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AFOSR 40-64

UNIVERSITY OF UTAH DEPARTMENT OF CHEMICAL ENGINEERING

AFOSR 40-64

Technical Report

on

IGNITION AND COMBUSTION OF SOLID PROPELLANTS

Under Air Force Grant 40-64

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SUMMARY

This report summarizes the work performed under Air Force Grant AFOSR 40-64. The results of the study of propellant ignition by high convective heat fluxes have shown that the gas velocity effect often observed in convective heating tests can be attributed to surface roughness. If this surface roughness effect is eliminated by the use of very smooth propellant surfaces or by use of very high gas velocities which prevent ignition of projections on the surface, the relationship between ignition time and surface heat flux is simply the extrapolation of the low-flux ignition data. Also, it appears that the effect of a burning rate catalyst is to increase the rate of reaction of propellant-component decomposition products at the propellant surface.

Modification of the thermal ignition theory to include the effects of surface regression for high igniter heat fluxes has lead to results which indicate that an ignition-pressure effect on the overall ignition process can be observed with practical ignition systems even when the thermal response of the propellant itself is independent of pressure. The problem of transition from ignition to steady-state burning can be approximately treated by this model. Polymer (PBAA) decomposition studies have shown that, while reactions and some weight loss may occur at temperatures below 300°C, at the heating rates of interest in propellant ignition, the thermal effect of these reactions can probably be neglected for temperatures below at least 350°C. The results of a re-evaluation of the hot-wire ignition technique have been encouraging. It is possible to accurately measure ignition times from 10 msec to 10 sec, and these results are comparable to data from low flux radiation tests.

I. INTRODUCTION

As part of a continuing research effort, several phases of the ignition of composite propellants have been studied. This work was supported by the Air Force Office of Scientific Research under Air Force Grant AF-AFOSR 40-64 and is being continued under Air Force Grant AF-AFOSR 40-65.

The study of the ignition characteristics of several special propellant formulations employing high convective heat fluxes has been essentially completed. The polymer decomposition study is beginning to yield interesting quantitative results and is continuing We have resumed the extinguishment studies employing the rarefaction tube and have confirmed previously observed phenomena. This work is now progressing into new areas Work on a solid-phase oriented ignition model is progressing, and the introduction into the model the possibility of surface regression during high flux ignition has opened what appears to be several interesting areas for study. We have started a small program to re-evaluate the hot-wire ignition method for ignition studies and present preliminary and encouraging results. Each of the above studies is discussed in the following sections of the report Separate conclusions are presented in each section

II IGNITION THEORY

The thermal theories of ignition present a quite adequate description of the ignition of both composite and double base propellants exposed to low heat fluxes For the case of exposure to high heat fluxes, which are of most interest for practical ignition, the agreement between the simple thermal theories and experiment is not always good A somewhat more complicated model than the one assumed by the simple theories but which reduces to the simpler models for the case of low flux ignition is required A clue to the nature of the more complex model is obtained by a consideration of the order of magnitude of the surface-ignition temperatures calculated from the simple ignition theories. By appropriate selection of reasonable parameters, a calculated surface-ignition temperature for the low flux case of about twice the absolute ambient temperature can be obtained If the same parameters are used for the high flux case, however, it is found that the calculated-surface temperatures are about three times ambient temperature A true surface-ignition temperature of about 600°K may be reasonable, however, before a temperature of 900°K would be reached, all the propellant components would gasify by endothermic processes Significant regression of the solid surface would occur A propellant ignition model which considers this regression should perhaps explain the propellant response to high surface-heat fluxes It can be argued, on the basis of steady-state burning rates, that the solid regression need not be considered for ignition, but such arguments are not entirely satisfactory The ignition heat flux may be much greater than the steady-state-burning-feedback flux, thus the temperature gradient in the propellant would be steeper in the ignition case, and the loss of even a few molecular layers at the solid surface would be important To a good approximation, the vaporization of any material near the surface can be treated as surface regression.

The consideration of surface regression in the ignition model introduces one problem and some interesting possibilities In the case of the simple thermal theories, ignition is assumed to be complete when a run-away reaction occurs, but if regression is considered no run-away reaction occurs, since presumably, the surface regression rate must increase as needed to establish a reasonable bound on the surface temperature A new ignition criterion which is analogous to the go-no-go experimental criterion must be used The minimum time at which the external flux can be cut off with transition to steady-state

burning (or at least a continuous increase in the surface temperature) still occurring would be the ignition time If the transition to steady-state burning must be considered, the model must then treat ignition, transition to burning and steady-state burning

Proposed ignition model

Preliminary calculations have been made in which it is assumed that the ignition process can be described by the following one-dimensional, nonlinear, partial differential equation in terms of solid temperatures.

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} = \left(\frac{k}{\rho c}\right) \frac{\partial^2 v}{\partial x^2} + \frac{A}{\rho c} \exp\left[-\frac{E_a}{Rv}\right] \tag{1}$$

The initial and boundary conditions which apply are

For $t = 0$, $v = v_o$.

For $t > 0$ and $x \longrightarrow \infty$, $v = v_o$.

For $t > 0$ and $x = 0$,

$$-k \frac{v}{x} = F_s + F_g(t)P^n + \frac{PC \exp\left[-\frac{E_c}{Rv}\right]}{1+PC \exp\left[-\frac{E_c}{Rv}\right]} B \exp\left[-\frac{E_b}{Rv}\right]$$

The velocity, u, is assumed to be a function of the surface temperature, or for temperatures evaluated at $x = 0$

$$-u = V_r \exp\left[-\frac{E_r}{Rv}\right] + \frac{PC \exp\left[-\frac{E_c}{Rv}\right]}{1 + PC \exp\left[-\frac{E_c}{Rv}\right]} \left\{ C_b \exp\left[-\frac{E_b}{Rv}\right]\right\}.$$

In these equations, v is the solid absolute temperature; v_o is the initial solid temperature, t is time, x is the distance measured from the position of original solid surface, B, A and C, and E_b, E_a, and E_c are respectively the product of frequency factor and heats of reaction and the activation energy for surface, bulk and surface absorption reactions, E_r is the activation energy for the thermal regression rate and V_r would be the rate for unity value of

the exponential; C_b transforms the surface reaction rate to the regression rate which is a result of surface reaction; k, ρ, and c are respectively the assumed constant propellant thermal conductivity, density and heat capacity; P is the pressure in atms., F_s is the external heat flux; and R is the gas constant. The term $F_g(t)$ represents the heat flux from the gas phase to the solid surface and is assumed to be zero for surface temperatures below a certain value This term is modified by the factor P^n to account for the effect of pressure on this heat flux. The gas-phase feedback must only be considered near the end of the ignition process and for steady-state burning. If certain simplifying assumptions concerning the solid response are introduced, the nature of this gas-phase feedback flux can be determined [5]. The value of n is chosen to approximate the results of the gas phase studies. The present model is solid phase oriented and is complementary to the gas-phase studies. In most gas phase studies relatively simple solid phase boundary conditions are assumed, in this study a relatively simple gas-phase feedback term is assumed Since simultaneous treatment of the solid phase and gas phase problems is probably beyond the capacity of present day computing systems, separation of the problem in this manner would represent a reasonable approach to the whole problem

The transformation of these equations into dimensionless form and the details of the setup for the numerical solution are discussed in Appendix A.

Preliminary results of computations.

Figure 1 shows qualitatively the type of information obtained by use of this ignition model In this case propellant parameters for the F-propellant were used and no simple gas-phase feedback term was included ($F_p(t) = 0$). The time scale was adjusted for each run to bring all the surface-temperature-time curves into the same range. For ignition heat fluxes much greater than the calculated steady-state-burning feedback flux (from surface reaction in this case), the transition to burning does not occur

Although the parameters selected for these runs may give results which exaggerate this effect, it should be noted that too high an ignition flux could produce regression and not ignition Since at higher pressures the steady-state feedback would be higher, higher ignition fluxes could be used. For near equality of these fluxes, the surface temperature appears to pass through a maximum before reaching stable burning. The high burning rates resulting from this high surface temperature during ignition could contribute to the transient over pressure observed with practical igniter systems.

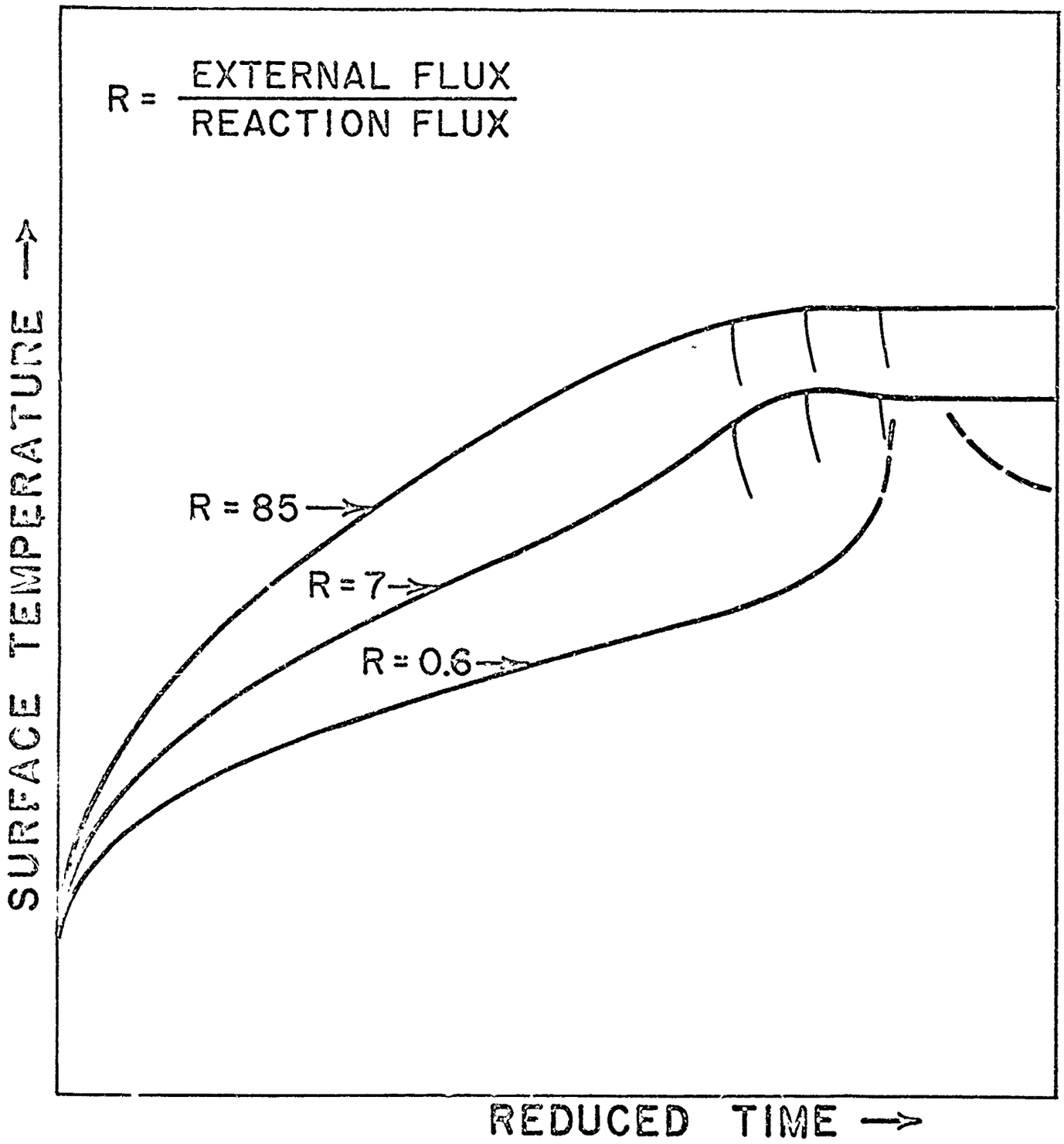

Figure 1. Typical qualitative results from the ignition model which treats surface regression. A feed-back flux which depends on surface temperature was considered. R propellant parameters were used in the model and the calculated surface regression rate was only about 10 per cent of the normal burning rated under predicted steady state burning conditions. Different time scales apply for each value of R. For R greater than one the surface temperature continuously dropped when the external flux was cut off.

Steady-state burning.

The ignition criterion for a model including the effects of surface regression requires at least an approximately correct steady-state-burning model In order to select reasonable parameters for the steady-state model, solutions to the ordinarily differential equation obtained from Equation (1) by elimination of the time-dependent term were obtained. The parameters used should permit the model to predict the normal dependence of burning rate on pressure, reasonable values of the steady-state-burning rate and the qualitative aspects of steady-state burning. Figure 2 shows the result of one set of calculations in which the parameters obtained by ignition results were selected to correspond to the F-propellant; the feedback flux from the gas phase was assumed to depend upon the square root of pressure and to be equal to about one-tenth of the heat flux from surface reactions at 1 atmosphere; and a negligible effect of condensed phase reactions was assumed

In the pressure range of 1-50 atms , the burning rate exponent would be about 0.4 At low pressures the burning rate appears to approach a steady value, but if a surface heat loss term, which would be important at low pressures, is added to the model an extinction pressure would be observed. At high pressures the burning rate exponent begins to decrease. Although not characteristic of most propellants, such an effect is noted with composite propellants containing volatile fuel-binders [1]. The calculated, steady-state surface temperatures were almost independent of the pressure. The model appears to contain enough parameters that a forced fit could be achieved by varying these parameters, and with certain limits, this is true. However, in common with the results from the ignition model, it is found that certain terms must be included or eliminated, and only a limited range for the variables is allowed if a reasonable result is to be obtained.

Preliminary conclusions

The ignition model considering solid regression satisfies the requirement of reducing to the simpler model at low fluxes and of producing ignition times at higher flux levels which are in qualitative agreement with experiment It represents a first attempt to handle the problem of transition from ignition to burning The general model appears to be selective with respect to terms

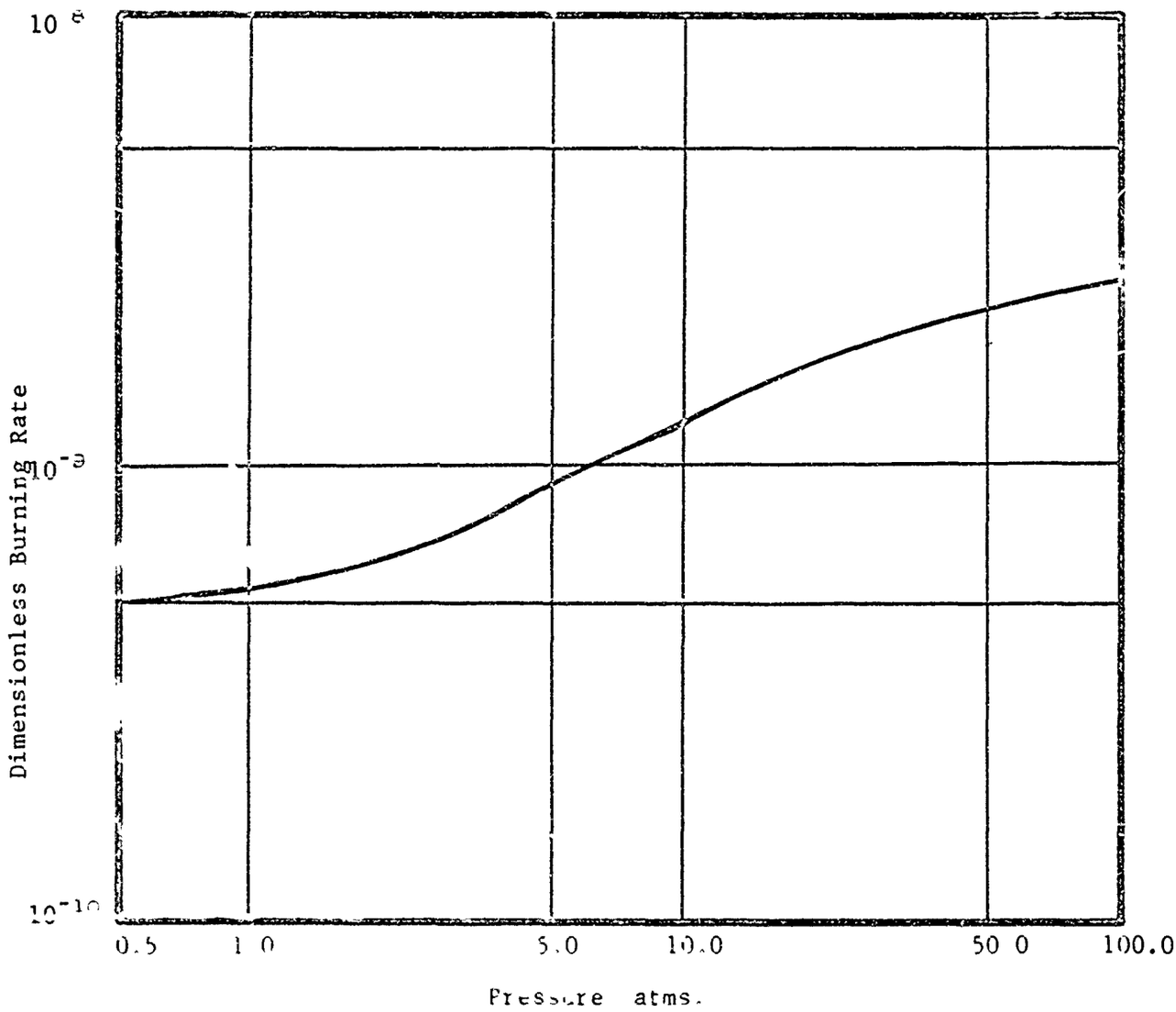

Figure 2. The effect of burning rates on steady-state burning rates calculated from ignition model which treats surface regression. The values of parameters used in Equation (1A) of Appendix A are as follows:

Y	0 02	E =	-0.30
CB =	43 5	EE =	6.0 x 10^{-}
CA	2 0 x 10^{-}	R =	1 00
CN =	0 5	RR =	1 10
D	0 50		
DD	1 0 x 10^{-}		

which may be included and their order of magnitude A great deal is known about ignition and burning, and it may be that only a single arrangement of terms and parameters will be able to produce a model which will make predictions in agreement with this knowledge. For example, the detailed model containing the parameters used to generate Figure 2 appears to be unstable when treated in Equation (1) Although a solution to the non-time dependent form exists, any deviation from this steady-state condition results in the beginning of a run-away reaction or in extinction. A high gas-phase-feedback flux appears to be required to stabilize the system. A flux-limited regression rate may be required.

It appears that the results of this type of analysis may be useful in the interpretation of our low-frequency combustion instability work and our extinguishment studies.

III. IGNITION OF PROPELLANTS BY HIGH CONVECTIVE HEAT FLUXES

The planned work employing the shock tube to study ignition by convective heat transfer from hot gases has been completed Appendix B is a summary of part of this work, and a discussion of the apparatus is presented there The material from this Appendix formed the basis for a paper presented at the 1964 Fall meeting of the Western States Section of the Combustion Institute. The following paragraphs summarize the major conclusions from this work, only a limited amount of experimental evidence is presented here Additional details are presented in Appendix B and in a technical report to be issued in the first quarter of 1965.

Propellant composition studies.

Thermal decomposition studies on ammonium perchlorate at fairly slow heating rates relative to those used in the ignition of solid propellants indicate that several metal oxides can be used to increase the rate of thermal decomposition as well as the extent of decomposition of otherwise pure ammonium perchlorate The addition of these metal oxides drastically lowers the temperature at which the ammonium perchlorate will undergo spontaneous deflagration (critical temperature). One of the most extensive studies of the effect of catalysts on decomposition of ammonium perchlorate was reported by Kuratani [8]. The results of this work are summarized as follows.

1. Cupric oxide, cuprous oxide, cuprous chloride, and zinc oxide were found to promote both the low temperature and high temperature ammonium perchlorate decomposition reactions.
2. Nickel oxide and chromic oxide (Cr_2O_3) promoted primarily the low temperature decomposition reactions
3. Manganese dioxide and copper chromite promoted primarily the high temperature decomposition reactions
4. Aluminum oxide, titanium dioxide, ferric oxide, and vanadium pentoxide did not appear to promote any of the decomposition reactions of ammonium perchlorate

The low temperature decomposition reactions are those which take place below about 350° C and appear to be associated with the decomposition of intermosaic ammonium perchlorate

Other studies which appear to be useful relative to ignition of propellants are those by Hermoni and Salmon [6]. They found by careful experiments that carbon, manganese dioxide, and copper chromite mainly influence ammonium perchlorate decomposition reactions in the solid phase, while chromic oxide and cuprous oxide influence gas-phase decomposition reactions

Investigations by Solymosi and Revesz [11] on the effect of ferric oxide on decomposition of ammonium perchlorate showed ferric oxide to have only a slight effect in the temperature range of 210-240 °C. A noticeable contribution to the decomposition of ammonium perchlorate was observed in the region of 245-270 °C.

Since considerable work has been done on ammonium perchlorate decomposition, it appeared that some information on the mechanism of ignition of solid propellants could be obtained by making an ignition study on propellants containing metal oxides as catalysts. The ignition of five different propellants was studied under high convective heat fluxes. The compositions of these propellants is shown in Table I.

Samples of propellant with freshly cut surfaces were exposed to convective heat fluxes in the range of 40 to 130 cal/(cm^2)(sec). Since the shock tube was used for these studies, the maximum testing time was limited to less than 25 msec Under these conditions it was found that only the propellant containing two per cent iron oxide (designated as AD) would ignite over the entire range of surface heat fluxes Propellant Z which contained two per cent zinc oxide and one per cent iron oxide ignited, but ignition times were about 50 per cent longer than for propellant AD. Propellants Y and AA containing zinc oxide and chromic, respectively, showed some indication of reaction at the surface as indicated by a small deflection of the photocell signal. This small amount of luminosity was only observed at a flux level of about 100 cal/(cm^2)(sec). The time for the appearance of this slight luminosity, which did not lead to steady deflagration, was about the same as that for the ignition of propellant Z Propellant AB which contained cuprous oxide occasionally ignited when subjected to fluxes of 90-110 cal/(cm^2)(sec).

Microscopic examination of the surfaces of samples which did not ignite showed that for all samples which gave a slight indication of reaction at the surface there was some ablation of both polymer and ammonium perchlorate In the case of the propellant containing zinc oxide there was considerable charring of the polymer for high flux runs, although no light signal was observed

Because of the test period limitation encountered with the shock tube it was not possible to obtain adequate data to determine the relative effects of the catalysts studied on ignition of ammonium perchlorate propellants. A general observation which can be made at this time is that catalysts which appear to be most effective in promoting the thermal decomposition of ammonium perchlorate are not necessarily effective in promoting ignition. Apparently thermal decomposition studies of ammonium perchlorate at very low heating rates do not give information which can be applied directly to the ignition of propellants. Furthermore, it is observed that non-volatile iron oxide, which does not effect greatly the thermal decomposition of ammonium perchlorate, appears to be an extremely effective ignition catalyst.

The ignition of a propellant may be greatly influenced by the ability of the catalyst to promote reactions between ammonium perchlorate decomposition products and the binder-fuel or of the ammonium perchlorate decomposition products themselves. It is known that both iron oxide and the so-called copper chromite, which also is an ignition catalyst, are oxidation catalysts. Although additional experimental work is required, it appears that when these ignition catalysts are used, steady deflagration of the propellant is initiated by surface catalyzed reactions. At least two mechanisms seem possible:

1. The promotion, by heterogeneous catalysis, of reaction between initial AP decomposition products; subsequent reaction occurs between the resulting fragments and either solid polymer or polymer decomposition products; or

2. The heterogeneously catalyzed reaction between the decomposition products of both propellant ingredients.

Either of these mechanisms could explain the results of ignition tests in which large, pressed pieces of AP were in contact with the PBAA polymer. Although complete transition to steady-state burning never occurred, significant reaction was observed only when the catalyst was present in the AP and when the gas flow direction was from the polymer to the AP.

Although the results of tests in which catalyzed propellants were formed by use of non-volatile carbon black as fuel-binder were obscured by questions concerning surface roughness, the ignition of these materials was similar

to that of polymer-fueled propellants and indicated that the direct surface oxidation of the fuel-binder is possible

A number of propellants have been tested each of which represented variations in the basic F-propellant composition. Variations in oxidizer loading and particle size were studied For the limited variation (± 5 per cent) in AP loading, no significant effect on ignition response was noted No significant effect was noted for variations in the AP-particle size except when all fine particles were used. The propellant containing all fine AP was more difficult to ignite than F propellant by convective heat fluxes (see Appendix B); this is probably because a smoother surface can be cut with this propellant and is not the result of a true difference in ignition response.

Gas velocity effects and surface roughness.

When the ignition response of a solid propellant to convective heating is studied, an effect of high gas velocities is often noted [3,10]. The normal procedure is to determine the gas velocity above which the effect is first noted and to make subsequent tests below this velocity. The existence of this gas velocity effect is often considered as evidence that the rate controlling ignition reactions occur in the gas phase. Although a major objective of this work was not the study of this gas velocity effect, enough data were obtained to indicate a rather novel explanation of the phenomenon. Appendix B presents some of the data from this study.

In the case of the ignition in nitrogen of the catalyzed propellants studied, the following characteristics of the gas velocity effect were noted:

1. Higher velocities result in longer ignition times. At pressures of 250-350 psia, an effect is noted at gas Mach numbers as low as 0.1.
2. The gas Mach number appears to determine the magnitude in shift of the ignition times from the zero velocity case.
3. If the catalyst is changed from copper chromite to ferric oxide, the ignition times and gas velocity shift remain essentially unchanged.
4. The gas velocity effect is almost eliminated when the propellants contain only fine ammonium perchlorate. Under the same test conditions the ignition times of these propellants are always longer than the ignition times of propellants containing the same loading of AP but with a normal size distribution.

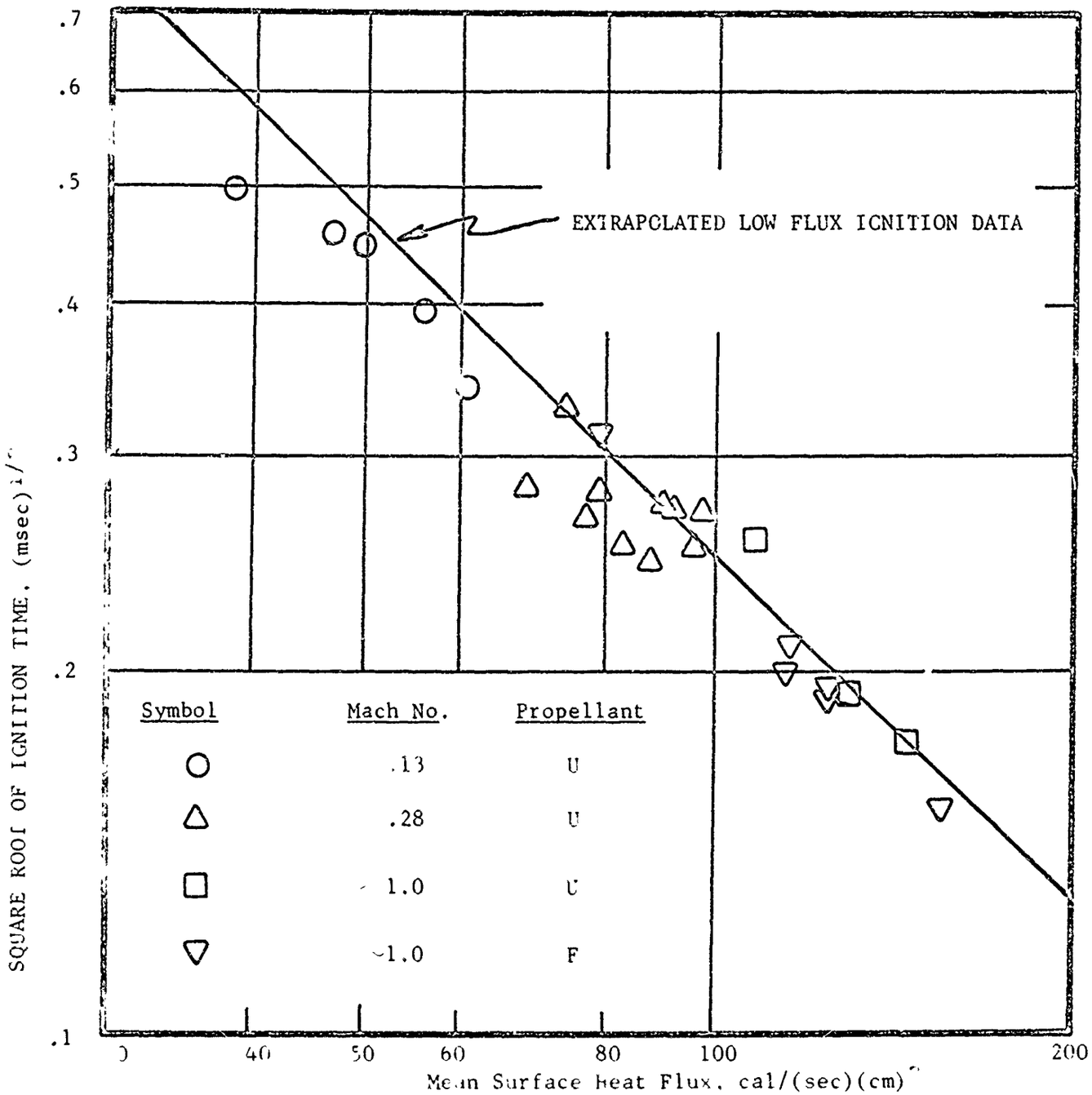

Figure 3. A comparison of ignition data for catalyzed Ammonium Perchlorate propellants obtained under different experimental conditions. The labled line represents an extrapolation of low-flux ignition data for AP propellants. (See reference 10). The data for the F and U propellants were obtained at 25 atms in the shock tube by high convective heat transfer to razor cut surfaces. The U-propellant contains only minus 15-micron AP particles and exposes a very smooth surface to the hot gases The indicated Mach number is for the gas flow past the propellant surface

The last of these conclusions is the most important. The cut surface of an all-fine AP propellant is much smoother than the cut surface of a propellant which contains coarse AP. Microscopic examination indicates that the surface roughness of the fine AP propellant is $\pm$ 2-3 micron while the roughness of the F propellant would be $\pm$ 10-15 micron or the same order of magnitude as the fluid-dynamic boundary layer. Because of the surface roughness, the exposed AP particles are exposed to two-dimensional heating. At low velocities, ignition of the rough surfaces would occur at abnormally low apparent surface temperatures. At high velocities, the decomposition products from the exposed particles would be diluted by the heating gases and would not be effective in promoting ignition. In the case of either very high velocities or very smooth surfaces, true one-dimensional heating and ignition would occur. Figure 3 shows a plot of the F-propellant-ignition results from the low-flux radiation furnace and from the shock tube for a gas velocity of nearly Mach one. Also shown are the ignition data for the U propellant (all 15-micron AP) at low and high velocities. The agreement between these three sets of data obtained under apparently vastly different conditions is remarkable. The procedure of studying convective ignition at low velocities only is apparently the sure way of not detecting the true one-dimensional ignition response of the propellant. Since gas velocities approaching a Mach number of one are often used in practical ignition systems, the surface roughness effect is eliminated and one-dimensional heating is of primary importance.

If this gas-velocity effect on ignition comes solely from a sweeping away of gas-phase decomposition products, changes in the ammonium prechlorate particle size would not influence the results. In fact, it would appear likely that if a diluting effect were the only consideration, a smoother surface would result in less dilution and ignition of smooth surfaces would be easier than for the rough surfaces. The opposite is observed.

Since it is obvious that the transition to burning requires the establishment of an easily observable gas-phase flame, anything which prevents the establishment of the flame will prevent transition to burning. At high velocities the exposed AP crystals on a rough surface are not effective in establishing a steady-state deflagration wave. When ignition occurs by one-dimensional heating, the transition to steady-state burning is apparently quite rapid, and the limiting reaction for ignition is probably the decomposition of the propellant ingredients.

IV. HOT WIRE IGNITION TESTS.

Most of the techniques used for the study of ignition of solid rocket propellants are not entirely satisfactory because they require complicated apparatus use indirect measurement of energy fluxes and/or are accurate only over a limited range of energy fluxes. Often the data are quite imprecise. None of these factors are problems when ignition is studied by use of electrically heated wires. The major objection to this hot-wire technique is that the sample pressure can not be easily defined, but since it appears that pressure does not have a great effect on the ignitions of the composite propellants of interest, this may not be a serious objection. As a result of these considerations, a program was started to reevaluate the hot-wire method for the study of composite propellant ignition. The first phase of this work was similar to the work of Altman and Grant [2] except in this case, the propellant was cast around the wire. Appendix C elaborates the technique and presents the initial results. This appendix formed the major portion of a paper presented at the Autumn 1964 meeting of the Western States Section of the Combustion Institute. Table II presents values of the integral which must be evaluated to form the solution to the heat conduction equation for the case of an infinitely long wire of finite conductivity embedded in an infinite body of propellant. The major conclusions from this work are:

1. At the time of ignition the voltage drop across the heated wire suddenly decreased. This is probably the result of ionization of the confined high-pressure-combustion products. Go-no-go tests were used to confirm that this drop was coincident with ignition. Since ignition could be detected by measurement of the voltage across the wire, ignition times from 10 msec to 10 sec were measured with this simple apparatus.
2. Linear-surface-temperatures at ignition and interface heat fluxes can be calculated by use of wire energy generation rates measured during each test.
3. The calculated surface temperatures were 40-50 °C higher than those calculated from radiation furnace data. This difference is probably the result of a polymer layer forming around the wire which pre-

vented direct AP-wire contact. Such a surface condition would be typical of propellant surfaces cast against casting mandrels.

Some additional work is being done in evaluating the hot-wire method. Different diameters of nichrome wire are being used and a number of different propellant compositions are being studied. Because the temperature coefficient of resistance of the nichrome wire is very low, the voltage drop across the wire is almost constant during a constant-current run. When the nichrome wire is replaced by nickel, which has a high temperature coefficient of resistance, it is expected that the wire temperature-time relationship can be measured directly and that irregularities in this relationship can be used to determine when gasification of the propellant begins.

V. EXTINGUISHMENT OF BURNING PROPELLANTS.

The study of the extinguishment of burning propellants by use of the rarefaction tube was reactivated during the last quarter of the grant period. Initial tests were made in which the burning surface was in the plane of the closed end of the rarefaction tube during the period of pressure decrease. In this case the sample is exposed to a decreasing pressure with no parallel nor normal gas velocity at the surface. The preliminary results confirm previous conclusions that a catalyzed propellant cannot be extinguished by pressure decay rates as high as 100,000 psi/sec. The uncatalyzed composite G propellant was extinguished by a rapidly decreasing pressure, and a study is being made with this propellant. Preliminary results indicated that long time constant phenomena are associated with the extinction. Tests are planned in which the burning surface will be exposed to varying intervals of cold gas flow parallel to the surface.

VI. FUEL-BINDER DECOMPOSITION STUDIES.

This work was initiated in an effort to characterize the propellant fuel-binder decomposition reactions that are of importance in composite propellant ignition. Data from steady-state regression rates measured by hot-plate techniques are probably not applicable, since by these techniques the strongest bonds which yield large polymer fragments must be broken while the breaking of weak bonds which yield lighter fragments may occur during ignition.

Conventional pyrolysis studies.

Small samples of polymer (1 x 0.1 x 0.2 cm) were injected into flowing nitrogen or oxygen in a heated stainless tube. The tube was 3/8-inch i.d. and was heated over a 4-foot length to insure that the gas temperature was uniform at the point where the sample, held in a coiled wire sample holder, was thrust into the flowing gas. The sample holder, mounted on a rod, was injected and removed through an air-lock which permitted high pressure operation of the system. The gas flow rate in the tube of 250 standard cc/min was high enough to insure that the sample was heated to the gas temperature in less than one second. The polymer used in this study was prepared by mixing polybutadiene, acrylic acid and an epon resin (No. 828) in the weight ratio of 81, 4 and 15. and by curing at 170 °F for seven days.

Pyrolysis rates were measured in nitrogen and in oxygen below the ignition temperature by measuring the weight loss of samples exposed to the hot gases. Figure 4 shows results obtained at 22.5 psia and 285 °C and 275 °C in nitrogen and oxygen. The data can be fit to no simple rate law, probably because of competing reactions, and are presented as per cent loss versus time. Except for short exposures, the pyrolysis rates in nitrogen were much greater than in oxygen. An activation energy of 25-30 kcal was calculated for the initial pyrolysis reaction in nitrogen. Samples pyrolyzed in nitrogen changed from a golden color to a dark brown and from a rubber-like material to a tough plastic. Apparently thermal polymerization occurred. Samples pyrolyzed in oxygen became brittle and were a glossy black. Apparently cross-linking involving oxygen occurred. In all cases, the sample size was not diminished by the loss of material, and pyrolysis occurred uniformly throughout the sample. The polymer fragments evolved were quite large and could be condensed

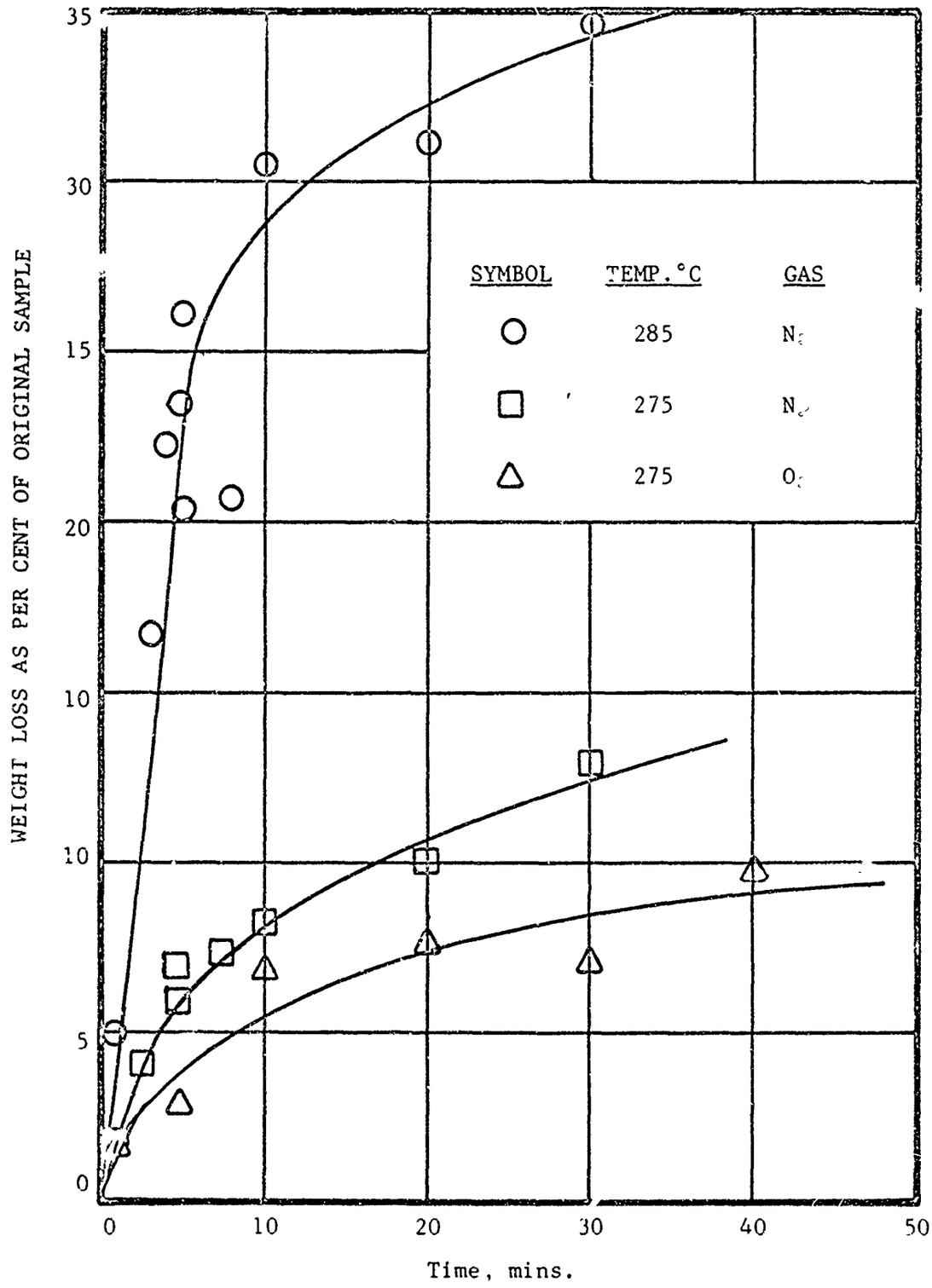

Figure 4. Pyrolysis of PBAA polymer in flowing nitrogen and oxygen at a pressure of 22.5 psia. The polymer samples were 0.1 x 0.1 x 0.2 cm. in size and weighed 0.1 gram.

at room temperature.

Ignition in oxygen occurred at higher temperatures. Figure 5 shows the minimum temperature required for ignition in pure oxygen as a function of pressure. At these temperatures, ignition occurred in 5-30 seconds after insertion of the sample.

Although these tests were not intended to form a comprehensive study, a number of fairly firm conclusions are apparent

1. In order to characterize the polymer reactions, tests must be made in the time scale of interest. The importance of each competing reaction such as decomposition, thermal polymerization or oxygen cross-linking varies according to the conditions and duration of a test.

2. This polymer decomposes at significant rates in the temperature range of 250-350 °C by homogenous decomposition. Reactions in this temperature range are of prime importance in composite propellant ignition.

3. One might be tempted to draw conclusions concerning the nature of the oxygen-polymer ignition reaction on the basis of these tests, but an objective view would shown that a firm conclusion cannot be established. A proponent of a heterogeneous oxidation mechanism can point out that the oxygen cross-linking reaction would probably be exothermic. When the energy release rate of this reaction exceeded the rate at which energy could be transferred to the gas phase, the polymer temperature would rise; and the cross-linking reaction would soon be replaced by a direct oxidation reaction. Most of the evidence, however, would support a gas-phase ignition mechanism. The temperature and pressure range required for ignition corresponds to the range normally required for the homogeneous ignition of gaseous hydrocarbon-oxygen mixtures. The mass-flux of polymer at the sample surface was about one per cent of the oxygen mass-flux past the surface; thus, in the boundary layer, a wide range of fuel to oxygen ratios would exist. The observed "induction" period of 5-30 seconds for these tests is of the same order as that of a hydrocarbon-oxygen ignition. This question, concerning the nature of the oxidation reaction, is possibly of academic interest only. In the case of propellant ignition in a neutral atmosphere, the primary oxidizing agent is unlikely to be oxygen.

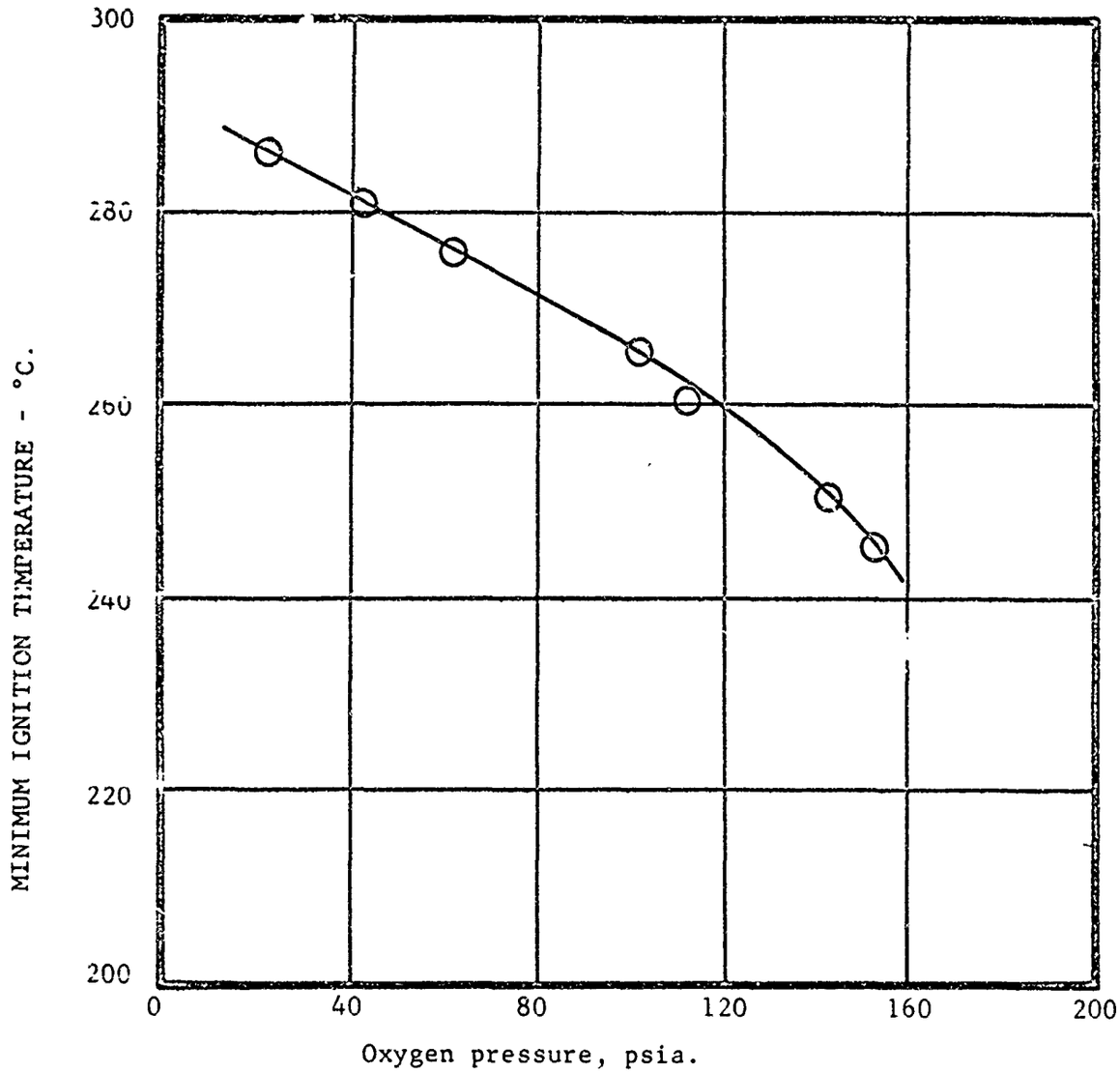

Figure 5. The minimum ignition temperature of PBAA polymer in flowing oxygen as a function of pressure. At these temperatures ignition occurred after 5 to 30 seconds of exposure. At higher temperatures ignition was very rapid, and at lower temperatures the oxygen appeared to contribute to polymerization and cross-linking.

Fast pyrolysis studies.

PBAA polymer decomposition studies were made for the time intervals of interest in ignition. Films of polymer were coated on the surface of thin-film heat-flux gages. The gages were 1 cm diameter x 5 cm long pyrex cylinders, and a platinum resistance thermometer was formed on one flat end by firing an organic platinum paint onto the surface. Opaque polymer films, which contained 4% carbon black, covered the resistance thermometer. The polymer-coated heat flux gages, which were shielded to insure one-dimensional conduction, were pushed into the radiation furnace. The platinum film measured the interface temperature of polymer and pyrex; and the gage output, which was proportional to this temperature, was displayed as the photographically recorded trace of an oscilloscope. These time-temperature data were converted to a time heat-flux at the gage surface relationship by well-known techniques [7].

Early in this work it was observed that the products of the pyrolysis reactions irreversibly altered the resistance of the platinum resistance thermometer, and in later tests the platinum film was coated with a very thin layer of SiO_2 formed by vacuum deposition. In most cases, the SiO_2 film adequately protected the platinum.

Even with SiO_2 coated gages, the preliminary tests with this technique were confusing. As a check on the technique, tests were made to determine whether black-body-radiation fluxes in the furnace could be measured. As a result of these tests, it was found that when the gage surface temperatures exceeds 100 °C, two corrections to the heat-flux-gage readings were required. First the variation in thermal properties of the gage must be considered. Also the temperature coefficient of resistance of the gage was found to change from 2.65×10^{-3} °C^{-1} to 2.41×10^{-3} °C^{-1} rather abruptly at about 110 °C. By use of the best available data on the effect of temperature on the thermal properties of pyrex [4, 9] and the results of extensive computer calculation, a simple by satisfactory technique for treating the thermal property variation was developed. When the black-body-radiation flux measurement data were corrected, it was found that the measured fluxes were constant with time and were within 2 per cent of the values calculated from the Stefan-Boltzmann equation and the measured furnace temperature.

The fast pyrolysis data obtained with SiO_2 coated gages were then corrected for variations in the pyrex properties and for the observed change in the film temperature coefficient of resistance. The final results, although not highly reproducible, are rather significant. Figure 6 presents typical results of the best of these pyrolysis tests under vacuum (.01 atm). Shown on the same time scale are the measured temperatures and fluxes at the polymer-gage interface. Also shown are the results of computer calculations for temperatures and heat fluxes which should agree with the measured values if no reactions occurred, the polymer-film thickness was .01 cm and the assumed thermal properties of the polymer and gage were correct. Considering the nature of the assumptions, the agreement between observed and calculated values of temperature and flux are good. Table III summarizes the computer calculations, and indicates that for time intervals greater than about five seconds, the temperature change across the inert polymer film should be within one per cent of the asymptotic value of 54.6 °C, and the heat flux at the interface should be 98 per cent of the surface heat flux. For exposure times greater than 2-3 seconds, to a good first approximation, the polymer surface temperature was 50 °C above the interface temperature shown in Figure 6 and deviations of the interface-heat flux from the observed maximum value can be attributed to reactions within the polymer film.

The interface-heat-flux relationship in Figure 6 is quite interesting. This heat flux is much below the anticipated value for the first five seconds of the run. During this period absorbed water is apparently evaporating from the polymer. Since in a closed system the amount of water evolved could be determined and since the energy required to remove the water is close to the heat of vaporization of pure water, this phenomena can be used as a check or to calibrate the method. For exposure times of 5-10 seconds, the interface flux was nearly constant and presumably approaches the surface heat flux. When the interface temperature reached about 210 °C (a polymer surface temperature of 260 °C) an endothermic reaction began and the interface heat flux dropped continuously. If the maximum value of the interface-heat flux is assumed to be equal to the surface heat-flux and the difference between this value and the observed flux is attributed to reaction within the film, an activation energy

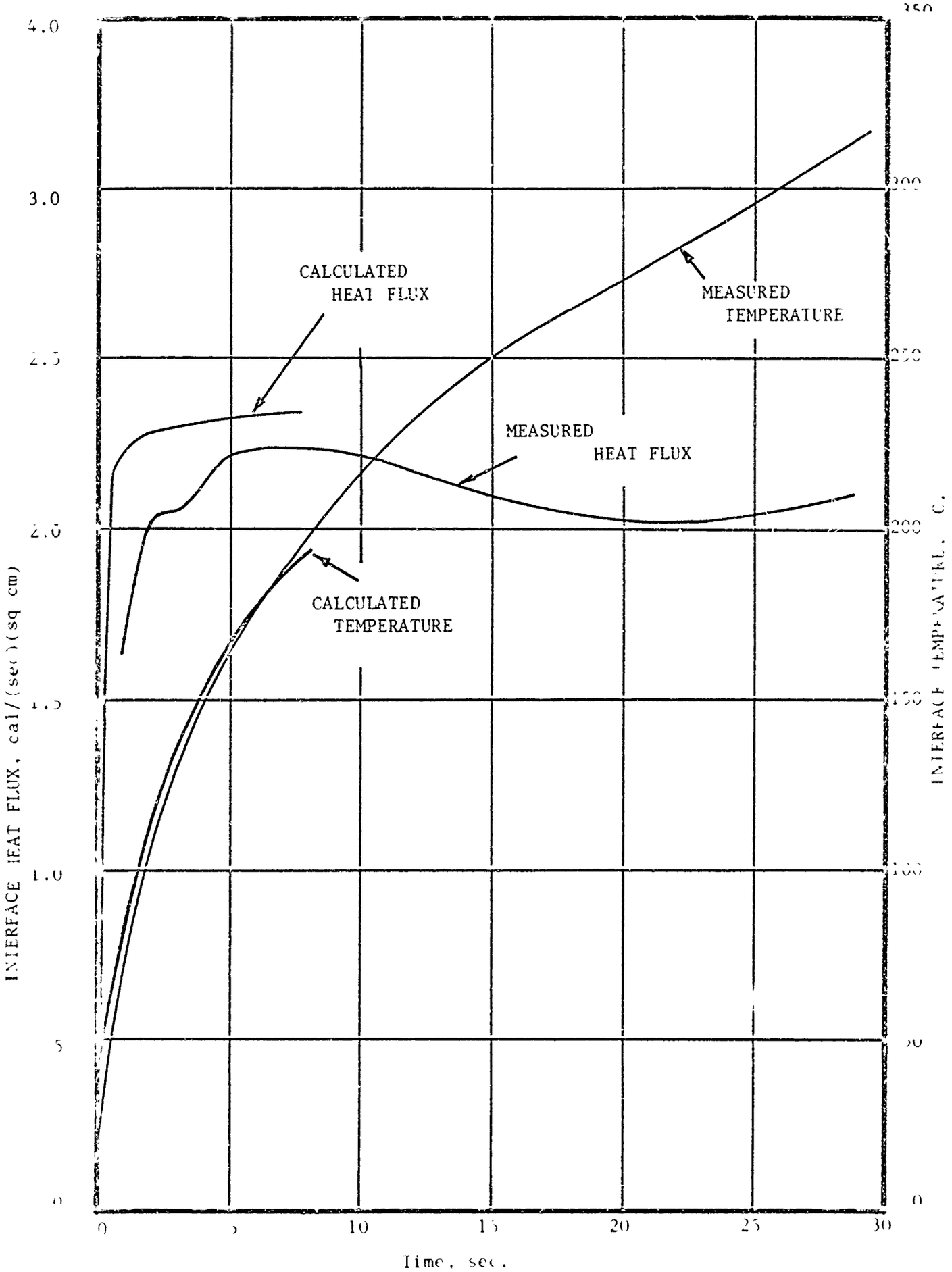

Figure 6. Measured and calculated interface temperatures and heat fluxes for fast pyrolysis of thin films of PBAA on heat-flux gage. The furnace temperature was 880 C (a black body heat flux of 2.38 cal/(sec)(sq cm)) the pressure was .01 atms and the polymer film thickness was .01 ± .003 cm. See Table III for a tabulation of calculated values.

for this endothermic reaction of 25-30 kcal can be calculated. The interface heat flux ceased to decrease after about 20 seconds of exposure. The surface temperature would be about 340 °C at this time. At this time regression of film occurred or else the reactants for the endothermic reaction were exhausted. In these tests the polymer film was lost from the gage. The measured heat-flux at the surface of the gage approached the surface value at later times.

Figure 7 shows the results of a similar test in which the polymer film was exposed to .85 atms of oxygen. In oxygen the period of water removal is noted, and a decrease in heat flux signifying reaction at a surface temperature of about 250 °C is noted. Once reaction starts, a smoothly decreasing heat flux is not observed. The irregularities in the heat-flux-time relationship shown in Figure 7 are typical of oxygen tests and are always observed. Some oxygen-polymer reaction occurs. Ignition occurs soon after what appears to be regression starts (at a surface temperature of 340 °C).

Although further development of the fast pyrolysis method is required, some conclusions can be drawn from this work.

1. Although some polymer reactions occur at temperatures less than 350 °C, the net reduction in effective surface heat flux would be only about 0.1 cal/(sec)(sq cm) and could be neglected for high surface-heat fluxes.

2. Significant surface regression of this polymer appears to start at about 340 °C which is above the calculated linear surface temperature at ignition for the low-flux ignition of a catalyzed AP propellant made from this polymer and is in the range of calculated ignition temperatures expected at high heat fluxes.

3. Endothermic pyrolysis reactions may occur below 300 °C which do not result in weight loss of the polymers. This technique can detect such reactions.

4. Exothermic oxygen-polymer reactions apparently occur before ignition. Ignition in oxygen appears to start when regression of the polymer begins.

5. The results of the fast pyrolysis reactions appear to be reasonable extrapolations of the results from the conventional tests. Pyrolysis activation energies and oxygen ignition temperatures determined by the two methods are comparable.

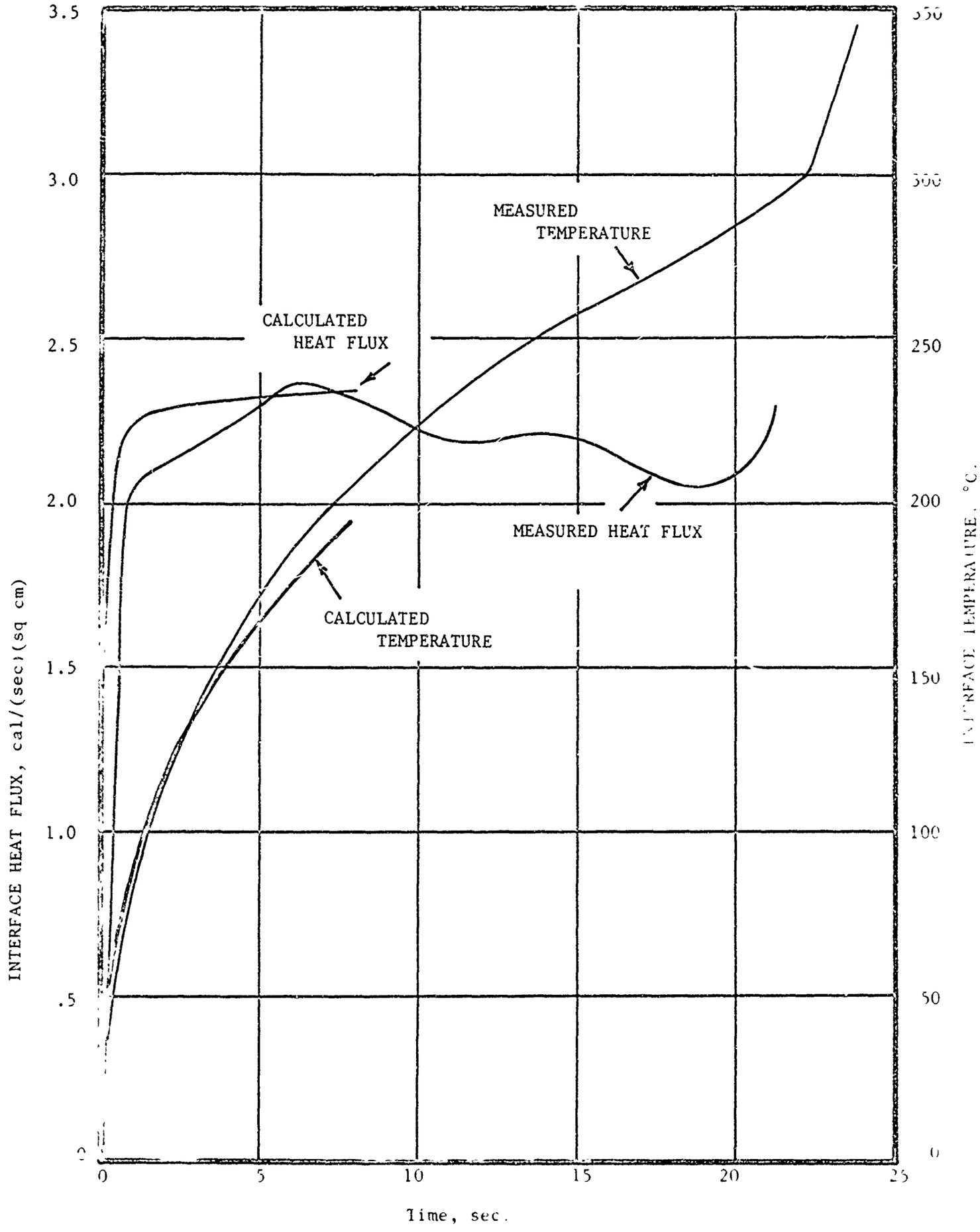

Figure 7. Measured and calculated interface temperatures and heat fluxes for fast pryolysis and oxidation of thin films of PBAA on a heat-flux gage. The furnace temperature was 880 °C (a black body heat flux of 2.38 cal/(sec)(sq cm)); the pressure was .85 atms oxygen and the polymer film thickness was .01 ± .003 cm. See Table III for a tabulation of calculated values.

The fast pyrolysis work is continuing, and tests are being made in an imaging furnace. A GE DFD 1000-watt projection lamp is used as an energy source, and replaces a carbon arc in the furnace for this purpose. Energy flux levels to 20 cal/(sec)(sq cm) can be obtained with this system. At the sample position a uniformly radiated ($\pm$ 0.5%) one-centimeter square area is obtained. Because the position of the lamp filament is fixed, the reproducibility of heat-flux distribution tests is excellent. Since the sample can be contained in a sealed chamber, pyrolysis products can be collected and analyzed. In order to avoid problems associated with correction of the heat-flux gage data, polymer films are being mounted on copper discs of known weight, and the disc temperature is measured by use of a thermocouple Once the technique for this study is perfected, several typical polymers will be considered.

APPENDIX A.

MATHEMATICAL DETAILS FOR THE IGNITION THEORY SOLUTION

In the following discussion the dimensionless form of the equations are in an approximate FORTRAN notation. Single variables are represented by one or a combination of several upper case letters (i.e., B or REX), and multiplication is indicated only by means of an asterisk. In this notation exp (b) denotes e^B. Equation (1) was put into dimensionless form by means of the substitutions shown in the following table.

TABLE IA.

Dimensionless Variables in FORTRAN Notation

	Dimensionless Quantity	Symbol	Definition in real notation from Equation (1)
1.	temperature	U	$\frac{R}{E_b} v$
2.	distance	X	$\frac{RB}{E_b k} x$
3.	time	T	$\left(\frac{RB}{E_b}\right)^2 \frac{t}{(k\rho c)}$
4.	heat flux	F	$\frac{F_s}{B}$
5.	velocity	REX	$-\left(\frac{E_b}{RB}\right)(\rho c)\ u$
6.	pressure	PRESS	P/1 atms
7.	activation energy ratio	D	E_a/E_b
8.	activation energy ratio	E	E_c/E_b
9.	activation energy ratio	R	E_r/E_b
10.	coefficient for exponential	DD	A/B
11.	coefficient for exponential	EE	C
12.	coefficient for exponential	RR	$\left(\frac{E_b}{RB}\right)(\rho c)\ V_r$
13.	coefficient for exponential	CB	$\left(\frac{E_b}{RB}\right)(\rho c)\ C_b$
14.	coefficient for gas phase feedback flux	GA	$F_g(t)/B$
15.	pressure exponential	GN	n
16.	initial temperature	Y	$\left(\frac{R}{E_b}\right) v_o$

In dimensionless form and in this notation, Equation (1) becomes·

$$\frac{\partial U}{\partial T} - REX * \left[\frac{\partial U}{\partial X}\right] = \frac{\partial^2 U}{\partial X^2} + DD * EXP\left[-\frac{D}{U}\right] \tag{1A}$$

For T = 0, U = Y

For T > 0 and X ∞, U = Y.

For T > 0 and X = 0

$$-\frac{\partial U}{\partial X} = F + GA * PRESS^{GN} + FACTR * EXP\left[-\frac{1}{U}\right]$$

where $FACTR = \dfrac{PRESS * EE * EXP(-E/U)}{1 + PRESS * EE * EXP(-E/U)}$

The dimensionless velocity is

$$REX = RR * EXP(-R/U) + FACTR * CB * EXP(-1/U)$$

whe.e U is the surface temperature.

Numerical solutions to Equation (1A) were obtained by means of a modified Schmidt Method.

In order to check the numerical solution, it was necessary to obtain a solution to Equation (1A) with the non-linear terms eliminated. The solution to the equation

$$\frac{\partial U}{\partial T} - REX * \left[\frac{\partial U}{\partial X}\right] = \frac{\partial^2 U}{\partial X^2} \tag{2A}$$

with initial and boundary condition of

T = 0, U = Y; T > 0 and X ∞ , U = Y; and T > 0 and X = 0, $-\frac{\partial U}{\partial X} = F$

with REX constant was derived. The surface temperature, U_s, is

$$U_s - Y = F * \left[\frac{1}{REX} + \left[\frac{T}{\Pi}\right]^{1/2} * EXP\left[-\frac{REX * T}{4}\right] - \frac{1}{REX} * \left[1 + \frac{(REX)^2 * T}{2}\right] * EFRC\left[\frac{REX * T}{2}\right]\right] \tag{3A}$$

This solution reduces to the well-known solutions for a zero velocity or for the steady-state ease; these reductions are not trivial. Satisfactory agreement between the numerical solutions to Equation (1A) and Equation (2A) were obtained.

APPENDIX B.

THE IGNITION OF COMPOSITE SOLID PROPELLANTS BY HOT GASES*

ABSTRACT

The University of Utah has been engaged in a research program directed toward understanding propellant ignition. One part of this program has been concerned with the behavior of solid propellants during ignition by convective heating. There is an obvious interest in this type of study since solid propellants are often ignited by sources which transfer most of their energy to the propellant surface by convection from hot combustion products.

In the experimental work described in this paper, propellant was ignited by shock-heated gases passing over the surface of a sample mounted in the wall of a test section at the end of a shock tube. Convective heat fluxes of 20 to 150 cal/(cm)^2(sec) were obtained at the propellant surface.

Various propellant compositions were studied to determine the effect of propellant ingredients on ignition behavior. It was found that propellants containing catalysts such as iron oxide and copper chromite, normally added to propellants to increase their burning rates, are more easily ignited than non-catalyzed propellants. Another interesting observation was that some propellants become more difficult to ignite as the velocity of the hot gases crossing their surfaces is increased.

INTRODUCTION

The ignition of composite solid propellants by convective fluxes is of considerable interest since igniter systems for many solid rockets depend on hot gases for ignition. Not all of the information from ignition experiments is directly usable for predicting the ignition requirements for rockets, since other considerations, such as flame spread, are important in large rocket ignition. Laboratory ignition experiments, however, do provide information on the response of a propellant surface to convective heating and on the effect

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* Reference, figure and table numbers refer to items in this appendix.

of additives that might be obscured in a large-scale rocket test. Furthermore, the behavior of composite solid propellants during ignition under convective heating has provided considerable insight into the mechanism of solid propellant ignition

Studies on ignition of composite propellants under convective fluxes have been reported by Baer, et al [1], Lancaster, et al [2], Grant, et al. [3], Hermance, et al. [4], and Bastress [5] In none of this earlier work however, was there reported an attempt to investigate the role of propellant ingredients in composite propellant ignition. In this work compositional changes were made in an ammonium-perchlorate propellant system to determine their effect on energy requirements and other ignition characteristics.

ADAPTATION OF THE SHOCK TUBE FOR IGNITION STUDIES

The shock tube used to generate hot gases in this work was 1-7/8-inch inside diameter with a 52-foot driver and 15-foot driven section This was the same tube used by Baer, et al. [1] for prior tests. For the experiments described in this paper, the driven end of the shock tube was modified to provide a means of passing shock-heated gases over the surface of a propellant sample Figure 1 shows a cut-away sketch of the driven-end of the shock tube and the test section used for ignition studies Figure 2 is an exploded view of the test section illustrating how the propellant sample holder, quartz window, and flow control orifice are fitted to the test section. The test section as shown in Figure 2 has a rectangular flow channel, 0 25 inches by 0.5 inches, with a bell-mouthed entrance The velocity of the hot gases passing through the test section is varied by the use of different critical flow orifices downstream of the propellant position

Before the ignition tests were performed, heat flux at the sample position was measured with a heat flux gauge (a thin-film platinum resistance thermometer on a glass or ceramic substrate). The results of the heat transfer study were correlated in terms of shock parameters and gas properties so that the heat transfer to the propellant surface could be calculated Baer, Ryan, and Salt [1] found, and it was verified by this work, that the transient heating process at the sample position could be represented by an instantaneous temperature rise resulting from the reflected shock, followed by a one-dimensional heating of a semi-infinite solid through constant heat transfer coefficient

$$\frac{T_s - T_j}{T_g - T_j} = 1 - e^{N^2} \operatorname{erfc} N \qquad (1b)$$

and

$$N = \frac{ht^{1/2}}{\Gamma}$$

where, t is time measured from arrival of the shock,

T_s is the surface temperature of the heat flux gauge at time (t),

T_j is the instantaneous temperature rise behind reflected shock,

T_g is the temperature of the shock-processed gases,

h is the heat transfer coefficient,

Γ is the thermal responsivity of the material undergoing transient heating (the square root of the product of the density, thermal conductivity and heat capacity of the material)

For the test section shown in Figure 1, it was found that the heat transfer coefficient could be correlated in terms of gas temperature, T_g (°K), and the mass flow rate (G g/cm^2 sec) of gas through the test section. An exponent of 0.75-0.80 on the mass velocity factor G would be predicted on the basis of steady-state heat transfer measurements. The higher value of 0.905 in Equation (2) is required to correlate the transient heat transfer coefficient. This difference may be the effect of the cold metal nozzle and duct upstream of the heat flux gauge.

$$h = 1.435 \times 10^{-4} (T_g)^{0.905} (G)^{0.905} \text{ [cal/(cm)}^2\text{(sec)(°C)]} \qquad (2B)$$

Use of this coefficient permitted calculation of the mean flux to the surface of the propellant sample up to the onset of ignition.

The shock tube is a useful tool for ignition research by convective heating since it provides a means for producing hot gases in a few microseconds, but there are some limitations to its use. One of these is the length of time processed gases are available for experimental work. Ideally this period is controlled by the length of the driven section of the shock tube. It was found, however, that because of the large amount of gas which flowed through the test section when large control orifices were used, cold driver gases mixed with processed gases at the interface, and the test times were greatly reduced. As a consequence, the usable test period was 25 milliseconds at 40 cal/(cm)^2(sec) and 9 milliseconds at 100 cal/(cm)^2(sec). Because of this limitation on heat flux duration some propellant compositions could not be ignited in the shock tube.

EXPERIMENTAL RESULTS ON IGNITION

Several different ammonium perchlorate propellants were tested The control propellant for this study is Utah F propellant. This propellant has a binder of polybutadiene-acrylic acid polymer cured with Epon 828 The complete compositions of this and other propellants tested are given in Table I. Some of the variables investigated were (1) particle size of ammonium perchlorate, (2) per cent of ammonium perchlorate in the propellant, and (3) the effect of additives used for modifying burning rates. All of the data reported here were obtained by use of nitrogen as the environmental gas to prevent chemical interaction between propellant decomposition products and heating medium.

Ignition of propellant was observed through a quartz window opposite the propellant position in the test section with an 1P40 photoelectric cell Both the direct light signal and a differentiated light signal from the photocell were displayed on an oscilloscope screen and recorded with a camera. Ignition of the propellant was taken as the time at which the differentiated photocell signal was rising almost vertically. High-speed motion pictures indicated that at this time steady deflagration was established on the propellant surface, and the flame was spreading rapidly over the surface.

In Figures 3, 4, 5, and 6 are presented ignition results on propellants studied. The data from ignition experiments are plotted in the form of mean surface heat flux, $\overline{F}$, cal/(sec)(cm)^2 versus square root of the ignition time, $t_i^{1/2}$, where t_i is in milliseconds. This method of presenting the data is suggested by the thermal ignition theories [6, 7]. The mean surface flux is defined as the constant flux which would bring the surface of the propellant to the ignition temperature in time t_i. Thermophysical properties of the propellants used for this calculation are given in Table II. Thermal diffusivity, heat capacity and density were determined experimentally for propellants F and G, and the thermal responsivity, Γ, was calculated. The thermal responsivities were estimated for propellants J, S, and U. It was assumed for the purpose of heat flux calculations that the thermal responsivity of the propellants remained constant at their 60°C values. Each data point in the figures represents one ignition run. It is estimated that the calculated flux at ignition is within five per cent of the true value.

The ignition data for propellant F shown by Figure 3 is representative of much of the ignition data obtained in this study. The composition of this propellant as given in Table I includes 2.0 per cent copper chromite catalyst

and 80.0 per cent of a bimodal blend of ammonium perchlorate (AP). The coarser AP has an average particle size of 200 microns, but some of the particles are as large as 400 microns. When the surface of the cured propellant is cut with a sharp razor blade, it is possible to cut through most of the AP particles, but some of the AP particles are fractured and a few are pulled from the propellant matrix. It is estimated that the surface roughness of the propellant is of the order of 20 to 30 microns when tested. The plot of heat flux versus the square root of ignition time on the logarithmic graph shows a set of data for each gas velocity in the test section. The gas velocity is expressed in terms of Mach Number. The gas velocity corresponding to a Mach Number of 0.13 is about 100 meters/second Note that the pressure in the test section when varied from 18-25 atmospheres does not appear to have a noticeable effect on the ignition time. Although not specifically indicated on the graph, the slopes for the two sets of data are the same, approximately -1 0 Because of the uncertainty in the heat flux results it is impossible to determine the exact slope of a set of data within perhaps 5 per cent. The fact that these ignition data have a slope of -1.0 means that the propellant ignites at approximately the same surface temperature regardless of the flux level This temperature is different for each gas Mach Number.

Ignition data for propellant S and U are given by Figure 4 and 5, respectively. These propellants are similar to F propellant in that they each contain 2.0 per cent copper chromite catalyst. However, both propellants have only 75.0 per cent of a single size AP. Propellant S has 85-micron AP and propellant U has 15-micron AP. Because of the finer particle size, the surfaces could be cut much smoother than on propellant F. It is estimated that the surface roughness was about 10-15 microns on S propellant and about 5 microns on U propellant. Propellant S, although having a finer particle size and lower level of AP, shows essentially the same ignition characteristics as F propellant. Propellant U with extremely fine AP does not ignite as easily as F propellant at low gas velocities (Mach 0.13), but ignites in about the same time as F propellant at intermediate gas velocities (Mach 0 28) Ignition data are also given for U propellant at extremely high gas velocities (approximately Mach 1). By comparing results from these three propellant compositions, propellant F, S, and U, it appears that the only significant difference in ignition characteristics occurs as the result of the extremely small particle size AP encountered with propellant U.

Except for the catalyst (iron oxide in J propellant), the F and J propellants have the same composition. Ignition characteristics for propellant F and J are almost identical, (compare data of Figure 3 with those of Figure 6 B). The only difference in ignition behavior is that at lower gas velocities, propellant J ignited more easily For a gas Mach Number at the propellant surface of 0.07, the data for F propellant (not shown) are coincident with the data obtained at Mach 0.13 for F and J propellant.

In addition to the propellants described above, an attempt was made to ignite propellant G which did not contain a burning rate additive. Otherwise, it is similar to propellant F. Propellant G was tested under the same conditions as the other propellants, but in none of these tests was there an indication of ignition as observed by the photocell. Examination of recovered samples from some of the runs under extremely high convective fluxes, 100 cal/(sec)(cm)^2, showed charring of the polymer at the surface of the sample. For one test on propellant G under both high flux and high gas velocity, some of the polymer had charred and carbon was deposited on the edge of the sample holder. Obviously, some AP had decomposed, but it was difficult to estimate the extent of this decomposition. It is believed that if the apparatus were not limited with respect to test time propellant G would have ignited at least at the low gas velocities.

ANALYSIS OF RESULTS AND CONCLUSIONS

Ignition data obtained by three different experimental methods are shown by Figure 7B in terms of heat flux versus the square root of ignition time. These data are for similar propellants. As these results show, data from the three types of experiments, although not coincident, are well represented by straight lines all of which have approximately the same slope Price, et al. [8] found that under high fluxes, greater than 50 cal/(cm)^2(sec), with the carbon-arc image furnace that the data could no longer be represented by a straight line. The line which describes the data for the carbon-arc image furnace and also the lines for the shock tube data have slopes near minus one. This slope agrees with the value found by Evans, et al 9; for ignition of pellets of AP, carbon black, and copper chromite. The thermal ignition theories which are the only presently available models for non-hypergolic ignition predict slopes from 0 80-0.95, but do not explain values equal to exactly minus one The slope of the line which describes the radiation furnace data, however, was determined to be -0.91.

The fact that the data from these experiments can be represented graphically as suggested by thermal ignition theories gives support to the theory that ignition of some composite propellants does indeed begin with a surface or bulk reaction. Because the pressure effect on ignition time is small in the presence of a non-reactive environmental gas it appears that the contribution of gas-phase reactions in the rate-controlling phase of the ignition process is small, at least, for propellants catalyzed with copper chromite or iron oxide The nature of the surface reactions which lead to steady deflagration cannot be described within the present state-of-knowledge on ignition

This work has shown that composite propellants are apparently ignited more easily by convective fluxes than by radiant fluxes, but the ignition time at a given flux level is influenced by the gas velocity over the propellant surface. Data for propellants containing different particle size AP showed that only very fine AP, such as that used in propellant U, significantly modified ignition characteristics. For coarser AP and different levels of AP, propellants F and S, no appreciable change in ignition time was observed. These results tend to indicate that surface roughness is important in the ignition of propellants under convective fluxes. There appears to be no easy way to explain the shift in ignition time with gas velocity An explanation of this effect must await further research. The presence of a burning rate catalyst in the propellant is extremely important for convective ignition, and more information is needed on the role of additives in the ignition process.

Table IB

Propellant Compositions

Propellant Code	Ingredients, Weight Per Cent: PBAA Binder(1)	Catalyst(2)	Ammonium Perchlorate	Ammonium Perchlorate Particle Size(3)
F	18.0	2.0 Copper Chromite	40.0 40.0	15 micron 200 micron
G	18.0	None	41.0 41.0	15 micron 200 micron
J	18.0	2.0 Iron Oxide	40.0 40.0	15 micron 200 micron
S	23.0	2.0 Copper Chromite	75.0	85 micron
U	23.0	2.0 Copper Chromite	75.0	15 micron

(1) Binder for these propellants was composed of 85.0 per cent liquid polybutadiene-acrylic acid copolymer cured with 15.0 per cent Epon 828. Propellant was cured seven (7) days at 80°C.

(2) The copper chromite was copper chromite catalyst Cu-0202P from the Harshaw Chemical Co., and the iron oxide was a pure red iron oxide, Code R-1599, from C. K. Williams and Company.

(3) Ammonium perchlorate of the designated particle size means that 50 weight per cent of the particles have a diameter less than the value indicated.

Table IIB

Thermophysical Properties of Propellants[1]

Propellant Code	Thermal Diffusivity cm^2/sec	Heat Capacity cal/(g)(°C)	Density at 25°C g/cc	Thermal Responsivity $cal/(sec)^{1/2}(cm)^2(°C)$
F	0.00170	0.316	1.63	0.0212
G	0.00171	0.311	1.60	0.0206
J	-	-	1.63	0.0206[2]
S	-	-	1.58	0.0203[2]
U	-	-	1.58	0.0203[2]

(1) These properties are for a temperature of approximately 60°C.

(2) Thermal responsivity was estimated for this propellant from experimental data on a similar propellant.

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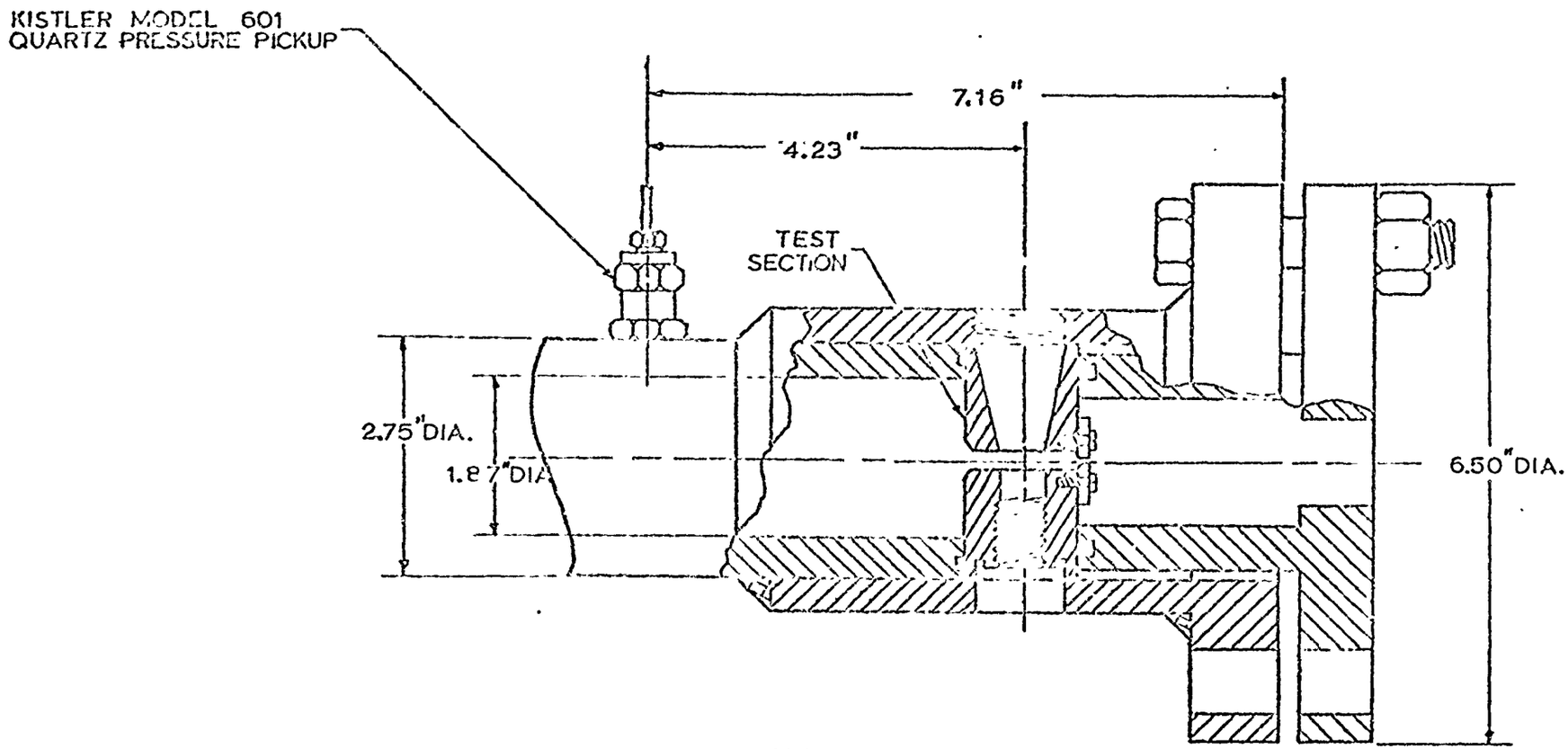

FIGURE 1B
CUTAWAY SKETCH OF DRIVEN END OF SHOCK TUBE
SHOWING POSITION OF TEST SECTION
½ SCALE

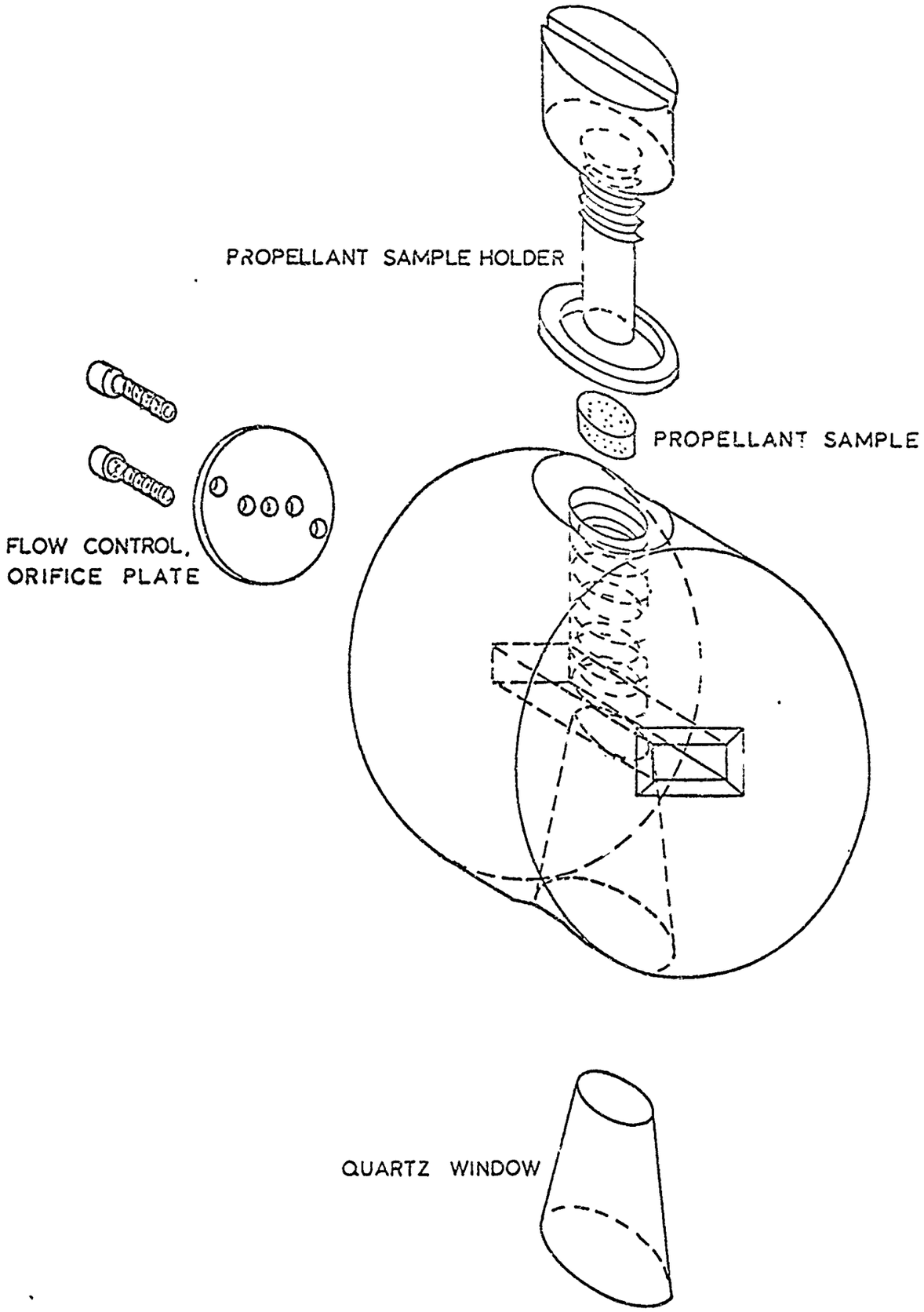

FIGURE 2_B
SKETCH OF TEST SECTION

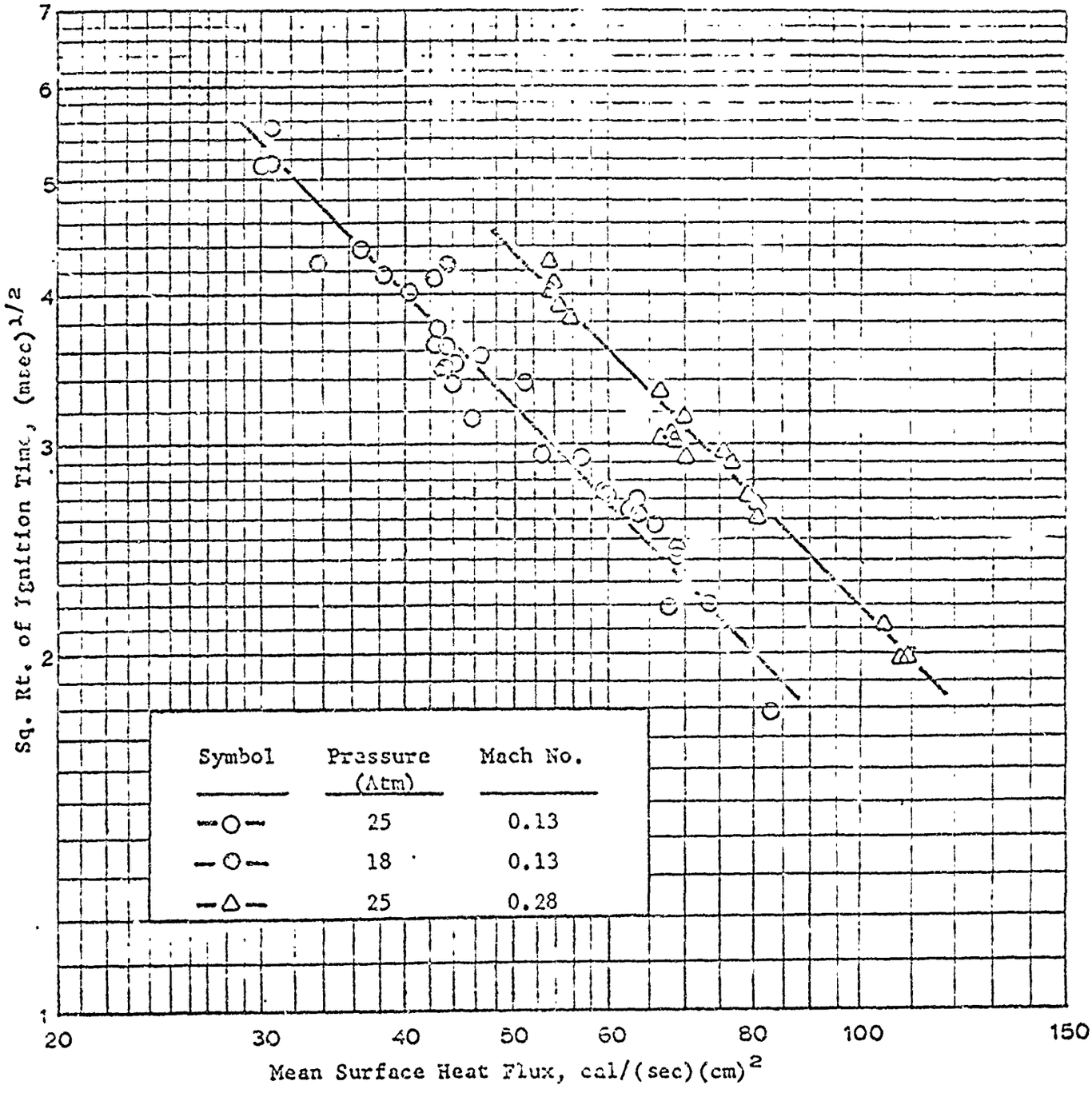

FIGURE 3 B

IGNITION OF "F" PROPELLANT IN NITROGEN

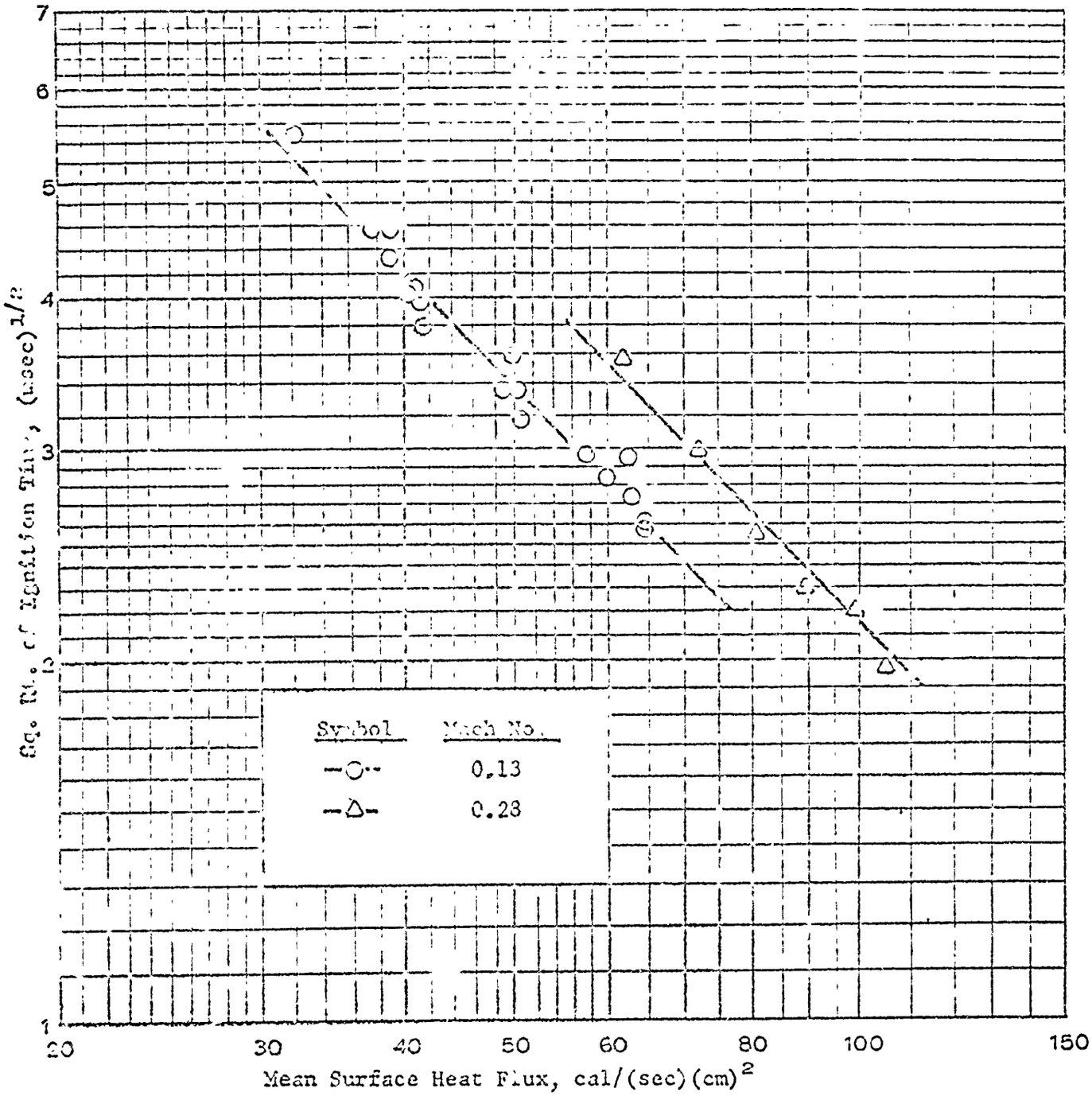

FIGURE 4 B

IGNITION OF "S" PROPELLANT IN NITROGEN AT 25 ATMOSPHERES PRESSURE

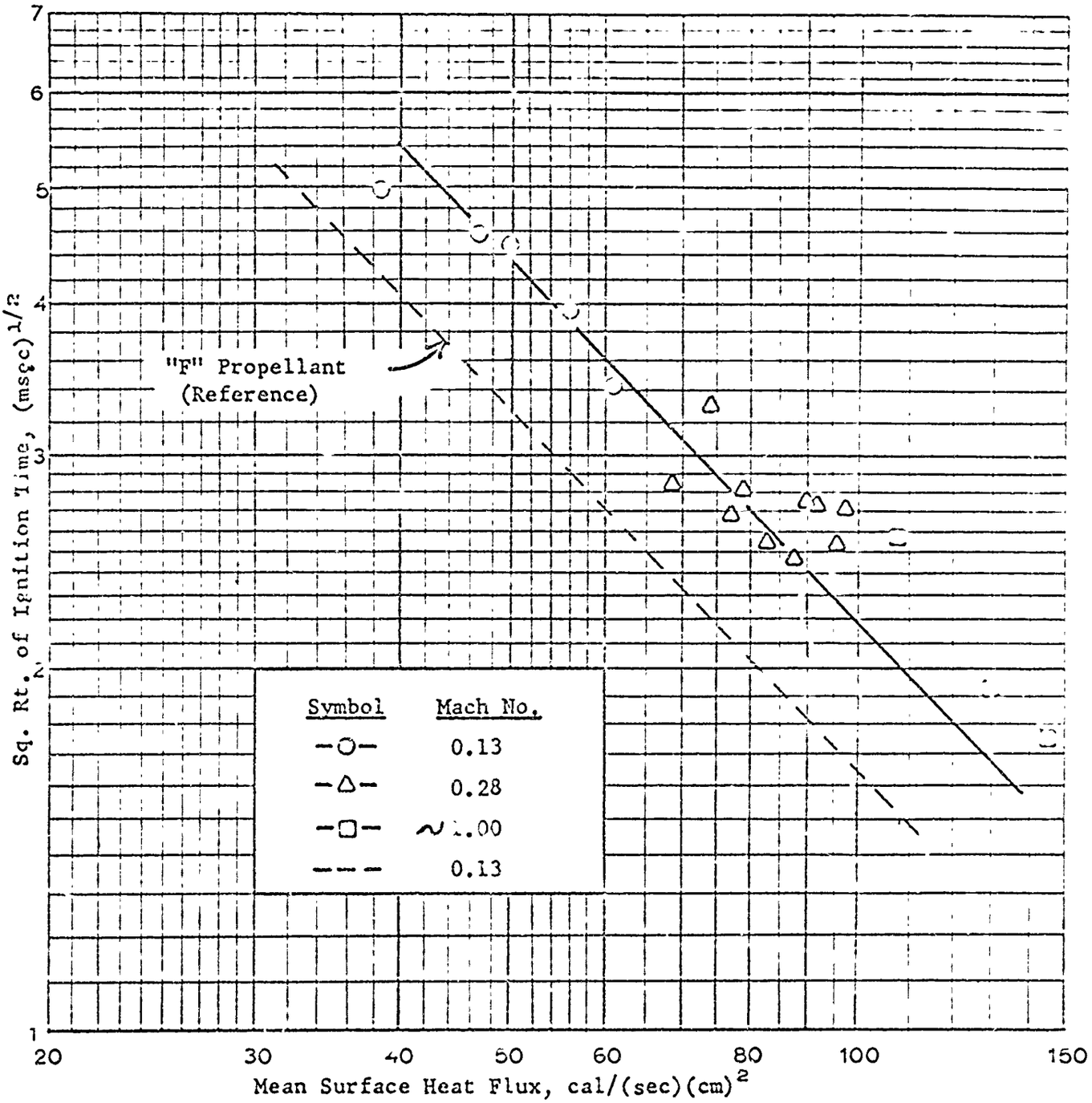

FIGURE 5B

IGNITION OF "U" PROPELLANT IN NITROGEN AT 25 ATMOSPHERES PRESSURE

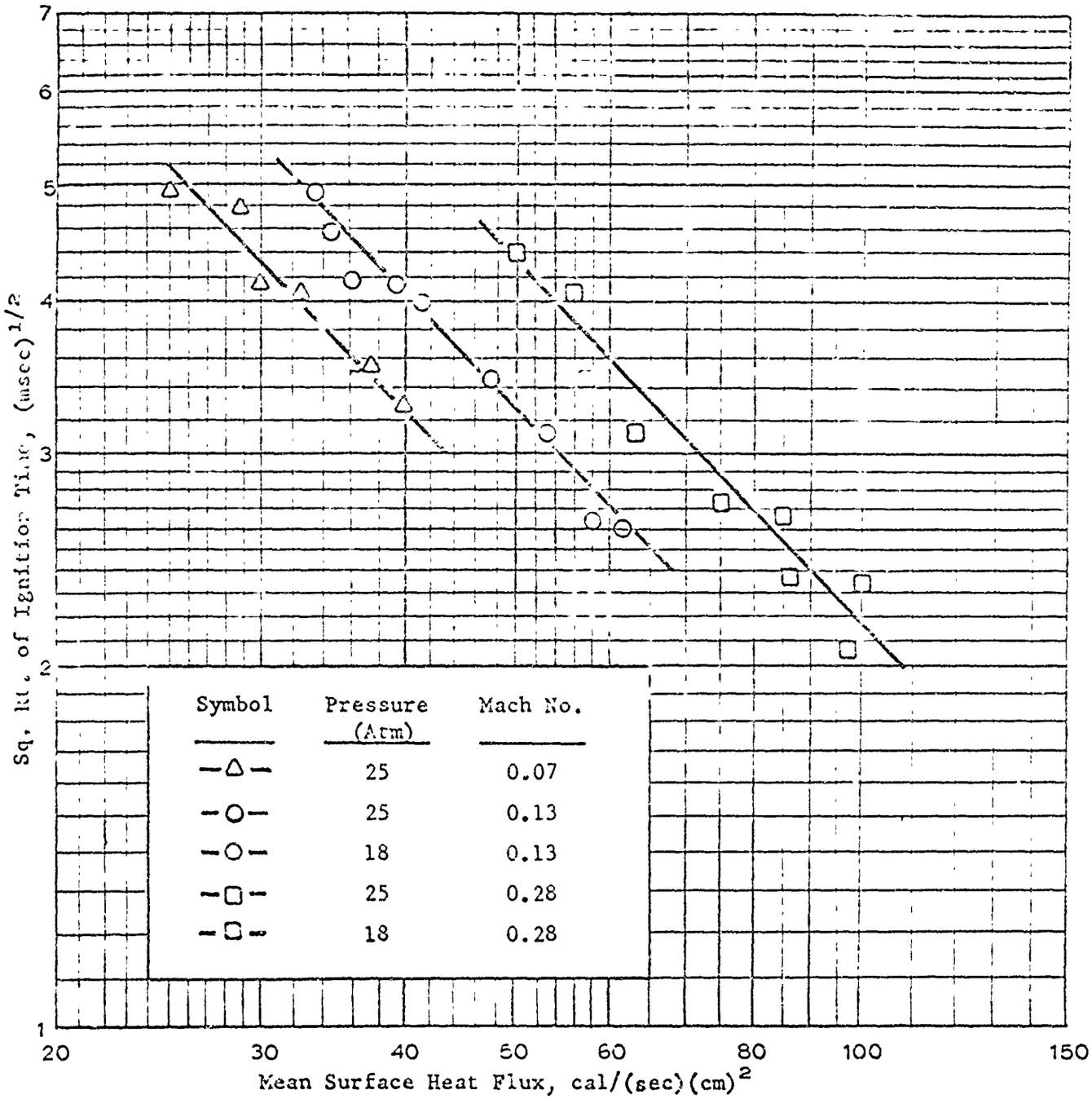

FIGURE 6

IGNITION OF "J" PROPELLANT IN NITROGEN

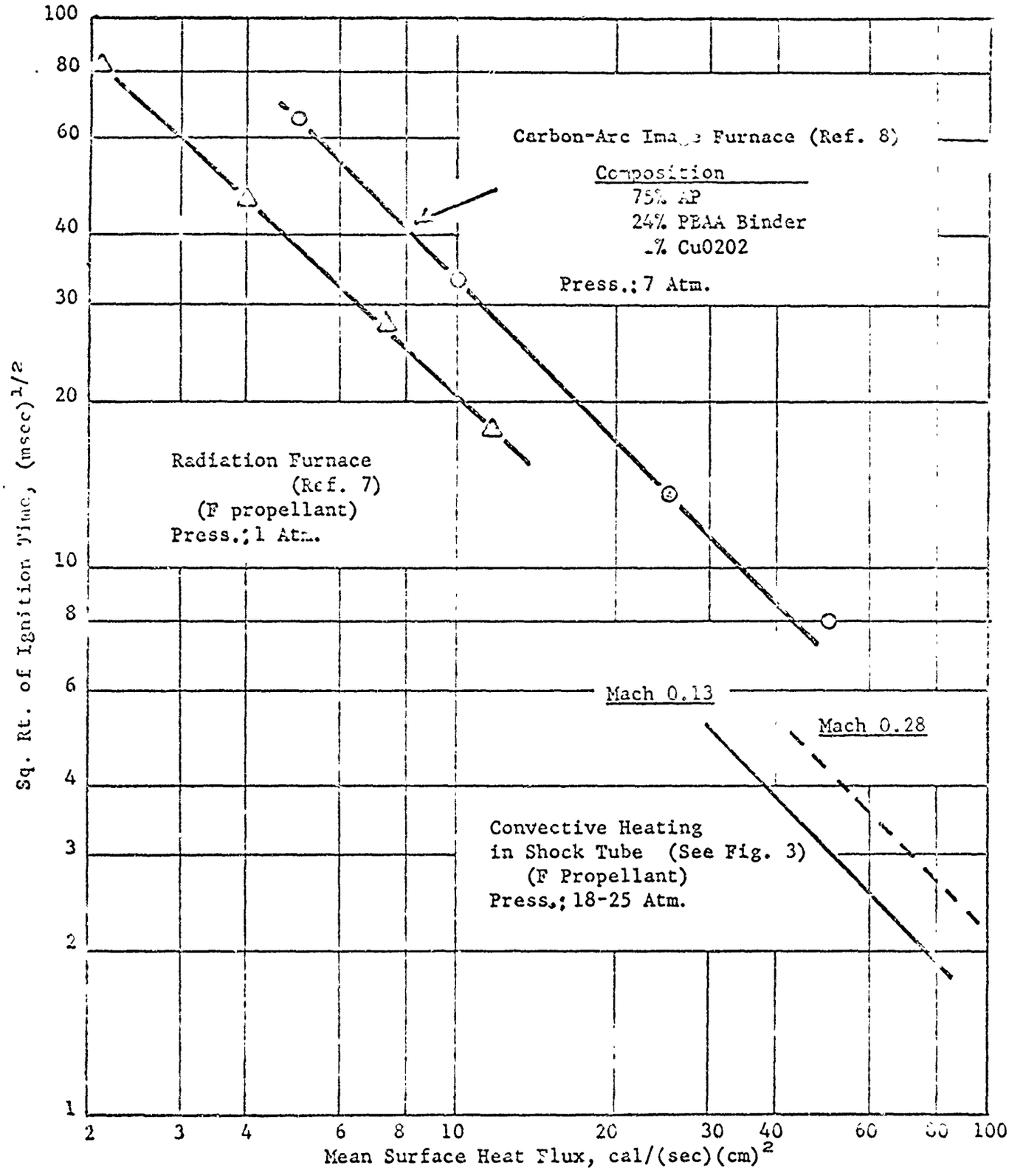

FIGURE 7

IGNITION DATA OBTAINED BY DIFFERENT EXPERIMENTAL METHODS

APPENDIX C.

RECENT RESULTS CONCERNING THE HOT-WIRE IGNITION OF COMPOSITE PROPELLANTS

ABSTRACT

Ignition times for composite propellant samples containing imbedded, electrically heated wires have been measured in the range from .01 to 10 seconds. It was demonstrated that the precise ignition time can be determined by carefully observing the voltage across the constant-current heated wire. Linear surface temperatures at ignition for the propellant were calculated from a known solution of the heat conduction equation which accounts for temperature gradients in the heated wire. These calculated temperatures are compared to the results from thermal radiation and forced convection ignition tests obtained from the same propellant.

INTRODUCTION

One of the most obvious methods proposed for the laboratory study of the ignition of solid propellants is to imbed electrically heated wires in small grains and to determine the relationship between the rate of thermal-energy generation in the wire and the ignition time. The apparatus and instruments required for such a study are the essence of simplicity; and, by suitable techniques, the energy-generation rates and the ignition times can be precisely determined. If the diameter of the wire is significantly larger than the diameter of the particles in the propellant, the propellant surface near the wire would be similar to that of the surface formed during motor casting. Such a surface is normally exposed to the motor igniter action. The major objections to hot-wire ignition are that the gaseous pressure at the wire-propellant interface cannot be precisely defined and that the effect of reactive gases on ignition cannot be studied. When pressure does not have a significant effect on the ignition process and if hypergolic ignition is not being considered, these objections are not important. Presumably the experiment can be designed to determine if gasification near the wire surface results in a significant difference between the wire and propellant surface temperatures.

The work by Altman and Grant [1] developed almost the only published data which were obtained by employing this technique. They found that their

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* Refer [illegible] numbers [illegible] as within [illegible] appendix.

ignition data could be explained by assuming a propellant ignition temperature of about 390°C. Because their method for determining ignition required the flame to travel through the propellant some distance in some unknown time interval, they were able to consider only ignition times greater than about one second.

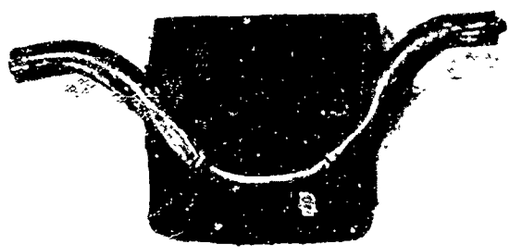
The objective of the work reported here was to evaluate the technique of ignition on hot-wires for time intervals shorter than one second. Pulses of energy were applied to wires for periods controlled by an electrical pulse generator. Ignition was originally defined in terms of a go-or-no-go criterion. Early in the work it was discovered that the ignition time could be precisely determined by observation of irregularities in the voltage signal from the heated wire, and use was made of this information in subsequent tests.

APPARATUS

Figure 1 shows a cross section picture (with one-half of the propellant cut away) of a propellant sample containing the imbedded heating wire. Nichrome V wire of 0.103 cm diameter (18-gage) was crimped between two short lengths of 1/8-inch o.d. copper tubing. The copper tubing served to produce good electrical contact to the resistance wire and to binding posts. The length of the Nichrome wire between the copper contacts was 1/2-inch. The resistance wire and ends of the copper tubing were cast into the propellant sample in the manner shown in Figure 1. The initial propellant temperature was room temperature, 27 ±2°C. The propellant sample size was always large enough to insure that it could be treated as an infinite body in the time scale of interest. The propellant was Utah "F" propellant, and Table 1 gives the thermal properties of this propellant. Table 1 also gives the thermal and electrical properties of the Nichrome V wire.

A schematic diagram of the electrical system is shown in Figure 2. Electrical current was supplied from a 12-volt automotive battery. The period for current flow through the imbedded wire was controlled by activating and deactivating a relay by means of the pulse generator. The magnitude of the electrical current was controlled by inserting fixed lengths of air-cooled Nichrome V wire in series with the battery and the heating wire. Controlled current-pulses of 20 to 300 ampere magnitude for durations from .01 to 10 seconds were easily obtained.

The current through the heating wire was determined by measuring the voltage across a known resistance in series with the wire. This voltage and



ONE INCH

Figure 1.

A section view of the cast propellant sample with imbedded wire and copper contacts shown in place One half of the propellant has been cut away to show the details of the wire placement.

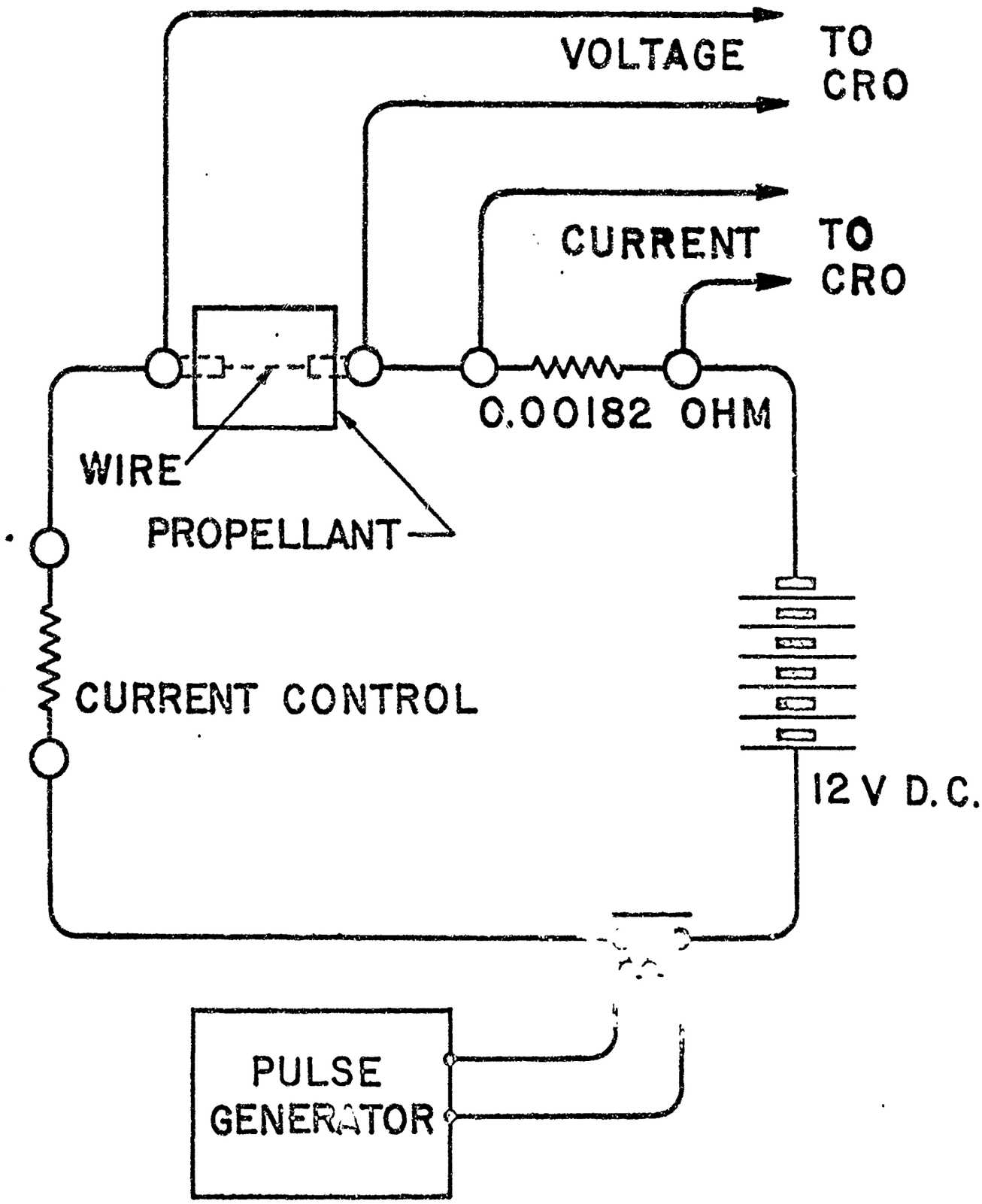


FIGURE 2 C.

The electrical schematic diagram of the hot-wire ignition system.

the voltage across the heated wire and contacts were displayed on separate traces of a dual beam oscilloscope. The oscilloscope trace was photographed to yield a permanent record. The oscilloscope sweep was triggered where voltage was first supplied to the relay or about 20 msec before the relay closed.

THEORY

Although data from hot-wire ignition tests may be useful when evaluating propellants and in developing ignition theories, the primary objective of this work was to evaluate the method for study. This evaluation is probably best made by comparison to other test methods, and the best quantitative evaluation is to compare the values of the linearly calculated surface-temperature at ignition for hot-wire ignition to values obtained from other methods of testing on the same propellant and under comparable conditions.

The linear-surface-temperature at ignition is calculated by considering the propellant to be chemically passive and to have constant thermal properties. In this case only the linear, partial differential equation describing heat flow in the solid need be solved. In the case of a long wire of infinite thermal conductivity imbedded in an infinite body and with perfect thermal contact, Carslaw and Jaeger [2] show that

$$T_s - T_o = \frac{2 R^2 Q_v \alpha^2}{\pi^2 K_2} \int_0^\infty \frac{(1 - \exp[-k_2 t u^2/R^2])\, du}{u^3 \Delta(u)} \qquad (1)$$

where T_s is the interface temperature between wire and propellant, T_o the initial, uniform propellant temperature, R the radius of the wire, Q_v the energy generation rate per unit volume in the wire, K_2 and k_2 the thermal conductivity and thermal diffusivity respectively of the propellant, and t is time. The parameter $\alpha = 2(\rho_2 C_2)/(\rho_1 C_1)$ where ρ and C are, respectively, density and heat capacity and subscripts 1 and 2 refer to the wire and propellant, respectively. The function

$$\Delta u = [u J_o(u) - \alpha J_1(u)]^2 + [u Y_o(u) - \alpha Y_1(u)]^2$$

where J and Y are the conventional designation for Bessel functions. When evaluated at the ignition time, T_s is the linear surface-temperature at ignition. Table II shows a short tabulation of the integral from Equation (1) obtained by numerical integration for parameters corresponding to the thermal properties shown in Table I.

Although the thermal conductivity of Nichrome V is much greater than the conductivity of the F propellant, the assumption of a negligible temperature gradient in the wire may not be valid at very high heating rates. The analogous result to Equation (1) in which the wire conductivity is considered to be finite is also given by Carslaw and Jaeger. In this case

$$T_s - T_o = \frac{4\, Q_v\, R^2}{\pi^2\, K_2\, k} \int_0^\infty \frac{(1 - \exp[k_1\, t\, \beta^2/R^2]\; J_o(\beta) J_1(\beta) d\beta}{\beta^4 [\phi^2(\beta) - \psi^2(\beta)]} \qquad (2)$$

where

$$\phi(\beta) = (K/k)\, J_1(\beta)\, Y_o(k\beta) - J_o(\beta)\, Y_1(k\beta) \text{ and}$$

$$\psi(\beta) = (K/k)\, J_1(\beta)\, J_o(k\beta) - J_o(\beta)\, J_1(k\beta)$$

The notation is the same as for Equation (1), and K and k are respectively the thermal conductivity ratio K_1/K_2 and thermal diffusivity ratio $\sqrt{k_1/k_2}$. Again the subscripts 1 and 2 refer to the wire and propellant, respectively. Table III is a short tabulation of the integral from Equation (2).

Table IV shows a comparison of calculated values of the interface (propellant surface) temperatures from Equations (1) and (2) for internal energy generation rates which would produce an interface temperature rise of 400°C in the indicated times. The properties of the wire and propellant were those of the present system. It appears that, except for very short time intervals, the temperature gradient in the wire may be neglected.

The rate at which energy is transferred from the wire to the propellant is simply the difference between the rate of energy generation and accumulation in the wire. The heat flux at the interface is this rate of transfer divided by the wire surface area. If the wire temperature is assumed to be uniform, the rate of energy accumulation in the wire may be obtained by differentiating Equation (1) with respect to time. The heat flux, F, can then be obtained as

$$F = \frac{RQ_v}{2} \left\{ 1 - 4\, \frac{\alpha}{\pi^2} \int_0^\infty \frac{\exp[-k_2\, t\, u^2/R^2]\, du}{u\, \Delta(u)} \right\} . \qquad (3)$$

Figure 3 is a plot of Equation (3) in which the thermal properties of Nichrome V and "F" propellant are assumed. For a given value of Q_v, the flux is low for time intervals less than about one-half second and is relatively constant for longer time intervals.

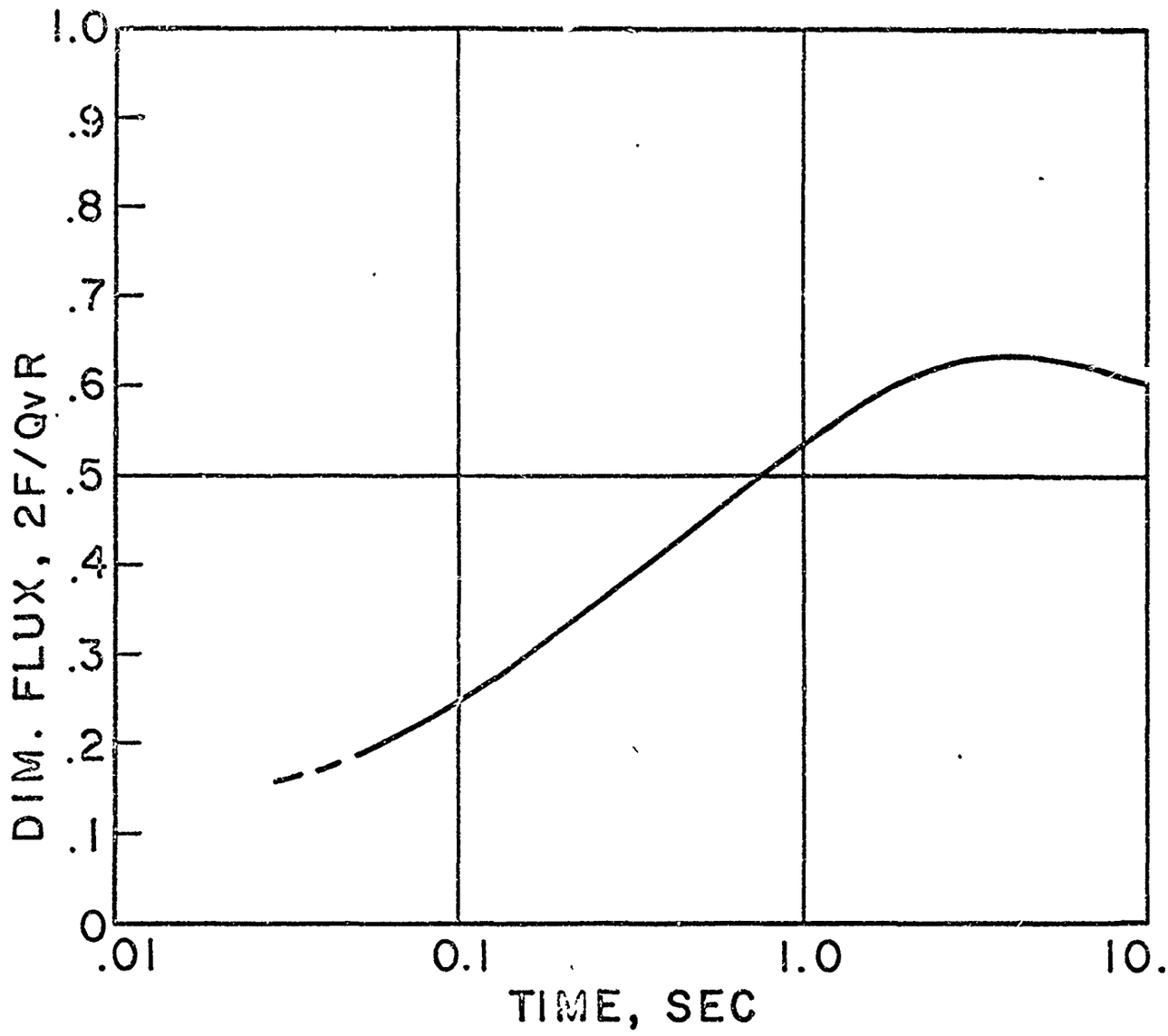


FIGURE 3 C.

Calculated dimensionless heat flux at the 18-gage Nichrome V wire "F" propellant interface plotted against the heating time. A uniform wire temperature was assumed. The dimensionless flux can be interpreted as the ratio of the rate at which energy flows to the propellant to the total rate of energy generation in the wire.

EXPERIMENTAL RESULTS

Early in the experimental program it was observed that coincident with propellant ignition a sudden decrease in the voltage drop across the heated wire occurred. It was concluded that this decrease in voltage was coincident with ignition (in the time scale of interest) since decreasing the heating interval of the wire produced a condition in which neither ignition nor this voltage decrease occurred. This decrease in voltage can be seen in Figure 4. The decrease occurred just before the relay opened and cut off the current. A pulse width slightly less than shown would not produce ignition. The decrease in voltage across the heated wire is possibly the result of ionization in the confined flame. Once it was confirmed that ignition could be detected by observation of the voltage trace, the ignition time was taken to be the period from the first current flow until the voltage decrease across the wire. A voltage increase before ignition would be interpreted as evidence of gasification which would insulate the wire surface and cause a rapid increase in temperature, resistance of the wire, and voltage drop. Such an increase was never observed.

Table V summarizes the test conditions and ignition results. Figure 5 shows the ignition data as a plot of the average volumetric energy generation rate, Q_v, versus ignition time. Except for an unexplained deviation of the data at the maximum heating rate, all results lie on a smooth curve. Also shown on Figure 5 is a line representing the Q_v-t_i relationship for a constant value (427°C) of the ignition temperature. Although the conclusion that ignition occurs at a constant ignition temperature appears attractive and could be supported by a casual inspection of Figure 5, the logarithmic plot is somewhat misleading. The "best fit line" definitely crosses the line calculated on the basis of a constant ignition temperature. It appears that the ignition temperature increases at shorter ignition times.

The energy generation rate was calculated as

$$Q_v = \frac{I^2 R_L}{A} \tag{4C}$$

where I is the average electrical current, R_L the wire resistance per unit length, and A the wire cross sectional area. The current decreased slightly during a test (see Figure 4), and an average value was used in Equation (4). Since the temperature coefficient of resistance of the Nichrome wire is quite low, room temperature resistance values were satisfactory for calculation purposes.

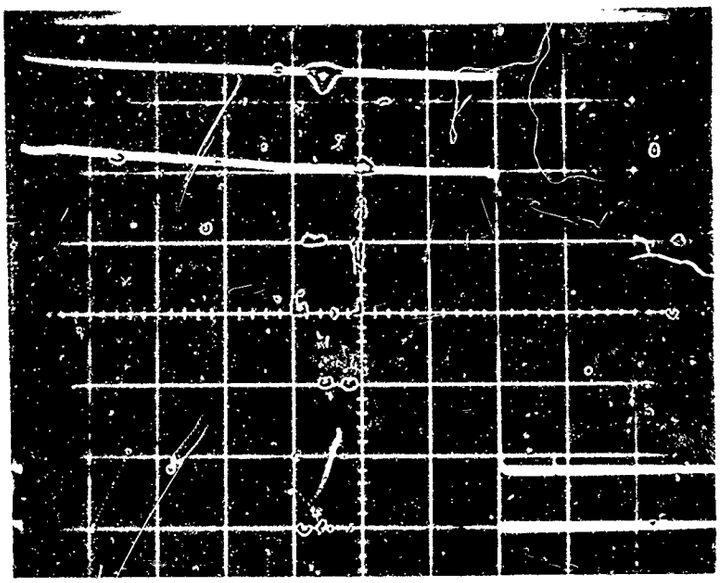


Figure 4C

The oscilloscope trace from a hot-wire ignition test. The upper trace is the current in the circuit (5.5 ampere/division), and the lower trace the voltage across the heated wire and contacts (0.2 volt/division). The time scale is increasing from left to right at 0.2 sec/division. Note the irregularity in the voltage trace which occurred just before the relay opens and the current goes to zero. This irregularity in the voltage signal is coincident with the propellant ignition.

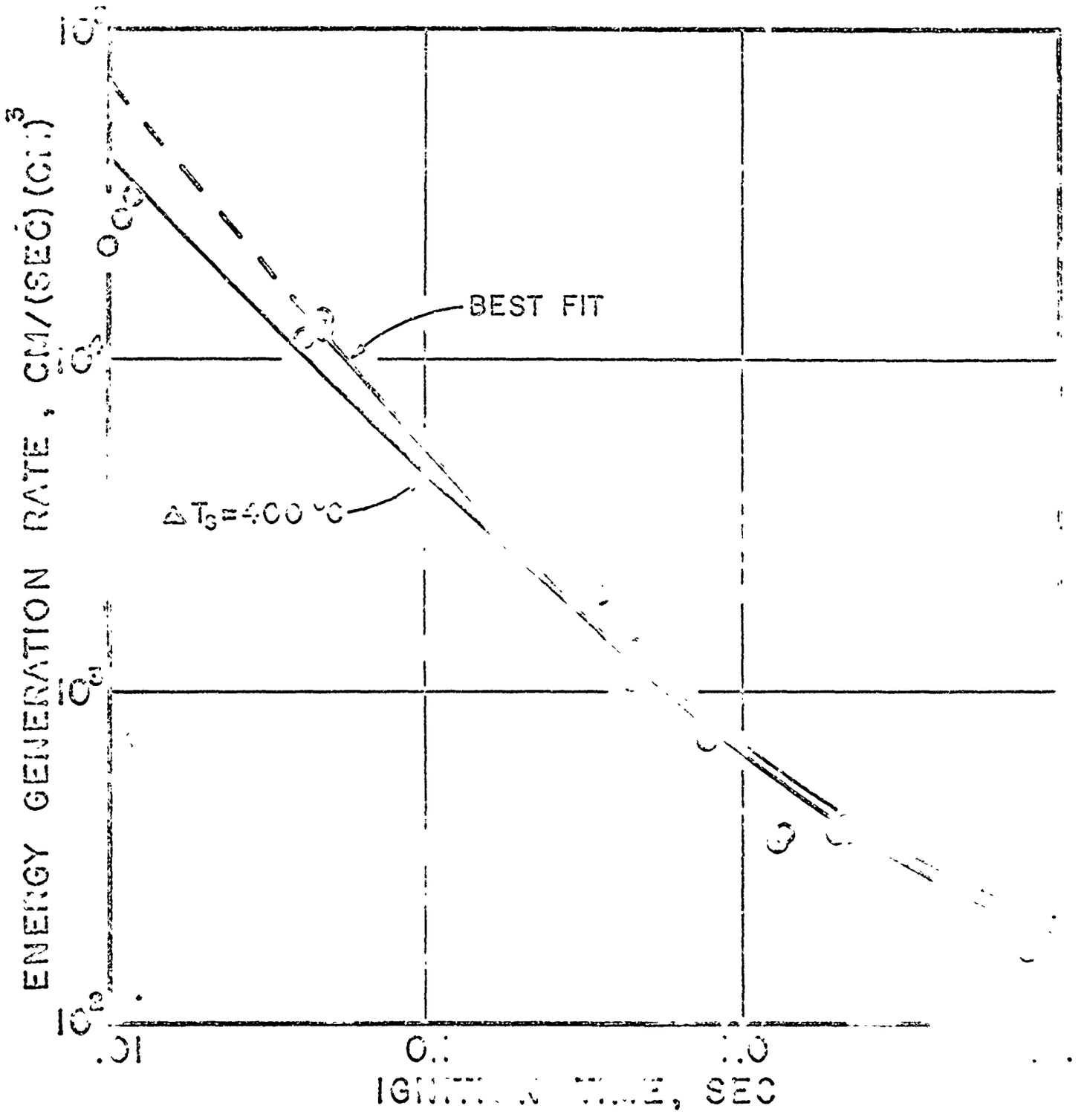


FIGURE 5C.

A summary plot of the hot-wire ignition data. The line labeled "Best Fit" was obtained by use of a least-squares analysis. The data at the highest heating rates were considered to be unreliable and were not included in the analysis. The line labeled 400°C was calculated by means of Equation (2) for an assumed interface temperature rise of 400°C and thermal properties corresponding to the 18-gage Nichrome V wire and "F" propellant

The relationship between the linear-surface-ignition temperature and the ignition time is shown in Figure 6 for the hot-wire ignition tests. Also shown are similar values obtained from ignition tests on the F propellant by thermal radiation in a high temperature furnace [3] and by high convective flux heating in a shock tube [4]. The hot-wire ignition temperatures lie above the values obtained from the radiation furnace and from the shock tube. The difference between the hot-wire and radiation furnace results might be rationalized by postulating that a polymer film over the heated wire tends to delay the ignition. The difference between the shock tube and hot-wire data is too great to be explained in this manner. Although the difference could be the result of a pressure effect, it appears more likely that the difference results from an effect of surface roughness when heating by convective means [4]. It would be difficult to determine which ignition values are more nearly correct. It is interesting to note that the hot-wire ignition data cover a range which overlaps the data from the low-flux radiation furnace and the high-flux shock tube.

CONCLUSIONS

This evaluation study showed that reasonable hot-wire ignition data can be obtained by using very simple apparatus; the data were quite reproducible and can be interpreted in a relatively simple manner. Energy generation rates are measured directly during a run, and propellant surface fluxes can be accurately calculated. Ignition can be detected by observation of the voltage signal across the electrically heated wire. This is one of the few ignition detection systems which does not depend upon light emission from a flame. Ignition times were measured from .01 to 10 seconds, a three order of magnitude range, and there appears to be no reason why the range cannot be extended to times less than 1 msec. Accurate measurement of ignition times over a two order of magnitude range is beyond the capability of most present laboratory apparatus used for the study of ignition.

No evidence was found to indicate that significant gasification occurred near the wire before ignition occurred. The hot-wire ignition data indicated that the linear-surface temperature at ignition increased as the ignition time decreased. This result is in agreement with the thermal ignition theories.

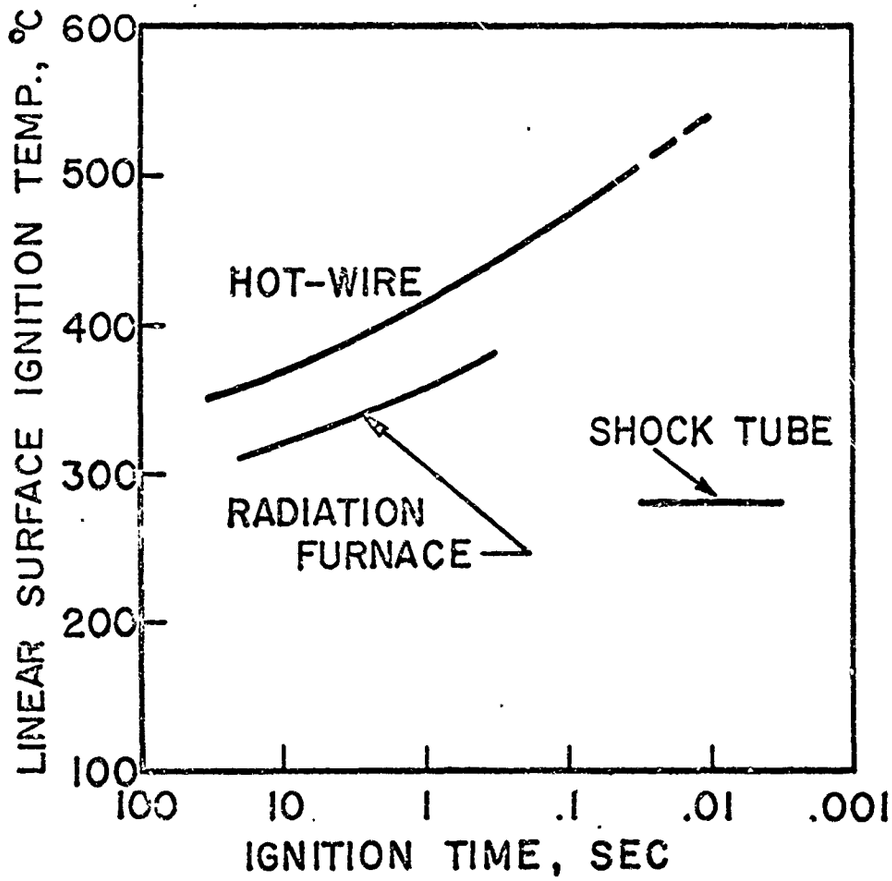


FIGURE 6 C.

The calculated surface-temperature at ignition for the "F" propellant as determined by use of low flux thermal radiation [3], high convective fluxes (shock tube) [4], and conductive transfer from hot-wires. The lines represent the average of smoothed data from each apparatus.

Table IC.

Summary of Thermal and Electrical Properties of "F" Propellant and Nichrome V Wire at 60°C.

Property	Propellant	Wire (18 gage)
Thermal Conductivity, cal/(sec)(cm)(°C)	8.8×10^{-4}	.026*
Heat Capacity, cal/(gr)(°C)	.316	108**
Density, gr/cc	1.63	8 22
Resistance, ohm/cm length	--	1.31×10^{-2}
Temperature Coefficient of Resistance, $°C^{-1}$	--	$1\ 3 \times 10^{-4}$***

* This value is from:
Silverman, L., "Thermal Conductivity Data", Jour. Metals, 5, 631-2 (1953).

** This value is from:
Douglas, T. B., and J. L. Dever, "Enthalpy and Specific Heat for Four Corrosion Resistant Alloys at High Temperatures", Jour. of Research National Bureau of Standards, 54(1), 15-19 (1955).

*** This is a value supplied by the manufacturer (Driver-Harris Co., Harrison, N.J.).

Table II C.

A Tabulation of the $\int_0^\infty \frac{(1-e^{-Mu^2})du}{u^3\,\Delta(u)}$

for $\alpha = 1.165$ where

$$\Delta u = [u\,J_o(u) - \alpha\,J_1(u)]^2 + [u\,Y_o(u) - \alpha\,Y_1(u)]^2$$

M	Value of the Integral
0.005	0.9953×10^{-2}
.010	$.1940 \times 10^{-1}$
.025	4611×10^{-1}
.050	$.8714 \times 10^{-1}$
.10	.1609
.25	.3448
.50	.5833
1.00	.9330
2.50	$.1570 \times 10^{1}$
5.00	$.2152 \times 10^{1}$
10.00	$.2779 \times 10^{1}$
25.00	$.3628 \times 10^{1}$
50.00	$.4270 \times 10^{1}$
100.00	$.4908 \times 10^{1}$

Table III C.

A Tabulation of the $\int_0^\infty \frac{(1-e^{-M\beta^2})\, J_0(\beta)\, J_1(\beta)\, d\beta}{\beta^4\, [\phi^2(\beta) - \psi^2(\beta)]}$

for K = 29.7 and k = 4.15 where

$\phi(\beta) = (K/k)\, J_1(\beta)\, Y_0(k\beta) - J_0(\beta)\, Y_1(k\beta)$

$\psi(\beta) = (K/k)\, J_1(\beta)\, J_0(k\beta) - J_0(\beta)\, J_1(k\beta)$

M	Value of the Integral
.10	0.1238
.25	.3032
.50	.5900
1.00	.1125 x 10
2.50	.2531 x 10
5.00	.4471 x 10
10.00	.7518 x 10
25.00	.1361 x 10^2
50.00	.1971 x 10^2
100.00	.2668 x 10^2

Table IVC.

A Comparison of the 18-Gage Nichrome V Wire - "F" Propellant Interface Temperature Rise as Calculated by Means of Equation (1) and Equation (2)

Time sec	Generation Rate, Q_v cal/(sec)(cm^3)	Interface Temperature, ΔT_s (°C) Equation (1)	Equation (2)
.01	3.75×10^4	400	273
.05	8.44×10^3	400	389
.10	4.39×10^3	400	396
.50	1.14×10^3	400	398
1.00	6.96×10^2	400	400
5.00	2.72×10^2	400	400
10.00	2.04×10^2	400	400

Table VC.

Summary of Hot-Wire Ignition Data

Run Number	Electrical Current (amperes)	Input Energy Rate (cal/sec-cm^3)	Ignition Time (sec)
1.	242	2.2×10^4	01
2.	267	2.68×10^4	011
3.	289	3.14×10^4	012
4.	182.5	1.25×10^4	048
5.	177.5	1.18×10^4	042
6.	188.3	1.33×10^4	048
7.	180	1.22×10^4	048
8.	87.5	2.88×10^3	.205
9.	88.8	2.96×10^3	210
10.	72.6	1.98×10^3	36
11.	72.6	1.98×10^3	32
12.	54	1.09×10^3	45
13.	60.3	1.37×10^3	46
14.	45.6	783	.78
15.	44.6	749	79
16.	31.7	378	1 38
17.	31 2	367	1 34
18.	31.7	377	2 00
19.	31 7	377	2 15
20.	30.1	341	2.55
21.	32 8	405	2 25
22.	32.8	405	2 10
23.	27 5	284	4.95
24.	26.7	267	4 90
25.	27.2	278	4 60
26.	24.4	224	7.60
27.	23.3	204	8 40
28.	21.1	168	8.00

NOMENCLATURE - Appendix C

A	cross section area of heated wire, cm^2
C_1	heat capacity of the wire, cal/(gr)(°C)
C_2	heat capacity of the propellant, cal/(gr)(°C)
F	heat flux at wire-propellant interface, $cal/(sec)(cm)^2$
I	electrical current, amperes or appropriate units
J_n	Bessel function of first kind of order n, dimensionless
K	thermal conductivity ratio K_1/K_2, dimensionless
K_1	thermal conductivity of the wire, cal/(sec)(cm)(°C)
K_2	thermal conductivity of the propellant, cal/(sec)(cm)(°C)
k	thermal diffusivity ratio $\sqrt{k_1/k_2}$, dimensionless
k_1	thermal diffusivity of wire, cm^2/sec
k_2	thermal diffusivity of propellant, cm^2/sec
Q_v	energy generation rate per unit volume in the wire, $cal/(sec)(cm)^3$
R	radius of the wire, cm
R_L	wire resistance per unit length, ohm/cm
T_s	wire-propellant interface temperature, °C
T_o	initial, uniform wire and propellant temperature, °C
t	time, sec
t_i	the ignition time, sec
u	a dummy variable, dimensionless
Y_n	Bessel function of the second kind of order n, dimensionless
α	the ratio $2(\rho_2 C_2)/(\rho_1 C_1)$, dimensionless
β	a dummy variable, dimensionless
ϕ	defined after Equation (2)
ψ	defined after Equation (2)

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3. Baer, A. D., and N. W Ryan, Ignition of Composite Propellants by Low Radiant Fluxes, AIAA Meeting, Palo Alto, Calif., Preprint 64-119 (1964).

4. Keller, J. A., Personal Communication (1964).

APPENDIX D

TABLES

TABLE I

The Compositions of Propellants Containing Various Ammonium Perchlorate Decomposition Catalysts

Propellant	Ammonium Perchlorate* (per cent)	Binder** (per cent)	Catalyst	Catalyst (per cent)
Y	75.0	23.0	Zinc oxide	2.0
Z	74.0	23.0	Zinc oxide Ferric oxide	2.0 1.0
AA	75.0	23.0	Chromic Oxide (Tech.)	2.0
AB	75.0	23.0	Cuprous oxide	2.0
AD	75.0	23.0	Ferric oxide	2.0

* A 50-50 blend of 15-micron and 85-micron weight average particle diameter ammonium perchlorate.

** The binder is composed of 85 per cent of polybutadiene-acrylic acid polymer and 15 per cent Epon 828 as the curative.

TABLE II.

A Tabulation of the Integral Useful for Evaluation of Hot-wire Ignition Data. *

For the
$$\int_0^\infty \frac{(1 - \exp[-M\beta^2])\, J_0(\beta)\, J_1(\beta)\, d\beta}{\beta^4[\phi^2(\beta)^2 - \psi(\beta)]}$$

where K and k (KAPPA) are respectively the thermal conductivity and thermal diffusivity ratios of the wire to propellant and

$$\phi(\beta) = (K/k)\, J_1(\beta)\, Y_0(k\beta) - J_0(\beta)\, Y_1(k\beta) \quad \text{and}$$

$$\psi(\beta) = (K/k)\, J_1(\beta)\, J_0(k\beta) - J_0(\beta)\, J_1(k\beta),$$

the following values are presented:**

KAPPA= 3.0
K=25.0

M	VALUE
100.00	0.1673912E 02
50.00	0.1257399E 02
25.00	0.8775506E 01
10.00	0.4861016E 01
5.00	0.2881587E 01
2.50	0.1622920E 01
1.00	0.7170036E 00
0.50	0.3745359E-00
0.25	0.1921522E-00
0.10	0.7840240E-01

KAPPA= 3.0
K=27.5

M	VALUE
100.00	0.1652355E 02
50.00	0.1229333E 02
25.00	0.8476525E 01
10.00	0.4619103E 01
5.00	0.2709346E 01
2.50	0.1513356E 01
1.00	0.6636716E 00
0.50	0.3455386E-00
0.25	0.1769651E-00
0.10	0.7214041E-01

KAPPA= 3.0
K=30.0

M	VALUE
100.00	0.1630864E 02
50.00	0.1201905E 02
25.00	0.8193892E 01
10.00	0.4308939E 01
5.00	0.2556126E 01
2.50	0.1417531E 01
1.00	0.6177029E 00
0.50	0.3207010E-00
0.25	0.1639980E-00
0.10	0.6680150E-01

KAPPA= 3.0
K=32.5

M	VALUE
100.00	0.1609482E 02
50.00	0.1175417E 02
25.00	0.7926791E 01
10.00	0.4197912E 01
5.00	0.2419008E 01
2.50	0.1333030E 01
1.00	0.5776728E 00
0.50	0.2991874E-00
0.25	0.1527965E-00
0.10	0.6219475E-01

KAPPA= 3.0
K=35.0

M	VALUE
100.00	0.1588249E 02
50.00	0.1149622E 02
25.00	0.7674363E 01
10.00	0.4013770E 01
5.00	0.2295628E 01
2.50	0.1257973E 01
1.00	0.5425017E 00
0.50	0.2803724E-00
0.25	0.1430225E-00
0.10	0.5817883E-01

* See Carslaw, H.S., and J. C. Jaeger, Conduction of Heat in Solids, 2nd ed., 347, Oxford University Press, Oxford (1959).

** The number .1673912E 02 should be read .1673912 x 10^2 etc. The values of the integrals should be accurate to .1 per cent.

TABLE II. (continued).

KAPPA= 5.0
K=25.0

M	VALUE
100.00	0.3572779E 02
50.00	0.2671928E 02
25.00	0.1887800E 02
10.00	0.1085956E 02
5.00	0.6672375E 01
2.50	0.3889088E 01
1.00	0.1780529E 01
0.50	0.9462264E 00
0.25	0.4899283E-00
0.10	0.2007671E-00

KAPPA= 5.0
K=27.5

M	VALUE
100.00	0.3537019E 02
50.00	0.2627089E 02
25.00	0.1839147E 02
10.00	0.1043066E 02
5.00	0.6341309E 01
2.50	0.3662152E 01
1.00	0.1661457E 01
0.50	0.8791564E 00
0.25	0.4541337E-00
0.10	0.1858635E-00

KAPPA= 5.0
K=30.0

M	VALUE
100.00	0.3501433E 02
50.00	0.2583081E 02
25.00	0.1792383E 02
10.00	0.1003152E 02
5.00	0.6040324E 01
2.50	0.3459831E 01
1.00	0.1557256E 01
0.50	0.8209641E 00
0.25	0.4232232E-00
0.10	0.1730304E-00

KAPPA= 5.0
K=32.5

M	VALUE
100.00	0.3465954E 02
50.00	0.2539890E 02
25.00	0.1747441E 02
10.00	0.9659561E 01
5.00	0.5765689E 01
2.50	0.3278394E 01
1.00	0.1465311E 01
0.50	0.7699950E 00
0.25	0.3962582E-00
0.10	0.1618615E-00

KAPPA= 5.0
K=35.0

M	VALUE
100.00	0.3430714E 02
50.00	0.2497595E 02
25.00	0.1704295E 02
10.00	0.9312410E 01
5.00	0.5514230E 01
2.50	0.3114813E 01
1.00	0.1383585E 01
0.50	0.7249819E 00
0.25	0.3725263E-00
0.10	0.1520508E-00

TABLE II. (continued).

KAPPA= 4.0
K=25.0

M	VALUE
100.00	0.2580264E 02
50.00	0.1934813E 02
25.00	0.1360823E 02
10.00	0.7704340E 01
5.00	0.4658784E 01
2.50	0.2672959E 01
1.00	0.1203391E 01
0.50	0.6342754E 00
0.25	0.3269544E-00
0.10	0.1336912E-00

KAPPA= 4.0
K=27.5

M	VALUE
100.00	0.2551320E 02
50.00	0.1897841E 02
25.00	0.1320910E 02
10.00	0.7364765E 01
5.00	0.4405966E 01
2.50	0.2505557E 01
1.00	0.1118634E 01
0.50	0.5873442E 00
0.25	0.3021404E-00
0.10	0.1234143E-00

KAPPA= 4.0
K=30.0

M	VALUE
100.00	0.2522479E 02
50.00	0.1861653E 02
25.00	0.1282807E 02
10.00	0.7051875E 01
5.00	0.4178404E 01
2.50	0.2357649E 01
1.00	0.1044996E 01
0.50	0.5468749E 00
0.25	0.2808286E-00
0.10	0.1146071E-00

KAPPA= 4.0
K=32.5

M	VALUE
100.00	0.2493778E 02
50.00	0.1826287E 02
25.00	0.1246455E 02
10.00	0.6762948E 01
5.00	0.3972619E 01
2.50	0.2226055E 01
1.00	0.9804273E 00
0.50	0.5116178E 00
0.25	0.2623241E-00
0.10	0.1069734E-00

KAPPA= 4.0
K=35.0

M	VALUE
100.00	0.2465252E 02
50.00	0.1791768E 02
25.00	0.1211785E 02
10.00	0.6495560E 01
5.00	0.3785718E 01
2.50	0.2108244E 01
1.00	0.9233526E 00
0.50	0.4806259E-00
0.25	0.2461052E-00
0.10	0.1002920E-00

TABLE III.

Calculated Surface Temperatures and Polymer-Gage Interface Temperatures for PBAA Coated Pyrex Heat Flux Gages.* The Surface Heat Flux was 2.385 cal/(sec)(sq cm).

Time sec	Surface Temp °C	Interface Temp. Calculated	°C Corrected**	Interface Heat Flux cal/(sec)(sq cm)
0	28.0	28.0	28.0	0
.069	76.2	34.5	36.0	1.41
.126	88.2	41.3	42.5	1.78
.296	106.5	55.7	56.0	2.06
.580	124.3	72.4	71.2	2.17
.864	138.0	85.4	83.0	2.24
1.15	148.6	96.0	92.5	2.28
1.43	158.4	105.3	100.6	2.28
2.85	194.6	141.1	131.0	2.30
4.27	222.0	168.2	152.8	2.31
5.68	244.9	191.0	170.6	2.31
7.10	265.0	211.1	186.8	2.33
7.80	274.0	220.1	192.3	2.33

* The polymer film was assumed to be .01 cm thick and the gage semi-infinite. The thermal responsivities were .0139 and .0378 cal/(sec)$^{1/2}$ (sq cm) (°C) respectively for polymer and gage, and thermal diffusivities were 0.98×10^{-3} and 3.36×10^{-3} cm^2/sec for the polymer and gage respectively.

** These temperatures were corrected to account for variation in the thermal properties of pyrex and should correspond to the measure gage interface temperatures.

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