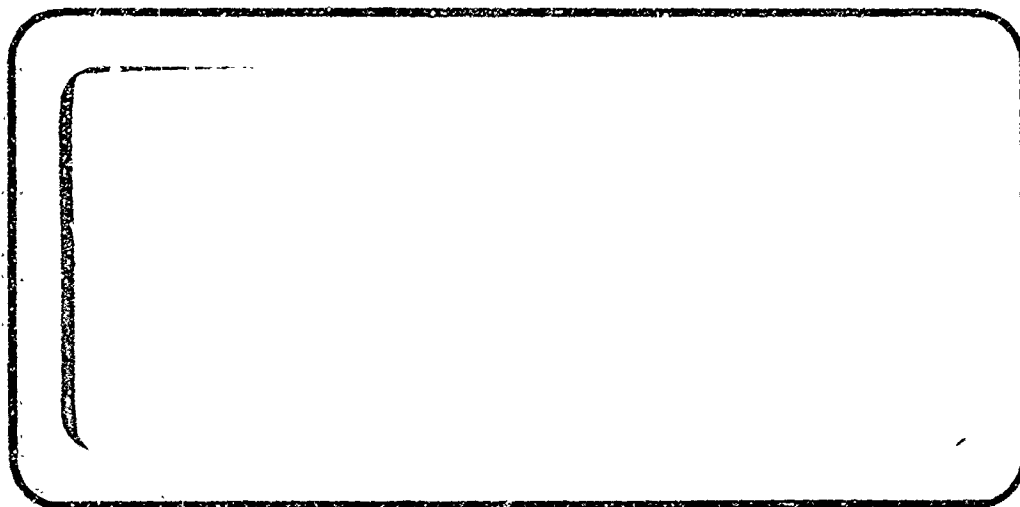


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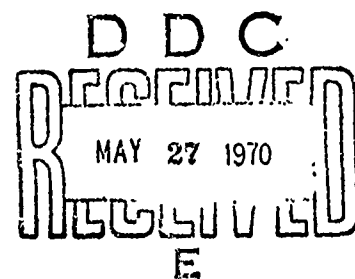
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MODEL FOR THE BURNING RATE AND EXTINCTION
OF ALUMINIZED POLYBUTADIENE AMMONIUM
PERCHLORATE COMPOSITE PROPELLANTS

Prepared by

E. D. Guth, J. S. Land, and G. Schlesinger

December 1969



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MODEL FOR THE BURNING RATE AND EXTINCTION OF ALUMINIZED POLYBUTADIENE
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ABSTRACT

A combustion model and burning rate equation for an aluminized polybutadiene ammonium perchlorate composite solid propellant was developed in terms of the rate of heat feedback to the propellant surface. It was found that the burning rate-pressure relationship for this propellant was well represented by an equation of the form:

$$r = c (T_2^4 - T_1^4) + d \frac{T_2 - T_1}{(T_2 + T_1)^{1/3}} p^{1/3} \quad (1)$$

where T_1 , c and d are constants. The feedback temperature in the equation, T_2 , was determined as a function of pressure using propellant ingredient physical chemical properties and subscale burning rate data. The equation was used to calculate the propellant extinction behavior in test chambers with low (or subsonic) exhaust flow, and the C^* extinction in test chambers exhausting with supersonic flow (i.e. rocket motors). These calculations agreed well with the observed extinction characteristics of the propellant.

* * * * *

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The purpose of this paper is to present a model and burning rate equation developed to describe the pressure effects on propellant burning rate and the propellant extinction characteristics of an aluminized polybutadiene ammonium perchlorate composite propellant. The analysis was performed using burning rate data measured by the Aerojet General Corporation, Sacramento, California, in subscale tests on cured strands about one inch in diameter (2 to 200 psia) and full scale tests in a 5000 pound motor (6 to 500 psia).

The propellant has a high solids loading and the primary fuel is aluminum. The burning rate is controlled by varying the quantities of coarse and finely ground oxidizer used in the particular batch of propellant. Using many large scale batches of the same propellant formulation burning rates were measured in full scale and subscale tests and the results were assessed to determine reproducibility and control. It was observed that the burning rate was strongly dependent on the design of the apparatus in which the burning rate was measured (i.e. strand bomb, 50 lb motor, large motor) under conditions where propellant erosion was not an important factor. In particular, the design with the best conditions for heat feedback to the burning surface resulted in the highest burning rate at a given pressure. A burning rate equation directly treating the rate of heat feedback was developed and the parameters determined from the accurately-known burning rate data.

This work differs from previous work on propellant burning rates in that the burning rate is related directly to the radiation and conduction contributions of the energy fed back to the propellant surface from the flame. The treatment reported in the literature providing the best description of propellant burning rates over wide pressure ranges is due to M. Summerfield.

The granular diffusion model of solid propellant burning developed by Summerfield and his associates¹ which relates chemical reaction and gas diffusion effects to propellant burning rates has been applied to correlate and predict the burning rates of many ammonium perchlorate propellants, and to interpret the mechanism of ammonium perchlorate composite propellants.² The equation describing propellant burning at high pressure based on the granular diffusion model is:

$$\frac{1}{r} = \frac{a}{p} + \frac{b}{p^{1/3}} \quad (2)$$

where a and b are constants determined by fitting the observed burning rate data.

In applying Summerfield's model to low pressure (below 10 psia) propellant burning, the effects of premixed chemical reaction time of ammonium perchlorate decomposition products, ammonia and perchloric acid, are taken into account.

The analysis presented here is based on the hypothesis that the burning rate of a solid propellant is determined largely by the thermal properties of the propellant components, and that the chemical reaction and gas diffusion effects are not rate determining. That is, the chemical reactions are assumed to be rapid at temperatures where the propellant ingredients gasify, or as the gaseous products are heated by the extremely high

temperature gradients in the flame. The model described below was developed using as inputs the results of thermochemical calculations of propellant properties (e.g. flame temperature, C^* , etc.) and data on the temperatures at which the major ingredients in the propellant under consideration gasify at rates comparable with the burning rate as follows:

<u>Major Propellant Ingredient</u>	<u>Gasification or Decomposition Temperature</u>
o Polybutadiene binder (and plasticizer) ^{3,4}	500°C
o Ammonium Perchlorate ⁵	600°C
o Aluminum ⁶	1000 - 1500°C depending on the partial pressure

As shown below, the burning rate equation developed from this model describes the observed burning rates at pressures from below 1 psia to 1000 psia, and in addition, provides a method for relating subscale and full scale data, and predicts propellant extinction properties.

A schematic representation of the combustion model used in this work is shown in Figure 1. The general form of this model for solid propellant burning has been verified by numerous experiments, as summarized in Reference 2.

It was assumed that in the burning process, solid particles of ammonium perchlorate and aluminum are released from the surface, and the solid surface recedes at the rate of binder pyrolyzes.⁵ Due to the thermal conductivity and heat capacitance properties of the binder, aluminum and ammonium perchlorate, the heat arriving at the solid surface generates gases initially at 500°C from the binder while the aluminum and ammonium perchlorate are at temperatures closer to 200°C when they leave the surface.

REGION	SCHEMATIC REPRESENTATION	CONDITION	THICKNESS	TEMPERATURE
Flame Zone		Gas: Binder, oxidizer combustion products; minor Al compounds Liquid: Al oxides	Depends on combustion Chamber geometry	Adiabatic flame temperature at equilibrium = T_2 at High Pressure
Boiling aluminum		Gas: Binder, oxidizer combustion products; oxygen - Al vapor Liquid: Al	Relatively thin. Not very pressure dependent	Isothermal at the Al boiling point at the pressure or partial pressure = T_2 at Low or Intermediate Pressures
Binder, Oxidizer Reaction		Gas: Binder, oxidizer combustion products; oxygen Liquid: Al	Defined by: $\ell_2 = M_2 \left(\frac{T_2 + T_1}{p} \right)^{1/3}$	All components - Al Boiling point = T_2 uniform gradient
Gasifying ammonium perchlorate; melting aluminum		Gas: H_2 , hydrocarbons and oxidizer decomposition products Liquid: some Al Solid: some Al		Al: 500 - 600°C ammonium perchlorate: 500 - 600°C Gas: 1200°C
Binder pyrolysis		Gas: H_2 , hydrocarbons Solid: Al, ammonium perchlorate	Defined by: $d\ell_1 = \frac{dT}{k \cdot q_2}$	Gas: $T \approx 1200^\circ C$ Solids: somewhat lower Gas: 500°C Solids: 200°C
Heated propellant		Surface: depressions and bumps from oxidizer and aluminum particles	Thin. Depends on binder thermal conductivity	Gradient
Ambient temperature propellant				

Key:

- - solid ammonium perchlorate
- ◊ - solid aluminum
- - liquid aluminum
- ⊙ - gasifying ammonium perchlorate
- ⊗ - vaporizing aluminum

- ℓ_1 - thickness of Zone 1
- ℓ_2 - thickness of Zone 2
- M_2 - constant relating ℓ_2 to oxidizer particle gas volume
- k - thermal conductivity of gases in Zone 1
- q_2 - heat flux from Zone 1 to the solid surface
- T_0 - solid propellant temperature
- T_1 - gas temperature at the top of Zone 1
- T_2 - gas temperature at the top of Zone 2, heat feedback temperature

In Zone 1, the pyrolysis gases from the binder are heated to about 1200°C (determined by fitting the data) while the solid aluminum and solid ammonium perchlorate are heated to an average temperature of $500^{\circ} - 600^{\circ}\text{C}$. At 600°C , under the transient heating conditions present in burning propellant, the ammonium perchlorate gasifies rapidly, thus identifying the end of Zone 1. It was assumed that the binder pyrolysis reaction and some endothermic decomposition of the binder gases are the only reactions occurring in Zone 1 and that the heat entering Zone 1 by conduction and radiation from the combustion products is all transferred to the propellant surface, or goes to decompose the binder and raise the temperature of the binder products, aluminum and ammonium perchlorate.

Since Zone 1 is defined in terms of the temperature of the ammonium perchlorate, the thickness of Zone 1 depends on the incident heat flux, the pressure and the mass of materials. The resulting thickness is essentially the path length necessary to conduct the heat from Zone 2 back to the surface. There is little, if any, contribution to the heat transfer in Zone 1 from radiation, since Zone 1 consists largely of particles of oxidizer and fuel which intercept most of the radiant energy.

Zone 2 starts when the ammonium perchlorate begins to gasify rapidly and ends at the temperature from which heat is fed back to the solid surface. At high pressure, heat is fed back from products at the flame temperature (which is lower than the aluminum boiling point). At intermediate and low pressures, heat is fed back from the region in which aluminum boils rapidly (1) in equilibrium with aluminum vapor at the burning pressure, or (2) at a partial pressure lower than the burning pressure. It is assumed that at intermediate and low pressures the aluminum liquid and vapor form a layer between the flame zone and the propellant surface, a.

shown in Figure 1, and the temperature of this layer, controls the rate of heat feedback to the propellant surface.

In Zone 2, the oxidizer gasifies and the oxidizer gases and binder pyrolysis products react. It is assumed that the thickness of Zone 2 is determined primarily from the volume occupied by pockets of the oxidizer gases at the average temperature in the zone. The oxidizer particles gasify rapidly once they reach about 600°C and form spheres of gas. These spheres occupy a volume of $\frac{\pi \ell_o^3}{6}$ where ℓ_o is the diameter and ℓ_o is related to the pressure by the ideal gas law (Equation 3)

$$\ell_o = \left[\frac{6 NRT}{\pi p} \right]^{1/3} \quad (3)$$

where N is the number of moles of gas produced by the oxidizer particle, R is the gas constant, T the temperature, and p the pressure.

The chemical reactions between the pyrolyzed binder and the gasified oxidizer are assumed to be rapid at the temperatures in Zone 2, since many of the species are free radicals (e.g., H, O and hydrocarbon radicals). The thickness of Zone 2 (ℓ_2) is:

$$\ell_2 = M_2 \left[\frac{\bar{T}}{p} \right]^{1/3} \quad (4)$$

where M_2 is a constant (determined in practice from high pressure fullscale motor burning rate data) and \bar{T} is the average temperature in Zone 2

$$\bar{T} = \frac{T_2 + T_1}{2}.$$

The surface recession rate (r_{rec}) of the binder in the propellant under consideration (equal to the burning rate, r) is expressed as a function of the heat flux, incident on unit area of Zone 1, \dot{q} , as follows:

$$r = r_{rec} = \frac{1}{\Delta H_B f_b \rho_p} \dot{q} \quad (5)$$

Where ΔH_B is the heat of decomposition per unit weight of binder plus the enthalpy change to heat the materials in Zone 1, f_B is the weight fraction of the propellant which is binder, and ρ_p is the density of the solid propellant.

The burning rate is expressed in terms of conduction and radiation contributions in Equation (1).

$$r = c(T_2^4 - T_1^4) + d \frac{T_2 - T_1}{(T_2 + T_1)^{1/3}} p^{1/3}$$

and

$$c = \frac{1}{\Delta H_B f_B \rho_p} \cdot \frac{A_1}{A_0} \epsilon \sigma \quad (6)$$

$$d = \frac{1}{\Delta H_B f_B \rho_p} \cdot k \cdot M_2 \frac{A}{A_0} \cdot \frac{1}{2^{1/3}} \quad (7)$$

Where A_0 is the area of propellant considered as a plane, A_1 the average area of propellant considering bumps and depressions, ϵ the emissivity of the materials in Zone 2, σ the Stefan-Boltzman constant and K the coefficient of thermal conductivity in Zone 1. The constants, c , d , and T_1 were determined from the fullscale motor burning rate data at high pressure, since they could not be calculated with sufficient accuracy for practical purposes. There is no convection term since by definition Zone 2 consists of materials moving away from the surface. Further, the model assumes that all the heat transferred back through Zone 2 is effective to pyrolyze the binder and heat the products in Zone 1.

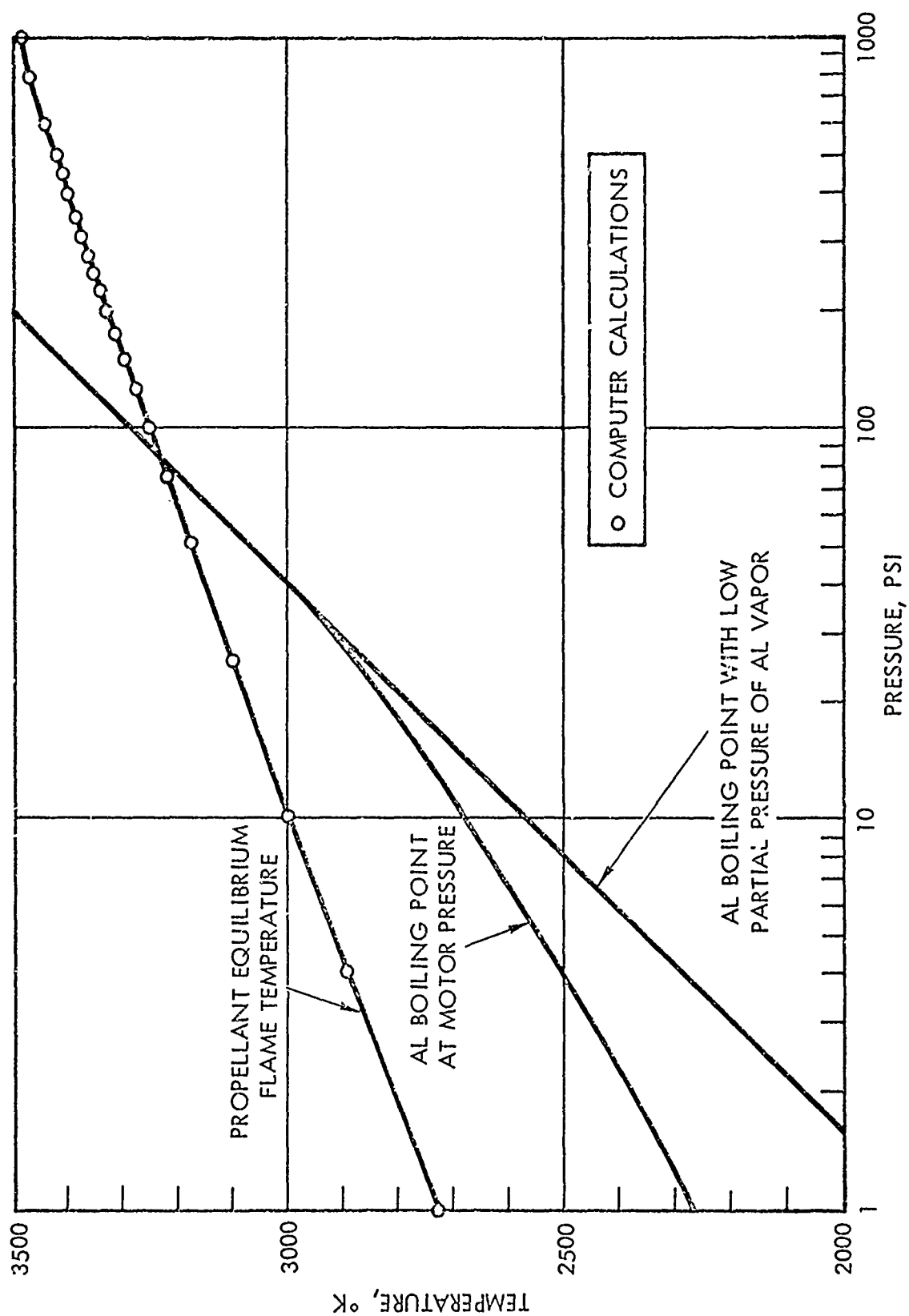
It is important to note that each of the constants c and d contain factors related to the surface area of the propellant. The actual area, including bumps and depressions, is not necessarily the planar area, but is related to oxidizer and aluminum particle size and concentration. The effect of changing oxidizer particle size, which changes the surface area, is a multiplying factor in the burning rate equation, and therefore the variations in burning rate due to particle size variations observed at high pressure can be used to calculate the variations at low pressure.

In using Equation 1, it is necessary to determine T_1 and T_2 . T_1 is a constant equal to 1200°C or about 1500°K , determined by fitting the data. T_2 is a function of pressure and the expected pressure dependence is shown in Figure 2. At high pressures, where T_1 , c and d in Equation 1 are determined from full-scale motor data, T_2 is the equilibrium propellant flame temperature (calculated from the thermodynamic considerations) which is lower than the boiling point of aluminum. Under these conditions, the aluminum boils and reacts rapidly and does not form a boiling layer at the top of Zone 2. At intermediate pressures, T_2 is the boiling point of aluminum. At low pressures, where diffusion lowers the partial pressure of aluminum, T_2 is described by the straight line (T versus $\log P$) tangent to the aluminum boiling point curve. This is justified by a relationship between the temperature and pressure for a boiling droplet of aluminum obtained by equating 1) the rate of vaporization by heat conduction to the droplet with 2) the rate of diffusion of aluminum into the surrounding bases. Using Maxwell's Diffusion Law, the relationship is:

$$dT = \frac{R}{F} \cdot \frac{\Delta H_V T}{K} \cdot \frac{dp}{p} \quad (8)$$

where R and F are constants from the diffusion equation, ΔH_V the heat of vaporization and K the coefficient of thermal conductivity. Since K is a function of T to the first power for a monotonic gas and ΔH_V for aluminum is virtually independent of the pressure, $\frac{\Delta H_V T}{K}$ varies by less than 5 percent for aluminum between 1500°C and 3000°C , and thus:

$$dT = A \frac{dp}{p} \text{ or } T = A \log P + B \quad (9)$$



where A and B are constants, The tangent point could occur for some propellants at pressures above the intersection of the flame temperature and aluminum boiling point curves. However, the curves of Figure 2 were drawn anticipating the results obtained below for this specific propellant.

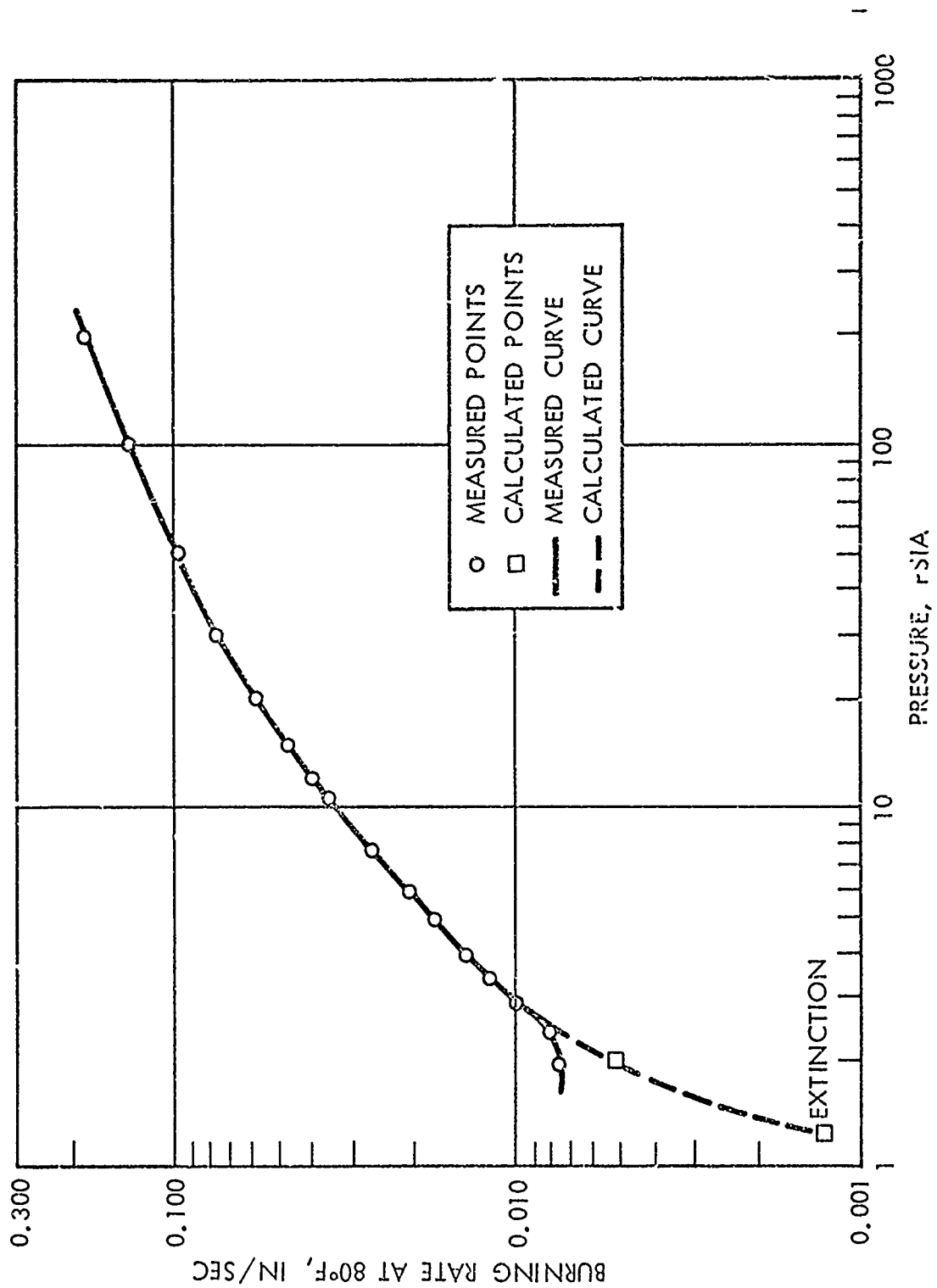
Figures 3 and 4 present, respectively, the data reported for cured, solid strands (approximately one inch diameter) burning at low pressure, and the calculated values for T_2 , using Equation 10, where T_1 , c and d were determined from the high pressure fullscale motor burning rate data at the same ambient temperature.

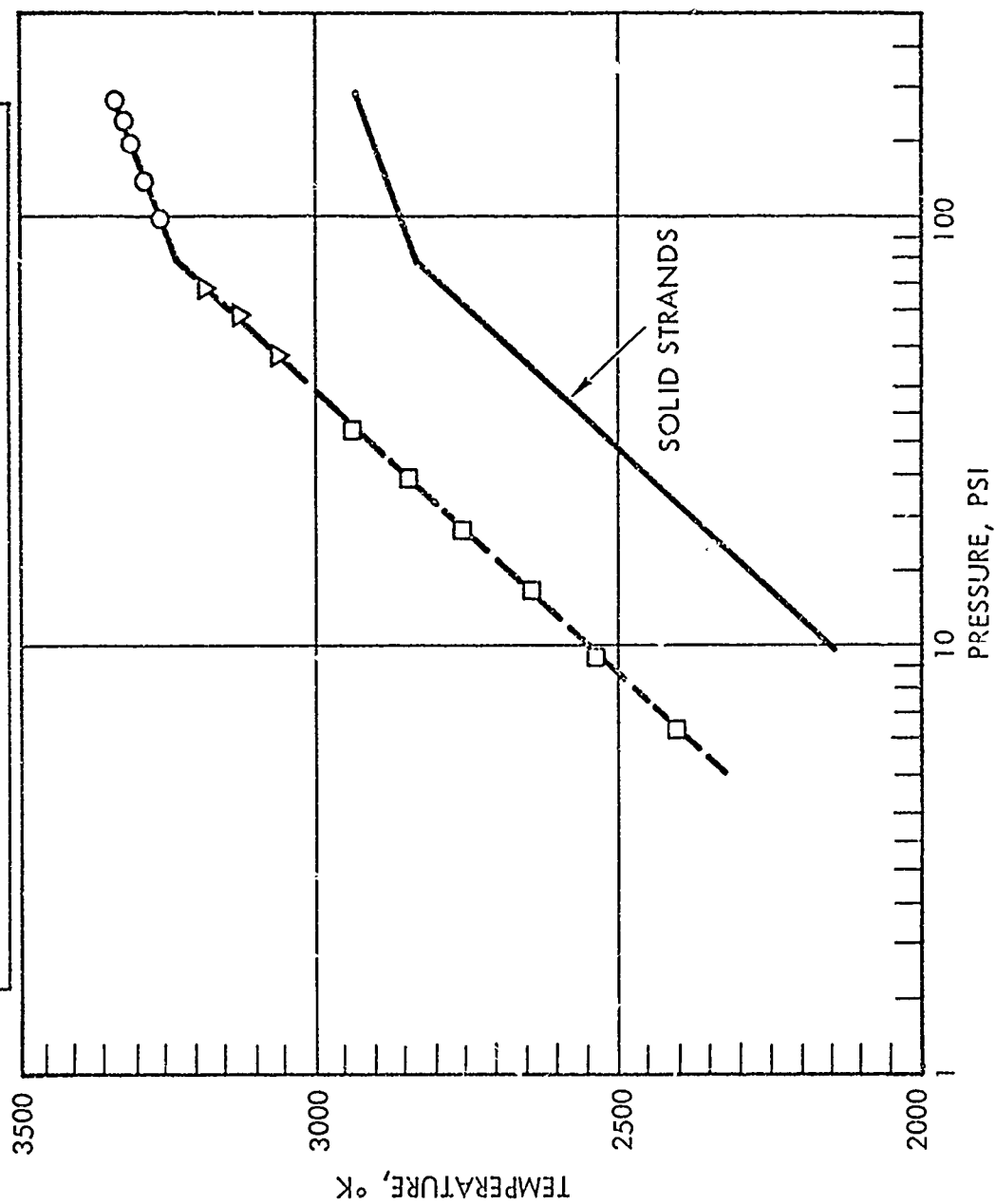
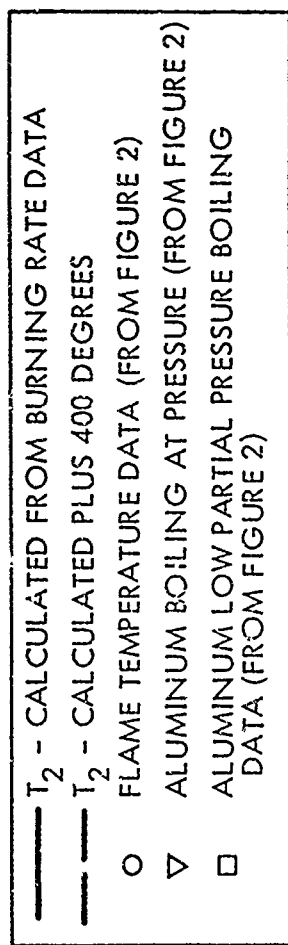
$$r = 2.53 \times 10^{-16} (T_2^4 - T_1^4) + 3.20 \times 10^{-4} \frac{T_2 - T_1}{(T_2 + T_1)^{1/3}} \rho^{1/3} \quad (10)$$

Figure 4 shows that at high pressure the calculated T_2 values for solid strands are 400°C below the equilibrium propellant flame temperature, and at intermediate pressures (85 to 45 psi) are 400°C below the equilibrium aluminum boiling point. Further, the low pressure results follow a straight line on the T versus log P plot.

These results can be interpreted to mean that the design of these solid strands and this particular solid strand burning apparatus resulted in inefficiency in heat feedback relative to the fullscale motor which lowered the heat flux to the propellant by an amount equivalent to lowering T_2 by 400°. Since the data were reduced, considering both the radiation and conduction contributions to the burning rate, this heat loss is assumed to occur in Zone 2.

Using T_2 calculated for solid strands plus 400°C, the T_2 curve at low pressures in Figure 2 was constructed as a straight line tangent to the



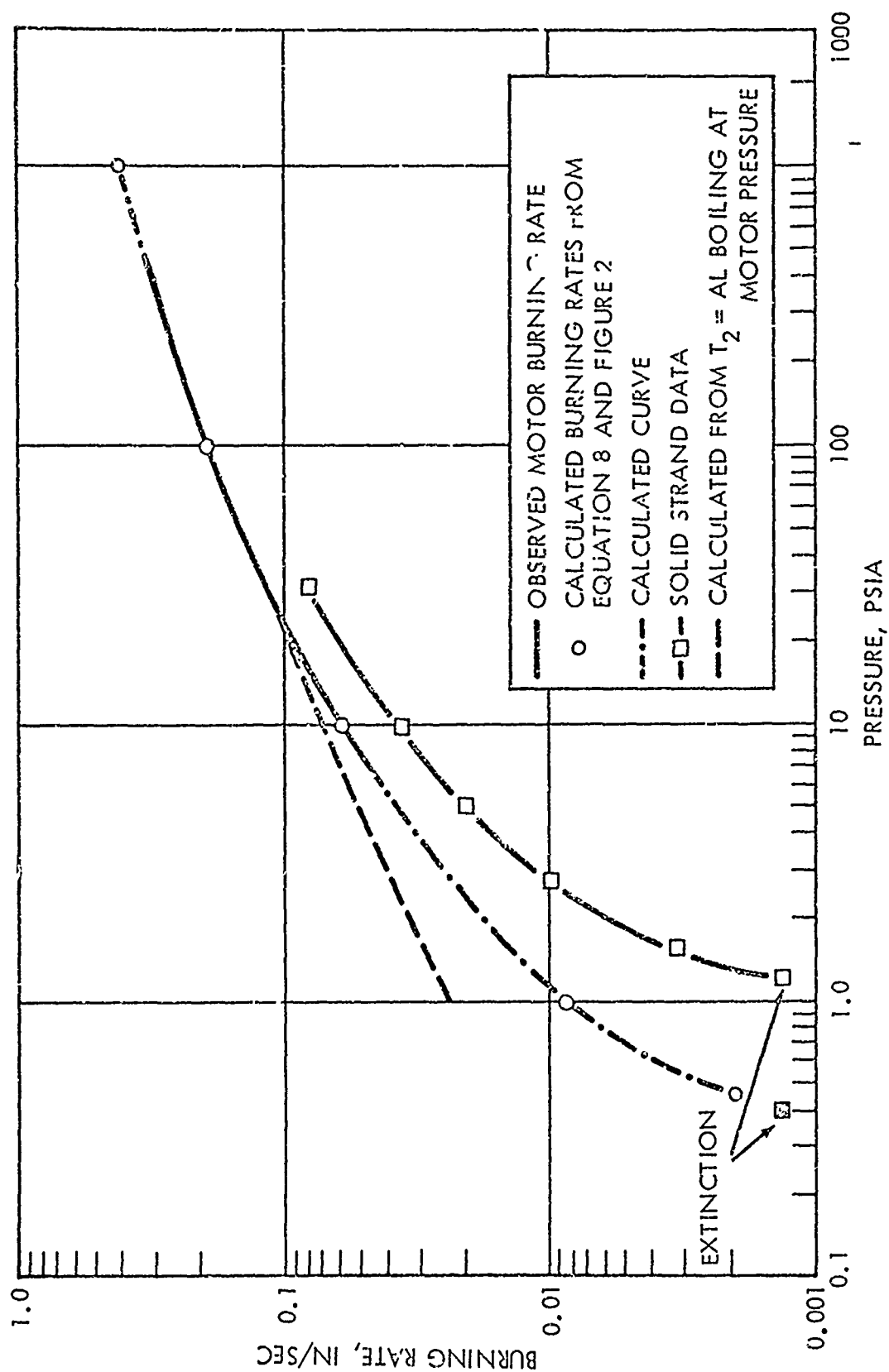


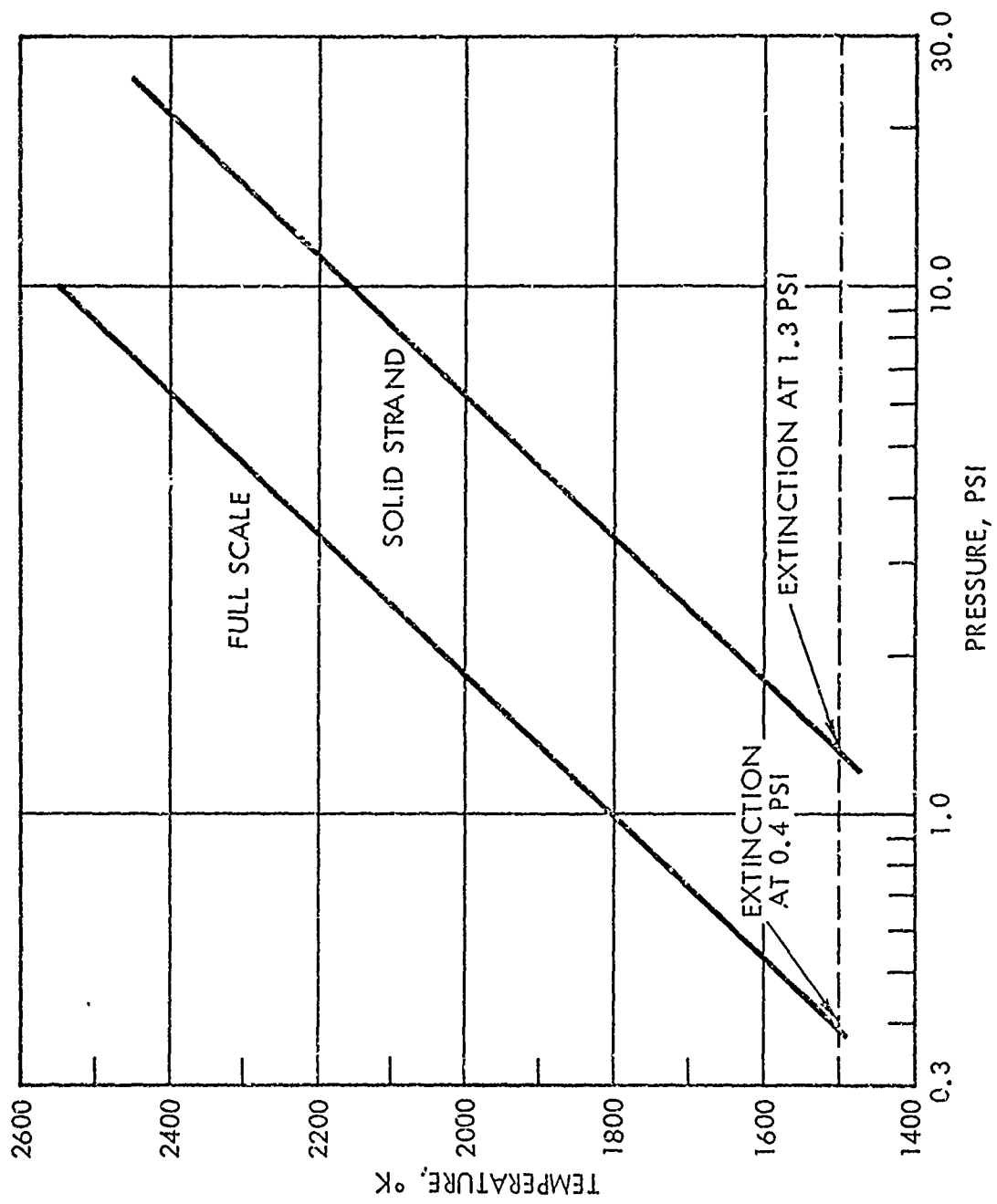
equilibrium aluminum boiling point curve at 45 psi. The calculated burning rates shown in Figure 5 were obtained from Equation 10 and Figure 2. It is seen that the observed full-scale data are reproduced exactly.

Using the model developed here, it is possible to reduce subscale burning rate data where measurements are reported at both high and low pressures to calculate values for T_2 which, when corrected, (using the flame temperature at high pressure as the T_2 applicable to fullscale burning rates) yield predictions to the fullscale burning rate at low pressures. It should be noted that the high pressure burning rates and the T_2 determined from equilibrium aluminum boiling point information (assuming that partial pressure of aluminum is not lowered by diffusion) can be used to predict an upper theoretical limit for the low pressure burning rate of the propellant in fullscale motors in the absence of any subscale data. Further, the true fullscale burning rate is bracketed at low pressure by the upper theoretical limit and any subscale data, thereby increasing the confidence in the predictions of T_2 from subscale results.

The model developed here can be used to predict the low pressure limit for propellant combustion for both subscale and fullscale tests.

In equation 5, if $T_2 = T_1$, there is no exothermic reaction which can feed heat back to the surface, and therefore self-sustained combustion is not possible below the corresponding pressure. The burning rate at extinction is zero, however, at pressures just above the extinction pressure, the burning rate can be plotted on a log-to-log scale as shown in Figures 3 and 5. The extinction pressures for subsonic flow are obtained by extrapolating the straight lines for T_2 versus log pressure down to $T_2 = 1500^\circ\text{K}$, as shown in Figure 6. The lowest observed burning pressures are 1.9 psi (compared to 1.3 calculated) for solid strands and 0.8 psi (compared to 0.4 calculated for fullscale motors) for a 50 lb motor.





Using the pressures and burning rates determined here, and calculated equilibrium C^* values for the propellant as a function of pressure, the throat areas necessary to extinguish a fullscale motor when supersonic flow is maintained (C^* extinction) were calculated using the mass balance equation with $\frac{d\rho_g}{dt}$ equal to zero.

$$V \frac{d\rho_g}{dt} = \rho_p A_b r - P A_t \frac{C^*}{P} = 0 \quad (11)$$

$$A_t = \frac{C^* \rho_p A_b r}{g P} = 13.0 \frac{C^* r}{P} \quad (12)$$

where

V = the chamber volume

ρ_g = the gas density

ρ_p = the solid propellant density

A_b = the burning area

A_t = the throat area

g = the gravitational constant

C^* = the characteristic velocity

The values of parameters describing the fullscale motors were used in Equation 12.

TABLE 1
CALCULATED THROAT AREAS

<u>Pressure (psi)</u>	<u>Burning Rate (in/sec)</u>	<u>C^* (ft/sec)</u>	<u>Throat Area (sq. in)</u>
2.0	.0165	4928	528
1.0	.0085	4888	540
0.9	.0074	4882	(522)
0.8	.0062	4876	(492)

The maximum value in the calculated throat area occurs at about 1 psi. At lower pressures, or higher throat areas, the mass generated by the propellant is less than the mass leaving the chamber and therefore there can be no steady-state pressure in the chamber. That is

$$V \frac{dp}{dt} = \rho A_b r - P A_t \frac{g}{C^*} \quad 0 \quad (13)$$

for all pressures and the pressure decreases rapidly to the extinction pressure where the propellant ceases to burn. It is noted that C^* extinction occurs at a higher pressure (1 psi) than low pressure extinction (0.4 psi) in the absence of supersonic flow.

CONCLUSIONS

From the results of the analysis, it is concluded that propellant burning rate variations with pressure for aluminized ammonium perchlorate polybutadiene propellants can be satisfactorily represented by a model based on heat feedback rates. The description of fullscale motor propellant burning rates at low pressure can be developed from

1. Fullscale data at high pressure
2. Subscale data at low pressure
3. Physical chemical property data on propellant components
4. Thermodynamic calculations of flame temperature, C^* , etc.

The approach leads to a direct way of assessing the relative heat feedback efficiencies of subscale propellant burning devices and permits the assessment of high pressure burning variations encountered in propellant production on low pressure burning rate. The burning rate equation leads directly to an accurate prediction of propellant extinction pressures for subsonic and supersonic flow conditions. Additional work is

required to develop a more fundamental derivation of the burning rate relationship and to test it on other types of propellants with different components, and where exothermic reactions occur in the surface, or in Zone 1.

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