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**EVALUATION OF IGNITION MECHANISMS
IN SELECTED SPACECRAFT MATERIALS**

by M. Gerstein and W. R. Yates

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FINAL REPORT
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FOREWORD

This technical report was prepared by Dynamic Science, a Division of Marshall Industries, under Contract NAS9-6873, entitled "Evaluation of Ignition Mechanisms in Selected Spacecraft Materials."

The contract was monitored by Mr. Jerry W. Craig of NASA Manned Spacecraft Center, Systems Engineering Division, Houston, Texas.

The period of work covered by this report was from 1 March 1967 through 30 June 1967.

Dr. W. Ross Yates was the contractor's principal investigator with assistance from Miss Mary McLain. Dr. Melvin Gerstein played a major role as consultant.



Harry A. Schmidt
Director of Special Projects

ABSTRACT

The present study was undertaken to identify ignition mechanisms for typical spacecraft materials in simulated operating environments. Accordingly, a variety of polymeric materials characteristically used in space cabin construction were tested in a small volume system containing pure oxygen at 5 psia. Among those variables receiving particular attention were the type of ignition source (both electrical and thermal) thermal behavior of the samples, locus of ignition, relative position of the test sample and energy sources, and the effect of various contaminating liquids.

Ignition was shown to occur in the vapor phase in the flammable decomposition products released by thermal degradation of the samples. Purely thermal ignition occurred above 450°F. for all of the solid materials studied, while ignition of samples soaked with glycol or MEK displayed ignition properties characteristic of the liquids. High voltage sparks drastically reduced the temperatures required for ignition. Ignition in wire-overload tests occurred as a result of impingement of molten and burning particles of metal and insulation, and not by direct transfer of energy from the arc.

The most important aspect of this work was our demonstration of the role played by gaseous thermal decomposition products in defining the ignition hazard. Relating such factors as heating and gas evolution rates and the sizes of enclosure and sample should form the basis for more quantitative design criteria with respect to materials application.

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I.

INTRODUCTION

Spacecraft, deep submergence vehicles and some high altitude chambers in medical research often utilize atmospheres in which the partial pressure of oxygen is greater than in the normal sea-level atmosphere. The fire hazard associated with increased oxygen concentrations has been recognized for many years. As a result, materials selection procedures for systems exposed to high oxygen partial pressures have been based on more severe requirements than for systems exposed to normal air. In spite of attempts to provide a greater margin of safety through more stringent material selection procedures, several fires have occurred in chambers having high oxygen partial pressures. These incidents have pointed out the need for a better understanding of the ignition and flame propagation process for solid materials as well as the need for advanced and improved materials screening and test methods.

The objective of the present test program was to identify ignition mechanisms for typical spacecraft materials, and to show how various features of actual environmental conditions contribute to the activation of these mechanisms. This information forms the stimulus for a materials selection and application program based upon more effective design criteria.

Since this program was of relatively short duration, and specific ignition data was desired rather early in the program, our overall technical approach was adjusted to meet these constraints. Our selection of equipment was also made on the basis of its immediate overall utility and the desirability to generate data rapidly through its use.

In this Final Report, we shall discuss the selection of experimental techniques and apparatus, and then proceed through our results in a historical manner, starting with the first of the materials studied. The development will thus appear to follow the course of evaluation of specific materials, though our most significant conclusions are of a general nature. The number and type of materials selected, however, should assure the generality of the conclusions, as well as their applicability to the particular problem at hand.

II.

RESULTS AND DISCUSSION

INTRODUCTION

The principal focus of attention in our study of ignition mechanism has been associated with two types of ignition sources, thermal and electrical. Three separate phenomena may be considered in a simplified discussion of the problem.

The first phenomenon is closely related to the process variously called thermal ignition, autogeneous ignition or spontaneous ignition. Heat acts as the energy source for ignition and in most cases also causes the formation of gases by vaporization, sublimation or decomposition. The ASTM autogeneous ignition apparatus and various modifications of it provide tests for this type of ignition.

The second process involves the ignition of a flammable vapor by means of a spark or glowing surface. The source of flammable vapor may be vaporization of a volatile combustible or, for low volatility materials, exposure to heat may (as in the thermal ignition process) generate flammable material by vaporization, sublimation or decomposition. The flash point and fire point tests are examples of standard procedures which provide this kind of information on materials. It should be emphasized that tests for these two processes are quite different. While heat may be the source of combustible vapor in both cases, in the flash point test an ignition source exists, such as a spark, flame or glowing surface. In thermal ignition tests, a critical temperature is sought, below which no ignition occurs. Thermal ignition is thus a measure of the minimum energy required for ignition; flash point is a measure of the heat necessary to provide a combustible mixture.

The third process involves ignition by a spark or arc where the arc is the source of energy producing the combustible vapor as well as the ignition source. Generally the energy in an arc is adequate to accomplish both purposes but the transfer of energy is very inefficient. In any event, this process simulates the events occurring when a circuit is over-loaded or when a short circuit exists.

In order to scan quickly a variety of configurations and to investigate all three mechanisms, several different ignition test configurations were used. Each configuration was selected to provide data in a given environment. There is a strong dependence of experimental apparatus on ignition but there was not adequate time to standardize the various methods in this exploratory study.

EXPERIMENTAL METHODS

Test Chambers and Gas Handling System

The test apparatus consisted of eight 2000-ml. Pyrex resin reaction flasks (Figure 1) mounted in an inverted position to resemble bell jars. Each test chamber could be isolated from the rest so that tests could be conducted in all eight in rapid succession and the test specimens replaced in one or more chambers without interrupting tests in the others. The ported lids were fixed in position and manifolded to a glass vacuum and gas handling system. The remaining ports were used to provide access for electrical connections inside the flasks. These were made vacuum-tight through the use of Kovar-to-Pyrex seals as shown in the example of Figure 2. The ground glass joints were sealed into the flask lids with Apiezon W wax and the main seal of each flask was effected with Kel F high vacuum grease. In all runs, the sample was mounted in a selected configuration with respect to sample size, type and location of heating devices, thermocouples, and arc or spark devices. The flask was then sealed, evacuated to less than 1 mm of mercury pressure, and filled with oxygen to 260 mm (5 psia). A variety of sample treatments and data collection techniques were utilized from this point and these are described separately in the following paragraphs.

Cylindrical Wire Test Configuration (a)

This arrangement (Figure 3) consisted of a cylindrical coil or helix of 20 gauge Nichrome wire approximately 1.5 cm diameter and 3 cm high. The sample was mounted on a 20 gauge iron-constantan thermocouple (TC) in the center of the coiled heater. Voltage was applied to the heater to create the desired heating rate in the sample while temperatures were monitored throughout the test on a strip-chart recorder. In some tests, 50 or 100 ml. beakers were mounted in an inverted position to cover the sample, heater and TC, in an effort to concentrate pyrolysis product gases in the vicinity of the ignition source. Another variation involved the use of high voltage sparks as sources of ignition

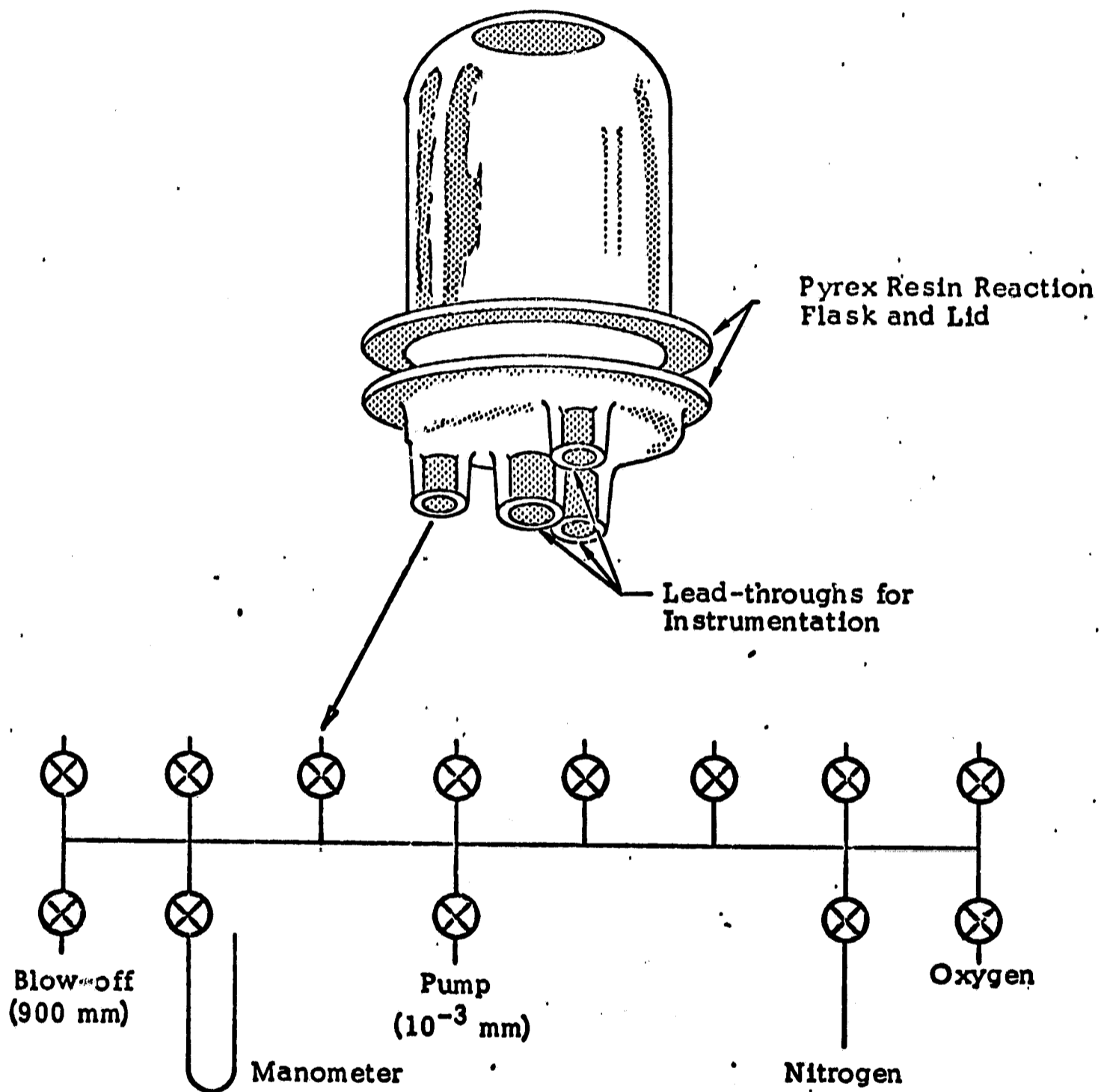


FIGURE 1. Test Chamber and Environment Control System.

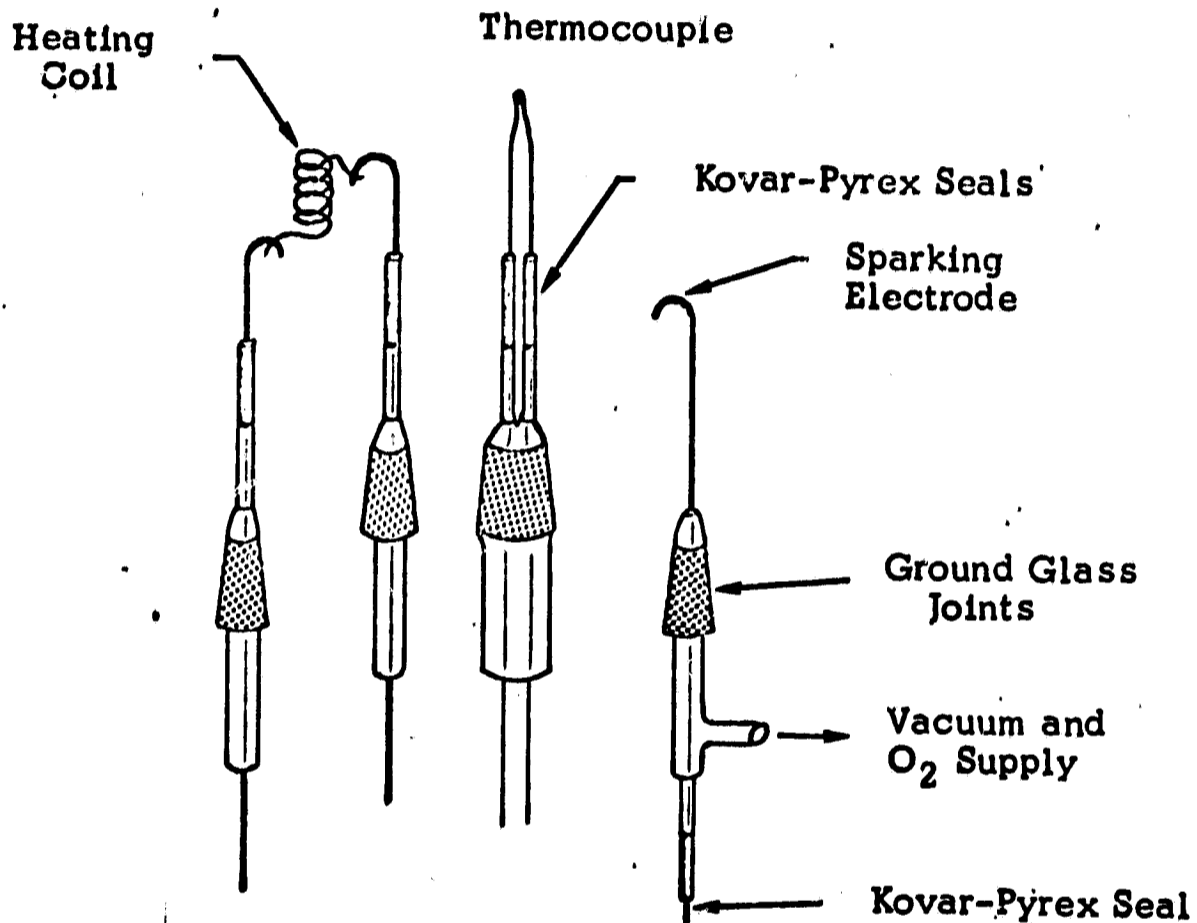


FIGURE 2. Vacuum-Tight Electrical Connections for Test Chambers.

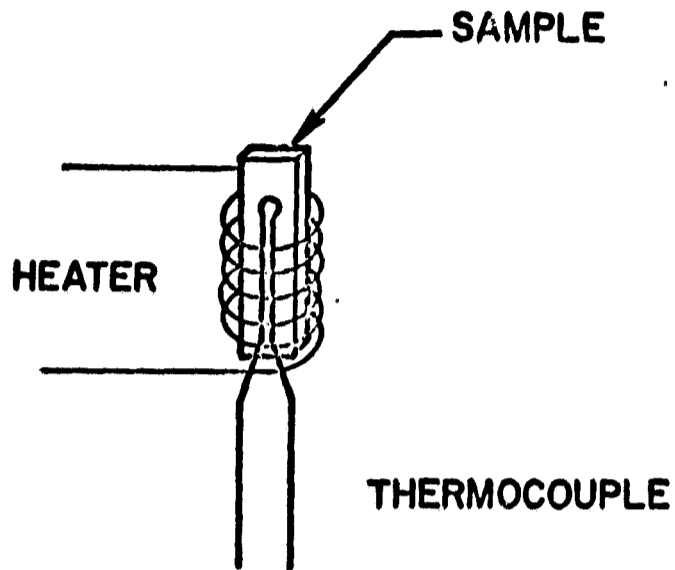


FIGURE 3. Cylindrical Wire Heater Test Configuration (a).

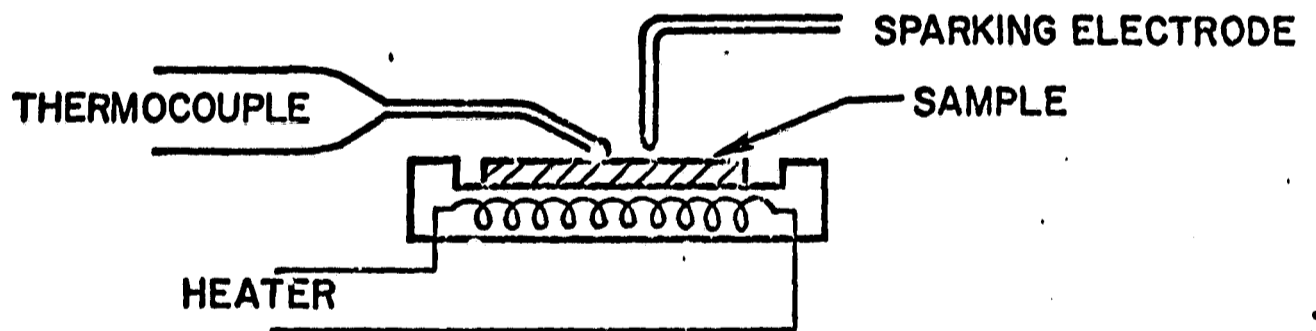


FIGURE 4. Ceramic Cup Heater Test Configuration (b) with Sparking Electrodes.

of the pyrolyzed gases. The additional electrode was usually positioned near the sample, with either the heater or TC acting as the grounded side of the high voltage circuit. In some experiments low energy sparks were obtained from a Tesla coil, while the more usual arrangement involved a 10,000-volt power supply for charging a capacitor, which could then be discharged across a gap in the vicinity of the sample. The capacitors used were 0.0023 - 0.017 μ fd, so that spark energies ($E = 1/2 CV^2$) ranged up to 0.87 joule at 10,000 volts.

Ceramic Cup Test Configuration (b)

Figure 4 shows this arrangement which was a Sauerisen cement-coated Nichrome wire heater in the form of a cup about 3 cm across and 0.5 cm deep. The 20-gauge TC was arranged to exert pressure downward against the sample. Sparking electrodes were used with this test configuration in the same manner as previously described.

Steel Tube Test Configuration (c)

This set-up consisted of a 1-inch diameter by 1.5 inch long stainless steel tube mounted horizontally (Figure 5). The heater wire was encapsulated in cement around the exterior surface of the tube, and a pair of electrodes was positioned in the center. A 20-gauge iron-constantan TC was silver-soldered to the inside surface of the tube, so as to provide measurement of the highest temperature to which the sample was exposed. Since this TC could not respond quickly to temperature changes in the gas phase, the point in time at which ignition occurred was noted visually. A few experiments were conducted with the ends of the tube closed in order to enhance the buildup of pyrolysis gas concentrations within the heater. In these tests, a second TC was placed in the center of the heater to provide information on the time of ignition.

Arc Testing Procedure

Both bare and insulated wires were used in these tests, with 1-5/8 inches of insulation left on in the latter case. These were suspended horizontally above a test sample of Nomex, Neoprene, etc. at distances ranging from 0 to 5 inches. When the atmosphere had been prepared, a current of 114 amperes at 24 volts D.C. passed through the test wire, using a helium arc welding power supply capable of supplying currents to 400 amperes. The current utilized in the tests was shown to be capable of breaking the 20-gauge test wire within one minute.

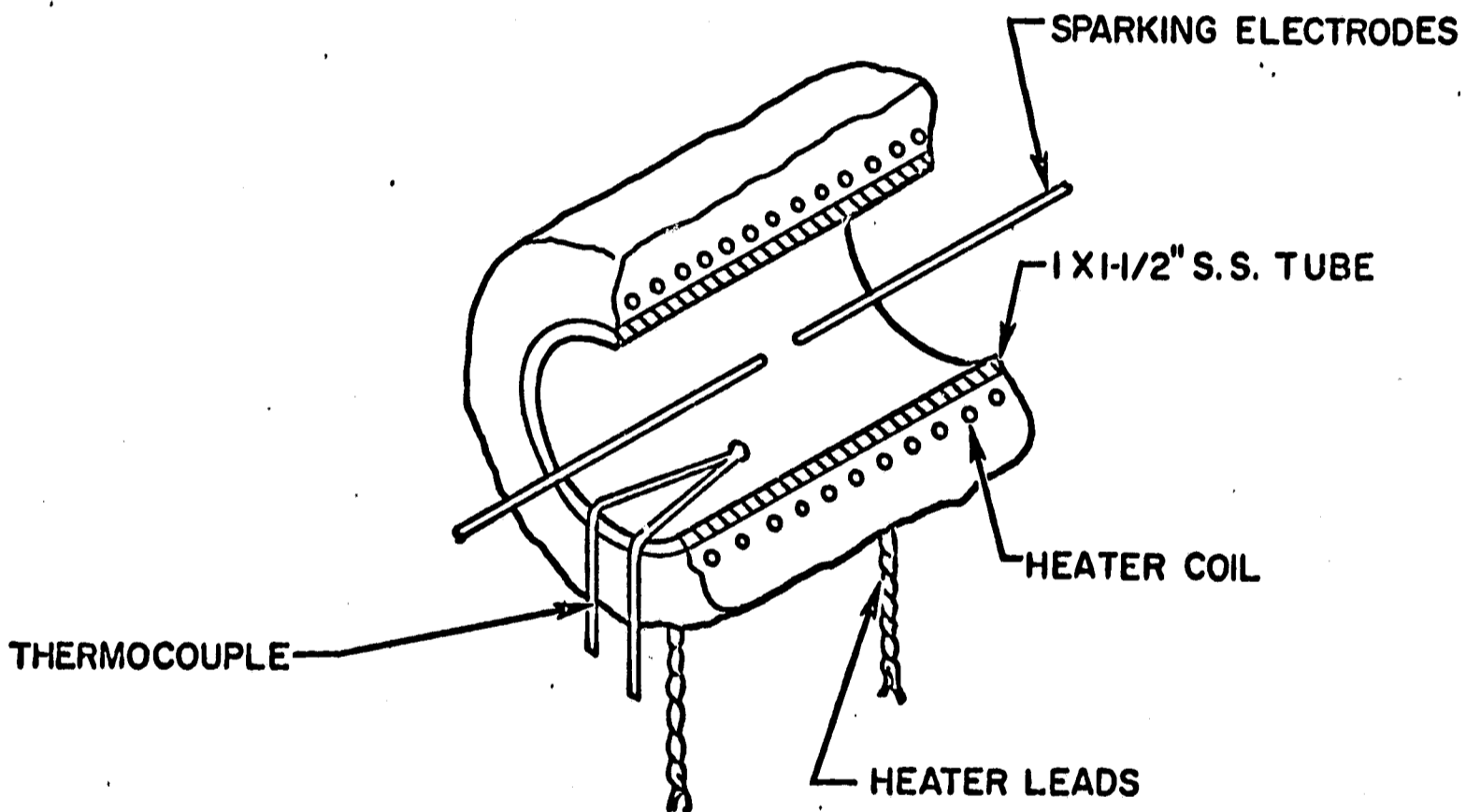


FIGURE 5. Stainless Steel Tube Test Configuration (c).

Photography

The eight test cells were arranged so that each could be viewed clearly and photographs taken of runs in progress. A Bolex 16-mm movie camera was used with Kodak Ektachrome ER449 film. Film strips were examined frame-by-frame with an L and W Photo-Optical Data Analyzer; the results are described in a separate section of this report.

Materials

Nomex (du Pont) was a Nylon fabric purchased in large sheets of 3, 10, and 30 mils thickness. Samples were cut from the sheets.

Neoprene vest fabric (MIL-C-19002) was a chloroprene coated Nylon fabric with a brilliant orange dye, and was obtained from Chemical Rubber Products, Inc. in the form of sheets.

Uralane polyurethane foam was obtained from Furane Plastics, Inc. It is available in a wide variety of properties, but Uralane 579 and 574 were chosen for testing because of their purported resistance to combustion. They are both prepared by mixing resin and hardener portions in place.

RTV-40 (General Electric) was a two-part silicone rubber potting compound which is mixed in place and cured at room temperature.

RTV-7 (General Electric) was a two-part silicone foam rubber, also room temperature cured.

TBS-757 (General Electric) was a two-part oven-cured silicone foam rubber, purported to have good flame resistant properties.

Silicone Sponge Rubber was obtained from L.A. Standard Rubber Co. in 1/4-inch thick sheets.

Armalon (du Pont) was a Teflon-coated glass fabric obtained in sheets.

Polyethylene sheet was a common packaging material of 1 - 3 mil thickness.

Epoxy Paint was a 3-M Velvet-coat 400 Series, obtained in pastel blue and black. The paint was mixed, brushed onto 1 x 1" squared of 1/16 aluminum sheet in a fairly heavy coat, and baked dry at 100°C. A test panel was then placed on top of the ceramic cup heater of Test configuration (b) and the experiment conducted in the usual manner with the TC in contact with the painted surface.

Insulated Wires were of two types, both 20-gauge stranded copper.

Kapton (du Pont) is a polyimide film and Teflon is polytetrafluoroethylene, both of which are purported to possess superior flame resistant properties.

Glycol (ethanediol-1, 2) was used as received and also as prepared to approximate Apollo specifications (Reference 1). For the latter, a solution was prepared containing 62.5% (wt.) glycol, 1.6% triethanolamine phosphate (TEAP), and 0.09% sodium mercaptobenzothiazole (MBT) in water. TEAP was prepared from H_3PO_4 and triethanolamine, while MBT was added in the form of a 50% solution (Nacap, R. T. Vanderbilt Co.).

RESULTS

Introduction

The goal of this program was to seek information concerning ignition mechanisms for spacecraft polymeric materials. Tests were performed on materials, one at a time, starting with the one which we could most readily mount in the test apparatus. Data for Nomex is therefore described first in this report.

As the tests progressed, we continually re-evaluated our techniques and our data and made suitable modifications which we felt desirable. Thus as our tests progressed from one material to another, we found ourselves able to provide greater meaning to our test results and to reduce the variety of different tests required. The results are herein described in that order, with the last several materials providing, in large part, only confirmation of earlier conclusions, and strengthening of the generalizations set forth earlier.

Nomex

A series of tests was conducted to determine the ignition characteristics of du Pont high temperature nylon known as Nomex.

The data obtained in the heated coil apparatus (a) are presented in Table I. The average value of ignition temperature from all runs is 446°C. To illustrate the effect of heating rate, Tests 12 and 23 are compared in Figure 6. Ignition occurred at 475°C and about 50 seconds after heating was initiated in Test 12 while ignition occurred at 350°C and about 50 seconds after heating was initiated in Test 23.

In most gas phase ignition studies the ignition temperature increased exponentially as ignition delay decreased. The opposite trend noted here may be explained by a number of mechanisms. There is a tendency, in some

TABLE I. Nomex Ignition Data in Heated Coil Test Configuration (a).

Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
5	26	475
8	28	510
9	26	475
10	29	530
11	23	420
12	26	475
14	27	490
18	25	455
19	26	475
19a*	19.5	360
19b*	19	350
20	26	475
21*	22	405
22	24	440
23*	19	350

* Fast Heating Rate

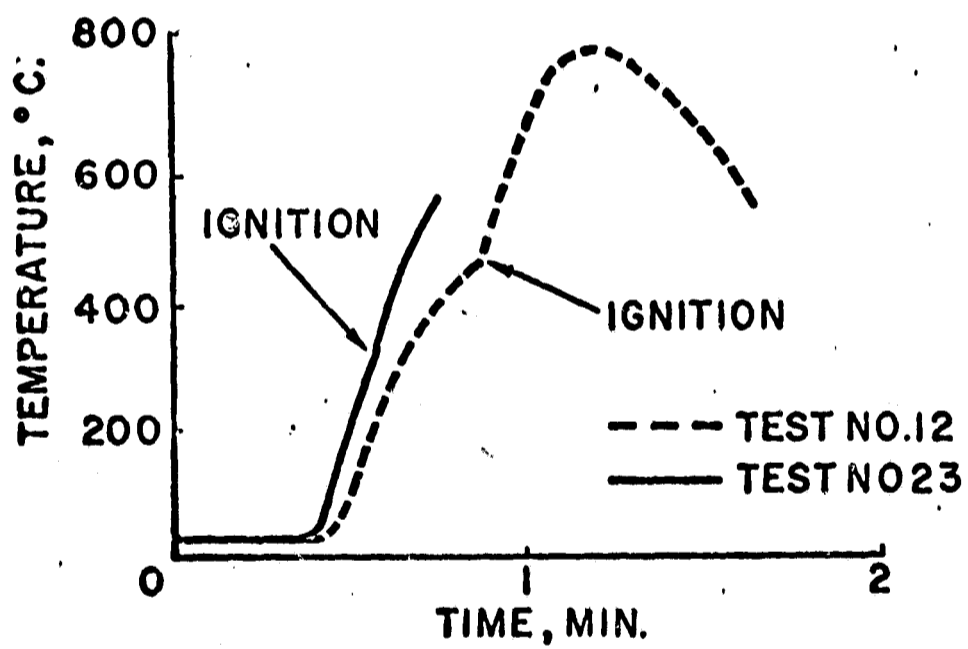


FIGURE 6. Effect of Heating Rate on Ignition of Nomex in Test Configuration (a).

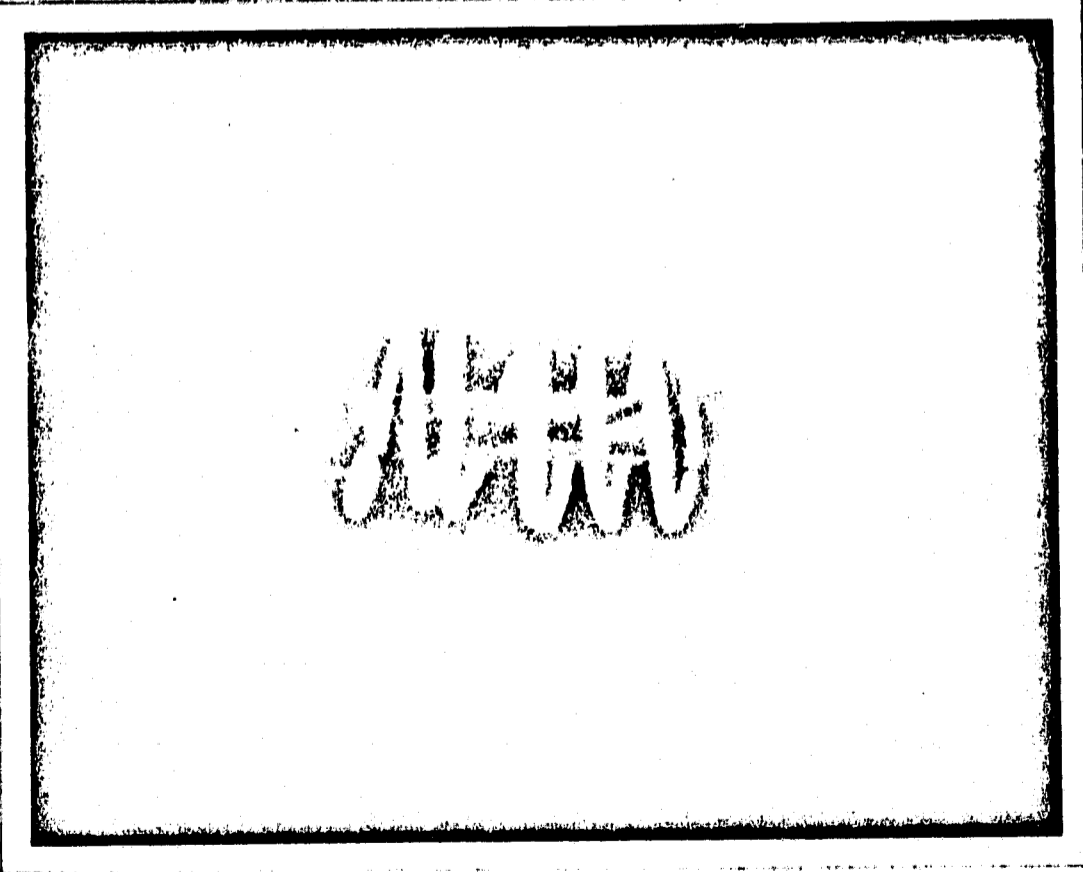
configurations, for the sample to shield the thermocouple from the heat source. This insulation coupled with the inherent lag in thermocouple response would create the situation in which the thermocouple displays greater temperature lags at faster heating rates. It was also evident during the experiments that large amounts of gas were evolved from a sample prior to ignition. Since gas evolution from a sample is a function of temperature, and the local concentration of sample vapors depends upon both temperature and time, the ignition temperature should depend upon the rate of heating. The rate of heating should then be a major factor in establishing the concentration of vapor at the time of ignition.

While it is not possible at this time to establish the exact reason for the decreased ignition temperature with increased heating rate, a dependence of ignition on the gas phase composition appears to be strongly indicated. This point will be discussed again in connection with other materials.

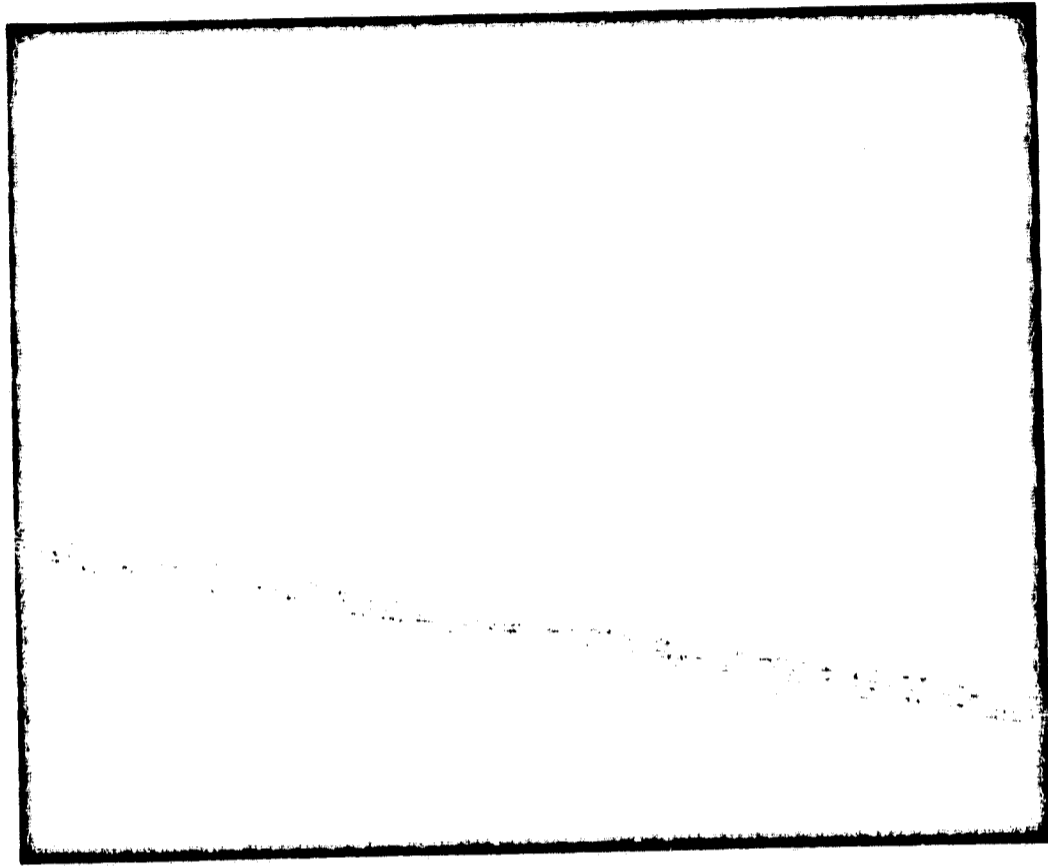
Frame-by-frame examination of motion pictures of some of these tests provided evidence that ignition occurred in the vapor phase, rather than at the solid sample surface. Figure 7 shows the appearance of a vapor flash outside the coiled heater and therefore clearly removed from the vicinity of the sample. The photographs of Figure 7 are 1/16 second apart, and the next frame (not shown) saw the entire sample engulfed in flame.

In order to investigate further the importance of evolved gas on the ignition phenomenon observed, a modified configuration of the heater was investigated. This heater consisted of an essentially flat, ceramic-coated cup and differed from the bare coil configuration in several important respects. The glowing coil, generally hotter than the sample, was removed as an ignition source. Even more important from the standpoint of isolating vapor effects, the heat was applied at one location, permitting the vapor to diffuse away from the heat source. The existence of flammable vapor could thus be detected by means of a spark to determine whether ignition could occur at temperatures below the thermal ignition point.

Several runs were made in test configuration (b) without a spark to provide a comparison with configuration (a). These runs are given in Table II. The average ignition temperature for these runs compares favorably with that from configuration (a) as shown in Table III.



(a)



(b)

**FIGURE 7. Nomex Test in Colled Heater Apparatus Showing Vapor Phase Ignition.
Photograph 1/16 Sec. Apart.**

TABLE II. Nomex Ignition Data in Ceramic Cup Test Configuration (b)		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
62	24	440
96	25.5	465
97	25	455
152*	32	580
Average	--	485
* Long Heating Time		

TABLE III. Nomex Ignition Data Average Results from Test Configurations (a) and (b)		
Configuration	Temperature (°C.)	
	All Runs	Normal Runs Only
(a)	446	474
(b)	465	455

The remainder of the Nomex tests in configuration (b) were performed with a spark ignition source. These results are summarized in Table IV. With minor exceptions, the sample produced sufficient vapor to permit spark ignition at temperatures well below the thermal ignition temperature, including a number of ignitions at sample temperatures below 200°C. There appeared to be some trend for ignition at lower sample temperatures with increased spark energy but the results were not sufficiently reproducible to provide a quantitative relationship.

Both apparatus (a) and apparatus (b) provide reasonably easy diffusion paths for the vapor produced by thermal decomposition of the sample. A third configuration (c) consisting of a heated cylinder was used. The sample was contained within the cylinder and provided a sheltered volume for the accumulation of decomposition products. The results obtained without a spark are given in Table V. These results are slightly higher than those found in configurations (a) and (b). In each case ignition appeared to occur at the open ends of the cylinder, suggesting that the mixture within the cylinder may have been extremely rich in vapor. The spark data (Table VI) obtained in configuration (c) also suggests the existence of vapor conditions differing from those in configurations (a) and (b) since the temperatures associated with spark ignition do not differ greatly from the purely thermal results. This suggests that the mixture within the cylinder may have been very rich in vapor and that the spark failed to cause ignition until the thermal ignition conditions had been achieved near the edge of the cylinder.

Neoprene

A series of tests was conducted to determine the ignition characteristics of Neoprene nest fabric (MIL-C-19002). The data obtained in heater configuration (a) are presented in Table VII. Included in the table are the heating times to ignition associated with each ignition temperature. These are plotted in Figure 8. The dependence of ignition delay on ignition temperature is clearly evident and confirms the less systematic data obtained with Nomex.

Similar data obtained in heater configuration (b) are presented in Table VIII. These data are also plotted in Figure 8 and are compared with the data obtained in configuration (a). Spark ignition data obtained in heater configuration (b) are presented in Table IX. These results appear to show no

TABLE IV. Nomex Ignition Data from Test Configuration (b), Using Spark Ignition Source

Test No.	I-C Thermocouple (mV.)	Temperature (°C.)
58	18	330
63	24	440
67	15	275
69	14.5	265
71	12	220
72	10	185
73	10	185
74	14	255
75	10	185
76	9	165
77*	25.5	465
78	16.5	305
79	17	315
80	17	315
81	15	275
83	18	330
85	17.5	325
86	16.5	305
89	19	350
90	15	275
92	18.5	340
93	20	365
94	15	275

* Weak Spark

TABLE V. Nomex Ignition Data from Test Configuration (c)		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
170	29	525
174	22	400
177	(41)	725
178	29	525
268*	35	630
269*	35	630

* TC attached to wall

TABLE VI. Nomex Ignition Data from Test Configuration (c) Using Spark Ignition Source		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
181	25	455
182	28.5	520
183	29.5	535
184	28.5	520

TABLE VII. Neoprene Ignition Data
from Test Configuration (a)

Test No.	I-C Thermo- couple (mV.)	Temperature (°C.)	Heating Time (Min.)
25	6	115	0.1
26	11	200	0.5
27	23	420	11.0
28	17	315	0.8
29	11	200	0.3
30	13	240	0.4
31	21.5	395	3.0
32	24	440	11.0
33	22	400	5.0
34	8	135	0.2
35	6	115	0.3

TABLE VIII. Neoprene Ignition Data from
Test Configuration (b)

Test No.	I-C Thermo- couple (mV.)	Temperature (°C.)	Heating Time (Min.)
118	29	525	5.5
124	8	135	0.2
125	16	295	1.0
126	28	510	3.3
127	31.5	570	2.0

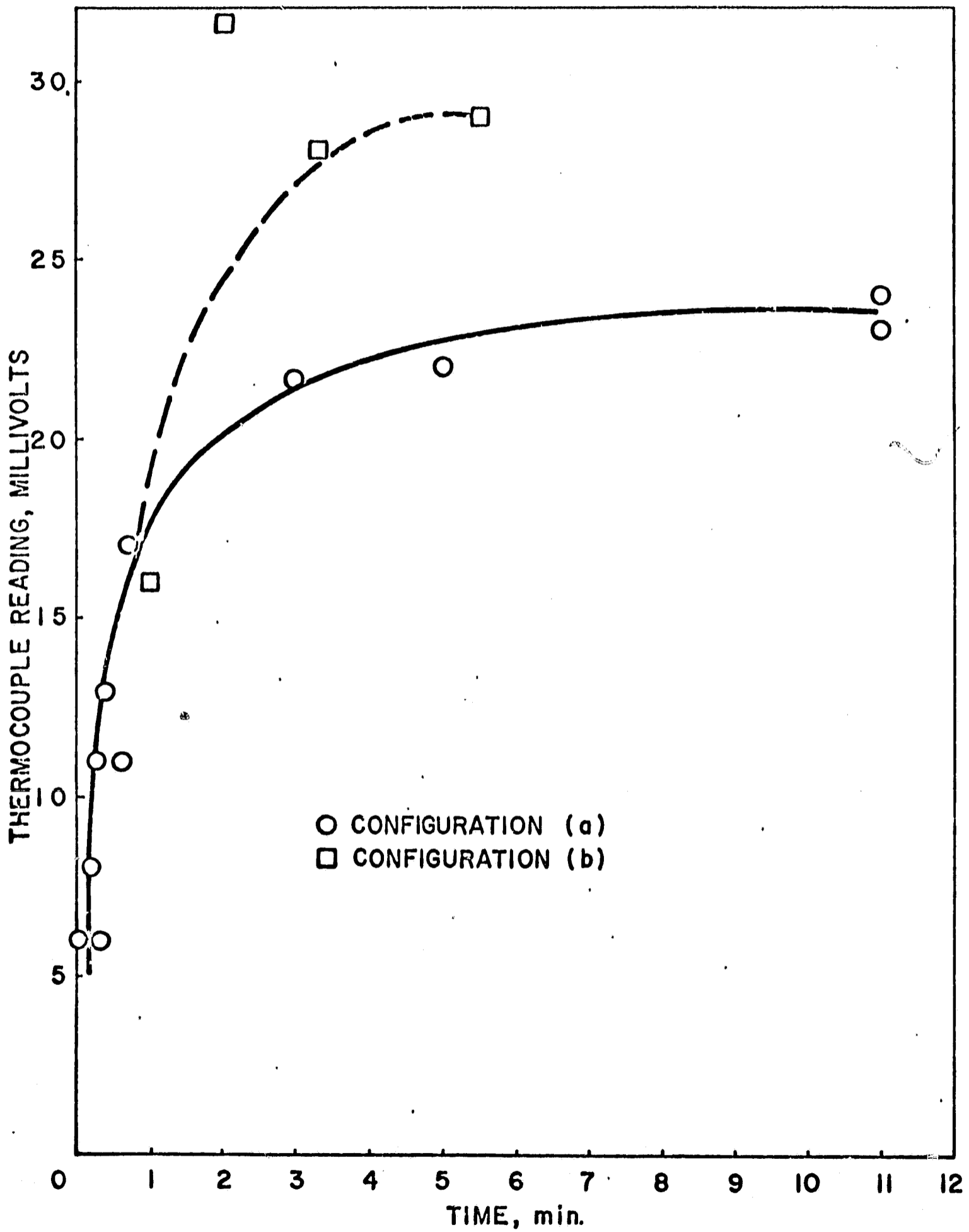


FIGURE 8. Variation of Ignition Temperature with Heating Time for Neoprene Vest Fabric.

TABLE IX. Neoprene Ignition Data for Test Configuration (b) Using Spark Ignition Source

Test No.	I-C Thermocouple (mV.)	Temperature (°C.)	Heating Time (Min.)
128	8.5	160	0.5
129	8.5	160	0.8
130	9	165	0.3
131	8.5	160	0.8
132	9.5	175	1.1
134*	11	205	1.1
135	12	220	1.5
136	9	165	0.8
137	10.5	195	0.8
138	8	150	0.8
139	9	165	0.8
142	10	185	1.0
143*	11	205	2.0
144*	13	240	0.7
145	12.5	230	1.0

* Spark 1.5 cm. above sample

✍

direct trend with ignition time and seem to correspond to the purely thermal ignition data obtained at short delay times.

These results strongly support the mechanism associating ignition temperature with vapor evolution. At rapid heating rates the heater achieves ignition temperature before appreciable vapor has diffused away. A low ignition temperature is thus measured. At slow heating rates, vapor diffuses away as the coil is heating up and a higher temperature is required to supply an adequate vapor concentration. The spark source acts as the site for ignition and is capable of causing ignition as soon as a favorable vapor mixture exists independent of the relationship between vapor formation and heating rate. In the purely thermal ignition mechanism, vapor production and ignition are coupled by their mutual dependence upon the temperature of the heat source. In those experiments where a spark is used, these processes are decoupled since vapor formation depends upon the temperature of the heat source but ignition does not. The spark acts as the ignition source in this case.

Silicone Sponge Rubber

Ignition data for Silicone sponge rubber are presented in Tables X and XI for the two test configurations used. Ignition temperatures are shown graphically as a function of heating time in Figure 9. The general trend is similar to that shown for Neoprene in Figure 8, but the agreement between results from apparatus (a) and apparatus (b) is not as close for Silicone as it was for Neoprene.

Silicone RTV-40

Ignition data for RTV-40 Silicone potting compound measured in the heated coil test configuration (a) are given in Table XII. An average value of 330°C was obtained for these runs at a moderate heating rate. Temperatures as low as 260°C were obtained with rapid heating and as high as 450°C with very slow heating rates.

The results in test configuration (b), the heated cup, are presented in Table XIII. An average value of 330°C was also obtained in configuration (b). Here, too, values in excess of 400°C could be obtained at very slow heating rates.

Ignition data for RTV-40 were also obtained in the heated cylinder test configuration (c). Most of the data used a spark ignition source. Three runs

TABLE X. Silicone Sponge Rubber Ignition
Data in Heated Coil Apparatus (a)

Test No.	I-C Thermo- couple (mV.)	Temperature (°C.)	Heating Time (Min.)
47	24	440	6.0
48	10	185	0.1
49	16.5	305	0.4
59	19.5	355	1.0
60	26.5	480	6.5
61	17.5	325	0.5
64	21.5	395	1.5
141	19	350	1.2

TABLE XI. Silicone Sponge Rubber Ignition Data
in Heated Cup Apparatus (b)

Test No.	I-C Thermo- couple (mV.)	Temperature (°C.)	Heating Time (Min.)
105	16	295	2.0
106	17.5	325	1.7
107	23	420	5.5
108	16	295	3.0
109	17	315	2.5
114	9.5	175	1.2
115	8	150	1.0
116	16	295	1.6
122	19	350	3.5
140	13	240	1.3

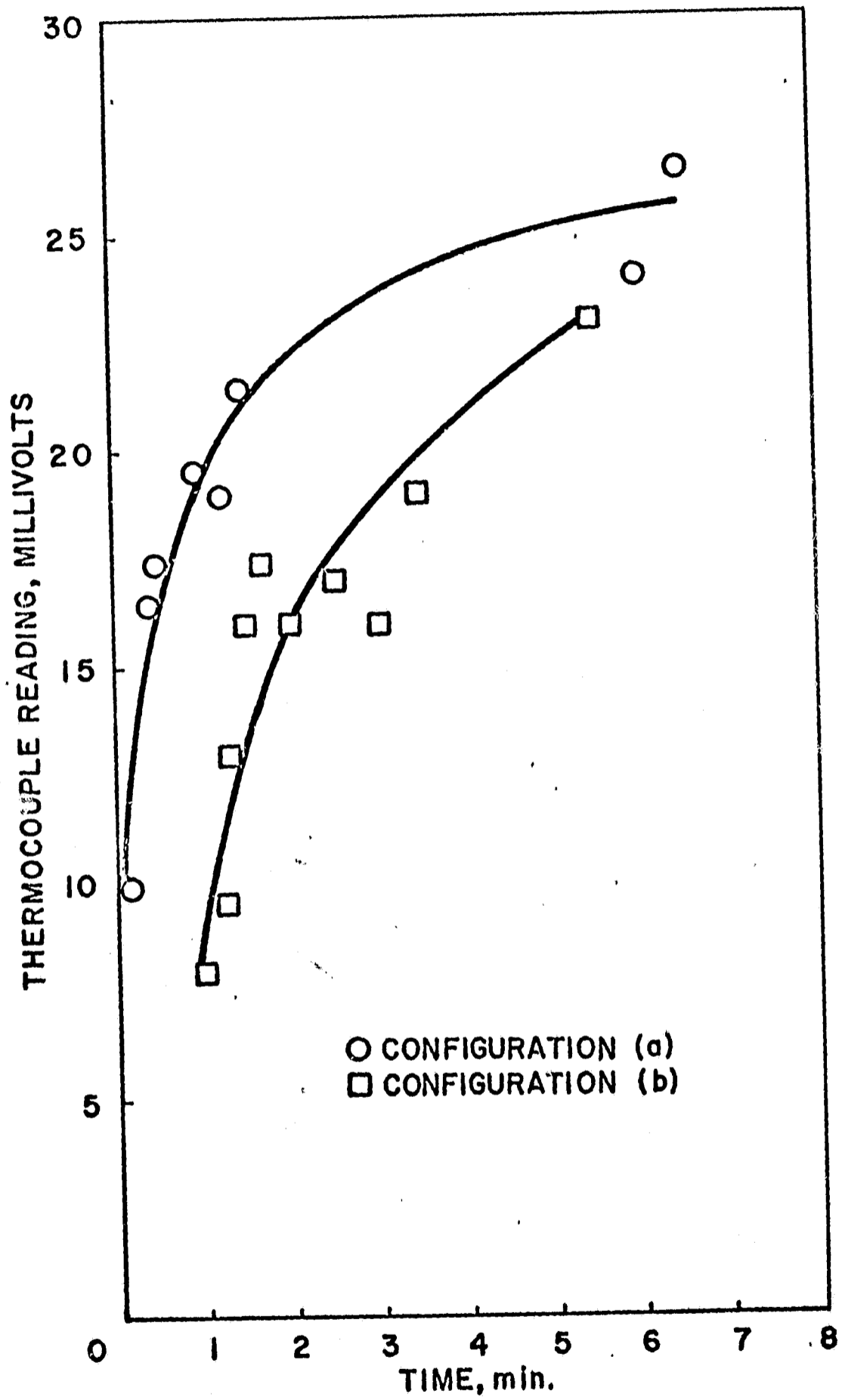


FIGURE 9. Variation of Ignition Temperature with Heating Time for Silicone Sponge Rubber.

TABLE XII. RTV-40 Silicone Potting Compound Ignition Data in Heated Coil, Configuration (a)		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
36	20	365
43	19	350
44	17	315
51	17.5	320
53	18	330

TABLE XIII. RTV-40 Silicone Potting Compound Ignition Data in Heated Cup, Configuration (b)		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
55	18	330
56	17	315
98	18.5	340
99	18.5	340
103	16.5	305
112	19.0	350

made without the spark are shown in Table XIV and indicate somewhat higher values than obtained with test configurations (a) and (b). As with previous materials, sparking showed little effect in configuration (c) as illustrated by the data in Table XV.

Silicone TBS-757

Ignition data for this heat resistant silicone sponge are given in Table XVI as measured in the heated cylinder, Test Configuration (c). Lower temperatures were observed in the same apparatus when a spark ignition source was used. These data are illustrated in Table XVII.

Armalon

The ignition temperatures of Armalon in Test Configuration (c) are presented in Table XVIII. Although there is a slight tendency for the spark data to show a lower ignition temperature, the difference is too small to be significant. This is consistent with other data obtained in Test Configuration (c). Test 220 is of interest since closing both ends of the tube apparently permitted the heated zone to contain a mixture too rich for easy ignition.

Polyethylene

Ignition data for polyethylene sheet are presented in Table XIX. Several runs were made in which thermocouples were placed at two locations within the heated cylinder. One was silver-soldered to the wall and the other placed in the center of the cylinder. These measurements are compared in Table XX.

The high value of the gas temperature compared to the wall temperature signifies considerable exothermic gas phase reaction and further confirms the importance of the gas evolved by thermal degradation on the ignition process. The thermocouple traces for Test 233 are shown in Figure 10 to illustrate the nature of the heating process. These results are in qualitative agreement with the Semenov thermal ignition model (Reference 2). This model establishes ignition by considering heat generated by chemical reaction (\dot{q}_R) and the heat lost from the reactor (heated by reaction) to the isothermal wall (\dot{q}_L). At ignition according to Semenov,

$$\dot{q}_R = \dot{q}_L \quad (1)$$

TABLE XIV. RTV-40 Silicone Potting Compound Ignition Data in Heated Cylinder, Configuration (c)		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
189	26	475
191*	34	615
192	31	565
* Slow heating		

TABLE XV. RTV-40 Silicone Potting Compound Ignition Data in Heated Cylinder, Configuration (c) with Spark		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
186	31	565
187	26.5	485
188	24	440
278	28	510
279	22	405
280	22	405
281	24	440

TABLE XVI. Silicone TBS-757 Ignition Data in Heated Cylinder Configuration (c).		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
266	32	580
267	32	580

TABLE XVII. Silicone TBS-757 Ignition Data in Heated Cylinder Configuration (c) with Spark		
Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
207	23	420
208	23	420
209	22.5	410
211	23.5	430
268	22	405

TABLE XVIII. Armalon Ignition Data in Heated Cylinder Test Configuration (c).

Test No.	I-C Thermo- couple (mV.)	Temperature (°C.)
215	34	615
216	37	665
217	36	645
218*	33	600
220**	No Ign. > 40	715
276***	34	615
277***	33	600

* One End of Tube Closed
 ** Both Ends of Tube Closed
 *** Spark Ignition Source

TABLE XIX. Polyethylene Ignition Data from Heated Cylinder Test Configuration (c).

Test No.	I-C Thermo-couple (mV.)	Temperature (°C.)
162*	22	405
171	18	330
173	22	405
175	18	330
176	18	330
221	26	475
222**	28	510
223	28	510
224***	10	185
225***	19	350
227	25	455
228	25	455
233	23	420
235	22	405

* Obtained in Test Configuration (b)
 ** Spark Ignition Source - Both Ends of Tube Closed
 *** Both Ends of Tube Closed

TABLE XX. Comparison of Wall and Gas Temperature in Configuration (c) for Polyethylene.			
Test No.	Temperature (°C.)		
	Wall	Vapor	ΔT
233	420	545	125
235	405	460	55

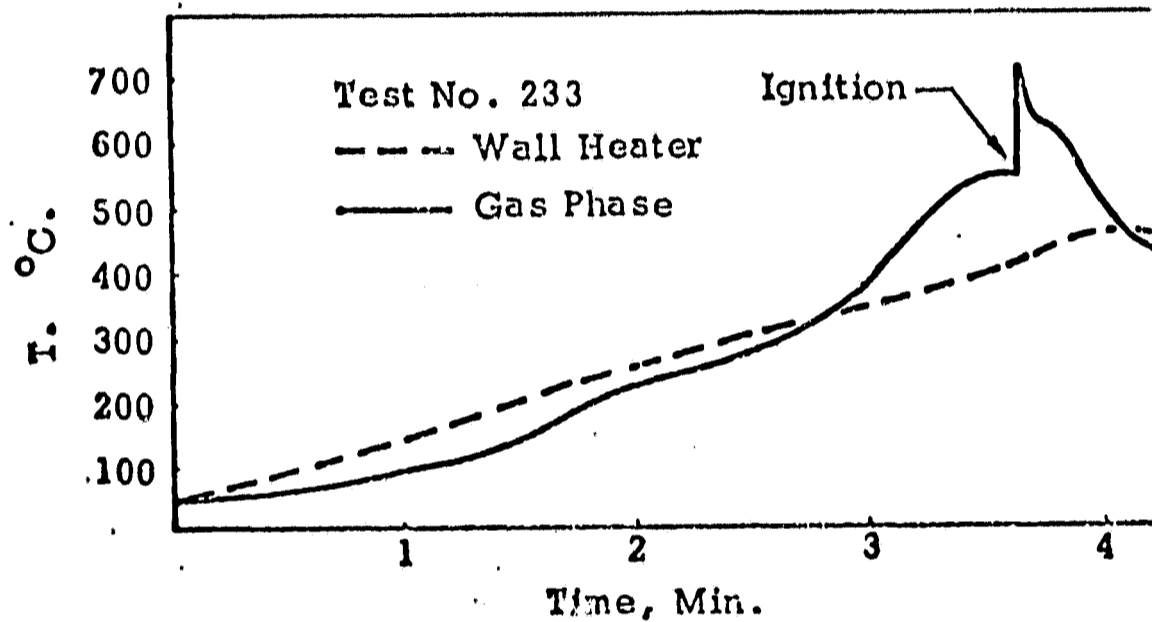


FIGURE 10. Thermal Ignition of Polyethylene

and
$$d\dot{q}_R/dT = d\dot{q}_L/dT \quad (2)$$

If \dot{q}_R and \dot{q}_L are written as

$$\dot{q}_R = f(c)\exp(-E/RT_g) \quad (3)$$

$$\dot{q}_L = h(T_g - T_w) \quad (4)$$

and substituted in (1)

$$h(T_g - T_w) = f(c)\exp(-E/RT_g) \quad (5)$$

Differentiating (3) and (4) with respect to T

$$d\dot{q}_R/dT = (E/RT_g^2)f(c)\exp(-E/RT_g) \quad (6)$$

$$d\dot{q}_L/dT = h \quad (7)$$

and substituting in (2)

$$h = (E/RT_g^2)f(c)\exp(-E/RT_g) \quad (8)$$

Comparing (5) and (8) yields

$$T_g - T_w = RT_g^2/E \quad (9)$$

Throughout the above derivation:

\dot{q}_R = rate of heat generation by chemical reaction

\dot{q}_L = rate of heat loss by conduction

T_g = gas temperature at center of reactor

T_w = wall temperature

$f(c)$ = chemical heat release rate dependence on concentration

E = reaction activation energy

R = universal gas constant

h = heat transfer coefficient

Thus the condition ensuring thermal initiation is that the initial self-heating of the mixture due to reaction must exceed a certain critical value $\Delta T > RT_g^2/E$. Using this relationship ΔT 's of 10 - 50°C. are found from reasonable assumed values for T and E. In other words, the result of Semenov's

model is a semi-quantitative prediction of our experimental findings.

Contamination and Clean-up

One of the possible environmental factors which can influence ignition of a material is its contamination by some other material. In the Apollo system there existed the possibility that some materials were contaminated by the spilling of an inhibited glycol-water heat transfer fluid. Such spills were, in practice, "decontaminated" by wiping the exposed surfaces with methyl ethyl ketone (MEK).

Our effort here was concerned with the determination of ignition characteristics of the Apollo glycol coolant (Reference 2). The data obtained are presented in Table XXI.

In almost all cases, a plateau in sample temperature was observed at about 175°C. This corresponds to the boiling point of glycol. Ignition was generally not observed until temperatures of the order of 220°C to 315°C were attained. In each case, ignition was caused by a spark in the gas phase flammable mixture. The differences in temperature probably correspond to variations in time associated with establishing a flammable mixture rather than with differences in ignition characteristics.

Several runs were made in which sample materials were wet with glycol and placed in the ignition apparatus. In the course of heating, dense clouds of vapor were released and the ignition was characteristic of glycol rather than of the sample material. It must be concluded, therefore, that under conditions where appreciable contamination of glycol can occur, the ignition will be characteristic of the glycol unless the sample has been heated slowly and all the liquid vapor driven out of the region of the ignition source before the latter is activated.

Similar results were obtained when the sample materials were treated with MEK. Data for mixtures of glycol and MEK are presented in Table XXII. The average temperature for spark ignition of the heated mixture is about 143°C., which is well above the boiling point of MEK (80°C.) but below that of glycol (197°C.), and possibly corresponds to the boiling point of the mixture. The values for glycol and MEK represent flash points and are well below the thermal ignition temperatures of about 430°C. (Reference 3).

TABLE XXI. Ignition Data for Apollo Glycol Coolant Mixture.

Test No.	I-C Thermo-couple (mV.)	Temperature
285	17	315
286	17	315
287	17	315
288	17	315
290	17	315
291	12	220
292	12	220

TABLE XXII. Ignition Data for Apollo Glycol, Coolant-
MEK Mixture

Test No.	I-C Thermo- couple (mV.)	Temperature (°C.)
293	10	185
294	11	205
295	6.5	120
296	7	125
297	5	95
298	8	150

Samples contaminated with glycol tend to show the ignition characteristics of glycol while those contaminated with MEK behave like MEK. Samples showed no unusual residue effects after having been soaked in these liquids and subsequently dried out.

Arc Ignition

In order to investigate the ignition process associated with electrical arcs, where the arc acts as both the heat and ignition source, a series of tests was conducted in which insulated wires were overloaded to destruction in the vicinity of various other materials.

Several preliminary experiments revealed the current overload level required to achieve reproducible destruction of the wires. It was found that 114 amperes at 24 volts D.C. invariably broke the wires 30-45 seconds after current application, regardless of whether the wires were bare or insulated with Kapton or Teflon.

The insulating materials invariably burned, melting and falling from the wire as they did so. The molten, burning insulation constitutes only one of two sources of ignition for materials located in the vicinity of the wire. At some time, independent of when the molten insulation left the wire, the wire would "explode," sending showers of molten copper in all directions. These droplets were capable of creating 1/16" deep pits in the Pyrex glass walls of the test chamber. They also caused frequent ignition of the materials being tested. This however seemed to require at least momentary contact with the sample. Rather, the droplet was often seen to bounce from the sample without causing ignition, especially in tests with hard-surfaced materials like Armalon.

These observations are illustrated in Figures 11 and 12. In Figure 11, a Silicone TBS-757 sample is seen to be ignited by the melted, burning Teflon after an impinging copper droplet had failed to cause ignition. Figure 12 shows a Uralane 579 sample ignited by a molten copper droplet.

Thus, it is seen that ignition of a test material located near an overloaded wire can be caused either by the molten metal of the wire or the burning insulation, and that no priority appears to exist between the two modes of ignition. Indeed, some experiments of this type resulted in no ignition from any source.

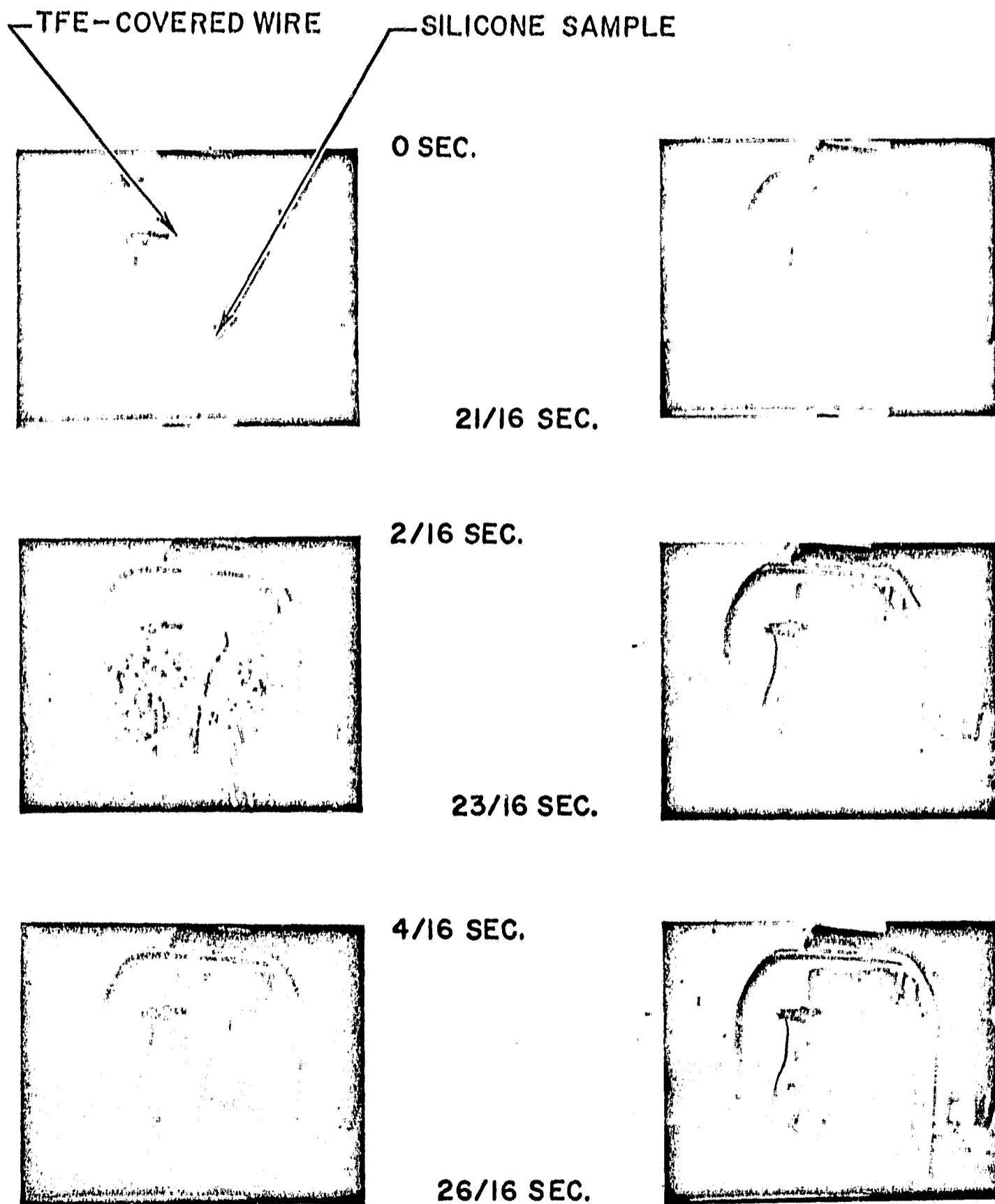
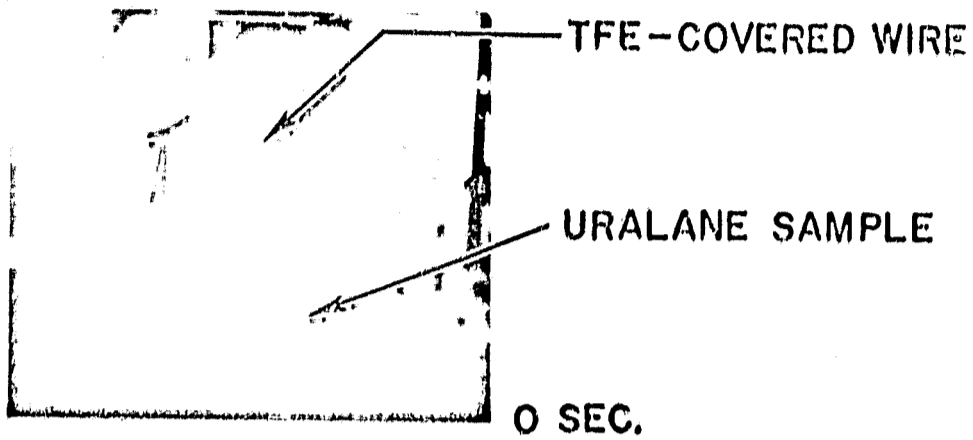
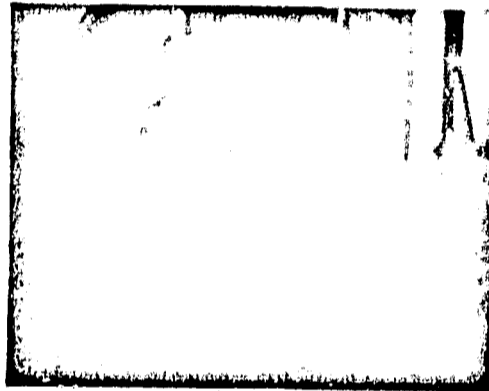


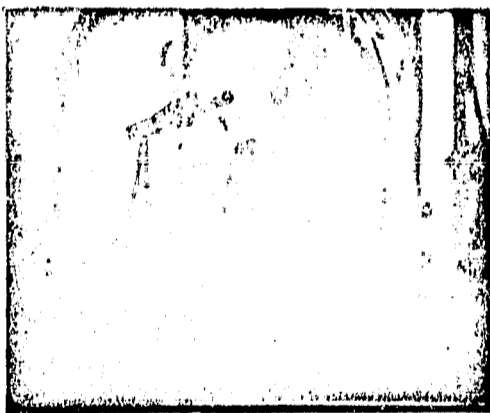
FIGURE 11. Wire Overload Test No. 464. TFE-Covered Wire 3" Above Silicone TBS-757 Sample.



69/16 SEC.



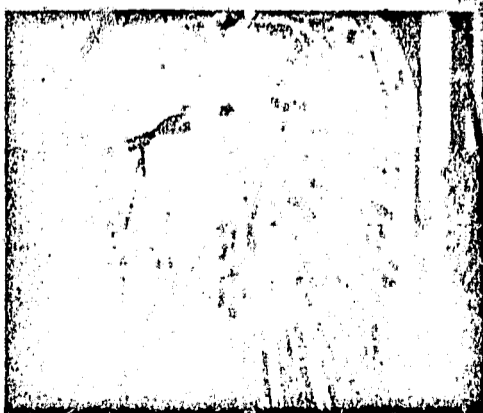
102/16 SEC.



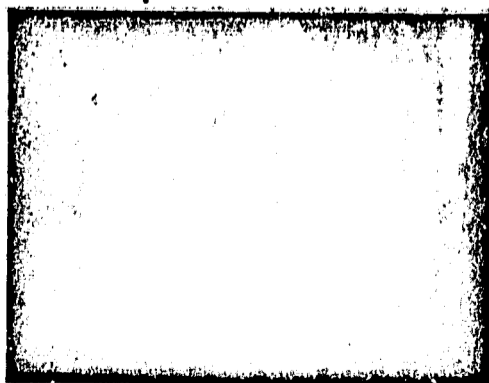
95/16 SEC.



103/16 SEC.



97/16 SEC.



108/16 SEC.

FIGURE 12. Wire Overload Test No. 601. TFE-Covered Wire 2 1/2" Above Uralane 579 Sample.

It should be noted that we originally intended to obtain data on exclusion distances for ignition of various materials by the arc. However, it was found that ignition often occurred in materials placed up to 5 inches (maximum for the test apparatus) away from the over-loaded wire. From our observations, the temperature of the molten particles and of the burning insulation was probably sufficient to ignite materials at distances significantly greater than those measured.

Flame Propagation and CF_3Br

A portion of this program was to have been devoted to the determination of flame propagation rates and the effects of CF_3Br .

We began our program with ignition experiments in 100% O_2 at 5 psia. Early in this phase of the work, we realized that the complexities of ignition in the presence of different types of ignition sources was going to consume the majority of the technical effort available for this program.

Rather than run a few hastily contrived tests on such an important subject, we felt it best to devote our entire technical effort to ignition and arc studies. To meet our contractual commitments with respect to flame spread and CF_3Br effects, we plan to draw upon the results of our current Air Force contract AF33(615)-2257 for this data. These tests are currently being conducted in oxygen-enriched atmospheres and in the presence of various potential extinguishing agents, including CF_3Br . Perhaps the most attractive aspect of this program is the fact that no experimental shortcuts need to be made, since the work will be carried out in the Dynamic Science combustion monitor at Wright-Patterson, utilizing personnel already highly skilled in the performance of such studies.

III.

SUMMARY

The following points summarize the results and conclusions of the work described in this Report:

A. Thermal ignition studies carried out on selected spacecraft materials showed that ignition occurs in the vapor phase of flammable decomposition products released in the thermal degradation of the polymeric sample. Purely thermal ignition tends to occur above 450°F for all of the solid materials studied.

B. The introduction of a spark ignition source nearly always reduces the sample temperature required for ignition. The presence of a potential contaminating liquid (such as glycol or MEK) on the solid sample tends to yield ignition characteristics of the liquid rather than of the base material. The presence of two liquids (glycol and MEK) produced ignition characteristics of the lower boiling liquid (MEK).

C. Electrical (arc) ignition of flammables in 100% oxygen at 5 psia occurred as a result of the impingement of molten and burning particles of metal and insulation and not by direct transfer of energy from the arc. The conversion of electrical energy to heat caused the ignition of insulating materials such as Teflon and ultimately to "explosion" of the wire. Either phenomenon was capable of causing ignition in other materials up to 5 inches away. This was the maximum distance used in our tests, but it appeared that ignition at significantly greater distances was certain. Contamination by glycol and clean-up by MEK affect the quantitative nature of the results by introducing volatile flammables but do not affect the basic mechanism of ignition.

D. Flame propagation data and the effects of flame suppression agents (such as CF_3Br) are currently being investigated by Dynamic Science under an Air Force contract at WPAFB. The results of these studies will be forwarded as an addendum to this Report as soon as they have been completed.

IV

REFERENCES

1. Jackson, J. D., P. D. Miller, F. W. Fink, and W. K. Boyd, "Corrosion of Materials by Ethylene Glycol--Water," Report 216, DMIC, Battelle Memorial Institute, Columbus, Ohio, May 10, 1965.
2. Semenov, N. N., "Some Problems in Chemical Kinetics and Reactivity," Volume 2, Translated by M. Boudart, Princeton University Press, (1959).
3. Mullins, B. D., "Spontaneous Ignition of Liquid Fuels," AGARDograph No. 4, Butterworths, London (1955).