 50 sec; 47.13% residue
791	1/2	515	456	55	23	Smoke at 17 sec, heavy smoke at 30 sec; no smoke at 1 min 18 sec; 47.93% residue
792	1/2	207	195	n.i.	n.a.	No apparent change to 10 min 94.43% residue
793	1/2	347	357	n.i.	n.a.	Very light smoke from 32 sec to 10 min when pellet removed 81.25% residue
794	0.85	347	358	n.i.	n.a.	Sampling run; pellet removed at 10 min; 81.98% residue
795	1/2	392	400	n.i.	n.a.	Smoke at 18 sec, heavy smoke at 50 sec; no smoke at 2 min 30 sec; 78.69% residue
796	0.85	390	400	n.i.	n.a.	Smoke at 42 sec, heavy smoke at 2 min 30 sec; no smoke at 7 min, 38 sec; 50.98% residue
797	0.85	396	395	n.i.	n.a.	Sampling run, smoke at 5 sec, heavy smoke at 1 min 10 sec; glow from 2 min 35 sec to 3 min 51 sec; 51.89% residue
798	1/2	438	455	n.i.	n.a.	Smoke at 22 sec, heavy smoke at 50 sec; glow from 1 min 25 sec to 1 min 59 sec; 54.41% residue
799	0.85	446	458	75	48	Smoke at 12 sec, heavy smoke at 30 sec; 48.51% residue
800	0.85	452	457	80	90	Smoke at 18 sec, heavy smoke at 40 sec; no smoke at 2 min 50 sec; 48.26% residue

TABLE XVI. (Continued)

Run No.	Pellet Diam. In[b]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[c]	Burn Time Sec[d]	Remarks
801	1/2	515	508	28	32	Smoke at 7 sec, heavy smoke at 15 sec; no smoke at 1 min; 49.80% residue
802	0.85	516	510	20	30	Smoke at 7 sec, heavy smoke at 15 sec; no smoke at 50 sec; 50.70% residue
803	1/2	474	483	34	26	Smoke at 7 sec, heavy smoke at 18 sec; no smoke at 1 min; 50.17% residue
804	0.85	471	483	28	31	Smoke at 8 sec, heavy smoke at 20 sec; 49.83% residue
805	0.85	471	481	42	28	Smoke at 15 sec; 51.58% residue
806	0.85	464	487	23	42	Sampling run; smoke at 10 sec, heavy smoke at 21 sec; 49.82% residue
807	1/2	508	430	n.i.	n.a.	Smoke at 12 sec, heavy smoke at 35 sec; glow from 1 min 13 sec to 1 min 30 sec; 46.59% residue
808	1/2	509	446	n.i.	n.a.	Smoke at 12 sec, heavy smoke at 25 sec, no smoke at 1 min 45 sec no glow observed;55.88% residue
809	1/2	509	442	n.i.	n.a.	Smoke at 14 sec, heavy smoke at 35 sec; glow from 1 min to 1 min 30 sec; 47.85% residue
810	1/2	551	426	n.i.	n.a.	Smoke at 10 sec, heavy smoke at 25 sec; no smoke at 2 min 15 sec no glow observed; 62.62% residue
811	1/2	553	437	32	23	Smoke at 10 sec, heavy smoke at 24 sec; 49.81% residue
826	1/2	467	450	n.i.	n.a.	Smoke at 10 sec, heavy smoke 1 min 14 sec, glow from 1 min 18 sec to 1 min 44 sec; 51.67% residue
827	1/2	469	479	34	24	Smoke at 10 sec, heavy smoke at 32 sec, no glow, no smoke at 58 sec; 50.51% residue
828	0.85	469	479	50	40	Smoke at 30 sec, no glow, no smoke at 1 min 40 sec; 47.64% residue
829	0.85	469	476	70	55	Smoke at 20 sec, heavy smoke at 50 sec, no glow, no smoke at 2 min 5 sec; 50.83% residue
830	0.85	469	477	58	47	Sampling Run, smoke at 18 sec, no glow, no smoke at 1 min 45 sec; 48.57% residue

[a] All temperatures were recorded just prior to Ladicote insertion.

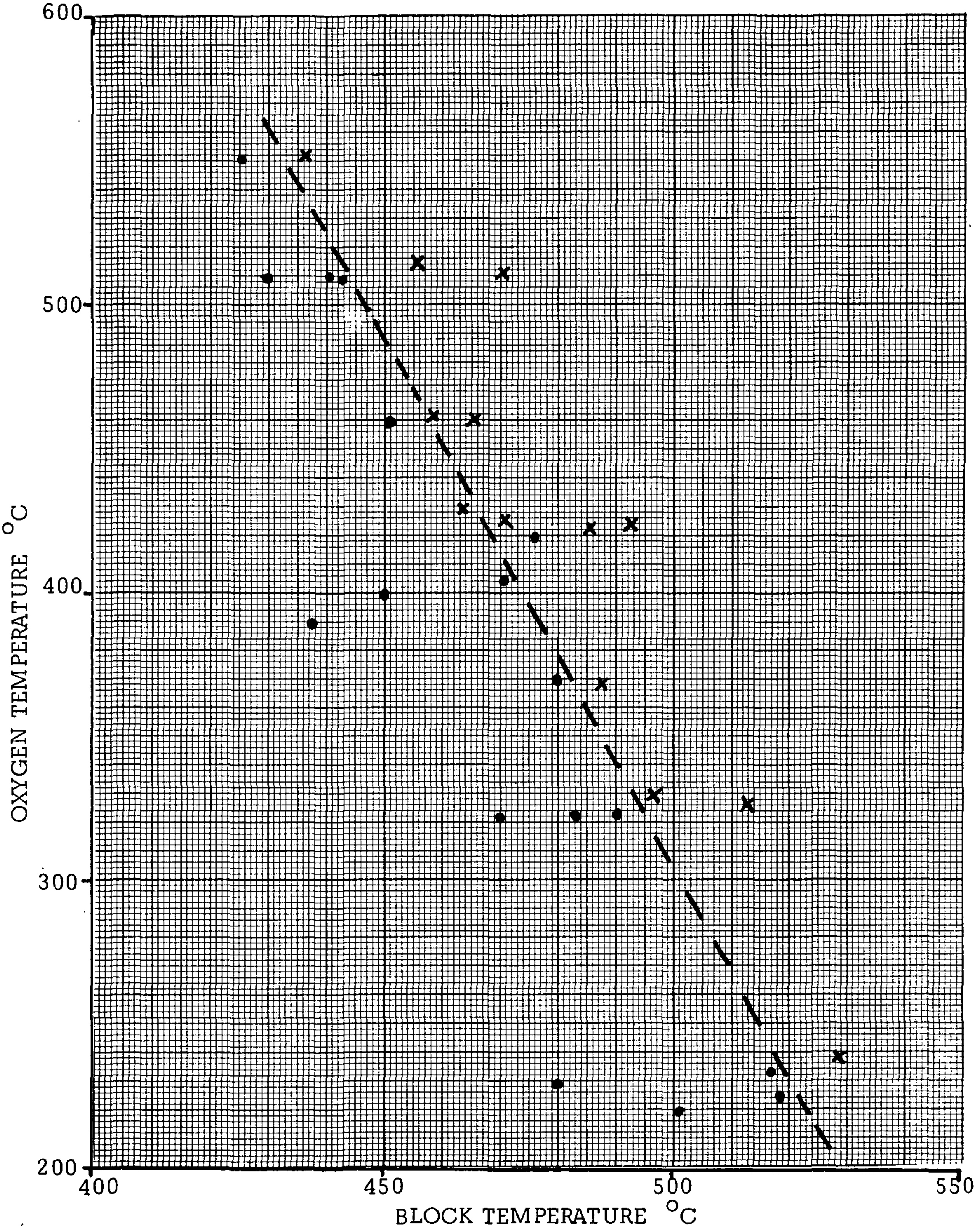
[b] The pellets of 1/2" diameter weighed between 120 and 200 mg, whereas the 0.85" diameter pellets weighed between 450 and 650 mg.

[c] Time measured from the insertion of Ladicote pellet.

[d] Time from ignition onset to conclusion of burning.

[e] No ignition.

[f] Not applicable.



X = Ignition
● = No ignition

Figure 14. Effect of Polymer Heating Block and Oxygen Temperature Upon Ladicote Ignition

The average residue after burning Ladicote in oxygen was found to be 50 ± 1% of the oven cured pellets. Based on the Ladicote Type II composition, allowing for the evaporation of the volatiles during the 55°C drying treatment, the pellets should contain approximately 53% of inorganic components. Under the conditions of the experiments, namely block temperatures in excess of 430°C (which appears to be the limiting ignition temperature) one would expect the carbonates to decompose, which would then make the inorganic residue equal to approximately 51.5%, which is fairly close to the found value. It should be pointed out that on ignition Ladicote flashed green, most likely due to some boron content.

To determine the type and relative concentration of the volatiles produced during the decomposition of Ladicote in oxygen, a number of sampling tests were performed. The pertinent data regarding temperatures, ignition onset, and sampling schedules are given in Table XVII, whereas the analytical results are summarized in Table XVIII. Examining Table XVIII, it is obvious that the tests were not performed in pure oxygen, which was due again to partial blocking of the sintered disc. This problem has been experienced with Fluorel gum and Refset and has been amply discussed previously.

From the Ladicote-oxygen tests it would appear that prior to ignition and even during the early stages of combustion the production of hydrogen fluoride (analyzed as SiF_4) is negligible. However, once the combustion is well established (see Table XVIII, 806-2 and 806-3) hydrogen fluoride is definitely formed (SiF_4 = 0.50% and 0.86%, respectively) accompanied by fluorinated hydrocarbons. It is thus reasonable to assume, in analogy with the Refset results, that in this particular case hydrogen fluoride does not originate from the Fluorel dehydrohalogenation (in the bulk of the specimen), but from the oxidation of the evolved fluorinated hydrocarbons, possibly via hydrolysis of carbonyl fluoride. If a mechanism as delineated above is truly operative then it is clear that the hydrogen fluoride absorbers present in the specimen cannot take care of the hydrogen fluoride generated during the combustion in the gas phase of the volatile pyrolysis products.

Examining Table XVIII, one can see that just prior to ignition hardly any oxidation took place (see Test 830-1) as evidenced by the relatively low content

TABLE XVII. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN THE LADICOTE-OXYGEN RUNS[a,b]

Run No.	Sampling Time Sec[c]	Ignition Delay Sec	Total Time Sec[d]	Gas Temp °C	Block Temp °C
794-1	300-305	n.i.[e]	n.a.[f]	347	358
797-1	175-180	155[g]	231	396	395
800-1	75-80	80	170	452	457
806-1	22-27	23	65	464	487
806-2	30-35	23	65	464	487
806-3	38-43	23	65	464	487
830-1	49-54	58	105	469	477
830-2	57-62	58	105	469	477

[a] All temperatures were recorded just prior to Ladicote insertion.

[b] Times are measured from insertion of Ladicote pellet.

[c] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[d] Time from insertion of Ladicote pellet to conclusion of burning.

[e] No ignition.

[f] Not applicable.

[g] In this case no ignition took place only glowing occurred.

TABLE XVIII. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING LADICOTE-OXYGEN TREATMENT[a]

Run No.[b]	Total %	O_2 %	Ar %	N_2 %	CO_2 %	CO %	SiF_4 %	CH_2CF_2 %	CHF_3 %
794-1	99.18	82.58	0.21	16.25	0.14	-	trace	-	-
797-1[c]	99.38	63.09	0.36	32.32	3.08	0.35	0.10	0.03	0.05
800-1	99.11	80.15	0.18	16.06	2.65	-	0.02	0.03	0.02
806-1[d]	100.35	62.51	0.36	30.51	6.08	0.84	0.02	-	0.02
806-2	99.54	49.15	0.36	31.05	16.04	2.04	0.50	0.16	0.24
806-3	99.82	48.65	0.37	31.36	17.34	0.99	0.86	0.10	0.15
830-1	100.63	65.26	0.41	34.00	0.95	trace	0.01	-	-
830-2[d]	100.52	26.33	0.44	35.49	34.38	3.85	0.03	-	-

[a] All analyses are given in mole percent.

[b] All these tests were performed using 0.85" pellets.

[c] This sample was taken while the material was glowing.

[d] This sample was taken during ignition.

of CO_2 and the absence of CO. Once combustion is well established (806-2, 806-3, 830-2) relatively high quantities of CO and CO_2 are produced. The unexplained finding is the low content of SiF_4 in the sample 830-2. Although, had the sampling been performed after additional few seconds of burning it is quite likely that SiF_4 would have been formed. It was noted earlier that hydrogen fluoride appears to be formed during the oxidation of the evolved volatiles in the later stages of combustion.

The experiments performed on Ladicote in air are summarized in Table XIX. It is obvious from the examination of these data that the ignition in air is very sporadic and not truly reproducible. This is contrary to the behavior in oxygen. In view of this the ignition curve could not be obtained. From the examination of Table XIX it is apparent that in the vicinity of 350°C (block and gas temperature) the rate of pyrolysis is relatively low (runs 836, 837), since under these conditions well above 80% of the material was left after up to 10 minutes on the heating block. At 400°C (run 838) the rate increased somewhat. Yet, in the vicinity of 450°C the residue amounted only to 54% of the original sample (runs 840, 841) indicating that most of the organic constituents were depleted. The analytical data for the Ladicote investigations in air performed at 350° and 400°C agree with the deductions based on the sample weight loss (see Tables XX and XXI). Examining Table XXI it is obvious that significant quantities of SiF_4 were found only in the run 841. The low level of SiF_4 in the other runs, as compared to run 841, cannot be readily explained. In all the tests, with the exception of the so-called low temperature experiments 837 and 839, the contents of CO and CO_2 were comparable if not higher than in the run 841 showing that oxidation was definitely taking place. On the other hand, all these tests were conducted at temperatures in excess of 500°C, whereas 841 was performed at gas = 455°C, block = 463°C. Furthermore, the sampling in the run 841 was done at a much later time after pellet insertion, than was the case in the other tests. It is believed that to get a better understanding of the processes occurring in any of these investigations a larger number of samplings than the customary three, which was necessitated by time limitation, would be required.

TABLE XIX. SUMMARY OF EXPERIMENTS CONDUCTED ON LADICOTE IN AIR ATMOSPHERE [a]

Run No.	Pellet Diam In[b]	Gas Temp °C	Block Temp °C	Ignition Onset Sec[c,d]	Total Time Sec[e]	Remarks
812	1/2	551	528	15	28	Heavy smoke at 10 sec; 50.46% residue
813	1/2	557	527	20	55	Heavy smoke at 12 sec, flashes at 20 to 30 sec; 60.54% residue
814	1/2	546	514	32	63	Smoke at 7 sec, heavy smoke at 15 sec, very heavy smoke at 25 sec, flashes at 32 and 35 sec; 52.34% residue
815	1/2	550	505	22	52	Heavy smoke at 19 sec, flashes at 22 sec, ignition at 24 sec, flame-off 33 sec; 52.08% residue
816	1/2	543	484	27	70	Smoke at 9 sec, heavy smoke at 21 sec, ignition at 31 sec, flame-off at 40 sec; 51.41% residue
817	1/2	541	465	n.i.[f]	70	Smoke at 14 sec, heavy smoke at 32 sec, very heavy smoke at 48 sec; 51.58% residue (after 10 min)
818	1/2	502	461	n.i.	100	Smoke at 13 sec, heavy smoke at 30 sec, very heavy smoke at 75 sec; 53.41% residue (after 10 min)
819	1/2	499	474	n.i.	93	Smoke at 11 sec, heavy smoke at 35 sec, very heavy smoke at 67 sec; 54.16% residue (after 3 min)
820	1/2	504	491	n.i.	88	Smoke at 14 sec, heavy smoke at 30 sec, very heavy smoke at 55 sec; 53.42% residue (after 2 min)
821	1/2	504	506	38	78	Smoke at 17 sec, heavy smoke at 35 sec, flashes at 38-45 sec; 57.13% residue
822	1/2	506	512	n.i.	75	Smoke at 15 sec, heavy smoke at 26 sec, very heavy smoke at 46 sec; 51.89% residue (after 10 min)
823	1/2	508	524	n.i.	55	Smoke at 10 sec, heavy smoke at 20 sec, very heavy smoke at 30 sec; residue 51.86%
824	1/2	508	527	n.i.	68	Smoke at 15 sec, heavy smoke at 23 sec, very heavy smoke at 35 sec; residue 49.23% (after 10 min)
825	1/2	508	535	n.i.	70	Smoke at 14 sec, heavy smoke at 25 sec, very heavy smoke at 39 sec; residue 49.82%
826	1/2	467	470	n.i.	104	Smoke at 16 sec, heavy smoke at 45 sec, very heavy smoke at 74 sec, glow at 77 sec, glow out at 104 sec; residue 51.67% (after 3 min)
827	1/2	469	479	34	58	Smoke at 10 sec, heavy smoke at 20 sec, very heavy smoke at 32 sec, flame off at 44 sec, glow off at 58 sec; residue 50.51%

TABLE XIX. (Continued)

Run No.	Pellet Diam In[b]	Gas Temp °C	Block Temp °C	Ignition Onset Sec[c,d]	Total Time Sec[e]	Remarks
828	0.85"	469	479	50	100	Smoke at 30 sec, heavy smoke at 45 sec, flame off at 67 sec; residue 47.64% (after 2 min)
832	1/2	455	445	n.i.	195	Smoke at 19 sec, heavy smoke at 60 sec; residue 61.44% (after 10 min)
833	0.85"	448	445	n.i.	192	Smoke at 30 sec, heavy smoke at 2 min 35 sec, glow at 2 min 45 sec; residue 55.97% (after 10 min)
834	1/2	403	404	n.i.	150	Smoke at 28 sec, heavy smoke at 65 sec; residue 82.10% (after 5 min)
835	0.85"	396	398	n.i.	230	Smoke at 30 sec, heavy smoke at 120 sec; residue 82.26% (after 5 min)
836	1/2	352	360	n.i.	600	Smoke at 37 sec, heavier smoke at 70 sec; residue 82.20% (after 10 min)
837	0.85"	357	360	n.i.	195	Sampling run; smoke at 41 sec, heavier smoke at 75 sec; residue 87.75% (after 3 min 15 sec)
838	1/2	404	397	n.i.	180	Smoke at 20 sec, heavy smoke at 56 sec; residue 76.77% (after 10 min)
839	0.85"	417	406	n.i.	135	Sampling run; smoke at 20 sec, heavy smoke at 90 sec; residue 81.26% (after 2 min 15 sec)
840	1/2	457	460	n.i.	155	Smoke at 14 sec, heavy smoke at 56 sec; residue 53.94% (after 10 min)
841	0.85"	455	463	n.i.	190	Sampling run; smoke at 12 sec, heavy smoke at 1 min 50 sec; residue 54.57% (after 3 min 10 sec)
842	1/2	511	513	n.i.	108	Smoke at 20 sec, very heavy smoke at 75 sec, glow at 1 min 30 sec, glow off at 1 min 48 sec; residue 54.56% (after 1 min 48 sec)
843	1/2	525	529	n.i.	87	Smoke at 19 sec, very heavy smoke at 50 sec; residue 52.52% (after 1 min 27 sec)
844	1/2	544	541	n.i.	70	Smoke at 14 sec, very heavy smoke at 30 sec; residue 50.16% (after 2 min)
845	1/2	448	546	27	60	Smoke at 9 sec, very heavy smoke at 25 sec, flashes at 27-35 sec; residue 53.96% (after 2 min)

TABLE XIX. (Continued)

Run No.	Pellet Diam In[b]	Gas Temp °C	Block Temp °C	Ignition Onset Sec[c,d]	Total Time Sec[e]	Remarks
846	0.85"	560	558	n.i.	70	Sampling run, smoke at 9 sec, very heavy smoke at 25 sec; residue 52.49% (after 2 min)
847	0.85"	544	524	n.i.	90	Sampling run, smoke at 17 sec, heavy smoke at 23 sec; residue 53.65%
848	1/2	597	574	15	50	Smoke at 5 sec, heavy smoke at 7 sec, flashes at 15-19 sec; residue 50.86%
849	0.85"	595	600	n.i.	60	Sampling run, smoke at 11 sec, heavy smoke at 25 sec; residue 52.2%

[a] All temperatures were recorded just prior to Ladicote insertion.

[b] The pellets of 1/2" diameter weighed between 120 and 200 mg, whereas the 0.85" diam. pellets weighed between 450 and 650 mg.

[c] Time measured from insertion of the Ladicote pellet.

[d] The occurrence of the first flash is denoted as ignition. Only in relatively few runs was actual combustion observed (815, 816, 827, 828).

[e] The time measured from the insertion of the Ladicote pellet to the complete absence of smoke.

[f] No ignition.

TABLE XX. SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS IN THE LADICOTE-AIR RUNS[a]

Run No.	Sampling Time Sec[b]	Total Time Sec[c]	Gas Temp. °C	Block Temp. °C
837	180-185	195	357	360
839	120-125	135	417	406
841	130-135	190	455	463
846-1	20-25	70	560	558
846-2	28-33	70	560	558
846-3	36-41	70	560	558
847-2	28-33	90	544	524
847-3	80-85	90	544	524
849-1	20-25	60	595	600
849-2	28-33	60	595	600

[a] All temperatures were recorded just prior to Ladicote insertion.

[b] Times are measured from insertion of Ladicote pellet. The interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[c] Time from insertion of Ladicote pellet to smoke disappearance.

TABLE XXI. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING LADICOTE-AIR TREATMENT [a]

Run No.[b]	Total %	Air %	Ar %	N_2 %	CO_2 %	CO %	SiF_4 %	CH_2CF_2 %	CHF_3 %
837	100.39	100.30	-	-	0.09	-	trace	-	-
839	100.28	99.37	-	0.68	0.22	-	trace	-	-
841	99.49	90.84	0.04	4.61	2.44	0.87	0.37	0.2	0.1
846-1	99.89	95.33	0.03	2.65	1.38	0.48	0.02	-	-
846-2	99.68	88.36	0.08	7.39	2.34	1.50	0.01	-	-
846-3	99.23	85.30	0.20	8.32	3.93	1.18	0.03	0.01	0.02
847-2	100.01	92.88	0.05	4.26	1.62	1.20	trace	-	-
847-3	100.52	89.68	0.09	7.92	2.13	0.69	trace	-	-
849-1	100.60	89.27	0.07	6.71	3.02	1.52	trace	trace	trace
849-2	100.36	90.01	0.08	5.99	2.76	1.08	0.01	0.2	0.2

[a] All the analyses are given in mole percent.

[b] All these tests were performed using 0.85 inch pellets.

Ignition Comparisons

No direct comparison of the ignition behavior of the three materials, namely Fluorel, Refset and Ladicote is really possible. The main difficulty is the unknown additive or additives in Refset and the conglomeration of ingredients in Ladicote II. The decreased autoignition limits of Refset in oxygen, as compared to the raw Fluorel gum, are in line with the expected reduced thermal stability of this system associated with the presence of cure and curing agent. In analogous manner, at first glance, one would also predict Ladicote to have lower ignition limits than Fluorel gum. This is not the case (compare Figures 11 and 14) and the compilation chart (Figure 17). It has to be remembered that in Ladicote II, Fluorel accounts for only 20% of the sample, accordingly the characteristics of the other ingredients must play a significant role. Furthermore, at any instant the concentration of the volatiles derived from the Fluorel component will be greatly diminished in view of the dilution effect.

Other valuable points were, however, brought into focus by this limited study: (1) an internal absorber of a toxic product, in this case of hydrogen fluoride, is effective for the removal of the dehydrohalogenation (within the sample) generated species, (2) the device cannot remove the hydrogen fluoride produced during the combustion of the gaseous fluorinated hydrocarbons, (3) in air environment, where no ignition seemed to occur (in our system), the internal absorber was found to be fully effective.

45B3 INTUMESCENT PAINT INVESTIGATIONS

The 45B3 intumescent paint was developed by NASA and a number of data pertaining to this and related materials have been published (Refs. 31, 32, 33, 34). The 45B3 paint is formulated by mixing A, B, and C (delineated in Table XXII) shortly before the actual use. As implied by its name the material intumesces on application of heat with the production of a foam-char. For the current investigation the material was supplied by the Sponsoring Agency. Due to the high intumescence capability of the Ames 45B3 paint, the type of pellet successfully employed in the

TABLE XXII. FORMULATION 45B3

Material	Weight
Part A	
Polysulfide polymer	14.1
Ammonium p-nitroaniline-o-sulfonate	57.0
Methyl ethyl ketone	28.9
Part B	
Epoxy resin, liquid	14.1
Toluene	14.7
Part C	
Tri(dimethylaminomethyl)phenol	2.8
Toluene	2.8

Ladicote paint investigation could not be used here. Therefore, for the ignition study nominally 1 mil thick, 0.85" diameter stainless steel discs were coated with 0.058-0.074 mm of the paint (20.0 ± 3.5 mg). In all instances the coating was allowed to dry for at least 72 hours at room temperature, to avoid solvent entrapment. It should be pointed out that the thickness of the coating was dictated by the limitation in the burner gap distance (0.6"), using the thickness given above resulted, especially at higher block temperatures (high heating rates), in "char-foams" which were up to 10 mm high; in some cases the foamed material filled even the burner gap (≈ 15 mm).

The tests performed in oxygen are summarized in Table XXIII, whereas the air experiments are given in Table XXIV. The graphical results of the ignition studies are presented in Figures 15 and 16. The gas sampling was attempted during the times when smoke evolution was observed, unfortunately the gaseous species were present in too low a concentration to allow mass-spectral detection, which is not surprising in view of the sample sizes used. Accordingly, sealed tube experiments, employing adequate material, were performed and these tests are discussed in a later portion of this report.

Examining Table XXIII, it is apparent that at 200°C only about 6% of the material is lost. This is in good agreement with TGA data obtained in nitrogen (Ref. 35). In the vicinity of 350°C (run 878) it would seem that about 40% (by weight) of material is lost during brief residence in burner, <u>ca</u> 30 sec. This again is in good agreement with TGA data. On prolonged (10 minutes) exposure to the burner atmosphere in oxygen this value approaches 70%, which tends to indicate oxidation of the char by hot oxygen. This assumption is supported by the results obtained in the air tests where even in the vicinity of 500°C (run 938, Table XXIV) the weight loss was only of the order of 50%. Based on the visual observations, smoking continued even after the intumescence ceased. It should be pointed out that in all the instances, where ignition did not take place the sample was removed only after smoking was no longer visible.

When ignition took place in oxygen what remained after combustion (which lasted 2-6 sec) appeared to be just the stainless steel disc; however, the weighing showed consistently 1-5% of residue pointing to some reaction with the stainless steel substrate. The lowest equitemperature in the oxygen tests was found to be <u>ca</u> 365°C.

It is noteworthy that in the air tests (Table XXIV) the residue left after ignition (combustion?) amounted to 30-40% of the original material and in no instance under the conditions employed was the combustion sustained. To check whether this self-extinguishing characteristic can also be observed at high temperatures one sample (run No. 945) was exposed to 585°C hot air with the heating block at the same temperature. Ignition

TABLE XXIII. SUMMARY OF EXPERIMENTS CONDUCTED ON 45B3 PAINT IN OXYGEN ATMOSPHERE[a]

Run No.	Film Wt mg[b]	Res. %[c]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Exp. Time Sec[f]	Remarks
865	32.3	94	200	200	n.i.(g)	n.a.(h)	600	3 min darkening, faint order
866	26.2	78	249	259	n.i.	n.a.	600	30 sec little intum., 1 min darkening
867	22.3	66	292	339	n.i.	n.a.	600	20 sec some intum., odor
868	13.2	32	354	361	n.i.	n.a.	600	1 sec intum.
869	16.5	56	368	300	n.i.	n.a.	600	2-10 sec intum. 10-65 sec smoke
870	19.7	3	236	443	1	5	306	---
874	17.8	61	301	358	n.i.	n.a.	40	4 sec intum., 7-15 sec smoke
876	17.8	63	362	310	n.i.	n.a.	35	3-6 sec intum., 5-8 sec smoke
877	22.5	66	355	326	n.i.	n.a.	45	4 sec intum.
878	16.9	60	357	346	n.i.	n.a.	30	4-8 sec intum.
882	15.3	5	462	370	1	2	30	---
883	18.7	2	548	355	1	5	30	---
884	14.8	3	555	349	1	3	30	---
885	16.9	2	548	342	1	4	30	---
886	18.5	4	555	331	1	5	30	---
887	21.3	3	564	317	2	3	30	---
888	26.5	2	562	309	1	4	20	---
889	22.5	3	553	301	3	4	30	---
890	21.0	3	546	283	2	3	20	---
891	16.1	3	551	261	2	3	15	---
893	20.7	2	548	237	2	6	20	---
894	19.2	3	532	238	2	6	20	---
896	16.6	62	506	248	n.i.	n.a.	60	5-30 sec intum.

TABLE XXIII. (Continued)

Run No.	Film Wt mg[b]	Res. %[c]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Exp. Time Sec[f]	Remarks
897	21.3	65	513	259	n.i.	n.a.	60	3-17 sec intum.
899	17.1	33	532	294	1	2	25	Self extinguish
900	15.8	69	530	212	n.i.	n.a.	60	3-17 sec intum.
901	18.0	11	511	236	3	5	30	Self extinguish
902	15.6	31	513	240	3	2	20	Self extinguish
903	19.0	73	515	227	n.i.	n.a.	60	3-18 sec intum., 12-18 sec smoke
904	19.5	72	214	333	n.i.	n.a.	40	4-10 sec intum., 6-10 sec smoke
905	18.9	71	208	360	n.i.	n.a.	40	2-8 sec intum., 5-20 sec smoke
906	14.0	3	219	478	1	3	30	---
907	15.7	57	222	454	n.i.	n.a.	30	3-5 sec intum., 4-12 sec smoke
908	23.0	3	249	460	1	5	20	---
909	19.1	3	250	445	1	4	20	---
910	21.2	59	252	426	n.i.	n.a.	30	3-7 sec intum., 5-15 sec smoke
911	18.8	57	313	397	n.i.	n.a.	30	2-5 sec intum., 4-12 sec smoke
912	18.7	1	319	417	1	4	20	---
913	16.9	1	325	407	1	2	35	---
914	18.2	5	389	370	1	5	20	---
915	17.9	58	392	350	n.i.	n.a.	30	2-6 sec intum., 4-12 sec smoke
916	19.9	1	385	363	1	5	20	---
917	17.6	3	464	348	2	6	20	---
918	23.4	2	469	330	2	5	20	---
919	20.9	1	457	317	1	5	20	---
920	15.7	1	462	306	1	4	20	---
921	25.9	-	468	295	n.i.	n.a.	-	Sample lost during removal from burner

TABLE XXIII. (Continued)

Run No.	Film Wt mg[b]	Res. %[c]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Exp. Time Sec[f]	Remarks
922	19.7	1	506	284	1	5	20	---
923	16.3	4	504	272	2	4	25	---
924	19.5	60	497	268	n.i.	n.a.	20	3-12 sec intum., 5-20 sec smoke
925	23.8	68	488	248	n.i.	n.a.	30	3-12 sec intum., 7-20 sec smoke
926	24.6	66	497	245	n.i.	n.a.	40	4-12 sec intum., 7-20 sec smoke

[a] All temperatures were recorded just prior to the paint insertion.

[b] The paint was coated onto 0.85" diameter, 1 mil thick stainless steel discs.

[c] The residue present is given with respect to the original coating.

[d] Time measured from the insertion of the sample.

[e] Time from ignition to conclusion of burning.

[f] Total time the sample remained in the burner.

[g] n.i. No ignition.

[h] n.a. Not applicable.

TABLE XXIV. SUMMARY OF EXPERIMENTS CONDUCTED ON 45B3 PAINT IN AIR ATMOSPHERE[a]

Run No.	Film Wt mb[b]	Res. %[c]	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[d]	Burn Time Sec[e]	Exp. Time Sec[f]	Remarks
927	20.3	49	229	508	n.i.(g)	n.a.(h)	25	1-6 sec intum., 3-15 sec smoke
928	18.8	54	233	514	n.i.	n.a.	25	1-6 sec intum., 3-12 sec smoke
929	24.1	39	242	530	1	1	20	1-5 sec intum., 2-10 sec smoke
930	16.4	?(i)	249	542	n.i.	n.a.	20	2-4 sec intum., 4-8 sec smoke
931	16.9	49	254	558	n.i.	n.a.	15	2-4 sec intum., 3-8 sec smoke
932	20.5	?[i]	259	583	n.i.	n.a.	15	2-4 sec intum., 2-8 sec smoke
933	21.9	33	266	595	1	1	15	---
934	20.6	32	294	613	1	1	15	---
935	26.3	41	387	551	1	1	20	1 sec intum., 2-5 sec smoke
936	24.3	23	427	512	n.i.	n.a.	30	1-3 sec intum., 3-10 sec smoke
937	21.2	37	452	527	1	1	25	1-2 sec intum., 2-4 sec smoke
938	20.8	44	450	513	n.i.	n.a.	25	1-2 sec intum., 1-12 sec smoke
939	19.0	36	504	501	1	1	25	2-10 sec smoke
940	22.1	46	511	470	n.i.	n.a.	30	1-2 sec intum., 2-12 sec smoke
941	13.5	37	513	489	1	1	25	2-12 sec smoke
942	18.5	37	569	460	1	1	25	2-15 sec smoke
943	21.7	38	569	446	0.5	0.5	25	1-10 sec smoke
944	24.6	48	569	433	n.i.	n.a.	20	1-2 sec intum., 2-10 sec smoke
945	17.1	30	585	585	0.5	0.5	25	1-10 sec smoke
946	23.7	45	296	574	n.i.	n.a.	20	1-2 sec intum., 2-10 sec smoke
947	22.7	21	291	589	n.i.	n.a.	300	1-2 sec intum., 2-10 sec smoke
948	12.3	41	340	556	n.i.	n.a.	20	1-2 sec intum., 2-10 sec smoke
949	16.1	42	383	610	n.i.	n.a.	25	1-2 sec intum., 2-10 sec smoke

TABLE XXIV. (Continued)

[a] All temperatures were recorded just prior to the paint insertion.

[b] The paint was coated onto 0.85" diameter, 1 mil thick stainless steel discs.

[c] The residue present is given with respect to the original coating.

[d] Time measured from the insertion of the sample.

[e] Time from ignition to conclusion of burning.

[f] Total time the sample remained in the burner.

[g] n.i. No ignition.

[h] n.a. Not applicable

[i] Sample was lost during removal from the burner.

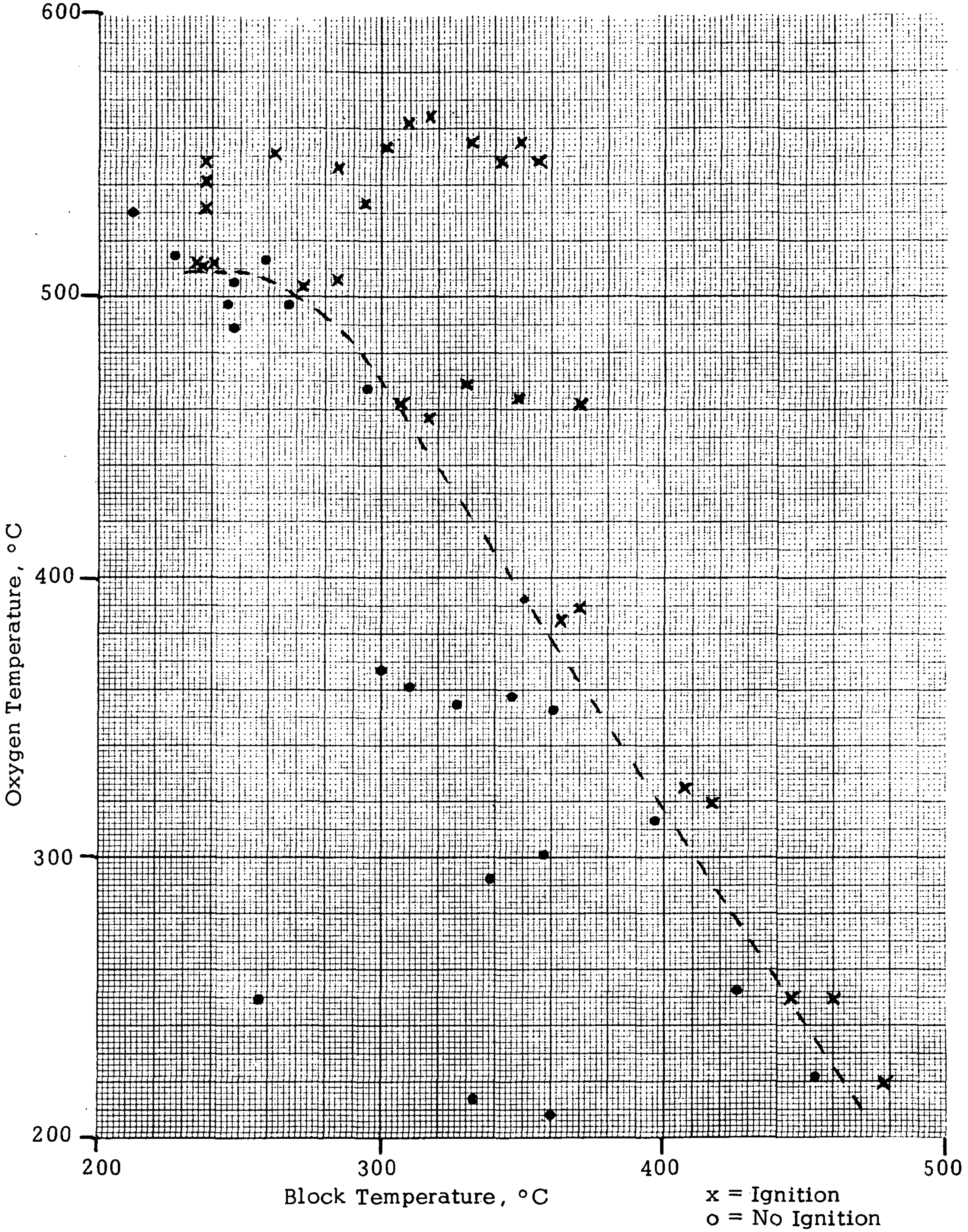
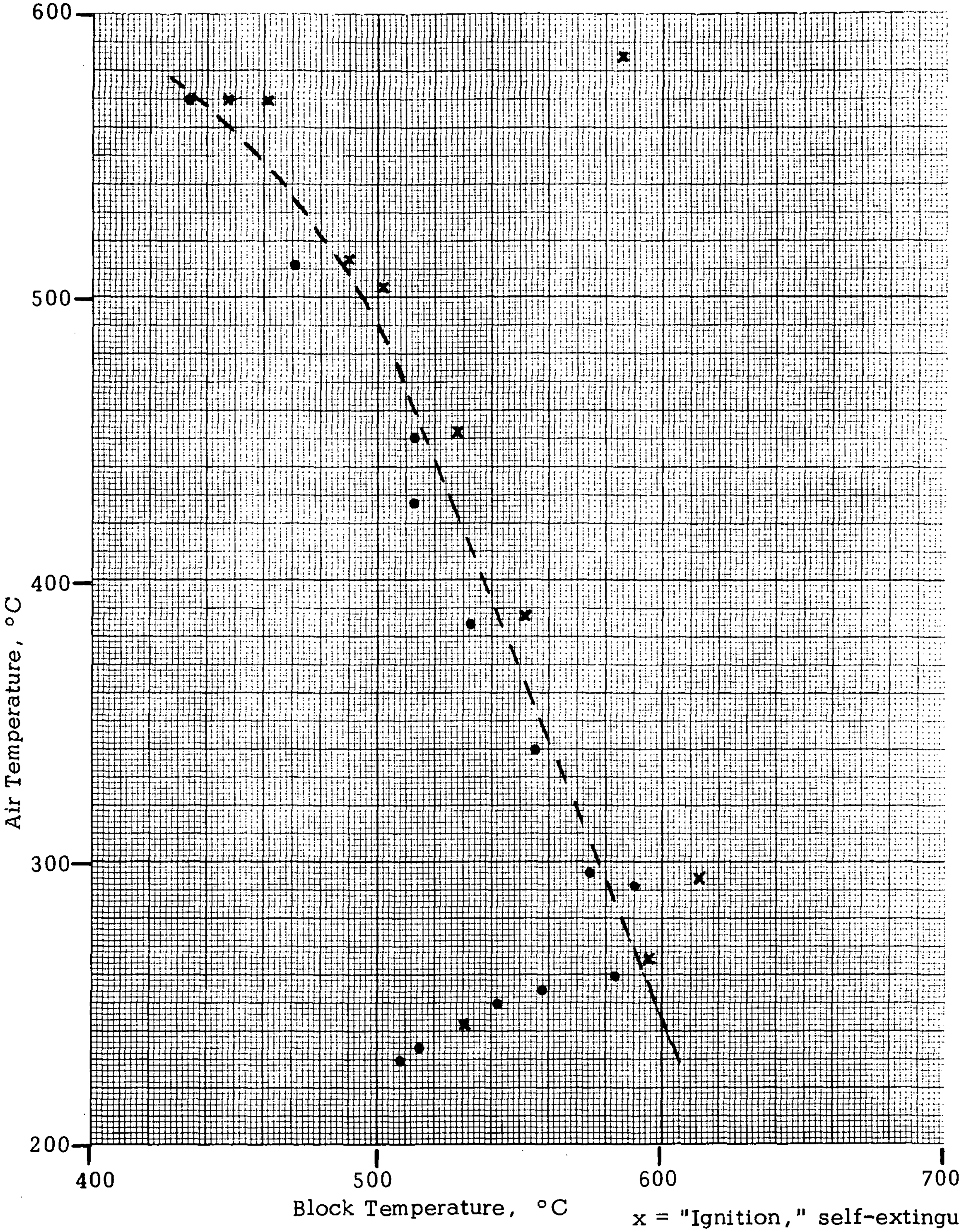


Figure 15. Effect of Oxygen and Block Temperature upon Ames 45B3 Paint Ignition



x = "Ignition," self-extinguished within 0.5-1 sec
o = No ignition

Figure 16. Effect of Air and Block Temperature upon Ames 45B3 Paint Ignition

took place within 0.5 sec after sample insertion, yet the flame died again within 1 sec. This finding would tend to indicate that the amount of combustible volatiles is almost negligible and that the remaining material will not burn in air. The majority of volatiles must be noncombustible since smoke evolution continued after self-extinguishment, as can be seen from Table XXIV. Based on Figure 16, the lowest equitemperature for gas and heating block, in the case of air was found to be ca 495°C.

The ignition curves for the 45B3 paint both in oxygen and air lie below similar curves for the tested fluorinated materials (see Figure 17) which implies much lower autoignition resistance. On the other hand it has to be stressed that in air the paint ignited only for a very short period leaving behind up to 50% of the char-foam. This behavior can be compared with that of Refset, which left a residue amounting to ca 48% in oxygen and ca 57% in air. The latter, furthermore failed to ignite in air, however, it glowed and thus could be regarded as potential ignition source.

As was noted in the preceding discussion no gas analysis could be performed using the stagnation burner arrangement in view of the small sample size employed (average weight, 20.0 ± 3.5 mg), necessitated by the intumescent nature of the paint. To conduct air off-gassing tests under somewhat dynamic conditions, a relatively large sample (40 mil coating on 1.5" x 1.5" stainless steel sheet) was heated with a Bunsen burner and when the yellow acrid smoke appeared the air samples were withdrawn using the probe employed in the stagnation burner experiments. The quantities of gaseous products which could be detected by a mass spectrometer were unfortunately insignificant (see Table XXV, the last two experiments). Accordingly, a sealed tube technique appeared to offer the best approach to the study of the volatiles evolved. The results of these tests are summarized in Tables XXV and XXVI. As shown in Table XXVI experiments were performed in sealed ampoules of known volume using a weighed sample of the dried paint and a known pressure of the gas (oxygen or air). If one were to consider the material (paint) to be composed entirely of $-CH_2-$ entities then the quantities of oxygen employed in the oxygen tests were sufficient to completely oxidize only ca 1/3 of the sample.

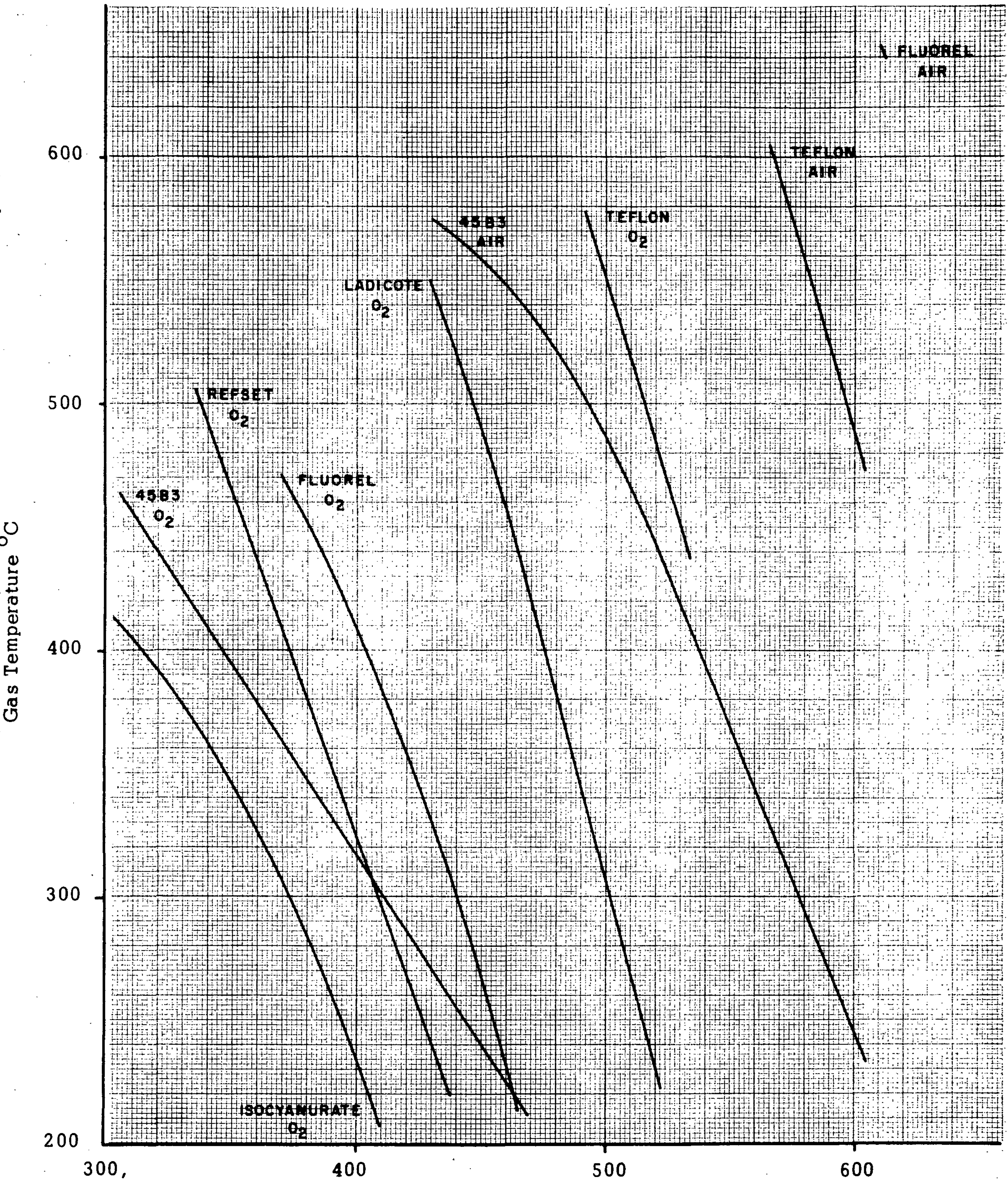


Figure 17. Ignition Curves in Oxygen and Air of the Compositions Studied

TABLE XXV. MASS SPECTRAL ANALYSES OF GASES PRESENT AFTER HEAT TREATMENT OF 45B3 PAINT IN OXIDIZING ATMOSPHERES[a]

Medium	Temp. °C[b]	Total Anal. %	O_2 %	Air[f] %	N_2[d] %	Ar[e] %	SO_2 %	CO %	CO_2 %	HCN %	COS[f] %
O_2	200	100.02	99.99	-	-	-	-	-	0.03	-	-
O_2	300	99.66	95.64	-	-	0.01	1.58	1.34	0.67	0.24	T
O_2	400	98.45	64.04	-	-	0.11	5.77	6.65	21.08	0.60	0.2
Air	300	100.50	-	74.32	19.21	0.43	3.29	1.08	1.39	0.56	T
Air	400	99.00	-	19.90	63.62	0.77	3.62	4.30	4.89	0.40	0.5
Air	500	96.87	-	0.94	71.82	0.87	0.71	13.39	8.77	0.31	1
Air	Burning[g]	99.69	-	99.39	-	-	0.03	-	0.27	T	-
Air	Burning[g]	100.13	-	99.80	-	-	0.01	-	0.32	T	-

[a] All the analyses are given in mole percent.

[b] All the tests with the exception of the last two were performed in sealed tubes.

[c] Air is taken as the total air composition which includes N_2, O_2, Ar, CO_2, etc., present in the air originally introduced into the ampoule.

[d] This is the nitrogen in excess of that present in the N_2, O_2, Ar, CO_2, etc., composition denoted as air. The excess of nitrogen is caused by the oxygen depletion.

[e] The same as applies to nitrogen applies also to argon.

[f] The mole percent of COS was determined from infrared spectra, based on the standard published by the Dow Chemical Company (Ref. 36) using Beer's law $\log P_o/P = A = abc$ (Ref. 37).

[g] These tests were performed using large samples of 45B3 paint and Bunsen burner as a heat source.

TABLE XXVI. SUMMARY OF SEALED TUBE EXPERIMENTS PERFORMED ON THE 45B3 PAINT IN OXIDIZING ATMOSPHERES

Sample Size mg	Ampoule Volume cc[a]	Initial Pres. mm[b]	Oxid. Medium	Temp. °C	CO_2 Wt[c] %	CO Wt %	SO_2 Wt %	COS Wt %	HCN Wt %	Remarks
123.4	132	403	O_2	200	0.05	-	-	-	-	No Intm[d]
91.2	127	407	O_2	300	1.0	1.2	3.6	T[e]	0.2	Intm
98.3	152	395	O_2	400	30.6	6.1	12.3	0.4	0.5	Intm
123.6	107	409	Air	300	1.3	0.7	4.5	T	0.3	Intm
114.7	120	412	Air	400	5.3	3.0	5.7	0.7	0.27	Intm
110.1	132	427	Air	500	11.6	11.3	1.4	1.8	0.25	Intm

[a] Volume of the sealed ampoule.

[b] The gas (air or oxygen) pressure prior to heating.

[c] Weight percent.

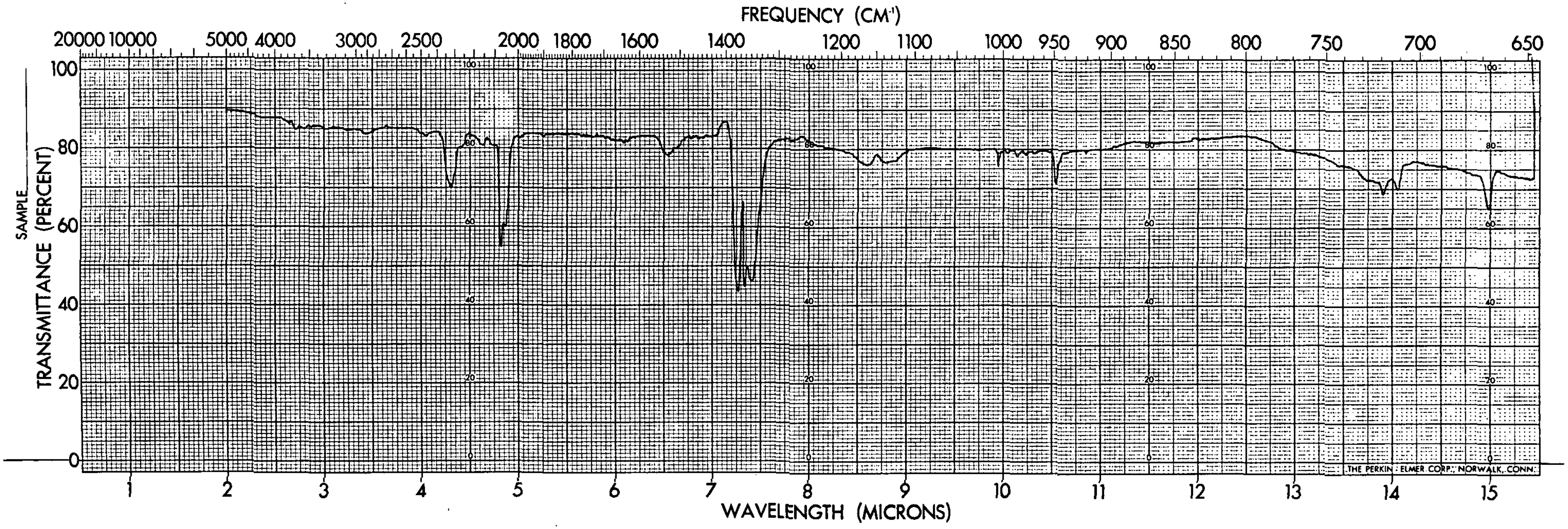
[d] Intumescence

[e] Trace

On the other hand the sample did not consist entirely of $-CH_2-$ units, but there were present fully oxidized SO_2 groups as well as sulfide moieties. Accordingly the amounts of oxygen employed were actually higher than needed for 30% combustion. To avoid undue product dilution we have deliberately employed these "rich" mixtures. The validity of this approach is shown by the results depicted in Table XXV, since in no instance was oxygen completely consumed in the pure oxygen tests. Actually under the most severe conditions only <u>ca</u> 36% of oxygen was used up. In the case of air the situation was less favorable since the quantities of air employed were sufficient to burn completely only <u>ca</u> 1/10 of the sample (based on calculations assuming $-CH_2-$ moieties to be present). Yet, only under the most drastic conditions (see Table XXV, run conducted at 500°C in air) was the oxygen almost completely depleted.

The pressures employed in all these tests were slightly above one half atmosphere (at room temperature). The sealed ampoules were heated at the selected temperature in an oven for a period of 15 minutes. After cooling to room temperature the ampoules were opened to a known evacuated volume and the volatiles present in every one ampoule were subjected to mass spectral analysis. Knowing the pressure and total volume the mmoles and weight of each constituent formed could be calculated and expressed as a weight percent of the original sample. In the case of the air-treated materials infrared spectra of the volatiles obtained after the treatment at 400°C and 500°C were also determined. These are shown in Figures 18 and 19, respectively. The two infrared spectra show the presence of the same components, namely: sulfur dioxide (4.0μ, 7.28μ, 7.34μ, 7.42μ, 8.57μ, 8.80μ), carbon dioxide (4.28μ, 13.89μ, 14.97μ), carbon monoxide (4.62μ, 4.72μ), carbonyl sulfide (4.82μ, 4.87μ), carbon disulfide (6.54μ), ethylene (10.52μ, and the typical fine absorptions on both sides of this band), and hydrogen cyanide (14.05μ). The main difference is the definitely higher relative concentration of ethylene in Figure 18, which is to be expected since at 500°C in air this material would be largely oxidized.

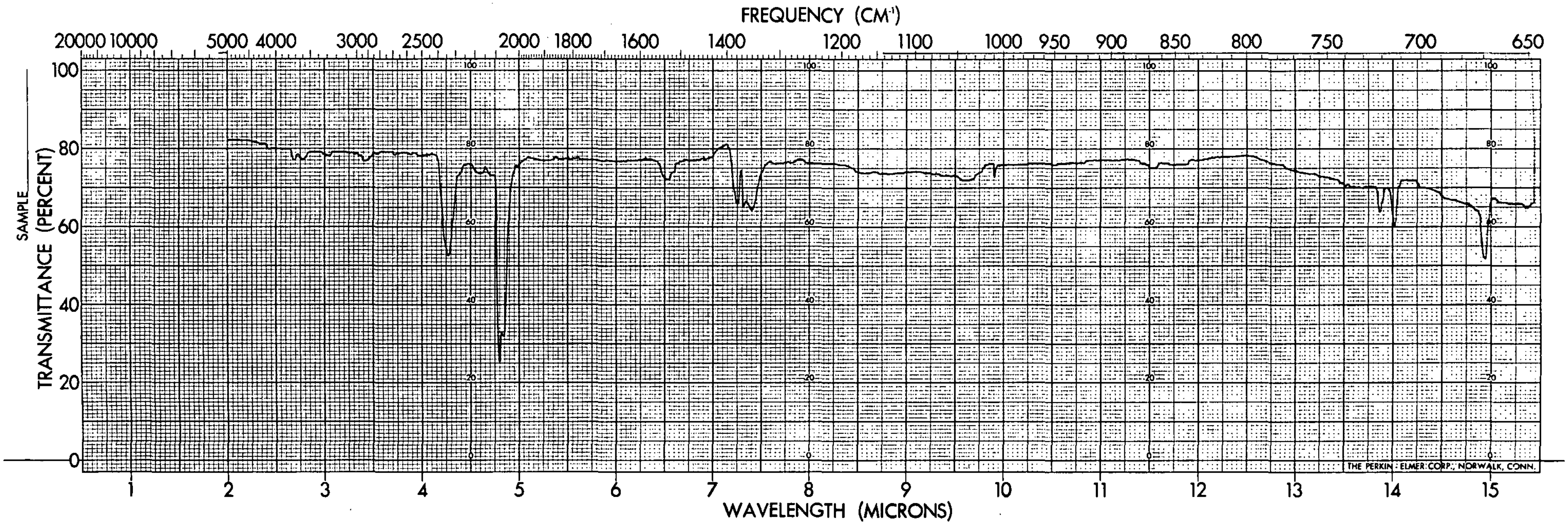
To concentrate the products, the total gaseous fractions were frozen in liquid nitrogen and the liquid nitrogen volatiles (O_2, air, CO) were pumped away. The liquid nitrogen condensibles consisted only of the products since oxygen, nitrogen and argon were removed. The only one of the products removable under these conditions is carbon monoxide, its absence in the spectra of the liquid nitrogen condensibles (see Figures 20,21) is shown by the absence of the absorption at 4.62μ and 4.72μ which were present in Figures 18 and 19. The infrared data supplement and support the mass spectral results (see Table XXV). The concentration of COS was determined in the samples Air-400°C and Air-500°C from the intensity of the 4.82μ infrared band in Figures 18 and 19, respectively. In the test, O_2-400°C, COS was determined based on the abundances at m/e = 60 (after calculating the sensitivity of COS from Air-400° and Air-500°C mass spectra). The relative amount of carbon disulfide could not be readily determined, furthermore, the origin of the absorptions centered at 11.50μ and 11.75μ (Figure 21) remains unknown.



10 cm cell

P = 120 mm

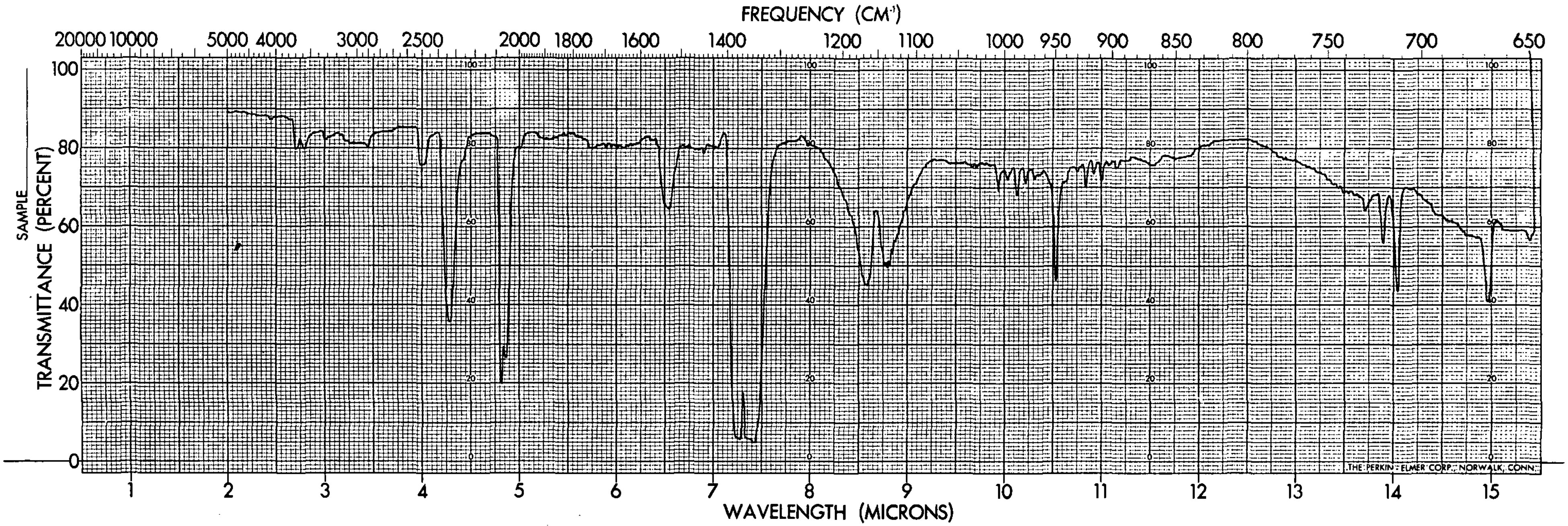
Figure 18. Infrared Spectrum of the Gaseous Atmosphere After the 400°C Heat Treatment of 45B3 Paint in Air.



10 cm cell

P = 137 mm

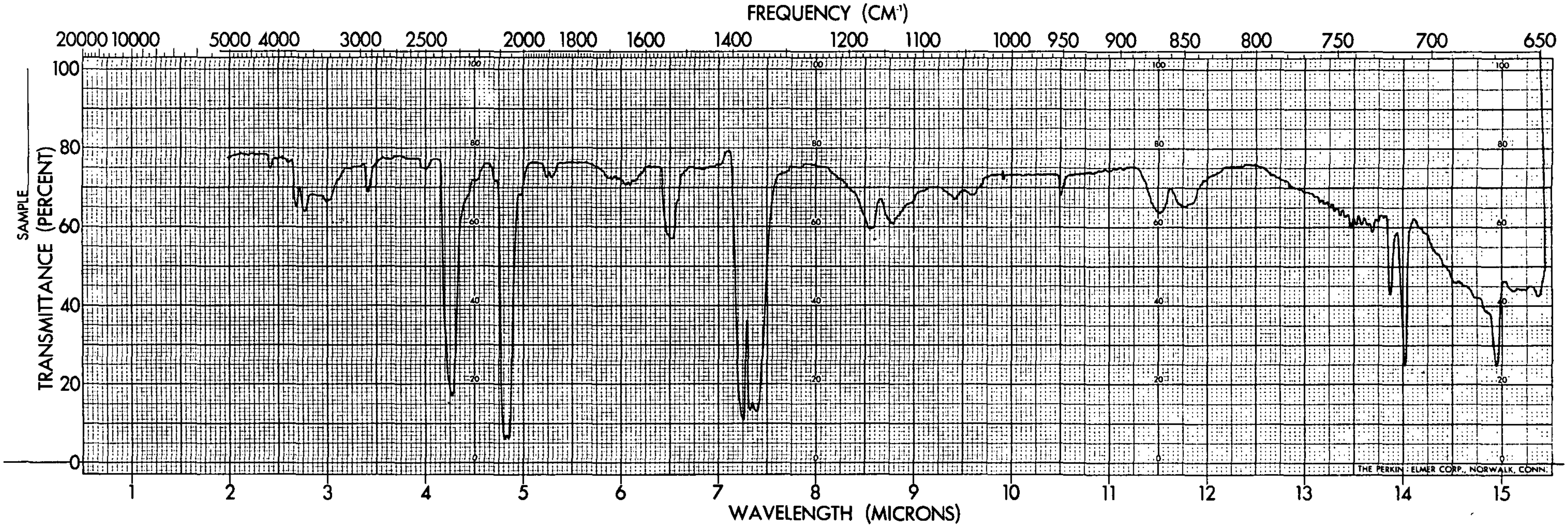
Figure 19. Infrared Spectrum of the Gaseous Atmosphere After the 500°C Heat Treatment of 45B3 Paint in Air.



10 cm cell

P = 150 mm

Figure 20. Infrared Spectrum of the Liquid Nitrogen Condensible Gaseous Products Formed During the 400°C Heat Treatment of 45B3 Paint in Air.



10 cm cell

P = 130 mm

Figure 21. Infrared Spectrum of the Liquid Nitrogen Condensible Gaseous Products Formed During the 500°C Heat Treatment of 45B3 Paint in Air.

The mass spectral results obtained at 200°C (see Table XXV) are in agreement with the burner tests and the TGA data, since in neither case significant quantities of material were lost. The appearance of the material in the tube after the 200°C exposure seemed hardly altered; at most the substance became slightly darker. All the other treatments at 300°C and above both in air and oxygen afforded intumescence (as evidenced by the black char-foam), yellow deposit and condensate on the sides of the tubes, and the volatiles analyzed and identified by infrared and mass spectral analyses. Examining Table XXVI it is obvious that the volatiles analyzed for in no way approach the weight loss shown at these temperatures by the TGA data (Ref. 35) and the burner tests even when all the oxygen present in CO_2, CO, COS and SO_2 is assumed to originate within the paint. This assumption, of course, is incorrect since a good portion of CO_2 is surely derived from carbon oxidation and some SO_2 is very likely obtained from the oxidation of the sulfur present in the polysulfide components. It is believed that this apparent discrepancy is due to the evolution of materials nonvolatile or of relatively low volatility at room temperature (one of these being water which can be considered under these conditions not amenable to mass spectral analysis). The presence of nonvolatile species manifested itself in all the sealed tube tests (except the one conducted at 200°C) as a yellow condensate and deposit. It should be stressed that the evolution of yellow fumes was also observed in the Bunsen burner-air experiments, as well as during stagnation burner testing. The nature of these materials has not been delved into, it is noteworthy, however, that both in the air and oxygen 400°C investigations a white crystalline material was also deposited.

Based on the mass spectral and infrared examinations the presence of CO_2, CO, SO_2, COS, CS_2, HCN and, in some instances, C_2H_4 has been definitely shown. The relatively low output of SO_2 in conjunction with the presence of COS in the tests conducted above 400°C can be explained by the reduction of SO_2 by the CO formed. This process has been observed to take place by Querido and Short (Ref. 38) in their studies of SO_2 reductions to elemental sulfur. One would expect the SO_2 output at 300°C either to be identical in air and oxygen or a higher value to be observed in oxygen. The opposite was found. The discrepancy, on the other hand, is relatively small. The formation of COS, as noted above, is due to the action of CO on SO_2 and the higher percentage of this material (Table XXVI) in the air-tests as compared to the oxygen series supports this assumption. The origin of CS_2 is rather obscure. It is believed that additional studies of the nature and the origin of the evolved species would help to understand the nature and the mechanism of formation of the "foam-char."

AMES ISOCYANURATE FOAMS INVESTIGATIONS

The foams were developed by NASA, some data relative to this and similar materials is published (Refs. 39-42) and actually a "Preliminary Material Specifications for Modified Polyisocyanurate Foam" has been issued.

The material used in the present investigation was supplied by the Sponsoring Agency in the form of cast rods which were then machined into 1/2" diameter 0.1" thick pellets; average weight 121 ± 15 mg (weight range 98 to 158 mg; the wide weight variation is due to the inhomogeneous nature of the foam). All the ignition tests and the oxygen sampling experiments were performed using these pellets. For the air-sampling, however, larger pellets 1.6" diameter, average weight 1041 ± 44 mg, were employed.

The results of the oxygen and air investigations are summarized in Tables XXVII and XXVIII, respectively. Examining Table XXVIII, it is apparent that no ignition occurred in air, even at gas and block temperatures of ca 600°C. However, at high temperatures the material glowed and the residue left after 3-5 minute residence in the hot environment amounted to about 15% (runs 999, 1000, 1001).

The oxygen ignition curve is depicted in Figure 22 from which it can be seen that in oxygen the autoignition took place at ca 325°C (gas and block temperatures). Comparing the ignition behavior in oxygen of the isocyanurate foam with that of the other materials studied under this contract, it is obvious that in oxygen this is the least flame retardant composition (compare Figure 17). On the other hand, it has to be remembered that his material failed to auto-ignite in air. It is noteworthy that the isocyanurate foams when heated smoked for a considerable period prior to ignition or glow onset, however, the last 2-5 sec before ignition usually no smoke evolution could be seen. Thus it

TABLE XXVII. SUMMARY OF EXPERIMENTS CONDUCTED ON AMES ISOCYANURATE FOAM IN OXYGEN ATMOSPHERE[a]

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[b]	Burn Time Sec[c]	Residence Time min:sec[d]	Remarks
950	243	484	55	25	2:00	20-50 sec smoke, trace residue
951	233	512	60	47	2:50	10-140 sec smoke, trace residue
952	224	482	190	30	4:30	15-105 sec smoke, trace residue
953	215	450	45	23	1:50	15-90 sec smoke, trace residue
954	203	418	104	41	3:30	20-90 sec smoke, 105-180 sec smoke; trace residue
955	189	323	n.i[e]	n.a.[f]	10:00	No apparent smoke, sample top surface discolored lightly, bottom surface blackened
956	193	340	n.i	n.a.	10:00	See run 955
957	198	370	n.i	n.a.	10:00	55-170 sec smoke, sample charred
958	207	394	n.i	n.a.	10:00	40-210 sec smoke, sample charred
960	238	384	295	28	4:25	40-105 sec smoke, 223-243 sec smoke, trace residue
961	252	332	n.i	n.a.	10:00	No apparent smoke, just light odor, sample discolored
962	259	342	n.i	n.a.	10:00	40-100 sec smoke, sample charred
963	265	351	n.i	n.a.	6:00	40-120 sec smoke, sample charred
964	268	382	n.i	n.a.	6:00	30-130 sec smoke; sample charred
965	271	399	127	28	3:00	25-80 sec smoke, 128-175 sec smoke, trace residue
966	336	367	80	30	2:35	28-65 sec smoke, 110-150 sec smoke, trace residue
967	336	347	n.i.	n.a.	7:00	30-120 sec smoke, sample charred
968	452	314	65	20	2:15	20-55 sec smoke, 85-100 sec smoke, trace residue
969	462	289	45	25	1:50	25-95 sec smoke, trace residue

TABLE XXVII. (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[b]	Burn Time Sec[c]	Residence Time min:sec[d]	Remarks
970	462	281	180	45	4:35	40-95 sec smoke, 225-245 sec smoke, trace residue
971	457	252	n.i.	n.a.	10:00	30-105 sec smoke, sample charred
972	462	245	n.i.	n.a.	10:00	55-145 sec smoke, sample charred
973	459	260	86	34	2:50	20-76 sec smoke, 87-150 sec smoke, trace residue
974	371	315	n.i.	n.a.	10:00	35-145 sec smoke, sample charred
975	371	315	n.i.	n.a.	10:00	30-132 sec smoke, sample charred
976	387	336	50	21	1:50	25-90 sec smoke, trace residue
977	392	369	32	23	2:00	22-90 sec smoke, trace residue
978	396	369	90	35	2:50	28-75 sec smoke, 92-155 sec smoke, trace residue
979	399	372	110	65	3:40	Sample is the residue of Run 957, no smoke before ignition, 175-195 sec smoke, trace residue
980	403	372	n.i.	n.a.	10:00	Sample is the residue of Run 955, no visual changes, residue 69%
981	406	372	n.i.	n.a.	10:00	Sample is the residue of Run 962, no visual changes, residue 79%
982	408	372	n.i.	n.a.	10:00	Sample is the residue of Run 963, no visual changes, residue 6%
983	411	377	110	30	3:20	Sample is the residue of Run 971, 112-170 sec smoke, trace residue
984	415	382	37	26	1:45	18-80 sec smoke, trace black residue
987	249	247	n.i.	n.a.	10:00	Sampling run, no visual changes, residue 96%

TABLE XXVII. (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Delay Sec[b]	Burn Time Sec[c]	Residence Time min:sec[d]	Remarks
989	315	317	n.i.	n.a.	10:00	65-130 sec light smoke, residue 81%
990	316	315	n.i.	n.a.	10:00	Sampling run, 45-115 sec light smoke, residue 80%
991	373	371	285	35	6:00	25-90 sec smoke, 320-340 sec smoke, trace residue
992	375	376	180	40	4:30	Sampling run, 25-125 sec smoke, 220-240 smoke, trace residue

[a] All temperatures were recorded just prior to sample insertion.

[b] Time measured from the insertion of the sample.

[c] Time from ignition to conclusion of burning.

[d] Total time the sample remained in the burner.

[e] n.i. No ignition.

[f] n.a. Not applicable.

TABLE XXVIII. SUMMARY OF EXPERIMENTS CONDUCTED ON AMES ISOCYANURATE FOAM IN AIR ATMOSPHERE[a]

Run No.	Gas Temp. °C	Block Temp. °C	Glow Delay Sec[b]	Glow Time Sec[c]	Residence Time min:sec[d]	Sample Type	Remarks
985	418	382	n.g.[e]	n.a.[f]	10:00	Small	30-105 sec smoke, residue 75%
986	420	449	n.g.	n.a.	10:00	Small	20-120 sec smoke, residue 59%
993	214	546	n.g.	n.a.	10:00	Small	10-75 sec smoke, residue 37%
994	256	617	110	135	10:00	Small	7-62 sec smoke, residue 20%
995	301	630	60	90	10:00	Small	5-35 sec smoke, residue 15%
996	357	629	60	115	10:00	Small	8-40 sec smoke, residue 19%
997	403	598	70	55	10:00	Small	10-35 sec smoke, residue 16%
998	466	613	60	70	10:00	Small	10-38 sec smoke, residue 14%
999	546	620	40	100	3:00	Small	10-30 sec smoke, residue 16%
1000	586	617	32	68	3:00	Small	4-28 sec smoke, residue 16%
1001	585	613	55	105	5:00	Large	10-75 sec smoke, residue 13%
1002	588	613	60	110	7:00	Large	Sampling run, 5-55 sec smoke, 30 sec v. heavy, residue 14%
1003	301	309	n.g.	n.a.	10:00	Large	Sampling run, no visual occurrance, residue 87%
1004	446	449	n.g.	n.a.	10:00	Large	15-240 sec smoke, 58 sec v. heavy, residue 50%
1005	446	445	n.g.	n.a.	10:00	Large	Sampling run, 5-250 sec smoke, 60 sec v. heavy, residue 46%

[a] All temperatures were recorded just prior to the foam insertion.

[b] Time measured from the insertion of the sample.

[c] Time from glow onset to glow disappearance.

[d] Total time the sample remained in the burner.

[e] n.g. No glow.

[f] n.a. Not applicable.

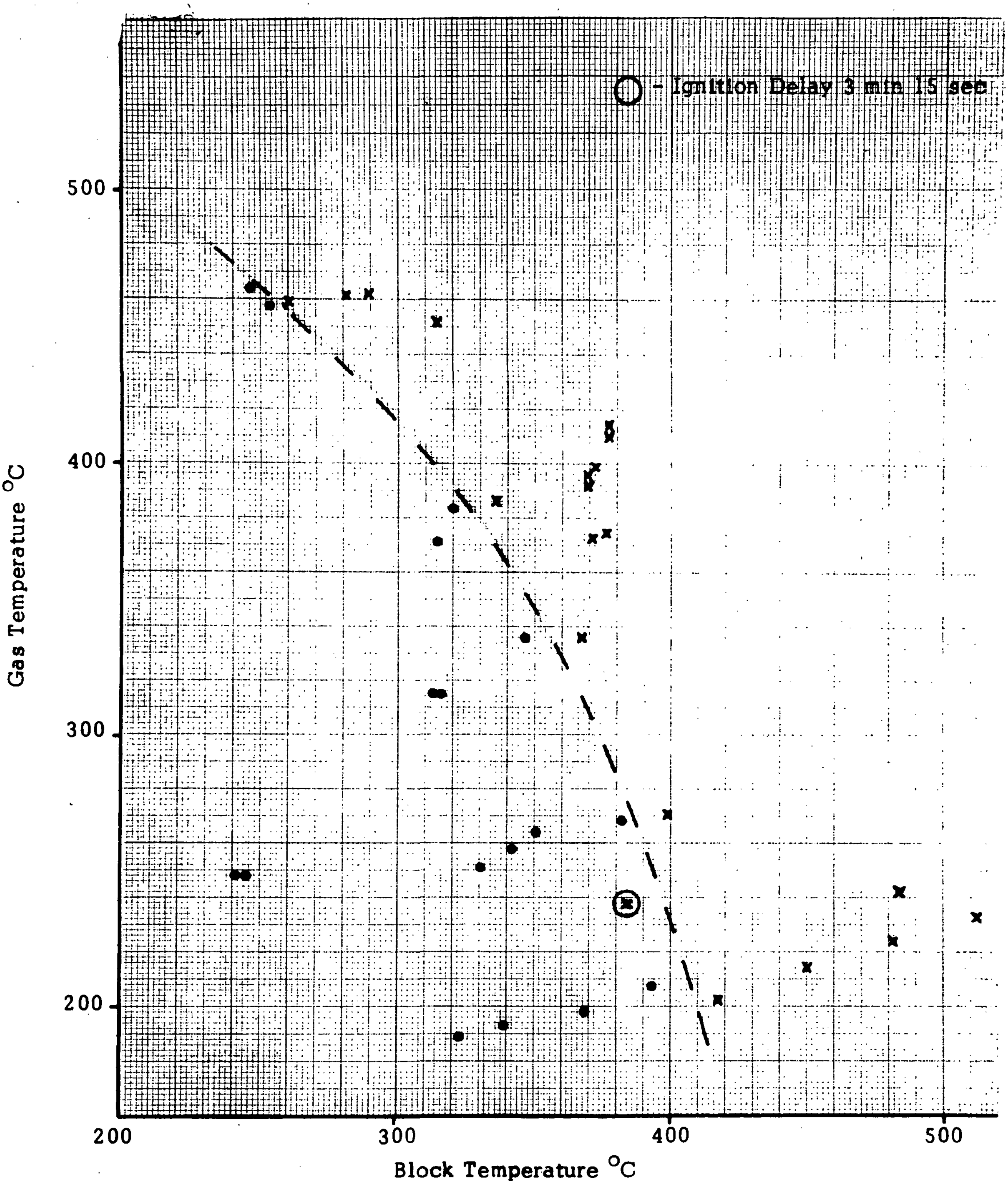


Figure 22. Effect of Oxygen and Block Temperatures Upon Ames Isocyanurate Foam Ignition

would appear that the residue left after the initial pyrolysis products were liberated, is the more readily ignitable species. This assumption was partly proven by the ignition of samples which were previously subjected to heat treatment (see runs 979-983). On the other hand not all of these samples ignited. Most ignitions appeared to be preceded by a glow or sparkling (1-2 seconds duration) which seemed to be attached to one point on the sample surface. The initial high flame lasted 1-3 seconds and the subsequent combustion was characterized by what could be described as a surface flame. The combustion was frequently accompanied by smoking and even after flame disappearance, in certain instances, light smoking was noted. However, invariably only a trace of residue was left. With an increasing number of tests performed, white and brown deposits were noted on all surfaces in the vicinity of the platinum sample dish, in some cases a white residue also could be seen on the dish.

The sampling runs, performed in oxygen, are summarized in Table XXIX whereas in Table XXX, the mass spectral results are presented. It is not surprising that no products were found in the tests 987-1, 987-2, 990-1, 990-2 since under the conditions employed in these particular experiments the samples lost only 4% (5 mg) and 10% (24 mg) respectively in a 10 minute period. In the run 992 sampling was performed during the period of heaviest smoking (992-1) and right after ignition (992-3). Yet, the sample 992-1 failed to show significant quantities of products, whereas in the sample 992-3 CO_2 and CO were found to be the main products. It seems worthwhile at this time to discuss certain aspects of the mass spectra obtained, this will become of significantly more importance in the air studies. In the first two gas samples from run 992 traces of aromatics appeared to be present as indicated by the abundances at m/e = 39, 41. The "CH", implying aliphatic carbon hydrogen linkages, are assumed to be the origin of the excess abundances at m/e = 28 (after subtracting N_2, CO, O_2, etc.). In view of the excess of the abundances at m/e = 28 the abundances at m/e = 26, 27 cannot be really ascribed to HCN. In the sample 992-3 excess of abundances at m/e = 44 was observed, after subtracting the output for CO_2. (m/e = 22 being taken as the base peak for CO_2). The output at 44 can be due to NCO containing species, oxygenated hydrocarbons, amine containing materials and others. Since the nature of the species responsible for the output at m/e = 44 is not known, it is impossible to assess

TABLE XXIX. SAMPLING SCHEDULES AND EXPERIMENTAL DETAILS IN THE AMES ISOCYANURATE FOAM-OXYGEN RUNS[a,b]

Run No.	Sampling Time min:sec - min:sec[c]	Ignition Delay Sec	Total Time min:sec[d]	Gas Temp. °C	Block Temp. °C
987-1	0:30 - 0:35	n.i.[e]	10:00	249	247
987-2	2:00 - 2:05	n.i.	10:00	249	247
990-1	1:05 - 1:10	n.i.	10:00	315	316
990-2	1:35 - 1:40	n.i.	10:00	315	316
992-1	0:50 - 0:55	180	4:30	375	376
992-2	1:10 - 1:15	180	4:30	375	376
992-3	3:00 - 3:05	180	4:30	375	376

[a] All temperatures were recorded just prior to sample insertion.

[b] Times are measured from insertion of sample.

[c] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[d] Time from the sample insertion to its removal.

[e] No ignition.

TABLE XXX. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING AMES ISOCYANURATE FOAM-OXYGEN TREATMENT[a,b]

Run No.	Total %	O_2 %	Ar %	N_2 %	CO_2 %	CO %	HCN %	Aromatic[c]	"44"[c]	CH[c]
988-1	100.17	99.85	-	0.32	-	-	-	-	-	-
988-2	100.11	100.11	-	-	-	-	-	-	-	-
990-1	100.03	99.97	-	0.03	0.03	-	-	-	-	-
990-2	100.16	99.95	-	0.19	0.02	-	-	-	-	-
992-1	99.79	99.32	-	0.21	0.26	-	?	T[d]	-	-
992-2	98.96	98.64	-	0.20	0.12	T	?	T	-	T
992-3[e]	99.29	92.30	0.02	0.82	5.78	0.37	?	T	Yes	Yes

[a] All the analyses are given in mole percent.

[b] All these tests were conducted using 1/2" diameter pellets of average weight 121 ± 15 mg.

[c] The meaning of these terms is explained in the text.

[d] Trace

[e] This sample was taken during combustion.

their contribution, etc. The almost complete analysis of the sample 992-1 (99.79% accounted for) would indicate that the majority of the species constituting the observed smoke are involatile or of low volatility at room temperature. One of these is most certainly water, however, other materials were definitely also evolved as evidenced by a pungent odor and by the presence of brown fumes. Based on the odor one is tempted to speculate that some of these materials are fused aromatics and biphenyls. To analyze for such compounds would require a heated sampling arrangement leading to a heated inlet and expansion chamber mass spectrometer. The problem encountered in the oxygen runs was further amplified in the air tests where 10 fold larger samples were employed to assure sufficient product concentration. These sampling experiments are summarized in Tables XXXI and XXXII. Again, the totals accounted for are fairly good, yet the ampoules after sampling appeared to be filled with smoke. In the mass spectra the left over output was present at m/e, 15, 16, 26, 27, 28, 39, 41 and 44, however, these outputs were relatively low. The infrared spectrum taken of sample 1005-1 (Figure 23) supports the mass spectral results. The only absorptions visible in this very weak spectrum are those ascribed to CH(3.4μ, 3.5μ), CO_2 (4.28μ, 13.89μ, 14.97μ), $CH_2{=}CH_2$ (10.52μ), $CH_3CH{=}CH_2$ (10.98μ) with carbon dioxide being by far the major constituent. It is noteworthy that no HCN seems to be present.

To clarify the data presented in Table XXXII, it should be emphasized that sample 1002-3 was taken during glow, actually when the glow was at its brightest. Again CO_2 was the main detected constituent, which was also the case in the sample 1002-2 taken during the heavy smoke evolution.

These rather inconclusive results dictate as an alternative or rather supplemental approach the sealed tube technique, which was found to give a large amount of information in the case of the 45B3 paint.

TABLE XXXI. SAMPLING SCHEDULES AND EXPERIMENTAL DETAILS IN THE AMES ISOCYANURATE FOAM-AIR RUNS[a,b]

Run No.	Sampling Time min:sec - min:sec[c]	Glow Delay Sec	Total Residence Time min:sec[d]	Glow Time min:sec[e]	Gas Temp. °C	Block Temp. °C
1002-1	0:20 - 0:25	60	7:00	1:50	588	613
1002-2	0:35 - 0:40	60	7:00	1:50	588	613
1002-3	1:30 - 1:35	60	7:00	1:50	588	613
1003-1	1:40 - 1:45	n.g.[f]	10:00	n.a.[g]	301	309
1005-1	1:00 - 1:05	n.g.	10:00	n.a.	446	445
1005-2	2:20 - 2:25	n.g.	10:00	n.a.	446	445

[a] All the temperatures were recorded just prior to sample insertion.

[b] Times are measured from insertion of sample.

[c] Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

[d] Time from the sample insertion to its removal.

[e] The time interval during which the glow was visible.

[f] No glow.

[g] not applicable.

TABLE XXXII. MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING AMES ISOCYANURATE FOAM-AIR TREATMENT[a,b]

Run No.	Total %	Air %	Ar %	N_2 %	CO_2 %	CO %	HCN %	Aromatic[c]	"44"[c]	CH aliphatic[c]
1002-1	98.99	96.55	0.05	-	2.39	-	?	T[d]	Yes	Yes
1002-2	99.60	96.41	0.05	1.00	1.99	0.15		Yes	Yes	Yes
1002-3[e]	98.49	78.47	0.22	16.11	3.69	-	?	-	Yes	Yes
1003-1	99.98	99.95	-	-	0.03	-	-	-	Yes	Yes
1005-1	99.45	98.90	-	-	0.55	-	?	Yes	Yes	Yes
1005-2	99.89	99.74	-	-	0.15	-	?	-	-	-

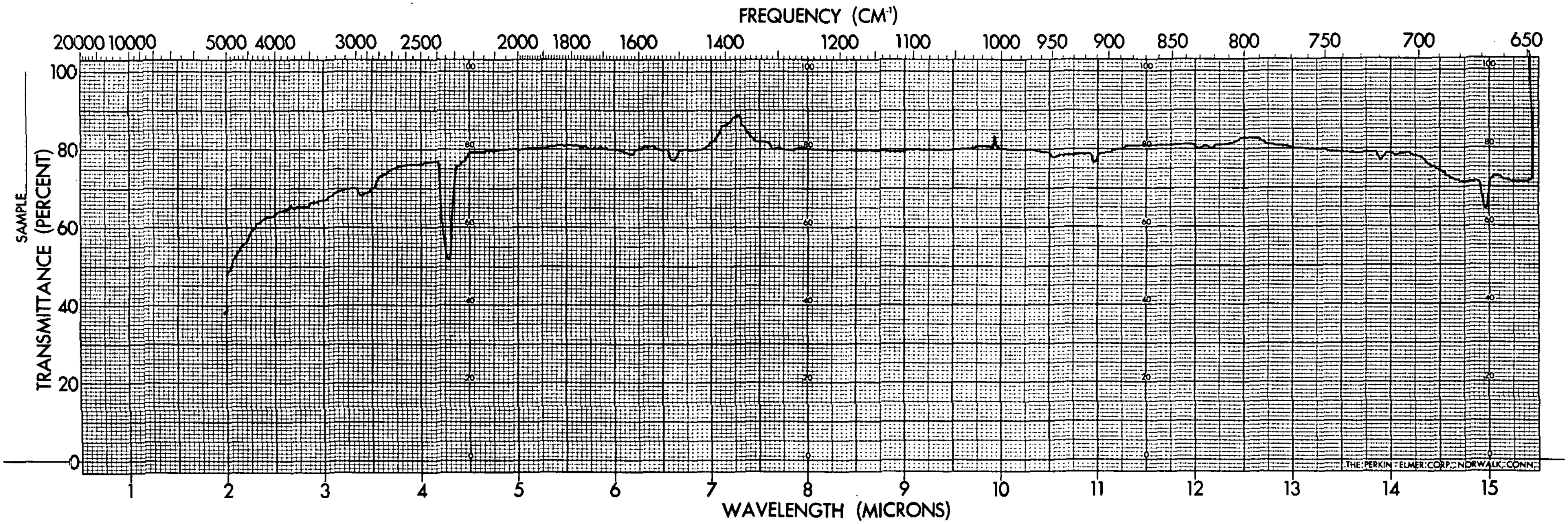
[a] All the analyses are given in mole percent.

[b] All these tests were conducted using 1.6" diameter pellets, average weight 1041 ± 44 mg.

[c] The meaning of these terms is explained in the text.

[d] Trace

[e] Sample taken during glow.



10 cm cell

P = atmospheric

Figure 23. Infrared Spectrum of the Gaseous Atmosphere in the Run 1005 (Sample 1005-1)

REFERENCES

1. K. L. Paciorek and L. B. Zung, "Fundamental Ignition Study for Material Fire Safety Improvement," Final Report, Part I, NASW-1921.
2. S. L. Madorsky, V. E. Hart, S. Strauss, and V. A. Sedlak, J. Research, Natl. Bur. Standards, 51, 327 (1953).
3. R. E. Florin, et al., ibid, 53, 121 (1954).
4. L. A. Wall and J. D. Michaelsen, ibid, 56, 27 (1956).
5. J. D. Michaelsen and L. A. Wall, ibid, 58, 327 (1957).
6. R. E. Florin, M. S. Parker, and L. A. Wall, ibid, 70A, 115 (1966).
7. J. C. Siegle, et al., J. Polymer Sci., Part A, 2, 391 (1964).
8. I. J. Goldfarb, R. J. McHenry, and E. C. Penski, J. Polymer Sci., 58, 1283 (1962).
9. E. E. Lewis and M. A. Naylor, J. Amer. Chem. Soc., 69, 1968 (1947).
10. G. P. Shulman, J. Macromol. Sci. (Chem), Al, 107 (1967).
11. H. C. Anderson, Makromol. Chem., 51, 233 (1962).
12. H. H. Jellinek and H. Kachi, Makromol. Chem., 85, 1 (1965).
13. R. E. Kupel, et al., Anal. Chem., 36, 386 (1964).
14. S. L. Madorsky, "Thermal Degradation of Organic Polymers," Interscience Publishers, 1964.
15. K. W. Graves, AIAA J., 4, 853 (1966).
16. E. Mathias and G. H. Miller, J. Phys. Chem., 71, 2671 (1967).
17. K. L. Paciorek and R. H. Kratzer, "Electric Discharge Reactions of Fluorinated Materials With Cyanogen," Abstracts of Papers presented at 158 ACS National Meeting, September, 1969.
18. R. C. Ferguson, J. Amer. Chem. Soc., 82, 2416 (1960).
19. T. G. Degteva, et al., Vysokomol. Soedin 7(7), 1198-202 (1965).
20. L. A. Oksentevich and A. N. Pravednikov, Vysokomol. Soedin., Ser. B10(1), 49-52 (1968).

REFERENCES (Continued)

21. K. L. Paciorek, et al., WADC-TR-59-129, Part I.

22. K. L. Paciorek, W. G. Lajiness, and C. T. Lenk, J. Polymer Sci., 60, 141-148 (1962).

23. K. L. Paciorek, et al., J. Polymer Sci., 61, S42 (1962).

24. D. K. Thomas, et al., Rubber Plastic Age, 46, No. 9, 1020 (1965).

25. K. L. Paciorek, "Fluorine-Containing-Polymers," Interscience Publishers, Editor L. A. Wall, to be released July 1971.

26. J. F. Smith, Rubber World, 142, 102 (1960).

27. J. Heicklen, V. Knight and S. A. Greene, J. Chem. Phys., 42, 221 (1965).

28. J. F. Smith and G. T. Perkins, J. Appl. Polymer Sci., 5, 460 (1961).

29. K. L. Paciorek and L. C. Mitchell, WADC 59-129, Part II.

30. K. L. Paciorek, L. C. Mitchell, and C. T. Lenk, J. Polymer Sci., 45, 405 (1960).

31. G. M. Fohlen, et al., "Intumescence: An In Situ Approach to Thermal Protection," Proceedings of the NASA Conference on Materials for Improved Fire Safety, NASA Manned Spacecraft Center, Houston, Texas, May 6-7, 1970.

32. N. Bilow, "A Study to Formulate Intumescent Coating Compositions" Proceedings of the NASA Conference on Supporting Research and Advanced Development on Fire Retardant Polymeric Materials," NBS Gaithersburg, Maryland, Oct. 30, 1970.

33. J. A. Parker, et al., "The Use of Salt of p-nitroaniline as a Component for Intumescent Coating," Sampe J., August-September, 1968.

34. J. A. Parker, "Development of Polyquinoxaline Foams," NASA Conference on Supporting Research and Advanced Development on Fire Retardant Polymeric Materials," NBS Gaithersburg, Maryland, Oct. 30, 1970.

REFERENCES (Continued)

35. D. Cagliostro, Private Communication.

36. D. S. Erley and B. H. Blake, "Infrared Spectra of Gases and Vapors- Volume II, Grating Spectra," The Dow Chemical Company, Midland, Michigan.

37. H. A. Szymanski, " The Theory and Practice of Infrared Spectroscopy," Plenum Press, New York, 1964.

38. R. Querido and W. L. Short, "Removal of Sulfur Dioxide From Stack Gases by Catalytic Reduction to Elemental Sulfur With Carbon Monoxide," Preprint, American Inst. of Chemical Engineers, New York, 29 p., 1970, 24 refs. (Presented at the American Institute of Chemical Engineers, 63rd Annual Meeting, Chicago, Ill., Nov. 29-Dec. 3, 1970, Paper 3e).

39. J. A. Parker, *et al.*, Sampe J., April/May, 1969, "Development of Polyurethane for Controlling Fuel Fires in Aircraft Structures."

40. S. R. Riccitiello, *et al.*, Paper presented at Symposium on Flammability of Plastics, Society of Plastic Engineers, New York, May 1970.

41. R. H. Fish, "The Performance of Lightweight Plastic Foams Developed for Fire Safety," Proceedings of the NASA Conference on Materials for Improved Fire Safety, NASA Manned Spacecraft Center, Houston, Texas, May 6-7, 1970.

42. J. Newland, "Processing of Fire Retardant Polyisocyanurate Foams," NASA Conference on Supporting Research and Advanced Development on Fire Retardant Polymeric Materials," NBS Gaithersburg, Maryland, Oct. 30, 1970.