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AFOSR 69-1250TR

COMPOSITE SOLID PROPELLANT IGNITION MECHANISMS

FINAL REPORT

APRIL 1969

CONTRACT NO. F44620-68-C-0053

Prepared for

THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
OF THE OFFICE OF AEROSPACE RESEARCH
UNDER CONTRACT NO. F44620-68-C-0053

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April 1969

COMPOSITE SOLID PROPELLANT IGNITION MECHANISMS

Research and Advanced Technology Department
UNITED TECHNOLOGY CENTER
Division of United Aircraft Corporation
Sunnyvale, California

FINAL REPORT

Prepared by

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The Air Force Office of Scientific Research
of the Office of Aerospace Research
Under Contract No. F44620-68-C-0053

FOREWORD

The author wishes to acknowledge the assistance of Mr. J. E. Erickson in conducting the experimental portions of this program. The research was performed in the Propulsion Research Branch under the cognizance of Dr. R. O. MacLaren. The program was under the overall management of the Air Force Office of Scientific Research, Directorate of Engineering Sciences, Propulsion Division (Dr. B. T. Wolfson).

ABSTRACT

This report describes the results of an experimental study of the thermal decomposition characteristics of composite solid propellant fuel components. Variations in heating rate, pressure, environmental gas, and polymer type were studied. Supplementary propellant ignition tests utilizing arc-imaging furnace and ionization gap techniques were conducted to obtain information relating onset time of a gas-phase reaction to propellant ignition times via radiant heating.

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ABBREVIATIONS

AP	ammonium perchlorate
CEC	Consolidated Electrodynamics Corp.
CENCO	CENCO Instrument Corp.
CTPIB	carboxy-terminated polyisobutylene
CTPB	carboxy-terminated polybutadiene
dc	direct current
DSC	differential scanning calorimeter
HAP	hydroxylamine perchlorate
HDP	hydrazine diperchlorate
Hy -Cal	Hy-Cal Engineering Company
ID	inside diameter
L/C	inductor/capacitor
NaCl	sodium chloride
OD	outside diameter
PBAA	polybutadiene-acrylic acid
PBAN	polybutadiene-acrylic acid-acrylonitrile
PBD	polybutadiene
PEK	PEK Inc.
PIB	polyisobutylene
PU	polyurethane
UTC	United Technology Center

SYMBOLS

a	constant
C_i	capacitor component, i^{th} component of capacitor/inductor unit $1 \leq i \leq 6$
Δh_{eff}	effective heat of decomposition
ℓ	critical depth of the solid
L_i	inductor component, i^{th} component of capacitor/inductor unit $1 \leq i \leq 6$
Q	calories/unit area
ΔT	temperature difference
w	weight loss/unit area

1.0 INTRODUCTION

Composition changes in composite solid propellants have resulted in significant differences in the ignition and combustion processes.(1, 2, 3)[*] The effects of compositional parameters on propellant ignitability were evaluated during previous research in which ignition characteristics of conventional composite solid propellants and model polymer-oxidizer composite systems were examined in a shock tube and an arc-imaging furnace.(1) The influence of systematic variations in the binder, oxidizer, catalyst type, metal additives, oxidizer particle size and concentration, and reactivity at the oxidizer/fuel interface on propellant ignition characteristics were assessed.

The binder and oxidizer components of the solid propellant exerted the major influence upon radiant energy ignition characteristics. In AP propellants, the minimum initial pressure for achievement of ignition was a function of the binder thermal stability. Propellants formulated from PIB and PU exhibited minimum pressures for which ignition can be achieved of 0.4 and 0.15 atm. These polymers were more susceptible to endothermic thermal decomposition than were CTPB and PBAN. As such, similar CTPB and PBAN propellants have a minimum pressure for ignition of 0.03 and 0.06 atm, respectively.

The effect of oxidizer variation on radiant energy ignition characteristics was explored using a series of perchlorate oxidizers. For propellants with the same fuel component, ignition ease and minimum ignition pressure were a direct function of oxidizer thermal stability. A PIB-AP formulation exhibits a minimum ignition pressure of 0.8 atm, while similar PIB-HAP and PIB-HDP propellants have minimum pressures of 0.03 and 0.005 atm, respectively.

Knowledge obtained from these studies has clarified some aspects of composite propellant ignition, but a multitude of fundamental questions remain to be answered regarding the chemistry of the ignition process. The kinetic process is the least understood because under actual combustion conditions the kinetic details are encumbered by the presence of hydrodynamic, energy, and mass transport processes. Moreover, the kinetic mechanism is complex. The decomposition kinetics of the

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[*] Parenthetical superscript numbers refer to references appearing on page 47.

simplest propellant ingredients are usually unknown, or known only at low temperatures. The rate expressions for the various parts of the kinetic mechanism are vital terms of the conservation and energy equations and their boundary conditions which govern the behavior of the system. Therefore, accurate kinetic data are requisite for experimental ignition and combustion data interpretation and for theoretical combustion model refinement.

Based on the present state of knowledge on composite solid propellant ignition and combustion kinetics, there is a serious lack of factual information on ingredient decomposition processes under actual ignition and combustion conditions. The problem is especially acute in the area of polymer decomposition.

It seems likely that the relative rates of competing pyrolysis mechanisms for polymers are changed as the temperature and heating rates increase. Heating rates less than 100°C/min typify most pyrolysis studies, while in propellant combustion the polymer is heated at the rate of thousands of degrees/second. Thus, because of the high-temperature gradient in combustion, low-temperature pyrolysis reactions do not proceed to a significant extent and high-temperature reactions are probably dominant.

The results of conventional bulk polymer decomposition studies provide an understanding of the parameters which influence polymer decomposition, but require critical interpretation when applied to composite propellant ignition and combustion processes analysis. Some fundamental mechanisms of polymer decomposition, such as random or weak-link scission, are expected to occur at various stages of the ignition and combustion process, but their rates and energetics may be markedly altered by high heating rates and the presence of solid and gaseous oxidizers.

The objective of this program was to investigate the decomposition mechanisms of organic polymers under transient heating conditions. In the course of the program it was planned (1) to study the factors affecting the decomposition of individual representative polymer systems, (2) to develop a description of the overall kinetic mechanisms for polymer degradation under propellant combustion conditions, and (3) to use the resultant information to foster development of quantitative propellant ignition and combustion theories.

2.0 SUMMARY

The thermal decomposition characteristics of composite solid propellant fuel components were studied using DSC, radiation furnace, and flash-heating techniques. PIB, PU, and PBDs were selected as representative fuel systems.

At a heating rate of 10°C/min and 1-atm nitrogen in the DSC, PIB began to darken at 225°C and commenced melting at 240°C. Bubbling and rapid fume-off occurred from 280° to 360°C, and decomposition was complete at 410°C. PU was observed to melt at 215°C with fuming beginning at 250°C; decomposition was complete at 400°C. Under similar conditions, the PBDs did not evidence any decomposition until 300°C with the major decomposition occurring in the temperature range of 450° to 500°C. The presence of oxygen promoted the decomposition of the polymers, particularly the PBDs; oxygen also lowered the temperature zone of decomposition and altered the mode of decomposition.

In the pyrolysis studies performed with the flash tube and radiation furnace, PIB and PU polymers exhibited a greater weight loss than the PBDs under equivalent incident energy levels. Following a thermal induction time, weight loss measurements in the radiation furnace showed that weight loss increased with heating rate at the same total energy input. Therefore, surface temperature is apparently the most important factor in the polymer decomposition reactions under these heating conditions. PBD decomposition appears to be dependent upon irradiance level, such decomposition being more endothermic for flash heating than for moderate radiant heating.

Supplementary propellant ignition tests utilizing arc-imaging furnace and ionization probe techniques were conducted to obtain information relating onset time of a gas-phase reaction to propellant ignition times via radiant heating. At moderate flux levels (10 to 20 cal/cm^2-sec) and pressures near 1 atm, ignition and onset times for gas-phase reaction nearly coincide. As the flux level is increased at atmospheric pressure, there is an indication of a minimum exposure time for ignition even though a gas-phase reaction is observed in a somewhat shorter time. The time difference between the gas-phase reaction onset and the ignition exposure time increases at subatmospheric pressure. For successful ignition of a PU propellant at a flux of 42 cal/cm^2-sec and 0.5 atm, the exposure

time must exceed approximately 132 msec, even though an ionization probe signal is noted at 95 msec. These results indicate that the establishment of a state of reactivity at the propellant surface and in the adjacent gas phase is a necessary, but not sufficient, condition for ignition.

3.0 EXPERIMENTAL APPARATUS AND PROCEDURES

A DSC, a radiation pyrolysis furnace, and a flash tube were the major experimental tools utilized to investigate polymer decomposition. Propellant ignitability tests using an ionization probe with an arc-imaging furnace were also conducted.

3.1 DIFFERENTIAL SCANNING CALORIMETER

The DSC used in this study was a Perkin-Elmer model DSC-1B. The sample enclosure has a see-through window permitting observation during decomposition. Figure 1 shows the auxiliary instrumentation and the DSC which has an operating temperature range of 173° to 773°K and can be programmed for heating rates up to 80°C/min.

3.2 RADIANT PYROLYSIS APPARATUS

The low-flux radiant pyrolysis equipment illustrated in figures 2 and 3 consists of a 1-in. OD quartz or Pyrex tube partly surrounded by 11 quartz lamps of 500 w each. The entire assembly is enclosed by a water-cooled nickel-plated stainless steel reflector. A graphite sample boat which fits into the tube is machined to hold a fuel sample and a Hy-Cal asymptotic water-cooled calorimeter. By connecting the Pyrex tube to a suitable gas supply, experiments can be conducted in a controlled atmosphere. A continuous gas flow of 30 cm/sec was maintained in all atmospheric pressure tests to sweep out decomposition products, thereby reducing attenuation of the radiant flux.

The heating unit is controlled by a variable autotransformer which supplies a maximum of 140 v. A voltmeter and ammeter are used to directly measure the power input to the lamps. The heat flux delivered to the surface is measured with a Hy-Cal asymptotic water-cooled calorimeter (model C-1302-A-100-004-072).

Polymer samples were prepared by casting the polymer solution into graphite containers having 0.625-in. OD, 0.50-in. ID and 0.25-in. length. Following curing of the polymer, the graphite container and cured polymer were inserted directly into the main sample holder. Pyrolysis runs were conducted by exposing individual fuel samples for measured time intervals. Sample weight loss as a function of flux level and exposure time was determined for each test.

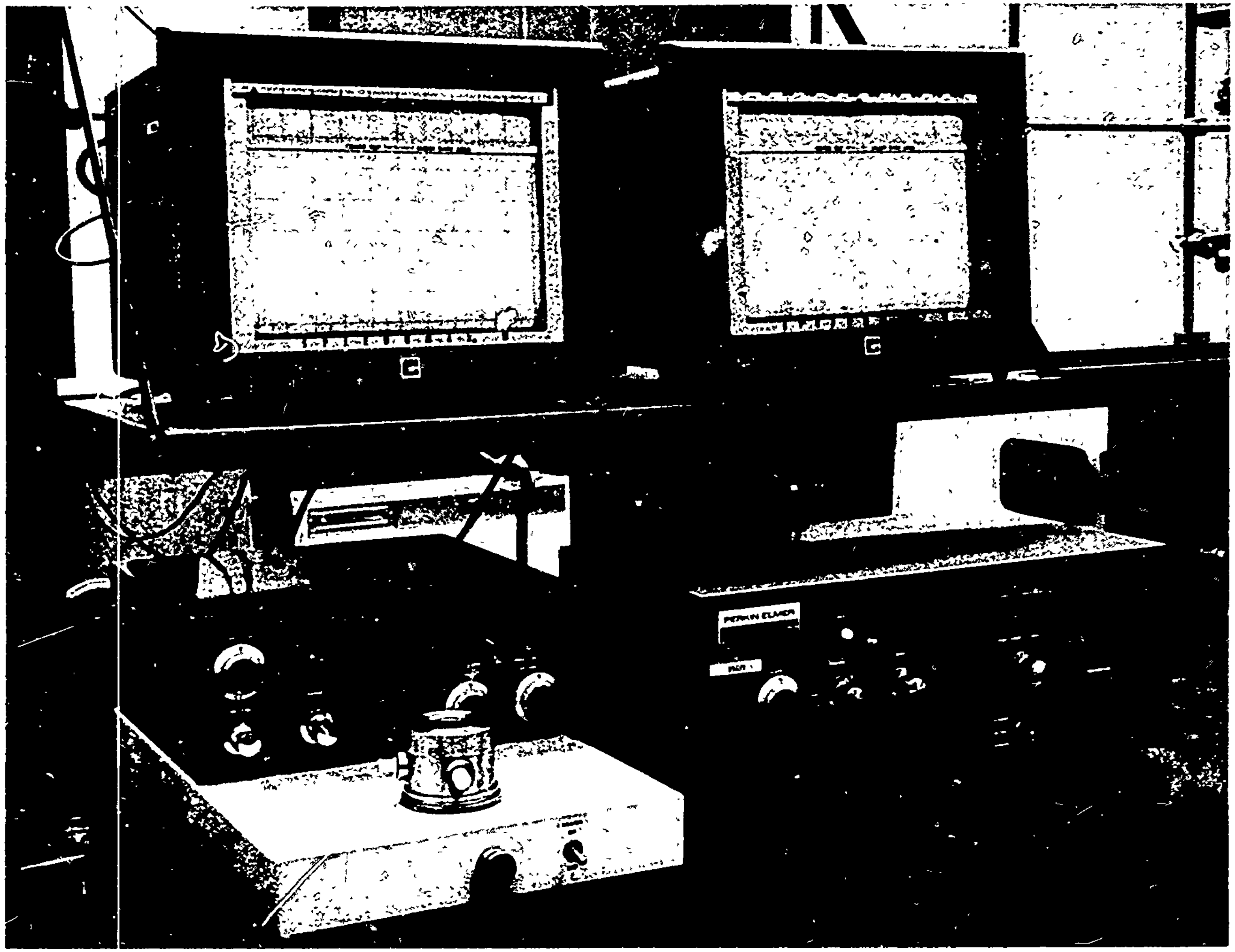

Figure 1. Differential Scanning Calorimeter and Auxiliary Instrumentation

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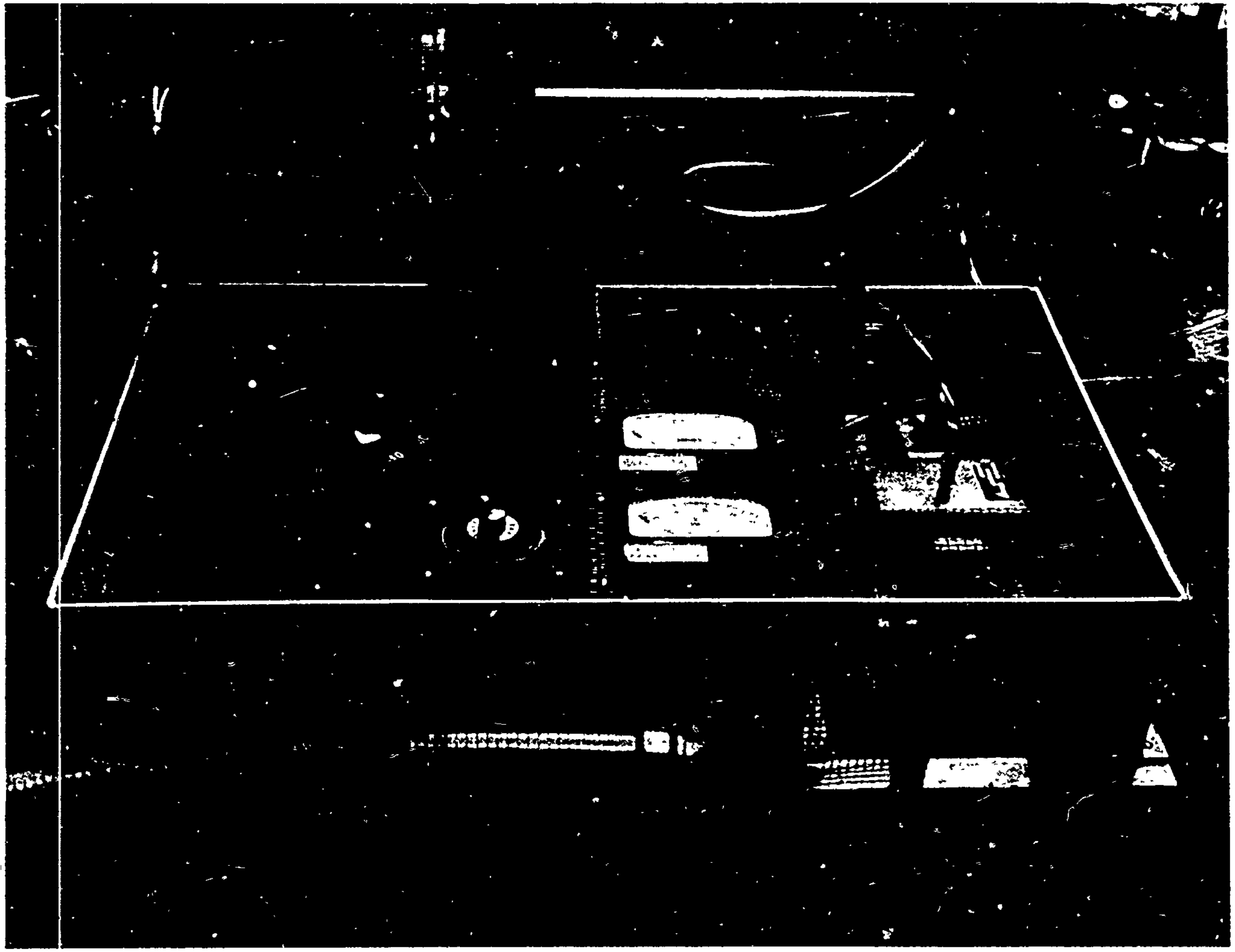

Figure 2. Radiation Furnace

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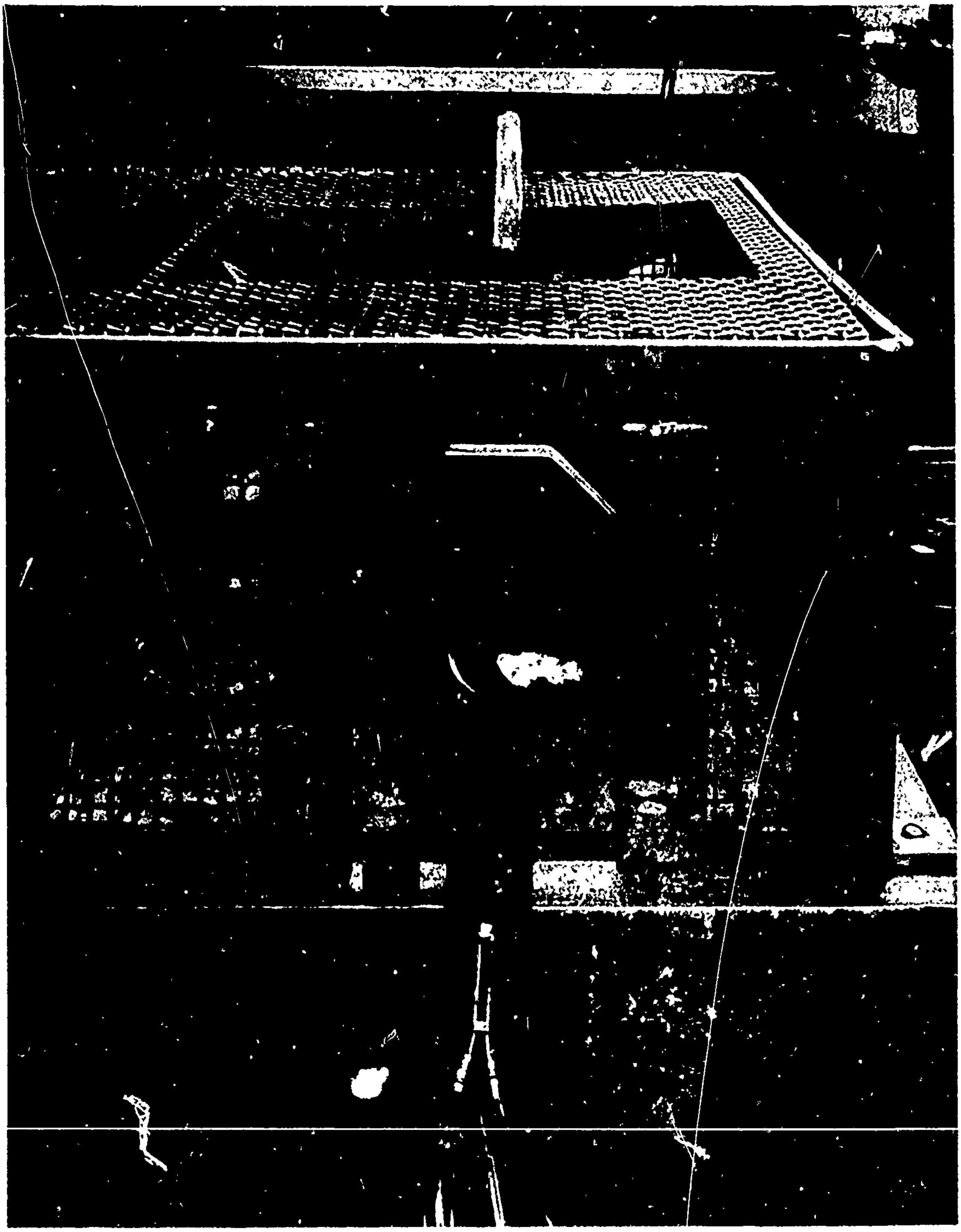

Figure 3. Sample Boat and Calorimeter for Radiation Furnace

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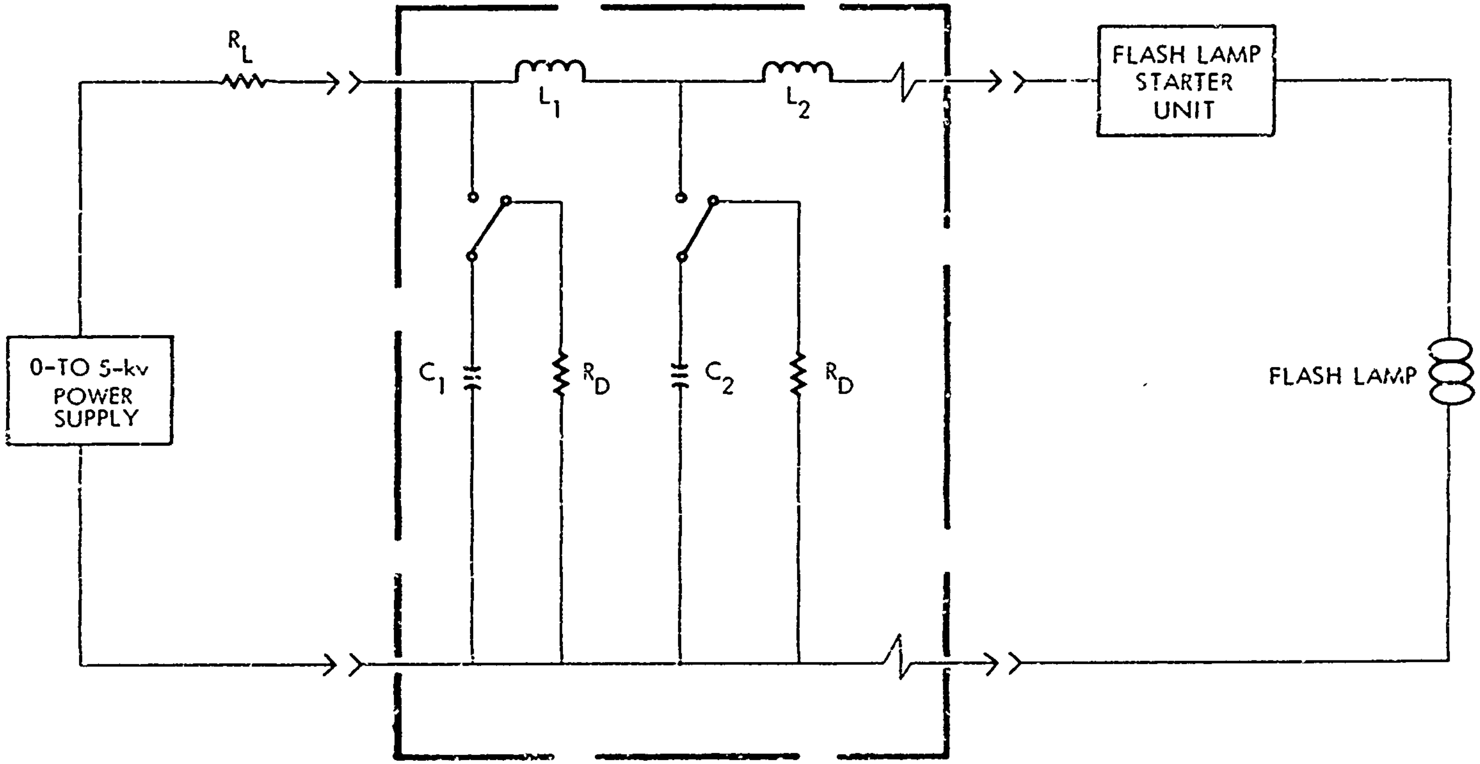
3.3 FLASH TUBE EQUIPMENT

The flash tube was designed to rapidly heat properly prepared solid materials via high-heating rates. As shown in figure 4, the flash discharge system consisted of four essential items: a dc power supply, a capacitor bank, a starter system, and a flash discharge lamp. The electronic circuitry used in this flash tube system is conventional except that the power dissipated through the flash lamp due to the capacitor bank discharge is essentially a square power pulse. The sample being irradiated is exposed to a constant heat flux over the duration of the test.

The circuit features inductor/capacitor (L/C) units schematically shown on figure 4 as C_i for the capacitors and L_i for the inductors. The capacitors (120μfarad) are a laser discharge type and may be charged to 5 kv. The inductors were specially fabricated and are rated at 7.8 mh. The present system has the capability of six L/C units. The duration of the energy pulse is determined by the number of L/C units in the circuit. The flash lamp starter unit is the trigger source, allowing the capacitors to discharge their energy through the flash lamp and resulting in ionization of the gas within the lamp. The capacitors are charged through a current-limiting resistor by a power supply continuously variable from 0 to 5 kv. As a safety feature, a capacitor discharge resistor is wired in parallel with each capacitor through a switch. A more complete description of the flash lamp and its operational characteristics is given in the appendix.

Polymer samples were prepared by casting polymer between NaCl crystal plates, curing the film, and then dissolving the NaCl in cold water leaving behind a polymer film. Film thickness was controlled by using a narrow border of masking tape affixed to one of the NaCl plates. Typical film thickness was 10 mils. Following dissolution of the NaCl, the resulting polymer films were dried, the masking tape trimmed away, and the film mounted on a cylindrical glass holder of 6-mm OD and 1-in. length. Due to the variation in film length (0.6 to 0.7 in.) introduced by trimming the masking tape, the length of the polymer sample was measured in each test. The microtome technique developed by Cheng(4) was also used to prepare a limited number of samples of each polymer. The sample holder was suspended from the crosspiece in a vacuum bottle of a Cahn electrobalance, and a Pyrex tube was placed around the sample. The vacuum bottle was then lowered so that the sample was at the midpoint of the flash lamp cavity. Pyrolysis tests were conducted by exposing polymer films to various energy input rates for a fixed time. Sample weight loss as a function of energy input rate and pressure level was determined. No significant differences were noted in the experimental results obtained with films prepared by the NaCl plate or the microtome technique.



R_L = Current-Limiting Resistor
R_D = Capacitor Discharge Resistor
C_i, L_i = i^{th} Component of Capacitor/Inductor Unit $1 \leq i \leq 6$

Figure 4. Flash Tube Electronic Circuit

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3.4 PROPELLANT IGNITION - IONIZATION GAP TECHNIQUE

Experiments utilizing an ionization gap technique in conjunction with arc-imaging furnace procedures were conducted to determine differences in the time required to initiate gas-phase reactions for various propellant systems. Figure 5, a schematic of the ionization gap equipment, shows the electric circuit and the physical placement of the probe in the furnace test chamber. Standard arc-imaging furnace test procedures(1) were used for these tests. A 200-v potential was maintained across the 0.5-mm air gap. Ignition tests were conducted by exposing individual propellant samples to various energy input rates and recording the time to initial deflection of the ionization probe signal and the ignition time (go/no-go criteria).

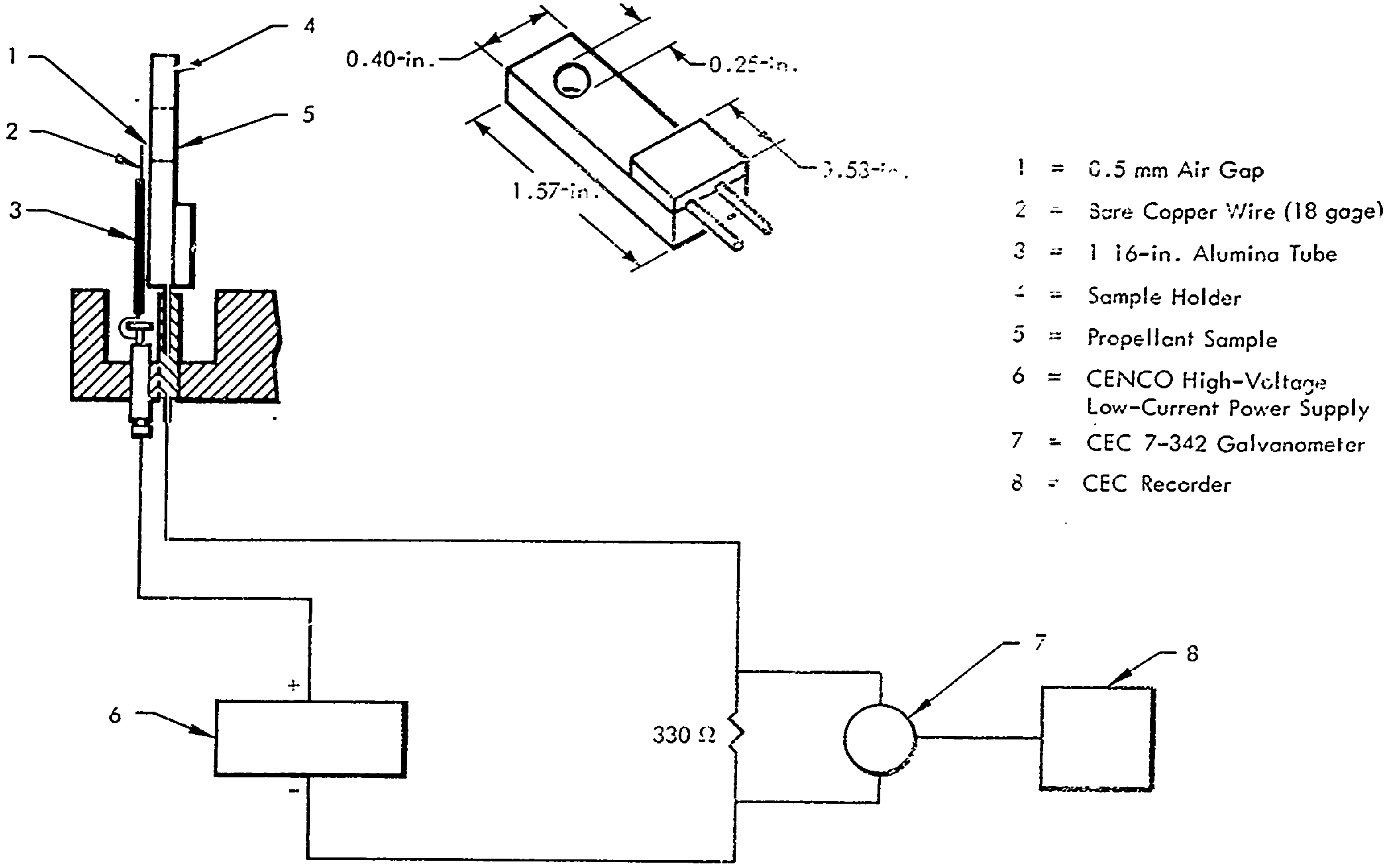

Figure 5. Ionization Probe Schematic

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4.0 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 POLYMER DECOMPOSITION - DSC TESTS

Decomposition studies were conducted on PBAN, PU, CTPB, and CTPIB. These polymers had been used in previous propellant ignition studies.(1) DSC traces for the binder systems are shown in figures 6, 7, and 8 for 1-atm nitrogen, air, and oxygen. Tables I, II, and III summarize the highlights of the DSC traces. In a nitrogen environment and at a heating rate of 10°C/min, decomposition of PIB first resulted in droplet formation on the viewport at 150°C. The polymer began to darken at 225°C and to melt at 240°C. Melting was completed at 270°C; bubbling and rapid fume-off occurred from 280° to 350°C. Decomposition was complete at 410°C.

PU was observed to melt at 215°C with fuming beginning at 250°C; decomposition was complete at 400°C.

Under similar conditions, the PBD polymers did not evidence any decomposition until approximately 300°C. The PBAN-EPOXY decomposition produced droplet formation on the viewport at 300°C. Darkening occurred at 375°C, rapid fume-off from a liquid-solid sample followed at 450° to 475°C, and decomposition was completed at 500°C. With the PBAN-MAPO binder, darkening was noted at 325°C and continued over the temperature range of 350° to 400°C. Rapid fume-off from a liquid-solid sample occurred at 470°C, and the reaction was complete near 500°C. The CTPB binder displayed initial decomposition and sample darkening at 310°C, extensive darkening near 400°C, rapid fume-off near 470°C, and reaction completion near 490°C. A small residue (0.05 mg) remained in all the PBD decompositions.

As can be seen in figures 7 and 8 and tables II and III, changing from nitrogen to an air or oxygen environment has a significant influence on binder decomposition. This is most clear in the case of the PBD polymers. The presence of oxygen shifts the entire decomposition range to lower temperatures and apparently alters the decomposition mechanism.

In the air environment, the decomposition of PIB and PU are not appreciably altered from their behavior in nitrogen. However, for PBD initial decomposition is observed at 200°C; a reduction of approximately 100°C compared with the initial decomposition temperatures in nitrogen.

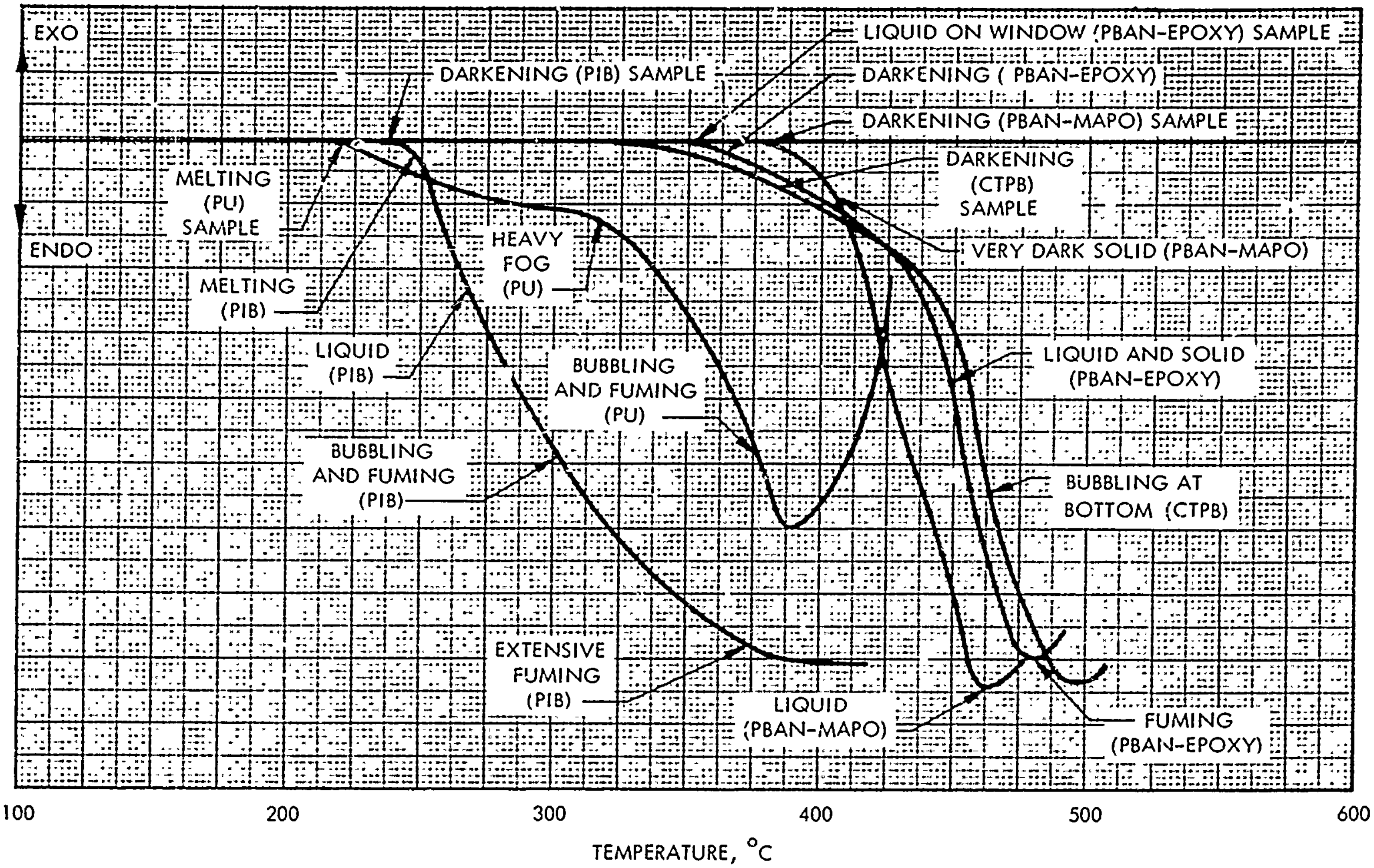

Figure 6. Polymer Decomposition, 1-atm Nitrogen in the DSC

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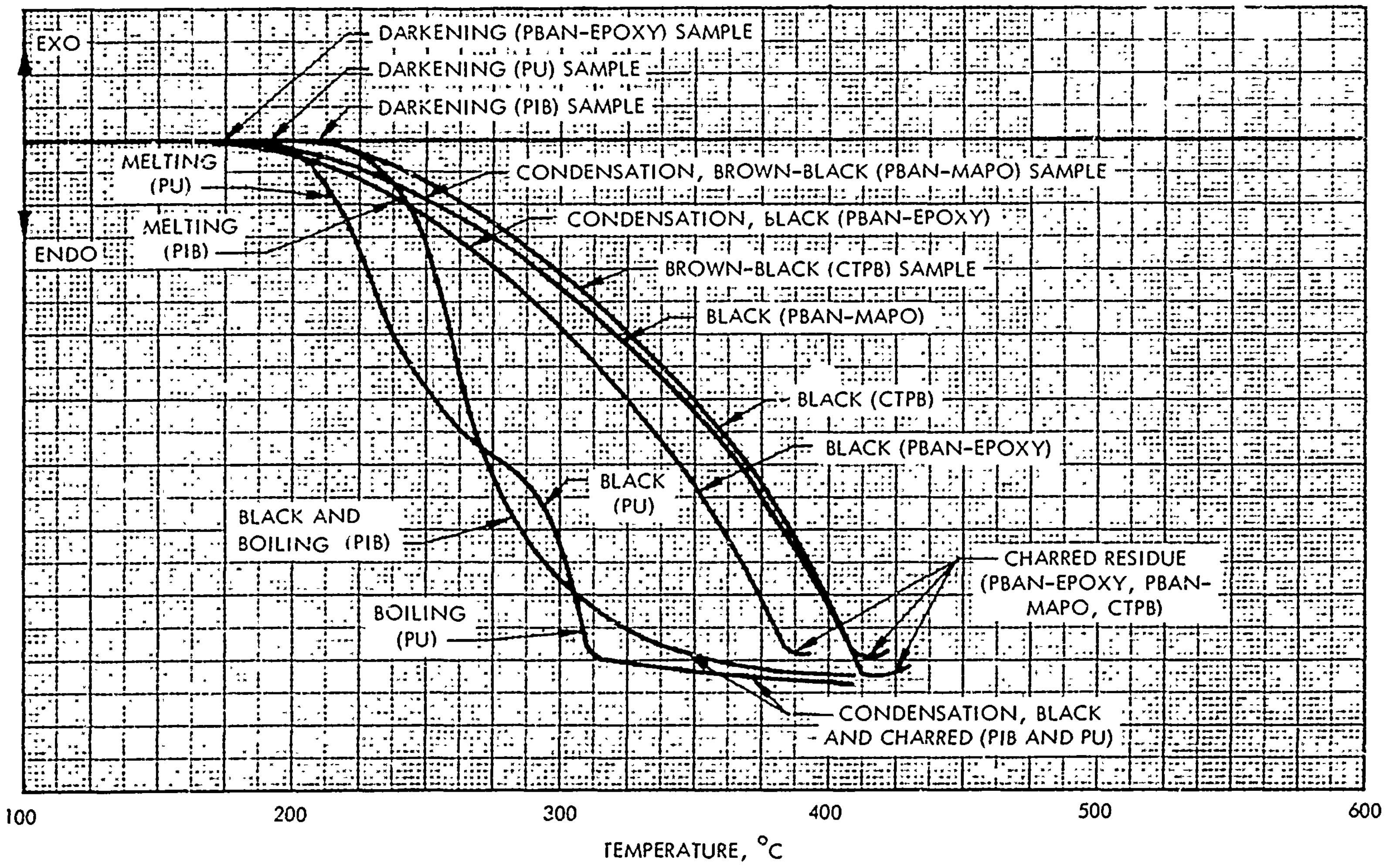

Figure 7. Polymer Decomposition, 1-atm Air in the DSC

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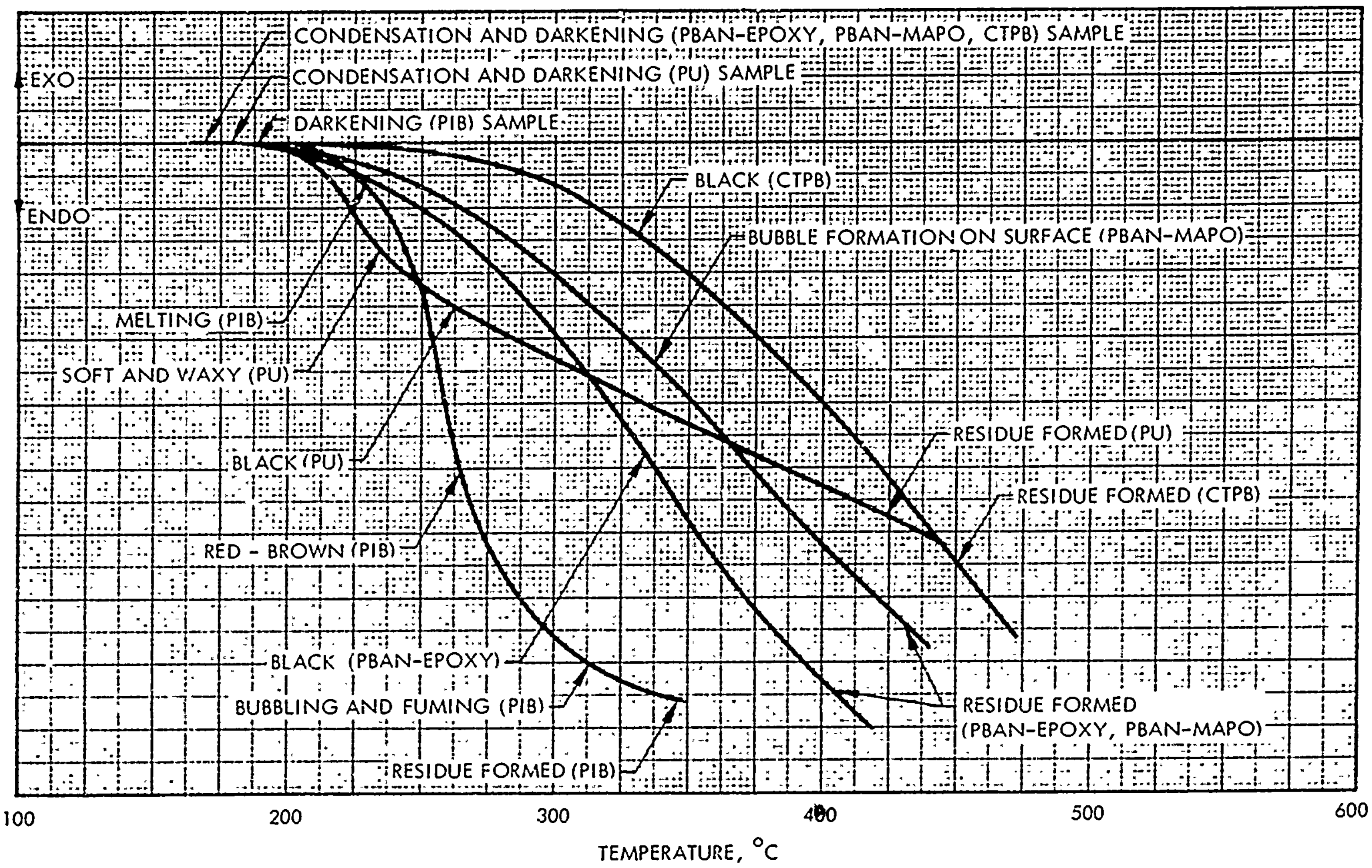

Figure 8. Polymer Decomposition, 1-atm Oxygen in the DSC

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TABLE I

POLYMER DECOMPOSITION - DSC TESTS

1-atm Nitrogen, Heating Rate 10°C/min

Polymer	200° to 250°C	250° to 300°C	300° to 350°C	350° to 400°C	400° to 500°C
PIB	Darkening-225°C Melting-240 C	Bubbling and fuming	Extensive fuming	-	-
PU	Melting-215°C	Limited fuming	Bubbling and fuming	-	-
PBAN-EPOXY	-	-	Condensate on viewing window	Darkening-375°C	Liquid and solid Bubbling in liquid layer. Fuming-475°C.
PBAN-MAPO	-	-	Darkening-325°C	Extensive darkening	Liquid and solid. Fuming-470°C.
CTPB	-	-	-	Darkening-390°C	Liquid and solid. Bubbling at bottom-470°C

TABLE II

POLYMER DECOMPOSITION - DSC TESTS

1-atm Air, Heating Rate 10°C/min

Polymer	200° to 250°C	250° to 300°C	300° to 350°C	350° to 400°C
PIB	Darkening-225°C Melting-240°C	Bubbling and fuming	Extensive fuming	-
PU	Melting-215°C	Limited fuming	Bubbling and condensation	-
PBAN-EPOXY	Condensation and darkening-200° to 220°C	Black-250°C	-	Limited decomposition*
PBAN-MAPO	Condensation and darkening-200° to 225°C	Increased condensation	Black-300°C	Limited decomposition*
CTPB	Darkening-204°C	-	Black-350°C	Condensation and decomposition*

* At completion of run, sample had original shape but was black and charred. Residue was hard and brittle.

TABLE III

POLYMER DECOMPOSITION - DSC TESTS

1-atm Oxygen, Heating Rate 10°C/min

Polymer	175°C to 250°C	250° to 300°C	300° to 350°C	350° to 400°C	400° to 500°C
PIB	Condensate on viewing window-190°C Melting-221°C	Red-brown liquid-267°C Bubbling and fuming	Extensive fuming	Carbon residue on sides of pan	Partial decomposition of residue*
PU	Condensate on viewing window-190°C Limited melting-210°C	Soft waxy appearance and discolored	Thick gel appearance and dark	Carbon residue on bottom of pan	↕
PBAN-EPOXY	Condensate on viewing window-200°C Darkening-205°C	Increased condensation	Extensive fuming	Swelling and char formation-400°C	↕
PBAN-MAPO	Condensate on viewing window-200°C Darkening-200°C	Increased condensation	Fuming	Char formation	↕
CTPB	Darkening-190°C Condensate on viewing window-200°C	-	Black-300°C	Char formation	Partial decomposition of residue*

* Runs were terminated at 500°C. A residue remained in each test. In the case of the PIB and PU polymers, this residue weighed 8% to 10% of the initial sample. In the case of PBAN and CTPB polymers, the residue weighed approximately 30% of the initial sample.

At completion of the decomposition runs with the PBD, the samples were found to have maintained their original shape but were black and charred, and the residue was hard and brittle.

When oxygen was used as the environmental gas, the initial decomposition temperatures of the PIB and PU were decreased approximately 25°C. In addition, these polymers did not melt completely as they had in nitrogen and air, but instead a carbonaceous residue was formed at 350°C. At the completion of the tests, a residue comprising 8% to 10% of the initial sample weight remained in the pan. With PBDs in oxygen, initial decomposition was noted at 190° to 200°C. Sample charring began at 350°C and a residue comprising approximately 30% of the initial weight was found at completion of the tests. Tests were also conducted at 0.5 and 0.1-atm in nitrogen, air, and oxygen. No significant shifts were noted in the decomposition temperatures of the polymers as a function of pressure.

The observations of the DSC results compared with the data for the rapid heating of polymeric fuel binders reported by investigators at the University of Utah prove interesting. Using a convective heat-flux furnace, Baer(5) has reported an endothermic reaction at 350°C for a PBAA binder with nitrogen at 760°C and 7.7 atm. Cheng reported that PBAA polymer vaporization occurred at 510°C with some endothermic reaction taking place around 400°C at 7.7-atm nitrogen.(4) In the presence of oxygen at 450°C and 0.85 atm, Cheng noted that an exotherm occurred at temperatures more than 100°C below those at which an endotherm was observed during heating in nitrogen at the same pressure. These temperatures, particularly for the PBD polymer, are in reasonable agreement with the temperatures noted in the DSC tests reported herein.

4.2 POLYMER PYROLYSIS - RAPID HEATING CONDITIONS

The flash lamp and radiation furnace were used to simulate polymer decomposition under a heating rate typical of a propellant ignition and combustion environment. Carbon (3 to 4 wt-%) was mixed into the polymer formulation to render the test samples opaque to thermal radiation. Flash pyrolysis studies were conducted in vacuum, nitrogen, air, and oxygen environments. Flash duration, defined as the time between the 1/e peak power points on the oscilloscope trace of the radiant output versus power input (see the appendix), was maintained as a constant. Heat flux was varied by changing the charging voltage to the capacitor bank. Sample weight loss was determined as a function of energy input rate, pressure level, and environmental gas.

The radiation furnace vas utilized to obtain information on polymer degradation at flux levels intermediate between the DSC and flash lamp heating rates. In the radiation furnace experiments, the heating rate was maintained as a constant and the exposure time was varied. Sample weight loss was determined as a function of heating rate, exposure time, and environmental gas. Nitrogen, air, and oxygen were used as test gases. A gas purge velocity of 30 cm/sec was employed in both the flash lamp and radiation furnace tests at atmospheric pressure to minimize clouding of the test chamber and subsequent attenuation of radiant energy. Under vacuum conditions in the radiation furnace, a black residue was deposited on the Pyrex tube shortly after the onset of decomposition. Decomposition tests in vacuum were limited to low-flux levels because of excessive radiant energy attenuation by this residue at high-flux levels.

Figures 9 through 13 summarize the decomposition data obtained in neutral environments in the flash lamp and radiation furnace. The flash lamp data refer to vacuum conditions, while the radiation furnace data refer to vacuum and nitrogen at 1-atm pressure. In the flux ranges studied, it was noted that a linear relation resulted when data were presented in the form of total incident radiant energy per unit area versus weight loss per unit area.[*] The slope of such a plot can be identified as the effective heat of decomposition, Δh_{eff}. The lines representing the individual data points in the figures are the best-fit lines obtained by least-mean-squares techniques, assuming that an equation of the form $Q = a + \Delta h_{eff} w$ provides a valid description of the data. In this equation Q = cal/unit area, a = constant, Δh_{eff} = cal/unit weight, and w = weight loss/unit area. Table IV summarizes the correlating equations for the various polymers.

Several aspects of overall polymer decomposition can be noted from the flash lamp and radiation furnace data.

A. Weight loss is slightly higher under vacuum than at 1-atm nitrogen pressure in the radiation furnace.

B. The PIB and PU polymers exhibit a greater weight loss than the PBDs at equivalent incident energy levels.

C. A thermal induction time occurs in the radiation furnace with a small rate of weight loss for short exposures which increases rapidly as exposure time is lengthened. Weight loss data show that at the same total energy input, the

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[*] A thermal induction time exists at the flux levels characteristic of the radiation furnace and this correlation was only applicable for exposure times exceeding the induction time.

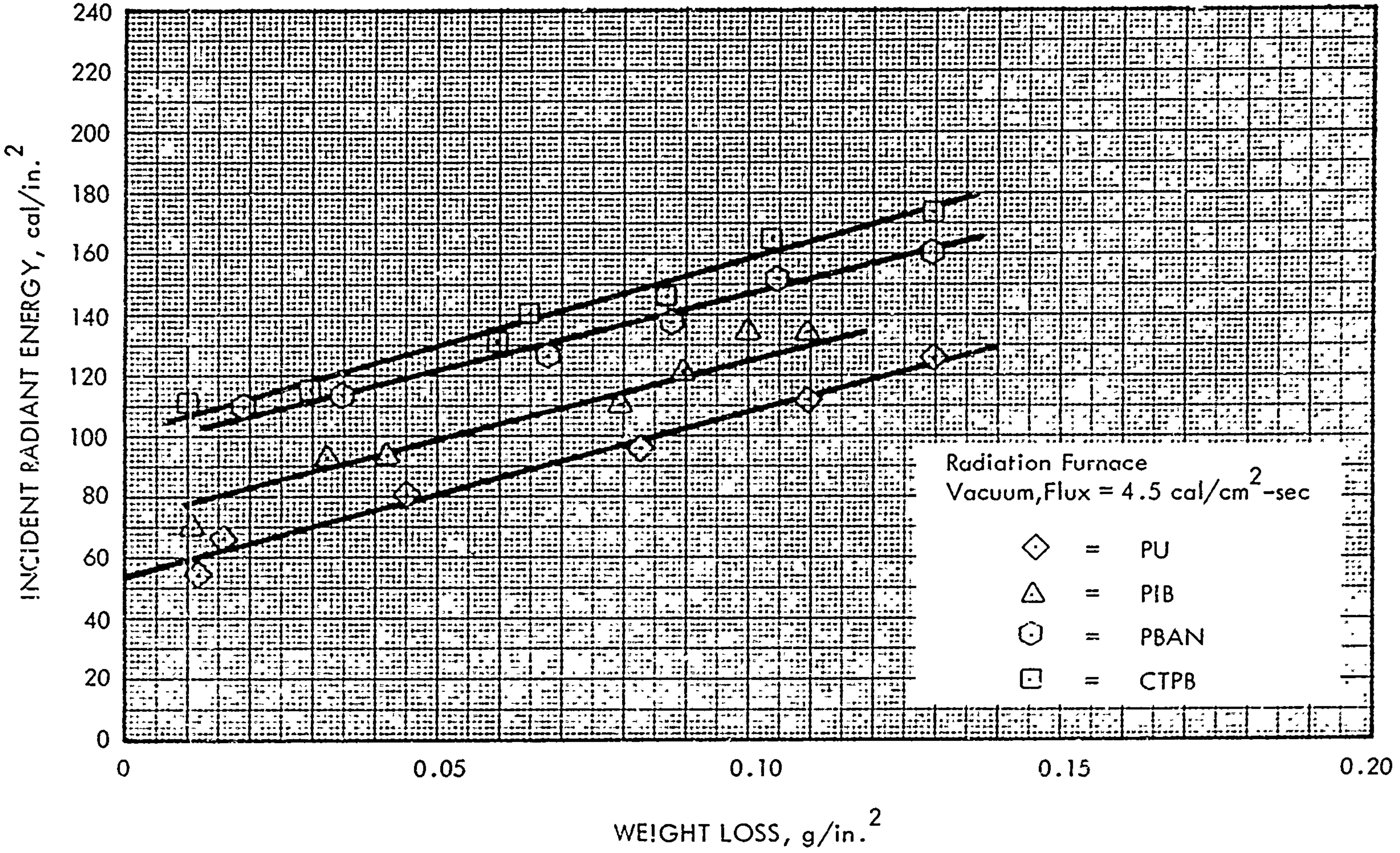

Figure 9. Polymer Weight Loss as a Function of Incident Radiant Energy

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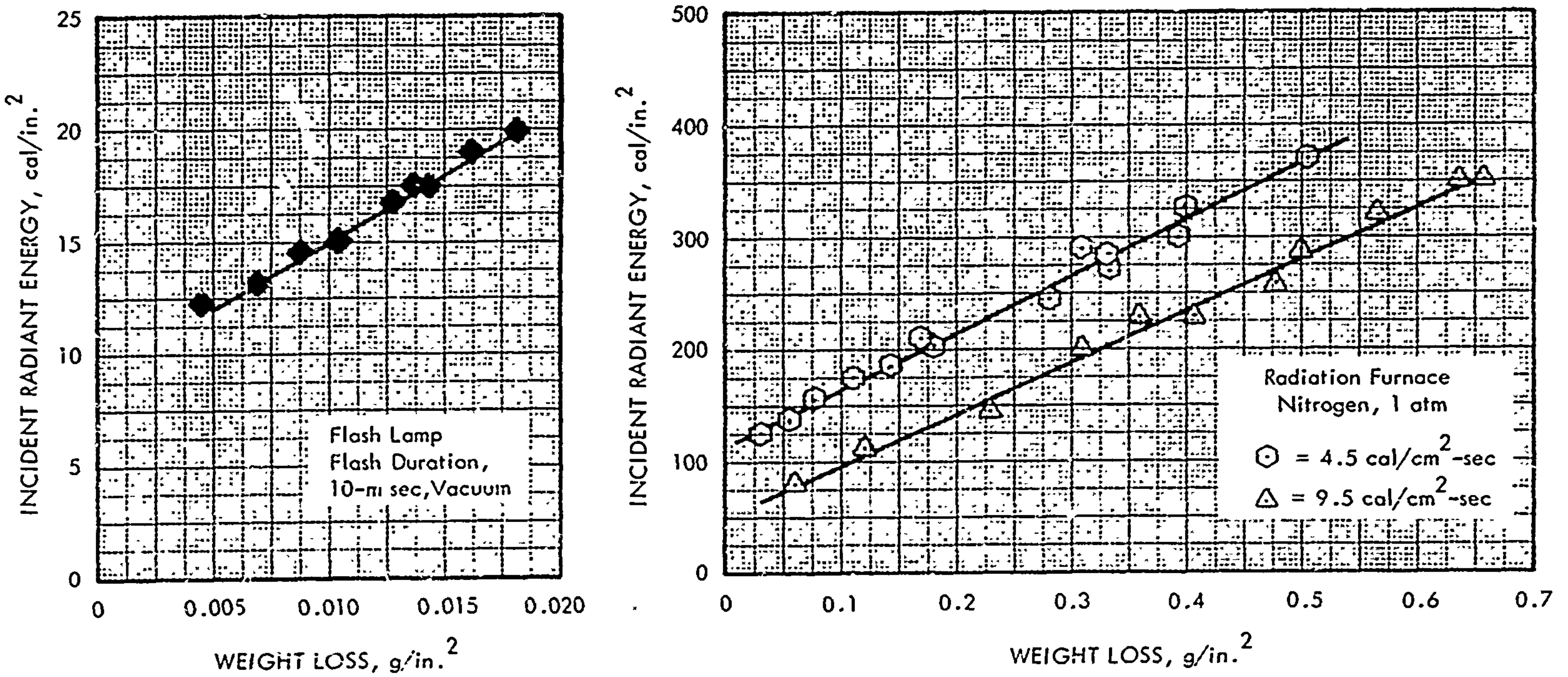

Figure 10. Polymer Weight Loss as a Function of Incident Radiant Energy (PBAN)

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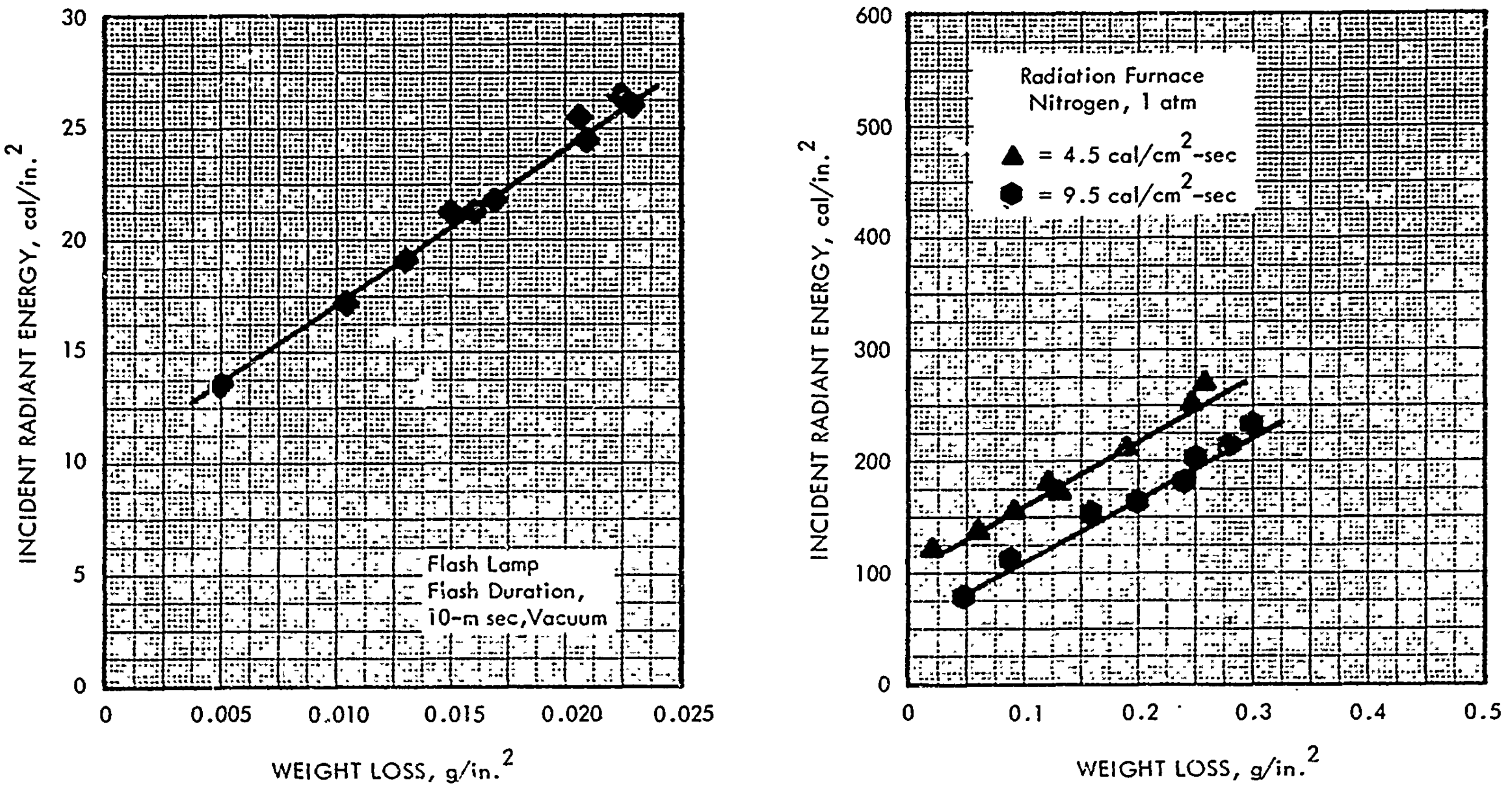

Figure 11. Polymer Weight Loss as a Function of Incident Radiant Energy (CTPB)

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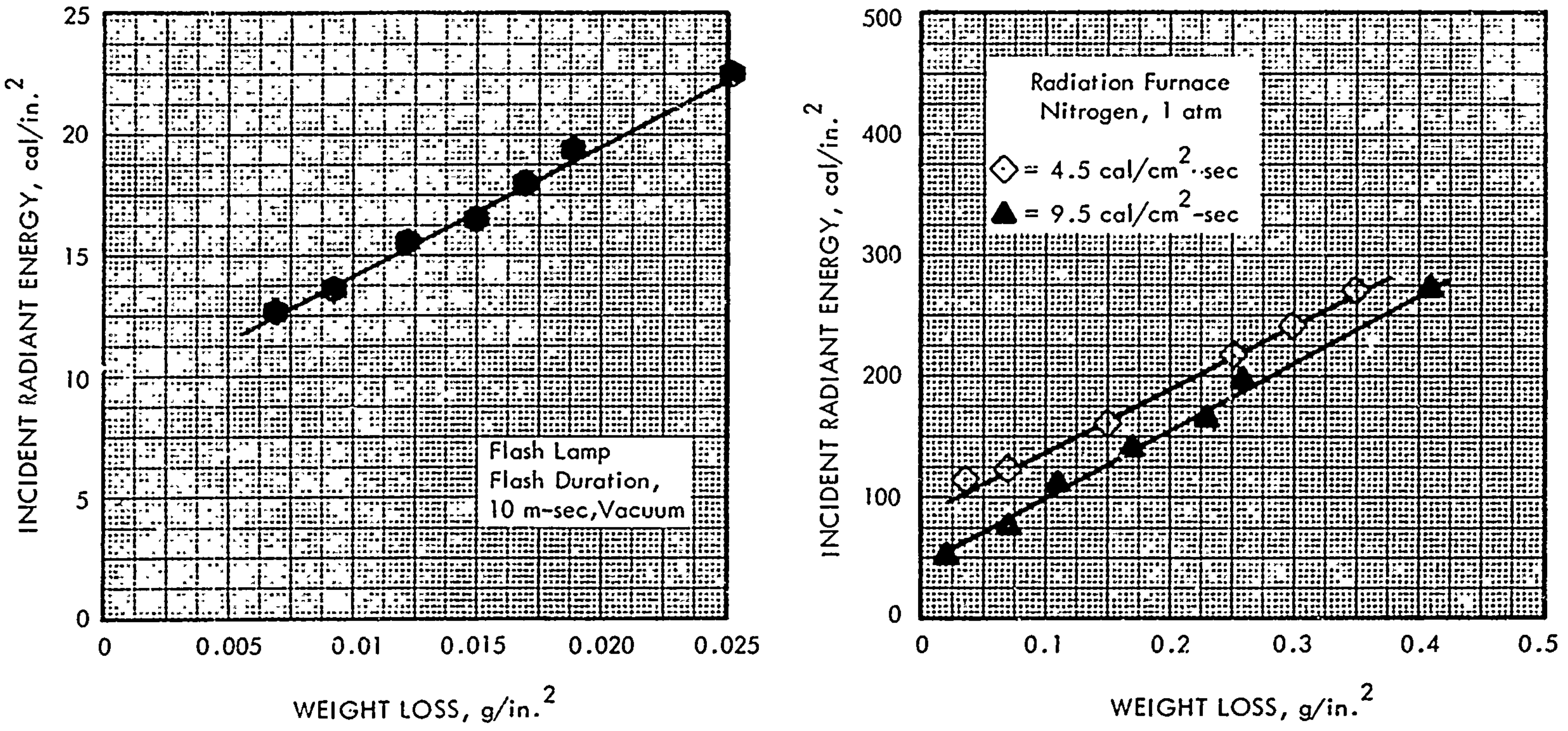

Figure 12. Polymer Weight Loss as a Function of Incident Radiant Energy (PIB)

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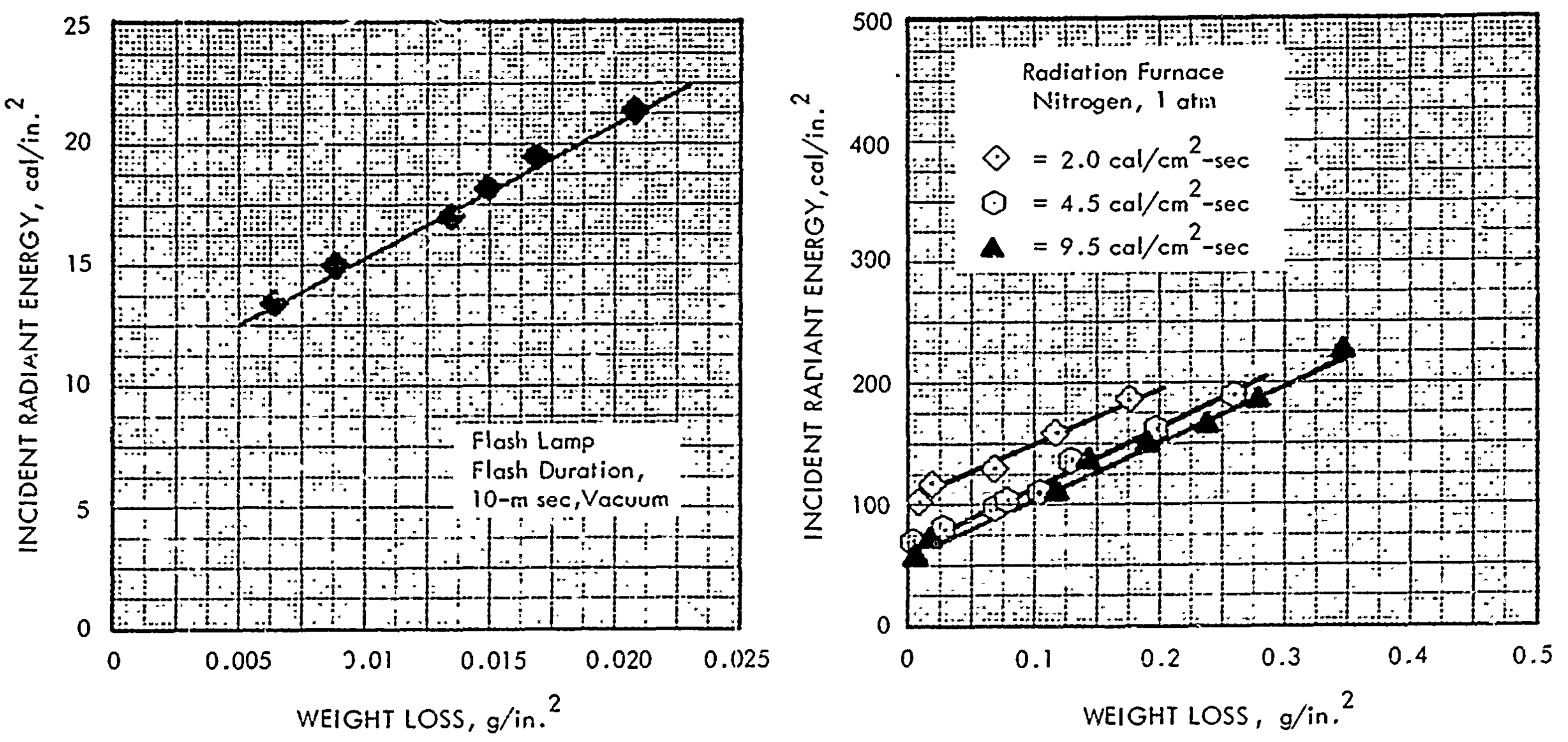

Figure 13. Polymer Weight Loss as a Function of Incident Radiant Energy (PU)

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TABLE IV

CORRELATING EQUATIONS FOR POLYMER DECOMPOSITION

Polymer	Test Mode	Pressure	Flux cal/cm^2-sec	Equation
PBAN	Flash lamp	Vacuum	-	Q = 9 + 600 w
	Radiation furnace	Vacuum	4.5	= 97 + 500 w
	↕	1-atm Nitrogen	4.5	= 111 + 516 w
	Radiation furnace	-	9.5	= 44 + 482 w
CTPB	Flash lamp	Vacuum	-	Q = 10.25 + 705 w
	Radiation furnace	Vacuum	4.5	= 102 + 570 w
	↕	1-atm Nitrogen	4.5	= 103 + 596 w
	Radiation furnace	-	9.5	= 52 + 572 w
PIB	Flash lamp	Vacuum	-	Q = 8.9 + 530 w
	Radiation furnace	Vacuum	4.5	= 73 + 516 w
	↕	1-atm Nitrogen	4.5	87 + 520 w
	Radiation furnace	-	9.5	45 + 560 w
PU	Flash lamp	Vacuum	-	Q = 10 + 542 w
	Radiation furnace	Vacuum	4.5	= 54 + 540 w
	↕	1-atm Nitrogen	2.0	= 104 + 460 w
	↕	-	4.5	= 64 + 510 w
	Radiation furnace	-	9.5	= 56 + 490 w

weight loss increases with the heating rate. Surface temperature is apparently the most important factor in the pyrolysis reactions.

D. The effective heat of decomposition of the PBDs seems to be dependent upon the heating mode. In the flash heating tests, PBAN exhibited a Δh_{eff} = 600 cal/gram while in the radiation furnace $\Delta h_{eff} \cong$ 500 cal/gram. Under similar conditions, Δh_{eff} for CTPB was found to be 705 cal/gram and $\approx$ 585 cal/gram. The PIB and PU binders exhibited little or no dependence of heating mode on Δh_{eff}.

In a nitrogen or air environment at atmospheric pressure, carbon and soot generation occurred in the flash pyrolysis tests. Within the accuracy of these tests and considering that the incident radiant beam attenuation could not be eliminated entirely by the gas purge, no significant shifts in weight loss occurred with 1-atm nitrogen at low energy levels. Typical data for PBAN, PIB, and PU are shown in table V.

Carbon and soot generation are also somewhat dependent on the incident energy level. In the case of PIB polymer with 1-atm nitrogen, a grey smoke typical of vacuum decomposition was observed at energy levels below 3.0 cal/cm^2. Above this level, black smoke and soot began to appear in the decomposition gases and at 3.6 cal/cm^2 soot was extensive. For the PU polymer, black smoke and soot began to appear at 3.6 cal/cm^2. The PBAN polymer formed soot at all energy levels and large quantities of carbon and soot appeared at energy levels above 2.5 cal/cm^2. In the presence of air, PBAN generated extensive quantities of black smoke and soot at all energy levels, and above 3.6 cal/cm^2 the test chamber was coated with a black deposit.

In contrast to the flash pyrolysis data, radiation furnace tests with 1-atm nitrogen did not result in carbon or soot formation, except for a small amount from PU after long exposure. Microscopic examination of the PBAN, PIB, and CTPB surfaces following exposure showed no evidence of char formation. The PIB polymer had completely melted, but the PBAN and CTPB melting was limited to a thin surface layer. Char formation was noted on the PU surface after about 5 sec of exposure.

The substitution of air for nitrogen (1 atm) in the radiation furnace did not produce any significant change in the weight loss of the PBAN, CTPB, or PIB. Representative data for the PBAN polymer are given in table VI. At most, a slight increase in weight loss may have occurred, but it was within experimental error and not deemed significant. Microscopic examination of the polymer surfaces following air exposure did not disclose any important changes from corresponding nitrogen tests.

TABLE V

COMPARISON OF POLYMER WEIGHT LOSS IN VACUUM AND 1-atm NITROGEN ENVIRONMENTS (Flash Lamp Tests)

Polymer	Gas Environment	Weight Loss mg/cm^2	Input Energy cal/cm^2
PBAN	Vacuum	2.1	3.8
		2.7	4.2
		3.0	4.4
	1-atm Nitrogen	2.1	3.9
		2.7	4.2
		3.0	4.4
PIB	Vacuum	2.1	3.1
		3.3	3.7
		3.4	3.8
		4.0	4.1
	1-atm Nitrogen	2.1	3.2
		3.3	3.5
		3.4	3.8
		4.0	4.2
PU	Vacuum	2.3	3.4
		3.1	3.9
		3.4	4.0
		4.8	4.7
	1-atm Nitrogen	2.3	3.4
		3.1	3.9
		3.4	4.2
		4.8	4.6

TABLE VI

COMPARISON OF POLYMER WEIGHT LOSS IN NITROGEN AND AIR ENVIRONMENTS

(Radiation Furnace)

Polymer	Gas Environment	Wt. Loss g/in.^{2}	Energy cal/in.^{2}	Flux cal/cm^2-sec
PBAN	1-atm N_2	0.307	295	4.5
		0.396	325	4.5
		0.425	354	4.5
		0.50	382	4.5
		0.515	423	4.5
	1-atm Air	0.336	300	4.5
		0.40	330	4.5
		0.45	359	4.5
		0.56	384	4.5
	1-atm N_2	0.059	79	9.5
		0.24	141	9.5
		0.54	263	9.5
	1-atm Air	0.059	78	9.5
		0.20	147	9.5
		0.51	265	9.5

In the case of PU, the air environment increased the weight loss and markedly altered the polymer surface structure. Microscopic examination showed char formation on the surface after 1 sec of exposure at an incident flux of 9.5 cal/cm^2-sec. Small clumps of a powdery, red material were also noted on the polymer surface. The material was determined to be iron oxide, from which the char formation appeared to originate, probably resulting from the oxidation of a cure catalyst, ferric acetylacetonate. The degree of surface covered by the char increased with exposure time until the surface was nearly covered by a char layer at 3 seconds. Beneath and between the char areas, the PU surface had a molten-glassy appearance.

When oxygen was used as the test gas, ignition or flaming of all the polymers occurred in both the flash pyrolysis and radiation furnace experiments. Ignition was noted at oxygen concentrations of the order of 1×10^{-3} g/cc in the flash lamp. This corresponds closely with the limiting oxygen concentrations found in previous ignition work using shock tube techniques (3×10^{-3} g/cc for polymers and 1.5×10^{-3} g/cc for propellants).(1)

The dependence of soot formation on incident radiant energy level and pressure observed in the flash pyrolysis experiments indicates a change in the basic mechanism of polymer decomposition or a shift in the controlling process. Since diffusion is retarded with increased pressure, the pressure effect is probably due in part to increased thermal cracking of the initial polymer decomposition products occasioned by increased residence time in the hot zone near the polymer surface.

The occurrence of a heating rate effect on the polymer decomposition products in associated with residence times, local temperatures, and resultant shifts in dominant decomposition modes. In experiments of gradual or stepwise temperature increases typical of DSC, secondary reactions of the products of lower temperature reactions occur. Low temperature pyrolysis reactions are the key processes under these conditions.

Irradiances typical of the radiation furnace are in an intermediate range, and high-temperature mechanisms begin to exert more influence. Some secondary reactions are expected, particularly at the lower flux levels and longer exposure times. The char formation noted with PU at a heating rate of 4.5 cal/cm^2-sec after 5 sec is an example.

At intense heating rates characteristic of flash pyrolysis, high-temperature reactions are dominant. Flash pyrolysis studies on cellulose have shown that the amounts and kinds of volatiles produced by flash heating differ markedly from those resulting from slower heating rates.(6) The average weight of the products is much lower at high heating rates; flash heating simply breaks the cellulose into smaller pieces. The same phenomenon has been noted when coal is flash heated.

The observation that decomposition of PBDs apparently becomes more endothermic via flash heating indicates that the PBDs probably behave in a similar manner. The relatively low melting points of PIB and PU (240°C and 215°C, respectively) may be the prime reason that these polymers behave differently and do not become more endothermic when flash heated. The PIB and PU may decompose primarily by a vaporization process while the PBDs undergo more of a surface pyrolysis.

4.3 PROPELLANT IGNITION - IONIZATION GAP

The ionization gap experiments were conducted to obtain information relating the onset time of a gas-phase reaction to propellant ignition times via radiant heating. The propellants used were similar to those studied in previous research on solid propellant ignition.(1) Table VII summarizes the results of the tests using the ionization probe. The time to first deflection of the ionization probe signal is taken to be the time required to establish a gas-phase reaction.

At moderate flux levels (10 to 20 cal/cm^2-sec) and pressures near 1 atm, ignition time and gas-phase reaction onset time nearly coincide. Propellant heating time dominates the ignition process in this range of pressure and external flux. As the flux level is increased at atmospheric pressure, there is some indication of a minimum exposure time required to achieve ignition, even though a signal is noted from the ionization probe at a somewhat shorter time. When the irradiance level is high, energy deposition is limited to material very near the exposed surface with a resulting high surface temperature. Whether or not flame persists after cessation of exposure will depend upon the mean relaxed temperature in the solid. Flaming is sustained only when sufficient energy has been supplied to produce a minimum relaxed temperature in a slab of thickness, ℓ ; it is necessary to partially establish the steady-state thermal wave in the solid. If the exposure is terminated prior to establishment of this condition, thermal feedback from the incipient flame does little more than offset heat losses. The manner of flux termination would be important in this flux-pressure range. Ryan and Baer in their recent theoretical studies have investigated the influence of the igniter flux termination on propellant ignition.(7) At low flux levels, a trapezoidal pulse requires more energy than a sharply terminated pulse, mainly because ignition occurs before the flux decreases. At high flux levels, the trapezoid flux form requires less energy for ignition.

As the pressure is reduced below atmospheric, the time differences increase between the initial signal from the ionization probe and the minimum exposure or ignition time. For successful ignition of the PU propellant at a flux of 42 cal/cm^2-sec and 0.5 atm, the exposure time must

TABLE VII

IONIZATION GAP DATA

Propellant	Pressure atm	Flux cal/cm^2-sec	Time of First Deflection of Ionization Probe Signal msec	Propellant Exposure Time msec	Ignition (go/no-go)	ΔT_s K
PU (81% bimodal AP)	1.0	15	208	540	go	-
		15	209	225	go	-
		30	-	80	no-go	-
		↓	125	180	go	-
	0.75		140	210	go	525
	0.5		160	290	go	565
			-	120	no-go	490
	.25		170	290	go	580
	0.1		190	260	no-go, ignited but went out at termination of flux	615
			200	520	↓	630
		30	200	1, 260	no-go, ignited but went out at termination of flux	630
	1.0	42	70	85	no-go, flame started but decayed	523
		↓	70	105	go	523
			70	80	no-go, flame started but decayed	523
	0.5		90	135	go, pause at shutter close	595
			95	165	go	610
			95	115	no-go, flame started but decayed at shutter close	610
			95	145	go, pause at shutter close	610
	0.1		110	270	no-go, flame started but decayed at shutter close	655
	0.1	42	112	830	no-go, flame started but decayed at shutter close	661
PIB (84% bimodal AP)	1.0	15	224	520	go	334
		15	225	230	go	335
	1.0	30	190	215	go	610
		↓	-	110	no-go	470
			-	155	no-go	550
	0.75		-	250	no-go	700
			270	280	go	735
			268	275	go	733
	0.5		350	460	no-go, ignited but went out at termination of flux	830
		30	350	815	no-go, ignited but went out at termination of flux	830
	1.0	42	133	490	go	735
		42	130	325	go	730

TABLE VII

IONIZATION GAP DATA (Continued)

Propellant	Pressure atm	Flux cal/cm^2-sec	Time of First Deflection of Ionization Probe Signal msec	Propellant Exposure Time msec	Ignition (go/no-go)	ΔT_s K
		42	-	120	no-go	-
	0 75	↓	-	120	no-go	-
		↓	180	290	no-go	850
		↓	190	500	go, gradual rise in probe signal with pause at shutter close	860
	0 5	↓	190	420	no-go	860
	0 1	42	205	2,000	no-go	-
	0 5	75	50	60	go	765
		75	48	50	no-go	750
CTPB (84% bimodal AP)	1 0	15	342	480	go	412
		15	-	300	no-go	-
	1. 0	42	120	490	go	700
	0. 5	↓	125	420	go	712
		↓	-	100	no-go	-
	0. 1	42	150	420	go	765
	0 5	30	150	280	go	550
		↓	150	180	go, pause at shutter close	550
		↓	-	120	no-go	-
	0. 1	↓	240	780	no-go, ignited but went out at termination of flux	690
		30	250	1,020	no-go, ignited but went out at termination of flux	700
PBAN (84% bimodal AP)	1. 0	15	253	530	go	256
	1. 0	30	110	130	go	465
		↓	-	95	no-go	435
	0. 5	↓	110	200	go	465
		↓	↓	120	go	465
		↓	110	115	no-go, ignited but died	165
		30	-	95	no-go	435
	1. 0	42	85	135	go, momentary pause at shutter close	575
		↓	90	490	go	595
	0 5	↓	75	420	go	-
	0 1	42	95	1,500	no-go, ignited but died at shutter close	600
	1 0	75	20	25	go	500
			18	22	go	473
		75	20	18	no-go, signal started but decayed	500

exceed approximately 132 msec, even though an ionization probe signal is noted at 95 msec. The calculated propellant surface temperature is approximately 875°K at the time of the initial ionization probe signal. This surface temperature is at least 100°K above typical propellant ignition temperatures. In this flux-pressure regime, the incipient combustion wave is again quenched if the external flux is terminated too soon.

With a further pressure decrease toward the minimum initial pressure for ignition achievement at any flux level, ionization probe signals are noted, even though ignition cannot be achieved for infinite exposure time. Thus, even though propellant surface temperatures are high enough to generate products, energy release at the surface and in the gas phase from chemical reaction cannot support incipient ignition in the absence of external energy. Therefore, the establishment of a "state of reactivity" at the propellant surface and in the adjacent gas phase is a necessary, but not sufficient, condition for ignition.

These results indicate that propellant ignition cannot be achieved unless the following conditions are simultaneously satisfied: (1) the reactive composition is within the limits of flammability, (2) the temperature of the system is above the ignition temperature, (3) a critical reaction volume is formed in the gas phase, (4) the steady-state thermal wave is at least partially established in the solid, and (5) the pressure is above the ignition pressure limit for the particular propellant.

5.0 CONCLUSIONS

5.1 POLYMER DECOMPOSITION

A. The thermal decomposition mechanism of polymer materials changes with the heating rate.

B. PIB and PU decomposition at low heating rates typical of DSC occur after melting of the polymer, while PBD decomposition appears to involve a limited liquid state.

C. At low heating rates, oxygen clearly promotes the decomposition of the polymers, particularly the PBDs. The presence of oxygen also lowers decomposition temperature and alters the mode of decomposition.

D. At the intermediate flux levels produced by the radiation furnace, PU pyrolysis involves a liquid layer during initial decomposition, but at longer exposure times a carbonaceous residue is formed. In contrast, PIB and the PBDs undergo total pyrolysis.

E. Surface temperature is apparently the most important factor in polymer decomposition reactions at the moderate flux levels characteristic of the radiation furnace.

F. All polymers studied volatilize completely at the intense heating rates characteristic of flash heating.

G. PBD decomposition appears to be dependent upon irradiance level, such decomposition being more endothermic when flash heated.

5.2 PROPELLANT IGNITION

Data obtained by the ionization probe technique and the arc-imaging furnace demonstrate that the establishment of a "state of reactivity" at the propellant surface and in the adjacent gas phase is a necessary, but not sufficient, condition for ignition.

APPENDIX

1.0 FLASH LAMP SYSTEM

Flash lamp systems have been very useful in the fields of photography as light sources, as well as energy sources for flash photolysis and flash pyrolysis systems. In this latter sence, a flash lamp system has been constructed for use in polymer decomposition investigations.

In simplified terms, the operation of a flash lamp system involves storing electrical energy in a capacitor storage bank where it is available to be converted to radiant energy by ionizing a gas in a gas-filled tube. The energy pulse is triggered by an appropriate electrical circuit which provides a high-voltage spike that initially ionizes the gas. Typically, the wave shape of the energy pulse is similar to that of a discharging capacitor, i.e., a very fast rise time followed by an exponential decay. The duration of these pulses varies from microseconds to 1 or 2 msec. The energy pulse from the flash lamp system used has been shaped by the use of inductors placed in series with each energy storage capacitor. The resulting wave shape is essentially a square pulse of energy with durations of from 8 to 13 msec depending on the number of energy storage capacitors employed.

The assembled flash lamp system is shown in figures 14 and 15; a schematic of the electrical circuit is given in figure 4. The capacitors used are a Sangamo Laser Discharge-type, each rated at 120µ farad and 5 kv. The inductors specially produced by Tranex, Incorporated were designed to have ratings of 7.8 mh, and were limited to a resistance of 0.2 ohm each.

The lamp used was a PEK model XE 5-3793. The lamp is filled with Xenon gas and the case is would as a spiral to maximize the heat flux in its core. The lamp is a five-turn helix with a 1-1/4-in. ID and a 4-in. height. The trigger source for the lamp, built by PEK, is capable of generating a high-voltage pulse variable between 30 and 50 kv with a duration of less than 6µsec. A voltage pulse of 30 kv has been sufficient to consistently trigger the lamp.

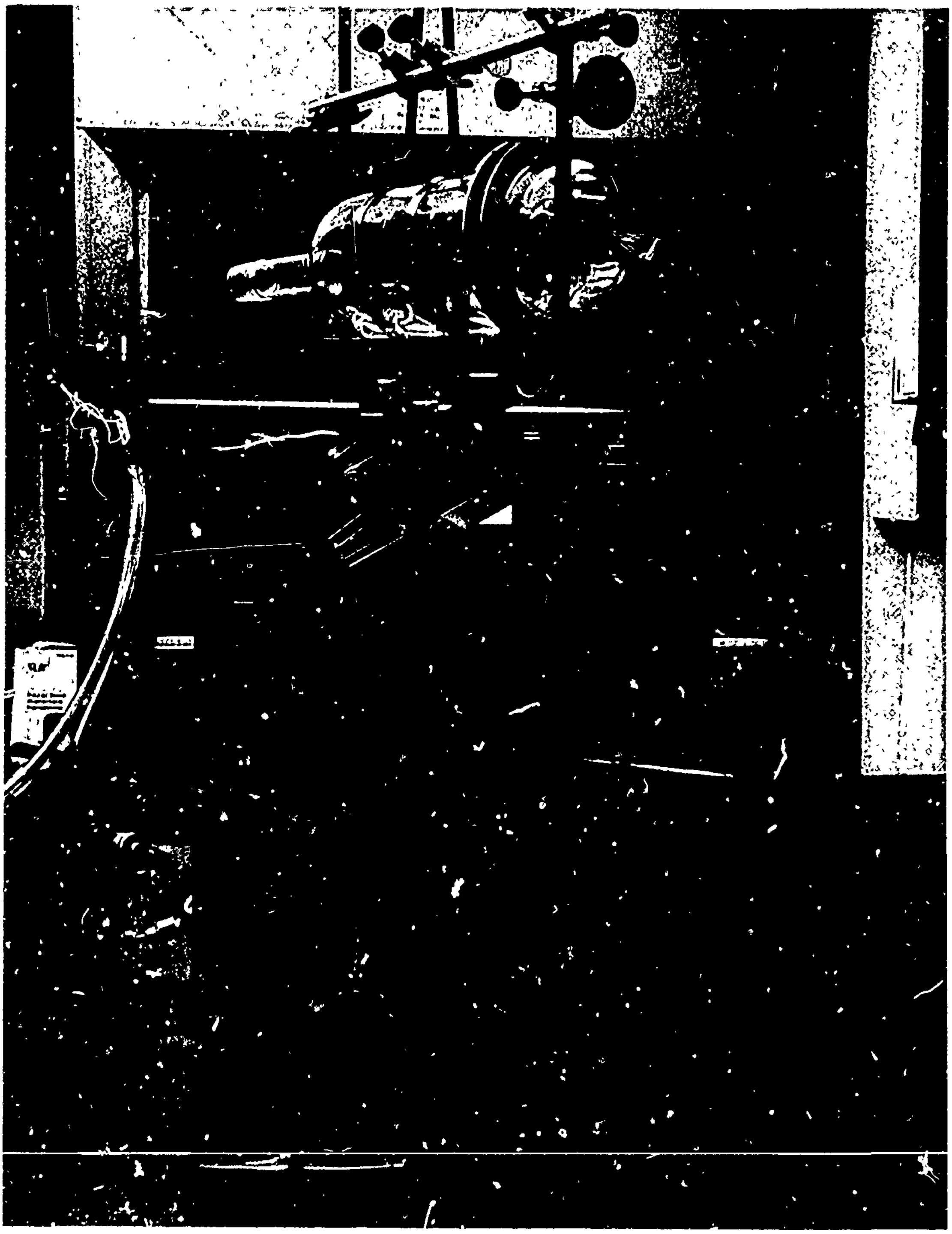

Figure 14. Flash Lamp Assembly

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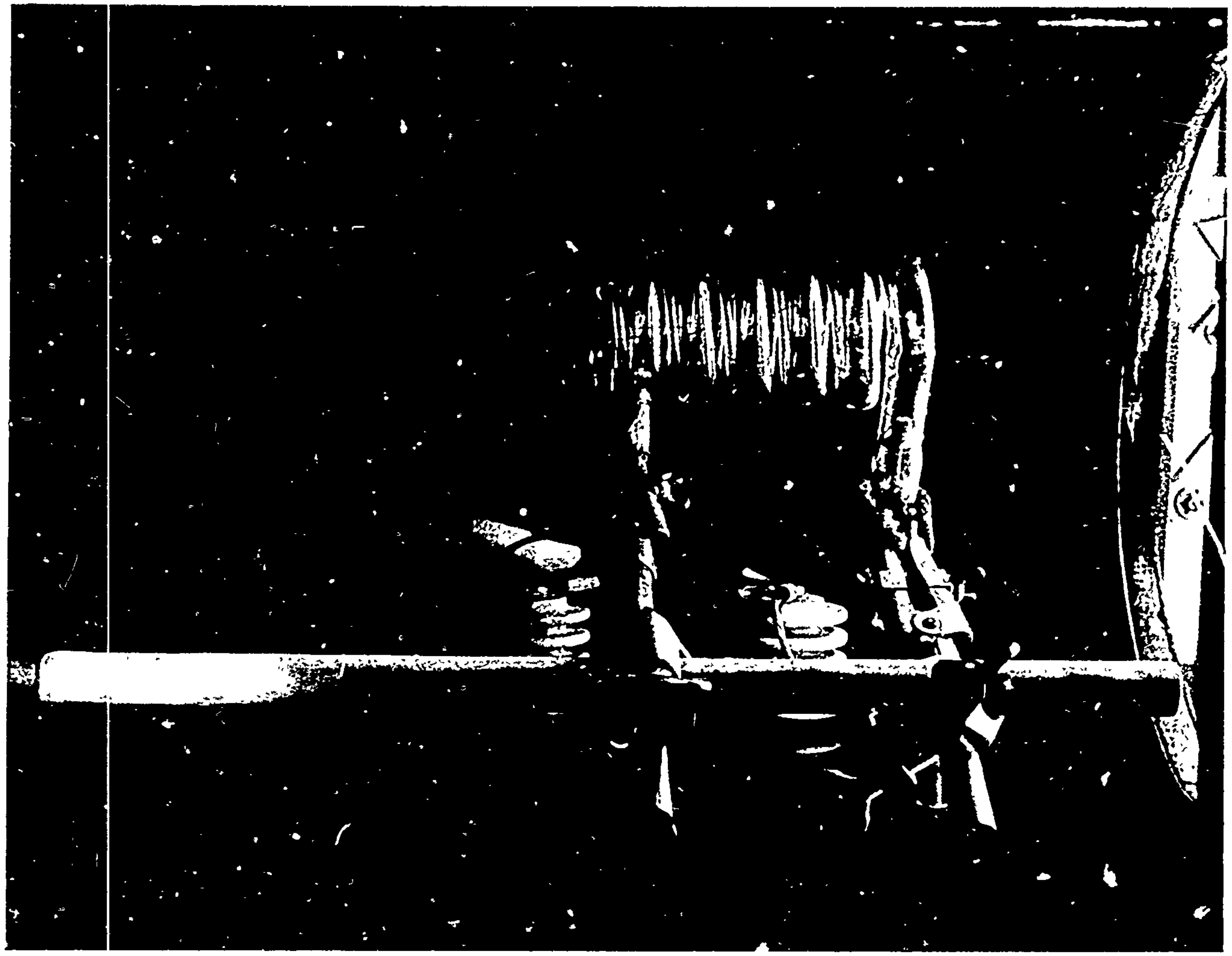

Figure 15. Flash Lamp

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2.0 SYSTEM OPERATION

There are two principal parameters which control the operation of the flash lamp system: (1) the total system capacitance and (2) the charging voltage. The capacitance influences the flash duration, while the charging voltage affects the level of the luminous heat flux. The capacitors are mounted in two chest-type cabinets and are accessible through hinged tops. There are a total of six capacitors, four of which are permanently wired into the circuit for proper shaping of the energy pulse. The remaining two can be individually switched in or out of the circuit with knife switches, as required.

The capacitor charging power supply is mounted in a console which is adjacent to the capacitor cabinets. It has a variable output of 2 to 5 kv at 0.7 amp and has a dc voltmeter on the front panel used to monitor the charging voltages. About 0.5 min is required to charge the capacitors to 5 kv. Ordinarily, the power supply is switched off after charging the capacitors so that they will not be recharged immediately after flashing the lamp. The capacitor bank will remain charged for several minutes without leaking any appreciable amount of charge. Both the capacitor cabinets and the control console are mounted on casters permitting mobility of the entire system.

For operation the lamp is initiated by closing a momentary-contract handheld switch which is connected to the PEK trigger source. At a BNC connector on the front of the trigger source cabinet, a sync pulse of 20 v is provided for triggering external monitoring equipment. The lamp itself is enclosed in a sheet metal box to protect operating personnel from the intense light.

Since there is sufficient energy stored in this system to be fatal to a person, safety has been a prime concern in the construction of the equipment. A resistor bank is installed in the system, operated by a relay, so that the capacitor bank can be discharged without firing the lamp, if that is necessary. In addition, it is used after firing the lamp to discharge any residual charge on the capacitors and is also used automatically through interlock switches on the capacitor cabinet tops when performing any manual operations on the capacitors.

3.0 SYSTEM CHARACTERISTICS

The available luminous heat flux from the lamp was measured by a technique described by Kuebler and Nelson.(8) Measurements were made to characterize the radiant output of the lamp as a function of charging voltage on the capacitor bank. In addition, measurements were made of the flash duration for various numbers of capacitors in the energy storage system by photographing the oscilloscope display of a photocell which monitored the optical intensity of the flash. The pulse duration is defined(9) as the time lapse between the 1/e points of the energy pulse as determined from the oscilloscope display. The measured pulse durations are shown in table VIII.

TABLE VIII

FLASH LAMP MEASUREMENTS

No. of Capacitors in Storage Bank	Pulse Duration msec
4	8.4
5	10.6
6	12.5

The results of the incident energy calibrations are shown in figures 16 and 17. Figure 16 shows the total energy/cm^2 incident upon the radiometer, while figure 17 shows the average heat flux incident upon the radiometer during the flash. Although the incident heat flux is of the order of 200 to 300 cal/cm^2-sec, the total energy absorbed by the radiometer is only 2 to 4 cal/cm^2.

Three different parameters are shown on the total energy plot corresponding to the number of capacitors in the system, but when the pulse duration is considered in the radiant energy plot, the resultant flux is a function of the voltage alone and is independent of the capacitance. Thus, it is possible to achieve a constant heat flux for varying times by varying the number of capacitors in the circuit and maintaining the voltage at a constant level. Conversely, since the flash duration is determined by the number of capacitors, it is possible to maintain a constant flash duration while varying the heat flux by changing the voltage to the capacitor bank.

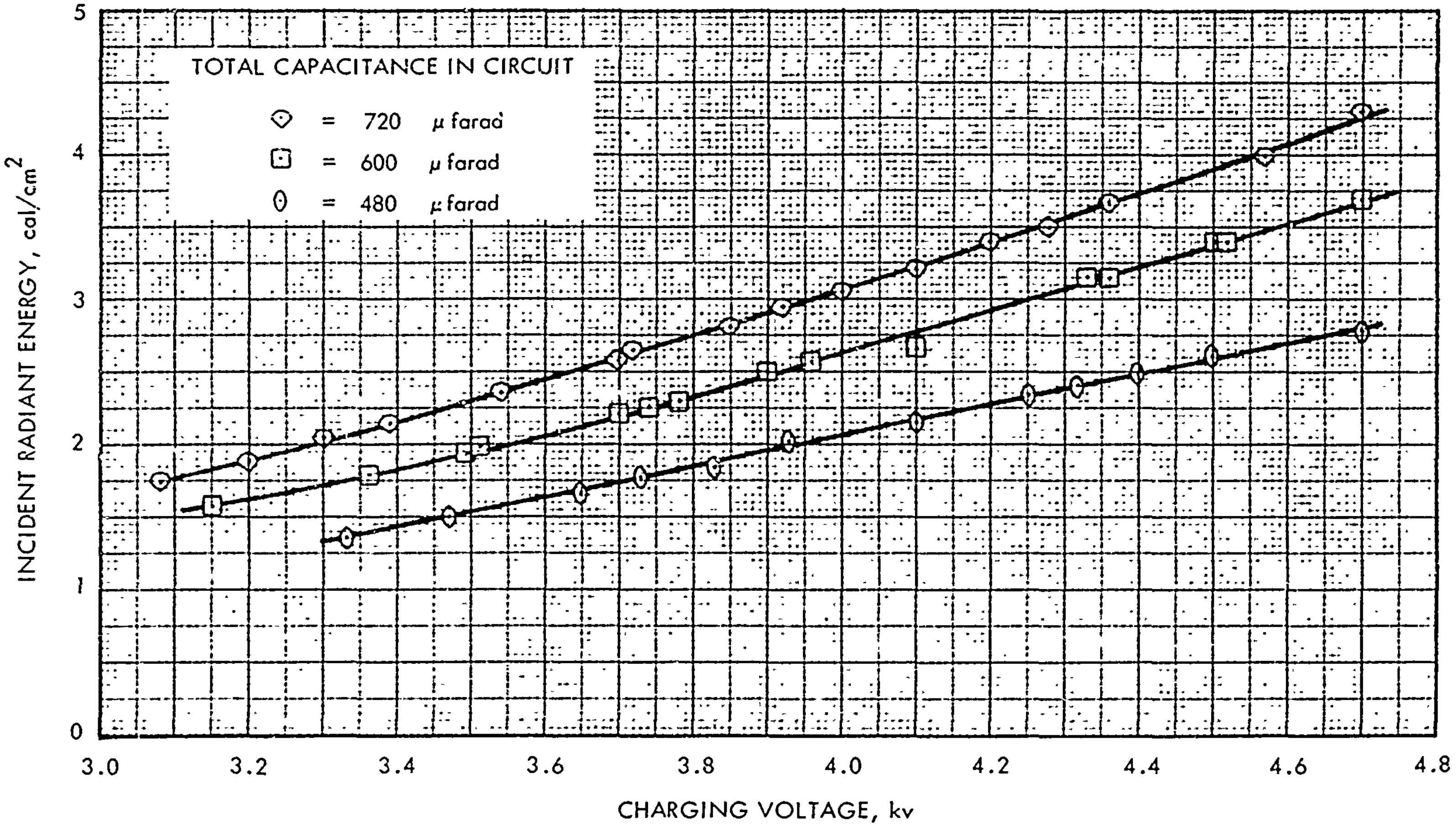

Figure 16. Incident Radiant Energy/cm^2 vs Capacitor Charging Voltage

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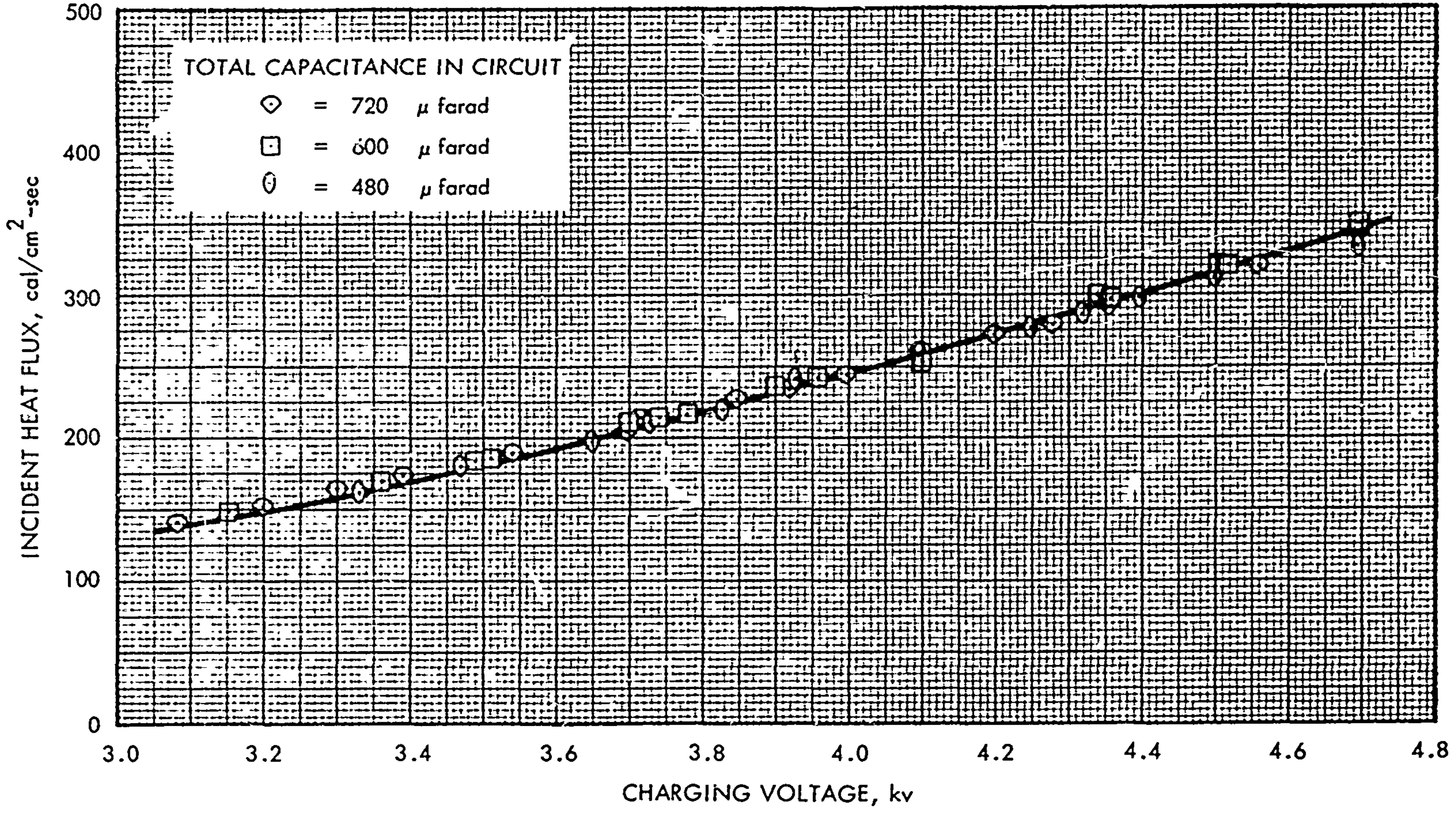

Figure 17. Incident Heat Flux vs Capacitor Charging Voltage

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The maximum flash duration using the current system is 12.5 msec. There is no reason, however, that this maximum could not be extended by adding additional capacitor-inductor units to the circuit.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

United Technology Center
Propulsion Research Branch
Sunnyvale, California 94088

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE

Composite Solid Propellant Ignition Mechanisms

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific Final

5. AUTHORS *name, middle initial, last name)*

Larry J. Shannon

6. REPORT DATE April 1969	7a. TOTAL NO. OF PAGES 49	7b. NO. OF REFS 9

8a. CONTRACT OR GRANT NO.
F44620-68-C-0053
b. PROJECT NO.
9711-01
c. 6144501F
681308

9a. ORIGINATOR'S REPORT NUMBER(S)
UTC 2316-FR

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
AFOSR 69-1250TR

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11. SUPPLEMENTARY NOTES
Tech. Other

12. SPONSORING MILITARY ACTIVITY
Air Force Office of Scientific Research
(SREP), 1400 Wilson Boulevard
Arlington, Virginia 22209

13. ABSTRACT

This report describes the results of an experimental study of the thermal decomposition characteristics of composite solid propellant fuel components. Variations in heating rate, pressure, environmental gas, and polymer type were studied. Supplementary propellant ignition tests utilizing an arc-imaging furnace and ionization gap techniques were conducted to obtain information relating time for onset of a gas-phase reaction to propellant ignition times via radiant heating.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Composite solid propellant						
Ignition						
Polymer decomposition						
Differential scanning calorimeter						
Radiation furnace						
Flash pyrolysis						