Model Describing the Erosive Combustion and Velocity Response of Composite Propellants

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A detailed model is presented which permits one to represent the response of the burning rate of an ammonium perchlorate solid composite propellant to pressure and velocity fluctuations. First, the steady regime response of the burning velocity of a propellant exposed to a turbulent boundary layer is described. The well-known granular diffusion flame model is employed, with the changes in the transport coefficients taken into account. It is shown (and not assumed) that, according to the present model, an additive law applies; a pressure and velocity sensitive erosive component is added to the normal pressure sensitive burning rate. By coupling the unsteady behavior of the propellant solid phase to the quasisteady flame zone, represented by the above-mentioned model, the linearized response of the propellant to pressure and velocity oscillations is obtained.

Nomenclature

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= parameter relative to the pyrolysis law of the propellant,
A
              Eq. (32)
         = c' \alpha R_{e\delta}, Eq. (12)
A
         = 2(\rho v)_w/c_f \rho_e u_e, injection strength parameter
B
В
         = parameter related to the energetic potential of the propellant,
              Eq. (38)
         = Eq. (37)
C(B)
         = c_f/c_{f_0}
         =2\tau_w/\rho_e u_e^2, friction coefficient
         = 0.16, Eq. (8)
C'
         = Eq. (38)
         = propellant heat capacity
         = gas heat capacity at constant pressure
c_g
D
         = diffusion coefficient
E_{s}
         = apparent surface activation energy for the pyrolysis law
         = enthalpy of formation at zero K
L
         = flame thickness, Eq. (16)
         = propellant burning mass flow rate
m
         = exponent in turbulent boundary-layer velocity profile, Eq. (4)
         = pressure exponent in v_b \sim p^n law
n
Q
         = heat required to heat the propellant to the surface tem-
              perature and to transform it into gases
R_{ex}
         = \rho_e u_e x/\mu, longitudinal Reynolds number
         = Reynolds number based on the boundary-layer thickness
R_{pr}, R_{pi} = pressure response function, real and imaginary parts R^{\circ} = universal gas constant
         = erosive component of the burning rate
         = normal (pressure influenced only) burning rate
T_n
         = temperature
         = burning rate
         = velocity components, parallel and normal to the surface
         = coordinates parallel and normal to the surface
X, y
         = exponent in turbulent boundary-layer velocity profile, Eq. (7)
α
α
         = thermal diffusivity
         = r_e/r_n, strength of the erosive effect
         = boundary-layer thickness

    boundary-layer momentum thickness

         = T/\bar{T}_s
φ
         = u/u_e, Eqs. (5) and (7)
η
         = v/\delta
         = thermal conductivity
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Index categories: Properties of Fuels and Propellants; Combustion in Heterogeneous Media.

 $\Omega = \omega \alpha_p / v_b^2$ $\mu = \text{viscosity}$ $\varepsilon = \text{turbulent momentum diffusivity}$ $\rho = \text{specific mass}$ $\tau = \text{shear stress}$ $\tau = \text{characteristic time}$ $\psi = \text{equivalence ratio for composite propellants, Sec. II}$ $\psi = \text{function expressing the effect of blocking, Eq. (26)}$ Subscripts and Superscripts e = outside the boundary layer g = gas phase p = propellant s, w = surface 0 = no injection

= physical frequency, rad/sec

I. Introduction

= all oscillatory quantities written as $q = \bar{q} + q' \exp(i\omega t)$

THE aim of this paper is, in the first place, to present a fairly detailed model which describes how the burning rate of an ammonium perchlorate (AP) solid composite propellant is modified when the propellant is exposed to a flow parallel to its surface, under conditions such that a turbulent boundary layer exists. This is the so-called erosive combustion regime. This model is then applied in order to determine the response of the propellant burning velocity to pressure and velocity fluctuations, considered to be small perturbations around the steady regime.

There does not seem to be, in the literature, any model which would permit one to evaluate the magnitude of the response of a composite propellant to velocity fluctuations. Insofar as this response, as well as the response to pressure fluctuations, can determine the stability of the combustion in a rocket motor, it seems interesting to attempt to describe it.

The model presented herein is based upon a description of the mechanisms which appear most likely to control the combustion of an AP composite propellant. Therefore, it seems relevant to review the various references concerned with the understanding and the modeling of the mechanisms of the combustion of composite propellants based on AP, exposed to pressure alone or pressure and velocity.

II. Background

When AP is combined with a combustible binder, the oxygen containing gases resulting from the combustion of the AP particles come into contact with the gases resulting from the

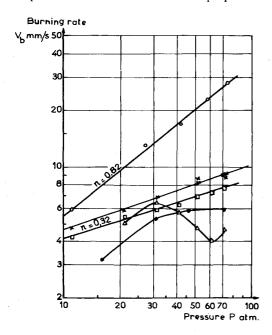
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pyrolysis of the binder, the result being a main flame which conducts heat to the surface of the propellant and allows it to be heated from the initial temperature to the surface temperature and be transformed into gases.

Summerfield and his colleagues¹⁻³ have proposed a model according to which, at low pressures, the mixing of oxidizer and fuel gases is very rapid, so that the flame is premixed and its height is determined by the kinetics of the chemical reaction. At higher pressures the mixing of the gases becomes slower and limits the combustion process. Assuming that the flame height is determined by the consumption, through laminar diffusion, of fuel pockets emanating from the pyrolyzing binder and that the heat flux is conducted from the flame to the surface in the laminar regime, one obtains the well-known result that the burning rate is affected by the pressure according to a $v_b \sim p^{1/3}$ law. In this granular diffusion flame (GDF) model the combustion of the AP particles is considered to be a surface process, provided that the pressure is above about 1 atm. This assumption is supported by the results of Ref. 4, in which a detailed model for the combustion of AP alone is presented and according to which about 70% of the AP exothermically decompose in a thin (a few microns) superficial liquid layer and the remaining 30% sublime into NH3 and HC104 which burn in a premixed flame very close to the surface (between 1 and 3 microns).

Several other, more detailed, models^{5,6} have been presented to describe the combustion of AP propellants. They all maintain the basic assumption, contained in the GDF model, that the flame height is determined, at high pressures, by the interdiffusion of oxidizer and combustible gases. In view of the fact that the GDF model leads to simple, analytical expressions for the basic parameters of the process and is in good agreement with experimental results,³ it will be employed in the present approach.

However, as pointed out by Steinz et al.³, it is not claimed that the GDF model should apply to all composite propellants. Several types of laws of burning rate vs pressure are displayed in Fig. 1. It can be seen that a propellant based on 80% AP and carboxyl terminated polybutadiene conforms to the $v_b \sim p^{1/3}$ law at pressures above 10 atm. Such a propellant is in the



- o 75% of 30 μ KP, CTPB . $\psi = 0.44$
- □ 80% of 90 μ AP, CTPB . Ψ = 0.44
- 72% of 90 µ AP, CTPB . ₩ = 0.29
- Δ 72% of 90 μ AP, Polyurethane. $\psi = 0.44$
- x 72% of 90 µ AP, Polyurethane + 3% copper chromite

Fig. 1 Various types of burning rate vs pressure laws.

range of validity of the GDF model as determined in Ref. 3, where the essential parameters are the mean AP particle size and the equivalence ratio ψ (ratio of mass fraction of oxidizing species to fuel mass fraction divided by the corresponding quantity for the stoichiometric composition). When the AP content is reduced, $\psi=0.29$ compared to 0.44 above, a plateau appears and the $p^{1/3}$ law cannot apply any more.

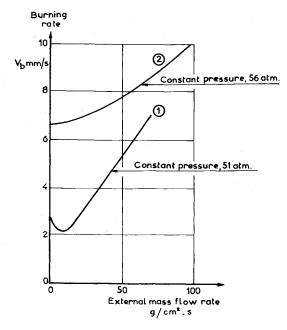
Also shown on Fig. 1 are results for a "normally" loaded AP propellant, $\psi = 0.44$, with a polyurethane binder. Nevertheless a very pronounced plateau effect can be seen. In the case of such a binder⁷ the AP particles become, at high pressures, deeply recessed into the binder matrix and might disappear locally, resulting in an inefficient combustion and a dip in the burning rate curve. As the pressure increases further, the plateau effect tends to disappear. It is known that the thickness of the heat wave into a regressing condensed phase is of the order of α/r , with α the thermal diffusivity of the solid and r the regression velocity. At high pressures it could be conceivable that the heat wave becomes smaller than the AP particle size, so that the complete disappearance of the particle becomes impossible and the mechanism for the plateau effect as well. It is also shown that with the introduction of small quantities of catalysts, such as copper chromite, the plateau effect is eliminated entirely and the $p^{1/3}$ law is recovered.

Finally, results for the burning rate of a propellant based on potassium perchlorate (KP), with an equivalence ratio equal to that of the propellants considered above, are displayed in Fig. 1. Such a composition gives rise to an evolution with a high exponent; 0.82 in the present case. Depending on the nature of the binder, ^{7–8} it appears that either a premixing of oxidizer and fuel gases can occur at the surface because of the partial spreading over the binder of molten KP, or that fairly large agglomerates of liquid oxidizer can cause the gaseous flow emanating from the surface to become turbulent, thus enhancing the intermixing of oxidizing and fuel gases and bringing the flame closer to the surface.

It can be said therefore that the GDF model is adequate to represent the combustion mechanism of composite propellants based on AP and specific binders (carboxyl terminated polybutadiene, polybutadiene acrylic acid, polysulfide, polyesterstyrene³...), provided that the AP content is high enough, and with the addition or not of catalysts. The model does not apply to the case of propellants based on AP combined with binders such that a plateau effect appears (some types of polyurethanes, polyisobutylene³...). However with the introduction of catalysts the law predicted by the GDF model is obtained again.

An extensive review of works concerned with the burning of propellants exposed to a high mass flow rate stream parallel to their surface has been given in Ref. 9. In most of these references¹⁰⁻¹³ it is assumed that the increase in the burning rate, in the erosive regime, exists because the heat flux to the propellant is enhanced by the presence of a turbulent flow. In the present approach this mechanism is subscribed to, but treated, it is believed, in more detail than in the above references. In particular, it should be interesting to establish in such an approach whether or not an additive law is valid, i.e., that to a normal pressure-sensitive burning rate is added an erosive pressure and velocity-sensitive component. It seems that this has always been assumed or inferred from not entirely convincing arguments.

As was mentioned before, the present approach cannot apply to propellants for which the burning-rate pressure law corresponds to the plateau effect because, in the first place, there is no quantitative model which can describe this effect. From the results of Ref. 14, reproduced in part in Fig. 2, it is seen that these propellants give rise to the so-called negative erosion regime (composition 1 in Fig. 2). It seems that, as the mass flow rate above the propellant increases, the heat flux to the surface is augmented and with it the drop of the burning rate, similarly to what is observed in Fig. 1 as the pressure increases, and probably due to the previously mentioned mechanism of



- 1 70% AP, 25% polyurethane, 5% Al
- ② " ", " " , " " +1% copper chromite

Fig. 2 Negative erosion effect for a plateau propellant. 14

recession and local disappearance of the AP particles. As the mass flow rate is further increased, Fig. 2, as well as Fig. 1 when the pressure is increased, the burning rate starts going up again, possibly, because the heat wave into the propellant becomes thinner. It is also interesting to note (Fig. 2), that when copper chromite is added to the propellant, and when the plateau effect is eliminated, the burning rate increases regularly with the mass flow rate, with no negative erosive effect occurring.

Section III of this paper will be devoted to an analytical treatment of the turbulent boundary layer on a flat plate, including the effect of blocking due to the injection of gas from the surface. From this treatment it will be possible to describe the transport coefficients in such a layer and, in Sec. IV, to insert them in an extended version of the GDF model, applicable to the erosive combustion regime. Finally, Sec. V will present an analytical treatment of the response of a propellant to small fluctuations around a mean fully developed turbulent boundary-layer flow.

III. Model for the Turbulent Boundary Layer on a Flat Plate with Injection

An incompressible flow, characterized by the external velocity and the longitudinal Reynolds number R_{ex} , is considered. Basic to all analytical descriptions $^{15-17,20}$ of a turbulent boundary layer with injection is a relationship for the evolution of the shear stress vs the ordinate, in an internal region close to the wall. The continuity and the momentum conservation equations are simplified by letting $\partial u/\partial x$ and $u \partial u/\partial x$ be negligible so that

$$\rho v \simeq (\rho v)_w, \qquad \tau \simeq \tau_w + (\rho v)_w u$$
 (1)

The latter equation can be rewritten as

$$d\phi/d\eta \simeq \frac{1}{2}c_f R_{e\delta}(1+\rho\varepsilon/\mu)^{-1}(1+B\phi)$$
 (2)

where $R_{e\delta}$ is the Reynolds number based on the boundary layer thickness, ε the coefficient for turbulent diffusivity of momentum, ε_{f} , the wall friction coefficient and

$$B = (\rho v)_w / \frac{1}{2} c_f \rho_e u_e, \quad \phi = u / u_e, \quad \eta = y / \delta$$
 (3)

Velocity Profile with Injection

In a way similar to that of Marxman, ¹⁶ Eq. (2) is used to obtain an analytical expression for the velocity profile. One writes

$$d\phi/d\eta = f(\eta, B)(1 + B\phi)$$

where, as $B \to 0$, $f(\eta, B) \to d\phi/d\eta(B = 0)$. It is known¹⁸ that, in the case of no injection, the velocity profile is fairly well represented by the empirical relationship $\phi(B = 0) = \eta^n$, with n a function of the Reynolds number (around 1/7 for $R_{ex} = 10^6$).

It can then be written

$$d\phi/d\eta = n\eta^{n-1}A(B)(1+B\phi) \tag{4}$$

with A(0) = 1. Marxman¹⁶ solves this equation by letting $1 + B\phi \simeq 1 + B\eta^n$. This approximation is not necessary since

$$\log(1 + B\phi)/B = A(B)\eta^n \tag{5}$$

where $\phi(\eta=0)=0$ has been used. This relation applied at $\eta=1$ leads to $A(B)=\log{(1+B)/B}$, and A(0)=1 as required, and to

$$\log(1+B\phi) = \eta^n \log(1+B) \tag{6}$$

as an explicit relationship for the velocity profile. It can be checked that for B small $\phi(B \to 0) = \eta^n [1 + (\eta^n - 1)B/2]$, an expression equivalent to that of Marxman, ¹⁶ whose solution is therefore valid only for very small injection intensities. However in practice the value of B can be very large even for small values of $(\rho v)_w/\rho_e u_e$ since $c_f/2$ is of the order of 10^{-3} .

Equations (1) and (2) are valid only in a region close to the wall. Results presented in Ref. 19 show that this region extends up to $y/\delta \simeq 1/10$. For $R_{ex} \simeq 10^6$, $\delta \simeq 3$ mm and this region is from the wall to about 300 μ and should include the flame height of the propellants which will be considered later. Although Eq. (2) strictly applies only in this internal region, its summation has been performed over the whole boundary-layer thickness, here as well as by Lees, ¹⁵ Marxman^{16,17} and others. ²⁰ To the extent that the evolution of the various quantities, the velocity profile for example, is steep close to the wall, the contribution to a summation over the boundary-layer thickness comes mostly from this region and the approach adopted here should be approximately correct. It is known, for example (see Ref. 18, p. 489), that by summing the relation $\tau(y) \simeq \tau_w$, corresponding to Eq. (1) for no injection, over the layer thickness, laws are obtained which represent fairly well the velocity profile.

It can be shown 19 that Eq. (6) can be very well approximated by the following expression, which is more appropriate for obtaining analytical relations for the parameters of a turbulent boundary layer with wall injection,

$$\phi \simeq \eta^{\alpha}, \quad \alpha = n \log (1+B)(1+B)/B \tag{7}$$

which, of course, for $B \to 0$ reduces to $\phi = \eta^n$ as required.

Reduction of the Wall Shear Stress due to Injection

It has been mentioned by many authors^{15–17,20,21} that wall injection reduces the shear stress at the wall. The comparison of the prediction of the present analytical approach to results from experiment or from more accurate numerical computations enables to put to test its validity.

From Eq. (2) and with the mixing length hypothesis of Prandtl¹⁸

$$\rho \varepsilon / \mu = R_{e\delta} \, c' \eta^2 \, d\phi / d\eta \tag{8}$$

where c' = 0.16 (assumed, as in Refs. 16, 17, and 21, to remain constant with injection), it is obtained

$$(1+\alpha)\phi \,d\phi/(1+B\phi) = c_f \,R_{e\delta} \,d\xi/2(1+R_{e\delta} \,c'\alpha\xi) \tag{9}$$

where Eq. (7) has been utilized and the change of variable $\xi = \eta^{\alpha+1}$ has been performed. This equation can be summed on ϕ from 0 to 1 and ξ from 0 to 1 (with the previous remarks on the validity of doing so applying again) and leads to an expression for the wall shear stress coefficient

$$\frac{1}{2}c_f = c'\alpha(1+\alpha)\frac{\left[B - \log(1+B)\right]}{B^2}\frac{1}{\log(1+R_{e\bar{o}}c'\alpha)}$$
(10)

As seen from Eq. (8) the quantity $R_{e\delta} c'\alpha$ represents the ratio of turbulent diffusivity to laminar diffusivity far from the wall. This quantity is therefore large compared to 1, as can be seen in Ref. 19.

For the case of no injection, Eq. (10) reduces to

$$\frac{1}{2}c_{f_0} = c'n\frac{(1+n)}{2}\frac{1}{\log(R_{e\delta}c'n)}$$
 (11)

As an example, for $R_{ex}=10^6$, this equation enables to obtain $c_{f_0}/2=2.06\times 10^{-3}$; for n=1/7, and 1.82×10^{-3} ; for n=1/8, as compared to 1.87×10^{-3} obtained from the well-known expression 18 $c_{f_0}/2=2.96\times 10^{-2}$ (R_{ex}) $^{-0.2}$. Equation (11) then gives a fair approximation of the wall shear stress for no injection.

Equation (10) can be written as

$$\frac{1}{2}c_f R_{e\delta} = (A/\log A)F(B) \tag{12}$$

where $A = c' \alpha R_{e\delta}$ and with F(B) easily obtained from Eq. (10). For the values of A which are considered, it can be written with fair accuracy19

$$A/\log A = (A/\log A)_{\text{ref}} (A/A_{\text{ref}})^{0.86}$$
 (13)

It is then obtained for the reduction of the wall shear stress

$$c_f/c_{f_0} = (\alpha/n)^{0.86} (\delta_0/\delta)^{0.14} F(B) \times 2/(1+n)$$
 (14)

It has already been mentioned that this reduction of the shear stress is sometimes 15-17 expressed under the form

$$c_f/c_{f_0} = \log(1+B)/B \tag{15}$$

This can be obtained from Eqs. (2) and (8) which lead to

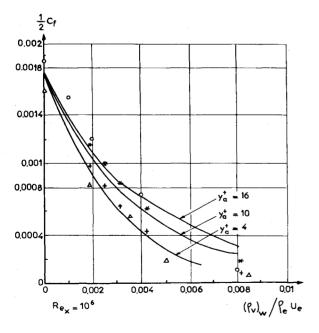
$$d\phi/(1+B\phi) = c_f R_{e\delta} d\eta/2(1+R_{e\delta} c'\eta^2 d\phi/d\eta)$$

and to Eq. (15), if the following approximations are made

$$\eta^2 d\phi/d\eta \to \eta^2 n\eta^{n-1} \to n\eta$$

and $\delta \to \delta_0$. From the present approach it is found that $\eta^2 d\phi/d\eta = \alpha \eta^{\alpha+1}$, with $\eta^2 d\phi$ ground for Eq. (15) which turns out to represent roughly the reduction in wall friction and has the advantage of being particularly simple.

In Fig. 3 various results concerning the wall shear stress reduction due to injection are compared. Those of Mills²¹ are obtained with a numerical computation scheme, more "exact" than the analytical one adopted here, for $R_{ex} = 10^6$ and for



of Simpson " Mc Quaid] As indicated by Mills [21] o Experimental points of Simpson

* Result of the present approach, eq. (14) with δ for constant $(\ell_V)_{\mu\nu}/\ell_e U_e$ + Result from Cf/Cfo = Log(1+B)/B

Numerical computation of Mills [21]

Fig. 3 Shear stress reduction due to injection.

different values of a damping parameter y_a^+ (Mills states that the value $y_a^+ = 10$ is the most representative). The experimental results of Simpson and McQuaid are also given, as they are indicated by Mills. The prediction of Eq. (14) is displayed in this figure. Since the results of Mills, as well as the experimental results, correspond to the case where the injection is constant along the abscissa, the boundary-layer thickness in Eq. (14) should be computed for this case. In the appendix of Ref. 19 a scheme was presented which allows to do so. Considering the approximations involved in the present approach it is seen that the agreement with the results of the numerical computation of Mills is fairly good and validates the approach adopted here. It is also seen that Eq. (15) can be considered as a convenient formula.

IV. Description of the Mechanism of **Erosive Combustion**

The case of a burning propellant exposed to a turbulent boundary layer is now considered. In Sec. II the opinion was expressed that the GDF approach ¹⁻³ is adequate to represent the combustion of many types of AP-based propellants. In this approach one considers the consumption of gaseous fuel pockets through diffusion mixing with oxygen containing gases resulting from the combustion of the AP particles. The basic assumption adopted here is that when a turbulent boundary layer has developed above the propellant surface, the transport coefficients of diffusion and heat conduction are modified in such a way that the heat flux to the surface of the propellant, and consequently its burning rate, can be enhanced.

If the characteristic mass of the gaseous fuel pockets is M(determined by the AP content and its mean particle size) and their size d, the time required to consume them is of the order of

$$\tau \sim d^2/D \sim M^{2/3}/\rho^{2/3}D$$

and the flame thickness is of the order of

$$L \sim v\tau \sim mM^{2/3}/\rho^{2/3}\rho D \tag{16}$$

where m is the propellant burning mass flow rate and D the diffusion coefficient. The burning rate is related to the flame thickness through the relation

$$mQ \simeq \lambda (T_f - T_s)/L$$
 (17)

where Q is the energy required to raise the propellant from its initial temperature to the surface temperature and to transform it into gases and λ is the thermal conductivity.

In the normal, non-erosive, combustion regime, the transport coefficients in Eqs. (16) and (17) are the laminar ones. Under erosive conditions, these coefficients are modified by turbulent components which depend upon the nature of the flow. If one adopts the assumption that the turbulent Lewis and Schmidt numbers are close to unity (an assumption which is supported by Ref. 21),

$$\lambda \simeq c_g \rho D, \qquad \rho D \simeq \mu (1 + \rho \varepsilon / \mu)$$
 (18)

one obtains from Eqs. (16) and (17)
$$L \sim \left[\frac{c_g(T_f - T_s)}{Q}\right]^{1/2} \left(\frac{M}{\rho}\right)^{1/3} \tag{19}$$

This result indicates that to the extent T_f and T_s do not change appreciably (a rather realistic assumption, which is contained anyway in the GDF approach^{1,3}), the flame thickness is not affected by the presence of a turbulent flow. The burning

mass flow rate, from Eqs. (17–19), is then given by
$$m \sim \left[\frac{c_g(T_f - T_s)}{Q}\right]^{1/2} \left(\frac{\rho}{M}\right)^{1/3} (\mu + \rho \varepsilon) \tag{20}$$

from which it is concluded that an additive law indeed applies. To the normal burning rate, sensitive to pressure following an $r_n \sim p^{1/3}$ law, is added a pressure and velocity sensitive (through the dependency of $\rho \varepsilon$ upon these parameters) component r_e . The ratio of these two components is

$$r_e/r_n \simeq \rho \varepsilon/\mu$$
 (21)

The model developed in Sec. III enables one to obtain a fairly simple analytical expression for the evolution of the turbulent eddy diffusivity coefficient ε as a function of the ordinate. Of course, Sec. III was relative to an incompressible turbulent boundary layer, with injection at the wall of a gas identical to that of the main flow. The application of the results of Sec. III to the problem under consideration is a rough approximation, to the extent that the nature of the gases as well as their temperature changes from the surface to the flame. It can be hoped, nevertheless, that rather than a fairly good magnitude of the erosive component, the present approach can yield its dependency upon the main parameters.

From Eqs. (7) and (8) one obtains

$$\rho \varepsilon / \mu = R_{e\delta} c' \alpha \eta^{\alpha + 1} \tag{22}$$

with α defined in Eq. (7). The turbulent diffusivity of course varies with the ordinate in the flame zone and some sort of average value should be introduced in Eq. (20). The simplest way to do so is to write

$$(\rho \varepsilon/\mu)_{\rm av} = 1/L \int_0^L \rho \varepsilon/\mu \, dy = R_{e\delta} \, c' \alpha/(2+\alpha) (L/\delta)^{\alpha+1} \tag{23}$$

It is interesting to note that $(\rho \varepsilon/\mu)_{\rm av}$ is indeed of order 1 for realistic values of the parameters and, from Eq. (21), so is the ratio r_e/r_n . Thus, as an example, for $R_{ex}=10^6$ and B=10, from Ref. 19, $R_{e\delta}\,c'\alpha=2.4\times10^3$ and for $\delta\simeq3{\rm mm},\ L\simeq30$ μ . $(\rho\varepsilon/\mu)_{\rm av}=1.7$.

The parameter α was found to be, Eq. (7), $\alpha = n \log(1+B) \times (1+B)/B$. It is known¹⁸ that the coefficient n varies with the Reynolds number R_{ex} . From Eq. (11), expressing the wall shear stress coefficient as a function of R_{ex} and n (for no injection), and from Eq. (13) which can be written as $A/\log A = 0.38A^{0.86}$, is obtained $\frac{1}{2}c_{f_0}R_{e\delta_0})^{0.86}$, which can be solved for n vs R_{ex} so that

$$c'n \simeq 8.3 \ 10^{-2}/(R_{ex})^{0.1}$$
 (24)

Finally from Eqs. (17, 23, and 24) the burning mass flow rate under erosive conditions is

$$m \simeq c_g \frac{(T_f - T_s)}{Q} \left[\frac{\mu}{L} + \frac{8.3}{10^2} \frac{\rho_e u_e}{(R_{ex})^{0.1}} \left(\frac{L}{\delta} \right)^n \psi \right]$$
 (25)

where the function ψ expresses the blocking effect of the gases injected into the boundary layer and can be written taking into account Eq. (4), as,

$$\psi = \frac{\log(1+B)}{B} \left[1 + B \left(\frac{L}{\delta} \right)^{\alpha} \right] \frac{1}{(2+\alpha)}$$
 (26)

As an illustration, the evolution of ψ with B is displayed in Table 1 (for a fixed value of L, 30 μ , δ_0 computed at x=20 cm and $R_{\rm ex}=10^6$ and δ computed 19 for the case of constant B along x).

Table 1 Evolution of the blocking effect factor with the injection strength

| В | | 5 | 10 | 20 | 100 |
|------------------|---|-----|------|------|------|
| $\psi/\psi(B=0)$ | 1 | 0.7 | 0.52 | 0.35 | 0.11 |

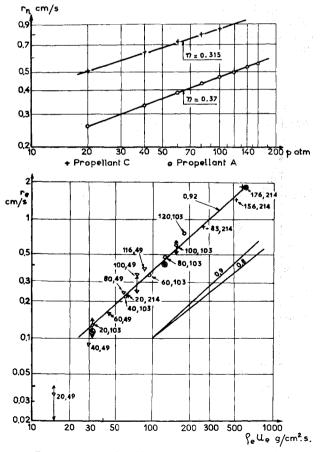
Aside from the effect of the blocking, it is seen from Eq. (25) that the erosive component depends upon the external mass flow rate, $\rho_e u_e$, according to a $(\rho_e u_e)^{0.9}$ law, to the extent that n being small the changes in the $(L/\delta)^n$ factor are fairly small, as will be confirmed later. Upon this evolution the blocking effect is superimposed, which is high for large values of B, that is for large values of $m/\rho_e u_e$. This blocking effect can give rise to the appearance of a "threshold velocity," below which the normal burning rate is little affected, as has been pointed out elsewhere. This threshold effect will be particularly noticeable for propellants with a high normal burning rate. Conversely the erosive effect will be felt more for propellants with a low normal burning rate.

Of all the published experimental results dealing with the erosive combustion of AP-based composite propellants, it seems that only those of Marklund and Lake¹² are presented with

enough details for a meaningful comparison to be made with the present approach (work has been performed at ONERA on this topic, ^{9,13} but was concerned mostly with plateau propellants, to which, as was explained in Sec. II, the present model cannot apply). Their results were obtained by exposing burning propellant samples to the flow which resulted from a main charge (of the same propellant, in most cases) and which developed a turbulent boundary layer for about 20 cm in a 3 cm diam tube before reaching them, under conditions such that, its thickness being small compared to this diameter, it can be considered as that on a flat plate.

The evolution of the normal burning rate with pressure of two of the propellants of Ref. 12 (composition A: 65% 30 μ AP; 35% polyester; composition C: 75% 30 μ AP, 25% polysulfideepoxy) is displayed in the upper part of Fig. 4. It can be seen that these two propellants conform approximately to the prediction of the GDF model, $r_n \sim p^{1/3}$, and therefore should be appropriate for an application of the approach presented herein. Also displayed in Fig. 4 is the erosive burning rate (total rate minus the normal rate at the same pressure) of propellant A as a function of the mass flow rate, $\rho_e u_e$. The line represents that indicated by Marklund and Lake and the various points have been taken from their figures of burning rates vs pressure at different given external stream velocities (sometimes with the error margin given by the authors). It is seen that these results are fairly well set on a single line, with a slope of 0.92. It is only at the very low mass flow rates that they depart from this line. It is believed that, in the experiments of Ref. 12, the boundary layer flowing over the propellant sample has not yet been affected by the injection of gases, at least for propellant A and for $\rho_e u_e$ higher than about 30 g/cm²s.

In Fig. 4 are shown a few points computed from the present



+ a ▼ Experimental results of MarkLund and Lake for propellant A (Figures represent the pressure and velocity respectively)

Computed points (matched at 176 at m, 214 m/s)

Fig. 4 Normal and erosive burning of propellants. 12

model under the following conditions. If the blocking effect is not taken into account, it is obtained from Eqs. (21) and (22), $r_e/r_n = R_{e\delta_0} c' n (L/\delta_0)^{n+1}/(2+n)$, with *n* from Eq. (24) and $R_{e\delta_0}$ computed for x = 20 cm, $\mu = 5.7 \ 10^{-4}$ CGS (an estimate for the viscosity of combustion gases at 1 700 K). If this formula is compared to the experimental result at 176 atm and 214 m/sec $(r_e/r_n =$ 2.95), a value of $L \simeq 7 \mu$ can be obtained (which should be viewed more like an efficient flame thickness than an actually measurable parameter). From Eq. (17), applied to the normal burning rate, with $T_f = 1690 \,\mathrm{K}^{12}$, $T_s = 1000 \,\mathrm{K}$ and $\lambda \,(\mathrm{laminar}) = 3.10^{-4} \,\mathrm{CGS}$, Q is found to be 300 cal/g. The results of the linear pyrolysis experiments of Cohen et al.²² indicate that the heat of pyrolysis of polysulfide (which, from the results of Ref. 12, compare propellant A and B, seems to be energetically close to polyester) is 750 cal/g. The contribution to Q from the binder would then be about 260 cal/g. The above result therefore seems to be reasonable. With the value of L thus computed, and taking into account its evolution with the pressure, points at other values of the pressure and the velocity could be computed from Eqs. (21) and (22) (with no blocking effect) and plotted in Fig. 4.

It can be seen that the good agreement between the computed values and the experimental results seems to validate the present approach and the assumption that the blocking effect is not felt in the experiments on propellant A of Ref. 12. As shown in this reference, propellant C, which has a higher normal burning rate than propellant A (see Fig. 4), gave results which fall below a straight line for a larger range of external mass flow rates. It is likely that in this case the blocking effect was more felt than for propellant A, but it is believed that the result of Eq. (25), for a turbulent boundary layer fully affected by this blocking effect, should not be applied. Results mentioned in Ref. 19 indeed indicate that a step in injection is fully felt only several cm downstream, for Reynolds numbers of the order of those considered here (the propellant samples of Ref. 12 are only about 1 cm long).

V. Evaluation of the Response of the Propellant to Pressure and Velocity Fluctuations

Several works ^{9,23-26} (a rather exhaustive review can be found in Ref. 25) have dealt with the modeling of the response of a solid propellant to pressure oscillations. Most of these works consider that the unsteadiness of the process arises from the condensed phase, with the gas phase responding quasi-steadily (an exception being Ref. 26, which considers the nonsteady behavior of the latter). Furthermore all of these works consider the flame to be laminar and premixed (sometimes without saying so explicitly), although it seems to be fairly well established that, for pressures higher than about 10 atm, the flame thickness is conditioned by the diffusive intermixing of oxidizing and combustible gases. This contradiction is also pointed out by the author of the GDF model.²⁷

It is known that the characteristic response time of the propellant solid phase is $\tau_p = \alpha_p/v_b^2$, with α_p the thermal diffusivity. For $v_{\bar{b}} \simeq 0.5$ cm/sec τ_p is about 4×10^{-3} sec, so that for oscillations even under 10^3 cps the inertia of the solid phase has to be taken into account. The response time of the flame zone is given by $\tau_g/\tau_p = (\rho_g/\rho_p)(\lambda_g c_p/\lambda_p c_g)$ and, since both the heat capacities and thermal conductivities of the solid and the gas are of the same order of magnitude, it is about a hundred times smaller than τ_p . It seems safe to consider that the flame zone responds quasi-steadily to external oscillations.

In most models for the response of a propellant to pressure oscillations, it is assumed that the surface decomposition of the propellant is described in the nonstationary regime by the law which applies in the stationary regime (an Arrhenius law most of the time). This is true if the thin subsurface decomposition zone responds quasi-steadily. It can be shown^{28,29} that its thickness is of the order of $\alpha_p/v_b \, \mathscr{E}_p$, where $\mathscr{E}_p = E_p/R^0 \, T_s$ and E_p is the activation energy of the in-depth decomposition reaction. The characteristic response time of this zone is then τ_p/\mathscr{E}_p . For AP it is found⁴ that $E_p = 60 \, \text{kcal/mole}$ and therefore $\mathscr{E}_p \simeq 30 \, \text{(for the propellant to pressure of the surface of the propellant to pressure of the surface of the propellant to pr$

 $T_s \simeq 1000\,$ K). It will be considered here that the superficial decomposition layer responds quasi-steadily. Depending on the actual values of α_p , E_p , the burning rate, and the frequency range considered, this assumption might break down. In the case where the nonsteadiness of the decomposition zone has to be taken into account²⁹ for a related problem, it is shown that the response of the solid phase can be modified. This point therefore deserves attention

When considering the response of the propellant to fluctuations of the velocity outside the turbulent boundary layer it is exposed to, one more characteristic time has to be considered. This is the response time of the boundary layer itself. Were this time to be larger or of the order of the oscillation time, then the boundary layer would have to be considered as fully unsteady. It is known (for example, Ref. 29) that the response time of a boundary layer is of the order of d^2/v , where d is a characteristic thickness and v is the momentum diffusivity (turbulent). It seems that, in the case of a turbulent boundary layer, one should consider the momentum thickness θ as the characteristic parameter, rather than the thickness δ which has no real physical meaning. From Eq. (22) it can be found $\theta^2/\varepsilon \simeq \delta/10u_e\,c'n$ and, for $R_{ex} \simeq 10^6, \, x \simeq 20$ cm, $u_e \simeq 100$ m/sec, it can be seen that this characteristic time is slightly above 10^{-4} sec. It should then be appropriate to consider that the boundary layer transmits instantaneously to the flame the external velocity oscillations. However, depending on the actual values of the parameters and as the oscillations approach a 1000 cps this assumption might hold less and less.

In view of the above remarks, it will be considered that only the propellant condensed phase introduces inertia in the process. The conservation of energy in the solid phase is expressed as

$$\frac{\partial^{2} \theta}{\partial \xi^{2}} - \left(1 + \frac{m'}{\bar{m}} e^{i\omega t}\right) \frac{\partial \theta}{\partial \xi} - i\Omega \theta' e^{i\omega t} = 0$$
 (27)

where $T/\bar{T}_s \equiv \bar{\theta} + \theta' \, e^{i\omega t}$, $\xi \equiv y v_b/\alpha_p \, (y \, \text{being the physical ordinate}, 0 \, \text{at the surface and } > 0 \, \text{into the gas phase}$, and $\Omega \equiv \omega \alpha_p/{v_b}^2$. By solving Eq. (27), we obtain the heat flux penetrating into the solid phase^{9,19}

$$q_{-s} = c_p \bar{m} \bar{T}_s \left[(1 - \theta_i) + \theta'_s s + \frac{m'}{\bar{m}} (1 - \theta_i) \frac{1}{s} \right]$$
 (28)

where $s = [1 + (1 + 4i\Omega)^{1/2}]/2$. By perturbating the Arrhenius law relating the burning mass flowrate to the surface temperature it is obtained

$$m'/m = \mathscr{E}_s \, \theta'_s \tag{29}$$

where $\mathscr{E}_s = E_s/R^{\circ}T_s$.

The consideration of the conservation of energy at the interface between condensed and gas phases and between the surface and a position downstream of the flame leads to the relationship

$$q_{-s} = m(h_p^{\circ} + c_p T_s - c_g T_f - h_{g,f}^{\circ}). \tag{30}$$

Equation (30) combined with Eq. (28) yields, for the steady part,

$$c_{g}\bar{T}_{f} - c_{p}\bar{T}_{i} + h_{g,f}^{\circ} - h_{p}^{\circ} = 0$$
 (31)

and, for the unsteady part, taking Eq. (29) into account,

$$(m'/\bar{m})[(s-1) + A/s - A] = -(c_g/c_p)\mathscr{E}_s \theta'_f$$
 (32)

where $A = (1 - \theta_i) \mathcal{E}_s$. This relation has been obtained from energy conservation considerations, independently of the flame structure being considered.

In the case under consideration, the combustion of AP composite propellants above about 10 atm, the flame is conditioned by the diffusional mixing of oxidizing and combustible gases. From the approach adopted in Sec. IV to describe the erosive combustion of AP propellants, the gas phase between the surface and the flame is characterized by the following relations, from Eqs. (16–18 and 23),

$$q_{+s} \simeq c_g (T_f - T_s) (\mu + \rho \varepsilon)/L$$
 (33)

$$L \sim mM^{2/3}/\rho^{2/3}(\mu + \rho\varepsilon) \tag{34}$$

$$\rho \varepsilon \simeq \rho u_e \frac{c'n}{(2+n)} L \left(\frac{L}{\delta_0}\right)^n \tag{35}$$

where, for the sake of simplicity, the effect of the blocking due to the injection of gases has not been taken into account in Eq. (35). From this equation it can be obtained

$$\frac{\mu' + (\rho \varepsilon)'}{\overline{(\mu + \rho \varepsilon)}} = \frac{1}{2(1 + \beta)} \frac{\theta'_f}{\overline{\theta}_f} + \frac{\beta}{(1 + \beta)} \left[0.9 \frac{\rho'}{\overline{\rho}} + 0.9 \frac{u'_e}{\overline{u}_e} + \frac{L}{\overline{L}} (1 + n) \right]$$
 (36) where the relation $\beta \equiv r_e/r_n = \overline{\rho \varepsilon}/\overline{\mu}$ has been utilized and $\mu \sim T^{1/2}$ assumed.

By combining Eq. (36) with the unsteady parts of Eqs. (33) and (34) a relationship is derived between q'_{+s}/\bar{q}_{+s} , m'/\bar{m} , p'/\bar{p} , u'_e/\bar{u}_e and θ'_f (after utilizing the perfect gas law to eliminate ρ). With Eq. (30) q'_{+s}/\bar{q}_{+s} can be expressed in terms of the other quantities, so that the following relation is found

$$\frac{m'}{\bar{m}} \left[\frac{C}{\mathscr{E}_s} \frac{(1+2\beta)}{2} + (1+\beta) \right] = 0.9\beta \frac{u'_e}{\bar{u}_e} + (\frac{1}{3} + 0.9\beta) \frac{p'}{\bar{p}} + \left[C\bar{\theta}_f \frac{(1+2\beta)}{2} + \frac{1}{6} - 0.9\beta \right] \frac{\theta'_f}{\bar{\theta}_f}$$
(37)

where $C = (\bar{\theta}_f - 1)^{-1} + c_g \bar{T}_s [c_g(\bar{T}_s - \bar{T}_f) + h_{g,s}^{\circ} - h_{g,f}^{\circ}]$. If now Eq. (32) is utilized to eliminate the relative amplitude of the flame temperature oscillation, a relationship between the oscillatory burning mass flow rate and the external velocity and pressure oscillations is arrived at, which characterizes the propellant response,

$$\frac{m'}{\bar{m}} \left[s - 1 + A \left(\frac{1}{s} - 1 \right) + ABC' \right] = 0.9\beta AB \frac{u'_e}{\bar{u}_e} + \left(\frac{1}{3} + 0.9\beta \right) AB \frac{p'}{\bar{p}}$$
(38)

with

$$B = \frac{c_g}{c_p} \, \bar{\theta}_f / (1 - \theta_i) \left[\bar{\theta}_f \, C(0.5 + \beta) + \frac{1}{6} - 0.9 \beta \right]$$
$$C' = 1 + \beta + C(0.5 + \beta) / \mathcal{E}_s$$

If $\beta=0$ is set in this relation, the response of the propellant under normal combustion conditions (pressure sensitive only) is found.

In order to illustrate the result of Eq. (38), the values found in Sec. IV for propellant A of Ref. (12) have been used, that is, Q = 300 cal/g, $\bar{T}_f = 1690$ K and $\bar{T}_s = 1000$ K. Since Q = 1000 K.

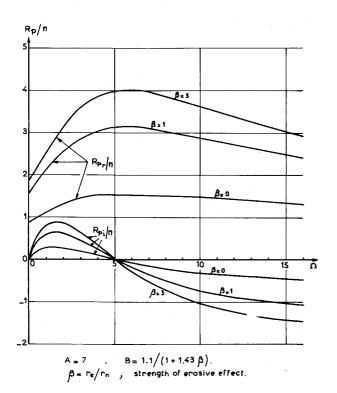


Fig. 5 Pressure response function with erosive effect.

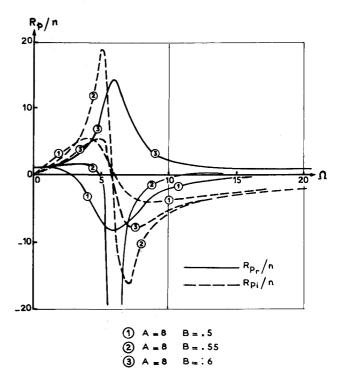


Fig. 6 Evolution of the normal pressure response function.

 $c_g \bar{T}_s - c_p T_i + h^\circ_{g,s} - h^\circ_p, h^\circ_{g,f} - h^\circ_{g,s}$ can be computed from Eq. (31) as well as C. The parameter A is computed with an assumed value of $E_s = 20$ kcal/mole and $T_i = 300$ K. Parameters A and B are then found as indicated in Fig. 5. In this figure the pressure response of the propellant, under erosive conditions (characterized by different values of the erosive strength parameter $\beta = r_e/r_n$), real and imaginary parts divided by the pressure exponent $n \approx 1/3$, is displayed. It is seen that, for the values of the fundamental parameter A and B utilized, the main influence of the erosive effect is to amplify the normal (no erosion) response curve. From Eq. (38) it is seen that the velocity response curve follows the same trend, being null of course for no erosive effect.

It can be noted that, for the no erosion case, $\beta = 0$, and for $\Omega \rightarrow 0$, R_{pr} is slightly different than n. This is due to the perturbation on T_s in Eq. (20).

It is well known, however, that the results obtained for the response function of a propellant are very sensitive to the value of the parameter B. In Fig. 6 the evolution of the normal pressure response function (that is, Eq. (38) for $\beta=0$) for a given value of A and slightly different values of B is displayed. It is seen that there exists a critical value of the parameter B on each side of which the trend of the pressure response is completely different. For a combination of values of Q, \bar{T}_f and \bar{T}_s which would set B in this vicinity the effect of an added erosive effect could then be very pronounced, changing the real part of the response function from highly positive values to highly negative values, or vice versa.

VI. Conclusions

The approach presented here was aimed at describing the erosive combustion and the response to pressure and velocity oscillations of ammonium perchlorate composite propellants. An analytical description of the turbulent boundary layer on a flat plate, taking into account the blocking effect due to the injection of gases at the wall, has been presented and has been found to yield results close enough to those of more complicated numerical approaches.

The erosive combustion of ammonium perchlorate propellants, exposed to a fully developed turbulent boundary layer, has been

represented by a modification of the granular diffusion flame approach, which takes into account the turbulent transport coefficients in the zone between the surface and the flame. It has been found that an additive law indeed applies, the normal pressure sensitive burning rate being increased by a pressure and velocity sensitive component. The prediction of the present model has been compared favorably to some of the experimental results of Marklund and Lake.

The linearized response of the burning rate of the propellant to small pressure and velocity oscillations, around a mean turbulent boundary-layer flow, has been obtained for conditions for which the unsteadiness of the process comes entirely from the unsteady response of the solid phase. In the case of a null erosive effect, this response is that corresponding to a flame conditioned by diffusion mixing phenomena. It has been found that the pressure response is rather strongly amplified when the erosive effect becomes more and more pronounced, with the velocity response following the same trend. It has been seen that, for critical values of a parameter related to the energetic potential of the propellant, the effect of an added erosive effect could reverse entirely the values of the response function.

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