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INVESTIGATION OF MATERIALS COMBUSTIBILITY AND FIRE AND EXPLOSION SUPPRESSION IN A VARIETY OF ATMOSPHERES

May 1966

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE

Prepared under Contract No. AF 33 (615)-2257

DYNAMIC SCIENCE CORPORATION
Monrovia, California

INVESTIGATION OF MATERIALS COMBUSTIBILITY AND FIRE
AND
EXPLOSION SUPPRESSION IN A VARIETY OF ATMOSPHERES

SUMMARY REPORT NO.SN-6401

Contract No. AF 33 (615)-2257

For the

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE

Prepared by:

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DYNAMIC SCIENCE CORPORATION
Monrovia, California

FOREWORD

This report was prepared by Dynamic Science Corporation, Monrovia, California, under Air Force Contract No. AF 33 (615)-2257. The work was monitored by the Air Force Aero Propulsion Laboratory, Research and Technology Division. The Project Engineer was Mr. Benito Botteri.

The program presented in this report was initiated in November, 1964, and will be concluded in November, 1966. The work has been directed initially by Dr. Jerome Ditter and later by Dr. H. Dwight Fisher as Program Manager for Dynamic Science Corporation. The experimental work was performed by the Program Managers and by laboratory assistants, Mr. K. A. Wix and Mr. J. Herr.

The work covered by this report was accomplished under Air Force Contract AF 33 (615)-2257 and presents a summary of the first year of effort. The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein, but is published for the timely dissemination of information.

ABSTRACT

The combustibility properties of polyethylene, polyvinylchloride and silicone rubber have been evaluated. The autogenous ignition temperatures of these materials have been determined as a function of atmospheric composition and pressure under standardized conditions in Dynamic Science Corporation's Combustion Monitor Model 164. The degradation and oxidation products from these materials were identified by gas chromatographic analysis. In addition, the burning rate of these materials was determined under test conditions simulating the environment found in missile silos and high performance aircraft.

Two candidate agents have been synthesized for evaluation as first-aid fire extinguishing agents on Class B fires (liquid).

The combustion properties of selected flammable materials in enriched oxygen environments and zero gravity flight conditions will be evaluated.

A survey has been made to select fire extinguishing agents for use in an orbiting manned spacecraft. Four candidate agents have been selected for evaluation under enriched oxygen atmospheres. The effectiveness of these agents will be evaluated during the coming year. Methods of application of these agents under zero gravity flight conditions will be evaluated.

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I. INTRODUCTION

The rapid evolution of aircraft and spacecraft has brought with it the ever increasing difficulty of designing for prevention of fires and explosions. In spacecraft, the sealed cabin with its limited work space, oxygen-enriched atmosphere and lack of flexibility in emergency situations has brought new and ill-defined fire hazards into the picture. The Supersonic Transport and other high performance aircraft with their high temperatures and unique operating problems, also places these materials in regions where the available combustion and fire hazards data is not applicable.

In the past, a great deal of data has been compiled on the fire and explosion characteristics of combustible materials. Unfortunately, most of the data is not pertinent to the actual operational problems that one faces in these new vehicles.

The work under this program is designed to evaluate such combustion properties as autogenous ignition temperature, burning rate, and degradation products of representative materials found onboard aircraft and spacecraft. We have attempted to gather this data over a range of atmospheric conditions, varying the oxygen composition from normal air (21% oxygen) to 100% oxygen at pressures between 5 psia and 1 atmosphere. The purpose of this program is to provide quantitative data which can be used by designers who are developing future spacecraft and aircraft equipment in assessing the potential fire and explosion hazards for systems containing these materials.

Another aspect of this project is the examination of new candidate agents which may prove more effective in the extinguishment of liquid fires under ambient conditions. Tests will be performed on hydrocarbon fires initiated in the combustion monitor. In support of this phase of the program, two candidate extinguishing agents have been synthesized. These compounds are 1-bromo-2, 2, 3, 3,-tetrafluoropropane, $(H(CF_2)_2CH_2Br)$ and 1-bromo-2, 2, 3, 3, 4, 4, 5, 5,-octafluoropentane, $(H(CF)_4CH_2Br.)$

A third area of investigation, which presents a unique challenge, is fire extinguishment within a manned spacecraft. The extinguishing agent must be useable under zero gravity conditions and compatible with an enriched oxygen environment. In addition, it must have the following properties:

1. It must not support combustion in an oxygen-enriched atmosphere.

2. The extinguishant and its degradation products must not exhibit toxic or anesthetic properties to man under the conditions of application.

3. The extinguishant and its degradation products must not be corrosive to onboard equipment under the conditions of application.

4. The extinguishant and its degradation products must not interfere with visual observation.

5. The extinguishant and its degradation products must not result in liquid or solid residue which will contaminate the spacecraft.

An extensive literature survey has been conducted in order to aid in the definition of candidate extinguishing agents suitable for use under these conditions. Four compounds have been selected for further evaluation under oxygen-enriched environments. These compounds are bromotrifluoromethane, bromochlorodifluoromethane, dibromodifluoromethane, and 1, 2-dibromotetrafluoroethane.

II. MATERIALS IGNITION

A. INTRODUCTION

One objective of this program is the determination of autogenous ignition temperatures of typical materials which might be used in a spacecraft environment. The oxygen-enriched low pressure atmosphere in a space vehicle might change the ignition characteristics of some materials and, if so, is important to determine whether these changes occur in a manner which affects the potential fire hazard. Therefore, particular emphasis is being given to the effects of oxygen concentration and total pressure upon ignition characteristics. Relevant data from three materials which have been studied is reported here.

B. EXPERIMENTAL PROCEDURE

1. Equipment

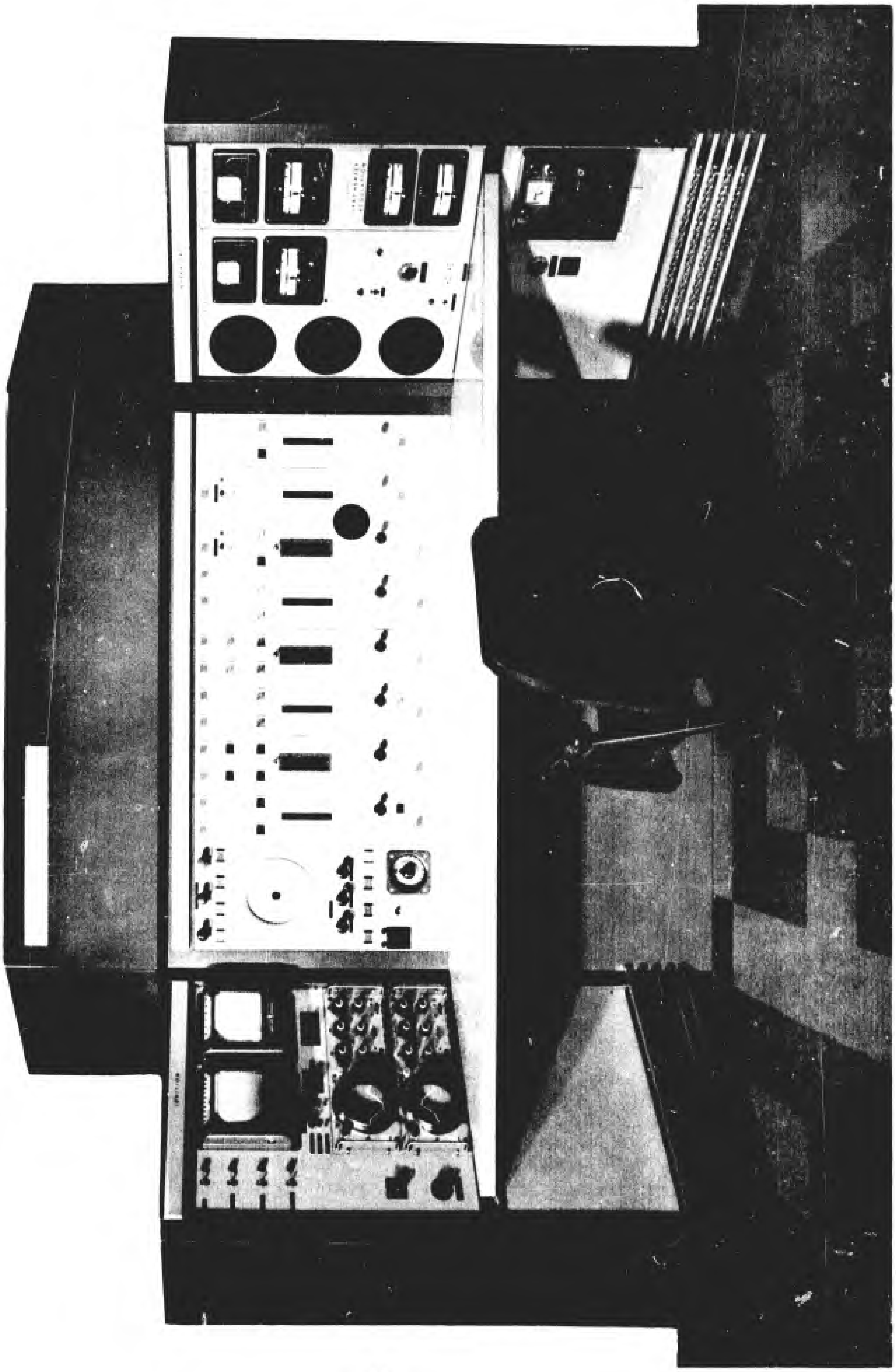
a. Test Chamber

The ignition tests were made in the Dynamic Science Combustion Monitor Model 164, illustrated in Figure 1. A complete description and operating procedure for this equipment is presented in Reference 6. A diagram of furnace No. 2, used in the tests, is shown in Figure 2.

The cylindrical, stainless steel ignition chamber is twelve (12) inches in diameter and eighteen (18) inches high. The wall temperature of the chamber can be controlled from room temperature to 1650°F. Oxygen, nitrogen or other diluents can be admitted as shown in Figure 2. The sample is placed on a tray equipped with a separate heater which allows tray temperature to be controlled independently or slaved to the temperature within the test chamber.

b. Auxiliary Vacuum Rack (used in conjunction with the combustion monitor)

This vacuum rack is equipped with a mechanical forepump and an air-cooled oil diffusion pump, and its high vacuum system is capable of reducing the pressure to less than 10^{-6} mm.Hg. A Pirani gauge is used to measure the residual pressure within the vacuum system. This vacuum rack also contains a high vacuum fractionating train, calibrated gas measuring bulbs, manometers, Toepler pump, and valves for removing gases and volatile vapors



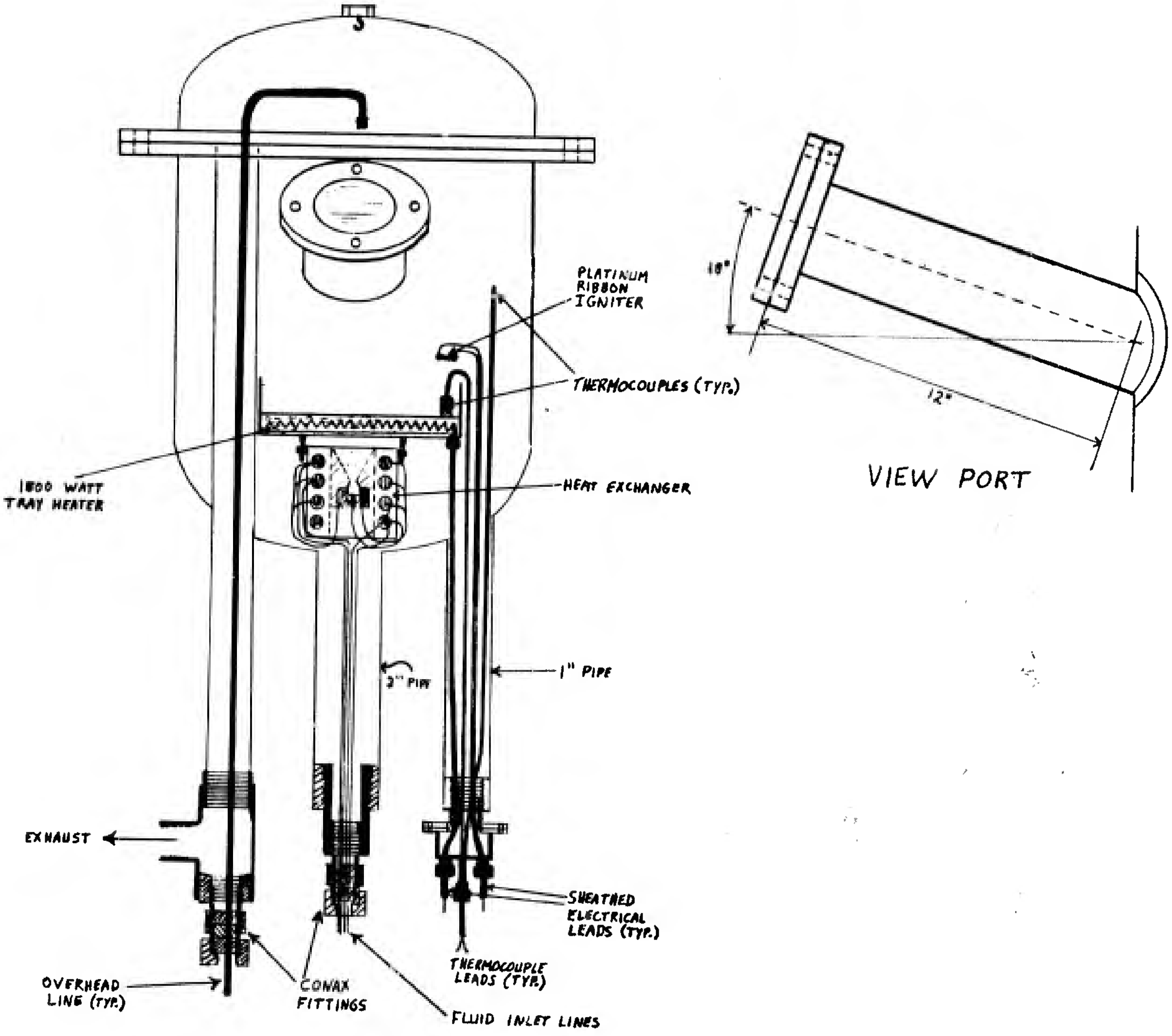


FIGURE 2 - NO. 2 FURNACE CHAMBER

from the combustion monitor reaction chambers. A second mechanical pump is used whenever it is not necessary to utilize high vacuum. The function of the auxiliary vacuum rack for the purposes of this project are as follows:

1. To assist in pumping the two reaction chambers in the combustion monitor;

2. to extract and collect volatile combustion and degradation products from the reaction chamber;

3. to fractionate, transfer, and measure gases and volatile liquids;

4. to calibrate the flow meters on the combustion monitor.

The operation of this type of system is amply described by Sanderson (Ref. 57).

c. Instrumentation

1. Thermocouples are used to control and/or indicate temperature at critical areas within the ignition chamber. One unit is mounted in the chamber atmosphere to control and measure the environmental temperature. A second thermocouple is attached to the bottom of the heating tray and also functions as both a control and measurement device. A third, moveable thermocouple is fixed directly to the test sample in order to measure temperature changes within a given film.

2. Pressure is monitored with a Statham Pressure Transducer of 0-30 psia range and the output presented graphically on a strip chart recorder.

3. Visual observations are made through a window mounted in the control panel of the combustion monitor.

4. A Beckman Oxygen Analyzer is used to monitor the oxygen content of the environmental gases.

5. A Micro-Tech 2500R gas chromatographic analyzer was connected by a manifold system between the gas inlet valve and sample loop on the chromatograph and the sample bulb, manometer and vacuum pump on the combustion monitor to facilitate quantitative introduction of gas samples. This maniford allows the

sample loop to be evacuated by the vacuum pump, either in conjunction with or separately from the remainder of the system, up to the sample bulb. After evacuation, a gas sample can be introduced and its pressure measured with the manometer. The sample is then injected into the column by depression to the gas injection valve.

The Micro-Tech chromatograph was fitted with two ten-foot columns in parallel. One column contained molecular sieve 5-A and the other silia gel. The columns have been operated at 150°C with a helium carrier gas flow rate of 60cc/minute in each column.

d. Calibration of Instruments

Since the purpose of this program is to define the effect of gas phase composition and pressure on the spontaneous ignition temperature of various flammable materials, all thermocouples, pyrometers and recorders used to sense the temperature of the system were calibrated. The various atmospheres involved in the test procedures are prepared from neat gases by flowing them into the system at predefined rates. The calibration of the flowmeters used to introduce these gases is therefore essential. Calibration of the gases under operating conditions is also necessary, because the combustion tests are conducted at varied pressures of 14.7, 11, 7 and 5 psia.

1. **Calibration of Temperature Sensing System.** The Varian G-11A Type T-2 recorder which is used to record the temperatures sensed by the various thermocouples was calibrated by the Standard Laboratory of Wright-Patterson Air Force Base. The two West Instrument Company's indicating-controlling pyrometers were set by placing their respective thermocouples in a bath of known temperature and positioning the pointer after allowing sufficient time for the system to equilibrate.

The temperature indicating systems, thermocouples, pyrometers and recorder were calibrated and true temperature versus indicated temperature curves were prepared. Although the calibration procedure used for the sensing system was simple, this system is capable of greater accuracy and precision than either pyrometers or recorders. The active portion of the thermocouple was inserted 2-4 inches into a hole in an electrically heated aluminum block and a precision calibrated thermometer was placed in a second hole in the block. A variable auto transformer was then used to apply controlled current to the heater in order to bring the aluminum block to thermal equilibrium. When the block reached thermal equilibrium, the thermometer was read and these readings were compared to those of the pyrometer or recorder. This procedure was repeated at 50° intervals from room temperature to 600°C. Correction curves constructed from these measurements were used throughout the combustion tests to correct the indicated temperatures. (All thermocouples within the No. 2 chamber were calibrated in the aforementioned manner.)

2. Calibration of Flowmeters. The gas flowmeters on the combustion monitor were calibrated under operating conditions, using oxygen, nitrogen, air and helium. These calibrations were performed by collecting the gases issuing from the test chamber in a calibrated volume which had previously been evacuated for a specified time period after which the pressure in the calibrated volume was measured. The flow rates were then calculated from the pressure increase in the standard volume. The flow rate at room temperature was determined from the relationship.

$$\text{flow rate (liters/min)} = \frac{P\,V}{760t}$$

where:

P = pressure increase in mm Hg.

V = volume of calibration system in liters

t = time of flow in min.

The specific procedure used to calibrate the Flowmeters is as follows:

a. Set Sterer valve at the desire reference pressure.

b. Fill chamber with the test gas until it flows through Sterer Valve.

c. Adjust the gas flow through the flowmeter under calibration to the desired float reading.

d. Energize the solenoid valves on the vacuum rack to direct the gas flow into the standard volume for a preset time after which the pressure is read from the manometer. The standard volume must be large enough to prevent the pressure rise from exceeding 2 or 3 cm. or the flow rate will be attenuated.

e. Calculate the standard flow rate. Since the room temperature is normally 22°C, the flow volumes are standardized at this temperature.

3. Vapor Phase Chromatograph. The Micro-Tech chromatograph was calibrated to qualitatively and quantitatively determine several gases which were expected to be found in the first chamber

during a run. These gases were methane, ethane, ethylene, acetylene, propane, carbon monoxide, carbon dioxide, oxygen, and nitrogen. The chromatograph was standardized at 150°C column temperature with a 60 cc per min. helium flow rate through each column. Ten foot columns packed with molecular sieve 5-A and silica gel were used in these calibrations and subsequent analytical runs.

For the purpose of calibration, a sample of known gas was admitted into the manifold system and sample loop and its pressure measured. The sample was then injected into the column gas stream and the retention time and peak area were determined from the strip chart. This procedure was repeated for several pressures with each of the test gases. A plot of peak area versus pressure for the various gases was then constructed which permitted the quantitative determination of these gases in the various combustion gas samples.

e. Test Procedures

1. The test sample is placed on the surface of the tray heater located in the No. 2 furnace chamber. The specimen thermocouple is placed in contact with the upper surface of the sample. The standardized sample size used in these tests are as follows:

a. Solid (cast) samples 5.0 gms ± 0.5 gms.

b. Woven fabric 2.0 gms ± 0.2 gms.

The materials which have been examined were polyethylene, polyvinylchloride and silicone rubber. The materials were obtained from commercial sources.

2. The furnace chamber is sealed, evacuated and checked for leaks.

3. The chamber is isolated from vacuum, the desired atmosphere is introduced, and the chamber pressure is set by adjusting the reference pressure on the Sterer valve to the desired operating level. When the operating pressure level is reached, the gas flow rate is adjusted. The flow rates of the gases are selected so as to change the chamber atmosphere at a constant rate, independent of operating pressure. The S.T.P. flow rates used at various chamber pressures are shown in Table I.

TABLE I

14.7	psia	(760 mm)	4.0	liters/min
11	psia	(569 mm)	3.2	liters/min
7	psia	(362 mm)	1.87	liters/min
5	psia	(259 mm)	1.33	liters/min

The test pressure and composition of the chamber atmosphere under which the test series is conducted is shown in Table II. This scheme was selected to provide the maximum information concerning the effect of pressure, composition and nature of diluent gas on the autogenous ignition temperature of the test sample.

TABLE II

COMPOSITION AND PRESSURE OF TEST ATMOSPHERES

	21% O_2 - 79% N_2	60% O_2 - 40% N_2	60% N_2 -40% He	100% O_2
760	X	X		X
567	X	X	X	X
362	X	X		X
259	X	X		X

4. After selection and adjustment of atmosphere and pressure, the furnace heater is activated and the power level is adjusted to 80% of the maximum with the tray heater set on null operation.

5. The chamber pressure and specimen temperature recorders are started.

6. Visual observation of the sample, chamber temperature and tray temperature are noted as a function of time. The temperature at which ignition occurs, the duration of burning, flame appearance and other pertinent data relating to the specimen are recorded.

f. Variables Studied

1. Pressures
2. Temperatures
3. Sample Size
4. Heating Rates
5. Flow Rates
6. Oxygen Concentration
7. Atmospheric Composition
8. Sample Location

C. RESULTS

1. Polyethylene

In order to determine the importance of such variables as sample size, heating rate, chamber temperature, flow rate, pressure, oxygen concentration and sample locations, a series of experiments were made in which one of the given factors was altered while the others remained essentially constant. Ignition temperatures for polyethylene samples in direct contact with the tray, ranged from 223°C for 100% oxygen at 1 atmosphere to 319°C for 100% oxygen at 259/760 atmospheres. Higher ignition temperatures resulted when the sample was not in contact with the tray. Autogenous ignition temperatures for polyethylene for the previously stated variables are given in Table III. In the following paragraphs, portions of the data are cited for the purpose of presenting and explaining our interpretation of the results.

a. Tests were made in which the sample weights were changed by a factor of approximately 18. These runs showed that within the range and conditions studied, variations in sample size had no significant effect upon the ignition temperatures. This observation is supported in the following comparison of data from runs 118 and 119.

Run	%O_2	Pressure (mm)	Sample Wt.	Sample Size	Ign. Temp.°C
118	100	760	4.907gm	1x1x3/8	248
119	100	760	89.896gm	4x4x3/8	250

TABLE III. CONTRACT AF 33(615)-2257 AUTOGENOUS IGNITION TEMPERATURE OF POLYETHYLENE

Run No.	Per cent O_2	Per cent N_2	Per cent He	Pressure MM Hg	Flow Rate L/Min	Ignition Temp. °C	Furnace Temp. °C	Flame Duration Sec.	Ignition Delay Sec.	Sample Weight Grams	Sample Size	Heating Rate (Final)	Remarks
101	100	-	-	259	1.1	305	121	-	5720	-	1x1x3/8	4.4	
102	100	-	-	362	1.4	300	105	60	2400	-	"	5.4	
103	100	-	-	569	1.9	250	142	90	3240	-	"	2	
104	100	-	-	760	2.3	250	92	270	2450	-	"	3	
105	100	-	-	259	2.9	302	103	105	2160	-	"	4	
106	50	50	-	760	4.8	262	100	125	3330	5.607	"	3.5	
107	50	50	-	362	3.0	No ign at 380				7.558	"	-	
108	50	50	-	569	5.25	282	93	94	1980	7.674	"	-	
109	50	-	50	259	3.2	No ign at 352				5.983	"	-	
110	20	80	-	569	5.2	No ign at 330				5.639	"	-	
111	20	80	-	569	5.6	No ign at 350				6.364	"	-	
112	75	-	25	760	4.1	242	78	270	1380	5.502	"	-	
113	75	25	-	569	4.4	244	90	100	1080	5.780	"	12	
114	25	-	75	760	4.0	No ign at 376°C				5.297	"	-	
115	100	-	-	760	4.2	223	75	260	900	5.531	"	7.5	
116	75	25	-	362	4.2	291	95	540	1180	5.796	"	14	

TABLE III (Continued) - AUTOGENOUS IGNITION TEMPERATURE OF POLYETHYLENE

Run No.	Per cent O_2	Per cent N_2	Per cent He	Pressure MM Hg	Flow Rate L/Min	Ignition Temp. °C	Furnace Temp. °C	Flame Duration Sec.	Ignition Delay Sec.	Sample Weight Grams	Sample Size	Heating Rate (Final)	Remarks
117	75	25	-	259	4.2	315	105	665	1180	6.318	1x1x3/8	16	
118	100	-	-	760	0	248	80	80	1750	5.907	"	6	
119	100	-	-	760	0	250	81	55	2225	89.896	4x4x3/8	5.5	
120	100	-	-	760	6.5	264	208	220	1000	5.763	1x1x3/8	10	
121	100	-	-	259	0	319	121	60	2410	5.911	"	10	
122	100	-	-	760	0	410	222	90	2330	5.630	"	4	Sample set off tray
123	100	-	-	760	0	425	252	103	2477	71.131	3-1/2 x 3-1/2 x 3/8	4.6	Sample set off tray
124	100	-	-	259	0	(510)	(402)	No ign					Sample set off tray
125	100	-	-	569	0	300	264	55	3480	50.089	3x3x3/8	9.8	Gases detonated
126	100	-	-	362	0	450	385	55	8015	52.156	9-1x1x3/8	1	Gases detonated(off tray)
127	60	40	-	362	0	(569)	(453)	-	-	52.375	"	-	No ign off tray
128	100	-	-	259	0	(395)	(395)	-	-	52.454	"	-	Sample held at 395 for 1 hr (No ignition)
128A	100	-	-	259	1.4	310	349	90	3820	5	1x1x3/8	4	
129	100	-	-	259	1.4	-	350	-	-	5.818	1x1x1/8	4	
130	100	-	-	259	1.4	311	358	97	3640	5.745	"	6	
131	100	-	-	760	-	230	282	70	2655	5.887	"	3.5	Sample oxygen soaked 30 days

b. Heating rate also had a minimal effect upon the ignition temperatures as is shown below in the data from runs 115 and 131:

Run	%O_2	Chamber Pressure	Chamber Temp. °C	Heating Rate	Ign. Temp.°C
115	100	760	75	7.5°C/min	223
131	100	760	282	3.5°C/min	230

Note that a greater than two-fold change in heating rate produced only a 7°C variation in ignition temperature. Observations made over the entire range of conditions studied confirms the absence of a consistent and significant effect of heating rate upon the ignition temperatures.

c. The general trend of the data indicates that variations in the chamber temperature had little effect upon ignition temperatures, however, its role is not as clearly defined as those of sample size and heating rate. For example, in the previous table, the furnace temperature varied by a factor of almost 4, yet the combined effect of furnace temperature and heating rate produced only a 7°C change in the ignition temperature. Similarly, runs 101 and 128A, in which the heating rate was held constant, resulted in only a 5°C difference in ignition temperature for an almost three-fold change in chamber temperature.

Run	%O_2	Chamber Pressure	Chamber Temp. °C	Heating Rate	Ign. Temp.°C
101	100	259	121	4.4°C/min	305
128A	100	259	349	4.0°C/min	310

Runs 120 and 115, however, tend to indicate that chamber temperature does have an effect upon ignition temperature. A comparison of these runs show that a variation of chamber temperature from 75°C to 208°C produced a change in ignition temperature from 223°C to 264°C. (Correction for the difference in flow rate to be discussed next does not eliminate this deviation.) Run 120 does tend to deviate in other comparisons and may be in error. Since the results of run 120 don't follow the general trend of other data, subsequent tests have been run on the assumption that chamber temperature has no effect on ignition temperatures.

d. The flow rate of the ambient atmosphere of the chamber apparently has a small but significant effect during the ignition period. Typical flow effect data for two pressure levels, 1 atmosphere and 1/3 atmosphere, are shown in Figure 3. Although there is some scatter in the data, two straight lines have been drawn through the experimental points. For the purpose of correlating data at different flow rates within the range studied, the information has been re-plotted in Figure 4 as the difference between the ignition temperature at zero flow rate against the flow rate where:

$\Delta SIT = (SIT)_0 - (SIT)$ The data can be approximated by the equation:

$\Delta SIT = 6 \times \text{flow rate}$

It is evident from the data that, in the range studied, the ignition temperature decreases as the flow rate increases. Presumably, this may be accounted for by the fact that the relatively low velocity flow supplies oxygen to the surface and hence promotes the reactions leading to ignition. However, this effect has a limited range of application because the flowing gas has a temperature below the ignition temperature and a condition must exist where the cooling effect of the gas would more than compensate for the oxygen diffusion effect. In this case, the ignition temperature would increase with the increase in flow rate.

e. Pressure has a pronounced effect on the ignition temperature, Figure 5, in which ignition temperature is plotted against pressure, shows that the ignition temperature increases as the pressure decreases.

Figure 6 illustrates the definite effect of oxygen concentration upon ignition temperature. As expected, the ignition temperature increases as the oxygen concentration decreases. The dependence of the ignition temperature on oxygen concentration is consistent with the concept of ignition which requires that the reaction rate must exceed a critical value before ignition occurs. If the reaction rate is given by the usual Arrhenious rate equation, then one would have:

$$\text{rate} \quad (CO_2)^m (C_{fuel})^n e - E/RT$$

where CO_2 = oxygen concentration
C_{fuel} = fuel concentration
m, n = exponents on concentration
E = activation energy
R = gas constant
T = temperature

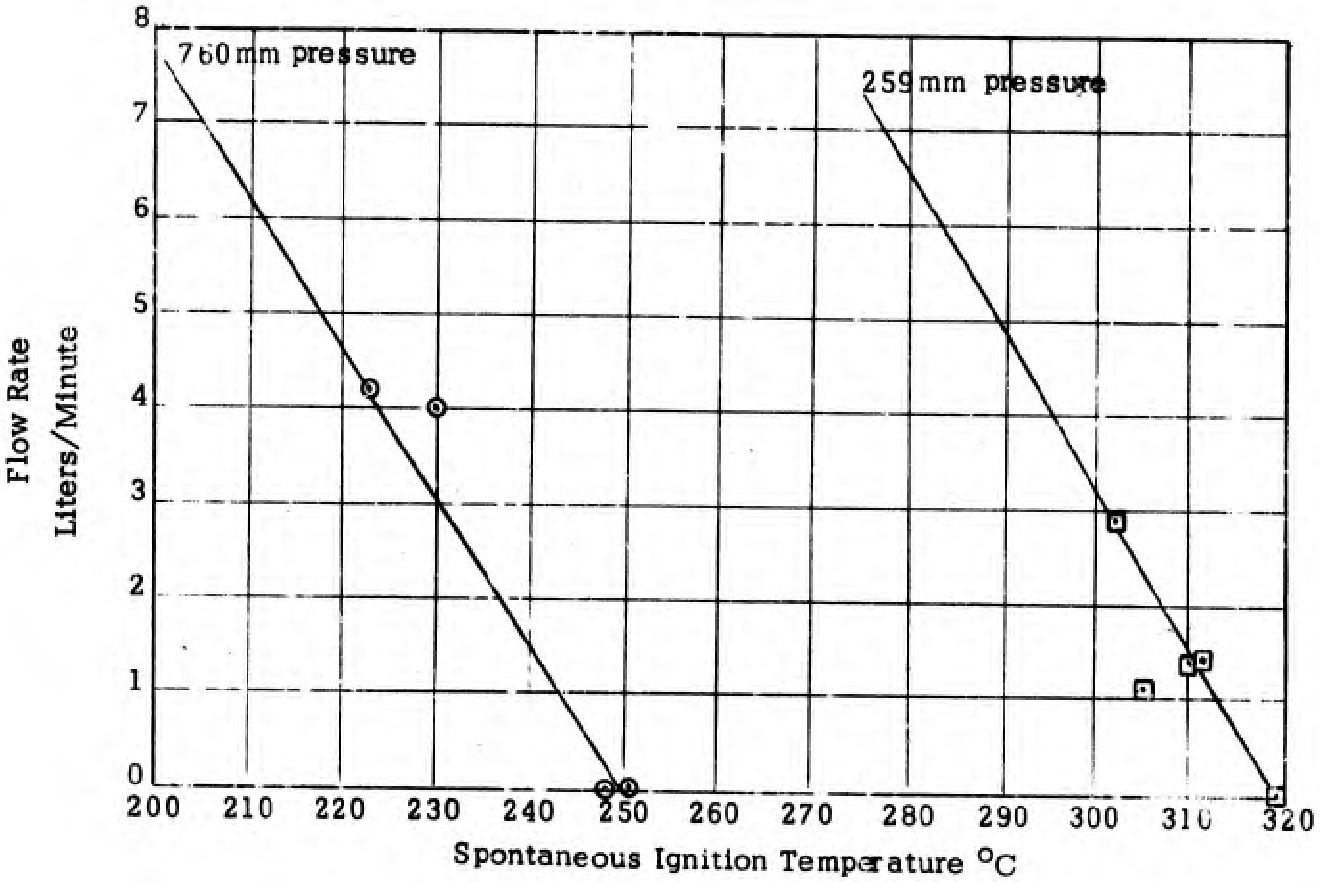


FIGURE 3

EFFECT OF FLOW RATE ON SPONTANEOUS IGNITION TEMPERATURE FOR POLYETHYLENE

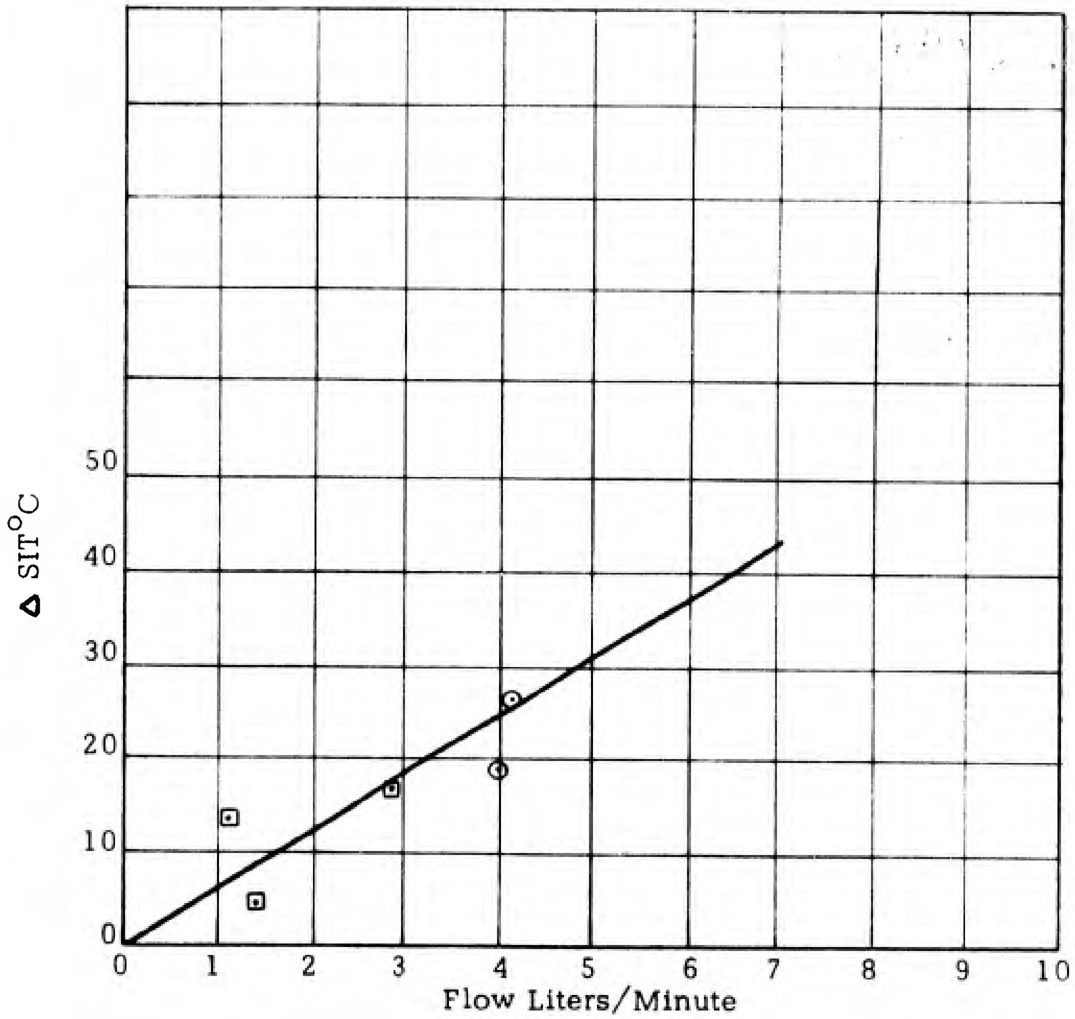


FIGURE 4

FLOW RATE VS SIT AT 1 ATMOSPHERE FOR POLYETHYLENE

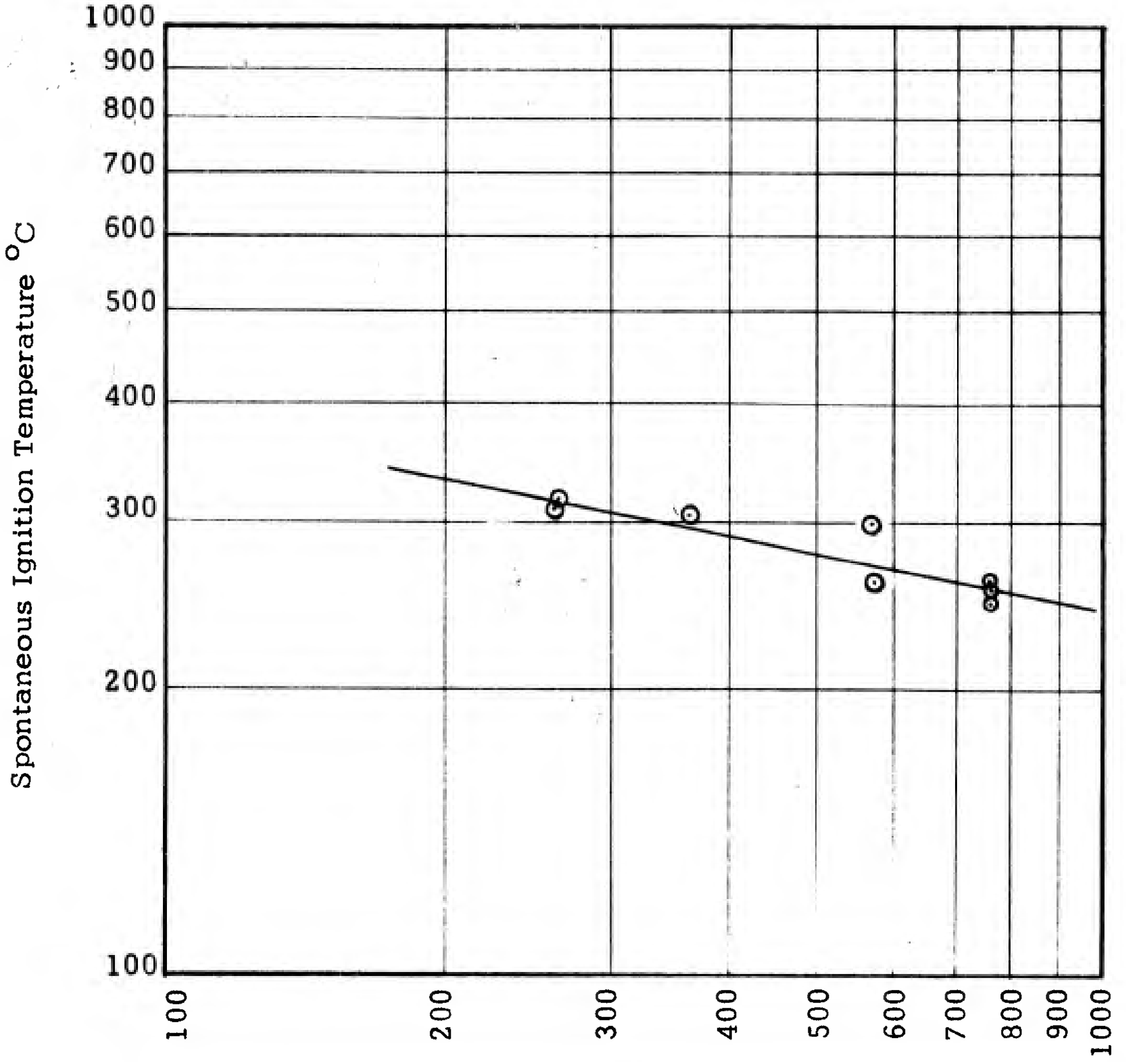


FIGURE 5

EFFECT OF OXYGEN PRESSURE ON SIT FOR POLYETHYLENE

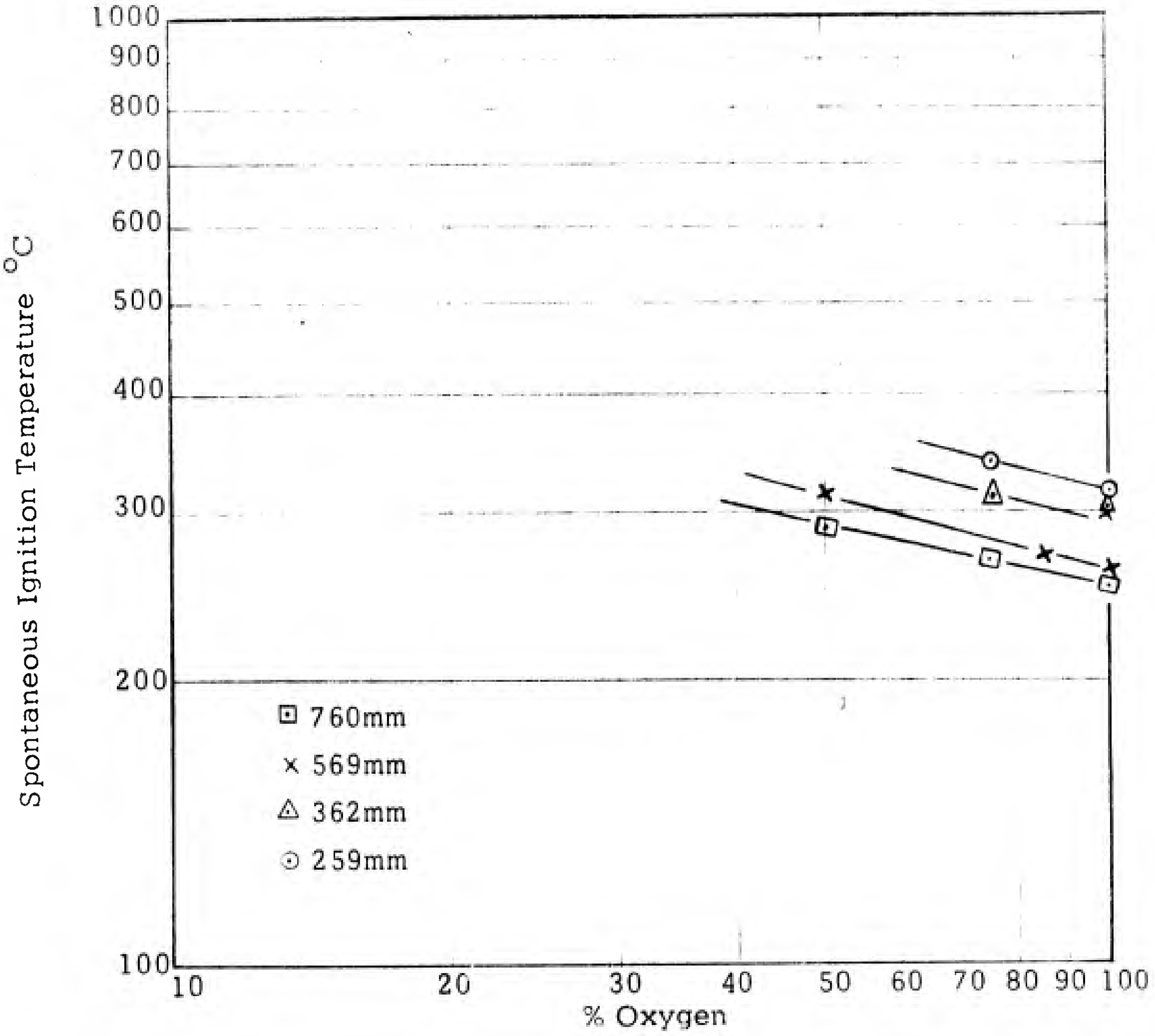


FIGURE 6

EFFECT OF PRESSURE ON SIT FOR POLYETHYLENE

Since a reduction of total pressure is equivalent to a reduction of partial pressure of oxygen, the effect of pressure on ignition temperature may be largely represented by the change in oxygen concentration. The data of Figures 5 and 6 have been re-plotted in Figure 7 where the partial pressure of oxygen has been corrected to zero flow rate for the purpose of comparison.

Frequently, the combustible material is some distance from the heat source in an actual hazard condition. This condition was simulated by removing the sample from the heating tray and using the chamber gases as the only heat source for the specimen. The apparent ignition temperature, based on the environmental temperature of the tray surface, was considerably higher than that required for ignition when the sample was in contact with the tray heater.

Since the heat transfer path is less direct when the sample is separated from the tray, it is reasonable to assume that the heat source temperature must be higher than the sample temperature. However, this data is only applicable to the conditions within this test program. In order to determine the source temperature required to produce ignition under other conditions, heat transfer calculations must be made which are based on all the environmental factors.

f. Analysis of Combustion Products and Pyrolytic Degradation Products of Polyethylene

1. Analysis of Combustion Products

The atmosphere within the test chamber was analyzed at various times prior to ignition and during the combustion process. The products which were detected in the chamber prior to ignition were ethylene, ethane, carbon monoxide and traces of carbon dioxide. The chamber gases during the time of burning contained carbon dioxide, traces of carbon monoxide with no hydrocarbons being detected.

On two occasions, a gas phase detonation occurred in the chamber coincident with ignition of the solid sample. The hydrocarbon species, particularly since these are primarily unsaturates, undoubtedly accounts for the existence of an explosive mixture in the vapor phase.

A complete analysis of the combustion products from the polyethylene tests was not possible due to a series of breakdowns of the Micro-Tech chromatograph. This unit was in operation for approximately four months.

2. Analysis of Pyrolytic Degradation Products

The pyrolysis experiments were carried out using a pyrex tube having an inside diameter of 68 mm surrounded by a tube furnace. The tube was first evacuated to 10^{-5}mm Hg and filled with helium. A helium flow rate of 200 cc per minute was maintained during the experiment. The furnace was turned on and the temperature increased to 500°C. Two liquid nitrogen traps were placed around traps in this exit line of the pyrolysis apparatus after which a one gram sample of the polyethylene was suspended within the heated tube. The heating was continued for one hour to insure complete pyrolysis. At the end of this period, the furnace was shut down and the helium flush stopped. The system was evacuated to transfer any volatile gas into the liquid nitrogen cooled traps. The volatile gases were fractionated by standard high vacuum techniques and analyzed by vapor phase chromatography and infrared spectroscopy.

The only components which have been identified in the volatile gases and their approximate percentages are as follows:

Ethylene	40%
Propylene	30%
1-Butene	20%
1-4 Pentadiene	10%

There appears to be only a very minute quantity, if in fact any, of any hydrocarbons between the pentadiene and those products which are hard wax-like materials.

2. Polyvinylchloride

Since the tests on polyethylene show that changes in sample size, heating rate, and chamber temperature have little or no effect upon the autogenous ignition temperatures, these variables have not been considered significant factors in the tests on polyvinylchloride or silicone rubber. The tests on these two materials were run using a standard size sample established on the basis of the polyethylene data and defined under the section on Experimental Procedure in this report. Chamber temperatures were maintained as close to tray temperatures as possible. During the runs on polyvinylchloride and silicone rubber, heating rates were varied to facilitate equipment operation, rather than for experimental purposes.

a. When the partial pressure of oxygen is varied, the autogenous ignition temperature of polyvinylchloride changes in the same manner as that of polyethylene. A decrease in the partial pressure of oxygen produces an increase in the autogenous ignition temperature whether the change in the oxygen partial pressure is produced by lowered total pressure or dilution with inert gases. The ignition temperature of polyvinylchloride increases from 390°C, @ 760 mm oxygen, to 514°C, @ 155 mm oxygen partial pressure. This relationship between the AIT of polyvinylchloride and oxygen pressure is graphically illustrated in Figure 8. The temperatures of both the tray and sample surface are plotted, and the data have been corrected to zero flow rate through the use of the equation derived for polyethylene. Both curves show an approximately equal dependence upon pressure.

b. The autogenous ignition temperatures for polyvinylchloride relative to varied environmental pressures and oxygen concentrations are presented in Table IV.

Figure 8 also shows that, on the average, the sample temperature is about 60-70°C higher than the tray temperature which indicates a surface or near surface reaction prior to ignition. This self-generation of heat by the reactants prior to ignition is a characteristic of the autogenous ignition process. Presumably, the heat source increases the temperature to a point where the chemical reactions generate heat at a greater rate than it is removed. The increase in temperature prior to ignition for homogenous gas reactions is approximately stated in:

$$T = \frac{RT^2}{E_a}$$

where:
T = temperature increase
R = gas constant
T = sample temperature, °K absolute
E_a = activation energy

The following table gives ΔT values for the surface temperature extremes of 773°K and 873°K as a function of activation energy.

Ts°K	E_a Cal.	ΔT °K
773	10,000	120
	20,000	60
	40,000	30
873	10,000	152
	20,000	76
	40,000	38

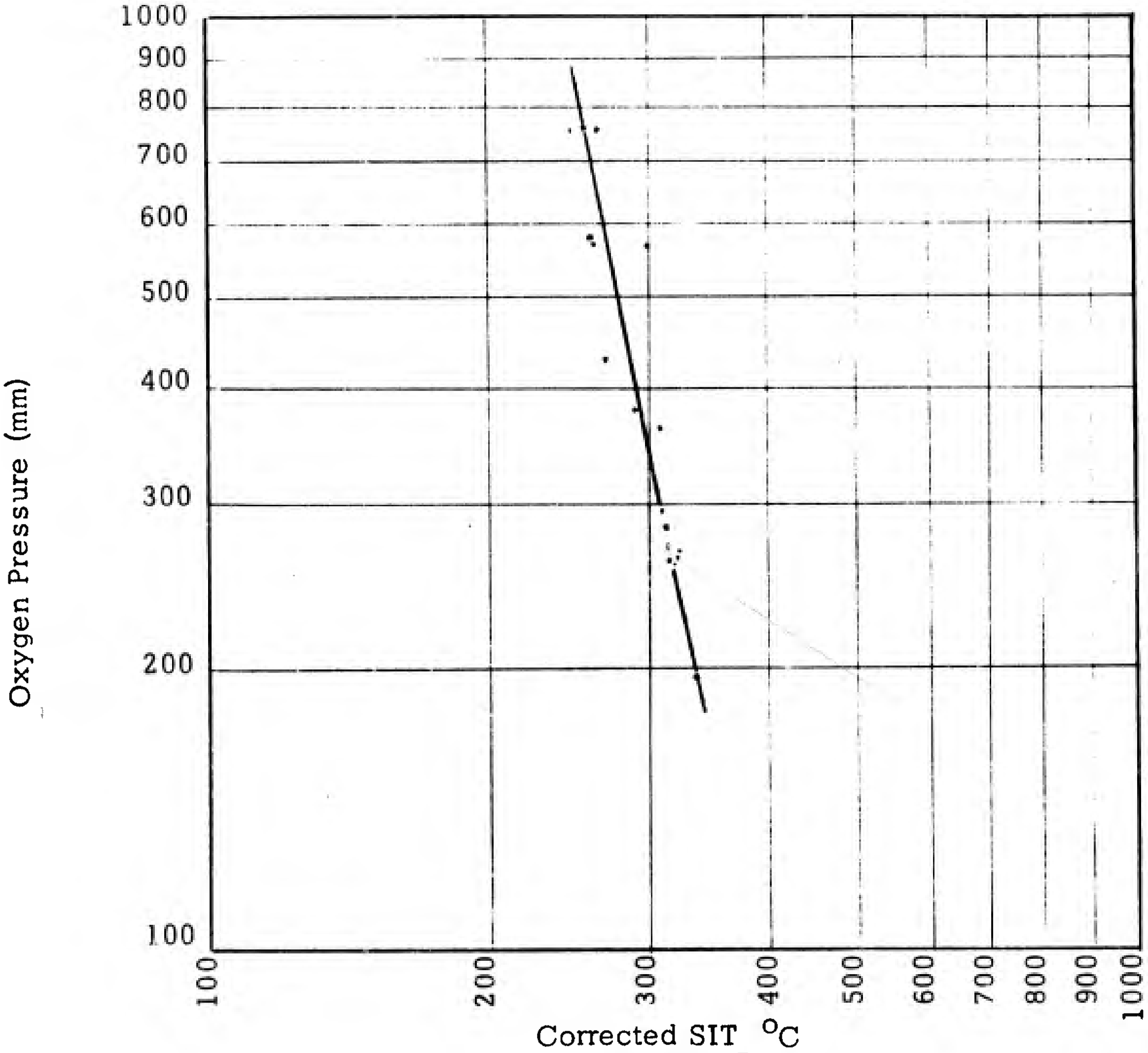


FIGURE 7

CORRECTED SPONTANEOUS IGNITION TEMPERATURE AS A FUNCTION OF OXYGEN PRESSURE FOR POLYETHYLENE

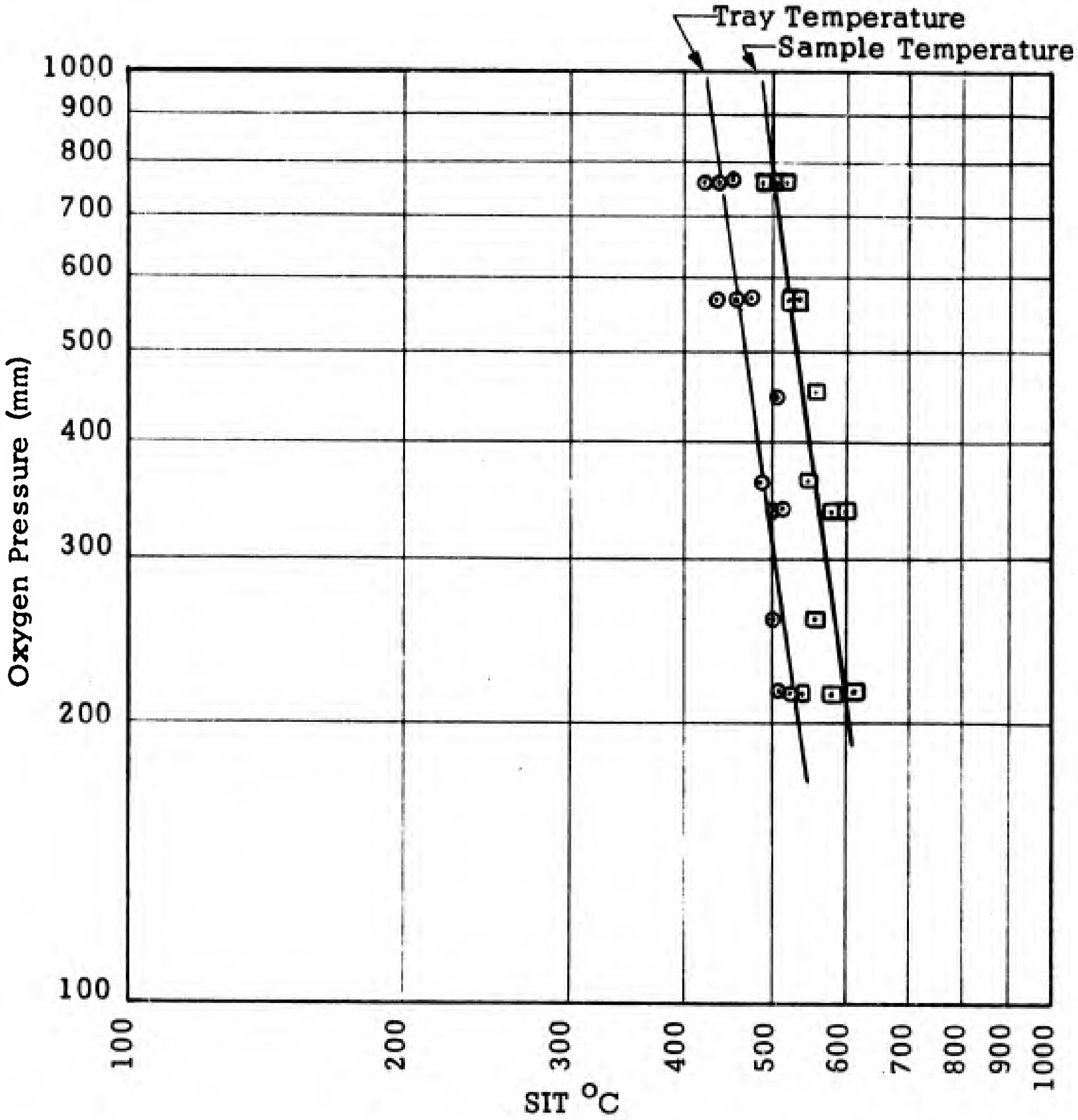


FIGURE 8

EFFECT OF OXYGEN PRESSURE ON SIT FOR POLYVINYLCHLORIDE

TABLE IV. - AUTOGENOUS IGNITION TEMPERATURE OF POLYVINYLCHLORIDE

Run No.	Per cent			Pressure MM Hg	Flow Rate L/Min	Ignition Temp. °C (Tray)	Ignition Temp. °C (Sample)	Furnace Temp. °C	Flame Duration Sec.	Ignition Delay Sec.	Sample Weight Grams	Sample Size	Heating Rate (Final)	Remarks
	O_2	N_2	He											
201	100	-	-	760	4.0	415	480	410	135	2940	5.294	4-1x1x 1/16 in	5	
202	60	40	-	760	4.0	480	537	480	555	3120	5.596	"	5	
203	20	80	-	760	4.0	-	No ignition at 650°C				5.579	"	-	
203A	20	80	-	760	4.0	-	No ignition at 645°C				5.551	"		
204	100	-	-	760	4.0	392	452	398	210	4770	5.811	"	3.5	
205	100	-	-	760	4.0	411	462	418	310	5760	5.591	"	3.5	Sample oxygen soaked for 30 da prior to test.
206	100	-	-	569	3.2	414	462	418	300	5730	5.566	"	4	
206A	100	-	-	569	3.2	415	452	425	320	4740	5.554	"	5	
207	60	40	-	569	3.2	485	562	485	700	5720	5.532	"		
208	20	80	-	569	3.2	562	No ignition at 588°C				5.668	"	5	
208A	20	80	-	569	5.2	562	No ignition at 590°C				5.605	"	5	
209	100	-	-	569	5.2	445	502	450	420	2550	5.578	"	7.5	
210	60	-	40	569	5.2	480	568	465	415	3760	5.577	"	10	

TABLE IV. (Cont'd) - AUTOGENOUS IGNITION TEMPERATURE OF POLYVINYLCHLORIDE

Run No.	Per cent O_2	Per cent N_2	Per cent He	Pressure MM Hg	Flow Rate L/Min	Ignition Temp. °C (Tray)	Ignition Temp. °C (Sample)	Furnace Temp. °C	Flame Duration Sec.	Ignition Delay Sec.	Sample Weight Grams	Sample Size	Heating Rate (Final)	Remarks
211	20	80	-	569	5.2		No ign at 575°C				5.660	4-1x1x 1/16 in	-	
212	100	-	-	362	1.9	476	539	460	570	3670	5.540	"	8	
213	60	40	-	362	1.9	502	535	502	670	2650	5.624	"	5	
214	20	80	-	362	1.9	-	No ign at 560°C				5.625	"	5	
215	100	-	-	259	1.3	496	552	478	660	2715	5.621	"	5	
216	60	40	-	-	1.3	514	600	502	840	4000	5.681	"	5	
217	20	80	-	259	1.3	No ignition at 570°C					5.621	"	5	
218	60	40	-	362	1.9	516	572	498	915	3040	5.656	"	5	
219	20	80	-	259	1.3	No ignition at 550°C					5.642	"	5	
220	100	-	-	569	3.2	439	510	418	435	2400	5.643	"	6.5	

Although the equation is approximate and applies to a homogenous gas in a spherical container rather than the locally heated, solid surface representative of the experiments reported here, it is evident that a $\Delta T = 70$ is within a logical value range for the differences between the temperatures of the sample surface and heat source.

Based on E = 40,000 calories, a value characteristic of many hydrocarbon reactions, the value $\Delta T = 70^{\circ}C$ is relatively high. The greater heat loss associated with experiments in which the furnace and gas temperatures are below the plate temperature may be a partial reason for this high value. The data in Table V tends to support this possibility.

TABLE V

Run	Plate Temp.$^{\circ}C$	Furnace Temp.$^{\circ}C$	$\Delta T, (T_s - T_p)^{\circ}C$
202	480	480	57
204	392	398	60
205	411	418	51
206	414	418	48
206A	415	425	37
207	485	485	77
209	445	450	57
213	502	502	33
		Avg.	$52^{\circ}C$

The average value of ΔT is about $52^{\circ}C$ for those runs in which furnace temperature is equal to or slightly higher than tray temperature. Values for those runs in which furnace temperatures were lower than temperatures are listed in Table VI for the purpose of comparison.

TABLE VI

Run	Plate Temp. °C	Furnace Temp. °C	ΔT (T_s - T[illegible]) °C
201	415	410	65
210	480	465	88
212	476	460	63
215	496	478	56
216	514	502	86
218	516	498	56
220	439	418	71
		Avg.	61°C

c. During the combustibility studies of polyvinylchloride, two regions of exothermic reaction were observed at temperatures considerably lower than the ignition region. These reactions resulted in a temperature increase which was detected by the thermocouple in contact with the specimen surface. The temperature of these exothermic reactions increased as the oxygen concentration increased. This would be expected in a surface oxidation process. The first reaction occurred between 220°C and 230°C and the second at approximately 282°C. Above 282°C the sample surface temperature remained higher than those of the tray or chamber gas.

An increase in sample volume occurred in conjunction with the surface oxidation reaction. The sample began to swell at approximately 280°C and changed to a carbonaceous, honeycomb mass of four times the original volume. Upon ignition, a mantle of flame surrounded the specimen and remained for about one half of the burning period. When the flame disappeared, the sample continued to glow in the manner of charcoal. The burning time for the standardized sample of polyvinylchloride increases as oxygen pressure is decreased. The data are presented, graphically, in Figure 9, but no attempt has been made to correlate these results at present because of the large spread.

d. Analysis of combustion product of polyvinylchloride. No analysis of chamber gases during the combustion tests on polyvinylchloride were performed. The Micro-Tech chromatograph was inoperative during this series of tests.

3. Silicone Rubber

a. The ignition test data on silicone rubber indicates that the behavior pattern of this material differs considerably from the general

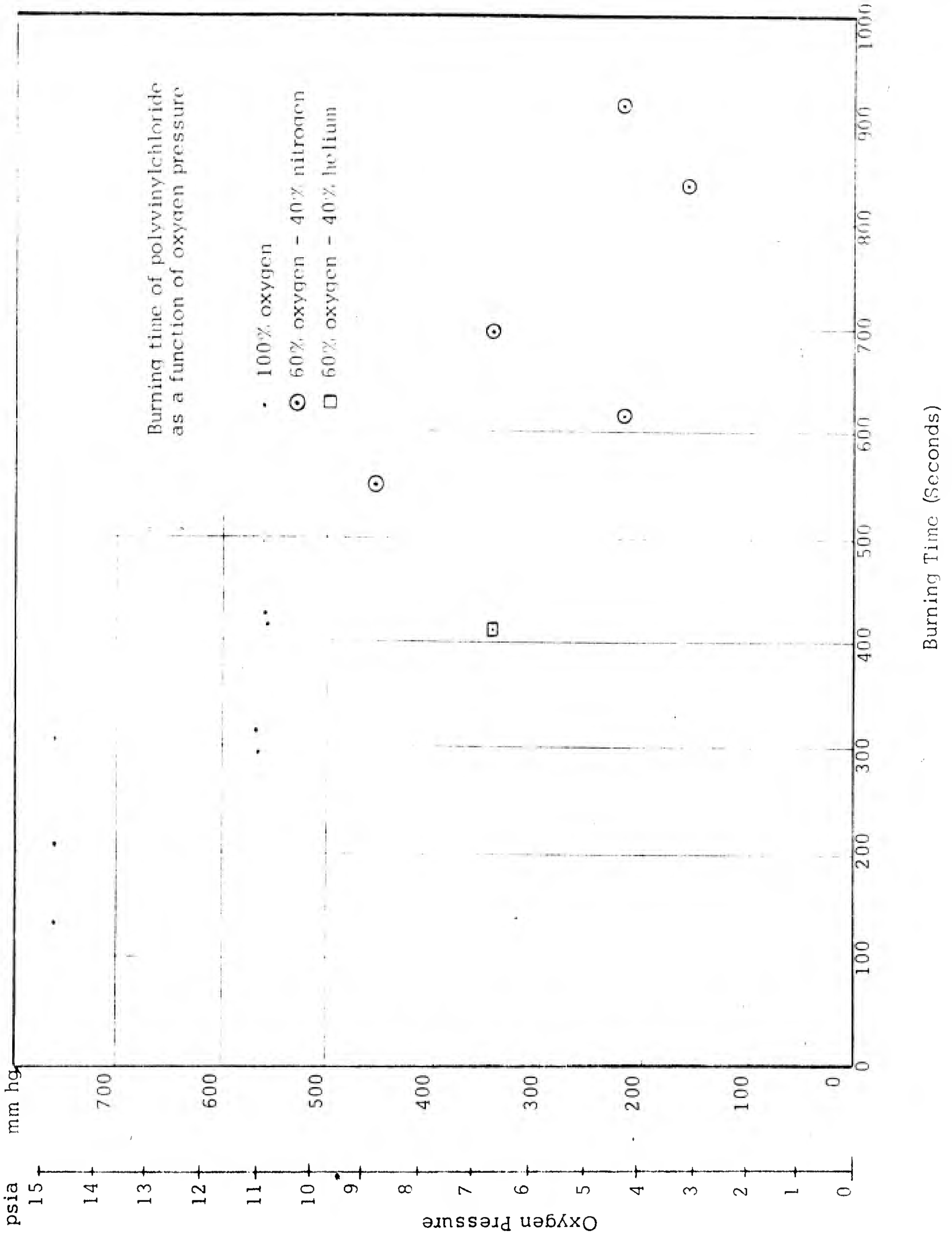

Burning time of polyvinylchloride as a function of oxygen pressure
• 100% oxygen
⊙ 60% oxygen - 40% nitrogen
☐ 60% oxygen - 40% helium
Burning Time (Seconds)
0
100
200
300
400
500
600
700
800
900
1000
Oxygen Pressure
psia
mm hg
0
100
200
300
400
500
600
700
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

FIGURE 9

trends established by the tests on polyethylene and polyvinylchloride. During the silicone rubber combustion experiments, an oil evolved from the specimen at approximately 200°C. This apparently volatile silicone condensed on the cool view window and oxidized as the heat increased. This reaction left a heavy, white film on the window and a suspension of fine silica in the chamber. Although these degradation products partially interfered with visual observation, some significant information was obtained in this area. The test sample began to expand at approximately 400°C and increased to about eight times its original volume. Ignition began with a brilliant yellow flame which rapidly diminished in size and extinguished itself after fifteen to twenty seconds. Thereafter, the sample continued to glow for one to five minutes. The duration of the glow depended upon the conditions peculiar to each test run. The suspended particles which formed prior to ignition and obstructed the visual observations could create similar problems in actual spacecraft operations. For example, the following difficulties could arise:

1. visual interference
2. fouling of the filter system
3. deposition of residue throughout the system.

Table VII contains the data relevant to the effect of atmospheric variables upon the autogenous ignition temperatures of silicone rubber.

b. Dependence upon the partial pressure of oxygen is illustrated in Figure 10. Notice that, when the flow rate correction is applied, there is essentially no pressure effect. This is in contrast to the measurable effect of pressure upon polyethylene and polyvinylchloride. However, it should be remembered that this flow rate correction, which seems to eliminate the apparent pressure effect on silicone rubber is related to the surface availability of oxygen. It is possible that the pre-ignition reactions, described in the preceding paragraph, inhibited the oxygen supply at the samples' surface.

c. At ignition, the surface temperature of the silicone rubber sample is lower than the tray temperature. This is not the case with polyvinylchloride. However, there are several possible reasons which could account for this difference. In each case, the polymer insulates the upper surface of the sample from the tray. This suggests that a lower temperature could exist at the sample surface during most of the heating period. If the activation energy for the silicone oxidation is higher than that for the polyvinylchloride oxidation, the surface temperature rise for silicone rubber may not occur until just before ignition. Such a condition could make it difficult to distinguish between the temperature rise caused by the samples self-generated heat and that due to ignition.

TABLE VII. AUTOGENOUS IGNITION TEMPERATURE OF SILICONE RUBBER

Run No.	Per cent O_2	Per cent N_2	Per cent He	Pressure MM Hg	Flow Rate L/Min	Ignition Temp. °C (Tray)	Ignition Temp. °C (Sample)	Furnace Temp. °C	Flame Duration (Sec.)	Ignition Delay Sec.	Sample Weight Grams	Sample Size	Heating Rate (Final)	Remarks
501A	100	-	-	760	4.0	520	496	502	90	4300	4.911	2-1x1x 1/8	3.5	
501B	100	-	-	760	4.0	522	498	510	75	4720	5.041	"	3.3	
502	100	-	-	569	3.2	520	495	522	60	3810	5.026	"	3	
502A	100	-	-	569	3.2	515	495	510	150	4510	4.967	"	3.3	
503	100	-	-	562	1.9	No ignition at 560°C					4.972	"	(3.3)	Sample ignited upon admission of air
503A	100	-	-	562	1.9	532	510	520	180	4620	4.976	"	3.3	
503B	100	-	-	562	1.9	532	500	522	190	4590	5.007	"	3.5	
504	100	-	-	259	1.3	538	500	525	270	4710	5.002	"	3	
505	60	40	-	760	4.0	530	495	520	160	4640	4.985	"	3.5	
506	60	40	-	569	3.2	535	498	525	-	4570	5.095	"	4	
507	60	40	-	562	1.9	535	498	525	110	4930	4.995	"	2.5	
508	60	40	-	259	1.3	535	498	525	330	5590	5.048	"	3.3	
508A	60	40	-	259	1.3	545	505	532	290	5000	5.129	"	3.4	
509	20	80	-	760	4.0	545	510	535	-	4630	5.180	"	3.5	

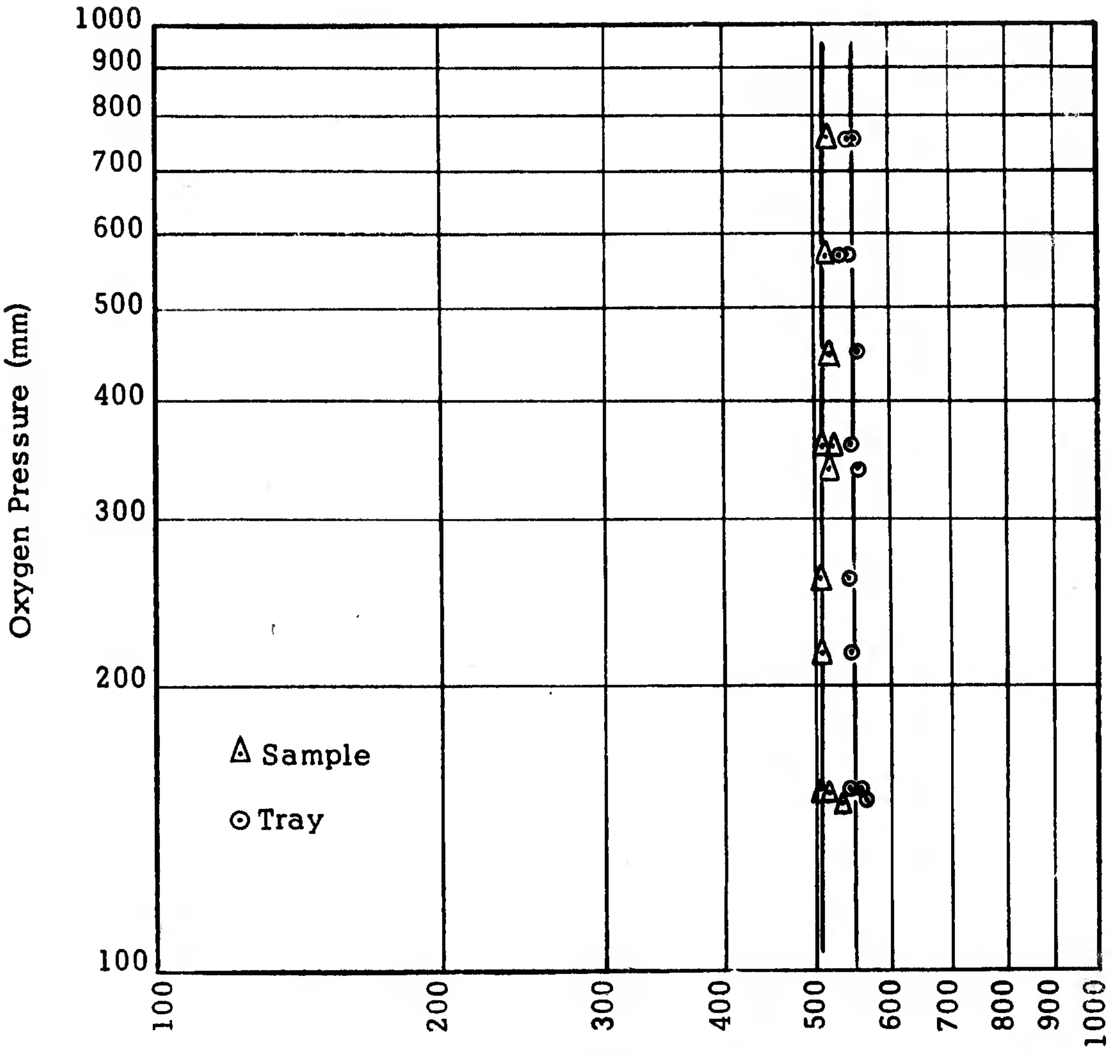


FIGURE 10

CORRECTED SPONTANEOUS IGNITION TEMPERATURE AS A FUNCTION OF OXYGEN PRESSURE FOR SILICONE RUBBER

A more detailed examination of the pre-ignition temperatures may assist in the evaluation of this possibility. The occurrence of endothermic pyrolysis on the surface of the silicone rubber and the exothermic, self-heating reaction taking place in the gas phase, is another feasible possibility.

The possibility of a high activation energy, with its implications of negligible oxidation prior to ignition, is an appealing explanation for the absence of a self-heating temperature rise because it can be qualitatively related to the absence of a pressure effect. In all cases, the small exponent on pressure indicates a diffusion controlled rather than a gas phase kinetic process. The pre-ignition reactions of polyethylene and polyvinylchloride consume oxygen and the reaction products dilute oxygen. These effects tend to reduce the local surface concentration of oxygen when the chamber concentration of oxygen is low. Therefore, an increase in the partial pressure of oxygen should affect the ignition temperature. During the silicone rubber reactions, there may be less dilution and depletion of the surface concentration of oxygen prior to ignition and therefore less dependence upon the partial pressure of oxygen.

d. At this stage of the program, the reasons for the difference between the behavior pattern of silicone rubber and those of polyethylene and polyvinylchloride have not been determined. The speculative explanations presented in this report will be studied further during the future courses of experimentation in an attempt to isolate those variables which may lead to a greater comprehension of these mechanisms.

e. The burning time for the standardized sample of silicone rubber increases as the oxygen pressure is decreased. The data are presented graphically in Figure 11, but no attempt has been made to correlate these results at present.

f. Analysis of combustion products of silicone rubber. The compositions of the atmospheres within the combustion chamber during the combustion tests on silicone rubber are given in Table VIII. The temperatures of the sample surface and heating tray are also given in this table at selected times from the initiation of the test. The data from these tests show the partial pressure of oxygen is decreased appreciable prior to the onset of flame and that the partial pressure of carbon monoxide increases to a high level, five to twelve mm, prior to ignition. Upon ignition, the partial pressure of oxygen decreases rapidly as would be predicted. In addition, the pressure of carbon dioxide increases rapidly and the partial pressure of carbon monoxide is decreased at the onset of flame. The concentration of carbon monoxide prior to and during

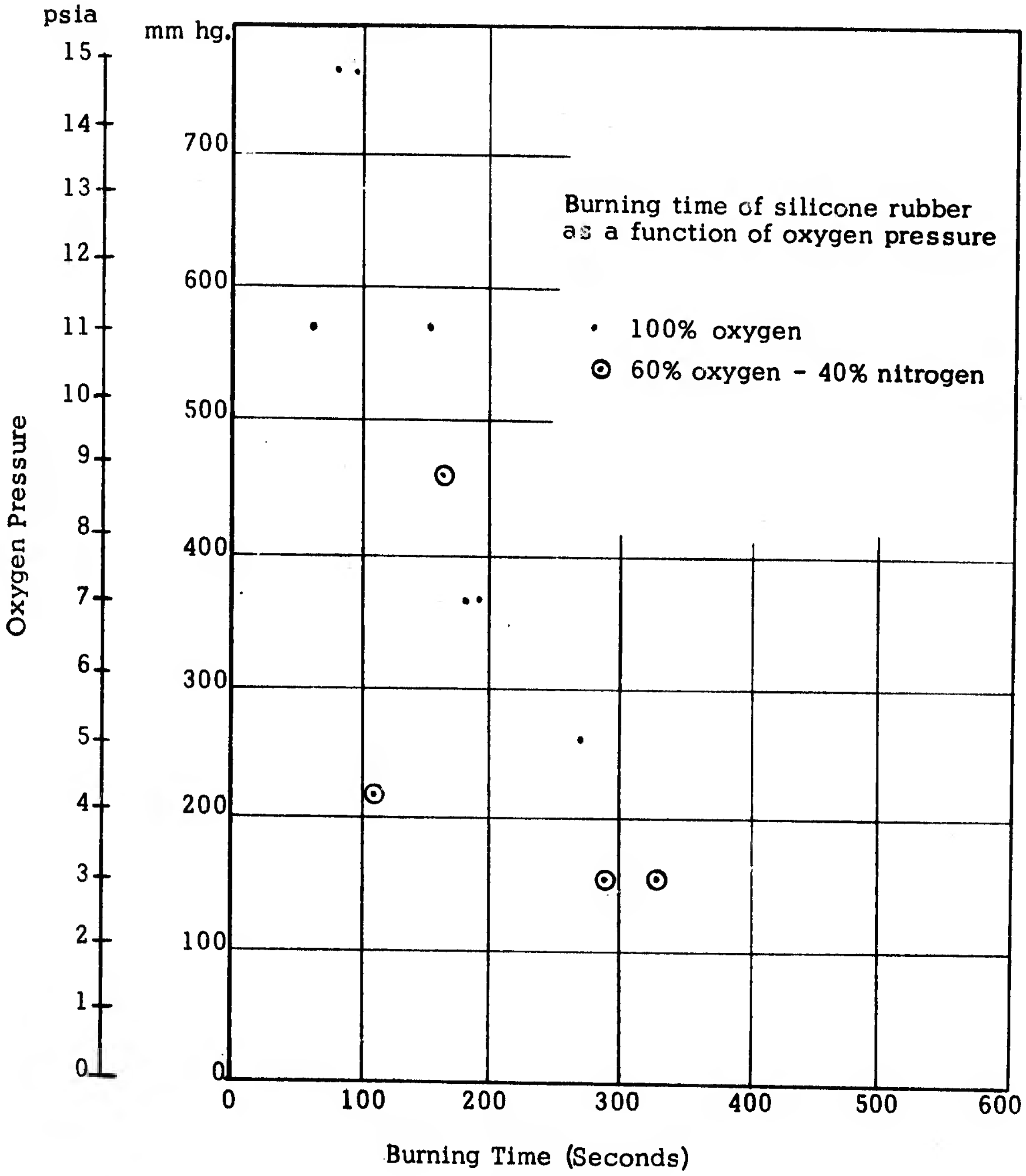

psia
mm hg.
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
Oxygen Pressure
Burning Time (Seconds)
Burning time of silicone rubber as a function of oxygen pressure
• 100% oxygen
⊙ 60% oxygen - 40% nitrogen

FIGURE 11

TABLE VIII. TEMPERATURE AND ATMOSPHERE COMPOSITION OF SILICONE RUBBER AS A FUNCTION OF TIME

Run No.	Time (Min)	Tray Tempera- ture (°C)	Sample Tempera- ture (°C)	O_2 Pressure (MM)	CO Pressure (MM)	CO_2 Pressure (MM)	Remarks
502A	24	232	215	569	0	0	
(Pressure -	31	310	280	672.1	7.55	0	
569 MM	41	385	350	560.2	-	-	
100% oxygen)	51	435	400	672.1	1.53	-	
	59	472	440	553.3	9.63	2.15	
	65	500	465	511.3	12.76	3.94	
	68	510	475	489.3	13.27	-	
	73.30	-	-	424.3	6.54	22.3	Slow ignition Orange
	74.0	535	700	-	-	-	Slight glow
	75	552	790	392.3	3.44	4.02	Slight glow
303	30	375	345	362	-	-	
(Pressure -	35	408	380	411.6	0.71	1.85	
362 MM	40	445	410	308.4	6.13	3.33	
100% oxygen)	45	472	440	355.9	9.55	8.99	
	50	500	460	350.2	10.9	13.6	
	52	512	472	281.4	6.28	11.1	
	56	530	493	182.9	3.27	3.10	
	60	543	515	163.2	2.30	2.68	
	63	550	520	153.7	1.75	2.61	
	67	-	-	-	-	-	System exhausted to atm. smp. igniter returned to press. to 362 mm Hg sample burned for short period & went out
305	40	560	338	454.0	-	-	
(Pressure -	55	442	410	462.3	3.51	1.16	
760 MM	61	475	438	430.6	9.88	2.21	
60% oxygen	70	508	470	429.2	11.9	7.48	
40% nitrogen)	75	522	488	421.7	12.9	13.7	
	77.20	530	495	424.0	10.4	17.6	Ign. - yellow flame
	79	545	770	421.4	5.41	-	

TABLE VIII. (CONTINUED)

Run No.	Time (Min)	Tray Tempera-ture (°C)	Sample Tempera-ture (°C)	O_2 Pressure (MM)	CO Pressure (MM)	CO_2 Pressure (MM)	Remarks
306 (Pressure - 569 MM 60% oxygen 40% Nitrogen)	45	398	368	359	-	-	
	55	452	415	368.9	1.92	-	
	65	493	455	366.5	7.59	2.01	
	74	528	490	304.7	8.15	7.99	
	76:10	535	498	355.9	5.92	8.02	Ign. orange flame
	78	550	705	-	-	-	View Obscured
307 (Pressure - 362 MM 60% oxygen 40% nitrogen)	51	412	375	216.53	-	0.47	
	60	458	420	227.9	2.07	-	
	66	485	440	192.2	6.53	2.24	
	70	500	460	214.7	6.71	3.54	
	77	525	485	174.6	5.88	9.69	
	82:10	538	498	195.8	2.22	28.54	Ign. - orange flame
	83	545	650	-	-	-	Flame dying
	84	550	650	-	-	-	No flame - red glow
	86	555	615	189.2	2.93	24.2	Appears out
308A (Pressure - 259 MM 60% oxygen 40% nitrogen)	30	272	245	155	-	-	
	50	395	365	175.4	-	-	
	65	460	428	163.7	3.39	1.75	
	75	498	462	192.7	6.36	3.30	
	85	525	490	156.3	4.78	8.21	
	89:10	545	508	149.6	2.81	1.81	Ign. - orange flame
	91	-	-	-	-	-	Flame died then flared
	92	-	-	-	-	-	Glow
	94	-	-	-	-	-	Out
309 (Pressure - 760 MM 100% air)	31	280	280	152	-	-	
	51	418	400	122.3	0.27	0.16	
	60	465	440	120.5	4.00	0.71	
	72	520	490	139.1	6.73	5.32	
	77:15	545	510	118.2	5.56	12.45	Ign. View obscured.
	82	565	585	115.6	1.63	1.47	

the period of flame exceeds the lethal limits. In addition, the carbon dioxide concentration during this flame is also sufficient to result in physiological damage or death. It appears from these data that the onset of a flammable condition due to overheating within a closed environment may result in a unhabitable atmosphere. It may then be necessary for a man in this environment to utilize some form of emergency breathing system.

III. LOW PRESSURE LIMIT

A. INTRODUCTION

In most combustion processes, ignition cannot occur below a certain partial pressure of oxygen. Generally, hydrocarbon-air mixtures will not ignite at atmospheric pressure when the oxygen concentration falls below 11% with inert gases such as nitrogen used as diluents. This corresponds to an oxygen partial pressure of about 84 mm. Lower partial oxygen pressures can support the combustion of vapor-air mixtures when the partial pressure of oxygen is accomplished by the reduction of total pressure rather than dilution. Since the combustion tests in this program were not performed under normal atmospheric conditions, pressure limits were studied in conjunction with the materials ignition experiments.

The data on pressure was obtained during the ignition test, therefore, the experimental procedure for this study remains the same as that previously described in this report.

B. RESULTS AND DISCUSSION

As pointed out in the previous discussion on ignition, the gas phase experiments under the condition of this program appear to depend on gas phase chemical reaction rates while the solid-gas reactions appear to depend on diffusion processes. In the case of solid-gas ignition, one might expect that the partial pressure of oxygen is the critical variable independent of how a particular partial pressure is achieved.

A low pressure limit of about 180 mm was observed for polyethylene and 155 mm for polyvinylchloride. There is no obvious reason for the fact that this value is greater than that observed for gas phase mixtures. The different mechanism could account for the larger pressure limit. In addition, the dilution of oxygen near the surface during pre-ignition reactions in the diffusion controlled solid-gas reaction could account for the higher apparent oxygen limit. It is interesting that silicone rubber could be ignited at an oxygen partial pressure of 155 mm. This is consistent with the postulate presented in the ignition discussion that less pre-oxidation occurs prior to ignition in silicone rubber.

IV. EXTINGUISHING AGENTS FOR FLAMMABLE LIQUID FIRES

The evaluation of selected bromine and chlorine substituted fluorocarbons as agents for the suppression and control of hydrocarbon fires will be undertaken in the future portion of this program. The evaluation will be performed using the No. 2 furnace chamber of the combustion monitor. Liquid hydrocarbon fuel, JP-6 and a hydraulic fluid, will be placed in the tray contained within the main chamber. The air flow to the chamber will be initiated and the liquid fuel ignited. The candidate agents under evaluation will then be applied to the flame by means of overhead lines.

The candidates which will be evaluated include the compounds listed in Table IX.

TABLE IX

1. $H(CF_2)_2\ CH_2Br$
2. $H(CF_2)_4\ CH_2Br$
3. $CF_2Br\ CFCl\ \ CF_2CFClH$
4. $CF_3\ CBrClH$
5. $CCl_3CF_2CFCl_2$

In support of this phase of the program, two of these candidate agents have been synthesized. These compounds are: 1) 1-bromo 2, 2,3,3,-tetrafluoropropane, item No. 1 above; and 2) 1-bromo 2,2,3,3, 4,4,5,5,-octafluoropentane, item No. 2 above. These compounds were synthesized by replacing the hydroxyl group of the corresponding alcohol with bromine by the method of Tiers et al, (Ref. 61). These compounds are on hand for evaluation when this phase of the program is initiated.

A. SYNTHESIS OF BROMINE SUBSTITUTED FLUOROCARBONS

1. Materials

a. $HCF_2CF_2CH_2OH$ - Technical C_3 fluoroalcohol - DuPont Organic Chemicals Department.

b. $HCF_2CF_2CF_2CF_2CH_2OH$ - Technical C_5 fluoroalcohol - DuPont Organic Chemical Department

c. Para-toluene sulfonylchloride, practical grade - J. T. Baker Company

d. Potassium Bromide NF - Van Waters & Rogers Inc., Braun Division

e. Diethylene glycol, technical grade - Van Waters & Rogers Inc., Braun Division

f. Sodium sulfate - anhydrous granular, J.T. Baker Co.

g. Sodium hydroxide - Reagent pellets, J.T. Baker Co.

B. EXPERIMENTAL: PREPARATION OF 1-BROMO 2,2,3,3, TETRAFLUOROPROPANE AND 1-BROMO 2,2,3,3,4,4,5,5, OCTAFLUOROPENTANE

The following procedure was used for the preparation of the paratoluenesulfonyl (tosyl) esters of the C_3 and C_5 fluoroalcohols.

In a 2-liter flask were placed 228 gms (1.72 moles) of the alcohol $HCF_2CF_2CH_2OH$, 400 gms (2.10 moles) para-toluenesulfonylchloride, and 600 ml of water. The mixture was vigorously stirred and heated to 50°C and 80 gms (2.0 moles) of sodium hydroxide dissolved in 320 ml water was added over a period of about one-half hour. Heat was liberated during the reaction and the rate of base additive was controlled to maintain the reaction temperature between 60°C and 65°C. The vigorous stirring was continued and the pH of the solution tested and sodium hydroxide in water was added until the solution was neutral. The reaction mixture was cooled and filtered through filter-aid to remove the dispersion of the brown solid residue, and the water layer separated. The product was washed five times with 100 ml portions of concentrated aqueous ammonia and then with water. The crude tosylester was dried over anhydrous sodium sulfate. The ester obtained was adequate for conversion to the bromide without further purification; yield 395 gms, 80.9%.

The procedures for preparing the C_3 and C_5 fluorobromide were similar in each case. The following is a typical experiment:

In a 2-liter round bottom flask fitted with a stirrer, distillation take-off head and thermometer were placed 572 gms (2.0 moles) $HCF_2CF_2CH_2O$ tosylate, 358 gms (3.0 moles) KBr and 600 ml diethylene glycol. The mixture was heated with stirring and the product which distilled over between 180°C and 220°C was collected. Heating was regulated to maintain the reaction temperature below 240°C. The distillate was washed three times with equal volumes of water and dried over anhydrous sodium sulfate; yield 349.4 gms (89.5%). The infrared spectrum of the 1-bromo-2,2,3,3,-tetrafluoropropane showed the material to be free of starting materials and reactants.

V. COMBUSTION PROPERTIES OF MATERIALS UNDER ZERO GRAVITY CONDITIONS

The combustibility of representative flammable materials under zero gravity flight conditions will be investigated. The properties which will be evaluated will include burning rate, flame intensity, self extinguishment properties, and combustion products.

Three types of flammable materials will be investigated in this program. The first, a liquid hydrocarbon fuel of low volatility, has been selected as an example of a vaporizing fuel, i.e., one which need only be vaporized in order to burn. Ideally, hexane would be preferred for these tests, however, the danger of explosion of such a volatile material is too great. The low volatility fuel should provide the same information and yet be safe. The exact fuel to be used will be determined in the laboratory tests conducted at Dynamic Science Corporation.

The remaining two combustible materials are representative of those materials which must undergo pyrolytic degradation prior to ignition and combustion. Molded polyethylene is a high molecular weight hydrocarbon, with a minimum of surface area which must be degraded in order to burn. Polyethylene is a material which is being used onboard present day spacecraft in several places, i.e., food containers and gear storage. For these reasons, polyethylene has been selected as one of the flammable materials to be evaluated under zero gravity conditions.

The third combustible material to be evaluated is a woven fabric representative of the materials which may be onboard a spacecraft in various places. The material which will be evaluated in this class will be dacron. This is similar to polyethylene in that it must undergo pyrolysis prior to combustion, but differs in that it exhibits a high surface to volume ratio.

The material under evaluation will be supported within a sealed test chamber and the preselected atmosphere introduced. Ignition of the sample will be accomplished by energizing a nichrome wire in contact with the test specimen. The ignition and combustion process will be recorded photographically by a 16mm motion picture camera. The materials will be fully evaluated under laboratory conditions to establish a base line for the tests to be carried out in the zero gravity test apparatus at Wright-Patterson Air Force Base, Ohio.

VI. FIRE EXTINGUISHING AGENTS FOR USE IN ENRICHED OXYGEN ATMOSPHERE

This portion of the program has been directed primarily to the selection of fire extinguishing agents to be utilized for fire protection within a space vehicle cabin. In addition to being useful as first aid fire protection in a space vehicle, the agent would also be useful in any situation where an enriched oxygen atmosphere would be encountered or where atmospheric contamination is a problem. The requirements for an extinguishing agent to be utilized within an orbiting spacecraft are as follows:

1. The agent must be capable of application under zero gravity conditions.
2. The agent must be capable of extinguishing Class A and Class C fires under enriched oxygen atmospheres.
3. The agent and its degradation products should exhibit negligible toxic and anesthetic effects.
4. The agent and its degradation products should exhibit negligible corrosion effects on materials used within a spacecraft.
5. The agent and its degradation products must not leave liquid or solid residues which would adversely affect visibility, contaminate on-board equipment, or cause undue clean-up problems.

An extensive literature survey has been conducted in an effort to identify suitable candidate material which would meet the above listed requirements. The reference to the literature which has been surveyed is given in the Appendix to this report.

A large number of compounds have been shown to exhibit fire extinguishing or fire retardant properties. The bulk of the available data relates to the effectiveness of these agents under normal atmospheric conditions. The candidate agents listed in Table X are representative of the various classes of materials which have been shown to exhibit flame extinguishing properties. It must be emphasized that the evaluation of these materials has been demonstrated using normal air (21% oxygen) as the source of oxygen. It is, therefore, necessary to carefully screen these materials prior to their utilization in oxygen enriched environments. This is particularly true of those compounds which are substituted hydrocarbons or contain hydrocarbon type groupings. Any compound which contains carbon can serve as a fuel in the proper

		Toxicity of Agent	Toxicity of Products	Solid Residue	Liquid Residue	Corrosiveness of Agent or Products	Compatibility With Oxygen-Enriched Environments	Cleanup
1.	CO_2							
2.	H_2O	X	X					
3.	N_2				X			X
4.	Inert Gases							
5.	CCl_4	X	X		X		X	
6.	CH_3Br	X	X					
7.	CH_2Br_2	X	X				X	
8.	CH_2BrCl	X	X				X	
9.	CH_3I	X	X				X	
10.	CH_3Cl		X				X	
11.	CF_3Br		-					
12.	CF_2BrCl	-	-					
13.	CF_2BrCF_2Br	X	-					
14.	CF_2Br_2	X	-					
15.	$CCl_3CF_2CFCl_2$	-	X		X			X
16.	$CHF_2CF_2CH_2Br$	-	X		X			X
17.	(Higher Members of Series)	-	-		X			X
18.	Br_2	X	X			X		
19.	BBr_3	X	X			X		
20.	PCl_3	X	X			X		
21.	PBr_3	X	X			X		
22.	$POCl_3$	X	X			X		
23.	$PSCl_3$	X	X			X		
24.	$(CH_3)_3PO_4$	X	X	X	X	-	X	X
25.	$(CF)_3PO_4$	X	X	X	X	-		X
26.	$SiCl_4$	X	X	X	X	X		X
27.	$SnCl_4$	X	X	X	X	X		X
28.	$TiCl_4$	X	X	X	X	X		X
29.	$Fe(CO)_5$	X	X	-				-
30.	CrO_2Cl_2	X	X	-		-		-
31.	HBr	X	X			X		
32.	SF_6		X			-		
33.	$NaHCO_3$			X				X
34.	$KHCO_3$			X				X
35.	K_2CO_4			X			X	
36.	SiO_2	X		X			X	

X = Exhibit Properties
\- = Unknown

TABLE X

CANDIDATE FIRE EXTINGUISHING AGENTS

environment of oxygen concentration and temperature. In addition, the presence of hydrogen with the molecule will increase the combustibility of the material. The fully fluorinated hydrocarbons, such as tetrafluoromethane and hexafluoroethane, exhibit desirable combustibility properties. They are, however, very poor extinguishing agents. These materials extinguish a fire in a manner similar to nitrogen, by blanketing the area with an inert gas and preventing the flame from receiving sufficient oxygen. The fluorinated compounds exhibit a high degree of stability and, therefore, do not enter chemically into the extinguishing mechanism.

The compounds which appear to offer the greatest potential as fire extinguishing agents contain bromine and/or chlorine since these agents undergo thermal degradation yielding halogen atoms in the hot fire zone. It is generally accepted that the extinguishing properties of the vaporizing fire extinguishing agents are due to the presence of free radicals, such as the halogen atom, which are capable of entering into the reaction of the combustion process and thereby extinguishing the flame. Compounds such as bromomethane and dibromomethane have been shown to serve as extinguishants while bromochloromethane is very effective under ambient conditions and is currently being used by the Air Force as an onboard extinguishing agent. These materials, however, cannot be used in an enriched oxygen environment due to their flammability under these conditions. The analogs of these compounds in which the hydrogen has been replaced with fluorine also exhibit good extinguishment properties in normal air. It is anticipated that these fluorinated analogs would perform satisfactorily in an enriched oxygen environment.

The utilization of carbon dioxide, nitrogen or the inert gases as extinguishing agents would most ideally meet the requirements of minimum toxicity, corrosion, oxygen compatibility, clean-up and utilization on Classes A and C fires. Carbon dioxide has had a long history as an extinguishing agent. The utilization of nitrogen and inert gases would not be satisfactory due to their mechanism of extinguishment. The mechanism of extinguishment for these gases is by "blanketing" the fire, thereby preventing oxygen from entering the reaction zone. This would result in the use of an unacceptably large amount of material thereby creating a problem of space and weight.

The last four compounds listed are representative of dry powder extinguishing agents. These materials are sodium bicarbonate, potassium bicarbonate, silica and potassium oxylate. This type of agent has proven to be very effective on all classes of fire and would undoubtedly perform satisfactorily under enriched oxygen conditions. These types of extinguishing agents would not be suitable, however, in a spacecraft under zero gravity conditions. This is because they are solids which would result in contamination of exposed electrical and mechanical components. This contamination could interfere with their operation resulting in systems failure. In addition to component contamination, these materials would be suspended within the spacecraft impairing the crew's vision. It is, therefore, concluded that dry powder fire extinguishing agents would be unsatisfactory for use in an enclosed environment under conditions of zero gravity.

Many of the inorganic compounds listed such as BBr_3, PBr_3, $Fe(CO)_5$ have been shown to be very effective in decreasing the flammability of many compounds and would also be expected to perform satisfactorily in an enriched oxygen atmosphere. However, these materials exhibit extremely undesirable properties with respect to toxicity, corrosion, contamination and post-fire clean-up. It is therefore concluded that none of the inorganic compounds which have been investigated to date would be acceptable as an onboard extinguishing agent for a closed environment system.

The chlorine and bromine substituted fluorocarbons have been shown to be effective as extinguishing agents. These materials and their degradation products exhibit minimal corrosion properties and are also generally compatible with an enriched oxygen environment. Compounds such as 1,1,1,3,3, pentachloro 2,2,3 trifluoropropane, 1-bromo 2,2,3,3, tetrafluoropropane, and higher members of these series of compounds have relatively low vapor pressures. Their use under zero gravity conditions would result in droplets being dispersed throughout the cabin area. Since these materials are liquids, they would attach to any surface in which they can be in contact and would result in a severe clean-up problem after they had been used. In addition, the vapors from these compounds would be released into the cabin atmosphere until all of the material had evaporated, thus resulting in a long-term contaminant within the closed environment. The remaining four compounds listed are gases or highly volatile liquids which would not result in long-term contamination of the atmosphere or clean-up problems within the spacecraft cabin. These compounds are listed in Table XI.

TABLE XI

1. Trifluorobromomethane
2. Bromochlorodifluoromethane
3. 1,2 Dibromotetrafluoroethane
4. Dibromodifluoromethane

The information available at this time indicates that trifluorobromomethane or its decomposition products do not possees hazardous toxicological properties. The preliminary data on the other compounds indicate varying degrees of anesthetic and toxic properties. The physiological properties of all of these compounds and their degradation products must be further evaluated prior to their usage in a manned environment.

The information which is available at this time indicates that five compounds in Table XII meet the basic requirements, with the exception of toxicity, as extinguishants for oxygen enriched atmospheres under conditions of zero gravity. These compounds are:

TABLE XII

CANDIDATE AGENTS FOR USE IN ENRICHED OXYGEN ENVIRONMENTS

1. Carbon dioxide
2. Trifluorobromomethane
3. Dibromodifluoromethane
4. Bromochlorodifluoromethane
5. 1,2 Dibromotetrafluoroethane

The possible use of these materials as extinguishments should not be excluded even though they may exhibit undesirable toxicological properties. The presence of highly toxic gases produced by the fire may produce an atmosphere which is incompatible with the crew. The information on the atmosphere within the test chamber on the combustion tests of silicone rubber and very probably many other materials, indicates the presence of carbon monoxide in sufficient concentration to be fatal to man within a very short time. It may then be necessary for the crew of a spacecraft to utilize emergency breathing oxygen in the event of a fire. The use of these agents would then be acceptable should it prove desirable to furnish the crew with the emergency breathing system. Since these materials have high volatility, they would be rapidly removed from the closed environment by the normal circulatory and purification system.

The quantity of carbon dioxide required to extinguish a fire limits its usefulness in a space and weight limited spacecraft. It should not be entirely overlooked, however, since the requirements for extinguishment under conditions of zero gravity may be entirely different from those found under normal conditions. Its use has the advantages of not requiring any additional atmosphere purification system since the spacecraft will contain a carbon dioxide removal system.

It is proposed that the halogenated hydrocarbons listed in Table XI above be evaluated as candidate fire extinguishing agents in enriched oxygen environments. The relative effectiveness and boiling point of these compounds are given in Table XIII.

TABLE XIII

	Formula	Boiling Point	Effectiveness Static[1] Wt. %	 Discharge System[2] Pounds
Bromotrifluoromethane	CF_3Br	-58	5.6	0.1
Bromochlorodifluoromethane	CF_2ClBr	-4	2.9	0.105
Dibromodifluoromethane	CF_2Br_2	22.5	3.7	0.125
1,2,Dibromotetrafluoromethane	CF_2BrCF_2Br	46	7.4	0.12

1) Volume necessary to prevent downward propagation in an explosion burette (Ref. 17, 18, 19).

2) Weight required to extinguish a standard fire in a high discharge rate system (Ref. 20).

The ignition and combustion properties selected liquid and solid materials will be evaluated under conditions of zero gravity. The tests will be carried out in atmospheres of varying total pressure and oxygen partial pressures simulating those which may be found in present and future spacecraft. In addition, tests will be performed to evaluate possible methods of applying estinguishants under conditions of zero gravity. The candidate extinguishants which will be used are those listed in Table XI.

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13. ABSTRACT

The combustibility properties of polyethylene, polyvinylchloride and silicone rubber have been evaluated. The autogenous ignition temperatures of these materials have been determined as a function of atmospheric composition and pressure under standardized conditions in Dynamic Science Corporation's Combustion Monitor Model 164. The degradation and oxidation products from these materials were identified by gas chromatographic analysis. In addition, the burning rate of these materials was determined under test conditions simulating the environment found in missile silos and high performance aircraft.

Two candidate agents have been synthesized for evaluation as first-aid fire extinguishing agents on Class B fires (liquid).

The combustion properties of selected flammable materials in enriched oxygen environments and zero gravity flight conditions will be evaluated.

A survey has been made to select fire extinguishing agents for use in an orbiting manned spacecraft. Four candidate agents have been selected for evaluation under enriched oxygen atmospheres. The effectiveness of these agents will be evaluated during the coming year. Methods of application of these agents under zero gravity flight conditions will be evaluated.

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