Solid Propellant Sandwich Deflagration Analysis

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A theoretical solution has been obtained for the shape of a deflagrating ammonium perchlorate surface when it is adjacent to an inert, pyrolysing, dry binder. The eigenvalue, the regression rate, is shown to be independent of binder type and very close to the burn rate of pure *AP*, as has been experimentally observed. A slope discontinuity of the surface should exist at the binder-oxidizer interface and typical binders should incline very near to 90° to the nearly horizontal *AP* surface, at the junction of the two. The transition from *AP* to binder should take place on a distance scale of the order of microns and all results are quite insensitive to pressure level.

Nomenclature

a $= g+2q_R Y_F$
b = pyrolysis law constant of vapor pressure constant
$\tilde{b}$ = dimensionless pyrolysis law constant or vapor pressure constant
c_s = solid phase specific heat
c_p = specific heat at constant pressure for gas phase
c = flame standoff distance
C = deviation of c from planar *AP* case
E = activation energy
g $= T/T_o$
$\mathscr{G}$ = deviation of temperature from planar *AP* case
G_o, G_1 = solid phase temperature perturbation constants
k = preexponential factor in reaction rate law
$\tilde{k}$ = dimensionless preexponential factor in reaction rate law
m, m_g = constants in eigensolution
n = coordinate normal to the solid-gas interface directed toward the gas phase
p = pressure
Q = reaction integral defined by Eqs. (18)
q = exothermic reaction heat in gas phase, endothermic in solid phase
R = universal gas constant
Re = Reynolds number
r, r_n = burn rate and regression rate normal to surface, respectively
T = temperature
v = gas velocity in y direction
w_F = production rate of NH_3
x, y = coordinates
Y = perturbed y position of solid surface
Y_k = mass fraction of species k
γ = deviation of mass fraction from planar *AP* case
z $= (1+(dy_s/dx)^2)^{1/2}$
α = thermal diffusivity, $\lambda/\rho c_p$
δ = inclination angle of binder
ε = dimensionless activation energy, E/RT
$\tilde{\eta}$ $= c_s/c_p$
λ = thermal conductivity
ξ $= c_p \lambda_s/c_s \lambda_g$
ρ = density
θ = inclination angle of solid *AP* surface

Subscripts

B = binder
f = flame temperature
F $= NH_3$
g = gas phase
o = cold solid
s = solid phase or surface
1 = quantity evaluated at flame standoff position

Superscripts

$\bar{\ }$ = quantity evaluated for the one-dimensional *AP* deflagration
$'$ = ordinary derivative with respect to x
$*$ = dimensional quantity
$\sim$ = solid phase perturbation function

Introduction

A SUBSTANTIAL number of experimental investigations of composite solid propellant ingredient behavior have dealt with the sandwich configuration.[1-8] By a sandwich is meant a slab of oxidizer, usually ammonium perchlorate (*AP*) in the cited investigations, adjacent to a slab of polymeric fuel. This two-dimensional configuration is an important experimental configuration for the study of phenomena taking place near the binder-oxidizer interface during a deflagration process. By removing the difficulties of viewing the interface details in a real three-dimensional composite solid propellant, much information has been gathered concerning the behavior and existence of binder melts, catalytic additives, the relative importance of *AP*-binder reactions in driving the deflagration rate, fluid mechanical instabilities during deflagration, and the behavior of aluminum when placed into the sandwich.

In contrast to the many experimental studies there have appeared no analyses of the sandwich deflagration process with *AP* oxidizer which had as a goal the prediction of the actual shape of the gas-condensed phase interface. Bakhman and Librovich[9] theoretically investigated a semi-infinite slab of oxidizer adjacent to a semi-infinite slab of fuel, but the oxidizer was not assumed to be capable of self-deflagration. Nachbar[10] investigated a periodic, two-dimensional array of oxidizer and fuel slabs as a model of an actual propellant. The goal was to predict a mean deflagration rate without predicting an actual achieved two-dimensional surface shape. Again, the oxidizer was assumed incapable of self-deflagration.

The need for an analytical model capable of prediction of the surface shape for an *AP* oxidized sandwich becomes apparent when trying to reason the behavior which is experimentally observed. Even in this two-dimensional configuration the problem is highly complex due to a) the appearance of binder melts, b) three phase heat transfer and one phase (perhaps two phase) mass transfer, c) two-dimensional heat and mass transfer, d) nonlinearities in the governing equations due to at least chemical reaction and an unknown surface shape, e) multiple chemical reactions and condensed phase reactions, f) a mathematically elliptic problem in an infinite region and g) the appearance of an eigenvalue—the deflagration rate. Under these

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difficulties an attempt to reason on a qualitative basis, given experimental information, is hampered by the lack of some computational framework and predictive capability.

A previous initial step toward providing a theory of the sandwich deflagration process[13] failed to yield the burn rate as an eigenvalue of the problem. Furthermore, an analytical error has been discovered in that treatment and the results are consequently in error. The current treatment corrects the error and recovers the burn rate as an eigenvalue of the problem by a more complex solution of the problem.

From a practical standpoint there are two major reasons for treating this problem. The first is to obtain an idea of the distance scales involved in the problem. That is, how far do the influence of the binder and oxidizer penetrate into each other? If these distance scales are small enough, this interface theory may be used in theory of an actual propellant. Secondly, the actual burn rate is desired. Is the influence of the binder on the self-deflagrating *AP* strong or weak? The current analysis addresses these issues.

Analysis

Model Construction and Assumptions

Given the complicated nature of the problem, a model is first sought which uses available experimental information liberally but which still does not overly restrict the model in interpretation of experimental results. Accordingly, the initial model uses the following observations:

a) Far from the binder-oxidizer interface, the *AP* regresses as pure *AP*. Furthermore, for binder thicknesses of the order used in some of the experimental studies (≈ 150 μm) there is little effect of one side of a sandwich upon the other side even when dissimilar materials are used. Therefore, the initial model development is concerned with a semi-infinite slab of *AP* against a semi-infinite slab of binder.

b) A steady-state is achieved experimentally with *AP* oxidizer. Consequently, time dependence is assumed absent.

c) For uncatalyzed sandwiches, the experimental results show very little effect of the binder-oxidizer reactions upon the surface profile. That is, the heat feedback from the binder-oxidizer reactions does not drive the overall deflagration rate; the *AP* self-deflagration is responsible for the overall deflagration rate at pressures removed from the low pressure deflagration limit and below 2000 psia. The initial model is therefore constructed assuming binder-oxidizer reactions to have negligible rate. This does not mean that a diffusion flame between the binder and oxidizer is absent, but it means this flame is not close enough to the interface to play a role in the deflagration behavior. Furthermore, the effect of catalysis is not treated.

The initial model therefore asks the question of the surface shape attained by a semi-infinite slab of *AP* which pyrolyzes a semi-infinite slab of binder. Posed in this manner, it is immediately recognized that the problem has neither a unique solution nor a steady solution because a) the final shape would depend upon the geometry of ignition, and b) it would take an infinite time to establish a steady profile in a semi-infinite slab of inert binder. The ignition problem is seen by imagining two cases—one in which ignition is achieved by a line heat source (say an ignition wire) and a second in which ignition is achieved uniformly over the entire *AP* surface. In the first case the *AP* would take on the shape of ever-increasing circular radii from the ignition point. In the second case the *AP* would deflagrate in a planar fashion except in the vicinity of the binder. However, these comments neglect the fact that the inert nature of the binder may affect the shape attained by the *AP*, even far away from the binder. Surely, at long enough time the profile in the interface vicinity will have become shape-invariant, but it is not obvious that the *AP* will be horizontal (assuming top-to-bottom deflagration). In fact, this is to be determined by the solution. Concerning the binder, it appears clear that after a sufficiently long time the processes in the interface vicinity will not depend upon processes taking place at a large vertical distance from the interface. Consequently, local steadiness may be presumed, as, in fact, it experimentally occurs.

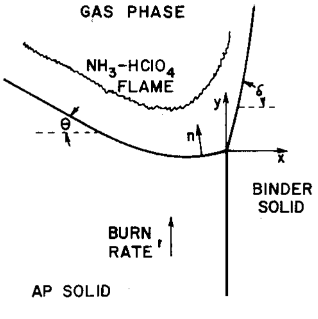

Fig. 1 Sandwich schematic and the coordinate system.

For this initial model, the absence of binder melts will be assumed. The limits of validity will then be determined by comparison of the model and experimental results. For the *AP* deflagration process, the Guirao-Williams model[11] is accepted with an equilibrium assumption for the gas-solid (or viscous liquid) *AP* interface. Some minor modifications are introduced into this model for computational convenience; these will now be described. Use of this model will restrict the sandwich theory validity to the pressure range 20–100 atm, because there is no *AP* theory capable of an explanation of observed phenomena above 100 atm and the low pressure deflagration limit of *AP* occurs near 20 atm.

Other usual assumptions are made to simplify the analysis which, while they lead to numerical error of order unity, do not alter significantly the scaling rules developed with respect to other variables. These assumptions are: a) the thermal and transport processes of the solid *AP* and binder are identical, b) the thermal and transport properties of all gas phase species are identical, c) the Lewis number is everywhere unity in the gas phase, d) the deflagration process takes place at constant pressure, e) heat conduction and mass transfer take place by temperature and concentration gradients, only, respectively, and the transport coefficients are independent of temperature in both the solid and gas phases. A final major assumption is that on any vertical line parallel to the binder-oxidizer interface the ρv product (density times velocity) is that as determined in the solid phase and all lateral velocities are zero (strictly true in the solid phase). This is in the spirit of the Burke-Schumann approximation as expounded in Ref. 12. This does yield error in convection effects upon heat transfer, but exact treatment of the problem appears too complex at the present time.

The configuration is shown in Fig. 1, in which the coordinate system is rendered stationary by a translation of the interface in the y direction at the rate r. Under the stated assumptions, the equations for solution and the boundary conditions are:

Gas Phase Species Continuity:

$$\lambda_g^* \left(\frac{\partial^2 Y_F^*}{\partial x^{*2}} + \frac{\partial^2 Y_F^*}{\partial y^{*2}} \right) = \rho^* v^* (\partial Y_F / \partial y^*) - w_F^* \tag{1}$$

$$\frac{\lambda_g^*}{c_p^*} \left(\frac{\partial^2 Y_B}{\partial x^{*2}} + \frac{\partial^2 Y_B}{\partial y^{*2}} \right) = \rho^* v^* \frac{\partial Y_B}{\partial y} \tag{2}$$

Rate Law:

$$w_F^* = -k^* Y_F^{\,2} e^{-E_g^*/R^*T^*} \tag{3}$$

Gas Phase Heat Transfer:

$$\lambda_g^* \left(\frac{\partial^2 T^*}{\partial x^{*2}} + \frac{\partial^2 T^*}{\partial y^{*2}} \right) = \rho^* v^* c_p^* \frac{\partial T^*}{\partial y^*} + 2 q_R^* w_F^* \tag{4}$$

Solid Phase Heat Transfer:

$$\lambda_g^* \left(\frac{\partial^2 T^*}{\partial x^{*2}} + \frac{\partial^2 T^*}{\partial y^{*2}} \right) = \rho^* v^* c_s^* \frac{\partial T^*}{\partial y^*} \tag{5}$$

Boundary Conditions:

$$\begin{aligned} Y_F(x,\infty) &= 0 & Y_F(-\infty, y) &= \bar{Y}_F(y) \\ T^*(x,-\infty) &= T_o^* & T^*(-\infty, y) &= \bar{T}^*(y) \\ T^*(\infty, y) &= T_o^* & T^*(x, \infty) &= T_o^* \end{aligned} \tag{6}$$

$$r_{n_B}{}^* = \vec{r}^*\cdot\vec{n}^*\big|_B = b_B{}^*\exp(-E_{s_B}{}^*/R^*T_s{}^*) \tag{7}$$

$$\lambda_g{}^*(\partial T^*/\partial n^*)\big|_{s+} = \rho_S{}^*r_n{}^*q_S{}^* + \lambda_g{}^*(\partial T^*/\partial n^*)\big|_{s-} \tag{8}$$

$$\rho^*D^*(\partial Y_F/\partial n^*)\big|_{s+,\,AP} = -\rho_s{}^*r_n{}^*(\tfrac{1}{2} - Y_{F_s}) \tag{9}$$

$$\rho^*D^*(\partial Y_B/\partial n^*)\big|_{s+,\,AP} = \rho_s{}^*r_n{}^*Y_{B_s} \tag{10}$$

$$p_{F_s}{}^* = b_F{}^*\exp(-E_{s_F}{}^*/R^*T_s{}^*) \tag{11}$$

where T^* is continuous, and ∇T^* is continuous within a phase. The products of AP gasification are assumed NH_3 and $HCl0_4$ which are assumed identical molecules for mass transfer computation. k^* is a rate coefficient for the assumed second-order reaction. As written in Eq. (3) k^* is not a fundamental pre-exponential constant but already has molecular constants and a factor p^{*2} absorbed into it. The factor 2 in front of $q_R{}^*w_F{}^*$ in Eq. (4) occurs because $q_R{}^*$ will be quoted per unit mass of AP rather than per unit mass NH_3. The equilibrium interface on AP is specified through Eq. (11). The formulation, as far as the AP deflagration process is concerned, differs from that of Ref. 11 in the following respects: a) no dilution of the NH_3 and $HCl0_4$ is assumed at the solid-gas interface, although it is tacitly accounted for by the choice of a number for $q_S{}^*$; b) calculations are simplified by taking the molecular weight of all species to be the same. The constants k^* and $b_F{}^*$ will be so chosen to recover the same burn rate and surface temperature results as in Ref. 10.

Equation (7) is the pyrolysis law for the binder, Eq. (8) is the energy conservation law at the solid-gas interface, and Eqs. (9) and (10) are the interface diffusion laws. Note in Eq. (8) that $q_S{}^*$ undergoes a discontinuity at the binder-oxidizer interface and Eqs. (9) and (10) are only valid on the AP side of the interface. Shown in Table 1 are typical values used in this work for the various parameters.

Table 1 Numerical values for various parameters

Quantity	Value	Reference
$T_o{}^*$	300 K	assumed
$\rho_s{}^*$	1.95 gm/cm^3	11
$c_p{}^*$	0.3 cal/gm K	11
$c_s{}^*$	0.3 cal/gm K	11
$q_R{}^*$	173 cal/gm	[to yield flame temperature of 1205 K of Ref. 11]
$q^*_{S_{AP}}$	− 100 cal/gm	11
$\lambda_g{}^*$	10^{-4} cal/cm sec K	11
$\lambda_s{}^*$	9×10^{-4} cal/cm sec K	11
$E_g{}^*$	15 kcal/mole	11
$E_s{}^*$	30 kcal/mole	11
$E_{s_B}{}^*$	8.7–17 kcal/mole	14
$b_B{}^*$	1–150 cm/sec	14
$q_{s_B}{}^*$	160–1004 cal/gm	14

Mathematical Character of the Problem

Equations (1–5) define an elliptic problem in the sense that what happens at one point in the field affects every other point. Furthermore an eigenvalue appears, $\rho^*v^* = \rho_s{}^*r^*$.

If the binder is hard to decompose and it assumes a nearly vertical surface, it appears obvious that the picture becomes one of a (nearly) flat plate of binder over which hot AP gases are flowing. If the Reynolds number based on distance along the binder were large enough this would revert to a parabolic problem because $\partial/\partial x \gg \partial/\partial y$ would result. However, exactly at the binder-oxidizer interface, the Reynolds number is zero. Since it is precisely this region that is of interest, the full elliptic problem must be solved. To gain an idea of magnitudes involved here the equations are nondimensionalized with respect to a distance scale $\alpha_s{}^*/r^*$ and temperature $T_o{}^*$. Heats of gasification are made dimensionless by $c_p{}^*T_o{}^*$ and activation energies by $R^*T_o{}^*$. To locate the condensed phase—gas phase interface at a constant position the y variable is replaced by $\eta = y - y_s(x)$. The resulting dimensionless equations and boundary conditions are

$$L[Y_F] = \tilde{k}Y_F{}^2e^{-\varepsilon_g/g}$$
$$L[Y_B] = 0$$
$$(\text{Gas})\ L[g] = -2q_R\tilde{k}Y_F{}^2e^{-\varepsilon_g/g}$$
$$(\text{Solid})\ L[g] = (1-\xi)g$$
$$L = \frac{\partial^2}{\partial x^2} + z^2\frac{\partial^2}{\partial\eta^2} - 2y'_s\frac{\partial^2}{\partial\eta\,\partial x} - y''_s\frac{\partial}{\partial\eta} - \xi\frac{\partial}{\partial\eta}$$
$$Y_F(x,\infty) = 0 \qquad Y_F(-\infty,y) = \bar{Y}_F(y)$$
$$g(x,-\infty) = 1 \qquad g(-\infty,y) = \bar{g}(y)$$
$$g(\infty,y) = 1 \qquad g(x,\infty) = 1$$
$$1/z_B = \tilde{b}_B\exp(-\varepsilon_{S_B}/g_s)$$
$$\partial g/\partial n\big|_{s+} = \xi[q_s/z + \tilde{\eta}\,\partial g/\partial n\big|_{s-}]$$
$$\partial Y_F/\partial n\big|_{s+_{AP}} = -(\xi/z)(\tfrac{1}{2} - Y_{F_s})$$
$$\partial Y_B/\partial n\big|_{s+_{AP}} = \xi(Y_{B_s}/z)$$
$$Y_{F_s} = \tilde{b}_F\exp(-\varepsilon_{s_F}/g_s) \tag{12}$$

where g is continuous, and ∇g is continuous within a phase. Since y' and y''_s are unknowns, the nonlinear character in Eqs. (12) is apparent. Nonlinearities also arise from the chemical reaction terms. The dimension $\alpha_s{}^*/r^*$ is known to be the "thickness" of the thermal wave which would occur in a planar regression. It is the reference dimension here. The parameter ξ in Eqs. (11) is nothing more than the ratio of a characteristic solid phase dimension $(\alpha_s{}^*/r^*)$ to the characteristic gas phase dimension $(\alpha_g{}^*/v^*)$. If there were no modification due to the reaction rate term, the gas phase distance over which significant heat transfer would occur would be of the order of $\alpha_g{}^*/v^*$. Using the parameters of Table 1, $\xi = 9.0$, showing that the gas and solid phase characteristic scales are quite different. Furthermore, constructing the Reynolds number based upon y, it is found that $Re_y = \xi y$, so that when y is of the order of $1/\xi$ a transition is taking place between "low" and "high" Reynolds numbers. If important field quantity variations are taking place only over a gas phase distance of the order of $1/\xi$, the problem must be treated as elliptic with no simplications possible through a boundary-layer assumption. However, a rather simple method of solution will emerge if at some point in the flowfield the boundary-layer approximation may be involved. The use of this approximation will be illustrated.

Solution by an Integral Technique

Pure AP deflagration

Far from the binder the AP must undergo a planar deflagration but the angle θ is unknown; it is the eigenvalue of the problem. All x-derivatives must vanish and Eqs. (12) become nonlinear ordinary differential equations in η along with the appropriate boundary conditions. The equation for the solid phase heat transfer may be solved exactly. The solution is

$$\bar{g} - 1 = (\bar{g}_s - 1)e^{\eta/z^2} \tag{13}$$

An overall energy balance yields the adiabatic flame temperature

$$\bar{g}_f = \bar{g}_s + q_R - q_s - \tilde{\eta}(\bar{g}_s - 1) \tag{14}$$

A first integral of the gas phase heat and mass transfer equations, subject to the boundary conditions, is

$$\bar{a}(\eta) \equiv \bar{g}(\eta) + 2q_R\bar{y}_F(\eta) = \bar{g}_f = \bar{g}_s + 2q_R\bar{Y}_{F_s} \tag{15}$$

The solution is completed by assuming a functional form for $g(\eta)$ as

$$\begin{aligned} \bar{g}(\eta) - \bar{g}_s &= (\bar{g}_f - \bar{g}_s)\frac{\eta}{\bar{c}} \qquad && \eta < \bar{c} \\ \bar{g}(\eta) &= \bar{g}_f && \eta \geqq \bar{c} \end{aligned} \tag{16}$$

where $\bar{c}$ is the η position where $\bar{Y}_F(\eta)$ vanishes, i.e. reaction is complete. Now integrating the gas phase energy equation between $\eta = 0$ and $\eta = \bar{c}$ using the assumed form for $\bar{g}(\eta)$ from Eq. (14), using the solid-gas interface boundary conditions and the equilibrium condition from Eqs. (12), the solution for the AP deflagration is completed as

$$\bar{c} = [Y_{F_s} z^2/\xi(\tfrac{1}{2} - \overline{Y}_{F_s})]$$

$$Q(\bar{c}) = \tilde{k}\overline{Y}_{F_s}{}^2\bar{c}\int_0^1 \left(1 - \frac{\eta}{\bar{c}}\right)^2 \exp\left\{-\varepsilon_g \Big/ \left[\bar{g}_s + (\bar{g}_f - \bar{g}_s)\frac{\eta}{\bar{c}}\right]\right\} d\left(\frac{\eta}{\bar{c}}\right)$$

$$= Y_{F_s}\left(\frac{z^2}{\bar{c}} + \xi\right) = \xi/2, \quad \overline{Y}_{F_s} = \tilde{b}_F \exp(-\varepsilon_{s_F}/\bar{g}_s) \tag{17}$$

An extremely important point to note from Eqs. (17) is that they imply that the regression rate normal to the gas-solid interface is independent of $\overline{\theta}$, the inclination to the horizontal. For note, $Q(\bar{c})$ is an invariant. For a fixed $\bar{g}_s$, $\overline{Y}_{F_s}$ is fixed and $\bar{c} \propto z^2$. Therefore, $Q \propto \tilde{k}\overline{Y}_{F_s}{}^2\bar{c} \propto \tilde{k}z^2$. But $\tilde{k} \propto 1/r^2$ so that $r \propto z$ and $r_n = r\cos\theta = r/z$ is an invariant. Consequently, for any sandwich vertical regression rate r which is the eigenvalue of the problem, the AP far from the binder will regress normal to its surface at a fixed, unique value. The pertinent values for AP combustion are consequently only presented for $\overline{\theta} = 0$. To numerically complete the solution the following procedure is used: a) $\bar{g}_s$ is given as a function of pressure.[11] b) Equation (14) yields $\bar{g}_f$ (which is actually constant here because $\bar{\eta} = 1$ and q_R and q_s are assumed independent of pressure). c) Equation (15) determines $\overline{Y}_{F_s}$. d) Equations (17) determine $\bar{c}$, $\tilde{b}_F$, and $\tilde{k}$.

From the nondimensionalization procedure it may be recalled that $\tilde{k} \propto p^2/\bar{r}^2$. Therefore, if the rate $\bar{r}$ is known at one pressure, it is known as a function of pressure. Shown in Table 2 are complete calculations for two sample pressures. In Table 2 it will be noted that b_F is not quite constant. This is due to the use of a slightly higher E_{s_F} than in Ref. 10. Furthermore, $\tilde{k}$ is not quite proportional to $(p/\bar{r})^2$. This is because $\bar{r}$ in Table 2 is the experimental value, and it is known that between the two values of pressure of Table 2 the theory of Ref. 11 slightly overestimates the pressure sensitivity of the deflagration rate. These details are not considered important for the current theory because a precise model for AP deflagration is not sought; only the deviations from a planar regression, due to the binder presence, are required and the previous theory appears adequate to serve as a baseline for perturbations due to the binder.

Perturbed Solution

It is noted that there is only a very weak variation of the dimensionless parameters with pressure in Table 2 (because $\bar{g}_s$ variations are weak with pressure), and therefore Eqs. (17) are nearly pressure invariant. Consequently, all further work will be carried out for the conditions that $\bar{g}_s = 2.93$ corresponding to $p = 54.4$ atm $= 800$ psia.

Upon extensive investigation of the partial differential equations for small deviations from the one-dimensional regression it was determined that: a) the deviations from the planar case in the gas phase could be expected to be simple deviations from the planar solution, but b) the solid phase deviations may be complex. By "simple" it is meant that the deviation is not oscillatory. Thus, if $g(x, y) = \bar{g}(x) + \mathscr{G}(x, y)$ where $\mathscr{G}(x, y)$ is the deviation from the pure AP case, $\mathscr{G}(x, y)$ may be expected to have monatonic behavior in y between the two end values $\mathscr{G}[x, y_f(x)]$. Therefore it was decided to attempt an integral solution where

$$\begin{aligned}
Y_F &= Y_{F_s}(x)\{1 - [\eta/c(x)]\} && \eta < c \\
Y_B &= Y_{B_s} + (Y_{B_c} - Y_{B_s})(\eta/c) && \eta < c \\
Y_F &= 0 && \eta > c \\
g - g_s(x) &= [g_1(x) - g_s(x)][\eta/c(x)] && \eta < c
\end{aligned} \tag{18}$$

are guessed forms of the solution for the gas phase.

If the Eqs. (18) are placed in Eqs. (12) and integrated from $\eta = 0$ to $c(x)$ the result is three nonlinear ordinary differential equations in the unknowns Y_{F_s}, Y_{B_s}, Y_{B_c}, c, g_1, g_s, y_s', and the η derivatives of g and Y_B at $\eta = c$. These derivatives appear because no functional form is specified for $\eta > c$. It is anticipated that these derivatives will be very small beyond the reaction region and one possible assumption is that they are zero. An alternate assumption has been employed and will be discussed. The diffusion boundary conditions and the equilibrium interface boundary condition provide three more relations for the nine unknowns. At $\eta = c$ which is of the order of magnitude of $1/\xi$, the Reynolds number is making a transition from low to high values, and it appears at this point reasonable to assume that $(\partial/\partial x) \gg \partial/\partial y = (\partial/\partial\eta)$. Making this assumption in Eqs. (12) there results

$$\begin{aligned}
\left.\frac{\partial g}{\partial \eta}\right)_{\eta=c} &= \frac{1}{\xi}\left.\frac{\partial^2 g}{\partial x^2}\right)_{\eta=c} = \frac{1}{\xi}\frac{d^2 g_1}{dx^2} \\
\left.\frac{\partial Y_B}{\partial \eta}\right)_{\eta=c} &= \frac{1}{\xi}\left.\frac{\partial^2 Y_B}{\partial x^2}\right)_{\eta=c} = \frac{1}{\xi}\frac{d^2 Y_{B_c}}{dx^2}
\end{aligned} \tag{19}$$

Eqs. (19) eliminate two of the previous unknowns, and one further relation is needed. For algebraic simplicity another differential equation is obtained by taking an η-moment of the equation $L[a] = 0$ $a = g + 2q_R Y_F$, derivable from Eqs. (12), and integrating from o to c.

For a numerical integration to proceed smoothly to $x = -\infty$ an asymptotic solution is desirable. Consequently, a solution was first sought which is a small perturbation about the planar AP deflagration state. Letting

$$\begin{aligned}
Y_{F_s} &= \overline{Y}_{F_s} + \gamma_{F_s}(x) & g_1 &= \bar{g}_1 + \mathscr{G}_1(x) \\
g_s &= \bar{g}_s + \mathscr{G}_s(x) & c &= \bar{c} + C(x) \\
y_s &= Y(x) & Y_{B_s} &= \gamma_{B_s}(x)
\end{aligned}$$

$$Y_{B_c} = \gamma_{B_c}(x)$$

substituting these forms into the nonlinear ordinary differential equations and boundary conditions, making use of the AP solution properties, and neglecting products and squares of perturbation quantities, there results the following linearized set of equations and boundary conditions

$$\tfrac{1}{2}[\overline{Y}_{F_s}C'' + \bar{c}\gamma_{F_s}''] + Y''\overline{Y}_{F_s} + \bar{y}_s'\gamma_{F_s}' = Q_{g_1}G + Q_{Y_{F_s}}\gamma_{F_s} + Q_c C + Q_{g_s}\mathscr{G}_s \tag{20}$$

$$\tfrac{1}{2}[\bar{c}\mathscr{G}_1'' + \bar{c}\mathscr{G}_s'' + C''(\bar{g}_s - \bar{g}_1)] + \frac{z^2}{\xi}\mathscr{G}_1'' = (\mathscr{G}_1 - \mathscr{G}_s)\left(\frac{z^2}{\bar{c}} + \xi\right) + 2\bar{y}_s'(\mathscr{G}_1' - \mathscr{G}_s') - \left(\frac{-2Y'\bar{y}_s'}{\bar{c}} + \frac{\bar{z}^2 C}{\bar{c}^2}\right)(\bar{g}_1 - \bar{g}_s) + Y''(\bar{g}_1 - \bar{g}_s) - 2q_R(Q_{Y_{F_s}}\gamma_{F_s} + Q_{g_1}\mathscr{G}_1 + Q_c C + Q_{g_s}\mathscr{G}_s) \tag{21}$$

$$\tfrac{1}{2}\bar{c}(\gamma_{B_c}'' + \gamma_{B_s}'') + \frac{\bar{z}^2\gamma_{B_c}''}{\xi} = \left(\xi + \frac{\bar{z}^2}{c}\right)(\gamma_{B_c} - \gamma_{B_s}) + 2\bar{y}_s'(\gamma_{B_c}' - \gamma_{B_s}') \tag{22}$$

$$(\gamma_{B_c} - \gamma_{B_s})\frac{\bar{z}^2}{\bar{c}} - \bar{y}_s'\gamma_{B_s}' = \xi\gamma_{B_s} \tag{23}$$

$$\bar{y}_s'\gamma_{F_s}' = -\xi\gamma_{F_s} + \frac{\bar{z}^2 C\overline{Y}_{F_s}}{\bar{c}^2} - 2\bar{y}_s'\overline{Y}_{F_s}Y' - \frac{\bar{z}^2}{\bar{c}}\gamma_{F_s} \tag{24}$$

$$\gamma_{F_s} = (\overline{Y}_{F_s}E_{s_F}/\bar{g}_s{}^2)\mathscr{G}_s \tag{25}$$

$$\mathscr{G}_1(-\infty) = \mathscr{G}_s(-\infty) = \gamma_{F_s}(-\infty) = \gamma_{B_c}(-\infty) = \gamma_{B_s}(-\infty) = Y'(-\infty) = C(-\infty) = 0 \tag{26}$$

Here Q_{g_1} Q_c, Q_{g_s} and $Q_{Y_{F_s}}$ are partial derivatives of the reaction rate integral which may be numerically evaluated. Note that

Table 2 One-dimensional AP deflagration results

p (atm)	$\bar{r}$ (cm/sec)	α_s/r (μm)	$\overline{T}_s$ (K)	$\bar{g}_s$	$\overline{Y}_{F_s}$	$\bar{g}_f$	$\bar{c}$	b_F (atm)	$\tilde{k}$
54.4	0.735	20.9	880	2.93	0.285	4.022	0.1471	4.38×10^8	2.62×10^6
100.0	1.000	15.3	911	3.04	0.258	4.022	0.1183	4.06×10^8	3.39×10^6

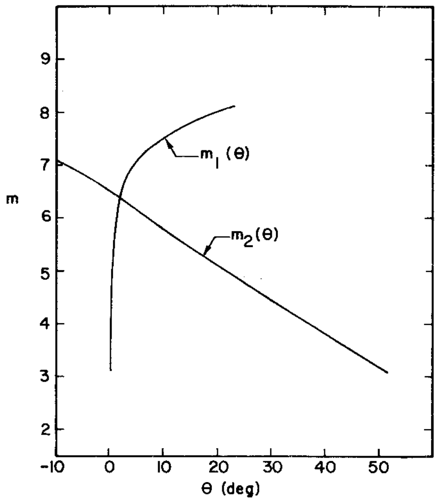

Fig. 2 Roots of the linearized sets of equations.

Eqs. (22) and (23) are decoupled from the rest of the system. Because Eqs. (20–26) are linear and homogeneous, they possess solutions like, say, $\mathscr{G}_1 = A_{\mathscr{G}1}\, e^{mx}$. Since $2Y_F + Y_B + Y_p = 1$, the binder equations must also have solutions $\gamma_{B_c} = A_{\gamma_{B_c}} e^{mx}$ where the m is the same. So there are two sets of equations which may be investigated. Since the equations are homogeneous, the determinant of the coefficient matrix must equal zero for a solution to exist. From Eqs. (20, 21, and 24) $m = m_1(\bar{\theta})$ is therefore developed. From Eqs. (23) and (24) $m = m_2(\theta)$ is developed and the results are shown on Fig. 2. Only real values of m were numerically investigated because the only unique solutions which will properly attach to the binder are for real m, as will be seen later. It is seen that there is a unique $\bar{\theta}$ for $m = 6.4$, $\bar{\theta} = 2°$. That is, an eigenvalue exists. The AP assumes a nearly horizontal surface far from the binder so that the burn rate is only slightly higher than the burn rate of pure AP. This result is independent of binder type and this is in accord with experimental observation. Since m appears in the equations only as m^2 or $m \tan\theta$, there exist solutions also for $m = -6.4$, $\theta = -2°$, which is merely the solution for the binder on the left and the oxidizer on the right in Fig. 1.

The perturbation solution is valid for $A_{\mathscr{G}1}$ positive or negative; however, the only physically realistic solutions occur for negative $A_{\mathscr{G}1}$ since the binder is a heat sink and will cool the gases of AP deflagration. In the perturbation solution (since the x and y origin is arbitrary) $A_{\mathscr{G}1}$ is set equal to -0.01 at $x = 0$ and all other quantities may be computed from the linear differential equations, knowing m and θ. The results for surface shape are shown in Fig. 3. Also shown are the temperature at the "edge" of the AP flame, the surface mass fraction of NGH_3, and the flame height. While this dimensionless solution is pressure invariant, the dimensional $x^* \propto \alpha_s^*/r^*$. At $p^* = 54.4$ atm this thermal wave depth α_s^*/r^* is 21 μm, and at 100 atm it is 15.4 μm. Consequently, the transition from planar AP regression to a severely changed profile occurs over very short distances and distances which are masked in the real case by binder melts and surface roughness. As one moves from left to right the solution predicts that all temperatures fall and the surface is convex from above. Also shown in Fig. 3 are the direction and relative magnitude of the solid phase heat transfer vector, which is analytically developed later.

The foregoing is an "eigensolution" to the AP problem and is independent of the binder causing the perturbation from a planar regression. However, the location of the binder depends upon the properties of this eigensolution and the physical properties of the binder. A question now to be asked is whether or not this linear solution may be used instead of a full nonlinear solution for binders of practical interest. The usual physical expectation is that a linearized theory will be reasonable if the perturbation quantities remain within some prescribed fraction of the corresponding baseline quantity. Viewing Fig. 3 and focusing on g_1, for example, if an arbitrary limit of validity is set that $(g_1 - \bar{g}_1)/\bar{g}_1 < 10\%$, it appears that the solution might be expected to be valid for $x < 0.6$. Adopting this criterion, a procedure to match to the binder is required for the linearized solution.

Location of the Binder

It will be noticed that the above solution is independent of the solid phase solution. In fact the heat transfer condition of Eqs. (12) and the surface temperature of the gas phase solution form boundary conditions for the solid phase heat transfer. Since the attempt here is to work with the asymptotic solution to a linear set of equations, the consistent linearized solid phase equation from Eqs. (12) is for $g = \bar{g}(\eta) + \mathscr{G}(x, \eta)$

$$\frac{\partial^2 \mathscr{G}}{\partial x^2} + \frac{\partial^2 \mathscr{G}}{\partial \eta^2} - \frac{\partial \mathscr{G}}{\partial \eta} = Y'' \frac{\partial \bar{g}}{\partial \eta} \tag{27}$$

where the simplifying assumption of $\bar{y}_s' = 0$ has been made in accordance with the forementioned gas phase solution. Letting $\mathscr{G} = \hat{g} + Y\,(\partial \bar{g}/\partial \eta)$, Eq. (26) becomes

$$(\partial^2 \hat{g}/\partial \eta^2) + (\partial^2 \hat{g}/\partial x^2) - (\partial \hat{g}/\partial \eta) = 0$$

which has the solution

$$\begin{aligned} \hat{g} &= e^{\eta/2}\, e^{mx}\,[G_o \cos m_g \eta + G_1 \sin m_g \eta] \\ m_g &= (m^2 - \tfrac{1}{4})^{1/2} \end{aligned} \tag{28}$$

This solution has a feature that $\mathscr{G}_s = G_o e^{mx} + Y(\partial \bar{g}/\partial \eta)(0)$ which determines G_o from the gas phase solution. A most important feature of the solution is the creation of an oscillatory ripple of very short wavelength (of order $1/m_g \approx 1/m$) superimposed on the monotonically varying temperature of the undisturbed solution. What happens, therefore, is that in both the solid phase and gas phase the distance scales over which rapid transitions are made are now of the same order of magnitude (of order $1/\xi$). In a sense, the short distance scale of the gas phase is imposed upon the solid phase.

To complete the solid phase solution, Eq. (28) is substituted into the interface heat transfer condition of Eqs. (12) and G_1 is determined. Now at any x position in the eigensolution to the AP problem, the heat transfer vectors in the gas and solid phases are known. Since this must be a continuous quantity and the

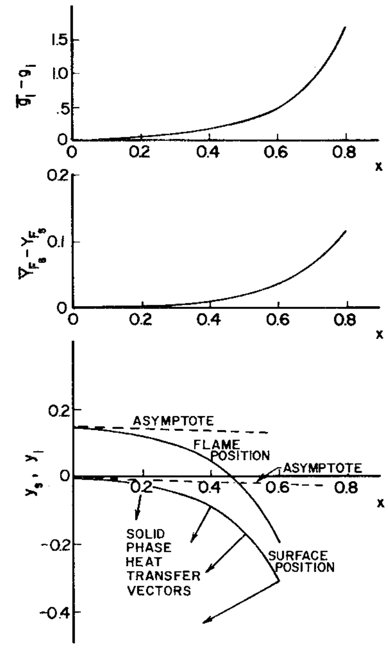

Fig. 3 Surface, flame standoff, surface NH_3 mass fraction, flame temperature and solid phase heat transfer vector profiles.

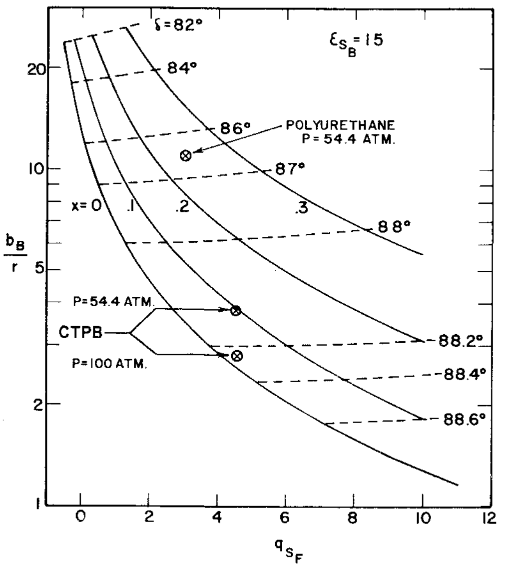

Fig. 4 Binder properties for attachment to the AP solution, $\varepsilon_{s_B} = 15$.

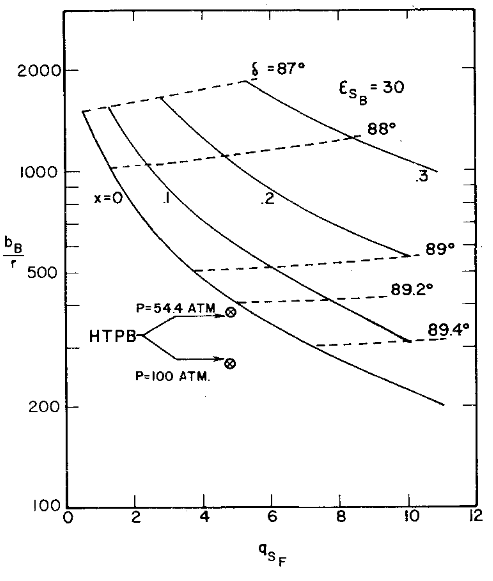

Fig. 5 Binder properties for attachment to the AP solution, $\varepsilon_{s_B} = 30$.

temperature is a continuous quantity, but q_s undergoes a discontinuity, there must be a surface slope discontinuity at the binder. In the interface energy conservation relation of Eqs. (12), the solid and gas phase heat transfer vectors may be computed from the AP solution, and this equation becomes a relation for the binder heat of gasification as a function of its surface slope. The result is

$$q_{s_B} = m\mathscr{G}_s y'_B \frac{(\xi-1)}{\xi} + (1+y'_B y'_s)\left\{\frac{g_1-g_s}{\xi c} - (g_s-1)(1+Y) - \frac{G_o}{2} - m_g G_1\right\} \tag{29}$$

The pyrolysis condition of Eqs. (12) gives an additional relation between the surface slope and the binder properties

$$(1/z_B) = \tilde{b}_B \exp(-\varepsilon_{s_B}/g_s) \tag{30}$$

At any x position, then, Eqs. (28) and (29) together with the AP eigensolution define an allowable binder attachment and a functional equation:

$$b_B = b_B(\varepsilon_{s_B}, q_{s_B}; x)$$
$$y'_B = y_B(\varepsilon_{s_B}, q_{s_B}; x)$$

For the case of $p = 54.4$ atm these results are shown in Figs. 4 and 5 for two values of ε_{s_B} which correspond closely to HTPB and CTPB binders.[14] Also, knowing q_s and b_B for HTPB and CTPB[14] the actual point at which these two binders would attach is shown on Figs. 4 and 5.† There are several points worthy of note. First, for these binders, the x position of compatability with the AP solution occurs where very little change from a flat AP surface has taken place. Consequently, the linear AP eigensolution can be used with confidence as a good approximation to the solution of the nonlinear problem. Polyurethane, shown on Fig. 4, would also attach to a nearly flat AP surface. A check of the fluorocarbon binder data of Ref. 14 also shows an attachment at negative x. The second important point is that the binder slope is very nearly vertical at the attachment point. This is the primary information desired, in addition to the AP surface profile, so no attempt is made to continue the solution to the right of the attachment point to find the binder profile. The third major point, refering back to Fig. 3, is that the solid phase heat transfer vector points from the binder toward the AP. This indicates that at least for a short distance above the interface the binder temperature must be increasing, probably because the highest temperature AP gases are at positive η.

Discussion of Results

A solution has been obtained for the shape of the deflagrating AP surface when it is adjacent to an inert dry binder. The eigenvalue, the vertical regression rate, has been found to be independent of binder type and to deviate only very slightly from the pure AP burn rate, as has been experimentally observed. Except for selected binders there would be very little visible effect of the binder upon the surface shape, and the result is virtually independent of pressure. The distance scale over which a visible transition would take place from planar AP to the binder is of the order of microns. The current theory assumes a dry binder; it is known, however, that binder melt flows exist for all binders tested heretofore in the sandwich configuration and that these melt flows run several hundred microns onto the AP surface. Furthermore, surface roughness dimensions of the order of microns develops during deflagrations. Consequently, few of the predicted phenomena are capable of being observed. A theory including the effects of melt flows is necessary.

The theory predicts, however, that if the melts do not occur there should be a sharp discontinuity in slope at the binder-oxidizer interface. This has recently been seen for catalyzed sandwiches[15] for which the melt extent is markedly reduced (for unknown reasons). Although the current theory is not directly applicable to catalyzed situations the interface conditions responsible for the slope discontinuity are applicable. It appears that melt flows dominate the development of the surface shape if melts occur.

The current theory shows that the heat flow vector near the gas-solid interface and AP binder solid interface is from the binder toward the AP in the solid phase. Consequently, there must exist a weak (hot) portion of the binder slightly up from the four-corner interface and into the binder. This might account for the appearance of "notches" in the binder sometimes seen in quenched samples.[1,2,4,15] The violence of the quenching process may eject the part of the binder which is weaker than surrounding parts.

The current analysis shows a very weak dependence of surface shape upon pressure. This independence has been observed experimentally, but the comparison between theory and experiment cannot be made precisely because binder melts have occurred in all the experiments.

If the AP particle size is sufficiently large the current analysis may form the basis for a deflagration theory of a heterogeneous

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† The activation energies for HTPB and CTPB do not exactly fit the numbers of Figs. 4 and 5. What has been done is to compute ab_B to fit the known binder pyrolysis data at a temperature g_s, assuming the activation energies of the figures.

propellant, if the binder were dry. The largest natural dimension which occurs in this theory is the thermal wave depth which is of the order of 20 μm at 800 psia. Consequently, for *AP* particle sizes larger than this dimension, there may be some merit in applying this technique to a real propellant. An extension to the case of a finite binder thickness would be required, however, unless *AP* particle sizes substantially in excess of the thermal wave depth were considered because the typical binder widths would be less than the typical thermal depth in the binder. Such an extension is not deemed difficult to attain.

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