Influence of Thermal Radiation on Solid Propellant Burning Rate

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Radiation assisted burning rate data $r(q_r)$ and temperature sensitivity of burning rate data $[r(p, T_o)$ and $\sigma_p = \partial r/\partial T_o)_p]$ were obtained for a well characterized double base propellant (nitrocellulose and metriol trinitrate). For example, at 14.6 atm, 70 cal/sec-cm^2 of xenon arc radiation increased the burning from 0.2 to 0.6 cm/sec. Analysis of the heat feedback from the flame revealed that once $r(T_o)$ data are available, $r(q_r)$ data does not permit additional properties of the combustion zone to be deduced. However, a simple analytical relationship between $r(q_r)$ and σ_p was developed that approximates the measured results. Propellant burning rate responsiveness to external thermal radiation increases with higher σ_p and lower burning rate.

Nomenclature

c = specific heat of propellant, cal/g-K
I = incident radiation, cal/sec-cm^2
p = pressure, atm
Q_s = surface heat release, cal/g
q_r = radiation absorbed by propellant surface, $I(l-r_e)$, cal/sec-cm^2
r = steady state burning rate, cm/sec
r_e = reflectivity of propellant surface
T = temperature, K
x = distance normal to surface, cm
λ = propellant thermal conductivity, cal/cm-sec-K
ρ = propellant density, g/cm^3
σ_p = temperature sensitivity of burning rate at constant pressure $(\partial \ln r/\partial T_o)_p$, (K)$^{-1}$

Subscripts:
eq = equivalent value
f = flame zone
n = no externally imposed radiation
ref = reference conditions for empirical $r(p, T_o)$ relation
s = surface
o = temperature of propellant before approach of thermal wave

Introduction

INVESTIGATIONS to understand and control solid propellant combustion processes must account for the influence of thermal radiation from the surroundings to the burning surface. For example, questions arise concerning the extent that radiation from chamber gases influence burning rate as a function of motor size, gas composition, flame temperature, etc. Also, it is of interest to speculate[1] on methods of increasing burning rate by devices that intensify radiant heating (e.g., by increasing the emissivity of the chamber gases or by decreasing the reflectivity of the propellant surface).

Konev[2] carried out direct measurements of burning rate vs externally imposed radiation using a double base propellant, (i.e., the Soviet's *N* powder). Konev was limited to rather low heat fluxes, 8 cal/sec-cm^2 at 1 atm and 4 cal/sec-cm^2 at 21.4 atm. Konev recognized that, under some conditions, externally imposed radiation is equivalent to increasing the initial temperature of the propellant. However, he did not develop the equations showing this relationship. Later Konev and Khlevnoi[3] considered analytically the complex interaction by which radiation transmitted below the propellant surface may accelerate (by simple heating) the condensed phase heating processes; they showed that the degree of acceleration depends on the ratio of radiation absorption length to subsurface reaction thickness.

At Princeton University,[4] experiments were carried out in which carbon-arc radiation was imaged onto burning ammonium perchlorate (AP) composite propellant. However, efforts to obtain consistent burning rate measurements as a function of radiant heat flux were hampered by ejection of AP particles from the surface. The radiation was partially transmitted through the individual AP crystals and concentrated at the AP/binder interface and, thereby, produced subsurface ignitions at the AP/binder interface.

Investigators at Brigham Young University[5-6] evaluated the effect of radiation on burning rate by placing propellants in a furnace (max temp was 1100K) at pressures between 0.4 and 1.4 atm. The maximum heat flux they obtained was 2.6 cal/sec-cm^2. Investigators at the University of Utah,[7] made measurements at one atm using heat fluxes up to 15 cal/sec-cm^2. They found that the effects of radiation on burning rate were appreciable.

Thompson and Suh[8] examined the same problem both theoretically and experimentally; they concluded that fluxes up to 1.5 cal/cm^2-sec have no significant effect on burning rate of M-2 double base propellant.

In this study, we directed our attention at obtaining burning rate data at higher pressures and higher heat fluxes and at providing a more complete treatment of the relationships between externally imposed energy and temperature sensitivity of burning rate data.

Analysis

Predictions of radiation effects on burning rate must account for the complex interplay between the increased gas velocities in the flame zone (resulting from the burning rate increase) and the changes in the heat feedback from flame and surface zones. A conventional analytical approach would be to add an externally imposed radiation term to one of the existing flame models. Predictions using such theories[6,7] require a rather

Received May 6, 1974; revision received August 19, 1974. Based on work performed in the Aerospace and Mechanical Sciences Department under Grant AF74-2602 from the Energetics Division, Air Force Office of Scientific Research.

Index category: Combustion Stability, Ignition, and Detonation; Fuels and Propellants, Properties of.

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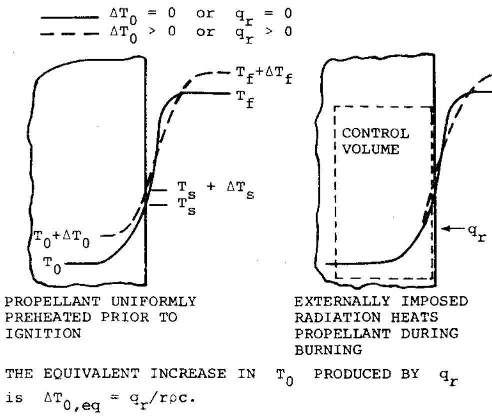

Fig. 1 During steady-state burning, externally imposed radiation produces increased burning rates similar to those obtained by increasing the initial temperature of the propellant.

detailed knowledge of surface temperature, surface reaction processes, and flame zone kinetics. In this paper, we have avoided the uncertainties of those parameters and processes and employed a prediction technique that requires only $r(p, T_o)$, specific heat, and density data.

In the equation development, we assume that the important condensed phase reactions occur in a layer that is thin compared to both the thermal wave depth and the radiation penetration depth. The former comparison is generally accepted to be valid for the range of burning rates encountered here (at 0.2 cm/sec the reaction layer in a PNC/MTN propellant is less than one-tenth the thermal wave thickness[9]). The latter comparison is similar; the radiation penetration is comparable to the thermal wave thickness (see absorptivity data below). Temperature sensitivity of burning rate, σ_p, was taken to be constant, a good approximation for most propellants. Writing the energy balance across the control volume shown in Fig. 1 and noting that under steady-state conditions (with the above assumptions) the spatial distribution of temperature and the transmitted radiation need not be accounted for when the control volume includes the significant portion of the temperature profile and the depth to which radiation is absorbed

$$r\rho c T_o = r\rho c T_s(r) - \lambda dT/dx)_s - q_r \tag{1}$$

where q_r is the portion of incident radiation that is absorbed.

There is some equivalent value of initial temperature, $T_{o,\mathrm{eq}}$, that corresponds to the burning rate enhancement by external radiation, q_r. Thus,

$$\lambda dT/dx)_s = r\rho c[T_s(r) - T_{o,\mathrm{eq}}] \tag{2}$$

From the definition of constant σ_p, the $T_{o,\mathrm{eq}}$ corresponding to a particular burning rate r is

$$T_{o,\mathrm{eq}} = (1/\sigma_p)\ln(r/r_{\mathrm{ref}}) + T_{o,\mathrm{ref}} \tag{3}$$

Substituting Eqs. (2) and (3) into Eq. (1) and simplifying yields

$$r = r_{\mathrm{ref}} \exp[\sigma_p(T_o - T_{o,\mathrm{ref}}) + \sigma_p q_r/(r\rho c)] \tag{4}$$

which is an implicit expression for r in terms of the externally imposed heat flux abosrbed by the propellant. Note that since T_s is eliminated, $T_s(r, p, \ldots)$ data are not required. The secant method was used to solve Eq. (4) for r.

As shown in Fig. 1 and Eq. (4), q_r produces an effect equivalent to increasing the initial temperature by an amount $\Delta T_o = q_r/r\rho c$. If the surface temperature is expressed in terms of an Arrhenius type pyrolysis law, $r = A_s \exp(-E_s/RT_s)$, the corresponding increase in surface temperature is

$$\Delta T_s = (RT_s^2\sigma_p/E_s)(q_r/r\rho c) \tag{5}$$

The increase in flame temperature is

$$\Delta T_f = q_r/(r\rho c_f) \tag{6}$$

Comparison of Theory with Experimental Results

A xenon arc-image furnace was modified to obtain $r(p, I)$ data. A drive mechanism was devised to maintain the burning surface of a strand at the focus of the arc. Thus, as the strand was burned, the linear positioning rate was adjusted until it was equal to the burning rate. Using this technique, several centimeters of the strand were burned while the linear rate was recorded on an oscillograph. A purge flow was used to rapidly sweep away propellant gases. This and the small diameter (0.25 cm) of the samples minimized the scattering gas/particle layer the incident radiation passed through. Thus, although no direct measurement was made, the attenuation of the flux by the flame is assumed to be negligible.

As indicated on Fig. 2, $r(I)$ data were obtained for two double base propellants. The nonplatonized propellant contains 53% nitrocellulose, 39% metriol trinitrate, 7% triethylene glycol dinitrate, 0.1–0.2% carbon powder plus stabilizers. The platonized propellant is similar but contains 1% lead salicylate and 1% copper salicylate added to accelerate burning rate and to produce plateau burning. For detailed information on these

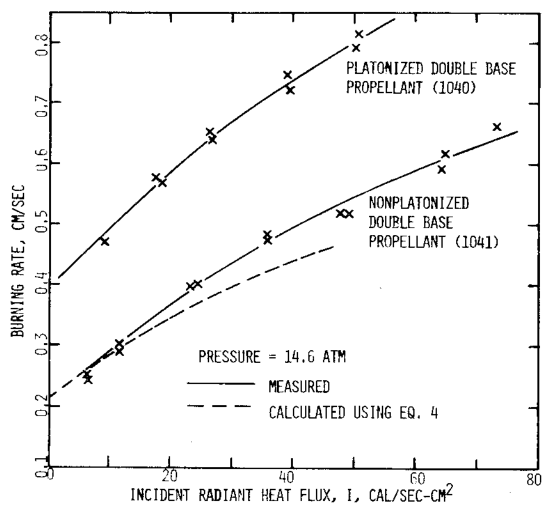

Fig. 2 Increase in burning rate produced by xenon arc radiation.

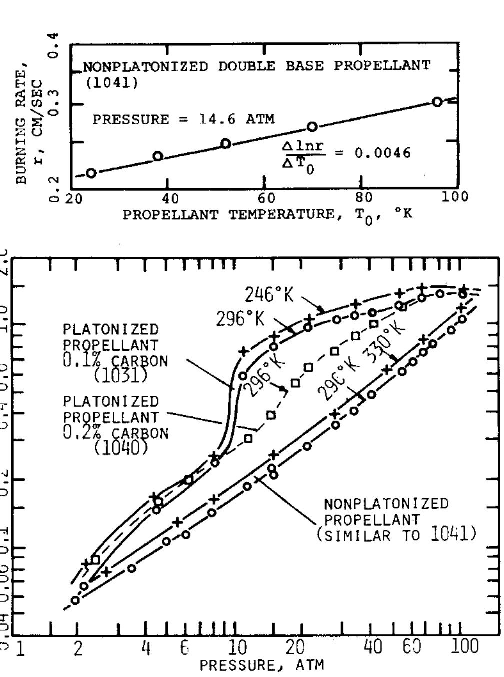

Fig. 3 Burning rate and temperature sensitivity data of three double base propellants.

propellants see propellants 1040 and 1041 described in Ref. 9. Burning rate data (Fig. 3) were obtained for the propellants at two temperatures over the pressure range from 2 to 100 atm using 0.6×0.6 cm strands in a temperature conditioned chimney burner. The nearly equal separation distances of the 296 and 330 K lines for the nonplatonized propellant indicate that σ_p is nearly constant over the pressure range. A wider range of temperatures was taken at 14.6 atm (the pressure of the $r(I)$ data], and from the $\ln r$ vs T_o plot the σ_p values were found to be nearly constant over the test range. The $r(p, T_o)$ data for the other platonized propellant (1031) are included to show the influence of ΔT_o on burning rate of a platonized propellant; $r(I)$ data are not available for 1031.

The measured[10] reflectivity of the cut propellant surfaces, averaged after weighting in accord with the spectral distribution of the arc, is approximately 0.06. Since the burning surface is generally covered with carbonaceous material there is no reason to believe that the reflectivity of the burning propellant is greater than the unburned surface. Reflectivity measurements[2] of extinguished propellant surfaces may not approximate the reflectivities of burning double base propellants since the extinguishment process removes much of the surface deposits.

The particulate additives tended to opacify the propellants.[10] Near the wavelength of the peak intensity of the xenon arc, the extinction coefficient of propellants 1040 and 1041 are about 80 and 50 cm^{-1} respectively, while the extinction coefficient of the basic propellant without particulate additives is about 5 cm^{-1}. Thus the propellants were opacified sufficiently that the catastrophic decomposition triggered by the absorption of radiation deep into the solid (i.e., wormholing) was not a consideration.

Table 1 Properties of nonplatonized double base propellants used in calculations

$p =$	14.6 atm
$r =$	0.215 cm/sec
$c =$	0.34 cal/g-K
$\rho =$	1.54 g/cm^3
$\sigma_p =$	0.0046 (K)$^{-1}$
Reflectivity $=$	0.06
$T_o =$	298 K

The values listed in Table 1 were used in Eq. (4) to obtain the calculated results shown on Fig. 2. Considering the simplicity of Eq. (4), the agreement between experiment and theory is reasonable. We do not have a complete explanation for the higher experimental burning rates; errors in the Table 1 values cannot account for the difference. It should be noted, however, that the higher fluxes correspond to quite large values of ΔT_o. The assumptions leading to Eq. (4) may break down if these high fluxes induce extensive surface reactions and, in effect, change the value of σ_p. In our continuing studies, we are also evaluating the possibility of photochemical effects enhancing the subsurface heat release or that near-surface "micro-wormholing" may increase the burning area at high fluxes. Still another possiblity is that radiative heating of the carbonaceous material above the propellant surface may accelerate reactions in the fizz zone of the double base propellant flame structure.

According to Konev and Khlevnoi (whose theory implicitly accounts for temperature sensitivity of burning rate in the nonradiation case),[3] the maximum purely thermal effect of external radiation occurs when the radiation penetration is large compared to the subsurface reaction layer thickness; this maximum effect is then equivalent to the same initial temperature increase utilized above. In other words, their maximum allowable increase is the same as that computed here by more straightforward means. Yet the experimental data appear to significantly exceed this limit.

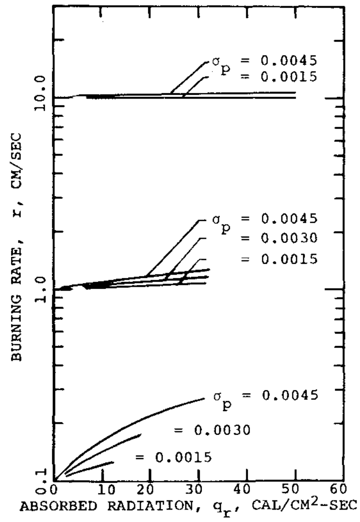

Fig. 4 Calculated results showing that degree of burning rate enhancement increases with decreasing burning rate and increasing temperature sensitivity.

It has been suggested[7] that radiation assisted burning experiments would provide sufficient information to determine the surface heat release, Q_s. However, since the externally imposed radiation alters the heat feedback from the flame zone, the experiment introduces an additional unknown into the energy equation, $\partial q_f/\partial q_r$, i.e.,

$$q_f \approx q_{f,n} + (\partial q_f/\partial q_r)q_r \tag{8}$$

Writing the energy equation so that it includes the gas phase adjacent to the surface,

$$r\rho c T_o = r\rho c T_s - r\rho Q_s - q_f - q_r \tag{9}$$

where Q_s is the heat of reaction at the surface. Solving for r yields,

$$r = \frac{q_{f,n}}{\rho[c(T_s - T_o) - Q_s]} + \frac{1 + (\partial q_f/\partial q_r)}{\rho[c(T_s - T_o) - Q_s]} q_r \tag{10}$$

While the magnitude of the factor multiplying q_r is the slope of the curves on Fig. 2, the experiment does not provide sufficient information to evaluate $\partial q_f/\partial q_r$. Thus, Q_s cannot be established from the $r(I)$ data alone. In Ref. 8, Q_s was determined from micro-thermocouple data and the energy balance at the burning surface.

Figure 4 illustrates the conditions under which external heating can be significant. The curves are calculated from Eq. (4). As burning rate increases, the effect is of secondary importance, as one would expect, because external radiant flux becomes small compared to the conductive fluxes in the flame zone.

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FEBRUARY 1975 AIAA JOURNAL VOL. 13, NO. 2

Sensitivity of Laser Absorption Wave Formation to Nonequilibrium and Transport Phenomena

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Experiments have shown that laser absorption waves (LAW's) may be ignited in air from aerosols or solid surfaces at laser intensities below the clean air breakdown threshold. We present detailed numerical calculations of the formation and structure of such LAW's made with a two-temperature, Lagrangian hydrodynamic computer program containing a fully coupled nonequilibrium breakdown chemistry, electron diffusion, and radiation transport. The detailed LAW structure is then interpreted to delineate the roles of the nonequilibrium, radiative, and transport processes in various regimes.

Nomenclature

c = velocity of light = 3×10^{10} (cm sec^{-1})
ΔE = $I_1 - I_2$
e = electron charge (esu)
f = laser flux (W cm^{-2})
$I_1(I_2)$ = ionization energy of the ground (first excited) state (ev)
I = $4\pi e^2/mc\omega^2 \simeq 2 \times 10^{-11}$ (ev cm^2 watt^{-1}) for $\hbar\omega$ = 0.12 ev
$m(M)$ = electron (atom) mass (gm)
n = electron number density (cm^{-3})
$N = N_1 + N_2 + n$ = total number of heavy particles (cm^{-3})
$N_1(N_2)$ = number density of atoms in the ground (first excited) state (cm^{-3})
$N_n = N_1 + N_2$ = total number of neutral particles (cm^{-3})
P = pressure (erg cm^{-3})
$R_a(T_g)$ = electron attachment rate = $\begin{cases} 1.7 \times 10^{-12} N(n-1) \text{ (Ref. 1)} & T_g < 0.4 \text{ ev} \\ 0 & T_g \geqq 0.4 \text{ ev} \end{cases}$
$R_{i1}(R_{i2})$ = electron impact ionization rate from the ground (first excited) state $\simeq$ $\bar{v}_{i1} \exp(-I_1/T_e)[\bar{v}_{i2} \exp(-I_2/T_e)]$ (Ref. 2)
R_r = radiative recombination rate $\simeq$ $1.3 \times 10^{-13} T_e^{-1/2}$ (Ref. 2)
R_x = electron impact excitation rate $\simeq$ $1.6 \times 10^{-8} \exp(-\Delta E/T_e)$ (Refs. 3, 4)
$\bar{R}_x, \bar{R}_{i1}, \bar{R}_{i2}$ = inverse rates of R_x, R_{i1}, R_{i2} from detailed balancing
$T_e(T_g)$ = electron (gas) temperature (ev)
$\bar{v}_{ei}(\bar{v}_{en})$ = electron ion (neutral) elastic collision rate $3.0 \times 10^{-6} T_e^{-3/2} (1.3 \times 10^{-7} T_e^{1/2})$ (Refs. 2, 4)
$\bar{v}_{i1}(\bar{v}_{i2})$ = electron impact ionization rates from ground (first excited) states $\bar{v}_{i1} \simeq 10^{-3}$ (cm^2 sec^{-1}) (Refs. 2, 5) $\bar{v}_{i2} \simeq 3.2 \times 10^{-7}$ (cm^2 sec^{-1}) (Ref. 2)
α = $\bar{v}_{i1} N_1$
β = $(Lf\bar{v}_{en}/\Delta E \bar{v}_x)^{I_1/\Delta E}$
γ = specific heat ratio = C_p/C_v
δ = $(1+\phi)\bar{v}_{en} N_1 I f/(I_1 + \phi I_2)$
θ = $\bar{v}_{i1}/\bar{v}_x$
ϕ = $\bar{v}_{i1}/\bar{v}_{i2}$
ρ = density (g cm^{-3})
σ = photoionization cross section in nitrogen, $\simeq 8 \times 10^{-18}$ cm^2 (Ref. 2)
ω = laser frequency (sec^{-1})

Presented as Paper 74-229 at the AIAA 12th Aerospace Sciences Meeting, Washington, D.C., Jan. 30–Feb. 1, 1974; submitted Feb. 14, 1974; revision received July 15, 1974.

Index categories: Lasers; Plasma Dynamics and MHD.

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Introduction

COLD clean air breaks down at a threshold CO_2 laser flux of a few times 10^9 W/cm^2,[6,7] but it has been found that in the presence of either solid surfaces or aerosols it may break down in fluxes considerably lower than the clean air breakdown threshold. Once formed, the resulting plasmas may be maintained by fluxes as low as a few times 10^4 W/cm^2.[8,9] These plasmas, which propagate up the beam at well-defined velocities, are called laser supported absorption waves, or "LAW's." The evolution of such LAW's may be divided into three consecutive phases: ignition, formation, and maintenance, each of which is, at present, better understood than the last. These phases refer respectively to the detailed evolution of the solid target material into a plasma, the formation of a LAW in the air ahead of this plasma, and its steady-state propagation in air up the laser beam.