STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

October 12, 1965

Quarterly Report No. 1 | *July 1 - September 30, 1965*

PROPELLANT COMBUSTION PHENOMENON DURING RAPID DEPRESSURIZATION

Prepared for:

CHIEF, SOLID PROPULSION TECHNOLOGY
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

ATTN: CODE RPS

CONTRACT NAS7-389

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SRI Project FRU-5577

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FOREWORD

The experimental and theoretical studies described in this report are respectively the responsibilities of E. L. Capener and G. A. Marxman. The over-all program is under the direction of L. A. Dickinson.

The program is under the over-all management of the Chief, Solid Propulsion Technology, Code RPS, OART, NASA, Washington, D. C. (R. W. Ziem), with technical management by High Temperature Materials Branch, Langley Research Center (A. R. Saunders). Administration of the project is under the direction of NASA-Western Operations Office (E. F. Wyszpolski).

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INTRODUCTION AND SUMMARY

This first quarterly report under Contract NAS7-389 describes the progress made in developing an understanding of the processes, occurring during rapid depressurization of burning solid propellants, that can result in an extinguishment of combustion.

In brief, one phase of the initial approach being followed is development of a theoretical model that can accommodate the physical and chemical processes that occur in the combustion wave; the model is being made compatible with known experimental facts. The second, and parallel, experimental phase covers the influence of propellant formulation characteristics on extinction and other related transient phenomena such as ignition.

The model proposed for describing the response of a burning solid propellant to pressure transients already appears capable of explaining a large volume of combustion instability data obtained at the Institute in another program.[1] (Aspects of these data contributed to the concepts utilized in forming the model; analysis of the model accurately predicted the trend of the stability bound vs pressure for AP-based propellants.)

The experimental studies sought to investigate the limits of stable combustion as pressure is reduced. A profound influence of oxidizer and binder characteristics was observed, which appears readily explained by our theoretical model. An additional observation was that, without exception, a simple burning rate law does not appear justified in the quasi steady state analyses of the extinction process developed elsewhere.[2,3] A more significant problem appears to reside in the fact that the relaxation times for combustion processes at, or close to, the solid surface are commensurate with the extinction time; hence, a simple linear or exponential pressure-dependent type of burning law cannot adequately explain non-steady state phenomena.

EXPERIMENTAL STUDIES

General

In support of this research program, a variety of experimental techniques were selected for studying the relevant combustion phenomena. These include a strand burner for lower extinction limit determination, and a variable area plug nozzle motor in association with a vacuum chamber; an arc image furnace is used for associated ignition studies.

Recognizing the importance of propellant composition in combustion phenomena, it was decided that a wide range of composite and double base formulations would be studied. In addition, the influence of unconventional propellant modifications such as specially coated oxidizers can be examined, since a fluidized bed coater is available.

Burning Rate Studies

The initial studies on burning rate were made with a modified Crawford strand burner. While the burning rate was determined by conventional techniques, the lower limit for combustion was monitored, using a photocell to detect burning as the pressure was slowly lowered.

The initial investigations were concerned with composite propellants based on two different binders, PBAN and PU, and two different oxidizers, AP and KP (the influence of a catalyst, Fe_2O_3 and aluminum was also studied).

A Nitrasol propellant was examined; this was a composite modified propellant. The propellant formulations studiedare detailed in Table I.

Burning rate plots for PBAN propellants with variable oxidizer loading, aluminum contents, and iron oxide catalyst levels are given in Figs. 1, 2, and 3. Figure 4 is the plot for propellants containing $KClO_4$ and Nitrasol. It is readily apparent that the classical equation $r = ap^n$ is unsatisfactory to represent the burning rate much below 60 psia.

Table I

PROPELLANT FORMULATIONS

Formulation	Weight Percentages			
	Oxidizer	Al	Binder	Ballistic Modifier
PBAN 103	80 NH_4ClO_4		20	
PBAN 285	80 NH_4ClO_4		19.5	0.5 Fe_2O_3
PBAN 286	80 NH_4ClO_4		19.0	1.0 Fe_2O_3
PBAN 287	80 NH_4ClO_4		18.5	1.5 Fe_2O_3
PBAN 288	80 NH_4ClO_4		18.0	2.0 Fe_2O_3
PBAN 289	72.5 NH_4ClO_4	7.5	20.0	
PBAN 290	70.0 NH_4ClO_4	10.0	20.0	
PBAN 291	67.5 NH_4ClO_4	12.5	20.0	
PBAN 292	65.0 NH_4ClO_4	15.0	20.0	
PBAN 293	84 NH_4ClO_4		16.0	
PBAN 294	86 NH_4ClO_4		14.0	
PBAN 295	88 NH_4ClO_4		12.0	
PBAN 109	80 $KClO_4$		20	
PU 144	80 $KClO_4$		20	
NIT 101	35 NH_4ClO_4	15.0	50	
PBAN 244	79 NH_4ClO_4		20	1 LiF
PBAN 284	79.5 NH_4ClO_4		20	0.5 $SrCO_3$

PBAN = Polybutadiene/acrylic acid/acrylonitrile binder

PU = Polyurethane binder

NIT = Nitrasol double base binder

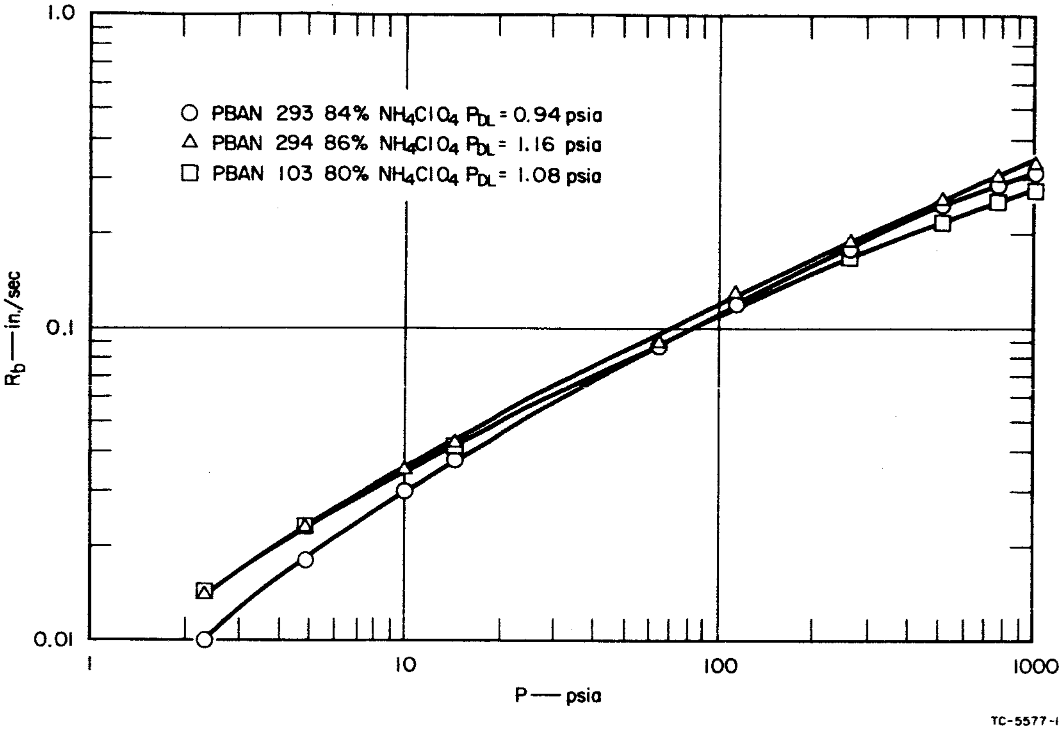

FIG. 1 BURNING RATES FOR OXIDIZER VARIATIONS

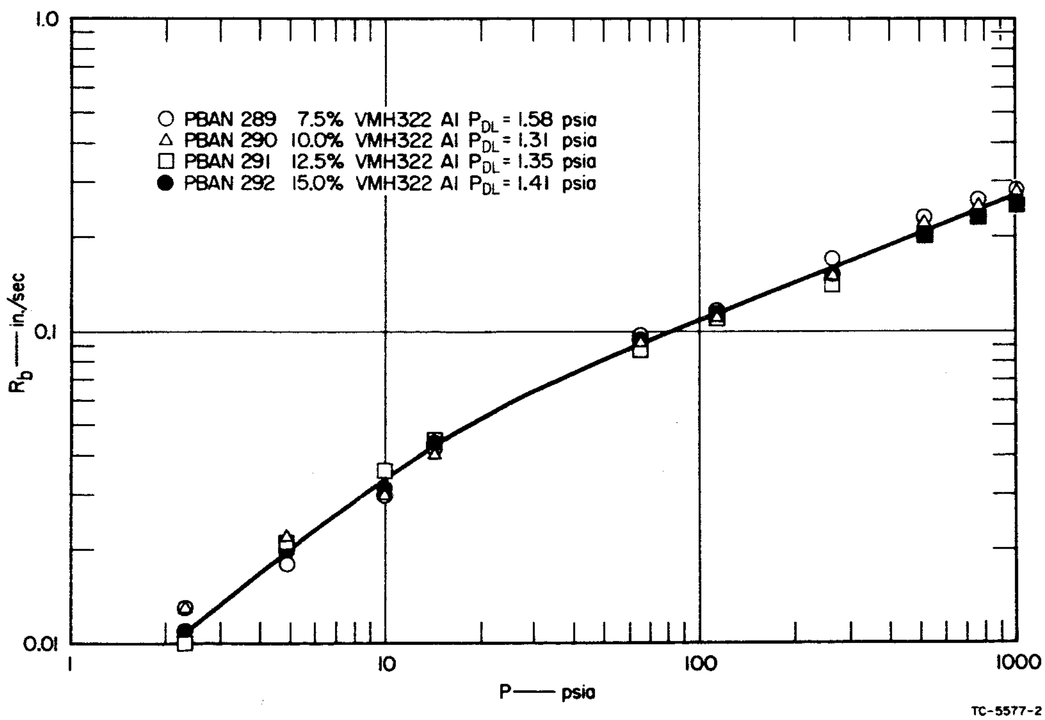

FIG. 2 BURNING RATES FOR ALUMINUM VARIATIONS

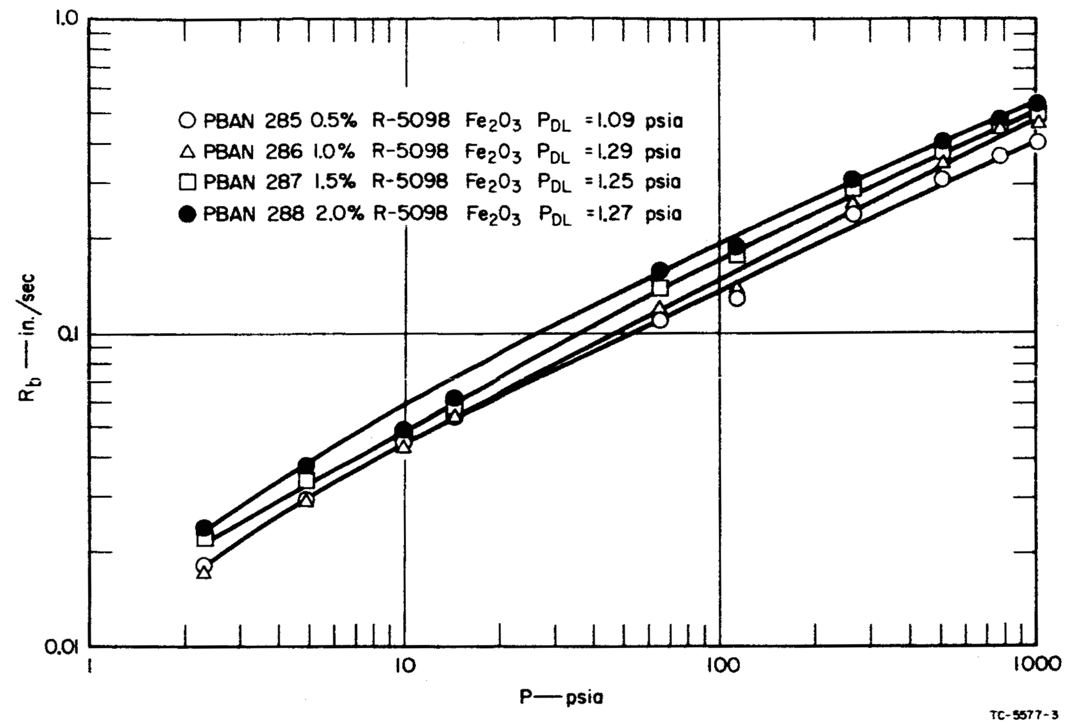

FIG. 3 BURNING RATES FOR IRON OXIDE VARIATIONS

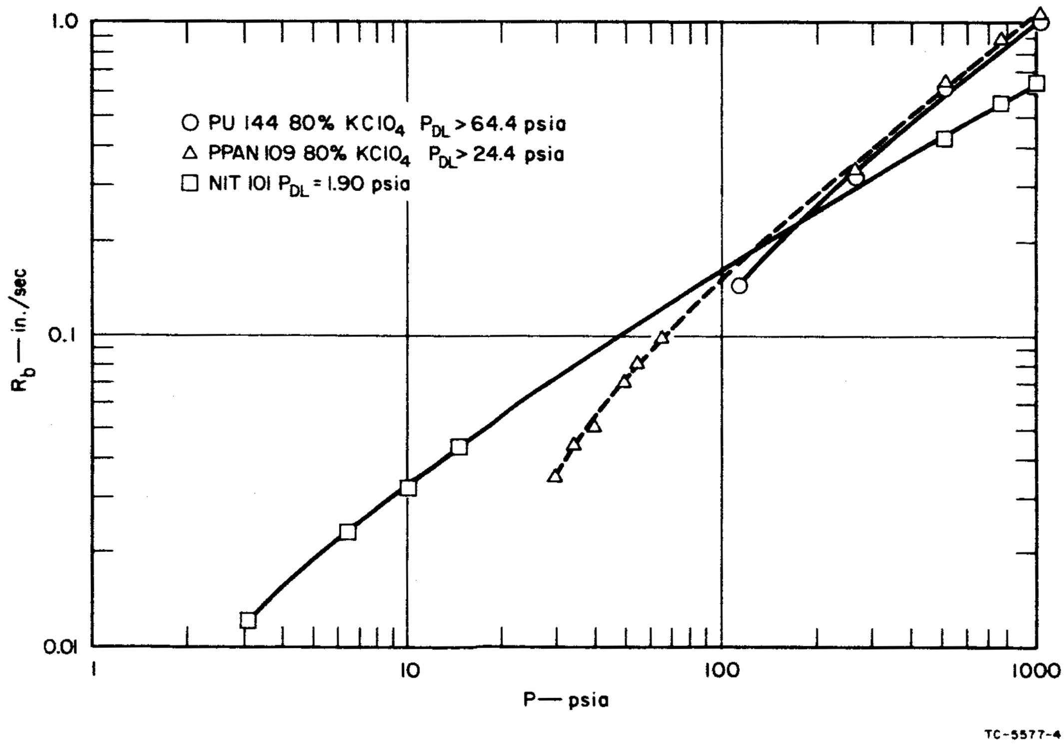

FIG. 4 BURNING RATES FOR POTASSIUM PERCHLORATE PROPELLANTS AND NITRASOL

The deviations appear to be greater with aluminized propellants. Summerfield[4] has proposed that the equation,

$$\frac{1}{r} = \frac{a}{P} + \frac{b}{P^{1/3}}$$

is more applicable from theoretical considerations. The pressure range considered was 1 to 140 kg/cm^2; whereas the present study extends to 0.08 kg/cm^2. The Summerfield equation can be expressed as:

$$\frac{P}{r} = a + bP^{2/3}$$

and a plot of Log P/r versus Log P should give a straight line. In Fig. 5 the burning rate data for one propellant from each variation study are plotted. The deviations at lower pressures for the aluminum and NH_4ClO_4 variants appear to be about the same as with $r = aP^n$. The catalyzed propellants appear to be correlated better at all pressures by the Summerfield criterion.

Lower deflagration pressures were measured in the strand bomb, using a photocell to detect extinction. The output voltages of the photocell and a pressure transducer were recorded on an oscillograph. The lower deflagration pressure (P_{DL}) was taken as the pressure at which the photocell output became zero during a steady pressure decrease. About 20 seconds were required for the pressure to drop from 14.4 psia to 0.3 psia. Duplicate runs were made with each propellant. The data are listed in Table II. One of the striking features of these data is the remarkable consistency of the lower deflagration pressure for PBAN propellants containing ammonium perchlorate. Variation of AP from 80 to 86%, aluminum from 0 to 15%, and iron oxide from 0 to 2% did not change the lower deflagration pressure in the range from 0.94 to 1.58 psia.

In view of the invariance of NH_4ClO_4 propellants with regard to P_{DL}, other oxidizers and binders were investigated. The use of $KClO_4$ raises P_{DL} to about 24 psia. Surprisingly, a change from PBAN to PU binder with $KClO_4$ oxidizer resulted in a propellant that did not burn below 64 psia; a change to Nitrasol propellant containing both aluminum and AP gave a

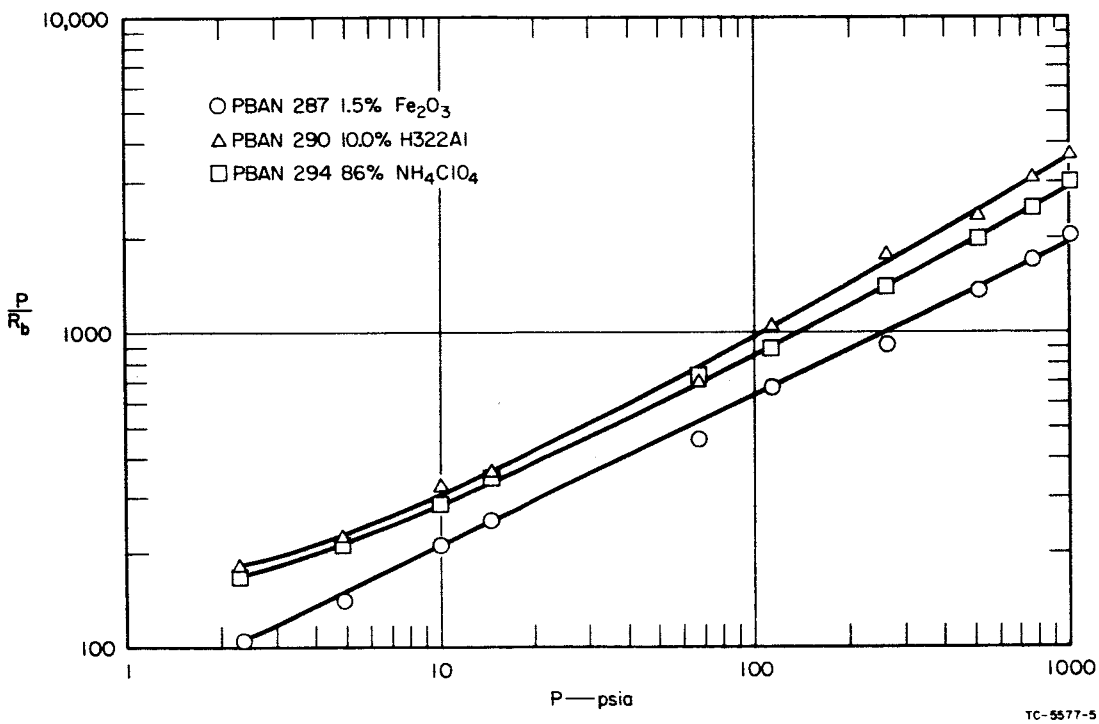

FIG. 5 SUMMERFIELD BURNING RATE

Table II

LOWER DEFLAGRATION PRESSURES

Formulation[1]	Variable	Pressure Psia
PBAN 103	80% NH_4ClO_4	1.08
PBAN 293	84% NH_4ClO_4	0.94
PBAN 294	86% NH_4ClO_4	1.16
PBAN 295	88% NH_4ClO_4	1.36
PBAN 289	7.5% V.M. H-322 Al	1.58
PBAN 290	10.0% V.M. H-322 Al	1.39
PBAN 291	12.5% V.M. H-322 Al	1.35
PBAN 292	15.0% V.M. H-322 Al	1.41
PBAN 285	0.5% R-5098 Fe_2O_3	1.09
PBAN 286	1.0% R-5098 Fe_2O_3	1.29
PBAN 287	1.5% R-5098 Fe_2O_3	1.25
PBAN 288	2.0% R-5098 Fe_2O_3	1.27
PBAN 109	80% $KClO_4$/PBAN Binder	>24.4
PU 144	80% $KClO_4$/PU Binder	>64.4
NIT 101	15% Al/Nitrasol Binder	1.90
PBAN 244	1% LiF	2.10
PBAN 284	0.5% $SrCO_3$	1.40

[1]Formulation Ingredients are in Table I

P_{DL} in the same range as that found for other AP-containing propellants. Another possible method of changing P_{DL} is by catalysis. Numerous investigators have reported on the effects of such rate depressants as lithium fluoride and potassium fluoride. Ciepluch[5] reported that potassium fluoride made extinction easier, whereas a binder change from PBAA to PU did not influence extinction under his experimental conditions. In lithium-fluoride- and strontium-carbonate-catalyzed propellants, we find little change in P_{DL} from propellants not containing these ingredients.

The investigation of threshold limits for ignition has revealed also that for propellants containing the same oxidizer, NH_4ClO_4, the threshold ignition pressure ranges only from 1.8 to 3.2 psia. Tests were made in the arc image furnace with an incident flux of 65-70 cal/cm^2 per second. The data are in Table III. As with P_{DL} the only significant change in threshold limit is given by changing the oxidizer to $KClO_4$. A significant change also occurred when polyurethane binder was used with $KClO_4$ instead of PBAN binder.

Interpretation of Experimental Results

The consistency of lower deflagration pressures and ignition threshold pressures for propellants of the same general composition implies that the fundamental measurement in each case relates in some way to heat transfer. As the pressure above burning propellant is reduced, the expanded flame front reduces the heat flux flowing back to the propellant surface until the flux can no longer maintain the required surface temperature, T_s, to sustain combustion. It may be argued that T_s is therefore the same for all of the variations tested, since P_{DL} varies little. A change in either oxidizer or binder is required to change P_{DL} significantly.

In measuring threshold pressures for ignition, a similar argument may be advanced. Part of the measured time to ignition is taken up in bringing the propellant surface to temperature T_s. However, if the flux feedback from the expanded flame front (being pressure dependent) is not enough to maintain the surface temperature T_s, then the propellant does not continue burning when the incident heat flux is turned off.

Table III

IGNITION THRESHOLD PRESSURES FOR INCIDENT FLUX OF 70 cal/cm^2 PER SECOND

Formulation	Variable	Threshold Limit, psia
PBAN 103	80% NH_4ClO_4	2.5
PBAN 293	84% NH_4ClO_4	1.8
PBAN 294	86% NH_4ClO_4	2.2
PBAN 295	88% NH_4ClO_4	3.2
PBAN 289	7.5% V.M. H-322 Al	2.0
PBAN 290	10.0% V.M. H-322 Al	2.7
PBAN 291	12.5% V.M. H-322 Al	2.6
PBAN 292	15.0% V.M. H-322 Al	3.2
PBAN 285	0.5% R-5098 Fe_2O_3	2.3
PBAN 287	1.5% R-5098 Fe_2O_3	2.5
PBAN 288	2.0% R-5098 Fe_2O_3	2.3
NIT 101	15% Al/Nitrasol Binder	3.8
NIT	Nitrasol (no AP)	100.0
PBAN 109	80% $KClO_4$/PBAN Binder	34
PU 144	80% $KClO_4$/PU Binder	80

THEORETICAL STUDIES

General

G. von Elbe[2] and investigators at Aerojet-General Corporation[3] have independently developed essentially identical analyses of the response of a burning solid propellant to a pressure transient. These analyses incorporate the following assumptions.

1. The rate-of-change of heat flux (or pressure) is considered to be sufficiently low that there is no appreciable lag in the relaxation of the temperature profile in the grain. Thus there is always a steady-state profile corresponding to the instantaneous heat flux.
2. The steady-state burning rate of the propellant is assumed to be described by the empirical expression $r = bP^n$. In addition, this expression is assumed to relate the instantaneous burning rate and pressure during transients.
3. The surface temperature is assumed constant.

These assumptions permit a quasi-steady treatment of the response of the propellant to pressure transients. In this approach the empirical steady state burning-rate law is combined with an energy balance at the gas-solid interface, and the resulting equation is differentiated with time to relate instantaneous burning rate to pressure-decay rate.

The limitations of the quasi-steady approach may be deduced by examining the characteristic relaxation times associated with the gas-phase and solid-phase processes involved in the combustion mechanism. Orders of magnitude of these relaxation times are[6]

$$\tau r_{solid} \sim \frac{K_s}{r^2}$$

$$\tau r_{gas} \sim \frac{K_g}{r^2}$$

where K_s and K_g are the thermal diffusivities of the solid and gas phases, respectively. A typical value for K_s is 2.5×10^{-4} in.^{2}/sec, so for a burning rate of 0.1 in./sec the thermal relaxation time in the solid is on the order of 0.025 sec; for a burning rate of 0.5 in./sec it is about 0.001 sec. The gas-phase thermal diffusivity K_g is about an order of magnitude smaller than K_s, with a corresponding reduction in gas-phase relaxation times. Consequently, the solid-phase thermal lag should be the rate-limiting mechanism in extinguishment of burning solid propellants, as assumed by the analyses mentioned above, if unanticipated slower mechanisms do not appear during the transient period. However, this conclusion also implies that characteristic times for extinguishment will be comparable to the solid-phase relaxation time, and, indeed, the extinguishment times observed by Aerojet investigators[3] are in the range 0.005-0.040 sec, or about the same as the relaxation times quoted above. Under these circumstances the quasi-steady analytical approach to the problem is somewhat questionable; such an approach is truly valid only when all relaxation times are negligibly small relative to the characteristic time of the process under consideration.

The empirical steady-state burning rate law $r = bP^n$ describes a behavior that results from an enormously complex interaction of gas-phase and solid-phase processes. For example, the over-all pressure sensitivity, represented by the exponent n, encompasses the individual pressure sensitivities of many reactions, both in the gas phase and at the interface, and is determined by the order of these reactions and other factors. Inasmuch as the relaxation times of gas-phase and solid-phase processes differ by an order of magnitude, it is likely that the relative contributions of these portions of the burning mechanism to the over-all pressure sensitivity are substantially altered during transient operation. This means that the pressure exponent n may itself be a function of dP/dt, in which case a representation of the burning rate during transient periods by the steady-state expression $r = bP^n$ would be misleading.

It is undoubtedly true that the surface temperature of a burning solid propellant is nearly constant, even with wide excursions in the burning rate. This observation merely reflects the fact that the effective activation energy E for the surface volatization process is generally quite large, so that $E/RT_w \sim 10$ or greater. Therefore, purely from the standpoint of determining a temperature profile, the surface temperature may be considered constant. On the other hand, to be self-consistent an analysis to determine the transient behavior of the burning rate may be required to account for changes in the surface temperature, because large changes in the burning rate actually are inseparably coupled through the burning mechanism to small, but finite, surface temperature variations.

Because all relaxation times are neglected in the quasi-steady analyses of propellant extinguishment, these theories predict an instantaneous response of the burning rate to an imposed pressure gradient. This implies that at the very instant a sufficient pressure gradient has been introduced, before the pressure itself has responded, burning will cease. In practice, of course, a finite decay rate (with a time constant on the order of 5-40 milliseconds, as noted above) is observed. To account for this lag, the Aerojet workers have introduced an arbitrary, empirical lag factor in their quasi-steady analysis.[3] This device allows a reasonable correlation of data, but is of somewhat limited value, in that the empirical constants in the lag factor vary with experimental conditions; i.e., the lag factor is not universally applicable.

In summarizing the foregoing remarks, one may conclude that presently available theories based on a quasi-steady approach will offer at least qualitative insight into the requirements for extinction of solid propellant burning. Moreover, they should provide an approximate basis for correlation of experimental data, and, in fact, this capability has already been partially demonstrated.[3] However, the quasi-steady assumption is difficult to justify relative to the extinction times of greatest practical interest, and the necessity of introducing empirical lag factors, for example, illustrates the inherent limitations of this approach. Although current theories delineate certain aspects of the mechanism, they clearly neglect others that may be of equal significance.

An endeavor to overcome this difficulty, within the practical bounds imposed by inadequately understood combustion kinetics and by mathematical considerations, has been initiated as a part of the present program. We are undertaking development of a more comprehensive and fundamental model of solid propellant combustion under transient conditions, which is intended as an aid in clarifying and relating the mechanisms of combustion instability, propellant-flame extinction, and other transient phenomena. The philosophy underlying this analysis will be that the mathematical complexity should be consistent with the available pertinent information, such as data describing the kinetics of the reactions. Therefore, rather than performing an exhaustive analysis of a model that is highly restricted in deference to insurmountable mathematical complexities, we shall seek a more neutral balance between a realistic model and mathematical tractability. Specifically, the model should encompass in a fundamental way, rather than through purely empirical relationships, the recognized basic features of the combustion mechanism, with modifications or improvements dictated by experiments. At the same time, it is consistent with current quantitative knowledge of the combustion kinetics, and with the desirability of minimizing mathematical problems, to describe the reaction steps in highly simplified terms, e.g., by elementary Arrhenius kinetics. A preliminary treatment of this type, outlined below, suggests that such an approach may prove to be quite illuminating.

Simplified Model of Unsteady Combustion in Solid Propellants

Denison and Baum[7] have considered a simplified model of propellant combustion in which it was assumed (a) that gas-phase reactions may be represented in terms of a single reaction of arbitrary order that obeys Arrhenius kinetics and responds with negligible time lag to pressure disturbances; (b) that there is no erosive burning; (c) that the Lewis number is unity in the gas phase; (d) that surface vaporization follows an Arrhenius law; and (e) that there are no solid-phase reactions. Their perturbation analysis determined the response of this model combustion process, initially burning in steady state, to a sudden oscillation or step-change in pressure, and derived stability criteria in terms of thermochemical parameters of the propellant. Recently this analysis was extended by Imber,[8] using the same combustion model, to include the possibility of a time-varying temperature profile in the grain prior to the pressure perturbation, as during ignition; corresponding modifications in the stability criteria were derived. The basic approach taken in these analyses is commendable, but the results probably are of limited value owing to the rather unrealistic combustion model, which omits what may be key steps in the combustion mechanism.

To develop an improved theory of unsteady combustion, it seems desirable to retain the general approach of the perturbation analyses, while employing a less restrictive combustion model.

As a first step in this procedure we shall consider the combustion model of Fig. 6, in which exothermic (or endothermic) reactions are permitted within the solid phase, at or very near the interface. In this idealized model these solid-phase reactions will be assumed to occur in a surface layer of negligible thickness relative to the penetration depth of the temperature profile. This assumption greatly simplifies the mathematical analysis and is entirely consistent with the simple Arrhenius kinetics employed to describe the reaction processes.

The equation governing heat conduction in the solid phase beyond the surface reaction zone is:

$$\frac{\partial T}{\partial t} = r(t)\,\frac{\partial T}{\partial x} + K\,\frac{\partial^2 T}{\partial x^2}\,. \qquad (1)$$

The vaporization process at the wall is assumed to follow an Arrhenius

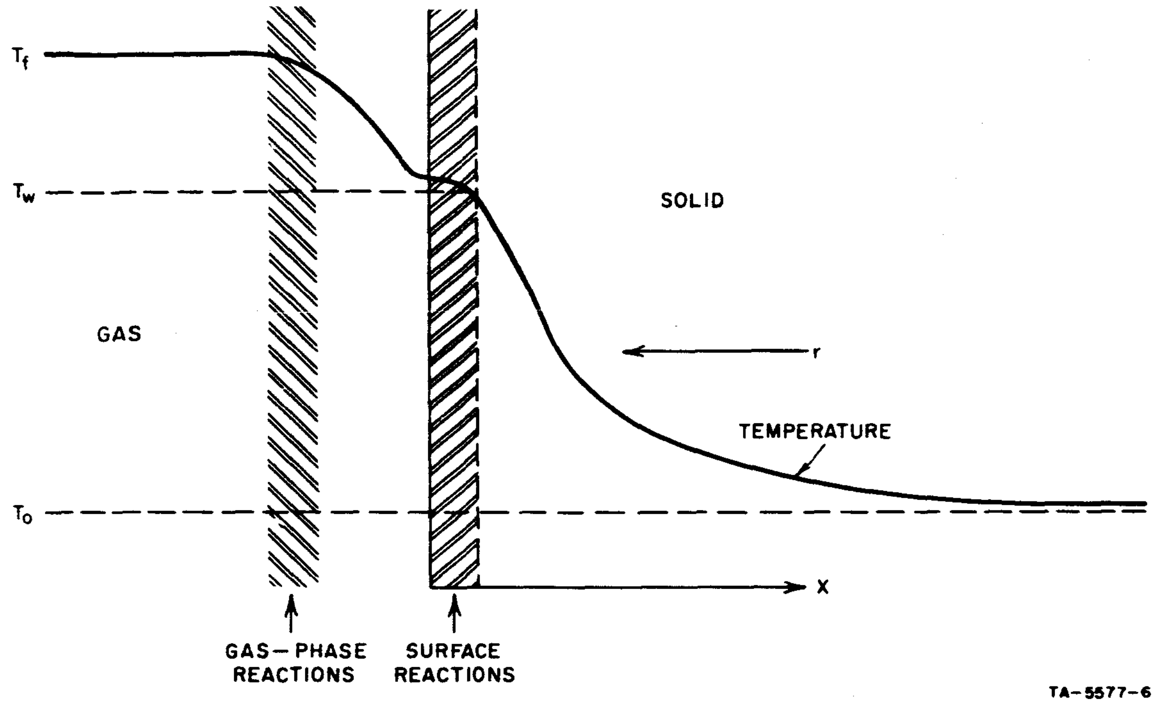

FIG. 6 COMBUSTION MODEL WITH GAS-PHASE AND SOLID-PHASE REACTIONS

law so that the burning rate is related to wall temperature as follows:

$$r = ae^{-E/RT_w}. \tag{2}$$

The following boundary condition is imposed upon the temperature:

$$x \to \infty;\ T \to T_0. \tag{3}$$

The remaining boundary condition is obtained through an energy-flux balance at the solid-gas interface. The net heat conducted into the unreacted solid propellant from the interface at the plane x = 0 is:

$$-k\left(\frac{\partial T}{\partial x}\right)_w = -k\left(\frac{\partial T}{\partial x}\right)_{g_w} - \rho_s r h_{g_w} + \rho_s r h s_w + Q_H + Q_D. \tag{4}$$

The first term on the right-hand side of the equality sign represents the energy coming from the gas phase; the second, the energy carried into the gas with the vaporizing propellant; the third, the energy carried by convection from the unreacted solid phase into the interface; the fourth, the energy released (positive) in heterogeneous decomposition reactions at the surface whose reaction rates depend upon the local gas-phase density; and the last, the energy released in solid-phase surface reactions with rates that are independent of gas-phase conditions. It is convenient to rewrite this expression as follows:[3]

$$- k\left(\frac{\partial T}{\partial x}\right)_w = - k\left(\frac{\partial T}{\partial x}\right)_{g_w} + \rho_s r[(C_s - C_p)T_w - L] + Q_H + Q_D. \tag{5}$$

Denison and Baum[7] have obtained a solution to the gas-phase conservation equations by assuming that the complex gaseous reaction process may be represented by a single-step reaction of order n, where in some cases n may not be an integer. For now we shall retain their gas-phase solution, which yields the following expression for the heat flux from the gas-phase to the wall:

$$- k\left(\frac{\partial T}{\partial x}\right)_{g_w} = \rho_s r[\epsilon_{r_w} Q_r - C_p(T_f - T_w)]. \tag{6}$$

This solution also relates the instantaneous flow of reactant into the gaseous reaction zone, $\rho_s r$, to the instantaneous gas-phase reaction rate, so that:

$$r = CP^{\frac{n}{2}} T_f^{\frac{n}{2}+1} e^{-\frac{E_f}{2RT_f}}. \tag{7}$$

Heterogeneous decomposition reactions at the interface will proceed at a rate proportional to the total mass flux through the surface reaction zone, $\rho_s r$. The fraction of this material involved in the heterogeneous reaction depends upon the density of the gas-phase reactant and on the Arrhenius law of the reaction. Thus:

$$Q_H = \rho_s r H_H \left(\frac{P}{T_w}\right)^m e^{-E_H/RT_W}. \tag{8}$$

Except that they are independent of the gas-phase density at the surface, the other decomposition reactions (represented here as a single step reaction, consistent with the gas-phase treatment) follow a similar law:

$$Q_D = \rho_s r H_D e^{-E_D/RT_w}. \tag{9}$$

Equations (5), (6), (8), and (9) may be combined to obtain:

$$-k\left(\frac{\partial T}{\partial x}\right)_w = \rho_s r\left[\epsilon_{r_w} Q_r - L - C_p T_f + C_s T_w + H_H\left(\frac{P}{T_w}\right)^m e^{-E_H/RT_w} + H_D e^{-\frac{E_D}{RT_w}}\right]. \tag{10}$$

Equations (1), (2), and (7), with the boundary conditions of Eqs. (3) and (10), complete the mathematical representation of the combustion model in terms of the dependent variables T_f, T_w, and r. Owing to the nonlinear character of these equations, a closed-form solution cannot be obtained, in general. Consequently, we resort to a small-perturbation analysis, assuming that each dependent variable, as well as the pressure, is the sum of a steady and a perturbed component:

$$\begin{aligned} P &= \bar{P}(1 + \tilde{P}) \\ T_f &= \bar{T}_f(1 + \tilde{T}_f) \\ T_w &= \bar{T}_w(1 + \tilde{T}_w) \\ r &= \bar{r}(1 + \tilde{r}) \end{aligned} \tag{11}$$

where, for example, $\tilde{P}$ is the ratio $\frac{P(t) - \bar{P}}{\bar{P}} \ll 1$. By introducing these expressions into Eqs. (1), (2), (3), (7), and (10), and retaining only first-order terms in the perturbed quantities, one can obtain a set of linear equations. The solution to these equations gives the first-order response of the combustion mechanism to a perturbation in the chamber pressure.

Denison and Baum[7] and Imber[8] have carried out such a solution for their simple combustion model, in which solid-phase exothermic or endothermic reactions are not permitted. In a later quarterly report it will be shown that the present problem, in which such reactions are allowed, can be made <u>mathematically</u> identical to that of the simpler model by redefining certain parameters in a suitable manner. This permits the use of earlier results, obtained from a rather complicated analysis, to determine the response of the present combustion model to pressure perturbations.

An Approximate Solution

Preliminary to the development of a precise solution, it may be instructive to obtain an approximate solution corresponding to the present combustion model. In so doing, the mathematical complexity of the problem can be greatly reduced, which should facilitate a physical interpretation of the results.

With this objective in mind, let us integrate Eq. (1) over x to obtain:

$$\frac{\partial}{\partial t}\int_0^\infty (T - T_0)dx = - r(t_w - T_0) - K\left(\frac{\partial \theta}{\partial x}\right)_w . \tag{12}$$

To evaluate the integral, which represents essentially the total energy stored in the grain at any instant, it is convenient to assume a steady-state temperature profile,

$$T - T_0 = (T_w - T_0)e^{-rx/K} . \tag{13}$$

As rapid changes appear in the heat flux, the temperature profile shape will reflect the corresponding small changes in surface temperature much more readily than it will respond to the much larger simultaneous changes in burning rate. Thus, for purposes of the approximate analysis, dT/dr will be neglected. Then Eq. (12) becomes:

$$\frac{K}{r}\frac{dT_w}{dt} = - r(T_w - T_0) - K\left(\frac{\partial T}{\partial x}\right)_w . \tag{14}$$

It is worth digressing briefly to note that the assumptions leading from Eq. (12) to Eq. (14) do not reduce the present analysis to a quasi-steady treatment comparable to those discussed in the introductory section. Here the surface temperature has been allowed to vary, and the primary transient in the temperature profile has been considered. Moreover, the possible shift in relative importance of solid- and gas-phase reactions under transient conditions is accounted for in the present approach, as no empirical burning rate law is used.

Equations (11) may now be substituted into Eqs. (2), (7), (10), and (14), and terms of equal order collected. Terms of the order of $\overline{P}$ (or $\overline{T}_f, \overline{T}_w, \overline{r}$) comprise the unperturbed equations, while those of the order of $\widetilde{P}$ form the linearized mathematical description of the response to pressure perturbations.

Combustion Without Pressure Disturbances

The equations for undisturbed burning of the solid propellant are:

$$\overline{r} = a e^{-E/R\overline{T}_w} \tag{15}$$

$$\overline{r} = C\overline{P}^{\frac{n}{2}}\, \overline{T}_f^{\frac{n}{2}+1}\, e^{-E_f/R\overline{T}_f} \tag{16}$$

$$\frac{K}{\overline{r}^2}\frac{d\overline{T}_w}{dt} = T_0 + \frac{\epsilon_{r_w} Q_r}{C_s} - \frac{L}{C_s} - \frac{C_p\overline{T}_f}{C_s} + \frac{H_H}{C_s} e^{-\frac{E_H}{R\overline{T}_w}} \left(\frac{\overline{P}}{\overline{T}_w}\right)^m + \frac{H_D}{C_s} e^{-\frac{E_D}{R\overline{T}_w}}. \tag{17}$$

These equations are nonlinear, and, except by numerical methods, no solution can be obtained, in general. Such a solution, if obtained, would describe the "normal" behavior of the combustion process, i.e., the behavior in the absence of disturbances caused, for example, by acoustical interactions in the chamber. The steady-state solution ($dT_w/dt = 0$) would correspond, within the limitation of the model, to the behavior usually described in terms of an empirical law such as $r = bP^n$.

The First-Order Response to Pressure Perturbations

The first-order response of the combustion model to pressure transients is obtained by collecting terms of the order of ratios of perturbed to unperturbed quantities, i.e., $\widetilde{P}$, $\widetilde{r}$, $\widetilde{T}_w$, and $\widetilde{T}_f$. Coefficients in these equations may be simplified by appropriate substitutions from

Eqs. (15), (16), and (17). After considerable algebraic manipulation, one obtains the following set of linear equations:

$$\tilde{r} = \frac{E}{R\bar{T}_w}\tilde{T}_w \tag{18}$$

$$\tilde{T}_f = \frac{\frac{E}{R\bar{T}_w}\tilde{T}_w - \frac{n}{2}\tilde{P}}{\Sigma} \tag{19}$$

where $$\Sigma = \frac{n+2}{2} + \frac{E_f}{2R\bar{T}_f}$$

$$\frac{K}{\bar{r}^2}\frac{\partial\tilde{T}_w}{\partial t} = \left[-\frac{K}{\bar{r}^2}\left(\frac{\partial\bar{T}}{\partial t}\right)_w\frac{1}{\bar{T}_w} + \theta_H\left(\frac{E_H}{R\bar{T}_w} - m\right) + \theta_D\frac{E_D}{R\bar{T}_w}\right]\tilde{T}_w$$
$$- \left[4\left(\frac{\bar{T}_w - T_o}{\bar{T}_w}\right) + \frac{1}{\bar{T}_w}\frac{K}{\bar{r}^2}\frac{\partial\bar{T}_w}{\partial t}\right]\tilde{r} - \bar{r}^2\frac{C_P}{C_s}\frac{\bar{T}_f}{\bar{T}_w}\tilde{T}_f$$
$$+ \bar{r}^2\frac{\theta_H m}{\bar{T}_w}\tilde{P} \tag{20}$$

where: $$\theta_H = \frac{H_H}{C_s\bar{T}_w}e^{-E_H/R\bar{T}_w}\left(\frac{\bar{P}}{\bar{T}_w}\right)^m; \qquad \theta_D = \frac{H_D}{C_s\bar{T}_w}e^{-E_D/R\bar{T}_w}$$

It is convenient to combine these equations to obtain the following differential equation for $\tilde{r}$:

$$\frac{d\tilde{r}}{dt} - C_1\tilde{r} = C_2\tilde{P} \tag{21}$$

where

$$C_1 = \frac{\bar{r}^2}{K}\left[\theta_H\left(\frac{E_H}{R\bar{T}_w} - m\right) + \theta_D\frac{E_D}{R\bar{T}_w} - \frac{C_P}{C_s}\frac{\bar{T}_f}{\bar{T}_w}\frac{E/R\bar{T}_w}{\Sigma}\right.$$
$$\left. - 4\left(\frac{\bar{T}_w - T_o}{\bar{T}_w}\right)\frac{E}{R\bar{T}_w} + \frac{K}{\bar{T}_w\bar{r}^2}\left(\frac{E}{R\bar{T}_w} - 1\right)\left(\frac{\partial\bar{T}}{\partial t}\right)_w\right] \tag{22}$$

$$C_2 = \frac{\bar{r}^2}{K}\frac{E}{R\bar{T}_w}\left[\theta_H m + \frac{n}{2}\frac{C_P}{C_s}\frac{\bar{T}_f}{\bar{T}_w}\frac{1}{\Sigma}\right]. \tag{23}$$

Response to Sinusoidal Pressure Oscillations or an Exponential Pressure Decay; A Stability Criterion

An oscillatory perturbation in the chamber pressure may be expressed as:

$$\tilde{P} = \epsilon \sin \omega t \tag{22}$$

where the ratio of the oscillation amplitude to the steady-state pressure is $\epsilon \ll 1$. The corresponding solution to Eq. (21), assuming $\tilde{r} = 0$ at $t = 0$, is:

$$\tilde{r} = \frac{C_2}{C_1^2 + \omega^2}\left[\omega e^{C_1 t} - C_1 \sin \omega t - \omega \cos \omega t\right]. \tag{23}$$

This equation indicates a very important stability criterion; if $C_1 > 0$ for a given propellant, imposed pressure oscillations may induce in that propellant an unbounded increase in burning rate with time; i.e., unstable combustion. Because instability-damping mechanisms present in an actual rocket chamber are excluded from the present model, it is not necessarily true that combustion instability <u>must</u> occur when $C_1 > 0$. However, the analysis indicates that combustion instability is <u>impossible only</u> if $C_1 < 0$.

The chamber-pressure decay introduced within the port of a solid rocket to terminate combustion typically has the form:

$$\tilde{P} = e^{-\beta t} - 1. \tag{24}$$

(Note that at $t = 0$, $d\tilde{P}/dt = -\beta$, or $\frac{dP}{dt} = -\beta\bar{P}$.) From Eq. (21), the approximate initial response of the burning rate to this pressure decay is:

$$r = \frac{C_2}{\beta + C_1}\left(e^{C_1 t} - e^{-\beta t}\right) + \frac{C_2}{C_1}\left(1 - e^{C_1 t}\right). \tag{25}$$

As in the case of a sinusoidal pressure oscillation, unstable combustion may occur when a sudden negative pressure gradient is imposed, unless $C_1 < 0$. In fact, this stability criterion holds quite generally, independent of the type of pressure disturbance that is introduced. Such a criterion is not derivable from the quasi-steady analyses discussed previously.

The physical meaning of the stability criterion may be explained qualitatively by examining the separate terms in Eq. (22). For stable burning it is required that the sum of the negative terms be greater in magnitude than the sum of the positive terms. An increase in the magnitude of the negative terms is accomplished primarily through an increase in the gas-phase flame temperature, which corresponds to an elevation of the energy release in the gas phase. (The other negative term is practically the same for all propellants.) A high energy release in the solid phase, e.g., from exothermic decomposition reactions, contributes to the positive terms and thereby promotes combustion instability. Consequently, for stable burning it is required that the heat release in solid-phase reactions remain less than a certain fraction of the total heat release in the combustion process. Highly exothermic solid-phase reactions are likely to exceed the permissible limit and cause unstable combustion. Moreover, owing to the positive $(d\bar{T}/dt)_w$ term, combustion instability may occur in an otherwise stable motor if there is a pressure disturbance while the steady-state temperature profile is still being established within the grain, e.g., just after ignition.

Pressure Gradient Required for Combustion Termination

Obviously, termination of the combustion process will ultimately occur as the chamber pressure fails to zero, regardless of the pressure gradient initially introduced. However, the rate at which the extinction occurs, i.e., the time required for the burning rate to drop to zero, is intimately coupled to the transient response of the combustion mechanism, and therefore to the pressure gradient. In practice, to stop solid-propellant combustion successfully will require achievement of the minimum possible lag in the response of the burning rate to a chamber pressure decay. In an actual motor the chamber pressure initially drops, then rises again as a result of the finite chamber volume and nozzle throat area. If the response of the combustion mechanism is slow, re-ignition may occur as the pressure starts to rise. It is a consequence of this lag effect that an empirical lag factor, which is not universally applicable, is unavoidable in using the quasi-steady theory.[3] This difficulty is removed with the present approach, because the finite response time of the combustion mechanism is considered.

To develop a criterion for minimizing the response lag time of the combustion process, it is necessary to consider the rate of change of the burning rate, given by the time-derivative of Eq. (25).

$$\frac{d\tilde{r}}{dt} = \frac{C_2}{\beta + C_1}\left(C_1 e^{C_1 t} + \beta e^{-\beta t}\right) - C_2 e^{C_1 t} \tag{26}$$

It has been established in the preceding section that unstable combustion, rather than a smooth extinction of combustion, may occur unless $C_1 < 0$. Consequently, in the following discussion this criterion may be assumed satisfied, as only a stable system is of interest here.

To determine the necessary conditions for reduction of the initial response lag in the combustion mechanism, it is convenient to expand Eq. (26) for small t, retaining the 2nd order term.

$$\frac{d\tilde{r}}{dt} \sim - \beta C_2 t - \frac{\beta C_2}{2}(C_1 - \beta)t^2 - \ldots$$

In general, the initial rate of change in the burning rate under an imposed pressure gradient is proportional to βC_2, where $dP/dt = \beta\bar{P}$. However, the algebraic sign of the second term, and of all even-numbered terms in the series, is fixed by the relative magnitude of β (the pressure gradient) and C_1 (which is negative). If $|\beta| < |C_1|$, the even-numbered terms are <u>positive</u>, meaning the burning rate falls off relatively slowly. This damping effect apparently is attributable to an out-of-phase interaction between the separate steps in the combustion mechanism. When $|\beta| > |C_1|$, all terms are <u>negative</u> and the burning rate extinction is sharply accelerated, because all steps in the combustion process respond in phase to the pressure decay.

In summary, the present analysis defines two criteria for successful extinction of solid propellant combustion: (1) to prevent unstable combustion as a result of pressure disturbances, it is required that $C_1 < 0$; (2) to ensure minimum lag in the burning-rate response of the combustion mechanism to an imposed negative pressure pulse, it is required that $|\beta| > |C_1|$.

The earlier, quasi-steady analyses of other investigators[2,3] lead to the following criterion for combustion termination by a negative pressure gradient:

$$\left|\frac{dP}{dt}\right|_{t=o} > \frac{\bar{r}^2}{K}\frac{\bar{P}}{n} \tag{27}$$

where

$$r = b\bar{P}^n .$$

The criterion developed in the present treatment, $|\beta| > |C_1|$, may be expressed in the following comparable form:

$$\left|\frac{dP}{dt}\right|_{t=o} > C_1\bar{P}, \text{ or}$$

$$\left|\frac{dP}{dt}\right|_{t=o} > \frac{\bar{r}^2}{K}|\lambda|\bar{P} \tag{28}$$

where

$$\lambda \equiv \theta_H\left(\frac{E_H}{R\bar{T}_w} - m\right) + \theta_D\frac{E_D}{R\bar{T}_w} + \frac{K}{\bar{r}^2}\left(\frac{E}{R\bar{T}_W} - 1\right)\frac{1}{\bar{T}_w}\left(\frac{\partial\bar{T}}{\partial t}\right)_w$$

$$- \frac{C_P}{C_s}\frac{\bar{T}_f}{\bar{T}_w}\frac{E/R\bar{T}_w}{\Sigma} - 4\left(\frac{\bar{T}_w - T_o}{\bar{T}_w}\right)\frac{E}{R\bar{T}_w} .$$

The common feature of these two criteria is evident: Both show precisely the same dependence on the burning rate, chamber pressure, and thermal diffusivity of the solid propellant. However, the present treatment reveals a basic distinction between different propellants that is not indicated by the quasi-steady analysis. According to Eq. (28), an array of propellants with identical burning rate characteristics, and operating at the same chamber pressure, might still require substantially different pressure gradients to terminate burning, owing to different values of the parameter λ. The magnitude of λ is determined by the relative importance of various reaction phases to the over-all combustion process, while the stability criterion developed above requires that $\lambda < 0$ for stable combustion. Therefore, it follows from Eq. (28) that propellants with relatively modest exothermic solid-phase reactions and high flame temperatures will not only be more stable, but also will require a stronger negative pressure pulse for termination of burning than will propellants having similar burning rate characteristics but a higher degree of exothermic reaction in the solid phase and less heat release in the gas phase.

Summary Comments on the Analytical Approach

The foregoing analysis and discussion suggests that a relatively fundamental approach to the solid propellant combustion problem may ultimately define and clarify significant mechanisms and interactions that heretofore have been overlooked. The theory developed above represents a preliminary effort to examine transient combustion problems in a somewhat more fundamental and unified manner than has been usual, while still retaining a meaningful combustion model. Future analytical studies will endeavor to relate the theoretical conclusions as directly as possible to observable quantities, and to extend the combustion model as required. Clearly, extensive experimental studies will be needed to provide continuous checks, inputs, and ultimate verification of theoretical concepts. The foregoing treatment provides a continuing basis for guidance of the experimental investigation.

CONCLUSIONS

The work to date has shown that a relatively sophisticated analytical approach can be effectively joined with an experimental study of transient pressure perturbation as represented by rapid depressurization of the burning pressure.

It appears probable, with the success achieved in explaining both limited extinction data and extensive combustion instability data, that planning of propellant development on other than an empirical or intuitive basis will be possible in the balance of the program.

Much remains to be done in improving the modelling concept further, but the success to date augurs well for a continued improvement in our knowledge of the relevant combustion processes.

ACKNOWLEDGEMENTS

The instrumentation and propellant formulation studies in support of this program are the responsibility of R. J. Kier and J. E. Baldwin. Technical supporting staff program coordinator is E. R. Wilson.

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NOMENCLATURE

a = frequency factor in Arrhenius law (Eq. 2)

b = coefficient in empirical burning rate law, $r = bP^n$

C = constant defined by Eq. (17)

C_1 = constant defined by Eq. (22)

C_2 = constant defined by Eq. (23)

C_s = specific heat capacity of solid

E = activation energy for vaporization of interface (Eq. 2)

E_D = activation energy for pressure-insensitive solid-phase decomposition reactions (Eq. 9)

E_f = activation energy for gas-phase reaction (Eq. 7)

E_H = activation energy for heterogeneous or pressure-sensitive solid-phase reactions (Eq. 8)

H_D = heat release (positive)/unit mass propellant in decomposition reactions (Eq. 9)

H_H = heat release (positive)/unit mass propellant (at a reference temperature and pressure) in heterogeneous reactions (Eq. 8)

K = thermal diffusivity (of solid unless otherwise specified) = $k/\rho_s C_s$

k = thermal conductivity

L = heat of vaporization/unit mass of propellant

m = order of heterogeneous reaction (Eq. 8)

n = order of gas-phase reaction (Eq. 7); also pressure exponent in empirical burning rate law

P = chamber pressure

Q_r = heat of reaction/unit mass of reactant in the gas-phase reaction

R = gas constant

r = burning rate

T = temperature

t = time

x = distance into the propellant from its surface

β = constant defined by Eq. (24)

ϵ = amplitude of pressure oscillation (Eq. 22)

ϵ_{Rw} = fraction of total mass flux at the wall associated with reactant (nearly unity at the wall)

λ = constant defined by Eq. (28)

ρ_s = density of solid propellant

NOMENCLATURE (cont d)

Subscripts

DL = lower deflagration limit

f = gas-phase flame

g = gas phase

o = conditions at $x \rightarrow \infty$

s = solid phase

w = conditions at the wall (gas-solid interface)

Superscripts

$(\bar{\ })$ denotes value of quantity prior to pressure disturbance

$(\tilde{\ })$ denotes difference between perturbed and unperturbed value, divided by unperturbed value; $\tilde{r} = (r(t) - \bar{r})/\bar{r}$.

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