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COMBUSTION PROBLEMS OF NITRAMINE PROPELLANTS

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Abstract

This report summarizes a theoretical investigation of the current problems of nitramine (composite) propellant combustion. This study has, as its distinctive feature, a detailed examination of the condensed-phase processes in the combustion of nitramine propellants. As a consequence of a recently developed model for the combustion of ammonium perchlorate (AP)/composite propellants, it is hypothesized that the condensed-phase degradation of the nitramine oxidizer particles to a vaporizable state is the overall rate-limiting step. It is also assumed that the gas-phase details are secondary in importance and need be studied only to the extent of supplying the correct boundary conditions on the condensed-phase/vapor-phase heat transfer. Because of our imprecise understanding of the gas-phase processes in the presence of combustion, several plausible models are considered for the gas phase. It is found that all of the gas-phase models considered lead to predictions sufficiently close to experimental trends for us to conclude that the precise details of gas-phase processes are not of critical importance in determining propellant combustion behavior. More to the point, we are led to believe that a thorough examination of the condensed-phase details may be sufficient in itself not only to interpret most of the available data on experimental regression rate vs. pressure of nitramine propellants but also to aid in the formulation of propellants to suit our needs.

Nomenclature

A	Constant in eq. (6) ($\text{gm cm}^{-3} \text{s}^{-1} \text{atm}^{-1}$)
a	Mean diameter of oxidizer particles (microns or cm) and also constant of the burning rate law ($r = a \cdot P^n$)
B	Pre-exponential factor in Arrhenius law for thermal degradation (s^{-1})
B_0	Reference value of B (s^{-1})
C_3, C_4	Defined in eq. (5)
c	Specific heat ($\text{cal gm}^{-1} \text{ } ^\circ\text{C}^{-1}$)
c_p	Gaseous specific heat at constant pressure ($\text{cal gm}^{-1} \text{ } ^\circ\text{C}^{-1}$)
D	Heat of degradation of solid (cal gm^{-1})
E	Activation energy for thermal degradation (cal mole^{-1})
FSV	Statistical mean fragment size vaporizing (dimensionless)
HEX	Heat of explosion (cal gm^{-1})

h	Normalized heat of degradation (dimensionless)
k	Coefficient of thermal conductivity ($\text{cal cm}^{-1} \text{s}^{-1} \text{ } ^\circ\text{C}^{-1}$) and Arrhenius thermal degradation rate constant (s^{-1})
δ	Thickness of surface melt layer (cm)
MW	Mean molecular weight of gaseous species (gm gm-mole^{-1})
m	Pressure exponent in eq. (6) (dimensionless)
\dot{m}'''	Gas phase combustion rate during uniform combustion ($\text{gm cm}^{-3} \text{s}^{-1}$)
n	Empirical pressure exponent in the propellant steady burning rate law (dimensionless)
P	Pressure (atm)
Q	Heat released by combustion gases upon complete combustion (cal gm^{-1})
R	Universal gas constant ($\text{cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$)
r	Linear regression rate (cm s^{-1})
T	Temperature ($^\circ\text{K}$)
T_v	Isochoric flame temperature ($^\circ\text{K}$)
v	Volume fraction of oxidizer in composite propellant (dimensionless)
X^*	Flame standoff distance (cm)
x	Distance coordinate (cm)
Z	Defined in eq. (5)
γ	Ratio of gaseous specific heats (dimensionless)
ζ	Normalized flame standoff distance (dimensionless)
κ	Thermal diffusivity ($\text{cm}^2 \text{s}^{-1}$)
Λ	Normalized mass burning rate in the gas phase (dimensionless)
ρ	Density (gm cm^{-3})
Ψ	Thickness of surface melt layer on oxidizer crystals in a composite propellant (cm)

Superscripts

—	Mean value
^	Value at regression rate breakpoint

Subscripts

b	Flame zone
mp	Melting point
o	Ambient solid

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s Solid phase
w Wall plane

I. Introduction

The limitations that the highly empirical nature of solid propellant design place on its technological applications are revealed clearly whenever new problems are encountered. This is particularly true when new applications are considered. Recently, the nitramine/composite propellants have been recognized as possessing very desirable properties for certain applications.¹ Offsetting the thermodynamic performance superiority is the combustion behavior, which has shown undesirable slope breaks in experimental regression rate vs. pressure curves. The undesirability of such a characteristic was amply described earlier.¹ It was thought to obviate this undesirable behavior, at least in the operating range of pressures (approx. below 30,000 psi), by making changes in propellant formulations. This was to be done in such a way as not to adversely affect the good features of performance, etc. In the absence of a theory of propellant combustion, however, efforts in this field cannot be well organized, and in the absence of a working model, at least, such efforts are conducted almost totally in the dark. In effect, what we now have is a set of experimental data that indicate general trends, and what we need, as a first requirement, is a model that can coherently interpret most, if not all, of the available data.

A very similar situation existed in the related field of ammonium perchlorate (AP)/composite propellant combustion until recently. A host of superficially diverse data could be found in the literature. The data covered the degradation, decomposition, and sublimation of the oxidizer (AP), and the degradation of the binder polymer; it also included similar data on AP doped with various chemicals, hot plate pyrolysis data on AP and the binder, single crystal deflagration data on AP, time-independent data on burning of composites, and similar time-independent data on composites with catalysts, oscillatory burning of composites, and all sorts of related experiments. An attempt was made to interpret this mass of data coherently in terms of a few simple postulates concerning the fundamental processes in propellant burning. A model was presented²⁻⁴ under the basic hypothesis that the fundamental degradation rate of AP to a vaporizable state is the overall rate-limiting reaction in propellant combustion. This CIT/JPL model successfully predicted the observed trends, including a few that were inconsistent with previous theoretical predictions.

In the present study this model has been explored to determine its applicability to nitramine propellant combustion. Aside from the obvious difference that the numerical data on rate constants and physicochemical properties would be different from those for AP/composites, there are also a few subtle differences, and these are mentioned in the report. In general, however, it is taken as a working hypothesis in this exploratory study that the essential details of the model are applicable to nitramine propellant combustion. Justification for this hypothesis can come only from examining the results, although - in a weak form - an indication of its general correctness comes from the simple reasoning that the rate-

limiting reactions are likely to be in the relatively low temperature, condensed-phase processes for nitramine propellant combustion also.

Lack of some of the input data needed to render the model completely self-contained has necessitated a parametric study of the problem. The oxidizer particle size, the volumetric loading, and the melt layer thickness (explained later) were varied over a range of model propellant formulations to predict theoretically the regression rate vs. pressure curves and related quantities (surface temperature, gas phase combustion zone extent, etc.). The predicted trends were found to be close to the experimentally observed trends. Most of the numerical constants used are available in the open literature or have been supplied by the USAF. The remaining few parameters are not arbitrary. They have been the subject of reasonable estimates in the past and should be within the grasp of experimental efforts in the near future.

The available literature is surveyed briefly in Section II. Section III goes into the details of the application of the CIT/JPL AP/composite propellant model to nitramine propellant combustion. The assumptions of constant wall temperature, uniform combustion rate, and the flame standoff distance being equal to the condensed phase heterogeneity are used to develop several possible models for the gas-phase processes in Section IV. A model incorporating the variation in flame standoff distance with pressure is also developed.

In general, this study has indicated that increasing the condensed-phase homogeneity (and hence increasing the heat transfer rate in the propellant) or decreasing the oxidizer particle size ought to have beneficial effects in reducing the high value of the burning rate exponent or avoiding the slope-break phenomena. These can be regarded as design hints as predicted by the model. Actual quantitative predictions of the burning rate vs. pressure curves for nitramine/composite propellants of specified formulations will require information on a few parameters that is not yet available and can only come from further research.

II. Review of Available Literature and Data

Literature surveys on nitramine combustion, in the particular context of current interest, have previously been carried out⁵⁻⁶. Rather than repeat these efforts, those papers and aspects will be discussed here that either did not receive much attention in those surveys, are more recent, or that affect this work directly. The available literature can logically be classified into two categories -- as experimental or theoretical work.

A. Experimental

Taylor⁷ found in his work on PETN, RDX, and HMX that, for any given pressure, the mass burning rate was practically constant at all loading densities and particle sizes of pressed strands of the material (up to the maximum pressure tested, 200 atm), although the apparent burning rate differed considerably as the oxidizer particle size was varied in the strands. High-speed motion pictures showed unmistakable evidence of a melt layer on the surface of the propellants. He postulated that the burning rate is controlled by the melt layer behavior on the surface, thus accounting for the neg-

ligible influence of particle size on the mass burning rate. Taylor also conducted burning rate experiments on the same oxidizers by lightly filling tubes of paper and Perspex (PMMA) in various mean particle sizes⁸. It was found that beyond a certain pressure the linear regression rate increased dramatically (with an increase also in the pressure exponent, n). The pressure at which this transition occurred increased to higher values with a reduction in oxidizer particle size. He attributed this phenomenon to convective heat transfer inside the pores. This "porous bed" burning is probably not directly relevant to the burning of nitramine propellants, which is our prime concern here.

Zimmer-Galler⁹ carried out thermal decomposition and combustion experiments with RDX, polyester binder propellants containing various burning rate catalysts. The degradation/decomposition kinetic constants that were obtained⁹ have been consistently used throughout the present work. Again, a reduction in oxidizer particle size was found to increase the pressure at which the burning rate pressure exponent markedly increased, Fig. 1. An interesting feature of this work is that burning rate experiments were conducted in widely different gas environments and the same curve of regression rate vs. pressure was obtained. This indicates that the fundamental rate-limiting reactions are unlikely to be in the gas phase.

Optical microscope examination of the surfaces of quenched samples of nitramine propellants in ref. 9 showed a glazed appearance, leading to the belief that a melt layer existed on the surface during combustion. More recently, high-speed micro-cinematography^{10, 11} and scanning electron microscopy of extinguished surfaces^{10, 12} also support the concept of a melt layer. The latter has revealed that the melt layer decreases in thickness with increasing chamber pressure.

The motion pictures of Cohen¹⁰ seem to show that there exists a fairly clearly defined bright "flame" zone some distance ($\sim 100\mu$) from the propellant surface. Cohen also showed that increasing the concentration of oxidizer in the propellant has an effect on the regression rate breakpoint similar to reducing the oxidizer particle size.

The effects of small variations in catalyst type and concentration, binder type (energetic or inert), and nitramine type, particle size and concentration have all been investigated at various pressures (refs. 5, 6, 13-16). However, the developmental nature of these efforts limits their scope where direct applicability is concerned.

According to Flanagan¹⁶ the addition of catalysts appears to have no effect on the burning rate slope-break phenomenon.

Very recent experimental work on RDX decomposition^{17, 18} has led to the postulation of a mechanism for the process. As such, the details are more appropriately considered theoretical than experimental.

B. Theoretical

The amount of theoretical work on nitramine combustion reported in the literature is rather limited and appears to have been done only in the general context of other propellants. Hence, it would appear that only those theoretical treatments that are sufficiently general to include in their scope different propellant ingredients need be examined in some detail. The basic objective of such an examination would be to extract information useful in arriving at a rational theory of nitramine combustion. Unfortunately, not many (sufficiently general) theories on composite propellant combustion exist. The well-known theories from Princeton¹⁹ address themselves to AP/composites and rely rather heavily on the available AP data. Hence, at least in their original form, the Princeton theories do not seem to have direct applicability to nitramine combustion.

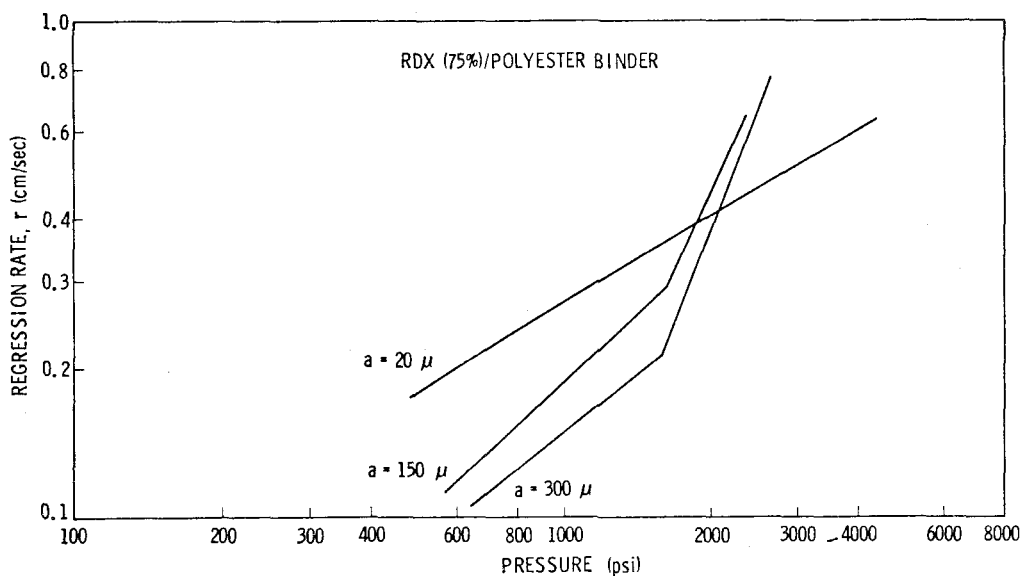


Fig. 1. Effect of RDX particle size on measured regression rate vs. pressure, replotted from ref. 9.

That essentially leaves us with the Beckstead, Derr, Price (BDP; refs. 20-22) model of composite propellant combustion. Here, applicability to nitramine combustion is definitely possible; as a matter of fact, the original work²¹ actually considered such a direct application to HMX (and its systems). Extension of that model to the specific problem on hand definitely seems feasible. This will not be discussed further here, because such an approach is currently being carried out by Cohen¹⁰.

The CIT/JPL model of composite propellant combustion is sufficiently general to be applicable to a host of problems in composite propellants*. In particular, applications to current problems in nitramine propellant combustion seem feasible²³.

Within the framework of any propellant combustion model, we recognize three regimes of importance to propellant combustion. These are the relatively low-temperature condensed phase, the medium-temperature vapor-phase/condensed-phase interface (wall), and the relatively high-temperature vapor phase. From the fact that, at any given pressure, we do observe a fairly well-defined regression rate, it is evident that an overall rate-limiting reaction is in operation in the system. The basic idea behind the CIT/JPL model is that the overall rate-limiting reaction in propellant combustion is likely to be in the relatively low temperature condensed phase. The vapor-phase heat transfer to the propellant surface matches the requirements of the degradation reactions and the sensible enthalpy rise. Since many of the oxidizers used in propellants are similar - crystalline solid particles and the binders are polymers of one form or another - and since the basic processes in the condensed phase (degradation and decomposition) are also similar, it would seem worthwhile to investigate the possibility of a single model being applicable to all such propellant combustion. If the key processes behind the overall burning rate are in the vapor phase, the prospects of the success of such an investigation appear bleak because of the rather varied compositions that occur in the vapor phase as determined by propellant chemistry.

Since the CIT/JPL model was based on the fundamental assumption that the key processes are in the condensed phase, fairly detailed calculations were performed of the regression rate vs. pressure curves and the related quantities (flame standoff distance from the surface, wall temperature variations, etc.). The theoretical results concerned only AP and AP/composite propellants. The predictions were found to be close to experimental observations in various applications including hot plate pyrolysis data of various investigators (compiled by Powling²⁴), AP single crystal deflagration data, initial temperature sensitivity, and the time-independent combustion data of propellants. In addition, the same model also gave predictions on oscillatory combustion characteristics (response functions) that were close to experimental observations, but unexplained by previous theories²⁵. Those gas-phase details needed to supply the proper boundary conditions on the condensed phase are modeled to be consistent with two of the popular pictures. It is found that either

*Only the essentials of the CIT/JPL model are presented here; additional details are contained in refs. 2-4.

is capable of handling the situation adequately, thereby de-emphasizing the importance of the precise details of the gas-phase processes to propellant combustion.

III. Postulated Mechanism of High Pressure Decomposition

A. Basic Postulates

The combustion of composite propellants involves extremely complicated processes in all of the three regions of interest (condensed phase, condensed phase - vapor phase interface, and vapor phase). Any completely realistic model would be so interactive analytically that it would be impractical to handle. What is needed is a model for the key processes that retains a degree of similarity to the actual physics and chemistry, at least to the extent of representing the fundamental parameters and phenomena. Since an adequate theoretical understanding of most of the details of propellant burning does not exist, the only real test of a model is the agreement (or otherwise) of the predicted results with experimentally observed trends. However, good agreement in one regime is no indication of the merits of the model when extrapolations to other regions are considered. If a model consistently predicts results close to experimental observations in several different regimes, it is tempting to apply the model to other systems as well.

The basic concept behind the CIT/JPL model is shown schematically in Fig. 2. The fundamental rate-limiting reaction is hypothesized to be the degradation of the oxidizer crystals in a thin melt layer on the interface between the oxidizer and the binder. Hence, the geometry of the propellant, as determined by the formulation, can be related to the degradation/decomposition of the propellant. It is to be clearly remembered, as has been emphasized several times^{3, 4}, that the model is an average representation only and is NOT to be interpreted literally.

Concentrating our attention on the condensed phase only, we may write the one-dimensional energy equation applied between the deep solid (∞) and the vapor/solid interface wall (o).

$$k \frac{d^2 T}{dx^2} + \rho c r \frac{dT}{dx} = D \rho c B \exp(-E/RT) \quad (1)$$

The source (or sink) term on the right hand side of the energy equation contains terms related to the actual degree of degradation at each plane in the propellant. This can be related to the fundamental degradation equation, which is, in the particular case at hand, an Arrhenius form of the equation. The pre-exponential constant B (in $k = B \exp(-E/RT)$) is assumed to be linearly dependent on the chamber pressure. The justification for this pressure dependence comes from the reasoning that the actual degradation is brought about by the diffusion of a catalytic species in the melt layer shown. The equations applied to AP/composite propellants lead to the regression rate expression:

$$r = \sqrt{\frac{\kappa \frac{6\psi v}{a} B_o P \exp(-E/RT_w)}{\left(\frac{E}{RT_w}\right) \left(\frac{T_w - T_o}{T_w}\right) \left[(h+1) \lambda n \frac{FSV}{FSV-1} - \frac{h}{FSV} \right]}} \quad (2)$$

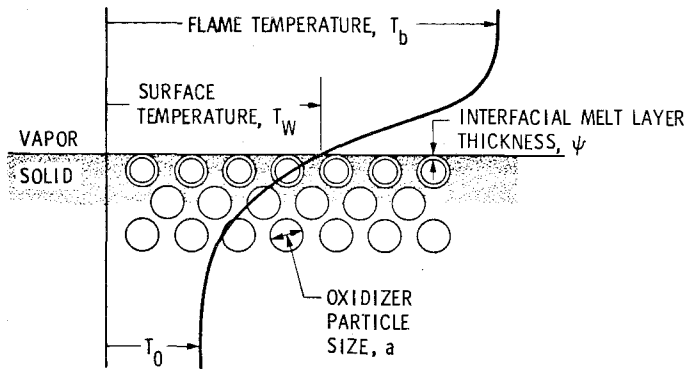


Fig. 2. Propellant Model

Detailed information concerning this equation is given in refs. 2-4.

As can be seen, ψ is the only parameter not precisely determined at the present time. However, since reasonable estimates of its values can be made, it is not a free parameter. For example, a ψ that is 5-10% of the oxidizer particle size seems reasonable, while 40-50% certainly does not. The numerical value of the wall temperature, T_w , has to be determined through proper matching with the gas-phase details, and several different models have been tried for the gas phase. Actually, experimentally measured values of the wall temperature may also be used when available. All of these approaches were used to predict various quantities of interest in the combustion of AP/composite propellants²⁻⁴.

Because of these and other²⁶ successes of the preliminary work, the CIT/JPL model was applied in the present study to the combustion of nitramine propellants. The basic aim was to postulate mechanisms of degradation/decomposition, so as to remove from the operating range the discrete slope breaks in the experimental regression rate vs. pressure curves. Essentially, the same analytical picture as for AP propellants was used. Obviously, the numerical constants were appropriately different. Also, in the original CIT/JPL model, as applied to the combustion of AP/composite propellants, the concept of Fragment Size Vaporizing (FSV) was introduced to signify the extent of propellant degradation at the vaporization step. An effort was made to determine the numerical value of FSV independently of propellant combustion details by observing similarities of vapor pressure equilibrium data of hydrocarbons. Here, in the combustion of HMX, RDX, etc., this second aspect of FSV relation seems to need some modifications. First, the pressures of interest are so high that, at all reasonable values of wall temperatures, the FSV is far less than unity, which makes degradation of the fundamental unit in the oxidizer RDX and HMX seem to be important. The FSV rule, in its original form², is not applicable to such a case. Second, the fundamental unit in the crystal (HMX and RDX) is not small or simple (as in AP) and therefore the concept of FSV needs careful interpretation.

Because of the considerations discussed above, the experimentally measured values of the degradation rates were used directly. These values are, inherently, influenced by variations of the

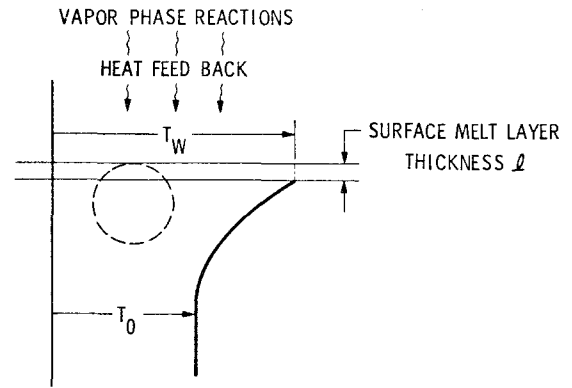


Fig. 3. High Pressure Behavior

surface details during combustion. Basically, we are assuming that the experimentally-determined fundamental degradation rate constants are directly applicable at pressures higher than those at which they were measured. The validity of such an approach can be established only by examining the results. The results obtained in the present study do appear reasonable in quantitative comparison with experimental data. Thus, it would appear that the new assumption concerning the vaporization step, in generalizing the original CIT/JPL model to nitramines, is a valid approach. Besides, as can be seen, the uncertainties in this respect (i. e., those concerning the value of FSV) are likely to make only minor variations in the quantitative regression rate predictions and hardly any at all in the qualitative trends. Thus, even if the new assumption on FSV should prove wrong later, our results here would still retain their utility.

As will become clear later, the basic assumption behind the derived equation (eq. 2) is that the condensed phase material (the propellant) may be considered homogeneous for the purpose of heat transfer calculations. It is this assumption that enables us to write the energy equation in the first place. When this assumption breaks down, the result (eq. 2) cannot be valid. Obviously, a second model is needed to represent the propellant combustion mechanics. The new model is shown in Fig. 3. It is assumed that all of the degradation reactions now take place in a surface layer of thickness l , and the regression rate is now given by

$$r = l B_0 P \exp(-E/RT_w) \quad (3)$$

Turning our attention to the elusive gas-phase details, the popular flame sheet model is envisioned as a possible means of exploring the wall temperature variations (and regression rates², too). The essence of the flame sheet approximation is that all of the gas-phase reactions are confined to a thin zone parallel to the surface but displaced a distance (X^*) from it. In other cases, it is possible that the reactions in the gas phase are uniformly distributed and are characterized by a mass consumption rate of $\dot{m}''' = A \cdot P$, where A is a constant and P the pressure. With this model, we may predict the wall temperature and regression rate variations if the value of A is known.

The task ahead now became fairly clear. The trends in propellant combustion behavior were examined as some of these parameters were varied.

Consideration was given to the applicability to nitramine propellant combustion and the implications of the results obtained in light of the available experimental data.

B. Break-Point Criteria

Breaks in the slope of solid propellant burning rate vs. pressure relationships are generally indicative of discrete dimensional effects. Discrete dimensions in heterogeneous propellants are obviously associated with the oxidizer particle (it is recalled that no slope breaks have been reported in tests with liquid oxidizers such as iso-DMED.¹⁴ Naturally, the question is "under what conditions do the discrete dimensions manifest themselves?" The natural dimension in propellant burning is the propellant thermal depth, κ/\bar{r} (propellant thermal diffusivity \div linear regression rate). When this dimension is large compared to the oxidizer particle size, a , we expect discrete dimensional effects to be smeared out. On the contrary, when κ/\bar{r} is small compared to a , discrete dimensional effects should be evident.

In this study, the breakpoints are predicted under the assumption that they occur when the characteristic thermal depth in the condensed phase becomes comparable to or less than the characteristic heterogeneity scale in the propellant (oxidizer particle size).

The equations used are as follows:

1) before the breakpoint

$$r = \sqrt{\frac{\kappa \frac{6\psi v}{a} B_o P \exp(-E/RT_w)}{(E/RT_w) \left(\frac{T_w - T_o}{T_w} \right)}} \quad [P \text{ in atm}] \quad (4)$$

2) at the point of slope discontinuity, i. e., the transition from subsurface reaction rate control to surface reaction rate control:

$$\hat{r} = \kappa/a \quad (5)$$

$$\hat{P} = \frac{\hat{r}^2 (E/RT_w) \frac{T_w - T_o}{T_w}}{\frac{6\psi v}{a} \kappa B_o \exp(-E/RT_w)} \quad (6)$$

3) after the breakpoint:

$$r = \iota B_o P \exp(-E/RT_w)$$

4) the value of the melt layer thickness is determined by matching regression rates at the breakpoint

$$\iota = \frac{\hat{r}}{B_o \hat{P} \exp(-E/RT_w)} \quad (7)$$

It is assumed to be constant in the post-breakpoint regime, at least in a reasonable range of pressure variations.

C. Discussion

In analogy with the available studies on AP single crystal deflagration (see, for example, Guirao and Williams²⁷), it is tempting to postulate the existence of a melt layer that gets progressively thinner with increasing chamber pressure. (Actually, the regression rate is more relevant than the pressure.) Beyond a certain value of the

regression rate, the melt layer disappears completely, and hence the regression rate vs. pressure curve is qualitatively different. Such ideas on AP deflagration need careful interpretation before they can be applied to nitramine combustion. It is to be remembered that the regression rate itself is continuous at the breakpoints observed in nitramine combustion, although the slope is not. If the reaction site (the melt layer) disappeared completely, we would expect a discontinuity in the regression rate, as indeed the AP regression rates are discontinuous at such a point. However, none is apparent in nitramine combustion. Similarly, discontinuous variations in either the wall temperature or the fundamental rate-limiting reaction would also be expected to be reflected in discontinuities in the regression rate, except in the fortuitous circumstance that two or more variations occur in a mutually compensating manner. These points reinforce the argument that the basic mechanisms behind the regression are probably not too different from each other on either side of the breakpoint.

If chemical processes were of crucial importance to the slope-break phenomenon, it would seem reasonable to expect that pressure would have a much stronger effect than it is observed to have. For example, we ought not to be able to shift the breakpoint position on the pressure scale, not to mention the complete elimination of the breakpoint (from the desired operating range, at least) through variations in a physical parameter such as the oxidizer particle size. On the other hand, the breakpoint seems to correlate with the regression rate more than it does with pressure.

If the high slope is caused by increased surface area due to mechanical cracking of the crystals, one would expect a fairly random behavior of regression rate with pressure in the post-breakpoint regime. None is evident. The data seem to be very reproducible, besides showing a well behaved n value.

IV. Gas Phase Treatments

A. Constant Surface Temperature

In the basic equation (eq. 2), all of the following are determined by the propellant formulation: the volumetric loading of the oxidizer in the propellant, v ; the oxidizer particle size, a ; the thermal diffusivity, κ ; and the kinetics constants B_o and E . The initial temperature, T_o , and the chamber pressure, P , are determined by the experimental conditions. The interfacial melt layer thickness, ψ , and the propellant wall (surface) temperature, T_w , are the only two variables that do not have unambiguous values at this stage of the analysis. Values for ψ have to come from experimental measurements. The correct way of treating T_w is to make no assumptions regarding its value, but to allow it to be self-determined by the gas-phase energetics and fluid dynamics.

For these initial calculations the wall temperature was assumed not to vary with pressure. From calculations that will be presented later, it was concluded that this assumption is reasonably justified for nitramine propellants of given formulations. It is not evident that the wall temperature is constant, only that this may be a reasonably good assumption at this stage. It is recognized

that the wall temperature may vary with variations in other formulation parameters (such as the oxidizer particle size, for example). In fact, the results obtained in the present section strongly suggest that the wall temperature probably decreases with increasing oxidizer particle size.

1. Parametric variation of a . The major propellant variable in the experimental regression rate measurements conducted to date has been the oxidizer particle size. Early in the development of the model, calculations were therefore carried out varying a parametrically to determine how well the regression rate breakpoint trends agreed with the experimental data. The numerical values used are given in Table 1.

For the pre-breakpoint region the effects of oxidizer particle size on the linear regression rate were not included in these initial calculations. These effects are available in the term $6\psi v/a$ (eq. 4), which is assumed here to be constant; i. e., at a specified oxidizer volumetric loading, the ratio, ψ/a , of the interfacial melt layer thickness to the oxidizer particle is assumed to be constant at a reasonable value of 5%.

The variation in the breakpoint \hat{r} value with a was calculated using eq. 5:

a in μ	2	10	30	50	100
\hat{r} in cm/s	7.5	1.5	0.5	0.3	0.15
\hat{r} in in./s	2.95	0.59	0.196	0.118	0.059

At 600°K, eq. 7 was used to calculate the melt layer thickness:

a in μ	10	30	50	100
l in μ	0.121	0.383	0.625	1.14

The calculated regression rate vs. pressure curves are shown in Figs. 4 and 5 for T_w values of 600° and 650°K, respectively.

2. Parametric variation of ψ . In this section the only parameter whose value is not thoroughly settled at this stage, the melt layer thickness ψ , was varied parametrically. In addition, the oxidizer particle size was again varied over the range of general interest. It was previously assumed that ψ was 5% of a . Its value was now varied from 1% to 9% to see its effect on the breakpoint in the regression rate vs. pressure curves. In eq. 2 it is seen that the regression rate varies as the square root of ψ . Even though the variation is mild, it can nevertheless have a noticeable effect on the breakpoint. A subtle point is that, although increases in oxidizer particle size decrease the regression rate, this result is valid only when all the other parameters are held fixed. For example, if the interfacial melt layer thickness is increased at the same time, the regression rate can actually increase with increases in particle size. Consequently, when ψ/a is specified as a certain percentage, the results have to be examined with care.

The results of the calculations showed that increases in the melt layer thickness increase the regression rate, as anticipated. In refs. 2 and 3 the basic regression rate formula (eq. 2) was derived under the assumption that ψ is small compared to a . Hence, when ψ/a approaches or exceeds 0.1 (for example), the results may not be valid. In such a case, physically speaking, the interfacial melt layer thickness on the oxidizer particle is becoming comparable to the oxidizer particle diameter itself, and the basic model becomes of questionable applicability.

In comparison with experimental values of linear regression rates, the results indicate that T_w probably decreases with increases in oxidizer particle size. The linear regression rate predictions were reasonable at the higher values of the wall temperature ($\approx 630^\circ\text{K}$) and the higher values of the melt layer thickness ($\sim 9\%$) for the smaller-oxidizer-particle propellants, while the regression rates of the larger-oxidizer-particle propellants were reasonable at the lower values of T_w . Such a variation in T_w is reasonable within the framework of a wide variety of gas-phase models (GDF, flame sheet, uniform combustion rate, etc.). This is so

Parameter	Value	Source
activation energy of degradation, E	48,000 cal/mole	ref. 9
pre-exponential constant, B	$10^{19.1} \text{ sec}^{-1}$	ref. 9
wall temperature, T_w	600°K, 650°K	assumed; to be supplied later by gas-phase details.
thermal diffusivity, $\kappa \equiv k/\rho c$	$15 \times 10^{-4} \text{ cm}^2/\text{sec}$	Eglin AFB data
volumetric loading of RDX, v , in the propellant	80 %	typical value; can be varied easily.
ratio of interfacial melt layer thickness to particle size, ψ/a	5 %	assumed as reasonable.
oxidizer particle size, a	2 μ , 10 μ , 30 μ , 50 μ , 100 μ	---

Table 1. Numerical Values Used (RDX) (Constant Wall Temperature).

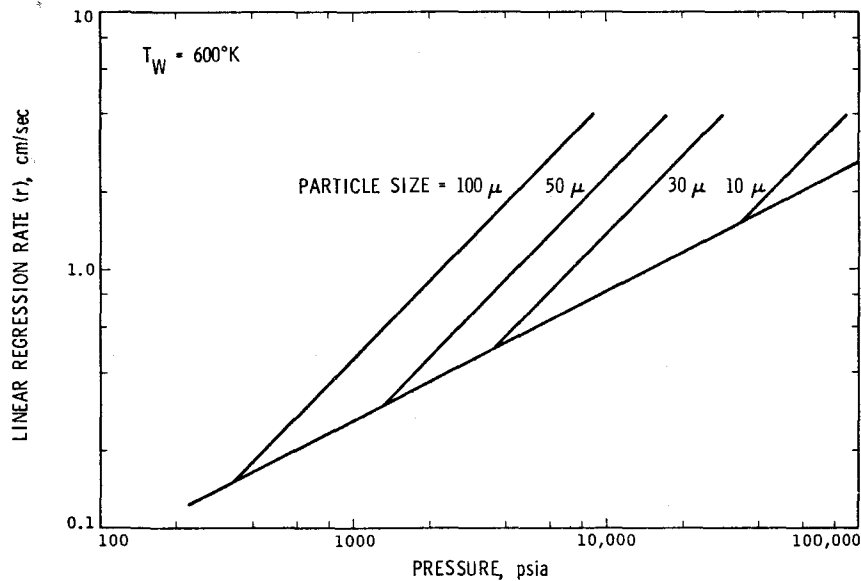


Fig. 4. Calculated regression rate vs. pressure for constant wall temperature of 600°K .

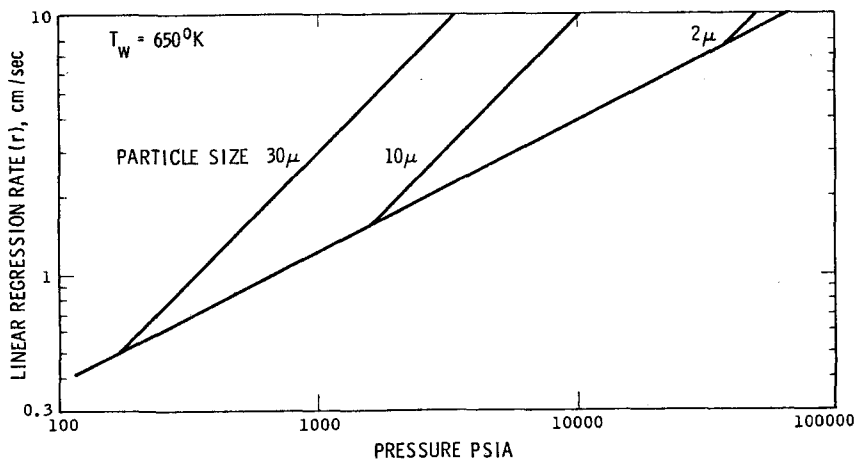


Fig. 5. Calculated regression rate vs. pressure for a constant wall temperature of 650°K .

because, as oxidizer particle size increases, the gas-phase combustion zone moves farther and farther away from the propellant surface (wall). This results in a decrease in wall temperature, since the basic energetics are not affected. However, this picture needs careful interpretation in the post-breakpoint regime since, by the very nature of the surface reaction model, oxidizer particle size is no longer a significant factor.

B. Uniform Combustion in the Gas Phase

In this section the previous work was extended to include consideration of gas-phase reactions, instead of assuming a constant wall temperature. The program that was developed is sufficiently general to permit determination of the regression rate as a function of pressure, when the condensed-phase and gas-phase parameters are specified. Further improvements to the program will be described later in the paper.

In accordance with the analyses in ref. 2, the regression rate is determined by the matching of the gas-phase mass combustion rate to the condensed-phase mass generation rate. The value of the wall temperature enters the expressions for both of these rates and iterative procedures are needed for solution, since transcendental functions are involved. The general method is described in detail on pp. 35-38 (particularly on p. 37) of ref. 2. In our application, the method is modified by elimination of the parameter FSV, which, as discussed previously, is believed to be of questionable applicability to the high pressure combustion of complex substances like nitramines.

Hence, the following equations (which result from a simplification of the general equations presented in ref. 2) are used:

1) condensed-phase mass generation rate:

$$\rho r = \rho \left[\frac{\left(\frac{6\psi v}{a} \right) B_o \cdot P \cdot \kappa \cdot \exp(-E/RT_w)}{(E/RT_w)(T_w - T_o/T_w)} \right] \quad (8)$$

2) gas-phase mass consumption rate (nondimensional):

$$\Lambda = \frac{\kappa \cdot Q \cdot \dot{m}'''}{\rho \cdot c_p \cdot (T_w - T_o) r^2} \quad (9)$$

where \dot{m}''' is the uniform combustion rate in the gas phase ($\text{gm cm}^{-3} \text{sec}^{-1}$) and Q is the heat of combustion (cal gm^{-1}).

Matching the heat flux from the gas to the condensed phase leads to

$$(\Lambda \cdot \zeta) + C_3 \exp(\zeta) + C_4 - 1 = \frac{Q}{c(T_w - T_o)} - 1 + h, \quad (10)$$

where $\zeta = \ln Z$; $Z = -\Lambda/C_3$; $C_3 = 1 + h - \Lambda$; $C_4 = 1 - C_3$; $h = \text{nondimensional heat of degradation, } D/c(T_w - T_o)$.

It is evident that there are no free parameters in the system. The gas-phase reaction rate, \dot{m}''' , uniquely specifies the regression rate since the other variables in the system ($B_o, E, D, Q, c, \kappa, \rho, T_o$) all have very definite numerical values.

The gas-phase mass consumption is now taken as adequately represented by two parameters, A and m ,

$$\dot{m}''' = AP^m \quad (11)$$

This is an assumption in the theory. However, it has been widely used and is seen, even in the simplest case ($m=1$), to yield very reasonable results for AP/composite propellants. The main support for the above form of gas-phase reaction rate, aside from the fact that it has been highly successful in other applications, is described in detail in ref. 2 (pp. 32-33).

Since the mass consumption rate in the gas phase is assumed to be completely determined by intermolecular diffusion of the reactants in the propellant, the numerical values of the constants are unlikely to be influenced by the chemical nature of those vapors.

Such reasoning leads, as a first approximation, to the same numerical values of A and m as were used in other propellant applications. This question of the numerical values of A and m has to be eventually settled through actual experimental measurements of the gas-phase reaction rate. The situation is analogous to the condensed-phase parameters E and B_o , which come from more fundamental experiments (DTA, TGA, DSC, etc.).

Details of the computer program are given in ref. 28. For one set of the parameters the results obtained are plotted in Fig. 6. The details of $\psi/a, v, \text{ binder, etc.}$ are not pursued at this stage, as this point was discussed in the previous section.

It is noted that the program is preliminary in form. It has been found to work for a few sets of values, for all of which $m=1$. It has not been tested extensively for various values of the parameters nor to optimize the cost considerations.

C. Flame Standoff Distance Model

Although the essence of this paper is a condensed-phase theory that hypothesizes that most of the interesting details in propellant combustion are controlled by the condensed-phase processes, a few essential details of the gas-phase processes do need to be considered in order to obtain a self-contained solution. In their simplest form the gas-phase details are adequately contained in the value of the temperature at the gas/solid interface popularly called the "wall temperature, T_w ." The value of the wall temperature determines the linear regression rate of the propellant through the condensed-phase equation (eq. 2). In the previous sections, two seemingly different models were proposed for the gas-phase processes; both were based on the assumption that the molecular mixing rate of fuel and oxidizer vapors controls the rate of chemical reaction in the gas phase: (1) the assumption of constant wall temperature (with a flame sheet model for the gas-phase combustion); (2) the assumption of uniform combustion in the gas phase.

Neither of the above two models attempted to interpret the gas-phase details in a mechanistic way. The present section makes a first attempt to overcome some of the limitations and actually relate the gas-phase details to propellant formulations.

1. Standoff distance proportional to a . The basic ideas of the analytical approach of this section are described below. The flame zone, or the zone of vigorous combustion, is established over the propellant surface. Because of the discrete nature of gas evolution from the particles, it is expected that considerable inhomogeneity exists in the gas phase above the burning surface. In fact, such gas-phase inhomogeneities are clearly visible in photographs of AP/composite propellant combustion²⁹. Far downstream, however, such inhomogeneities disappear because the combustion reactions reach completion. Therefore, it is clear that the scale of gas-phase inhomogeneity (reflected in the flame zone dimensions) is related to the physical extent of condensed-phase heterogeneity (reflected in the oxidizer particle size). Hence, a quantitative relation is sought between these two variables. The idealized representation of the flame zone dimensions is the "flame standoff distance." Analytically, one can predict the propellant regression rate if the flame standoff distance is specified. The flame standoff distance not only varies with the condensed-phase heterogeneity, but also with the chamber pressure. Any theoretical modeling of the flame standoff distance must predict both of these variations. The present model concentrates only on the variations with oxidizer particle size. Pressure variations are considered later. The essence of the present approach is written as

$$X^* \propto a \quad (12)$$

$$\text{or } X^* = (\text{constant}) \cdot a$$

A linear dependence was temporarily assumed between the flame standoff distance and the oxidizer particle size. Based on physical considerations, it can be expected that larger oxidizer particles would result in the flame zone being established farther away from the surface. However, the assumed linear dependence (eq. 12) is by no means obvious. It is merely one of several possible assumptions that enable us to obtain analytical solutions at this

stage. This form was chosen purely for the simplicity it affords. As can be readily appreciated, the representation of eq. 12 needs modification when different pressures are considered. For example, the numerical value of the constant can be expressed as a function of pressure to incorporate the fact that, for a given propellant formulation (oxidizer particle size), the flame standoff distance decreases with increases in pressure.

The analytical solution is straightforward. The propellant formulation specifies the values of a and v , along with the standard values of B_0 , E , μ , and T_0 . A reasonable (constant) value of the interfacial melt layer thickness, δ , is assumed ($\approx 5\%$ of a). The value of the wall temperature uniquely determines the regression rate. However, the wall temperature cannot have an ambiguous value if it is required that the adiabatic flame temperature (determined by the propellant formulation) be reached exactly at the "flame standoff distance," as specified by eq. 12. Hence, the gas-phase energy equation applied between the wall⁺ and the flame sheet⁻ is solved for the heat transfer rate at the wall (wall temperature gradient). There exists only one value of the wall temperature at which the heat transfer rate into the condensed phase from the gas phase vaporizes the propellant material at exactly the rate determined by the condensed-phase chemical kinetic degradation equation (eq. 2). Further details of the calculation are given in ref. 28.

The RDX constants in Table 2 were used for the representative propellant considered here. The results are presented in Figs. 7 and 8. It is most encouraging that: (1) the wall temperatures are predicted to be about 600°K, which is the generally accepted value for nitramine propellant combustion; (2) the regression rates are predicted to be around 0.4 cm/sec at 100 psia, which is again reasonable; (3) the wall temperature and the regression rates are predicted to decrease with increases in the oxidizer particle size.

The last of these is the most significant result of the present program. The widely observed experimental trend of decreasing regression rate

with increases in the oxidizer particle size is correctly predicted by this extremely simple modeling. This particular version of the model does not have for its aim the prediction of X^* variations with pressure. However, an analysis in the following subsection which predicts the X^* variations with mean pressure will show that the X^* decreases nearly logarithmically with pressure increase. When that fact is incorporated into the present model, the simple model should be very useful.

2. Variation of flame standoff distance with pressure. Here we consider the flame standoff distance variations in greater detail. The flame standoff distance is an analytically convenient concept which enables us to write a simple expression for the heat transfer rate from the vapor phase to the condensed phase. Obviously, for a given energetic scheme (as determined by the propellant formulation), this heat transfer rate must depend on the chamber pressures. This is nothing more than a statement of the fact that the regression rate is pressure dependent.

A theoretical prediction of the variations in the flame standoff distance with pressure would enable us to further evaluate our model regarding its applicability to nitramine propellant combustion. Also, as explained later, quantitative experimental determination of the flame standoff distance with pressure, which is relatively easy to measure (compared with the wall temperature T_w or the gas-phase combustion rate \dot{m}'''), may actually help us determine some of the other unknowns.

The computations here are subject to the same limitations as before. For example, the breakpoints are still predicted as being given by the ratio of the thermal diffusivity to the oxidizer particle size. Also, predictions based on the condensed-phase model are not valid beyond the breakpoint.

The key elements of the computation in this section are as follows:

1) The variations in the flame standoff distance are computed based on a reference value at a reference state. It is assumed that the flame standoff distance is proportional to the condensed-phase

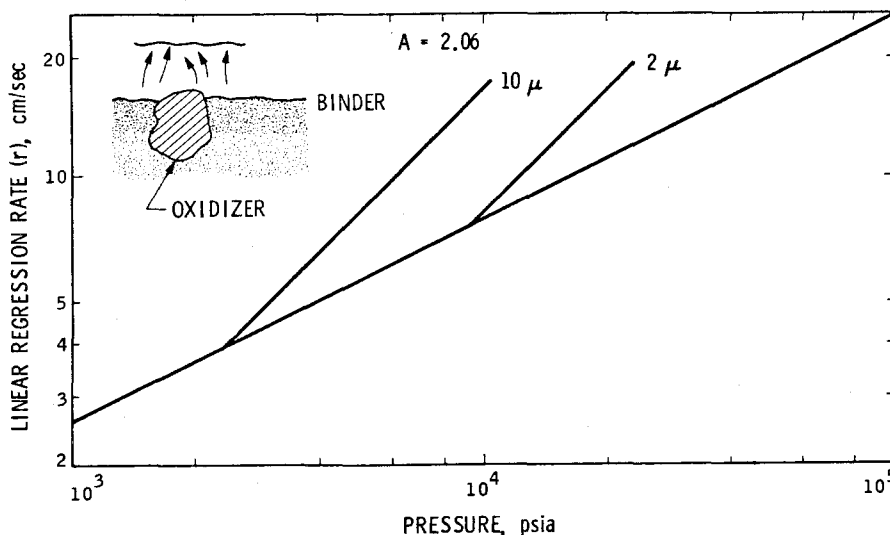


Fig. 6. Calculated regression rate vs. pressure assuming uniform combustion in the gas phase ($\dot{m}''' = A \cdot P$).

Parameter	Value	Source
activation energy of degradation, E	48,000 cal/mole	ref. 9
pre-exponential constant, B	$10^{19.1} \text{ sec}^{-1}$	ref. 9
thermal diffusivity, $\kappa \equiv k/\rho c$	$15 \times 10^{-4} \text{ cm}^2/\text{sec}$	Eglin AFB data
volumetric loading, v, of RDX in the inert binder propellant	80 %	typical value
ratio of interfacial melt layer thickness to oxidizer particle size, Ψ/a	5 %	assumed as reasonable
oxidizer particle size	$10\mu - 100\mu$ in steps of 10μ	
flame temperature of monopropellant RDX	3282°K	ref. 9
flame temperature (adiabatic) of propellant with 20 % inert binder	2640°K	Eglin AFB data
constant in $X^* = (\text{constant}) \cdot a$	1	assumed

Table 2. Numerical Values Used.

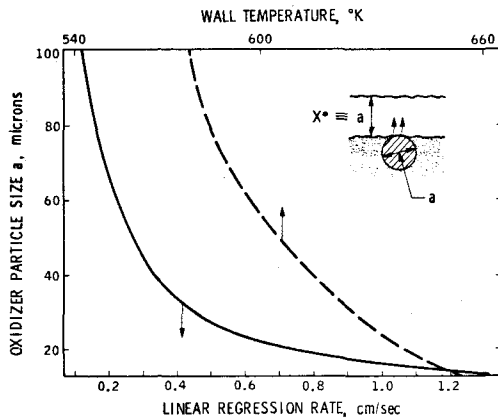


Fig. 7. Calculated regression rate, propellant wall temperature, and oxidizer particle size relationships assuming a simple flame stand-off distance gas-phase model; pressure = 1000 psia.

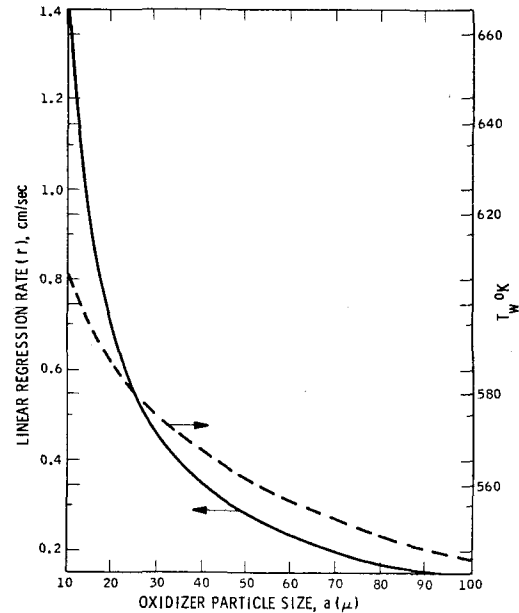


Fig. 8. Calculated regression rate, propellant wall temperature, and oxidizer particle size relationships assuming a simple flame stand-off distance gas-phase model; pressure = 21,000 psia.

heterogeneity (the oxidizer particle size). Moreover, at the reference pressure of 1000 psia, the flame stand-off distance is equated to twice the oxidizer particle size. This equality is somewhat arbitrary, but it is not thought to be of critical importance to the general conclusions of this study.

2) The wall temperature is assumed to remain constant as the pressure is varied. However, T_w variations with oxidizer particle size are considered.

The computational procedure is straightforward. The propellant formulation specifies the oxidizer particle size, a ; the volumetric loading of the oxidizer, v ; the flame temperature, T_b , which is assumed not to vary appreciably with pressure.

A reasonable value of the interfacial melt layer thickness is assumed (5% of the oxidizer particle size). The linear regression rate of the propellant is computed at incremental values of T_w using eq. 2. The flame stand-off distance is computed through $X^* = \zeta \kappa_s / r$. The surface melt layer thickness is not assumed constant, but its variation with pressure and oxidizer particle size (Fig. 9) is calculated using the expression

$$l = \frac{\kappa}{r} \ln \left(\frac{T_w - T_o}{T_{mp} - T_o} \right) \quad (13)$$

This expression was derived by solving the condensed-phase energy equation, neglecting the heat of degradation, and assuming that the surface region is molten between T_{mp} and T_w . It is recognized that the argument is not rigorously valid, since the quoted melting points refer to an equilibrium phenomenon, whereas propellant combustion is a non-equilibrium phenomenon, with residence times of the order of 10^{-3} sec. However, this crude argument is thought to be adequate as a first description of a complex process.

The computations have been carried out for wide variations in wall temperature, for oxidizer particle sizes of 20, 30, 40, 50, and 60μ and at pressures of 1000, 11,000, 21,000, 31,000, and

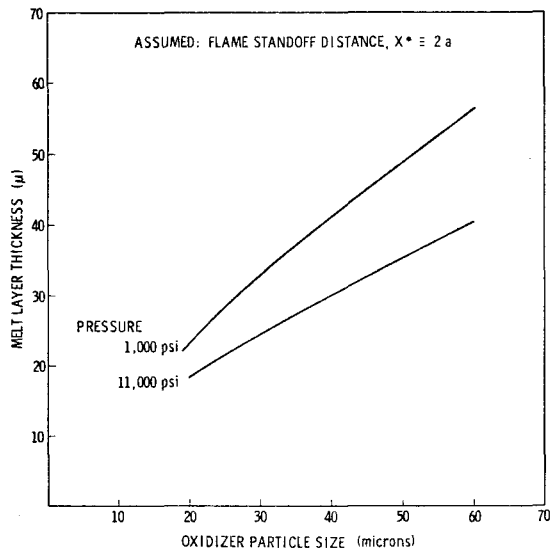


Fig. 9. Calculated variation in surface melt layer thickness with pressure and oxidizer particle size.

41,000 psia.

There exist several different ways of interpreting the extensive data obtained. Figure 10 presents the variations in the flame standoff distance with pressure variations. The calculations realistically predict that the flame standoff distance, X^* , decreases with pressure. It must be kept in mind that these predictions, using eq. 2, are not valid beyond the breakpoint, \bar{r} . However, in view of the crudeness of the breakpoint predictions (order-of-magnitude validity only), the predicted lines are continued with broken lines up to the highest pressure, 41,000 psia. The variations in the oxidizer particle size, as they influence the flame standoff distance, are considered. It is clear that the predictions in Fig. 10 are probably accentuating this effect somewhat. It is known from experiment that a variation in the oxidizer particle size from 50 to 20 μ is unlikely to increase the regression rate by more than a factor of 2. However, the trends are predicted well.

V. Concluding Remarks

A. General Remarks

The present theoretical work on nitramine propellant combustion has considered a parametric study of the various quantities of interest. The ultimate goal of all such studies would be to analytically predict the regression rate as a function of the propellant formulation and chamber pressure. If successful, we would be in a position to alter the formulations to suit specific needs of a propellant pressure-time history. In fact, that was precisely the main motivation of the present investigations. Since we have not achieved such a predictive ability even in the vastly explored AP/composites field, it is needless to add that the main task still remains open in the nitramine propellant field. However, this work has indicated the general trends fairly well. Probably the single most important result is the clear indication that the model, which started out with postulates and hypotheses, is indeed ap-

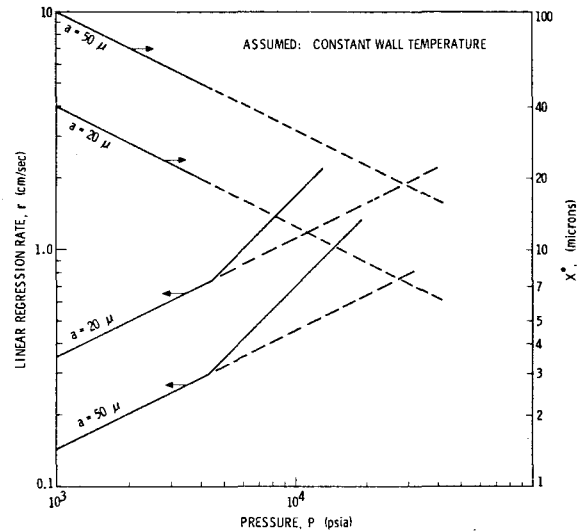


Fig. 10. Calculated variation in flame standoff distance and regression rate with pressure.

plicable to the problem of nitramine combustion. The fact that the fundamental rate data used, with no free parameters, predicts the observed trends cannot be indicative of the contrary.

In general, the model has relied rather heavily on AP/composite propellant data. This is true not so much with regard to the actual use of that data but more with regard to the position of the AP/propellant field. More specifically, in earlier work, the AP/propellant data were repeatedly used²⁻⁴ as the standard testing basis for our model. The model consistently predicted results close to experimental observations. Generalizations have since been attempted to cover the nitramine propellant field. It is natural to ask about the validity of such generalizations.

The similarities are thought to be profound. Both of these propellants (AP and nitramine) are composite propellants using a rather heavy loading of crystalline oxidizers. The binders form a rather small portion of the formulation and usually are also polymers of some form. The degradation reactions of the oxidizer and binder seem to obey the same general type of Arrhenius expressions. The pre-exponential factor was assumed to be linearly dependent on the chamber pressure, based on a picture of degradation. Later, it was found that experimenters had indeed encountered this pressure-dependent degradation of AP.³⁰ Based on the same picture, pressure-dependent degradation of nitramines has been assumed here. We are hopeful that a future effort, or a future discovery of an earlier experimental study, might indicate the assumed pressure dependence.

An extremely important aspect of the present study needs to be clearly understood. This model has been put forward to represent composite propellants as a family. Except for the numerical constants, it makes absolutely no distinction, at least in its present form, between AP composites and nitramine composites. The model says that beyond the homogeneous solid limit for composite propellants (i. e., when $a > \kappa/r$), we should observe changes in the propellant combustion behavior, no matter what the chemical formulations are. The natural

question would be whether such slope-break or similar phenomena are known to occur with AP/composite propellants. At first sight the AP/propellant family may appear to be totally devoid of all such special behavior. However, a closer examination of the data indicates that most AP/propellants have been meant generally for rocket applications where the operating pressures are rather low compared to the high pressure applications that the nitramine propellant data cover. Hence, we should examine the AP/propellant data in high pressure applications. Fortunately, such a study has been made and the report has been declassified recently³¹. That study, which involved closed bomb tests of high pressure combustion of AP/composite propellants of a variety of formulations, invariably found an increase in the slope, n , by almost a factor of two at the higher regression rate. The data presented³¹⁻³³ are indeed very impressive and show unmistakable changes in the slopes at high pressures. The slope breaks appear to be rather smooth and not as abrupt as those reported for nitramines. This could be due to the multimodal distribution of particles in the conventional AP/composites or could also be due to broader distribution of particle sizes in the AP case as compared with the nitramines case. (As a matter of fact, a fairly sharp break was observed²⁶ with a fairly narrow AP size distribution in a non-metallized AP/PBAN propellant.) Also, when an extremely unimodal distribution of nitramine oxidizer crystals was used in a propellant¹⁰, a drastically high slope break was discovered. The main "signal" in all of this is simply that the slope change anticipated by the CIT/JPL model for composite propellants in general is indeed observed not only in nitramine propellants but in conventional AP/composites as well. This must certainly be regarded as a strong support for the model.

The second aspect of this work has to do with specific propellant applications. All of the numerical data were obtained for a model composite propellant that has the properties of RDX oxidizer. Rate constants were found⁹ only for RDX. In any case, the results are not expected to be widely different for the other nitramine oxidizers. Superficially, it may appear that binder interactions have been completely ignored in this work. Actually, it is the binder interaction that determines such important parameters as the wall temperature T_w , the flame temperature T_b , and the other property values such as ρ , c , κ , etc. Thus, the binder interactions have been intimately interwoven into the model. Also, the gas-phase model used for AP/composites may appear, at first sight, to be totally inapplicable to the nitramine composites. This is mainly because of the fundamentally different roles that the binder vapors play in the combustion of these two classes of propellants. In AP/composites the AP monopropellant flame temperature is lower than the propellant flame temperature; the binder vapors undergo chemical reactions with the oxidizer vapors exothermally to reach the final flame temperature. In the nitramine propellants with the so-called "inert" binders, the monopropellant oxidizer flame temperature is higher than the propellant flame temperature, and the binder vapors actually lower the temperature with interaction. However, under the basic assumption that the diffusion-mixing process of the two vapors (oxidizer's and binder's) controls the gas-phase temperature profile, the same vapor-phase model is applicable for both propellants. In addition, we

have the interesting situation that the same numerical constants used for AP/composites may be used, as a first approximation, in describing this mixing process (and hence the heat release process). The important mixing process is non-laminar, and this diffusion-mixing is unlikely to depend strongly on the chemical nature of the vapors. In any case, the gas-phase processes are not the primary controlling factors in propellant burning in the present model.

It is encouraging that the predictions and the anticipations of one model are consistent with the main trends in the experimental literature. The model indicates that decreasing the oxidizer particle size should have a beneficial effect; indeed, it is observed to have a beneficial effect. The model places little emphasis on the metal content, special ingredients, and the chemical nature of the binder or oxidizer. Experimentally, it is found that "whether inert or energetic binder, cyclic or linear nitramine, metallized or non-metallized, the slope-break phenomenon is invariably exhibited."²⁸

In the context of the present model, the catalyst would be influencing the condensed-phase degradation rate and consequently the break in the regression rate vs. pressure would persist around the same value of the regression rate. However, the pressure at the breakpoint would be lower, because the catalyst addition would increase the regression rate at a given pressure. Hence, in the context of the CIT/JPL model, it would appear that the breakpoint would occur at lower pressure with catalyst addition, if no other changes are made at the same time. (However, the catalyst itself is obviously added at the expense of some other component, and we do not have, strictly speaking, the same composition any more.)

This model, admittedly, is highly idealized and needs improvements before handling more realistic features such as particle size distributions, multimodal oxidizers, etc. Also, further studies are expected to make the model more self-contained in that the wall temperature variations will be automatically handled. It is believed that more research effort will actually enable us to arrive theoretically at propellant formulations to meet specific applications criteria.

B. Salient Conclusions

The above parametric study on the combustion of nitramine propellants has led to the following conclusions:

- (1) The CIT/JPL model realistically predicts the observed trends with a minimum number of input parameters.
- (2) Different gas-phase models lead us to essentially the same analytical trends, thus de-emphasizing the importance of the gas-phase details.
- (3) The wall temperature of the propellant decreases with increases in oxidizer particle size; the interfacial melt layer thickness has a relatively minor influence on the propellant combustion behavior.
- (4) The hypothesis of gas-phase combustion zone dimensions being determined by the condensed-phase heterogeneity, a , leads to predictions of wall temperature and the regression rate that are both in agreement with the experimentally observed trends.

- (5) With regard to the widely held belief in the existence of a "melt layer" on the surface of the propellant, the model seems to be sufficiently general to be consistent with the reported observations.
- (6) Simplified relationships for the melt layer thickness and flame standoff distance give reasonable results which show them decreasing with increasing pressures, consistent with reported observations.

References

1. Heiney, O. K. "Status of the Air Force Problems with Nitramine Propellants," AFATL, Eglin AFB, presented at the JANNAF Workshop on the Combustion of Nitramine Propellants, Eglin AFB, Florida (16-17 Jan. 1973).
2. Kumar, R. N. "Some Considerations in the Combustion of AP/Composite Propellants," Daniel and Florence Guggenheim Jet Propulsion Center, California Institute of Technology (Aug. 1972).
3. Kumar, R. N. "A New Look at AP Composite Propellant Combustion," JPL Quarterly Technical Review, 3, 2 (July 1973), pp. 53-77.
4. Kumar, R. N. "Condensed Phase Details in the Time-Independent Combustion of AP/Composite Propellants," Comb. Sci. and Tech., 8, 3 (1973), pp. 133-148.
5. Stiefel, L. "Review of Workshop on the Combustion of Nitramine Propellants for Guns," 10th JANNAF Combustion Meeting, CPIA Publication 243, Vol. I (Dec. 1973), pp. 199-213, Silver Spring, Md.
6. Moy, B. K. Nitramine Combustion Problems, Technical Report AFATL-TR-72-190, (Sept. 1972), Air Force Armament Laboratory, Eglin AFB, Florida (and additional data supplied by author).
7. Taylor, J. W. "A Melting Stage in the Burning of Solid Secondary Explosives," Comb. and Flame, 6 (June 1962), p. 103.
8. Taylor, J. W. "The Burning of Secondary Explosive Powders by a Convective Mechanism," Trans. Faraday Society, 58 (1962), p. 561.
9. Zimmer-Galler, R. "Correlations between Deflagration Characteristics and Surface Properties of Nitramine-Based Propellants," AIAA J., 6, 11 (Nov. 1968), pp. 2107-2110.
10. Cohen, N. S. and Flaming, R. W. "Combustion of Nitramine Propellants," Lockheed Propulsion Co., Redlands, Calif., presented at AFATL-AFOCSR Explosive Combustion Meeting, Air Force Armament Laboratory, Eglin AFB, Florida (11 Apr. 1974).
11. Visnov, M. "Nitramine Combustion," Frankford Arsenal, Philadelphia, Pa., presented at AFATL-AFOCSR Explosive Combustion Meeting, Air Force Armament Laboratory, Eglin AFB, Fla. (11 Apr. 1974).
12. Derr, R. L. "HMX Deflagration," Naval Weapons Center, China Lake, Calif., presented at AFATL-AFOCSR Explosive Combustion Meeting, Air Force Armament Laboratory, Eglin AFB, Fla. (11 Apr. 1974).
13. Peterson, J. A. "Control of Pressure Exponent of Nitramine-Containing Gun Propellants," Thiokol/Wasatch Div., Brigham City, Utah, presented at JANNAF Workshop on the Combustion of Nitramine Propellants for Guns, Eglin AFB, Fla. (16-17 Jan. 1973).
14. Simmons, R. L. "Composition Effects on Nitramine Propellant Combustion," Hercules, Inc., Allegany Ballistics Laboratory, Cumberland, Md., presented at JANNAF Workshop on the Combustion of Nitramine Propellants for Guns, Eglin AFB, Fla. (16-17 Jan. 1973).
15. Caveny, L. H. and Summerfield, M. "The Ignition of Composite Propellants Containing HMX," Princeton U., Princeton, N. J., presented at JANNAF Workshop on the Combustion of Nitramine Propellants for Guns, Eglin AFB, Fla. (16-17 Jan. 1973).
16. Flanagan, J. E. "Composition/Ingredient Effects on the Burning Rate Versus Pressure Behavior of Nitramine Propellants," Rockwell International, Canoga Park, Calif., presented at JANNAF Workshop on the Combustion of Nitramine Propellants for Guns, Eglin AFB, Fla. (16-17 Jan. 1973).
17. Cosgrove, J. D. and Owen, A. J. "The Thermal Decomposition of 1, 3, 5 Trinitro Hexhydro 1, 3, 5 Triazine (RDX) - Part I: The Products and Physical Parameters," Comb. and Flame, 22 (Feb. 1974), p. 13.
18. Cosgrove, J. D. and Owen, A. J. "The Thermal Decomposition of 1, 3, 5, Trinitro Hexhydro 1, 3, 5 Triazine (RDX) - Part II: The Effects of the Products," Comb. and Flame, 22 (Feb. 1974), p. 19.
19. Summerfield, M., et al. "Burning Mechanism of Ammonium Perchlorate Propellants," in Solid Propellant Rocket Research, Progress in Astronautics and Rocketry, Vol. 1, Academic Press, New York (1960), pp. 141-182.
20. Beckstead, M. W., et al. "A Model of Composite Solid Propellant Combustion Based on Multiple Flames," AIAA J., 8, 12 (Dec. 1970), pp. 2200-2206.
21. Beckstead, M. W., et al. "The Combustion of Solid Monopropellants and Composite Propellants," 13th Symposium (International) on Combustion Proceedings, the Combustion Institute, Pittsburgh, Pa. (1971), pp. 1047-1056.
22. Combustion of Nitramine Propellants, Planning Document P-2706, Lockheed Propulsion Co., Redlands, Calif. (14 May 1973).
23. Kumar, R. N. and Strand, L. D. "Combustion Problems of Nitramine Propellants," Jet Propulsion Laboratory, Pasadena, Calif., presented at AFATL-AFOCSR Explosive Combustion Meeting, Eglin AFB, Fla. (11 Apr. 1974).

24. Powling, J. "Experiments Relating to the Combustion of Ammonium Perchlorate-Based Propellants," 11th Symposium (International) on Combustion Proceedings, the Combustion Institute, Pittsburgh, Pa. (1967), pp. 447-456.
25. Kumar, R. N. and Culick, F. E. C. "Role of Condensed Phase Details in the Oscillatory Combustion of Composite Propellants," AIAA Paper 73-218, Washington, D. C. (1973).
26. Kumar, R. N. and McNamara, R. P. "Some Experiments Related to L-Star Instability in Rocket Motors," AIAA Paper 73-1300, Las Vegas, Nev. (1973).
27. Guirao, C. and Williams, F. A. "A Model for Ammonium Perchlorate Deflagration between 20 and 100 Atmospheres," AIAA J., 9, 7, (July 1971), pp. 1345-1356.
28. Kumar, R. N. and Strand, L. D. Analytical Investigation of the Combustion Processes Occurring in Advanced Nitramine-Based Propellants, Final Report, Eglin AFB MIPR No. 7621-73-90062, Jet Propulsion Laboratory, Pasadena, Calif. (1974).
29. Maltzev, V "Certain Problems Related to Mechanisms of Combustion of Condensed Systems (Double-Base and Mixed Propellants)," Institute of Chemical Physics, USSR Academy of Sciences, Moscow (Aug. 1971 - Feb. 1972).
30. Shannon, L. J. Composite Solid Propellant Ignition Mechanisms, AFOSR Scientific Report 66-2103, UTC 2138-ASR1, United Technology Center, Sunnyvale, Calif. (Nov. 1966).
31. Cole, R. B. High Pressure Solid Propellant Combustion Studies Using a Closed Bomb, Special Report No. S-68, Rohm and Haas Co., Redstone Arsenal Research Div., Huntsville, Ala. (Aug. 1965).
32. Cole, R. B. Combustion of Solid Propellants at High Pressures - a Survey, Special Report No. S-71, Rohm and Haas Co., Redstone Arsenal Research Div., Huntsville, Ala. (20 May 1965).
33. Cole, R. B. Burning Rates of Solid Composite Propellants at Pressures Up to 20,000 Psi, Report No. S-80, Rohm and Haas Co., Redstone Research Laboratories, Huntsville, Ala. (Sept. 1966).