Theory of Dynamic Extinguishment of Solid Propellants with Special Reference to Nonsteady Heat Feedback Law

M. Summerfield,* L. H. Caveny,† R. A. Battista,‡ N. Kubota,‡ Yu. A. Gostintsev,§ and H. Isoda¶
Guggenheim Aerospace Propulsion Laboratories, Princeton University, Princeton, N. J.

Two methods for predicting instantaneous burning rates are described and compared: 1) theories based on models of the flame and 2) the Zeldovich-Novozhilov method which uses the steady-state burning rate data as functions of pressure p and initial temperature T_0 to deduce the appropriate nonsteady law for the heat feedback rate from the flame. The latter method offers the important advantage of not requiring detailed knowledge of the flame structure. Theoretical connections between the two methods are demonstrated. Burning rate data $r(p,T_0)$ were obtained for pressures from 1.3 to 40.0 atm and for initial temperatures from 130° to 350°K. The primary limitation encountered in the application of the Zeldovich-Novozhilov method is the inadequacy of techniques for obtaining $r(p,T_0)$ at ambient temperatures below 150°K. Calculated extinction boundaries agree with measured results for depressurization rates from 4,000 to 15,000 atm/sec and pressures from 20 to 60 atm. An interesting observation is that within a class of similar propellants, the propellant with a high temperature sensitivity of burning rate tends to extinguish more readily, ignite with greater difficulty, and be more prone to instability.

Nomenclature

A_s = pre-exponential factor in pyrolysis law, cm/sec
B = parameter defined in Eq. (17)
c = specific heat, cal/g-°K
E = activation energy, cal/g-mole
h = enthalpy, cal/g
H = surface heat release parameter, $Q_s/c_c(T_{s,i} - T_0)$
k = parameter defined in Eq. (16)
m = mass burning rate, g/sec-cm²
n = pressure sensitivity of steady-state burning rate $(\partial \ln r/\partial \ln p)_{T_0}$
$O[\ ]$ = the value is on the order of the number in the brackets
p = pressure
q = heat flux at surface, cal/sec-cm²
Q_s = heat release at the burning propellant surface, cal/g
r = burning rate, cm/sec
R = universal gas constant, 1.98 cal/g-mole-°K
t = time, msec, sec
T = temperature, °K
u = mean velocity in gas phase, cm/sec
α = thermal diffusivity, cm²/sec
β,ϵ = defined in Eq. (32), sec⁻¹, and in Eqs. (1) and (2), respectively
λ = thermal conductivity, cal/cm-°K-sec
ρ = density, g/cm³
σ_p = temperature sensitivity of burning rate at constant pressure $(\partial \ln r/\partial T_0)_p$, $(°K)^{-1}$
τ = characteristic time, sec
ϕ = temperature gradient (when nonsubscripted, value is at condensed phase surface), °K/cm
Φ = heat feedback parameter used in KTSS model, $q_{g,s}r^o$, cal/cm-sec²

Subscripts

c = condensed phase
f = fully reacted gas; final condition
g = gas phase
i = condition at onset of depressurization
0 = ambient conditions
ref = reference conditions for empirical $r(p,T_0)$ relation
s = surface

Superscript

o = steady-state condition

Introduction

INSTANTANEOUS burning rates of solid propellants in a rapidly changing pressure field depart greatly from the steady-state values (as measured in strand-burner experiments) that correspond to the instantaneous value of the pressure.[1-4] One approach for deducing the dynamic burning rate response is based on the use of a detailed model of the combustion wave, which in turn has to be deduced from various diagnostic experiments. This flame model approach has been used extensively in the USA.[1,3-5] Because of the differences in the flame structures and surface reactions of the various propellants, and the wide range of operating conditions, it is often necessary to reconstruct and modify the flame models. Also, when new propellant ingredients that influence the flame zone structure are examined, the flame model must be sufficiently complete so that it can account for the effects produced by the new ingredients.

This paper deals with an approach for analyzing unsteady burning that is not so well known in the USA** and which has been developed by Zeldovich,[7-9] Novozhilov,[10-12] and their colleagues[13-16] in the USSR. This theory does not require a detailed knowledge of the flame structure. In this paper, we demonstrate that in a narrow range there is a basic

Presented as Paper 70-667 at the AIAA 6th Propulsion Joint Specialist Conference, San Diego, Calif., June 15–19, 1970; submitted July 22, 1970; revision received November 30, 1970. Based on work performed under contract N00014-67-A-0151-0023 issued by the Power Branch of the Office of Naval Research.

* Professor of Aerospace Propulsion. Fellow AIAA.
† Member of Professional Staff. Associate Fellow AIAA.
‡ Ph.D. Candidate. Student Member AIAA.
§ Visiting Research Scientist on leave from the Institute of Chemical Physics, Moscow, USSR Academy of Sciences; Financial support was provided by the U. S. National Academy of Sciences and the USSR Academy of Sciences. Present address: Institute of Chemical Physics.
¶ Visiting Professor on leave from the University of Tokyo. Present address: University of Tokyo.

** In fact, the Princeton group misunderstood the underlying principle of this approach and as a result criticized it in Refs. 1 and 2. A similar misunderstanding resulted in the advantages of the approach not being reported in Ref. 6.

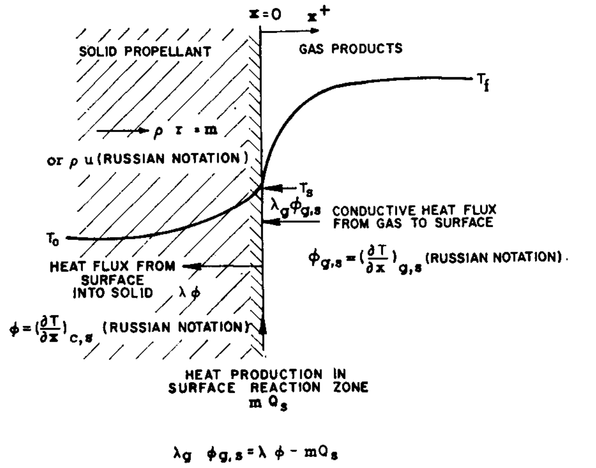


Fig. 1 One-dimensional energy balance at surface of burning solid propellant.

connection between theories based on flame models and the Zeldovich-Novozhilov (Z-N) theory. However, despite certain difficulties which we will point out, the potential for the Z-N theory is great, since a wide range of propellants will satisfy the assumptions of the method, and the method requires fewer physical measurements than do the flame model theories.

The Z-N method starts with measured steady-state burning rates as a function of pressure and ambient temperature. No detailed knowledge of the combustion wave structure is required, although it is necessary to know whether the part of the wave in which the heat release takes place is thin enough to be called quasi-steady (see explanation below). From $r(p,T_0)$ data, the heat feedback function from the gas to the solid is deduced in the proper instantaneous form for application to nonsteady burning problems (ignition, instability, rapid pressure transients, etc.). It will be shown that the feedback function deduced in this manner must be the same as that deduced in the flame models. Another important feature of the Z-N method is that it predicts the existence of low-temperature and low-pressure limits for combustion under steady conditions. The criterion for extinction under conditions of rapid depressurization is more difficult to establish analytically, but the method does yield an approximate criterion for the onset of extinction, defined as the point beyond which a flame can not be sustained without external heating.

Analysis

The unsteady burning theory presented in this paper is based on the original ideas of Ya. B. Zeldovich[7] and the extensions[8–16] of the theory made by him and other members of the Institute of Chemical Physics and the Institute of Problems in Mechanics, both in Moscow. The physical problem to be considered is a solid propellant grain burning in a chamber in which a rapid pressure change is taking place,

Table 1 Propellant properties[a]

λ_c cal/°K-cm-sec	0.0009
c_c cal/g-°K	0.30
α_c cm²/sec	0.00187
A_s for pyrolysis law, cm/sec	2241.
E_s for pyrolysis law, cal/g-mole	16,000
$r(p,T_0)$, cm/sec	Fig. 4
Temperature sensitivity, σ_p,(°K)$^{-1}$	Eqs. (25) and (26)

[a] Unless indicated otherwise the unimodal burning rates were used in the analytical studies.

e.g., small oscillations that may lead to combustion instability or sudden depressurization to achieve extinguishment. The objectives are 1) to predict the dynamic burning rate, $r = f(t)$, for a specified $p(t)$ and 2) to establish the conditions for the onset of unstable burning or extinguishment. We will accomplish these objectives by avoiding any detailed model of the flame and by using instead a solution to the condensed-phase energy equation and steady-state burning rate data, $r^o(p,T_0)$ and $T_s(p,r)$.

Assumptions

The assumptions used herein are intended to apply to conventional high-energy propellants and rocket-motor extinguishment conditions (i.e., $30 \leq p \leq 100$ atm, $0.5 \leq r \leq 3.0$ cm/sec, and $1000 \leq (dp/dt)_i \leq 15{,}000$ atm/sec). In particular, the discussion of oxidizers is directed at ammonium perchlorate (AP). Figure 1 shows the coordinate system and indicates the various zones and processes. The assumptions are as follows:

1) The rate processes in the gas phase and at the propellant surface can be considered quasi-steady†† in the sense that their characteristic times are short compared to that of the pressure transient. No such limitation is necessary for the thermal part of the wave in the solid.

2) No rate-controlling processes occur in the condensed phase. Although the surface reactions occur in a zone of finite thickness it is so thin that it can be considered as a plane.

3) The propellant is homogeneous and isotropic and has a uniform effective surface temperature.

4) The propellant and flame system is considered to be adiabatic and not influenced by external forces (e.g., acceleration and externally imposed shear forces).

For the conditions considered herein, assumption 1 is valid, as can be shown by comparing the magnitudes of the depressurization times and the characteristic times for the three zones:

$$\tau_c = \alpha_c/r^2 \qquad \tau_s \approx \epsilon\alpha_c/r^2 \qquad \tau_g \approx \alpha_g/u_g^2 \tag{1}$$

For practical extinguishment conditions, the characteristic time of the depressurization process is generally greater than 0.002 sec. For the datum case situation of Table 1, τ_c is 0.002 sec. The value of ϵ can be estimated from the theory of flame propagation as follows, on the assumption that the surface reaction zone has indeed some depth, an amount controlled mainly by the activation energy E for the condensed plane reaction:

$$\epsilon = RT_s/E \tag{2}$$

For $E = 16$ kcal/g-mole, $\epsilon = O[0.1]$. This means that the surface reaction is significant only within 10% of the depth of the thermal wave in the solid. The small value of ϵ indicates that the surface will respond more rapidly than the condensed phase. By using the mass conservation law, the relative characteristic time of the gas phase flame is

$$\tau_g/\tau_c = \lambda_g c_c \rho_g/(\lambda_c c_g \rho_c) = O[0.01] \tag{3}$$

because $(\lambda_g c_c)/(\lambda_c c_g) = O[1]$ and for pressures less than 100 atm, $\rho_g/\rho_c = O[0.01]$. (This result is consistent with the 10 μsec relaxation times for step changes in the gas-phase boundary conditions that were calculated using a Shvab-Zeldovich formulation of the energy equation.[17]) Hence, with respect to a hypothetical pressure transient, the gas-phase and surface reaction parts of the combustion wave may be taken to be quasi-steady; the thermal zone in the solid definitely is not quasi-steady.

†† Mathematically, this means that the time derivatives in the gas-phase and surface-reaction equations may be neglected. Therefore the differential equations of the quasi-steady gas phase and surface are identical to the differential equations of the steady-state conditions.

Assumption 2 is based, in part, on examinations of the condensed phase regions immediately below extinguished propellant surfaces. If subsurface reactions contributed significantly to the large amount of heat required to decompose and vaporize the condensed phase, it is reasonable to expect that microscopic examination of the subsurface region would reveal evidence (e.g., discoloration, pores, and structural changes) of subsurface decomposition. In the range of interest, extensive experimentation with AP-composite propellants have not revealed such evidence.[18–20] From the double-base propellant results performed in the 1940's[21] it was generally held that subsurface reactions were an important part of the combustion process in double-base propellants. However, recent experimental studies at Princeton University, Hercules, Inc.,[22] and the USSR Academy of Sciences have not detected evidence of subsurface reactions in extinguished propellants. However, when composite and double-base propellants are burned at $p < 1$ atm, evidence of subsurface decomposition is observed in both. A difficult question is whether at the low-pressure end of the extinguishment sequence subsurface reactions could be significant. It should be noted that the propellants that did not reveal evidence of subsurface reactions were extinguished by rapid depressurization. But these observations do not preclude that subsurface reactions are significant contributors in propellants that do not extinguish.

Assumption 3 applies by definition to the homogeneous propellants, such as the double-base propellants, and is reasonable for a wide range of propellants with gas-phase reaction zone thicknesses that are greater than or approximately the same magnitude as the surface roughness of the heterogeneous propellants. The types of propellants which satisfy the criterion are categorized in Fig. 3 of Ref. 23. For composite propellants, whose surfaces consist of distinct regions of oxidizer and binder, the concept of a surface temperature is valuable only to the extent that it accounts for the surface temperature in the mean.

Assumption 4 restricts the method to those rocket motors for which heat losses to the chamber and erosive burning effects are small. However, for particular applications, externally imposed radiant heating boundary conditions can be incorporated.

Development of Functional Relations

From the theory of flame propagation, a functional relationship for the mass burning rate in the gas phase is

$$m_g = m_g(p,T_f,\phi_{g,s},Q_s) \tag{4}$$

The energy balance at the solid-gas interface can be written in functional form as

$$m_c = m_c(\phi_{c,s},\phi_{g,s},Q_s) \quad Q_s = Q_s(T_s,p) \tag{5}$$

We introduce the thermochemical heat release Q_s as a variable in Eq. (4) since, in principle, the variation of Q_s implies variation of the composition of the combustible vapor coming from the surface and entering the gas flame. In Ref. 3, we took Q_s to be constant.

Since the gas-phase and surface reactions are both assumed to be quasi-steady during the fluctuation of pressure,

$$m_c = m_g = m = r\rho_c \tag{6}$$

The total (i.e., physical and chemical) energy conservation equation (also quasi-steady) written for a gas-phase control volume (with one boundary at the condensed-phase surface and the other boundary in the fully reacted gas) yields

$$mh_{c,s}(T_s) - \lambda_c\phi_{c,s} = mh_{g,f}(T_f,p) \tag{7}$$

The functional form of the pyrolysis law at the solid surface is

$$m = m(T_s,p) \tag{8}$$

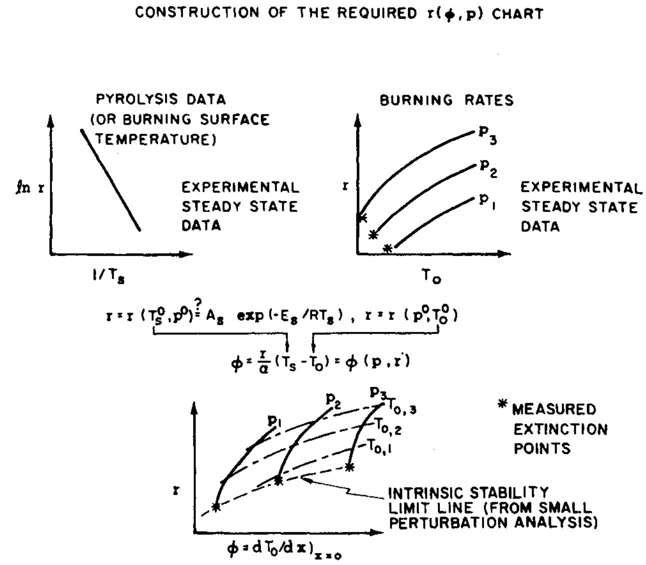


Fig. 2 Schematic drawing showing relationship between experimental data and the required heat feedback function.

The energy equation in the condensed phase ($-\infty < x \leq 0$) is

$$\rho_c c_c[\partial T/\partial t + r(t)\phi_c] = \lambda(\partial\phi_c/\partial x) \tag{9}$$

As indicated in Fig. 1, the origin is fixed at the surface and the solid is translating in positive x direction at velocity $r(t)$.

Since the essence of the Z-N method is to obtain the heat feedback from the gas-phase and surface reactions without having to consider the details of the gas-phase and surface reactions, it provides the first of the following boundary conditions required for the solution of Eq. (9):

$$\phi_{c,s} = \phi_{c,s}(t) \quad T_c \rightarrow T_0 \text{ as } x \rightarrow -\infty \tag{10}$$

Since we are considering extinguishment, the initial condition for many physical situations is the steady-state solution for the pressure immediately prior to the onset of depressurization;

$$T = [T_s(p_i,T_0) - T_0]\exp[xr(T_0,p_i)/\alpha_c] + T_0 \tag{11}$$

One approach to evaluating $\phi_{c,s}(t)$ is to formulate a complete flame theory (on the basis of diagnostic experiments) that provides the details of Eqs. (4, 5, 7 and 8), and then to couple the heat feedback gradient $\phi_{c,s}$ to Eq. (9) by means of Eq. (5). Five equations, (4, 5, 7, and 8) contain seven variables: $m,Q_s,\phi_{c,s},\phi_{g,s},T_s,T_f,p$. Thus, the flame theory formulation makes it possible to obtain one equation in three variables:

$$\phi_{c,s} = \phi_{c,s}[r(t),p(t)] \tag{12}$$

This is the desired boundary condition and has been employed previously in flame models.[4] Since Eq. (12) was developed under the quasi-steady assumption, and since the time dependency appears only through the instantaneous values of r and p, we can obtain the same result from steady-state considerations, i.e., $\phi_{c,s} = \phi_{c,s}(r^o,p^o)$. Indeed, in the following paragraphs, we show how $\phi_{c,s}(r^o,p^o)$ is obtained from steady-state data.

Now to avoid the development of a flame model, we will take advantage of the Z-N method. The following relationships are available in principle from laboratory experiments: $r^o = r^o(T_0,p)$, and $T_s{}^o = T_s{}^o(p,r)$. Whereas the steady-state burning rate r^o can be obtained by routine experiments (for a limited temperature range), experimental measurements of the dependence of T_s on p and r are much more difficult (see Ref. 24) and have yet to be accomplished over the desired ranges of r and p.

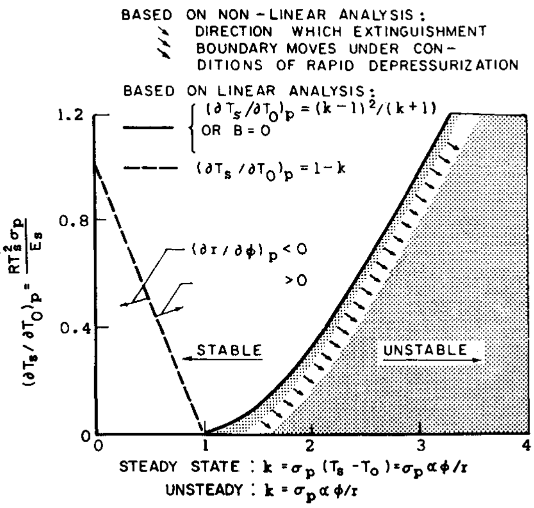


Fig. 3 Regions of stable burning in terms of parameters in the condensed phase and at the surface.

The Z-N method uses r^o data in conjunction with the following expression for the steady-state energy balance in the condensed phase

$$\lambda_c\phi = r^o\rho_c c_c(T_s^o - T_0) \tag{13}$$

As indicated in Fig. 2, $r^o(T_0,p)$ and $T_s^o(p,r)$ can be combined with Eq. (13) to obtain the following functional form, which is equivalent to Eq. (12) derived from a flame model:

$$\phi = \phi(r^o,p^o) = \phi[r(t),p(t)] \tag{14}$$

This relation, which is obtainable from steady-state experiments, is the key element of the Z-N method, since it expresses the heat feedback to the condensed phase in terms of two parameters, p, which is externally imposed, and r, which is the important explicit result desired from the solution. Assumption 1 is the justification for applying the steady-state result of Eq. (14) to transient conditions.

At a given p, there can be a wide range of r: 1) during steady-state conditions, r is varied by changing T_0, and 2) for dynamic conditions, r is controlled by the heat balance at the propellant surface. Based on the foregoing arguments, it is maintained that for a given r and p (regardless of how the value of r is obtained) the value of $\phi(r,p)$ is the same for both the steady-state and transient conditions. It is important to realize that even though Eq. (14) is obtainable from steady-state data, transient burning rate calculations can be performed only if the transients in the condensed phase are calculated, [i.e., $\phi(t)$] by solving the transient heat conduction equation [Eq. (9)] with Eqs. (14) and the second of Eqs. (10) as boundary conditions.

Stability and Extinction Limits

Extensive analytical developments within the basic framework of the Z-N method have been carried out[7–16] to establish the regions of stable burning§§ and to define criteria for events such as the onset of extinction and ignition. Recently V. B. Librovich¶¶ completed a monograph[24] that reviews and summarizes the analytical developments of these criteria. These criteria will be summarized in this paper; the reader is referred to Refs. 7–16 for the details of the analytical development and for a more complete explanation of the significance of the criteria.

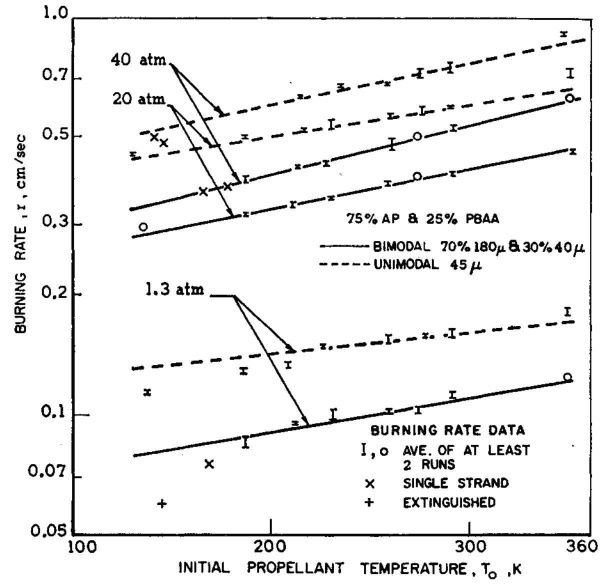


Fig. 4 Measured burning rate vs initial propellant temperature with pressure as a parameter.

The key factor in the stability and extinction criteria is the condensed-phase temperature gradient at the propellant surface ϕ. If during either transient processes or steady-state conditions, the thermal gradient is caused to exceed a certain maximum value for a particular instantaneous r, the balance between the heat conducted into the condensed phase from the gas-phase and surface zones is upset to the point that stable combustion cannot be sustained. The locus of such maximum values of the gradient is a line running across the (r,ϕ) plane. This limit line contains the intrinsically stable domain of the plane. Another physical definition of the limit line is as follows: if r happens to decline momentarily so as to cross the line, while the temperature gradient at the surface remains nearly constant, then the energy flow from the flame becomes too weak to enable the burning rate to recover and sustain itself. For depressurization, this corresponds to the onset of extinction. For constant-pressure conditions, crossing the line indicates that the pressure is below the lower deflagration limit.

For the special case of constant T_s (the earliest version of the theory[7]), the observation that increasing the propellant initial temperature T_0 increases r and decreases ϕ led to the following sufficient condition for stable burning, which is obtained by differentiating Eq. (13) and arguing that for a fixed $p,\phi(r)$ is single-valued:

$$(\partial\phi/\partial T_0)_p = (1/\alpha_c)(\partial r^o/\partial T_0)_p(T_s - T_0) - r^o/\alpha_c < 0 \tag{15}$$

This condition can be expressed in terms of a parameter k

$$k = \sigma_p(T_s - T_0) < 1 \tag{16}$$

Until recently this constant T_s criterion, Eq. (16), was widely referred to in the USSR literature; however it does not apply to most physical situations, since stable burning can occur even when $k > 1$. The theory was extended to allow for variable T_s, and a small-perturbation analysis of Eq. (9) and its boundary conditions was carried out to define more fully the regions of stable burning.[12] For extinguishment, the results of the small-perturbation analysis indicated 1) that stable burning was assured when $k < 1 - (\partial T_s/$

§§ For purposes of this paper, this region (also referred to as the region of intrinsic stability[3,5]) is the domain where a fully developed flame exists and is stable under small perturbations of pressure.

¶¶ Dr. Librovich prepared the monograph while he was a Visiting Research Scientist at the Guggenheim Laboratories of Princeton University, and on leave from the Institute of Problems in Mechanics of the USSR Academy of Sciences in Moscow. Financial support was provided by the U. S. National Academy of Sciences and the USSR Academy of Sciences. Also, the authors are indebted to V. B. Librovich for his stimulating discussions and lectures on combustion theories.

$\partial T_0)_p$ and 2) that for $k > 1 - (\partial T_s/\partial T_0)_p$, stable burning depends on an additional parameter B being less than zero

$$B = (k - 1)^2/(k + 1) - (\partial T_s/\partial T_0)_p < 0 \qquad (17)$$

The range of stable burning defined by Eqs. (16) and (17) is shown on Fig. 3. During a monotonic depressurization the locus of values in the $(\partial T_s/\partial T_0)_p$ vs k plot moves away from the stable region toward the unstable region. For the situation we examined when the locus of values crosses over the $B = 0$ line into the unstable region, the heat feedback from the flame rapidly decreases and extinction subsequently occurs, i.e., crossing over the $B = 0$ is the previously referred to onset of extinction. It is important to note that the foregoing criteria are based on the linear responses corresponding to small changes in p, and thus they might fail for the nonlinear rapid depressurization situation. The practical significance of the criteria based on linear responses and combustion situations that lead to departures from the linear responses are discussed in the section on analytical studies.

Plots of steady-state r vs q (or ϕ) at constant pressure, referred to as Zeldovich plots, are a convenient representation of the propellant burning characteristics. The slope $(\partial r/\partial \phi)_p$ is markedly different for different types of propellant.[25] The small-perturbation analysis gives the useful result

$$(\partial \ln r/\partial \ln\phi)_p = k/[k + (\partial T_s/\partial T_0)_p - 1] \qquad (18)$$

First, for constant T_s, we see from Eq. (17) that stable burning occurs when $k < 1$ and $(\partial \ln r/\partial \ln\phi)_p$ is negative. Secondly, when T_s is not constant,* the slope is determined as follows

$$k + (\partial T_s/\partial T_0)_p < 1 \rightarrow (\partial r/\partial\phi)_p < 0 \qquad (19)$$

and

$$> 1 \rightarrow (\partial r/\partial\phi)_p > 0 \qquad (20)$$

The boundary separating the regions of positive and negative slope on a Zeldovich plot is included in Fig. 3.

The transient burning characteristics can be more easily understood by expressing several of the parameters in terms of commonly used parameters. From the Arrhenius type pyrolysis law,

$$T_s = -E_s/R \ln(r/A_s) \qquad (21)$$

Differentiating with respect to T_0 at constant p yields

$$(\partial T_s/\partial T_0)_p = dT_s/dT_0 = RT^2{}_s\sigma_p/E_s \qquad (22)$$

An alternative expression for the parameter k which is suitable for nonsteady calculations is

$$k = \sigma_p\alpha\phi/r \qquad (23)$$

Temperature Sensitivity Measurements

Two 75% AP-25% PBAA/EPON propellants were tested; one containing bimodal 70% 180-μ and 30% 45-μAP, the other containing unimodal 45-μAP. These propellants, referred to as the bimodal and unimodal propellants, respectively, were duplicates of propellants 949 and 951 used in the extinguishment experiments in Ref. 1. The experiments were performed at pressures of 1.3, 20.0, and 40.0 atm, and $130°\mathrm{K} \le T_0 \le 350°\mathrm{K}$.

The strands, $\frac{1}{4} \times \frac{1}{4}$-in. cross-section, were temperature-conditioned and then burned in a standard chimney burner.[23] The r's were determined from the instant of melt of a sequence of five fuse wires placed 0.5 in. apart. A constant flow of pressurized N_2, preconditioned to the desired temperature by passing it through a heat exchanger coil in a temperature-conditioned liquid bath, maintained the strand at the proper temperature.

For $208°\mathrm{K} \le T_0 \le 350°\mathrm{K}$, the r's were reproducible within 1.0% in all but a few cases (see the scatter bars in Fig. 4), and the T_0 of the strand at each condition was kept within 3° of the desired temperature from run to run. The effect of T_0 on r for many propellants is usually expressed by the empirical relation

$$r = r_{\mathrm{ref}} \exp[\sigma_p(T_0 - T_{\mathrm{ref}})] \qquad (24)$$

Thus, on $\ln r$ vs T_0 plots, σ_p is the slope. The data presented in Fig. 4 represent the average of at least two runs unless otherwise indicated. The straight lines through the data are approximations at 20 and 40 atm, for $200° \le T_0 \le 300°\mathrm{K}$. However, at 1.3 atm and below 200°K the data are insufficient to recognize a definite trend of how T_0 and p affect σ_p. As indicated in Fig. 4, the existence of an intrinsic stability limit line predicted by the theory was indicated by the negative results of attempts to burn the bimodal propellant at 1.3 atm and ~150°K. The propellant would ignite and then extinguish after burning a few millimeters. Unfortunately, this was the only nonburning point encountered in the series, so it cannot be asserted with confidence that this represents the theoretically predicted Z-N limit line.

A relationship for σ_p in terms of p and T_0 has not been established. However, several trends influenced the manner in which the data were used in the calculations: 1) at 20 and 40 atm, σ_p is a weak function of T_0; 2) in the ranges of practical interest the stability criterion and ϕ must be calculated at pressures greatly above 1 atm; and 3) both the unimodal and bimodal propellants demonstrated similar temperature sensitivity characteristics at 20 and 40 atm. Also, the applicability of the Z-N method at the very low r's corresponding to 1 atm has not been established, since at sufficiently low r's, subsurface exothermic reactions with large time constants may become significant. Accordingly, the following relationships based on the 20- and 40- atm data were used in the calculations for the unimodal and bimodal propellants, respectively:

$$\sigma_p = 0.000030p + 0.00124 \qquad (25)$$

$$\sigma_p = 0.000024p + 0.00193 \qquad (26)$$

Analytical Studies

Connection Between Flame Models and Z-N Method

A convenient and physically intuitive method for demonstrating and recognizing the basic relationship between the flame model method[1,3,5,26–28] and the Z-N method is to use a flame-model method (any properly formulated flame model can be used) to calculate $r(p,T_0)$ results and to use an empirical pyrolysis law in place of the experimentally determined $r^o(T_0,p)$ and $T_s{}^o(p,r)$ data required by the Z-N method. We will first accomplish this for the KTSS model,[3] in which, as in the case of most flame models, $T_s{}^o(p,r)$ is deduced from experimental pyrolysis data, admittedly very sketchy, fitted to an Arrhenius type law. We begin by differentiating with respect to T_0 at constant p the following quasi-steady heat feedback equation from the KTSS model:

$$r\rho c_c(T_s - T_0) = \Phi(p)/r + r\rho Q_s \qquad (27)$$

which yields

$$\rho c_c(T_s - T_0)\sigma_p + r\rho c_c[\sigma_p(dT_s/dr) - 1] = \sigma_p[Q_s\sigma_p - \Phi(p)/r^2] \qquad (28)$$

* Surface temperature is generally thought to increase with increasing pressure. Of course, the surface temperatures of plateau and mesa propellants may not increase monotonically with pressure.

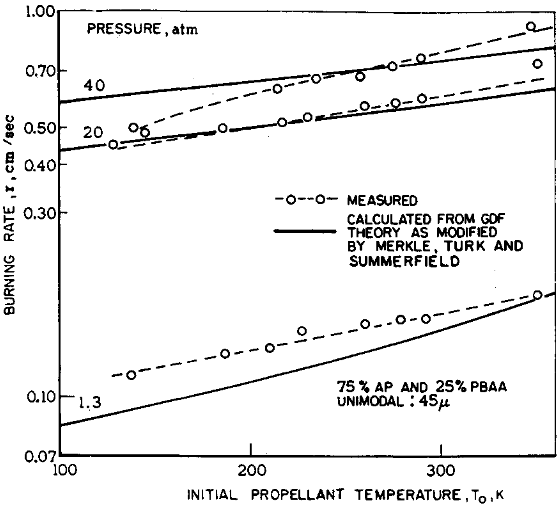


Fig. 5 Comparison of measured and theoretical burning rates as a function of pressure and initial temperature.

Solving Eqs. (27) and (28) for σ_p yields

$$\sigma_p = 1/[r dT_s/dr + 2(T_s - T_0)(1 - H)] \tag{29}$$

where $H \equiv Q_s/[c_c(T_s - T_0)]$ as used in the KTSS model. Expressing T_s by Eq. (21) and differentiating with respect to r and combining the result with Eq. (29), we have a result in terms of the propellant properties

$$\sigma_p = 1/[RT_s^2/E_s + 2(T_s - T_0)(1 - H)] \tag{30}$$

Using the values of Table 1 corresponding to about 20 atm, we calculated that $\sigma_p = 0.0020/°K$, which is very close to the measured values. Thus, Eq. (30) indicates the basic connection between the two approaches, since the KTSS model can be used to obtain $r°(p,T_0)$ over the broad $p - T_0$ domain.

In a similar manner, the basic connection between the two approaches can be demonstrated by using the granular diffusion flame model as modified by Merkle, Turk, and Summerfield (MTS) in Ref. 1. First we used the MTS flame model to calculate directly $r(t)$ by means of the heat feedback boundary condition obtained from the flame model in the manner described for Eq. (12). To complete the comparison, the MTS flame model and pyrolysis law of Ref. 1 was used to calculate the $r°(p,T_0)$ results in Fig. 5 from measured $r°(p, 300°K)$ data and the Z-N method then used the theoretical $r(p,T_0)$ results of Fig. 5 (as if they were experimental data) to calculate $r(t)$ by means of the heat feedback boundary condition obtained in the manner shown in Fig. 2. Figure 6 shows the expected exact agreement of the two approaches. By this demonstration, we do not want to give the impression that the Z-N method requires calculated $r°(p,T_0)$ data. It does not.

The effect of T_0 on the gas phase was also recognized by Glick.[29]

Extinguishment Boundary

A Zeldovich plot, Fig. 7, was prepared for the bimodal propellant using the measured $r(p,T_0)$ data, the properties of Table 1, and Eqs. (13), (17), and (21). The circles on Fig. 7 indicate the calculated limits of intrinsic stability for the pressures at which the experiments were carried out (i.e., 1.3, 20 and 40 atm). The propellant will not have a self-sustaining flame if its value of T_0 is below the value corresponding to the intrinsic stability limit. The fact that the extinction point observed at 1.3 atm is slightly below the calculated intrinsic stability point is interesting, but only partially convincing, since the low-temperature σ_p is not accurately known at 1.3 atm.

The most meaningful test of the Z-N method is to compare predicted and measured extinction boundaries. Accordingly, analytical predictions were made for each of the experimental points shown in Fig. 8. The experimental results of Fig. 8 were taken from Ref. 1 and are for the unimodal propellant. The properties in Table 1 and Fig. 4 were used. The analytical procedure was to carry out the numerical solution of Eq. (9) with the measured $p(t)$ history imposed on the solution by means of the boundary condition, Eq. (14). In each of the go or no-go cases, the calculated extinguishment result determined by observing whether the computed $r(t)$ declined to zero, agreed with the measured result (except for the single extinction point at the extinguishment boundary). The theoretical boundary is shown as a broad line, since r approaches zero very slowly whenever the extinction is marginal.

It is also interesting to note the behavior of the parameter B used in the intrinsic stability criterion: For each extinguishment case, B became greater than zero during the depressurization, and for each nonextinguishment case the B remained less than zero. For a given initial pressure, the pressure at which B becomes greater than zero increases as

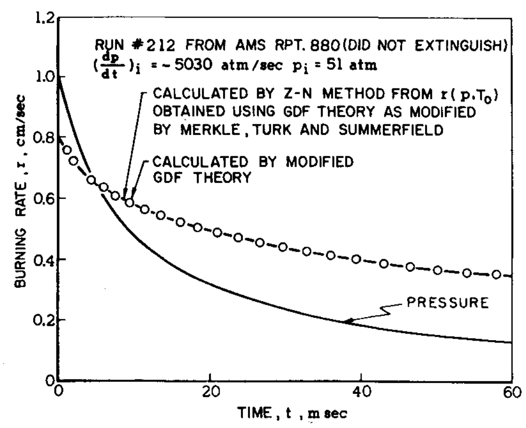


Fig. 6 Comparison of predicted transient burning rate behavior calculated by the Z-N method and GDF theory as modified by Merkle, Turk, and Summerfield (MTS).

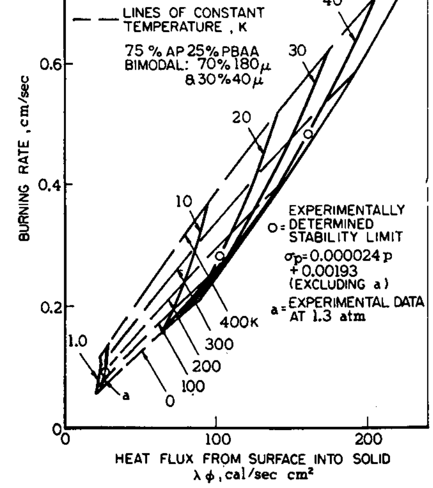


Fig. 7 Effect of pressure and initial temperature on the stability limit and on heat flux into condensed phase (Zeldovich plot).

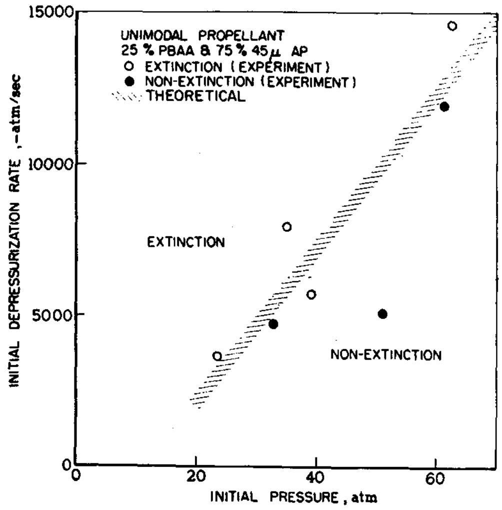


Fig. 8 Comparison of required depressurization rates for extinguishment with the measured extinction data of MTS.

$(dp/dt)_i$ increases. Thus, in situations where the depressurization rate greatly exceeds the minimum value for extinguishment, B provides an early signal that extinguishment will occur. As has been pointed out, the degree to which the intrinsic (linear) stability criterion, Eq. (17), can be relied on for the nonlinear case of extinguishment has not been established. However, for the monotonic pressure decay of extinguishment, our calculations show it to be very useful, particularly if the situation being analyzed can accommodate a small conservative tolerance margin on the depressurization rate. As this paper was being prepared, an analysis by Librovich[24] and computer experiments conducted at Princeton demonstrated that the dynamic conditions of extinguishment tend to shift the stability line based on B. This shift greatly exaggerated in Fig. 3 is to the right. However, we want to emphasize that for the monotonic pressure decay of extinguishment, the actual shift in the stability line is very small and does not detract from its usefulness.

Parametric Studies

Several series of parametric studies were conducted to investigate the manner in which depressurization rate and propellant properties influence the extinguishment characteristics and $r(t)$. The results of Figs. 9–11 were calculated using the unimodal propellant properties (except as noted) and an exponential pressure decay

$$p = p_f + (p_i - p_f)\exp(-\beta t) \tag{31}$$

where

$$\beta = (dp/dt)_i/(p_i - p_f) \tag{32}$$

Figure 9 shows that increasing σ_p increases the rate at which r is depressed. Similarly, Fig. 10 shows that increasing E_s of Eq. (21) increases the rate at which the r is depressed. When E_s is relatively high, small changes in T_s correspond to large changes in r. Accordingly, when E_s is

Fig. 9 Effect of temperature sensitivity on burning rate during depressurization.

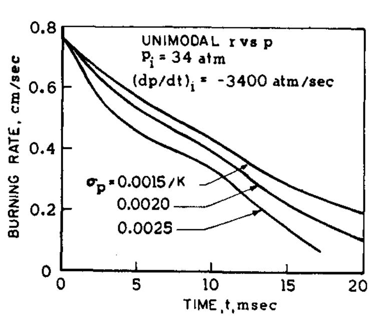
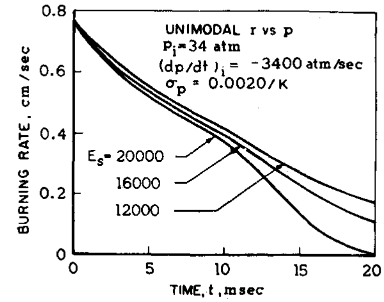


Fig. 10 Effect of pyrolysis law activation energy on burning rate during depressurization.



relatively high, r responds more rapidly to decreases in the heat feedback from the gas phase and surface zones. Other calculations demonstrated that increasing σ_p and E_s decreases the depressurization rates required for extinguishment.

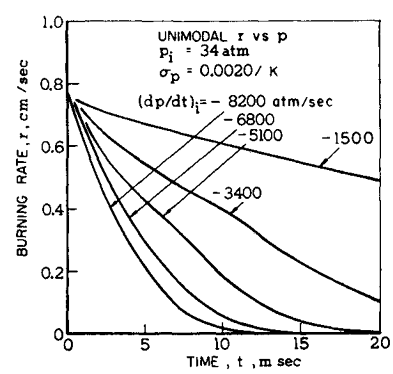
Figure 11 illustrates how $(dp/dt)_i$ influences $r(t)$. All of the cases in Fig. 11 extinguished except for the lowest $(dp/dt)_i$, -1500 atm/sec. The changes in slope of the $r(t)$ lines on Figs. 9–11 are a consequence of the steady-state $r(p)$ characteristics of the unimodal propellant.

The parametric studies revealed how low a range of T_0 is required in the measurement of $r^o(p,T_0)$ in order to calculate $\phi_{c,s}(r,p)$ during very fast depressurization cycles. For the cases in Fig. 9, the value of T_0 that corresponds to the point where B changes sign (i.e., where dynamic r crosses the limit line) are 200°, 17°, and < 0°K for σ_p of 0.0025, 0.0020, and 0.0015, respectively. Accordingly, in the case of the more difficult to extinguish propellants, the effective range of σ_p must be extended either by extrapolation or by a flame model. Recently, Novikov and Ryazantsev[16] reported that the $r(p,T_0)$ relations can be obtained by quenching the propellant in contact with a metal heat sink. Using this approach it may be possible to achieve effective values of T_0 that are much lower than those reported here (even to the extent that the effect is equivalent to the minus Kelvin range).

Just as the higher values of σ_p in Fig. 9 correspond to the more rapid response of r to changes in p, within a class of similar propellants, the propellant with the higher σ_p will be more prone to instability. This trend is clearly demonstrated in Fig. 3 if it is noted that increasing σ_p for a marginally stable case moves the case in the direction toward the region of instability.

In the previous paragraphs, the emphasis has been on depressurization and, therefore, on the need for $r(p,T_0)$ data at low temperatures. If we had been concerned with fast pressurization phenomena, as during rocket ignition, then $r(p,T_0)$ data would be required at elevated temperatures. Just as a heat sink is needed to evade the limitation in obtaining very low temperature data, so it is necessary to utilize a scheme (radiation input, for example) to evade the tendency to thermal explosion in obtaining $r(p,T_0)$ data at elevated temperatures. It is interesting to note that within a class of propellants, the propellants with higher σ_p ignite with greater difficulty when subjected to radiant heating.[30]

Fig. 11 Effect of initial depressurization rate on burning rate during depressurization.



Conclusions

The Zeldovich-Novozhilov (Z-N) method is superior in some situations to those dynamic burning theories that rely on flame models. It offers the important advantage of not requiring detailed knowledge of the flame structure, but makes use, instead, of directly obtainable steady-state burning rate data. For full use of the Z-N method, surface temperature data are also required; in the absence of such data, a partial Z-N method can be devised that relies on an estimated pyrolysis law. Unfortunately, for some propellants and for fast depressurization rates, it is practically impossible to obtain reliable $r(p,T_0)$ data over a sufficiently wide range of T_0. In these cases, some kind of theory for extrapolation purposes is needed; hence a flame model may be required.

Zeldovich and his colleagues have developed a broad attack on nonsteady burning problems of many kinds which deserves extensive study and parallel work by scientists and engineers working in the field. However, the success of the Z-N method should not be used as justification for relaxing current efforts to develop more fully the necessary flame models[1,3,26–28] and the corresponding nonsteady heat feedback laws, since in many practical situations the range of the Z-N method is inherently limited.

References

[1] Merkle, C. L., Turk, S. L., and Summerfield, M., "Extinguishment of Solid Propellants by Depressurization: Effects of Propellant Parameters," AIAA Paper 69-176, New York, Jan. 1969; also, AMS Rept. 880, July 1969, Princeton Univ., Princeton, N. J.

[2] Summerfield, M. and Krier, H., "Errors in Nonsteady Combustion Theory in the Past Decade (A Review)," AIAA Paper 69-178, New York, Jan. 1969.

[3] Krier, H., T'ien, J. S., Sirignano, W. A., and Summerfield, M., "Nonsteady Burning Phenomena of Solid Propellants: Theory and Experiments," *AIAA Journal*, Vol. 6, No. 2, Feb. 1968, pp. 178–185.

[4] Culick, F. E. C., "A Review of Calculations for Unsteady Burning of a Solid Propellant," *AIAA Journal*, Vol. 6, No. 12, Dec. 1968, pp. 2241–2255.

[5] Denison, M. R. and Baum, E., "A Simplified Model of Unstable Burning in Solid Propellants," *ARS Journal*, Vol. 31, No. 8, Aug. 1961, pp. 1112–1122.

[6] Wooldridge, C. E. and Dickinson, L. A., "Review of Soviet Transient Combustion Research," *ICRPG/AIAA 2nd Solid Propulsion Conference*, June 1967, pp. 104–110.

[7] Zeldovich, Ya. B., "On the Combustion Theory of Powder and of the Explosives," *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki*, Vol. 12, No. 11–12, 1942, p. 498.

[8] Zeldovich, Ya. B., "On a Burning Rate under Nonsteady Pressure," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 3, Jan.-Feb. 1964, pp. 126–130.

[9] Zeldovich, Ya. B., "On the Stability of the Combustion of the Powder in a Semi-Closed Volume," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 1, Jan.-Feb. 1963, pp. 67–77.

[10] Novozhilov, B. V., "Non-Linear Oscillations of the Powder Burning Rate," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 5, Sept.-Oct. 1966, pp. 31–41.

[11] Novozhilov, B. V., "Transient Process of the Burning Powders," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 5, Sept.-Oct. 1962.

[12] Novozhilov, B. V., "Non-Steady Burning of Powder Having Variable Surface Temperature," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 1, Jan.-Feb. 1967, pp. 54–63.

[13] Pokhil, P. F., Nefedova, O. I., and Margolin, A. D., "Anomalous Dependence of Powder Burning Rate on Initial Temperature," *Doklady Akademii Nauk SSSR*, Vol. 142, No. 4, July-Aug. 1962, pp. 860–862.

[14] Gostintsev, Y. A. and Margolin, A. D., "On the Nonsteady Propellant Combustion under Influence of a Pressure Impulse," *Zhurnal Fizika Goreniya i Vzriva*, Vol. 1, No. 2, March-April 1965, pp. 69–74.

[15] Librovich, V. B., "Ignition of Powders and Explosives," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 6, Nov.-Dec. 1963, pp. 74–80.

[16] Novikov, S. S. and Ryazantsev, Yu. S., "Extinction of Propellant Near the Contact with a Metal," *AIAA Journal*, Vol. 8, No. 2, Feb. 1970, pp. 358–359.

[17] Caveny, L. H., "Analysis of Transient Heat Feedback from Solid Propellant Gas Phase," to be submitted for publication to AIAA.

[18] Hightower, J. D. and Price, E. W., "Two-Dimensional Experimental Studies of the Combustion Zone of Composite Propellants," *Proceedings of Second ICRPG Combustion Conference*, Publ. 105, Vol. I, 1966, Chemical Propulsion Information Agency, p. 421.

[19] Caveny, L. H. and Pittman, C. U., "Contribution of Solid-Phase Heat Release to AP Composite-Propellant Burning Rate," *AIAA Journal*, Vol. 6, No. 8, Aug. 1968, pp. 1461–1467.

[20] Powling, J., *Advances in Tactical Rocket Propulsion*, Technivision Services, Maidenhead, England, 1968, p. 136.

[21] Huggett, C., "Combustion of Solid Propellants," *Combustion Processes, High Speed Aerodynamics and Jet Propulsion Series*, Vol. 3, Princeton University Press, Princeton, N. J., 1956, pp. 514–574.

[22] Miller, R. R., personal communication, Oct. 30, 1969, Hercules Inc., Cumberland, Md.

[23] Steinz, J. A., Stang, P. L., and Summerfield, M., "The Burning Mechanism of Ammonium Perchlorate-Based Composite Solid Propellants," AIAA Paper 68-658, Cleveland, Ohio, 1968; also AMS Rept. 830, Feb. 1969, Princeton Univ., Princeton, N. J.

[24] Librovich, V. B., *Theory of Nonsteady Flames*, to be published by Academic Press, New York, 1970.

[25] Novikov, S. S. and Ryazantsev, Yu. S., "Analysis of the Conditions for the Extinction of Solid Propellant Burning," *Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki*, No. 2, March-April, 1969, pp. 93–97.

[26] Beckstead, M. W., Derr, R. L., and Price, C. F., "The Burning Mechanism of Ammonium Perchlorate-Based Composite Propellants," Paper 102, Thirteenth (International) Symposium on Combustion, Aug. 1970, The Combustion Institute.

[27] Coats, R. L. and Horton, M. D., "Predicted Effects of Motor Parameters on Solid Propellant Extinguishment," AIAA Paper 70-664, San Diego, Calif., 1970.

[28] Wooldridge, C. E. and Marxman, G. A., "A Comparison Between Theoretical and Experimental Extinction Behavior of Composite Solid Propellants," AIAA Paper 70-666, San Diego, Calif., 1970.

[29] Glick, R. L., "Temperature Sensitivity of Solid Propellant Burning Rate," *AIAA Journal*, Vol. 5, No. 3, March 1967, pp. 586–587.

[30] Kondrikov, B. N., Ohlemiller, T. J., Caveny, L. H., and Summerfield, M., "Ignition Criterion and Self-Heating of Propellant Subjected to Intense Radiative Heat Fluxes," presented at the 1970 Technical Meeting of the Eastern Section of the Combustion Institute, Atlanta, Ga., Nov. 1970.