

Ignition of Composite Propellants by Low Radiant Fluxes

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The ignition characteristics of several composite propellants subjected to blackbody thermal radiation were experimentally determined. Surface heat fluxes ranging from 1 to 13 cal/sec-cm² were employed, and the effects of surface flux, initial propellant temperature, pressure, and surface geometry on the propellant ignition times were determined. Ignition tests on propellants formed by pressing ammonium perchlorate with nonvolatile carbon black and graphite showed that the surface ignition temperatures of these materials were the same as for normal propellants. A simple ignition theory is proposed which postulates that the ignition is controlled by a single surface reaction. The characteristic constants for this reaction (activation energy, etc.) may be determined from the effect of surface heat flux on the experimentally measured ignition times. Once the characteristic constants of the surface reaction are known, predictions of the variations in ignition times for changes in initial propellant temperature, pressure, and surface geometry are possible for flux levels in the range investigated.

Introduction

IN spite of a great deal of work on the ignition of solid propellants, very little is known about the mechanism of the ignition process. Practical ignition tests on small motors yield data that couple the igniter and propellant response, and most research in which the propellant response alone was studied has been an attempt to correlate ignition times or ignition energies in terms of surface heat flux, pressure, and composition of the gas in contact with the propellant. Such approaches are necessary in order to define the important variables and to supply data for the design of practical igniter systems concerned with specific propellants. In order to obtain more general information, it is necessary to gain a greater understanding of the propellant response; and, because of the complexity of this response, some simplifications must be introduced into the study of the problem. One simplification would be to study the reactions of single propellant constituents or of simple propellant systems. The approach used in the present work was to study the ignition of complex actual propellants but at surface fluxes somewhat lower than those developed by practical igniters. Thermal radiation fluxes ranging from 2 to 13 cal/sec-cm² were employed, and ignition times from 0.25 to 10 sec were observed. Under these conditions, the composite propellant can be treated as homogeneous material with respect to its thermal properties, the partial translucence of the propellant constituents to thermal radiation may be neglected or eliminated, and the external surface fluxes will always be less than the steady-state energy feedback of the burning propellant. Also, because of the relatively long time intervals involved, the propellant ignition time can be accurately taken to be the time of appearance of first flame; and, hopefully, if a chain of reactions occurs, the rate-limiting reaction may be easily identified. Direct extrapolation of ignition data obtained under these conditions to the conditions that exist in a rocket engine may be unsatisfactory; but, once ignition under low flux conditions is understood, a theoretical extrapolation may be possible.

Apparatus and Procedure

The chemical and thermal properties of the propellants used in this study are summarized in Table 1. The densities and thermal diffusivities of all materials were measured. Heat capacities were taken from published data on ammonium perchlorate,¹ and values were measured for the various fuel binders used. With the exception of the ammonium nitrate propellant *D*, all contained ammonium perchlorate *AP* as oxidizer. With the exception of propellant *G*, all contained burning rate catalysts. Propellants *A* and *B* contained 2% aluminum and were supplied by propellant manufacturers, as were propellants *C* and *D*. All other propellants were formulated for this study in a small-scale facility. Commercial grades of ingredients were used in all formulations. In all tests the exposed propellant surfaces were cut with a sharp razor blade just prior to a test. The *F* and *G* propellants were found to be slightly transparent to the thermal radiation. The surfaces of these propellants were coated with a thin film of carbon black to eliminate this problem. The coated *F* and *G* propellants were designated, respectively, the *FC* and *GC* propellants. Because of the relatively long times involved in these tests, the thin carbon-black film did not affect the observed ignition times.

Two furnaces were employed in this study, each containing a heated 2-in. i.d. \times 18-in.-long core. The sealed furnace shown diagrammatically in Fig. 1 was operated at pressures of 0.2–20 atm at temperatures up to 1000°C. An atmospheric furnace was used which operated at temperatures up to 1500°C. The sample holder, injection holder, and aluminum foil shielding system used for this work are shown in Fig. 2. The injection holder was mounted on an injection rod that could be thrust into the furnace. The rod was held in guides such that, when the injection holder was correctly positioned inside the furnace, the rod would strike a stop, the sample holder would then be carried through the foil shield by inertia, and the propellant surface was exposed to the essentially blackbody thermal radiation inside the furnace core. Tests showed that the propellant surface went from the completely covered to the completely exposed position in 20–30 msec. Ignition was detected by an infrared sensitive photocell, which viewed the exposed propellant surface in the furnace. An oscilloscope sweep was triggered when the injection rod contacted the stop. The photocell signal and timing markers were displayed on the oscilloscope screen, and the screen was photographed to yield a permanent record. Normally, five samples were run under each set of conditions and the results averaged.

Since the propellant sample was left in the furnace until ignition occurred, the surface was exposed continuously to

Presented as Preprint 64-119 at the AIAA Solid Propellant Rocket Conference, Palo Alto, Calif., January 29–31, 1964; revision received February 15, 1965. This work was supported by the U. S. Air Force under Contract No. AF 49(638)-170, Grant No. AF 62-99, and Grant No. 40-63, monitored by the Air Force Office of Scientific Research of the Air Research Development Command.

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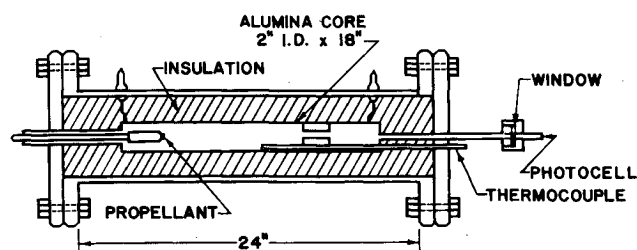


Fig. 1 A sectional view of the sealed, low-temperature radiation furnace. Propellant samples are pushed rapidly into the furnace from the left end of the furnace and are stopped in the position shown.

an essentially constant surface heat flux. Data presented in terms of surface heat fluxes are corrected for reradiation of the surface and for free convection heat transfer from the hot furnace gases. Free convection heat-transfer coefficients were calculated from published correlations.² Estimated values of surface absorptivity (usually 0.9) were used based upon data for similar propellants. In all cases, a neutral atmosphere was presented to the sample surface, and no surrounding gas-surface reactions occurred.

Theory

The low-flux ignition characteristics of the composite propellants studied can be adequately described by a simple mathematical model. The propellant slab is considered to be a homogeneous, semi-infinite body, originally at a uniform temperature, and subjected to a constant surface heat flux. These conditions were closely approximated by the experimental conditions. Ignition is assumed to be the result of a runaway exothermic surface reaction, which contributes to the surface heat flux. The mathematical relationship that describes this model is

$$\partial T / \partial t = (k / \rho c) (\partial^2 T / \partial x^2) \quad (1)$$

with boundary condition at $x = 0$,

$$-k(\partial T / \partial x) = F + Be^{-E/(RT)}$$

and as $x \rightarrow \infty$, $T = T_0$, and with the initial condition that, at $t = 0$, $T(x) = T_0$, where T is local absolute temperature, x is the positive distance from the surface into the solid, t is time, F the externally applied heat flux, B the product of the surface-reaction frequency factor and the quantity of

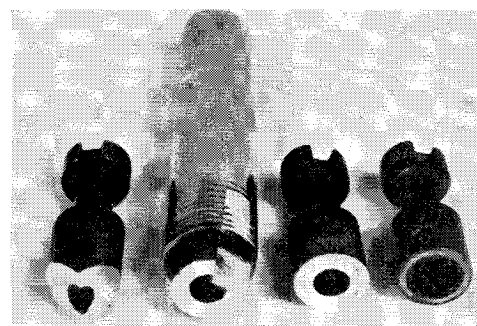


Fig. 2 Sample mountings for the radiation furnaces. From right to left the photograph shows 1) the propellant sample mounted in the sample holder, 2) the mounted sample with edge covered with foil shield, 3) the sample holder projecting from the injection holder as when in the furnace, and 4) the 90° corner sample holder that was used in some tests.

energy transmitted to the surface per unit reaction, E the effective reaction activation energy, and k , ρ , and c , respectively, the solid thermal conductivity, density, and heat capacity. The initial uniform solid temperature is T_0 . For the purposes of this paper, the thermal properties were assumed to be constant at their 60°C value. In most cases, comparative results only are considered, and since the major constituent of all materials was the same (AP), the effect of temperature dependence of the thermal properties should be the same for all materials. Equation (1) was put into dimensionless form, and numerical solutions were obtained for various reasonable values of the parameters. Ignition was assumed to occur when the surface-reaction term was greater than F and was changing rapidly with time.

It appears likely that the actual ignition process is considerably more complex than is indicated by Eq. (1); however, this model seems to be an adequate approximation to the controlling processes for the case of low surface flux ignition. A surface exothermic reaction was considered in the model presented here, because it was felt that this was a likely process in the case of a composite propellant. A reasonable mechanism, which could lead to Eq. (1), would be a surface or bulk endothermic reaction followed by a rapid exothermic surface reaction. Necessary assumptions for this model are that the rate of energy feedback from the exothermic reaction is a function of the propellant surface temperature, and that gas-phase reactions are rapid and con-

Table 1 Summary of propellant chemical and thermal properties^a

	Propellant					
	A	B	C	D	F ^b	G
Fuel binder	Polysulfide	Polyurethane	BD/MVP ^d Rubber AP	BD/MVP Rubber NH ₄ NO ₃	PBAA ^e AP	PBAA AP
Oxidizer crystal	AP	AP				
Approximate weight, %						
Oxidizer crystal	76	82	86	84	80	82
Aluminum	2	2	0	0	0	0
Catalyst ^c	1	In fuel	2	2	2 ^c	0
Fuel binder	21	16	12	14	18	18
Density, g/cm ³	1.75	1.70	1.70	1.53	1.63	1.60
Thermal diffusivity, cm ² /sec	0.00167	0.00139	0.00196	0.00196	0.00170	0.00171
Thermal responsivity, $\Gamma = (k\rho c)^{1/2}$ cal/sec ^{1/2} — cm ² °C	0.0229	0.0202	0.0233	0.0270	0.0212	0.0206

^a These values are at approximately 60°C. For calculation purposes, the surface absorptivity was assumed to be 0.9 for the propellants.

^b The F propellant was the same as F except a surface coating of carbon black was used during testing and an absorptivity of 1.0 was assumed.

^c The F propellant catalyst was Harshaw Chemical Co. Cu-0202-p copper chromite. The other catalysts were various compounds of iron.

^d Butadiene-methylvinylpyridine rubber produced by the Phillips Petroleum Co.

^e Polybutadiene-acrylic acid copolymer cured with 15% EPON 828 resin.

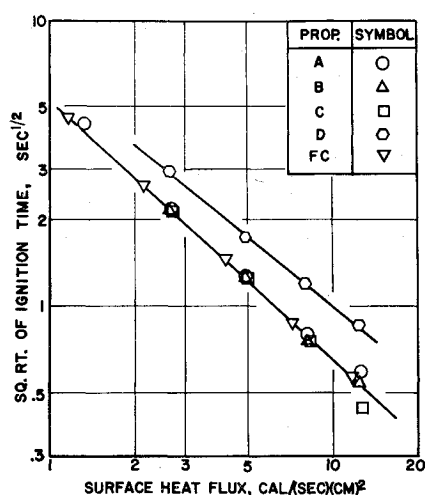


Fig. 3 The effect of surface heat flux on propellant ignition times.

trolled by the rate at which reactants are produced by the solid. The justification for the first assumption can be strengthened by identifying the exothermic reaction. The second assumption is in opposition to the gas-phase ignition theory proposed by Summerfield et al.^{3, 4} Since the gas-phase theory has not been placed on a quantitative basis for ignition in a neutral atmosphere, it is not yet possible to define the limits of applicability of this assumption. Summerfield et al.^{3, 4} have quantitatively treated the gas-phase theory for the case of ignition by gaseous oxygen. The problem of hypergolic ignition by oxygen was also treated by Anderson et al.⁵ in terms of a heterogeneous reaction model.

An analysis of the results of the numerical solutions of Eq. (1) indicates the following characteristics for the propellant ignition.

1) The square roots of the calculated ignition times $(t_i)^{1/2}$ are roughly inversely proportional to the surface heat flux. A plot of $\log(t_i)^{1/2}$ vs $\log F$ should be essentially a straight line of slope slightly greater than -1 . The slope of such a plot depends, to a very good approximation, only on

the activation energy assumed for the reaction. From the numerical calculations, it is found that

$$S = 4.2(RT_0/E) - 1 \quad (2)$$

where S is the slope of such a plot. Equation (2) can be used to obtain activation energies from experimental data. Since S is normally close to -1 , small errors in the determination of S can result in large errors in the calculation for E/R .

2) The effect of pressure on the ignition process is determined by the effect of pressure on the parameter B in the boundary-condition equation. If the final exothermic reaction in a chain proceeds as rapidly as reactants are formed, the parameter B and the ignition time would be independent of pressure. If B is proportional to pressure, as would be the case if excess reactants were present, numerical solutions indicated that, for the range of activation energies anticipated, $t_i \propto p^n$, where n ranges from 0.15 to 0.25. In either case, the ignition process would not be a very strong function of pressure.

3) A convenient parameter for use in characterizing solid propellant ignition is the linearly calculated surface temperature at ignition T_{si}^L . For the case of constant surface heat flux

$$T_{si}^L = T_0 + (2F/\Gamma)(t_i/\pi)^{1/2} \quad (3)$$

where Γ is the thermal responsivity of the propellant $(k\rho c)^{1/2}$. Equation (3) is just the solution to Eq. (1) with the chemical reaction term neglected. The numerical solutions to Eq. (1) indicate that T_{si}^L should be independent of the initial propellant temperature. By use of this fact, it is possible to summarize the results of the numerical calculations. It is found that, to an adequate approximation,

$$(t_i)^{1/2} = \frac{\Gamma(\pi)^{1/2}}{2F} \left[\frac{E/R}{1 - 1.04 \ln(F/B)} - T_0 \right] \quad (4)$$

It should be mentioned that the calculations by Hicks,⁶ in which he considered a bulk exothermic reaction, are in qualitative agreement with the results presented here. The only quantitative difference is that the activation energies calculated from a $\log(t_i)^{1/2}$ vs $\log F$ plot from Hicks' results are approximately twice the values calculated from Eq. (2).

Table 2 Effect of initial A-propellant temperature on the linear surface temperature at ignition T_{si}^L

Initial propellant temperature, °C	Furnace temperature, °K	Ignition time, sec	Surface flux, cal/sec-cm ²	Surface ignition ^a temperature T_{si}^L , °K, measured average
60	1083	8.78	1.78	592
30	1083	10.38	1.79	587
0	1083	13.40	1.79	595
-30	1083	14.94	1.80	586
-60	1083	17.80	1.81	588
60	1283	2.73	3.46	615
30	1283	3.20	3.48	609
0	1283	3.78	3.49	607
-30	1283	4.57	3.49	611
-60	1283	5.40	3.49	613
60	1483	0.96	6.12	628
30	1483	1.14	6.13	626
0	1483	1.25	6.16	612
-30	1483	1.64	6.14	631
-60	1483	1.94	6.14	635
60	1680	0.41	9.98	648
30	1680	0.47	10.00	641
0	1680	0.54	10.0	636
-30	1680	0.69	10.0	652
-60	1680	0.85	10.0	667

^a These values are probably high, since the thermal properties were assumed to be constant at their 60°C value.

Experimental Results

The predicted characteristics of the solid propellant ignition presented in the previous section have been experimentally checked and have been found to be substantially correct. The data of Wachtell and Roth⁷ on the low-flux ignition of double base propellants indicate the same ignition characteristics for these materials. The experimental results obtained in the present work are discussed in the following paragraphs in the same order in which the predicted characteristics were outlined.

1) The effect of surface heat flux on the ignition time was studied at atmospheric pressure with several propellants initially at room temperature ($28 \pm 2^\circ\text{C}$) by making a series of tests at different furnace temperatures. The results of this study are summarized in Fig. 3 as a plot of $\log(t_i)^{1/2}$ vs $\log F$. A slope of slightly greater than -1 is noted in all cases; and, if a constant value of surface absorptivity is assumed, the -0.91 slope of the line for the catalyzed AP propellants can be used with Eq. (2) to determine an apparent activation energy E/R , in this case, of $14,000^\circ\text{K}$.

2) The effect of pressure on the ignition times was determined in the sealed radiation furnace. Figure 4 shows typical data obtained for the A propellant. Little or no effect of pressure on the ignition times was observed. Because pressure was not an important variable, all subsequent tests were performed at atmospheric pressure.

3) Tests were made in which the initial temperature of propellant samples was varied from -60° to $+60^\circ\text{C}$. It was anticipated that, for a constant surface heat flux, the calculated values of $T_{s,i}$ would be independent of T_0 . Table 2 summarizes such data for the A propellant, and $T_{s,i}$ is found to be essentially independent of T_0 . By use of this result, ignition data can be corrected for initial temperature effects.

An additional test of the validity of the simple mathematical description of the ignition process was made by considering the ignition characteristics of a square corner section of propellant. The sample holder used in this study is shown in Fig. 2. If a two-dimensional (90°) corner is treated as an infinite solid in the direction perpendicular to each face (a semi-infinite corner), it can be shown that, for the case of a constant surface heat flux to each face, the temperature rise at the corner is twice the temperature rise of a semi-infinite body subject to the same surface heat flux. If t_i is calculated from Eq. (4) for the case of a semi-infinite body, then for the same values of E/R and B , t_i for the semi-infinite corner subjected to the same surface heat flux may be calculated from Eq. (4) if the value of F for the corner is taken to be twice F for the semi-infinite body. The ratio of the ignition time for the semi-infinite body to the ignition time

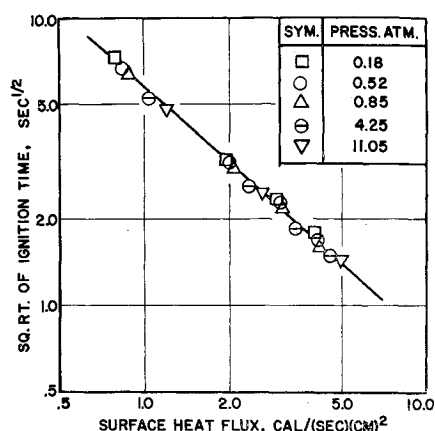


Fig. 4 The effect of pressure on the ignition times of the A propellant.

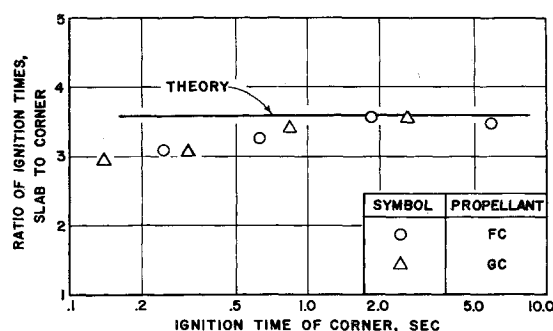


Fig. 5 A comparison of the ignition times of semi-infinite slabs of propellant to semi-infinite 90° corners. The line labeled theory represents the prediction of the simple ignition theory.

of a semi-infinite corner in the radiation furnace at the same temperature should be equal to 3.6. Figure 5 represents the results of an experimental check of this hypothesis for the FC and GC propellants and shows that for relatively long ignition times the ratio of ignition times is indeed 3.6. The values of E/R and B were determined from the $\log(t_i)^{1/2}$ vs $\log F$ plot for the semi-infinite body. If gas-phase reactions at any distance from the surface were important, this predicted relationship between corner and flat surface would not be valid. If ignition occurred at a constant surface temperature, this ratio would be 4.0. The deviation of this ratio from 3.6, in the case of shorter ignition times, is the result of the experimental impossibility of cutting a true corner from a propellant slab. Although the samples were carefully cut with a sharp razor blade, microscopic examination showed that the edge of the sample corner had a radius of curvature of about 0.002 cm . In the case of short-time ignition, the depth of penetration of the energy was not sufficiently greater than the radius of curvature to make the sample respond as a true corner.

An additional factor that was considered and about which the simple mathematical model is noncommittal is the effect of a burning-rate catalyst on the ignition process. A series of propellants was prepared in which 0, 0.5, 1.0, 2.0, and 4.0% Harshaw Cu-0202-p copper chromite burning catalyst replaced corresponding amounts of AP, and the ignition times of these materials were determined in the atmospheric radiation furnace. The propellants containing 0 and 2.0% catalyst were, respectively, the G and F propellants. Figure 6 summarizes the results of these tests. The addition of the burning-rate catalyst produced some reduction in the ignition times as more catalyst was added until about the 2% level was reached. The 2 and 4% materials showed essentially identical ignition times.

Figure 6 also shows the effect of coating the F and G propellants with carbon black to reduce the surface transmissivity of these propellants; an increase in absorptivity also resulted from coating the surfaces. Equation (1) can be modified by adding a term to account for absorption below the propellant surface. If the values of E/R and B , determined for the blackened surface samples, are used when obtaining numerical solutions to the modified Eq. (1) and if the absorptivity is assumed to change from 1.0 to 0.9 for the blackened vs the uncoated surface, it is found that observed ignition data for the uncoated F and G propellants can be calculated for assumed effective opacities of 125 and 40 cm^{-1} respectively.

Proposed Ignition Mechanism

It has been shown that a relatively simple model, which involves consideration of only a single exothermic reaction quite adequately describes the ignition process of composi-

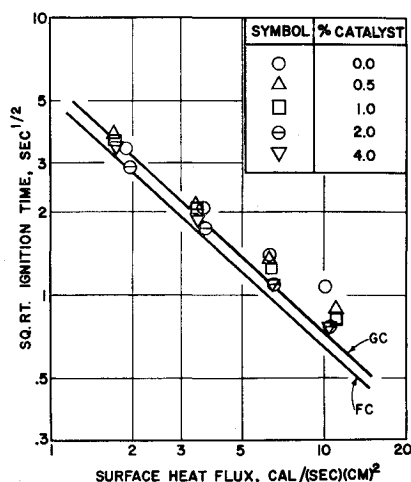


Fig. 6 The effect of the addition of copper chromite burning-rate catalyst to the G propellant. A comparison of the line for the GC and FC propellants to the data for the 0 and 2% catalyst materials, respectively, illustrates the effect of the transmissivity of the propellant surface.

propellants subjected to low-level radiant heat fluxes. Some consideration must be given to identifying this reaction in order to justify the simple model. The clue to resolving the gross mechanism of the ignition process of these composite propellants is found in Fig. 3. It appears that the ignition times of all catalyzed AP propellants are essentially the same when exposed to the same surface heat flux. Although the thermal properties of all these propellants are fairly similar, a variety of polymers, additives, solids loadings, and burning-rate catalysts are represented. The only common component of all the propellants is the ammonium perchlorate. An obvious and convenient hypothesis is that the ignition is controlled by the decomposition of the ammonium perchlorate. Subsequent reaction between the AP decomposition products and solid-fuel binder is also suggested, since the data in Fig. 3 do not indicate a dependence on polymer or, presumably, on polymer pyrolysis rates.

In order to test these hypotheses, a series of special propellants, containing as-nonvolatile fuel graphite and carbon black, were prepared by pressing mixed powders at 100,000 psi. The carbon black was fired at 1000°C in an inert atmosphere for two hours before use in the propellant. Table 3 summarizes the chemical and thermal properties of these materials. Ignition times for each propellant were deter-

mined in the radiation furnace. All propellants showed an easily identifiable flame, which was taken as an indication of the ignition and burning. The CB propellant (carbon-black fueled) burned at atmospheric pressure when removed from the furnace. Since ammonium perchlorate does not burn at low pressure, the nonvolatile carbon black must participate in the ignition and burning reactions. The graphite-containing propellant and the ammonium perchlorate, which contained 2% carbon black, would not burn when removed from the furnace.

Because the thermal properties of these materials were not similar, it was necessary to correct the ignition data to a common basis. As indicated previously, Eq. (1) was put into dimensionless form before numerical solutions were obtained. A consideration of the dimensionless groups involved in the solutions shows that, if the value of B and E/R for a series of propellants is the same, then a plot of $\log[(t_i)^{1/2}/\Gamma(RB/E)]$ vs $\log F/B$ should yield a single line for the series, and for the same surface flux at a given value of $(t_i)^{1/2}/\Gamma(RB/E)$, the surface temperatures would be the same. Figure 7 is such a plot for the series of propellants with non-volatile fuel binders; also included are data for the blackened F propellant. The values of E/R and B were, respectively, 14,000°K and 0.46×10^{10} cal/sec-cm². These values were determined from previous ignition data on the FC propellant. With the exception of two points that represent long-period ignition of the graphite propellant, a single line results for the FC, CB, and GR materials. APC, which was basically only AP, ignited at a surface temperature a little higher than the other materials. If APC contained somewhat more than 2% carbon black, the ignition times would probably have been identical to the other materials. The conclusion that the ignition proceeds by AP decomposition followed by an exothermic reaction between AP decomposition products and solid-fuel binder seems inescapable. This mechanism is compatible with the simple mathematical model previously proposed. The activation energy of 28 kcal/g-mole calculated from the ignition data is comparable to the activation energy for the anticipated AP decomposition reaction⁸; however, considering some of the approximations involved, this agreement may be fortuitous. Since the steady-state combustion of carbon-black fueled ammonium perchlorate propellants is similar in many respects to the combustion of polymer fueled propellants,⁹ it appears that a heterogeneous reaction between AP decomposition products and the solid-fuel binder may be important in steady-state combustion.

Summary

The ignition of composite rocket propellants subjected to surface heat fluxes in the range from 2 to 13 cal/sec-cm² can be described by a very simple mathematical model, which considers only a single exothermic propellant reaction. Under these conditions, pressure has little effect on the ignition process. The effect of initial uniform propellant temperature on the ignition time may be treated by making use of the fact that the linear surface temperature at ignition T_{si}^L is almost independent of the initial temperature. The ignition mechanism, which is consistent with this model, is that the ammonium perchlorate decomposition is the first step in the process, the ammonium perchlorate decomposition products react with solid-fuel binder, and the energy released by the decomposition products and fuel binder quickly brings the propellant to steady-state burning conditions.

In the case of ignition of solid propellants subjected to high surface heat fluxes, the situation appears to be more complicated. Although the high-pressure, high-convective heat flux data of Baer, Ryan, and Salt¹⁰ are reasonably consistent with the results of the low-flux ignition tests, most data obtained by use of the high radiant fluxes of the arc image furnace¹¹ show significant differences, particularly

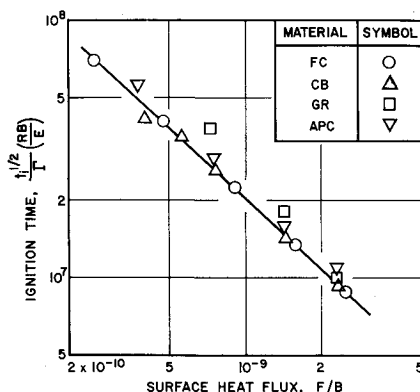


Fig. 7 The ignition characteristics of various materials that contain nonvolatile fuel binders and the FC propellant. Data points falling on the line indicate ignition at the same temperature as the FC propellant.

Table 3 Summary of chemical and thermal^a properties of pressed materials

	Material		
	CB	GR	APC
Fuel	Carbon black ^b	Graphite	Carbon black ^b
Weight, %			
Ammonium perchlorate	82.0	82.0	96.0
Fuel	16.0	16.0	2.0
Copper chromite catalyst	2.0	2.0	2.0
Density, g/cm ³	1.65	1.97	1.89
Thermal diffusivity, cm ² /sec ^a	0.0024	0.0078	0.0021
Thermal responsivity, $\Gamma = (k\rho c)^{1/2}$ cal/sec ^{1/2} cm ² -°C	0.021	0.046	0.025

^a These values are at approximately 60°C. For calculation purposes, the surface absorptivity of these materials was assumed to be 0.9.

^b The carbon black was commercial Phil Black-E previously fired at 1000°C for two hours.

with respect to the effect of pressure. Thus the simple model for low-flux ignition probably represents a special case of the general ignition process.

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