Composite Solid-Propellant Ignition by Radiant Energy

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Ignition characteristics of representative composite solid propellants were studied using an arc-imaging furnace to provide a radiant energy source. The variation of propellant ignitability with formulation changes was found to be small provided the binder and oxidizer were fixed. The minimum initial pressure for which ignition will occur appears to be predominantly determined by the thermal decomposition characteristics of the binder component in ammonium perchlorate-based propellants. It is proposed that a key step required to achieve ignition is the establishment of a critical gas-phase reaction rate threshold adjacent to the propellant surface.

Nomenclature

C_{ox} = gaseous oxidizer concentration
C_F = gaseous fuel concentration
E = activation energy
F = external radiant flux
P = pressure
R = gas constant
$(R_{xn})_{\text{critical}}$ = critical gas-phase reaction rate threshold
T = temperature
t_T = propellant heating time
t_c = chemical-diffusion lag time
Z = gas-phase Arrhenius factor
λ = mixture ratio
τ_{ign} = total time to ignition

Introduction

IGNITION is the first stage in solid-propellant combustion, and the ignition characteristics of composite solid-propellants depend on the simultaneous interaction of many physical and chemical processes. The study of propellant ignition is complicated by the fact that the contribution of individual unit processes may shift with changes in propellant composition, gaseous environment, hydrodynamic factors, heating mode and rate, and pressure. The magnitude of the ignition time and its dependence on measurable independent variables provide the principal clues for the determination of the significant processes.

Although it is an oversimplification, it is useful to consider the problem of ignition of solid propellants as primarily one of production of combustible volatiles. The process can be further defined by the consideration of two separate stages: 1) propellant heating and 2) ignition of the volatiles following propellant heating. The ignition event can be divided into time intervals representing these stages,

$$\tau_{\text{ign}} = t_T + t_c \tag{1}$$

where

τ_{ign} = total time to ignition
t_T = time of propellant heating by external energy source alone
t_c = time of heat addition by various chemical reactions plus time of transition to steady-state combustion.

During the chemical lag exothermic reactions occur at or near the propellant surface and the surface temperature rises faster than it would from externally applied energy alone. The rate of volatiles generation rises rapidly with temperature and will exceed any threshold value within a small temperature change. Therefore, ignition will usually occur when the solid reaches some fixed temperature, and this temperature will be substantially independent of heating rate and other parameters over a limited range.

However, if a complete understanding of the ignition mechanism is to be attained, the kinetic processes affecting the chemical time, t_c, must be defined in greater detail. The ignition research reported here was designed to explore the interrelationship among ignition characteristics and propellant compositional factors in order to determine chemical reaction sequences that may be important in determining t_c.

Experimental Apparatus

An arc-imaging furnace is a convenient tool for ignition research because the external heating rate can be controlled completely independent of other factors. Therefore, the observed effects of pressure, gaseous environment, propellant formulation variables, and heating rate can be assessed and directly related to the ignition process.

Minimum exposure times were obtained by using the go/no-go criterion. In this procedure, successive samples are exposed to energy pulses of known intensity and duration, and successful or unsuccessful ignition is noted. At low pressures, where ignition requires long exposure times, the exposure time was held constant and go/no-go limits of pressure were also determined.

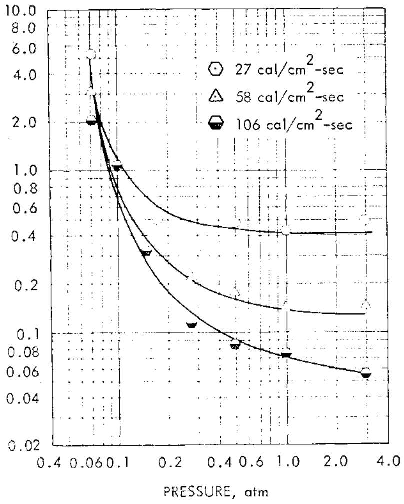

Fig. 1 Ignition time as a function of pressure—PBAN propellant.

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Test samples were disks of propellant 0.30 in. in diam × 0.50 to 0.75 in. thick. A cork-borer was used to cut specimens from a sheet of propellant prepared with a microtome knife. This procedure provided good reproducibility of sample surface. A nitrogen gas environment was maintained in all tests.

A variety of propellant formulations was employed. Polybutadiene-acrylic acid-acrylonitrile (PBAN), polyurethane (PU), carboxy-terminated polybutadiene (CTPB), polyisobutylene (PIB), and a nitrato-ester plasticized polyester (PEP) were used as the binders. Individual tests exhibited scatter, and 20–25 tests were used to establish a threshold. At some combinations of flux and pressure it was necessary to use additional tests to achieve consistent results. Complete details of the arc-imaging furnace and experimental procedure are given in Ref. 1.

Experimental Results

Ignition characteristics of representative composite propellants were investigated as a function of incident radiant energy level and pressure. The pressure effect on exposure or ignition time (τ_{ign}) can be depicted by plots of log τ_{ign} vs log P. The initial pressure is employed in all cases. A plot of τ_{ign} vs F on logarithmic coordinates was employed to represent the influence of radiant flux level on ignition time.

Figure 1 illustrates the pressure effect on ignition time for a PBAN propellant containing 84% ammonium perchlorate (AP), but no aluminum or carbon. Figure 2 depicts the flux dependence. Incident radiant flux levels and the upper bound of the go/no-go limit were plotted in all cases. No statistical techniques, such as that developed by Evans,[2] were applied.

Figure 3 illustrates the effect of the addition of aluminum and carbon on the exposure time of a PBAN propellant at an incident flux level of 58 cal/cm²-sec. Polymer weight percentage was maintained constant and the aluminum and carbon were added at the expense of ammonium perchlorate in this series of propellants. As is apparent, the ignition time decreases as the propellant is made more opaque, but the general shape of the τ_{ign} vs P plot is not altered by the addition of aluminum or carbon. The decrease in ignition time noted with the separate addition of aluminum and carbon is attributed to changes in the propellant surface optical absorption characteristics (i.e., propellant transparency is decreased). The increased opaqueness enhances absorption of the incident radiant energy at the propellant surface. The observed increase in ignition time for the propellant containing both aluminum and carbon in comparison to the propellant containing only carbon is attributed to increased propellant thermal conductance.

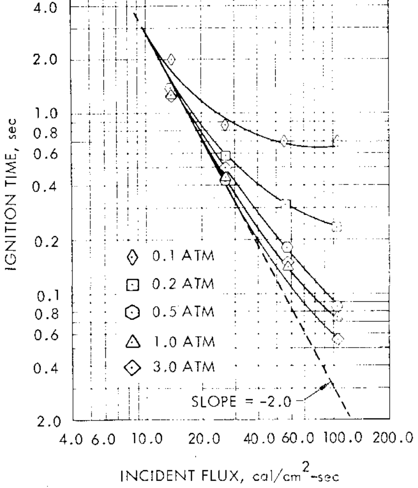

Fig. 2 Ignition time as a function of incident radiant flux—PBAN propellant.

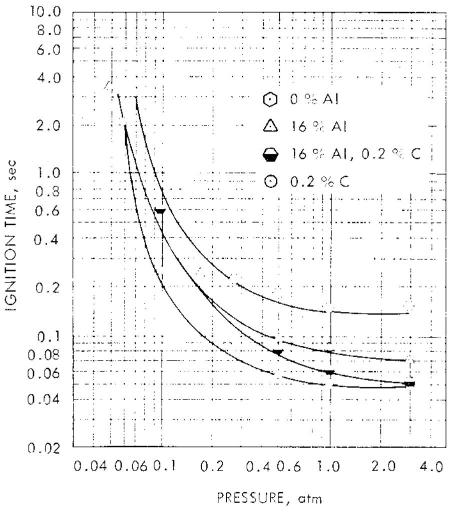

Fig. 3 **Effect of aluminum and carbon on ignition time of PBAN propellant (flux 58 cal/cm²-sec).**

Burning rate catalyst effects were investigated with the PBAN and PIB binders. This series of propellants contained 83.55% ammonium perchlorate (70/30 coarse:fine), 0.20% carbon, and 0.25% catalyst. Iron oxide, copper chromite and n-butylferrocene were used as catalysts. The addition of iron oxide had no effect on the ignition characteristics of the PIB propellant. With the PBAN binder, the catalysts tended to lower ignition time, as illustrated in Fig. 4.

A decrease in the oxidizer loading level from 84 to 75% resulted in an increase in ignition time and minimum initial pressure at which ignition can be achieved for a representative PBAN propellant. Figure 5 depicts the ignition data for these propellants which contained bimodal ammonium perchlorate (70/30 coarse:fine), 0.25% iron oxide, and 0.20% carbon.

Variation of ammonium perchlorate particle size from all fines (7 μ), to all coarse (190 μ), and to a 50-50 blend of 7-μ–190-μ resulted in no noticeable effect on ignition behavior in a CTPB binder system. This series of propellants contained 79.55% oxidizer, 0.20% carbon, and 0.25% iron oxide. Figure 6 summarizes the data for these propellants. Similar results were obtained with a series of uncatalyzed PBAN propellants.

The influence of an oxidizer coating on propellant ignitability was studied using the CTPB binder system and Kel-F as a coating agent. All propellants contained 78% AP (190 μ), 0.20% carbon, and 0.25% iron oxide. In one

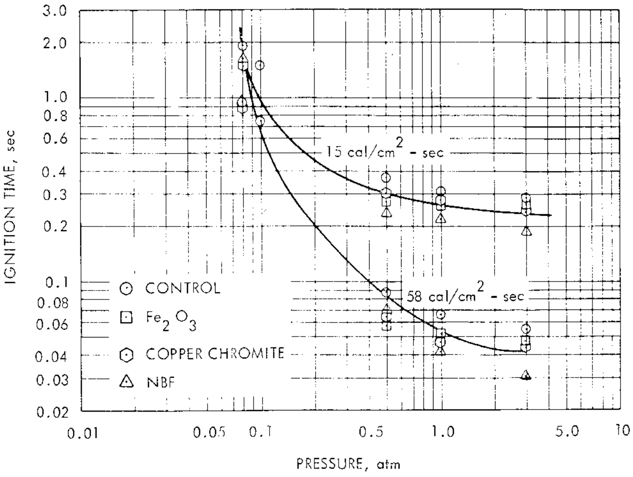

Fig. 4 **Effect of catalyst variation on ignition characteristics of PBAN propellant.**

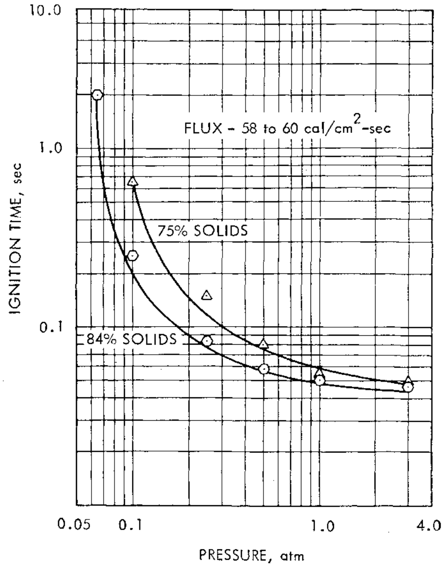

Fig. 5 Effect of solids loading on ignition time.

of the formulations, the oxidizer (AP) was coated with 1.5% Kel-F, while a second contained an equivalent amount of Kel-F added to the binder. A control propellant containing no fluorocarbon additive was also checked. As can be seen in Fig. 7 inclusion of Kel-F in the formulation results in an increase in the minimum initial pressure for successful ignition. However, the location of the Kel-F additive has no noticeable influence on the ignition characteristics.

Figure 8 depicts the effect of polymer variation on ignition time for an incident flux level of 58 cal/cm^2-sec. All propellants contained 83.5% AP (70:30 coarse-fine), 0.25% iron oxide, and 0.20% carbon. It is evident that the minimum initial pressure at which ignition can be achieved is markedly dependent upon the binder component.

The effect of oxidizer variation on propellant ignition was investigated using a series of perchlorate oxidizers. Figure 9 illustrates the effect of substituting potassium perchlorate (KP) for AP in a CTPB binder system. Both propellants contained 75% oxidizer (45 micron nominal particle size) and 0.2% carbon. The potassium perchlorate formulation exhibits longer ignition times and a higher minimum initial pressure for ignition.

Figure 10 compares the ignition times for hydroxylamine perchlorate (HAP) and hydrazine diperchlorate (HDP) propellants and an identical AP control formulation. The formulations containing the advanced oxidizers were easier to ignite at all pressure levels, and the HDP system exhibited an extremely low minimum initial pressure for ignition.

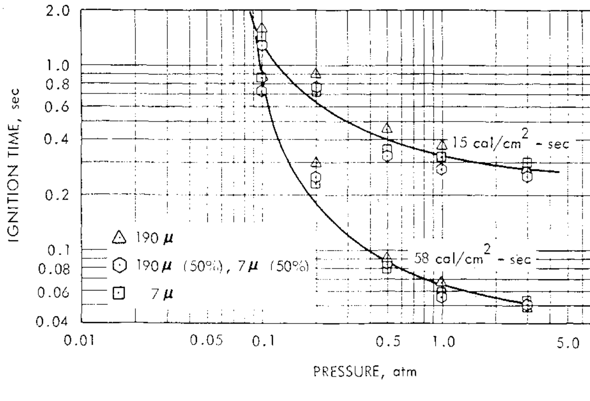

Fig. 6 Effect of oxidizer particle size on ignition characteristics of PBAN propellant.

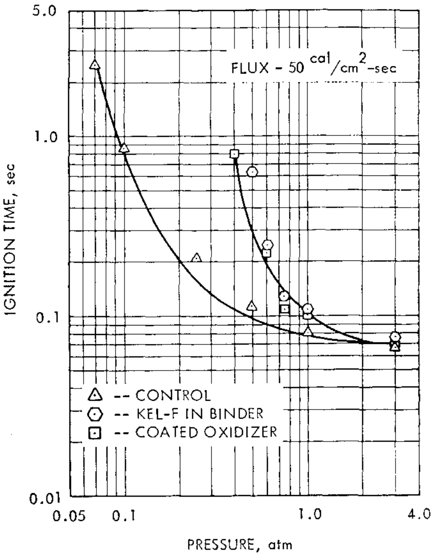

Fig. 7 Effect of oxidizer coating on ignition characteristics of CTPB propellant.

The influence of oxidizer particle size on ignition times of the HAP and HDP propellants was determined at an incident flux level of 50 cal/cm^2-sec. Figure 11 summarizes the data for the HAP system, and Fig. 12 illustrates the HDP data. No significant influence of particle size was noted in the HAP formulation. A modest reduction in ignition time with decreased particle size was noted with the HDP propellant. These propellants were handmixed, and the effect may be primarily the result of nonuniformity from batch to batch.

Photomicrographs of propellant surfaces exposed to radiant energy for a time just short of that required to cause ignition were used to supplement the ignition characterization data. A general feature of all the propellant surfaces was the appearance of polymer melting and flowing. An analysis of the surface structure of various propellants is given in Table 1.

Discussion

The objective of the experimental work reported in this paper was an attempt to distinguish the relative contributions of various chemical reaction mechanisms that may dominate the ignition process when radiant energy is used as the external energy source. Before discussing the experimental results

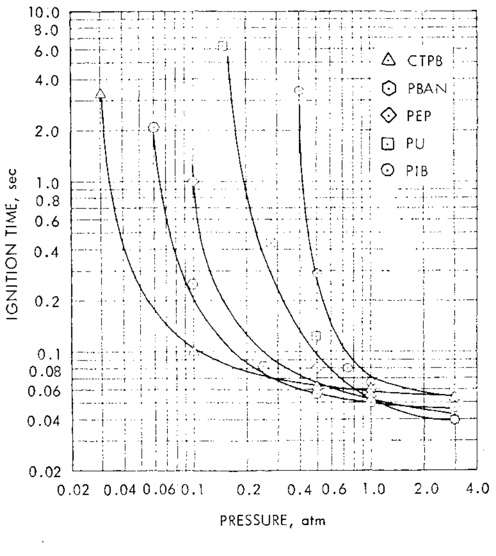

Fig. 8 Effect of polymer variation on ignition characteristics of AP-oxidized propellants (flux 58 cal/cm^2-sec).

Table 1 Surface structure of propellants exposed to radiant energy

Propellant	Flux level	Surface structure
Polyurethane-AP (84% AP, bimodal 0.25% Fe_2O_3)	30 cal/cm²-sec	Evidence of polymer melting and flowing. Large AP particles protrude from surface. Surface has a definite pitted appearance.
CTPB-AP (80% AP all coarse, 190μ)	25 cal/cm²-sec	Evidence of extensive polymer glazing and/or melting. Surface has a pebbled structure and some oxidizer particles are coated with a layer of glazed or molten polymer. AP particles protrude from surface.
CTPB-AP (80% AP all fines, 8μ)	50 cal/cm²-sec	Evidence of polymer melting and flowing. Surface has a fine grain structure.
PBAN-AP (84% AP, bimodal, 1% nBF)	50 cal/cm²-sec	Evidence of polymer melting. Very little coating of oxidizer by molten polymer. Large oxidizer particles protrude from surface.
PBAN-AP (84% AP, bimodal, 1% Fe_2O_3)	25 cal/cm²-sec	Evidence of polymer melting. Very little coating of oxidizer by molten polymer. Large oxidizer particles proturde from surface.
Polyurethane-AP (70% AP, 45μ, 0.25% Fe_2O_3)	50 cal/cm²-sec	Evidence of polymer melting and flowing. Surface has a fine pebbled structure.
Polyisobutylene-AP (84% AP, bimodal)	25 cal/cm²-sec	Evidence of polymer melting and limited flowing. Large oxidizer particles protrude from surface. Some particles covered with molten polymer.
Polyurethane-KP (70% KP, 45μ, 0.25% Fe_2O_3)	50 cal/cm²-sec	Evidence of polymer melting and flowing. Oxidizer also appears to have melted.

in detail, the major theoretical composite propellant ignition models will be briefly reviewed.

The first attempt at a general ignition model for solid systems was that of Hicks,[3] which led to a transient surface heating analysis with exothermic chemical heating in the solid with an exponential dependency of rate on temperature. Subsequent to the work of Hicks, other solid-phase models were proposed involving different assumptions regarding incident heating and the nature of the self-heating.[4,5] Baer and Ryan[4] have extended the calculations of Frazer and Hicks[6] by analyzing the effect of the activation energy of the propellant-heating reaction on the time to achieve ignition. Their calculations demonstrated that the slope on a plot of log $\tau^{1/2}$ versus log F is related to the activation energy by the expression

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

The studies of Hicks and Baer were based on a constant heat flux to the propellant surface. Price[7] considers the more important complex cases which have been analyzed, and the reader is referred to his work for the details. Ryan and Baer[4] and Wise and co-workers[8] have conducted experimental studies to define the nature of the condensed-phase reactions.

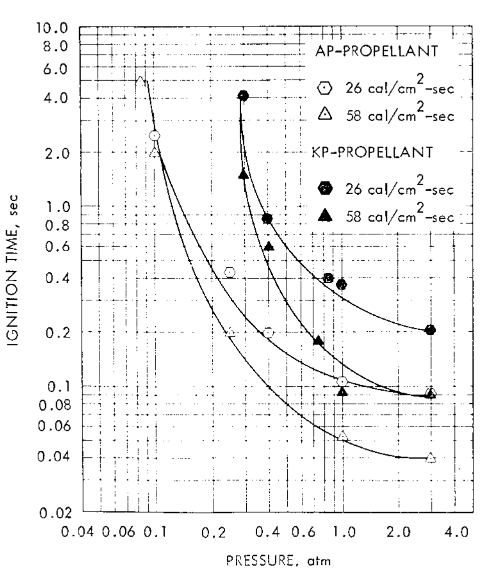

Fig. 9 Comparison of ignition characteristics of KP and AP propellants (CTPB binder).

The thermal-ignition theory correlates some observed ignition phenomena, but it possesses several deficiencies, the most serious being the lack of provision for the effect of external pressure on ignition time. These objections led investigators at Princeton University to postulate that the chemical reactions between propellant constituents which result in runaway heating conditions occur in the gas phase at some small but finite distance from the solid surface. A series of studies in the period from 1956 to the present[9,10] included development of a gas-phase model in which a hot oxidizing environmental gas and fuel vapors from the propellant mixed and reacted to provide a self-sustaining heat source. The analytical model represents the environmental oxidizer as diffusing toward the surface and the fuel as diffusing from the surface, with only secondary consideration given to the case where both vapors originate at the surface of the heterogeneous propellant. Hermance is currently working on an extension of the gas-phase model to include the latter possibility.[11]

A third concept of propellant ignition evolved from studies of hypergolic ignition by powerful oxidizing gases such as fluorine.[12] The hypergolic ignition theory consists of a one-dimensional model with diffusion of vapor-phase species and with heat conduction into the solid and gas from the reaction surface. In this model, the sole heat source is a

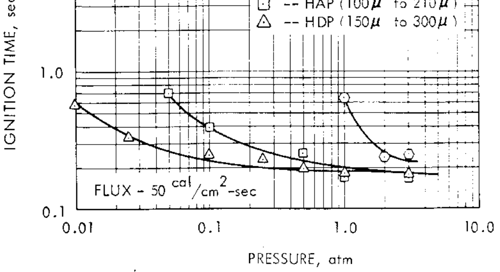

Fig. 10 Ignition characteristics of advanced oxidizer systems.

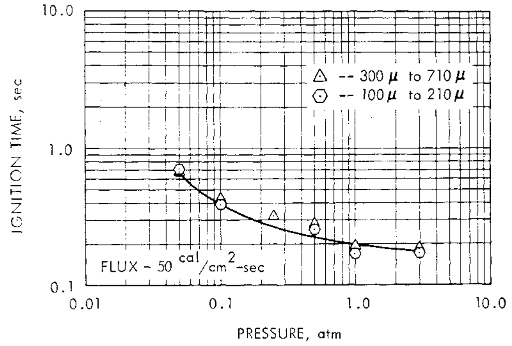

Fig. 11 Effect of particle size on ignition characteristics of HAP-oxidized propellant (flux 50 cal/cm²-sec).

heterogeneous surface reaction, which is assumed to obey an Arrhenius rate law.

The hypergolic model describes the behavior of externally applied oxidizing gases, but says nothing about what occurs within a composite propellant to achieve ignition in an inert environment. However, the fact that hypergolic reactions occur at temperatures below the characteristic propellant "ignition temperature," calculated from the thermal theory, does suggest that gas-solid reactions could contribute significant energy to the ignition process in neutral environments. To elucidate the possible role of gas-solid reactions in composite-propellant ignition, a qualitative ignition model has been proposed.[13] It is postulated that the primary preignition reactions occur at the propellant surface or in the subsurface layers, and that these reactions are generally between gaseous molecules, resulting from solid oxidizer decomposition, and the solid organic polymer matrix. For propellants with oxidizers that have high decomposition temperature or low thermal stability polymers, gas-liquid reactions may be important.

These models have all enjoyed some success in describing experimental propellant ignition data over limited parameter ranges. However, the clear-cut dominance or relative importance of any one chemical mechanism has not been established. The present program was conducted with the thought of obtaining a matrix of data relating propellant formulation variables and ignition characteristics, and using this data to assess the probable importance of various chemical mechanisms.

The over-all dependence of ignition time on pressure and incident flux level, as demonstrated in Figs. 1 and 2, is typical for all propellant formulations studied. The logarithmic plots of τ_{ign} vs P are curves bounded by an asymptote of infinite slope at the minimum initial pressure at which ignition can be achieved, and an asymptote of zero slope at sufficiently high pressure. The flux dependence plots indicate that the data are adequately described by a line of slope equal to -1.9 to -2.0 at flux levels below 20–25 cal/cm²-sec and pressures between 0.75 and 3.0 atm. This indicates that a constant surface temperature at ignition could be assumed in this flux-pressure range. Ignition temperatures calculated from the general heat conduction equation in the absence of chemical reaction are useful in estimating the general range of surface temperatures expected to prevail at ignition. Typical values at a low flux level are shown in Table 2. It should be pointed out that at the low flux levels, the ignition temperature of the propellants in Table 2 corresponds closely to that at which ammonium perchlorate begins rapid decomposition. This technique is of limited utility since ignition data are described by a line of -2 slope over only a limited pressure-flux range.

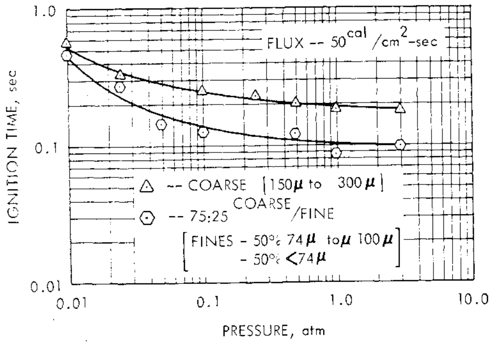

Fig. 12 Effect of particle size on ignition characteristics of HDP-oxidized propellant (flux 50 cal/cm²-sec).

Table 2 Surface temperature at ignition

Propellant	Flux, cal/cm²-sec	Pressure	Ts, °C
CTPB-AP	15	1 atm, N_2	395
PBAN-AP			342
PU-AP			330
PIB-AP			370

In this study the principal compositional variables found to have a significant effect on ignition characteristics were binder type, oxidizer type, and solids loading level. The unimportance of particle size suggests that gas-solid subsurface interfacial reactions are of minor importance. However, on theoretical grounds, Baer has pointed out that oxidizer particle size makes only a minor effect on the activation energy of the interface reaction and lack of a particle size effect does not necessarily rule out an interfacial reaction.[14] On the other hand, Bouck working on a two-dimensional model of propellant ignition, has found that inclusion of an interfacial reaction has only a minor effect on predicted ignition behavior.[15] The lack of an oxidizer particle size effect in the ammonium perchlorate oxidized propellants may be partly due to polymer melting.

A further indication of the apparent lack of importance of subsurface interfacial reactions is provided by the data obtained for coated ammonium perchlorate. As can be seen in Fig. 7, inclusion of Kel-F in the formulation results in a significant shift in the minimum initial pressure at which ignition can be achieved. However, the lack of any noticeable effect due to Kel-F placement suggests that the reactivity of the binder-oxidizer interface is of little importance at the flux levels studied. Fluorocarbons are well-known flame retardants for gaseous hydrocarbon flames, and the increase in the minimum ignition pressure is attributed to fluorocarbon quenching of gas-phase reactions.

The contribution of exothermic, particle size independent, condensed-phase reactions can not be readily assessed from the data obtained in this study. Investigations by Wise[8] and others indicate that exothermic homogeneous reactions in the solid (e.g., ammonium perchlorate decomposition) can contribute energy to the ignition process. The theoretical studies of Bouck indicate that the effect of an exothermic reaction at the surface of ammonium perchlorate can be quite pronounced.[15]

Burning rate catalyst effects on ignition were observed to be minimal. The catalysts tended to reduce the ignition time as illustrated in Fig. 4. The relative reduction of ignition time with catalyst variation follows their relative order of burning rate effectiveness; i.e., the more effective n-butyl ferrocene produces an easier-to-ignite propellant. The influence of catalyst addition can be attributed to their influence in accelerating AP decomposition or to their catalysis of gas-phase reactions. Rosser and co-workers and Inami and Wise have studied the possible role of copper chromite in AP propellant ignition and combustion in more detail.[16,17]

The nature of the polymer component was found to be the dominant formulation variable affecting ignition in the AP propellants. An examination of the data in Fig. 8 indicates that the influence of the fuel variation is related to the initial pressure. Two distinct regions of pressure-fuel interaction are discernible: A) Ignition times show a dependence on the nature of the fuel element at pressures below approximately 0.75 atm and the minimum initial pressure at which ignition can occur is dependent upon the fuel component. B) Ignition times exhibit little dependence on the nature of the fuel component at pressures above 0.75 atm.

The major differences between the propellants are the oxidative and thermal degradation properties of the binders. Although there is a real lack of quantitative data on polymer degradation under conditions of interest, available data indicate that the PU and PIB binders are less subject to exothermic (oxidative) degradation and more easily degraded by endothermic thermal decomposition. In contrast, the CTPB and PBAN polymers should show greater susceptibility to oxidative degradation and less to thermal degradation.[18–20] Howard[21] also found that over the temperature range of 350° to 475°C polyether-PU rubbers gasify more readily than PIB which, in turn, gasifies at a rate faster than polyester-PU rubbers.

Because of the difference in susceptibility to oxidative degradation of the fuel components, a more noticeable difference in ignition times in the 0.75 to 3 atm range might be expected if an interfacial heterogeneous reaction were a major energy source. However, perchloric acid (usually assumed to be the gaseous reactant in the heterogeneous reaction) is a very reactive oxidizer and may not show any selectivity among the polymers. The lack of an AP particle size effect and the negligible influence of oxidizer coatings in the CTPB and PBAN systems noted earlier indicate that a subsurface heterogeneous reaction is probably of minor importance in polybutadiene binder systems. A similar conclusion can be drawn for the PIB and PU binder systems because of their increased oxidative stability and lower thermal stability in comparison to polybutadienes.

In view of the apparent lack of importance of interfacial reactions under these conditions, variation of the minimum initial pressure for ignition with binder type is attributed to differences in their thermal decomposition characteristics. Qualitative correspondence between changes in minimum initial pressure at which ignition can be achieved and binder thermal stability is noted in the tested series of propellants.

The results of the investigation of oxidizer variation effects on ignitability show that for a propellant with a fixed fuel component, oxidizer decomposition controls ignition characteristics. Variation of the oxidizer type modifies surface temperatures, surface structure, the rate of gaseous oxidizer generation, and the nature of the gaseous species. This will result in longer or shorter ignition times depending upon individual oxidizer decomposition mechanisms and rates.

Viewed in total, the results of the present study indicate that the chemistry of propellant ignition in the pressure range below 3 atm and the 15 to 100 cal/cm²-sec flux range involves primarily a coupling between endothermic and exothermic homogeneous condensed-phase reactions and gas-phase reactions with a key step required to achieve ignition being the establishment of a critical gas-phase reaction rate threshold in the gaseous layer adjacent to the surface. The critical gas-phase reaction rate threshold

$$(R_{xn})_{\text{critical}} = (C_{ox}C_f)_{\text{critical}}\, Z \exp(-E/RT) \qquad (2)$$

is determined by the binder and oxidizer decomposition rates, the local gas temperature, and the local reactant concentrations. In an inert environment, both the oxidizer and binder must decompose at a rate sufficient to provide reactants in the necessary concentration to allow ignition to occur under the prevailing conditions of temperature and pressure. Because of the initial propellant heterogeneity, molecular mixing of fuel and oxidant is an important factor in the ignition process. The over-all consumption rate of fuel and oxidant is determined by the rate at which they can diffuse into a region where they form a combustible mixture. Also in the radiant ignition experiments, each initial reactant undergoes a temperature drop as it diffuses from the surface. Thus, ignition of the mixture will occur only if two conditions are simultaneously satisfied: 1) the composition of the mixture is within the limits of inflammability, and 2) the temperature of the mixture is above the ignition temperature.

If it is also assumed that for ignition of any type to occur and be sustained a critical volume of oxidizer-fuel must be heated to the ignition temperature of the mixture, the farther this critical volume is from the solid surface, the hotter the surface must become to cause ignition because of heat-transfer considerations. Because this critical volume will recede from the surface with decreasing pressure, ignition will become increasingly more difficult at low pressures. Coupling between the pressure dependence of the reaction rate, diffusion rate, propellant ingredient decomposition rates and the heat-transfer rate (both to and from the solid surface) results in a complex over-all pressure dependence of the ignition time. The interplay between these unit processes could easily result in the experimentally observed transition from the relatively pressure-insensitive region near 1 atm to the pressure-sensitive region, and finally, to a point of no ignition (i.e., minimum initial pressure for ignition).

Although the postulate that the key step in the ignition process is a gas-phase reaction can not be proved unequivocally, the recent work of Hightower[22] on the effect of environmental gases and pressure on the radiant energy ignition of AP propellants and individual propellant ingredients demonstrates the strong contribution of a gas-phase reaction. Ignition times of a PBAN-AP propellant in various inert atmospheres were found to increase with decreasing molecular weight of the environmental gas. Hightower also found that when air and oxygen were used as test gases, the dependence of the propellant ignition time on oxygen concentration was different if the concentration was varied by mole fraction or total pressure. Similar results were noted with a dummy propellant in which glass beads replaced the AP. Hightower's findings suggest a diffusion-limited reaction in which the binder is the first propellant constituent to begin a significant decomposition. These studies were conducted at pressures above 1 atm and at flux levels in the range 10 to 100 cal/cm²-sec. His results also indicate that for radiant ignition in inert atmospheres and this range of pressures and fluxes, the slow step is the decomposition of AP to supply oxidizing gases at a rate sufficient to permit ignition to occur. Sutton and Wellings[23] also noted a marked reduction in radiant energy ignition times when oxygen was used as an environmental gas. They attributed this result to a gas-phase reaction between vaporized fuel and gaseous oxygen in times short compared to times required for AP to decompose and provide a sufficient source of oxidizing gases.

To utilize the preceding ideas in analyzing the data on compositional variables and propellant ignitability obtained in this study, it is necessary to digress a moment to consider oxidizer decomposition rates, decomposition product distribution, and the nature of perchloric acid flames. Perchloric acid flames are important because it is assumed that $HClO_4$, or its decomposition products, are primary gaseous oxidizer species involved in the ignition process.

Ammonium perchlorate decomposition has been studied in considerable detail.[24,25] For the purposes of this discussion, AP will be considered to decompose at a temperature near 300°C and its product distribution is given by Eq. (3);

$$\begin{aligned}NH_4ClO_4 &\rightarrow 1.11\,H_2O + 0.45\,NH_3 + 0.33\,HCl + \\ &0.22\,N_2O + 0.11\,NO_2 + 0.11\,HClO_4 + 0.28\,Cl_2 + O_2 \qquad (3)\end{aligned}$$

HAP melts at 80°C, exhibits an endotherm at 167°C, and a major exotherm at 180°C. At temperatures above 190°

Table 3 Approximate upper flammability limits of $HClO_4$-hydrocarbon systems

Fuel	Mixture composition	Mixture ratio λ	Temperature, °K	Burning velocity, cm/sec
Methane	CH_4—84% $HClO_4$—4.2% H_2O—9.1% Ar—2.6%	20	1070	13
Ethane	C_2H_6—76% $HClO_4$—6.2% H_2O—13.5% Ar—4.5%	22	1050	10
Ethylene	C_2H_4—84.5% $HClO_4$—4.0% H_2O—8.7% Ar—2.9%	31	1050	10

$$\lambda = \frac{\text{ratio of fuel to oxidizer in mixture}}{\text{ratio of fuel to oxidizer in a stoichiometric mixture}}$$

to 200°C, there is detectable decomposition yielding a mixture of oxides of nitrogen and chlorine, water, and oxygen. The over-all decomposition can be represented as follows:

$$NH_3OHClO_4 \rightarrow 0.5\ N_2O + 0.143\ Cl_2 + 0.714\ HClO_4 + 1.64\ H_2O \quad (4)$$

Hydrazine is primarily a monoacid base and its diacid salts are rather weakly bound. When subjected to heat, they generally decompose to yield the monoacid salt[26]

$$N_2H_42HA_{(s)} \rightarrow N_2H_5{}^+A^-{}_{(s)} + HA_{(g)} \quad (5)$$

The mechanism of sublimation of the monosalt is analogous to that of the ammonium salts: $N_2H_5{}^+A^-{}_{(s)} \rightarrow N_2H_{4(g)} + HA_{(g)}$. Equation (6) gives the over-all product distribution for HDP[27];

$$N_2H_6(ClO_4)_2 \rightarrow 0.5\ NH_4ClO + 0.74\ N_2 + 0.2O_2 + 0.29\ HCl + 0.06\ N_2O + 1.2\ HClO_4 + 0.7\ H_2O + 0.55\ H_2 \quad (6)$$

In the case of transient processes such as ignition it might well be pertinent to consider using transient decomposition products rather than over-all product distributions. It was decided that such a discussion exceeded the scope of the paper and that the relative yield of $HClO_4$ could be used to characterize the degree of reactivity of the gaseous decomposition products. Normalizing $HClO_4$ yield to a unit weight of solid oxidizer decomposed, the following order is obtained:

$$AP/HAP/HDP = 1/5.8/6.6$$

The relative rates of decomposition of the oxidizer are also important. Existing data suggested the following order of thermal stability:

$$AP > HAP > HDP$$

These results indicate that at a constant temperature, more HDP would decompose than HAP. Thus, although the relative yield of $HClO_4$/unit mass is similar for these oxidizers, more $HClO_4$ would be liberated with the HDP oxidizer because of increased mass consumption.

Hydrocarbon-perchloric acid flames have very wide flammability limits. The upper limits have not been accurately determined. Table 3 summarizes the existing data for a limited number of $HClO_4$-fuel systems.[28] There is effectively no lower limit of perchloric acid-fuel flames because a decomposition flame of perchloric acid vapor can be stabilized for an initial temperature just above boiling point of the acid. However, because pure AP will not burn at atmospheric pressure, the $HClO_4$ flame alone is not sufficiently exothermic to sustain propellant ignition.

The preceding brief discussion of perchloric acid flames and perchlorate oxidizer decomposition has direct application to the analysis of the ignition data. Consider first the case of AP oxidized propellants. In practical cases, where high heat fluxes are involved, it is likely that fuel pyrolysis and vaporization occur before there is appreciable decomposition of AP. It also seems reasonable to assume that the initial binder decomposition products contain considerable light hydrocarbon fractions. The fact that such a fuel-rich mixture, as shown in Table 3, is flammable is in accord with the practical situation and consistent with experimental ignition data.

At pressures on the order of 1 atm, the propellant heatup time dominates the ignition process. In this pressure range and with relatively volatile fuels, the chemical lag time is primarily controlled by the exothermic condensed phase thermal decomposition of AP. Because sufficient fuel decomposition products are assumed to be present, the binder will exhibit only a secondary influence.

As the pressure is decreased, the degree of surface endothermicity, the rate of decomposition of the fuel component, and the heat of combustion of the polymer will begin to exert a more pronounced effect. Reed[29] has noted that the heat of combustion of polybutadiene polymer is greater than that of PU-polyether. The degree of endothermicity of the binder and its decomposition rate will influence the average surface temperature; a more endothermic binder will produce a lower surface temperature at a given time. A lower surface temperature will be reflected in a lower gas temperature and a longer time to establish a gas-phase reaction. In addition, as the pressure is decreased less energy will be transferred from the gas-phase reactions back to the surface (because of increased heat-transfer distance) to sustain oxidizer and fuel decomposition. As a result, ignition time will increase. Furthermore AP decomposition apparently becomes endothermic below approximately 300 mm Hg.[30] Below this pressure, if the energy supplied by gas-phase chemical reactions does not exceed the surface endotherms, ignition will not be achieved because the surface temperature will not attain a sufficiently high level to sustain reaction following termination of the external energy source.

For a propellant with a fixed fuel component, differences in ignitability characteristics are determined by the decomposition characteristics of the oxidizer. Variation of the oxidizer modifies the degree and energetics of condensed-phase reactions, the rate of gaseous oxidizer generation, and the nature of the gaseous species. Replacing AP with KP which has a decomposition temperature exceeding 400°C and generates less active gas species than AP, will produce a propellant that is harder to ignite at atmospheric pressure levels. HAP and HDP have relatively low decomposition temperatures in comparison with AP. With HAP and HDP systems, it is likely that oxidizer decomposition or vaporization will occur before or at approximately the same time as appreciable fuel pyrolysis. This, in turn, means that a combustible mixture can be established at a lower surface temperature and at a distance closer to the surface. For these oxidizer systems, a lean mixture may exist at the point of ignition. The lack of a lower flammability limit for $HClO_4$ flames is very pertinent in this case. In addition, because of the relatively low decomposition temperature of these oxidizers, interfacial reactions and exothermic oxidizer decomposition reactions may contribute more energy at all pressure levels than in similar AP propellants. Therefore, less energy may need to be supplied from the gas-phase reactions to support material generation. Propellants containing these oxidizers would be expected to be easier to ignite than AP propellants, and they should exhibit lower minimum initial pressure for ignition.

The qualitative model discussed in the preceding paragraphs presents a general picture of the over-all aspects of the radiant ignition process in the pressure range below 3 atm and the 15 to 100 cal/cm^2-sec flux range. Admittedly it is quite speculative, but it seems to be consistent with existing information. The proposed model is based quite strongly on the interaction of kinetic, heat, and mass transfer processes, for which very little reliable data are available under the conditions of interest. It does point out the need for more detailed knowledge of propellant ingredient decomposition mechanisms.

Objectively, it must be considered that no single controlling chemical mechanism can be proposed. It is likely that condensed-phase, catalytic, and gas-phase reactions each contribute energy to the ignition process. For a specific case, the relative importance of any single reaction process will depend upon interrelated factors such as local concentrations, local temperature, interface chemical and physical structures, external heating rate, and external pressure. A reasonable comprehensive analytical model must be used in conjunction with experimental ignition and kinetic data to establish the roles of various unit processes over the complete spectrum of pressure and heat flux. Efforts along these lines have been initiated[31,32,11] and more definitive conclusions may be forthcoming.

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