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TABLE OF CONTENTS (Concluded)

<u>Section</u>	<u>Title</u>	<u>Page</u>
IV.	EXAMINATION OF THE MODEL IN THE CONTEXT OF THE AFOSR/AFATL EXPLOSIVE COMBUSTION MEETING	45
	A. KEY ELEMENTS	45
	B. DISCUSSION	46
V.	CONCLUDING REMARKS	49
	A. GENERAL REMARKS	49
	B. SALIENT CONCLUSIONS	53

Analytical Investigation Of The Combustion Processes Occurring In Advanced Nitramine-Based Propellants

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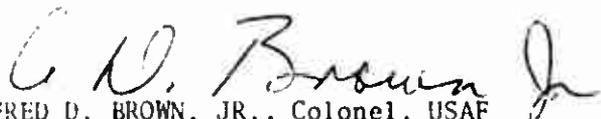
FOREWORD

The work described in this report was performed during the period from June 1973 through July 1974 by the Propulsion Division of the Jet Propulsion Laboratory, California Institute of Technology under MIPR No. FY 7621-73-90062 with the Air Force Armament Laboratory, Air Force Systems Command, Eglin Air Force Base, Florida.

Program managers for the Armament Laboratory were Lt William S. Bulpitt and Mr Otto K. Heiney (DLDL).

This report has been reviewed and is approved for publication.

FOR THE COMMANDER


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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.

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TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
I.	INTRODUCTION	1
II.	EVALUATION OF AVAILABLE LITERATURE AND DATA . . .	5
	A. AVAILABLE LITERATURE	5
	1. Experimental Work	5
	2. Theoretical Work	7
	B. USAF-SUPPLIED BURNING RATE DATA	10
	C. CATALYSTS AND THEIR EFFECTS	10
	D. OXIDIZER PARTICLE SIZE EFFECTS	12
III.	POSTULATED MECHANISMS OF HIGH PRESSURE DECOMPOSITION	13
	A. BASIC POSTULATES	13
	B. EFFECT OF VARIATIONS IN WALL TEMPERATURE ON THE SLOPE OF THE BURNING RATE LAW CURVE	18
	C. CALCULATIONS ASSUMING CONSTANT WALL TEMPERATURE	19
	D. CALCULATIONS ASSUMING UNIFORM COMBUSTION IN THE GAS PHASE	23
	1. Method	23
	2. Computer Program	25
	E. PARAMETRIC VARIATIONS OF ψ and a	27
	1. Computer Program	29
	2. Discussion	30
	F. GAS-PHASE DETAILS AS INFLUENCED BY THE OXIDIZER PARTICLE SIZE	30
	1. Method	31
	2. Computer Program	33
	3. Numerical Data	33
	4. Results	33
	5. Breakpoints	36
	G. MELT LAYER COMPUTATIONS	36
	H. VARIATIONS OF FLAME STANDOFF DISTANCE WITH PRESSURE	40

TABLE OF CONTENTS (Concluded)

<u>Section</u>	<u>Title</u>	<u>Page</u>
IV.	EXAMINATION OF THE MODEL IN THE CONTEXT OF THE AFOSR/AFATL EXPLOSIVE COMBUSTION MEETING	45
	A. KEY ELEMENTS	45
	B. DISCUSSION	46
V.	CONCLUDING REMARKS	49
	A. GENERAL REMARKS	49
	B. SALIENT CONCLUSIONS	53

LIST OF FIGURES

<u>Figures</u>	<u>Title</u>	<u>Page</u>
1.	Effect of RDX particle size on measured regression rate vs. pressure, replotted from Ref. 12	12
2.	Propellant model	14
3.	High pressure behavior	17
4.	Calculated regression rate vs. pressure for a constant wall temperature of 600°K	22
5.	Calculated regression rate vs. pressure for a constant wall temperature of 650°K	22
6.	Calculated regression rate vs. pressure assuming uniform combustion in the gas phase ($\dot{m}''' = A \cdot P$)	26
7.	Calculated regression rate, propellant wall temperature, and oxidizer particle size relationships assuming a simple flame standoff distance gas-phase model; pressure = 1000 psia	35
8.	Calculated regression rate, propellant wall temperature, and oxidizer particle size relationships assuming a simple flame standoff distance gas-phase model; pressure = 21,000 psia.. . . .	35
9.	Melt layer behavior on a model propellant	39
10.	Schematic view of the model for melt layer computations	39
11.	Calculated variation in surface melt layer thickness with pressure and oxidizer particle size	42
12.	Calculated variation in flame standoff distance and regression rate with pressure	43

LIST OF TABLES

<u>Tables</u>	<u>Title</u>	<u>Page</u>
1.	Nitramine propellant experimental data gathered from literature	11
2.	Numerical values used (constant wall temperature)	20
3.	Numerical values used	34

LIST OF ABBREVIATIONS AND SYMBOLS

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 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 ($\text{cal gm}^{-1} \text{C}^{-1}$)
c_p	Gaseous specific heat at constant pressure ($\text{cal gm}^{-1} \text{C}^{-1}$)
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 ($\text{cal cm}^{-1} \text{s}^{-1} \text{C}^{-1}$) and Arrhenius thermal degradation rate constant (s^{-1})
l	Thickness of surface melt layer (cm)
MW	Mean molecular weight of gaseous species (gm gm-mole^{-1})
m	Pressure exponent in Eq. (6) (dimensionless)
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 ($\text{cal mole}^{-1} \text{K}^{-1}$)
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)

LIST OF ABBREVIATIONS AND SYMBOLS (Concluded)

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
\wedge	Value at regression rate breakpoint

Subscripts

b	Flame zone
mp	Melting point
o	Ambient solid
s	Solid phase
w	Wall plane

SECTION 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 (Ref. 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 (Ref. 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 manner 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 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 presented (Refs. 2-4) 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.

Because we lack some of the input data needed to render our model completely self-contained, we have made a parametric study of the problem. The oxidizer particle size, the volumetric loading, and the melt layer thickness (explained later) are varied over a range in 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 are 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 burning rate data and additional USAF-supplied data are evaluated in Section II, after a brief literature survey. The literature survey is restricted to those models of propellant burning that show promise of application here. The effects of burning rate catalysts and oxidizer particle size are mentioned.

Section III goes into the details of the application of the CIT/JPL AP/ composite propellant model to nitramine propellant combustion. This material was presented in the monthly technical reports made by JPL to the U.S. Air Force over the period of this contract. 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. The thickness of the widely accepted "melt layer" is computed using a very simple model.

In general, our 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 our 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.

SECTION II

EVALUATION OF AVAILABLE LITERATURE AND DATA

A. AVAILABLE LITERATURE

A literature survey on nitramine combustion, in the particular context of current interest, has been made by Ludwig Stiefel (Ref. 5). Rather than repeat his effort, we will concentrate on those papers and aspects that either did not receive much attention in Ref. 5 or that affect our own work directly. The available literature can logically be classified in two categories - as experimental or theoretical work.

1. Experimental Work

Among the experimental work on the subject, a large number have to do with developmental type of research aimed at increasing our understanding of combustion behavior in an empirical manner. The effects of small variations in catalysts, in binder type (energetic or inert), and in particle size, have all been investigated at various pressures. The available data should, in principle, be helpful in designing new nitramine propellants for specific applications. However, the empirical nature of all of these efforts (Refs. 6-9) limits their scope where direct applicability is concerned. Obviously what is needed is more fundamental experimental work, possibly on the oxidizer and the fuel separately, even if such efforts appear to be rather isolated from technological applications. It is encouraging to observe that two such efforts have indeed been reported in the open literature.

J. W. Taylor (Ref. 10) 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 negligible influence of particle size on the mass burning rate. Taylor also conducted experiments on the same oxidizers, PETN, RDX, and HMX, by lightly filling tubes of paper and Perspex (PMMA) in various mean particle sizes (Ref. 11). It was found that beyond a certain pressure the linear burning rate was dramatically higher, with an increase in the pressure exponent, n (in $r = ap^n$) also. He attributed this phenomenon to convective heat transfer inside the pores. This "porous-bed" burning, although very relevant to the overall situation in the cartridges, is not directly relevant to burning of single strands of nitramine propellants, which happens to be our prime concern in this report.

The work of Zimmer-Galler (Ref. 12) provides us with the numerical constants for the degradation/decomposition of the nitramines of interest in high pressure applications. Since the basic rate data enter into all fundamental models in a very direct manner, the work of Zimmer-Galler has proved extremely useful in our own predictions. An interesting feature of that work (Ref. 12) 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.

An examination of the surfaces of the quenched samples of nitramine propellants showed a glazed appearance, leading to the belief that a melt layer existed on the surface during combustion. This melt layer, which appears to make its presence felt at various stages of nitramine combustion modeling, is discussed in greater detail in Section III. To anticipate some of the future discussion, the melt layer seems to figure prominently in practically all of the modeling efforts, but whether the melt layer appears before or after the break-point has been a matter of doubt. At any rate, the kinetics constants determined by Zimmer-Galler have been consistently used throughout our work, and therein lies the value of that work for our discussions.

The very recent experimental work on RDX decomposition (Refs. 13 and 14) adds nothing fundamentally new to the field, and its relevance to propellant combustion studies is yet to be demonstrated. It postulates a mechanism for the decomposition of RDX and, as such, the details are more appropriately considered theoretical and not experimental.

2. Theoretical Work

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. Exceptions do exist (Ref. 15), but are few in number. 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 Princeton (Ref. 16) admittedly 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.

The modeling efforts at Georgia Institute of Technology (Ref. 17) are considering sandwich models of oxidizers and binders. Such studies definitely add to our knowledge and have the added advantage that they can be directly derived by simple experiments, some of which have already been performed in AP/binder systems (Ref. 18). It is not clear, however, as to how these sandwich studies can be generalized to handle the considerably more complicated heterogeneous mixture of oxidizer and binder that constitutes a technology propellant of our times. Until such a method of applying the sandwich results to actual propellants is indicated, their utility with regard to nitramine combustion will not be obvious.

That essentially leaves us with the BDP (Beckstead, Derr, Price; Refs. 19-21) model of composite propellant combustion, which is gaining popularity lately. Here, applicability to nitramine combustion is definitely possible; as a matter of fact, the original work (Ref. 20) 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 aspect of the literature will not be considered at length here because such an approach is the main theme of a contemporary study at the original BDP center (Lockheed Propulsion Co.) funded by AFOSR. The two efforts (LPC and JPL) are complementary, and several similarities will be mentioned below. As a matter of fact, one of the main objectives of the present work is to explain the experimental results of the LPC work.

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 feasible. In fact, such an application was indeed considered and the encouraging results obtained were presented (Ref. 22) at the Explosives and Combustion Meeting held at the Eglin AFB in April 1974.

At present, practically all of the useful design information on solid rockets is empirical. Because of a general lack of understanding of the fundamentals, costly programs are invariably needed in any solid propellant development. Hence there is a need for work at a fundamental level, to attempt to deempiricize propellant combustion data. Within the framework of any propellant combustion model, we recognize three regimes of importance to propellant combustion.

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

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 themselves only with 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 Powling, Ref. 23), 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 theories (Ref. 24). 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 is capable of handling the situation adequately, thereby de-emphasizing the importance of the precise details of the gas-phase processes to propellant combustion.

B. USAF-SUPPLIED BURNING RATE DATA

The USAF-supplied burning rate data on nitramines was evaluated in the framework of the CIT/JPL model. Rather a large number of parameters were varied, and the experimental output also varied; the parameters of direct relevance and importance to the CIT/JPL model are as follows: the burning rate exponents before and after the break point, the propellant formulation, the particle size of the oxidizer and, as explained later, the ratio of the thermal diffusivity to oxidizer particle size. This ratio (κ/a) has the dimensions of regression rate and figures prominently in our theory of nitramine combustion. The USAF-supplied data on regression rate vs. pressure is extensive and could be discussed at length in the context of our work. However, it is considered more appropriate to prepare a table of the relevant quantities to enable the reader to ascertain the general trends in the data (Table 1). As can be seen, although the pressure at the breakpoint is considerably different for different propellant formulations, the regression rates at the breakpoints do not differ greatly. In general, this leads us to believe that the basic hypotheses behind our condensed phase model may be valid, since, using only condensed-phase variables (thermal diffusivity, particle size, and regression rate), we have been able to unify some of the superficially diverse data on nitramine combustion.

C. CATALYSTS AND THEIR EFFECTS

There does not appear to exist in the open literature a systematic study of the nitramine propellant behavior as catalysts are varied in type or concentration. As already discussed the available information is almost entirely empirical and does not lend itself to a systematic classification of the effects of catalysts on burning rate or other effects. This state of affairs with catalysts is recognized by Stiefel also (Ref. 5).

Specifically, there does not appear to be any evidence (Ref. 1) that the addition of catalysts would either eliminate or make a significant improvement in this burning-rate slope-break phenomenon.

D. OXIDIZER PARTICLE SIZE EFFECTS

As already mentioned, the effect of oxidizer particle size offers a promising area for further investigation, since variations in this physical parameter appear to affect the slope-break phenomenon rather strongly (Ref. 1). In general, decreasing the oxidizer particle size seems to help avoid both the high slope and the slope-break phenomenon, as is shown in Fig. 1. In fact, using extremely small oxidizer particles (2μ) seems to remove the slope-break phenomenon completely from the operating range of pressures (Ref. 25). The experimental data available in this respect are summarized in Table 1. As can be seen, there is no conclusive evidence as to the precise nature of the systematic variations in the slope-break variations with oxidizer particle size. However, there apparently exist clear indications of these beneficial effects in other ways (Refs. 1 and 25). A systematic investigation of the effects of decreasing oxidizer particle size, intended to provide a solid ground for working models on this known beneficial effect, is in progress at the Eglin AFB and the experimental data are being received periodically at JPL. In the near future, it should be possible to process the systematic data in terms of the CIT/JPL model.

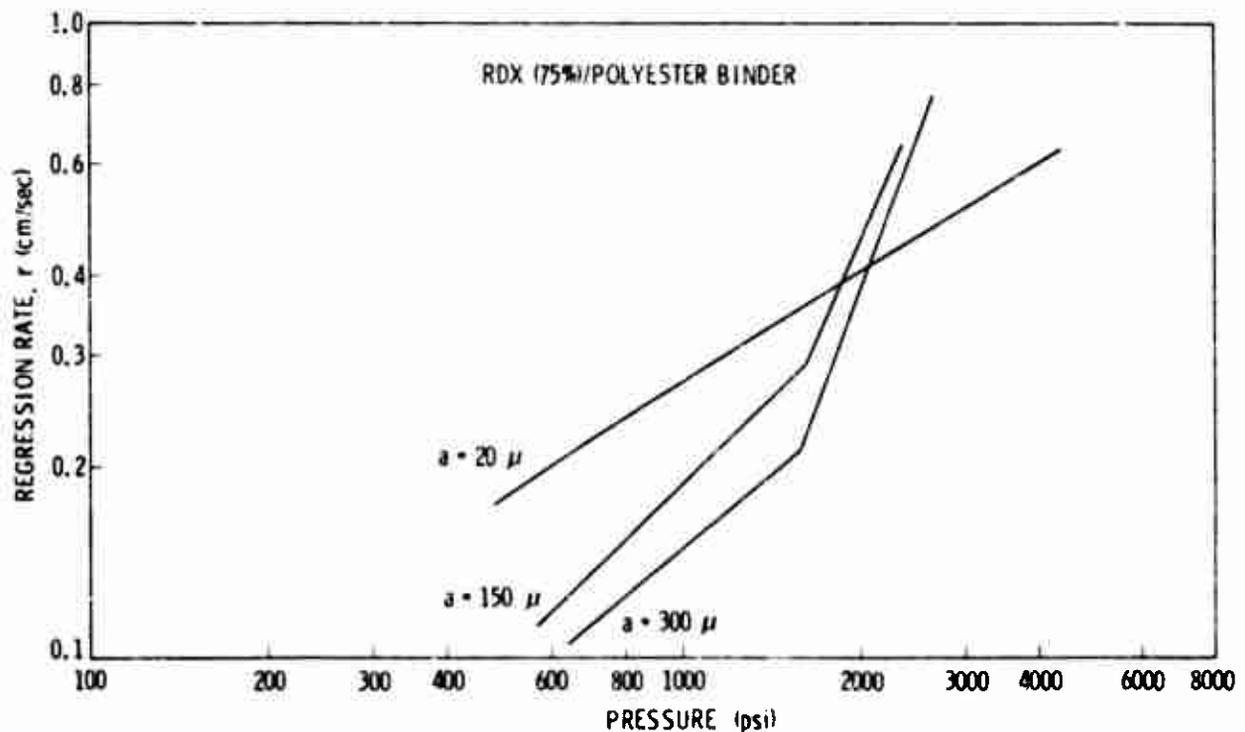


Figure 1. Effect of RDX Particle Size on Measured Regression Rate Versus Pressure, Replotted From Reference 12

SECTION III

POSTULATED MECHANISMS OF HIGH PRESSURE DECOMPOSITION

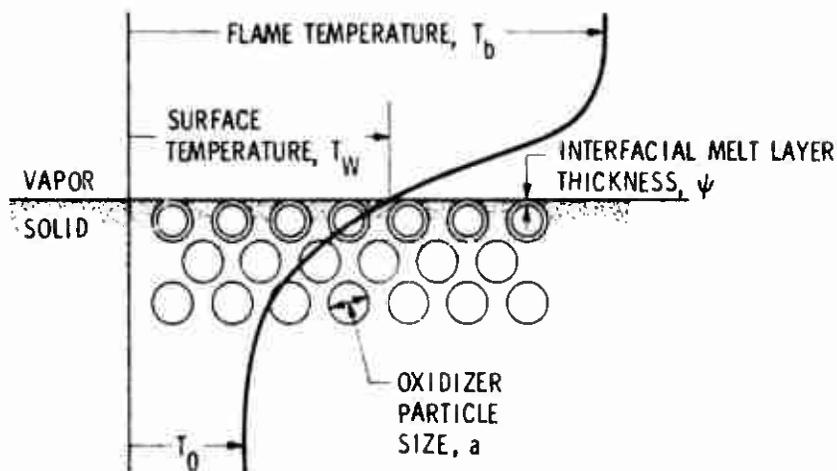
A. BASIC POSTULATES

The combustion of composite propellants involves extremely complicated processes in all of the three regions of interest (condensed phase, wall 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 (Refs. 3 and 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 (0).

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



$$r = \left[\frac{\frac{6\psi V}{a} \cdot \kappa B_0 P \cdot \exp(-E/RT_w)}{\frac{T_w - T_0}{T_w} \cdot \frac{E}{RT_w} \left[(h+1) \ln \frac{FSV}{FSV-1} - \frac{h}{FSV} \right]} \right]^{1/2}$$

Figure 2. Propellant Model

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:

$$r = \sqrt{\frac{\kappa \frac{6\psi V}{a} B_0 P \exp(-E/RT_w)}{\left(\frac{E}{RT_w}\right) \left(\frac{T_w - T_0}{T_w}\right) \left[(h+1) \ln \frac{FSV}{FSV-1} - \frac{h}{FSV} \right]}} \quad (2)$$

Detailed information concerning this equation is given in Refs. 2-4. To briefly recapitulate the definitions of the symbols,

κ is the thermal diffusivity of the propellant.

Ψ is the thickness of the interfacial melt layer on the oxidizer particles.

v is the volume fraction of the oxidizer particles in the propellant.

B_0 is the reference value of the pre-exponential constant in the degradation.

h is defined as $D/c (T_w - T_0)$, where D is the heat required by unit mass of the oxidizer to be degraded to the fundamental individual repeating units.

c is the specific heat of the propellant (solid).

T_0 is the temperature of the unaffected propellant.

FSV is the parameter Fragment Size Vaporizing, which essentially quantifies the extent of propellant degradation at the vaporization step.

As can be seen, Ψ , the interfacial melt layer thickness, 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 propellants (Refs. 2-4).

Because of these and other (Ref. 26) 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 form (Ref. 2), 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 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 .

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 rates (Ref. 2), 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.

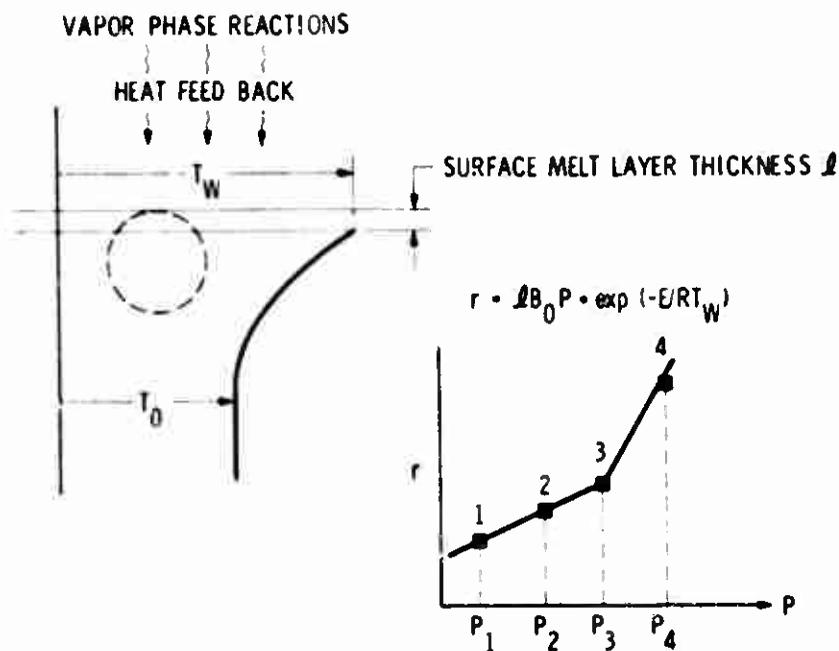


Figure 3. High Pressure Behavior

The task ahead of us now becomes fairly clear. The trends in propellant combustion behavior are to be examined as some of these parameters are varied. Consideration is also to be given to the applicability to nitramine propellant combustion and the implications of the results obtained in light of the available experimental data. Such an approach was undertaken, and the periodic progress was summarized in monthly reports. The results are presented here.

B. EFFECT OF VARIATIONS IN WALL TEMPERATURE ON THE SLOPE OF THE BURNING RATE LAW CURVE

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 (Ref. 7)]. 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 the present section, 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). For the pre-breakpoint region, the effects of oxidizer particle size on the linear regression rate were not included at this stage of the study. These effects are available in the term $(6\psi v/a)$, which is assumed here to be constant, i. e., at a specified oxidizer volumetric loading, v , the ratio, ψ/a , of the interfacial melt layer thickness, ψ , to the oxidizer particle size, a , is assumed to be constant at a reasonable value of 5%. Explicit variations of the oxidizer particle size throughout the entire regime are considered later. At the present stage of this discussion, the explicit variations in the post-breakpoint regime are considered. At the point

of slope discontinuity, i. e. , the transition from subsurface reaction rate control to surface reaction rate control, the matching of the two regression rates determines the value of the only external parameter (the melt layer thickness, l) which is not arbitrary.

C. CALCULATIONS ASSUMING CONSTANT WALL TEMPERATURE

In the calculations of the present section constant wall temperatures have been assumed. Of course, the correct way of treating the problem is to make no assumption regarding the wall temperature, but rather to allow it (T_w) to be self-determined by the gas-phase details; that is the next step, reserved for a later section. However, we may make a few comments here on the possible implications of such a treatment. It is known that the use of the gas-phase reaction rate expression in its simplest form, $\dot{m}''' = A \cdot P$, results in a pressure exponent slightly higher than that given by the constant T_w model. That is to say, the values of the exponent, n , revealed by the present calculations would increase slightly both before and after the breakpoint. To hazard a guess, the n 's may increase from the present values of 0.5 and 1 to ≈ 0.6 and ≈ 1.2 , which are much closer to typical experimental values (Thiokol and Hercules). The main point to note is that the present section gives a specific calculation only. More sophisticated calculations will be described in subsequent sections.

Slight modifications have been made in the basic CIT/JPL theory (Refs. 2 and 3) in attempting to apply it to the vastly different nitramine gun propellant system. The concept of FSV does not appear to be directly applicable:

- 1) The pressures are so high that, at all reasonable values of wall temperatures, the FSV is far less than unity.
- 2) Since the fundamental unit in the crystal is not small or simple for either RDX or HMX, the FSV concept needs careful interpretation.

In light of the above, the experimentally measured values of the degradation rates will be used directly. These values are, inherently, influenced by

variations of the surface details in degradation. The details of the procedure employed are:

- 1) In place of gas-phase reaction rates (to be used in subsection III-D), reasonable values of the wall temperatures are assumed (600°K and 650°K).
- 2) A modified form of subsurface degradation equation is used to predict the linear regression rate.
- 3) Recognizing that the subsurface-reaction model is of limited validity when the condensed phase is not homogeneous (i. e., when $\kappa/\bar{r} < a$, the predictions are stopped at $\bar{r} = \kappa/a$.)
- 4) At the point of discontinuity (in slope), the surface reaction rate equation is used and the prediction of r vs. P is continued. There are no arbitrary parameters at this stage; the value of the only external parameter, the melt layer thickness, l , is determined by matching the regression rates at the breakpoint

The numerical values used are given in Table 2.

TABLE 2. NUMERICAL VALUES USED (RDX) (CONSTANT WALL TEMPERATURE)

Parameter	Value	Source
Activation energy of degradation, E	48,000 Cal/mole	Ref. 12
Pre-exponential constant, B	$10^{19.1} \text{ sec}^{-1}$	Ref. 12
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	

The equations used are as follows:

1) Before the breakpoint:

$$r = \sqrt{\frac{\kappa \frac{6\psi v}{a} B_0 P e^{-E/RT_w}}{(E/RT_w) \left(\frac{T_w - T_0}{T_w}\right)}} \quad [P \text{ in atm}]$$

2) At the breakpoint \hat{r} :

$\hat{r} = \frac{\kappa}{a}$ which yields values of \hat{r} as follows:

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

3) After the breakpoint:

$$r = f B_0 P e^{-E/RT_w} \quad [P \text{ in atm}]$$

f is not assumed, but is determined by matching regression rates at the breakpoint.

Calculation Example: At 600°K T_w , the calculated values are:

a in μ	10	30	50	100
f in μ	0.1212	0.383	0.625	1.14

which look very reasonable.

The calculated regression rate vs. pressure curves are shown in Figs. 4 and 5.

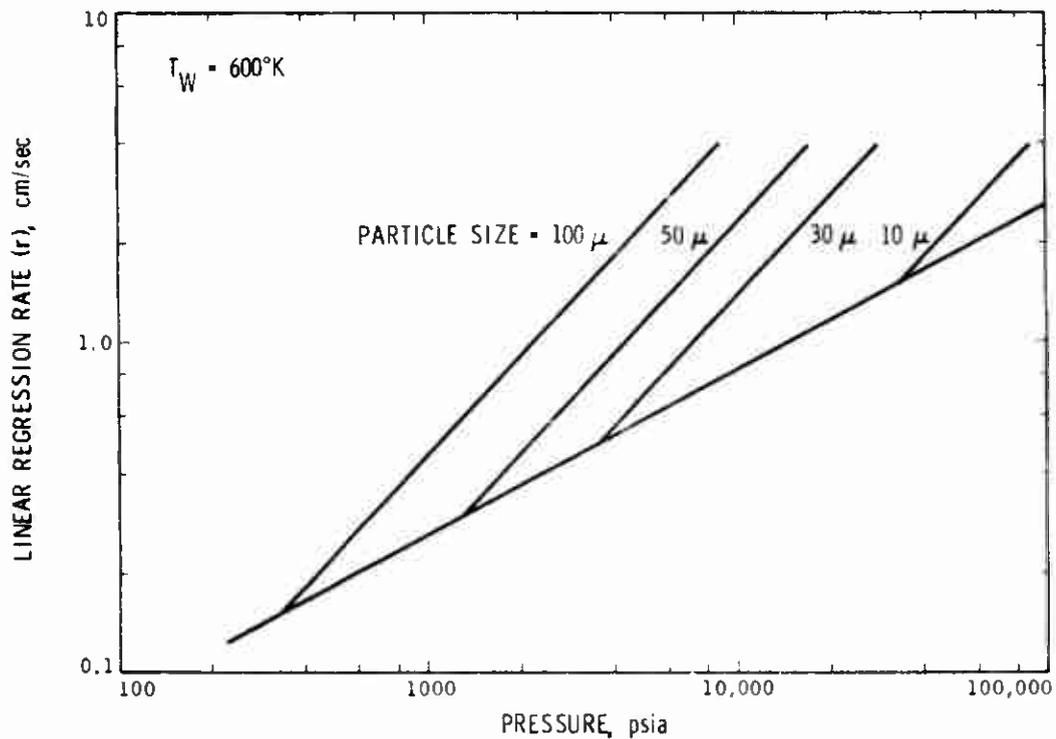


Figure 4. Calculated Regression Rate Versus Pressure For Constant Wall Temperature of 600°K

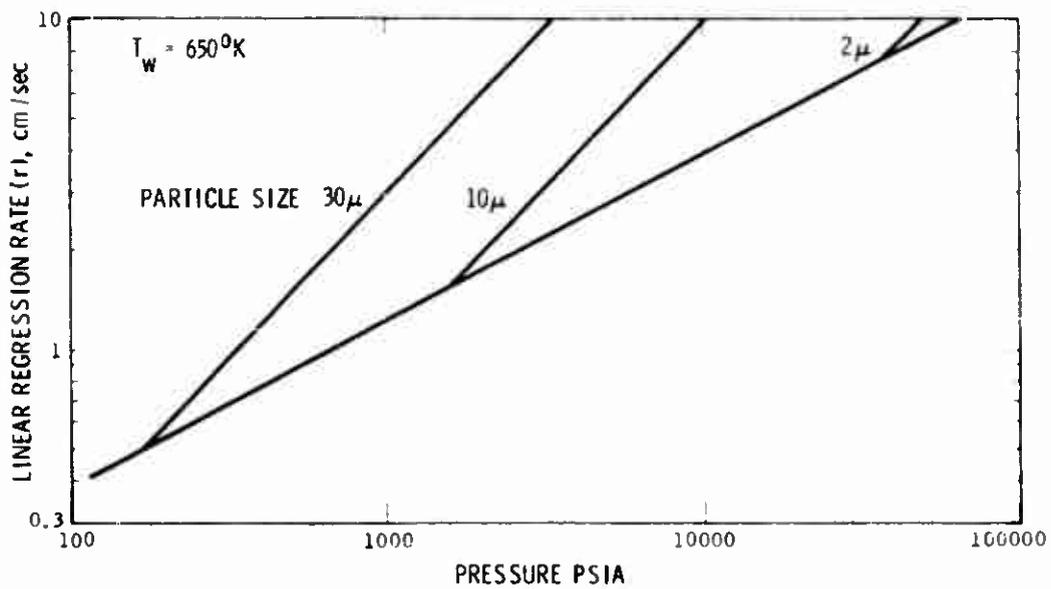


Figure 5. Calculated Regression Rate Versus Pressure For Constant Wall Temperature of 650°K

D. CALCULATIONS ASSUMING UNIFORM COMBUSTION IN THE GAS PHASE

In this section we extend the previous work to include consideration of gas-phase reactions, instead of assuming a constant wall temperature. In the process, we describe the preparation of a computer program; later in this report improvements to this program will be described. The program 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.

1. Method

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 page 37) of Ref. 2. In our application the method is modified by elimination of the parameter FSV, which 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:

$$\rho_r = \rho \left[\frac{\left(\frac{6\psi v}{a}\right) B_c \cdot P \cdot \kappa \cdot \exp(-E/RT_w)}{(E/RT_w) \left(\frac{T_w - T_o}{T_w}\right)} \right]^{1/2} \quad (3)$$

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

$$\Lambda = \frac{\kappa \cdot Q \cdot \dot{m}'''}{\rho \cdot c_p \cdot (T_w - T_o) r^2} \quad (4)$$

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

$$(\Lambda \cdot \zeta) + C_3 \exp(\zeta) + C_4 - 1 = \frac{Q}{c(T_w - T_o)} - 1 + h \quad (5)$$

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 , κ , ρ , T_o) all have very definite numerical values.

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

$$\dot{m}''' = A P^m \quad (6)$$

This is an assumption in the theory. However, it has been widely used and is seen, even in the simplest case ($m \equiv 1$), 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 very analogous to the condensed-phase parameters E and B_0 , which come from more fundamental experiments (DTA, TGA, DSC, etc.).

2. Computer Program

NOTE

A listing of this computer program and the deck of cards were sent to Eglin AFB earlier. The listing is self-explanatory.

Briefly, the computer program has in it the values of B_0 , E , κ , c , ρ , and T_0 . It reads in values of A , m , D , Q , trial T_w , ΔT_w , a , and v . The above values form one set in a data card. The number of such sets (the number of data cards) is specified in the program by the variable NUMBER. The program then uses the trial value of T_w to compute independently the two sides of the equation (Eq. 5) (called W1 and W2 in the program). The two independently calculated values must be equal for a proper solution. A 5% error bound has been established in the program. A 5% error in Eq. (5) results usually in a 1 or 2% error bound on the regression rate, which is felt to be adequate at this stage. The error bound can be easily altered. If the two values W1 and W2 do not match at the initial trial value of T_w , one of two things can happen:

- 1) If the wall temperature is too LOW, it is gradually incremented in steps of ΔT_w (called DT in the program) until a favorable agreement is obtained. In the process, if it is found necessary, the incremental step size ΔT_w (DT), is made smaller by factors of 10 at a time.

- 2) If the initial wall temperature is too HIGH, the following message should appear:

THE INITIAL VALUE OF TRIAL WALL TEMPERATURE, TRIAL T, IS TOO HIGH. CHOOSE A LOWER VALUE.

The regression rate is computed for four values of pressure: 1,000, 11,000, 21,000, and 31,000 psi. The output also contains the values of A and m used, the wall temperature computed, and the value of the regression rate at which breaks are likely to occur in the standard regression rate vs. pressure plot. For one set of the parameters the results obtained are plotted in Fig. 6.

The details of ψ/a , v , binder, etc. are not pursued at this stage. This point was discussed in the previous section.

It is noted that, at this stage, 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 or to optimize the cost considerations.

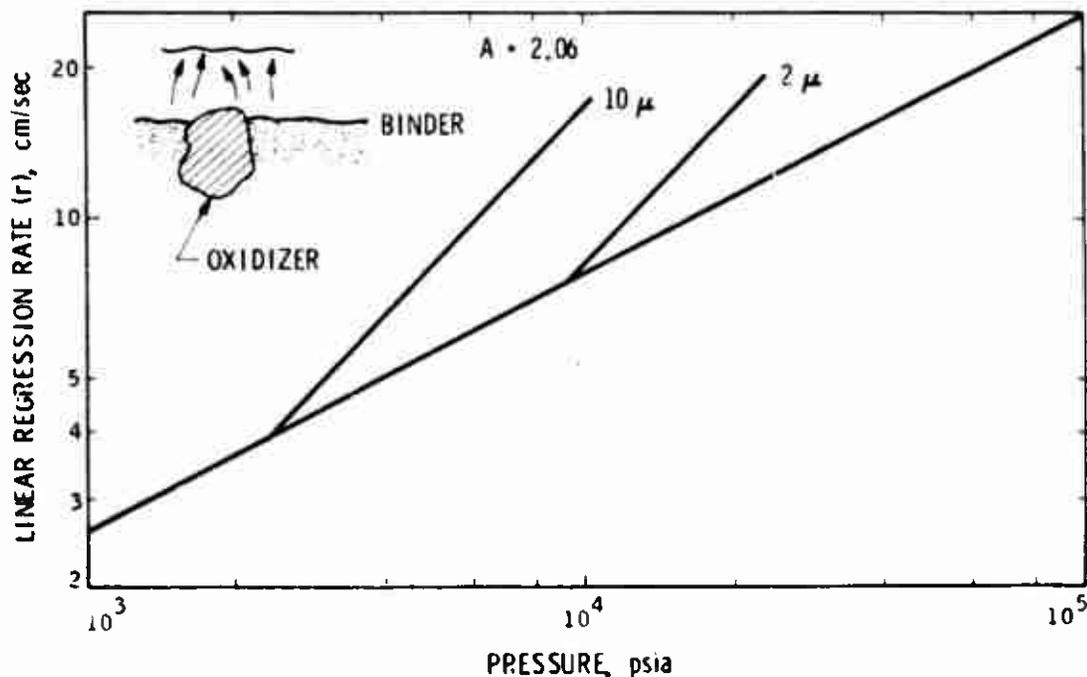


Figure 6. Calculated Regression Rate Versus Pressure Assuming Uniform Combustion in the Gas Phase ($\dot{m}''' = A \cdot P$)

E. PARAMETRIC VARIATIONS OF ψ AND a

In this section the previous work is extended to include cases in which the thickness of the interfacial melt layer is not constant, but variable, and in the process a computer program is prepared that is an improvement over the previous effort (subsection III-D-2). In addition, the other important parameter, namely the oxidizer particle size, is varied over the range of general interest. The program is simple enough to easily handle variations in the volumetric loading of the oxidizer in the propellant.

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_0 and E . The initial temperature, T_0 , and the chamber pressure, P , are determined by the experimental conditions; the propellant wall temperature, T_w , is determined by the gas-phase energetics and fluid dynamics; and the interfacial melt layer thickness, ψ , has to come from experimental measurements. T_w and ψ are the only two variables that do not have unambiguous values at this stage of the analysis. In Section III-D-2, the value of T_w was determined for two different values of the gas-phase reaction rate parameters. It was found that the T_w did not vary with pressure when the gas-phase reaction rate was assumed to be controlled by molecular mixing of the fuel and oxidizer vapors. Based on the above exploratory study of the possible variations in T_w , it was concluded that the assumption of constant T_w 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. Of course, this point has to be settled through careful measurements of the gas-phase reaction rates. Unfortunately, such experimental data are unavailable at this time; they are being obtained in a separate project at JPL. In any case, the wall temperature is assumed not to vary with pressure in the present calculations, although 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.

Using the above background, the only parameter whose value is not thoroughly settled at this stage, the melt layer thickness, ψ , is varied parametrically. The basic idea is to have available results that will find ready application once measurements are made of ψ variations. It has been previously assumed that ψ was 5% of a . Now its value is 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, ψ , is increased at the same time, the regression rate can actually increase with increases in particle size. Consequently, when we specify ψ/a as a certain percentage, the results have to be examined with care.

The breakpoint regression rate is predicted, as above, by

$$\hat{r} = \kappa/a \quad (7)$$

At regression rate values exceeding \hat{r} , since the propellant cannot be considered homogeneous anymore, surface reactions in a melt layer of thickness l are postulated and the regression rate is now given by

$$r = l B_0 P \exp(-E/RT_w) \quad (8)$$

The value of the melt layer thickness at the wall is not arbitrary, but is determined by proper matching at the breakpoint.

The procedure is as follows:

- 1) The breakpoint, \hat{r} , is determined by $\hat{r} = \kappa/a$

- 2) The breakpoint pressure is determined by

$$\hat{P} = \frac{\hat{r}^2 (E/RT_w) \frac{T_w - T_o}{T_w}}{\frac{6\psi v}{a} \kappa \cdot B_o \cdot \exp(-E/RT_w)} \quad (9)$$

- 3) The melt layer thickness at the breakpoint is determined by

$$\hat{l} = \frac{\hat{r}}{B_o \cdot P \cdot \exp(-E/RT_w)} \quad (10)$$

It is then assumed that the melt layer thickness is constant in the post-breakpoint regime, at least in a reasonable range of pressure variations.

1. Computer Program

NOTE

A listing and printout of this computer program were sent to Eglin AFB earlier. The listing should be self-explanatory.

THERDF is the thermal diffusivity, κ
 EL is the surface melt layer thickness, l
 PSI is the interfacial melt layer thickness, ψ

The computer program reads in values of the wall temperature, T_w , and volumetric loading of the oxidizer, v , in the propellant. It computes the linear regression at five discrete values of the pressure: 1,000, 11,000, 21,000, 31,000, and 41,000 psia. The program also considers four values of the oxidizer particle size (2 μ , 10 μ , 50 μ , and 100 μ) and five values of the interfacial melt layer thickness (1%, 3%, 5%, 7%, and 9% of the oxidizer particle diameter). The program automatically selects the correct regression rate equation, depending on the location, as pre-breakpoint or post-breakpoint. This is an improvement over the previous efforts. In the pre-breakpoint regime the

surface melt layer is nonexistent (at least within the framework of Refs. 2 and 3), and hence the melt layer thickness, is printed out as 0.0. The rest of the results should be self-evident. The computer costs are quite low (\$1.06).

2. Discussion

The results show that increases in the melt layer thickness increase the regression rate, as anticipated. In Refs. 2 and 3 the 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 present results indicate that the wall temperature, T_w , probably decreases with increases in oxidizer particle size. As can be seen in the printout, the linear regression rate predictions are reasonable at the higher values of the wall temperature ($\sim 630^\circ\text{K}$) and the higher values of the melt layer thickness ($\sim 9\%$) for the smaller-oxidizer-particle propellant, while the regression rates of the larger-oxidizer-particle propellants seem reasonable at the lower values of the wall temperature. Such a variation in the wall temperature is reasonable within the framework of a wide variety of gas-phase models (GDF models, flame sheet models, uniform combustion rate models, etc.). This is so 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.

F. GAS-PHASE DETAILS AS INFLUENCED BY THE OXIDIZER PARTICLE SIZE

Although we have all along been using a condensed-phase theory that hypothesizes that most of the interesting details in propellant combustion are controlled by the condensed-phase processes, we do need to consider a few

essential details of the gas-phase processes 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 our 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. Method

The basic ideas of the analytical approach of the present 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 the photographs of AP/composite propellant combustion (Ref. 27). Far downstream, however, such inhomogeneities disappear because the combustion reactions reach completion. It is clear, therefore, 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. At the present stage we concentrate only on the variations with the oxidizer particle size. The essence of the present approach is written as

$$X^* \propto a \quad (11)$$

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

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. (11)] 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. (11) needs modification when different pressures are considered. For example, the numerical value of the constant in Eq. (11) 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 , κ ($\equiv k/\rho c$), and T_0 . A reasonable (constant) value of the interfacial melt layer thickness, ψ , 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. (11). 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)].

2. Computer Program

NOTE

The listing of this computer program was sent to Eglin AFB earlier. The listing should be self-explanatory, in view of the programs sent before.

The computer program is written such that the value of the temperature at the flame sheet is printed out for incremental values of the wall temperature, T_w . A knowledge of the adiabatic flame temperature, T_b , for the propellant thus enables us to locate the exact value of the linear regression rate from the computer printout. The wall temperature is also printed out along with the regression rate. This provides an independent "check" on the solution. Since the wall temperature range for the nitramine propellant combustion is fairly well known, the wall temperature actually obtained (for the correct flame temperature) can be useful in evaluating the procedure.

3. Numerical Data

The RDX constants in Table 3 were used for the representative propellant considered here.

4. Results

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.

TABLE 3. NUMERICAL VALUES USED

Parameter	Value	Source
Activation energy of degradation, E	48,000 cal/mole	Ref. 12
Pre-exponential constant, B	$10^{19.1} \text{ sec}^{-1}$	Ref. 12
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 μ - 100 μ in steps of 10 μ	
Flame temperature of mono-propellant RDX	3282°K	Ref. 12
Flame temperature (adiabatic) of propellant with 20% inert binder	2640°K	Eglin AFB data
Constant in $X^* = (\text{constant}) \cdot a$	1	Assumed

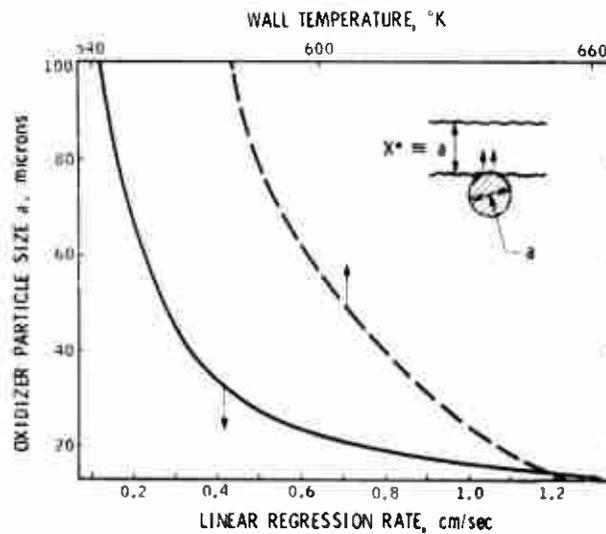


Figure 7. Calculated Regression Rate, Propellant Wall Temperature, and Oxidizer Particle Size Relationships Assuming A Simple Flame Standoff Distance Gas-Phase Model; Pressure = 1000 psia

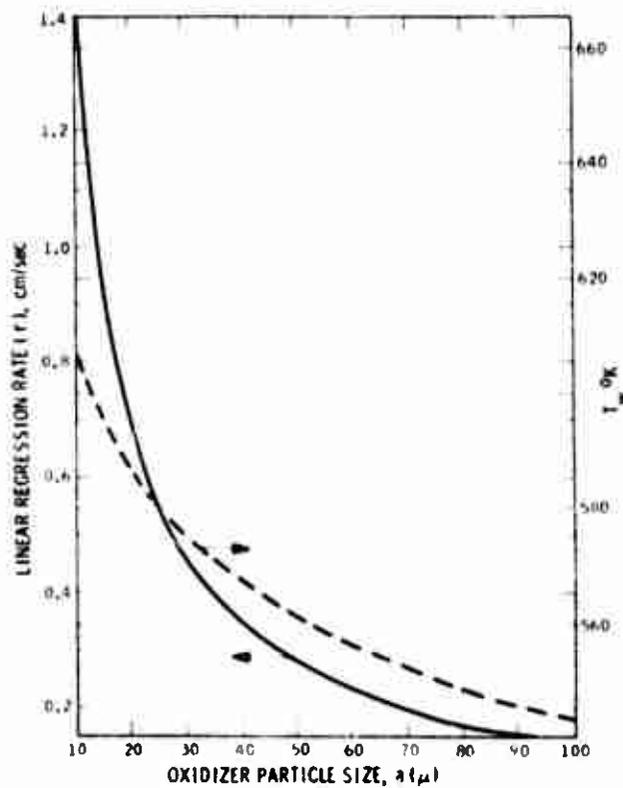


Figure 8. Calculated Regression Rate, Propellant Wall Temperature, and Oxidizer Particle Size Relationships Assuming A Simple Flame Standoff Distance Gas-Phase Model; Pressure = 21,000 psia

- 2) The regression rates are predicted to be around 0.4 cm/sec at 1000 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 subsection III-H 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 remarkably useful indeed.

5. Breakpoints

The breakpoints are predicted within the general context of the CIT/JPL model as occurring when the characteristic thermal depth in the solid becomes less than the characteristic heterogeneity scale (oxidizer particle size) in the propellant. As reported in the September 1973 technical monthly report of this program, the breakpoints are predicted to be as follows:

a in μ	10	20	30	40	50	60	70	80	90	100
\hat{r} ($\equiv \kappa/a$) cm/sec	1.5	0.75	0.5	0.375	0.3	0.25	0.214	0.1875	0.1667	0.15

G. MELT LAYER COMPUTATIONS

It is suggested that the observed melting phenomenon is associated with the thermal gradients in the condensed phase. The wall temperature is generally believed to be approximately constant, at about 600 - 650°K. The melting points of RDX and HMX are reported (Eglin AFB data) to be 204°C and 284°C, respectively. Hence, the propellant material, in its travel from the low temperature environment ($\approx 300^\circ\text{K}$) to the high temperature wall, may

undergo melting after the melting point; that is, the temperature difference ($T_w - T_{mp}$) is traversed through a melt layer. 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 nonequilibrium 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. Neglecting, for the moment, the heat of degradation in the condensed phase, the solution to the energy equation,

$$k \frac{d^2 T}{dx^2} + \rho c r \frac{dT}{dx} = 0$$

is

$$\frac{T - T_o}{T_w - T_o} = e^{\frac{-rx}{K}}$$

with x measured from the wall into the propellant material. Thus, at any regression rate (and hence pressure), the melting point, T_{mp} , specifies the thickness, l , of the melt layer for a specified wall temperature, T_w :

$$l = \frac{K}{r} \ln \left(\frac{T_w - T_o}{T_{mp} - T_o} \right) = \text{melt layer thickness} \quad (12)$$

In the very short time available (typically in the region $\tau \sim l/r \sim 10^{-3}$ sec) it is unlikely that mixing of binder and oxidizer can take place thoroughly through the melt layer; consequently, the present model, which considers spherical oxidizer particles with a thin interfacial melt layer on them, may still be valid. As has been pointed out in earlier reports (Ref. 3, for example), the CIT/JPL model is intended to be a highly idealized (but useful) representation of the complex mechanics in propellant combustion.

The data included in the September 1973 monthly technical report to Eglin AFB is the basis for the present computations. As a typical example, the

r vs. P curve for 10 μ oxidizer particles and 600°K wall temperature are chosen. The following table is easily generated through

$$\frac{T_{mp} - T_o}{T_w - T_o} = e^{\frac{-r\ell}{K}}$$

$$\frac{(204 + 273) - 300}{600 - 300} = e^{\frac{-r\ell}{15 \times 10^{-4}}}$$

$$\text{or } \ell = \frac{7.91}{r} \text{ microns}$$

Pressure, psia	1300	2000	3000	3650	5000	6000	7000	8000	10,000
Regression rate, cm/sec	0.3	0.37	0.45	0.5	0.58	0.64	0.69	0.74	0.825
Melt layer thickness, μ	26.4	21.4	17.6	15.8	13.6	12.4	11.5	10.7	9.6

The results are plotted in Fig. 9.

The following points should be borne in mind:

- 1) Heat of degradation has not been considered. The wall temperature gradients in actuality will be steeper and, consequently, the melt layers will be thinner than predicted, as shown in Fig. 10.
- 2) Wall temperatures are not precisely known at this time and 600°K is an approximate number only. A higher value of T_w leads to a lower value of the melt layer thickness.
- 3) Binder interactions have been totally ignored. These will lower the melt layer thickness because the binder heat sink leads to a steeper wall temperature.

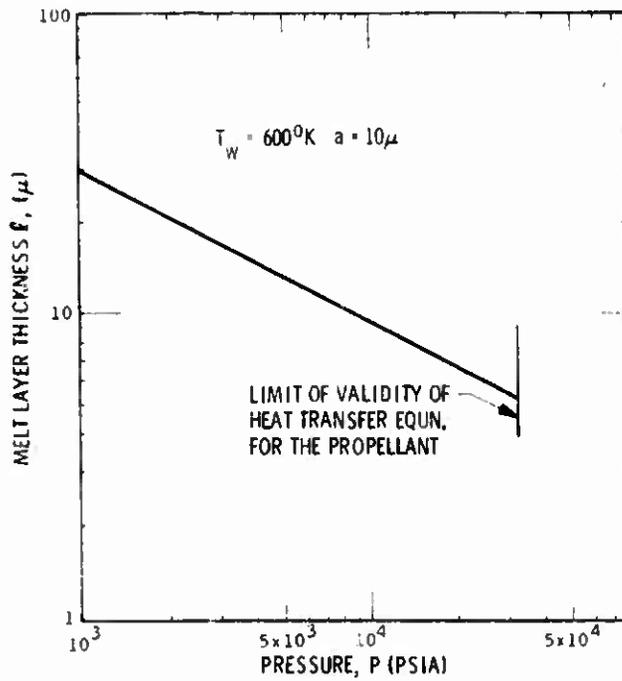


Figure 9. Melt Layer Behavior on a Model Propellant

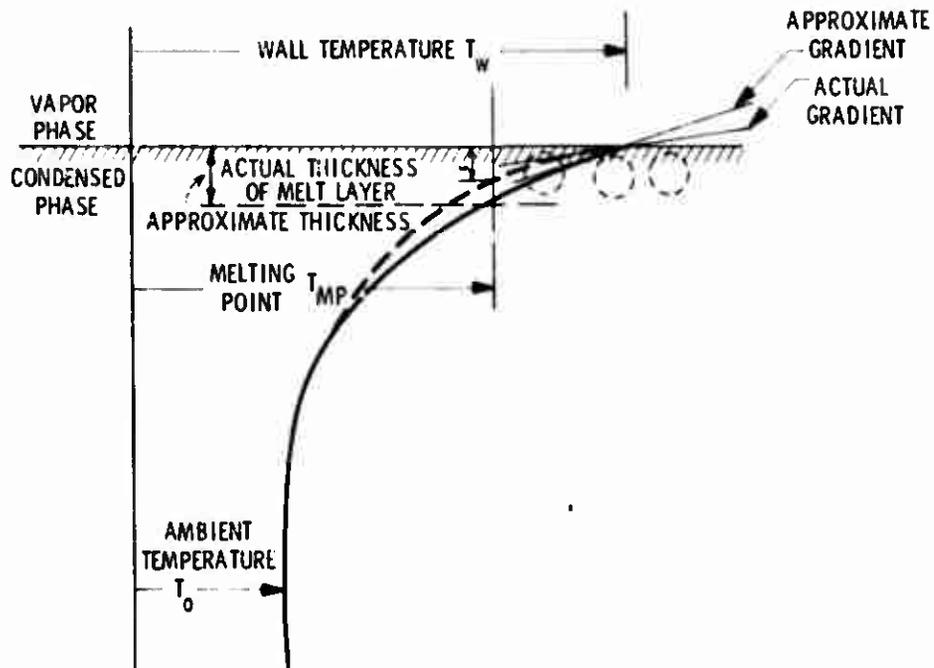


Figure 10. Schematic View of the Model for Melt Layer Computations

- 4) Variations in the value of the thermal diffusivity with either T_w or a could alter the values presented in Fig. 9.
- 5) The computations were performed using thermal and chemical parameters (T_{mp} , B , c , ρ , . . .) for a typical RDX propellant. HMX has a higher melting point--284°C. Hence, the melt layers are likely to be substantially thinner than for RDX propellants.

It is suggested that the melt layer thickness computed here be regarded as an upper bound only. As shown in Fig. 9, the theoretical results cannot be extended to the possible "disappearance" of the melt layer at higher pressures because of limitations on the validity of Eq. (12) used to compute the thickness. Equation (12) assumes that the propellant material may be considered homogeneous for the purposes of heat transfer calculations. The homogeneous solid assumption is of questionable validity beyond the regression rate at which the characteristic thermal depth, κ/r , equals the characteristic heterogeneity scale, a .

H. VARIATIONS 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 heterogeneity (the oxidizer particle size). Moreover, at the reference pressure of 1000 psia, the flame standoff distance is equated to twice the oxidizer particle size. This equality is somewhat arbitrary, but 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:

- 1) The oxidizer particle size, a .
- 2) The volumetric loading of the oxidizer, v .
- 3) The flame temperature, T_b , which is assumed not to vary appreciably with pressure.

We assume a reasonable value of the interfacial melt layer thickness (5% of the oxidizer particle size, a). The linear regression rate of the propellant is computed at incremental values of the wall temperature, T_w , using Eq. (2). The flame standoff distance is computed through $X^* = \zeta \kappa_s / r$, and the melt layer thickness (Fig. 11) is computed using the procedure discussed in the previous section [Eq. (12)]. The computations have been carried out for wide variations in the wall temperature for oxidizer particle sizes of 20, 30, 40, 50, and 60 μ and at pressures of 1000, 11,000, 21,000, 31,000, and 41,000 psia.

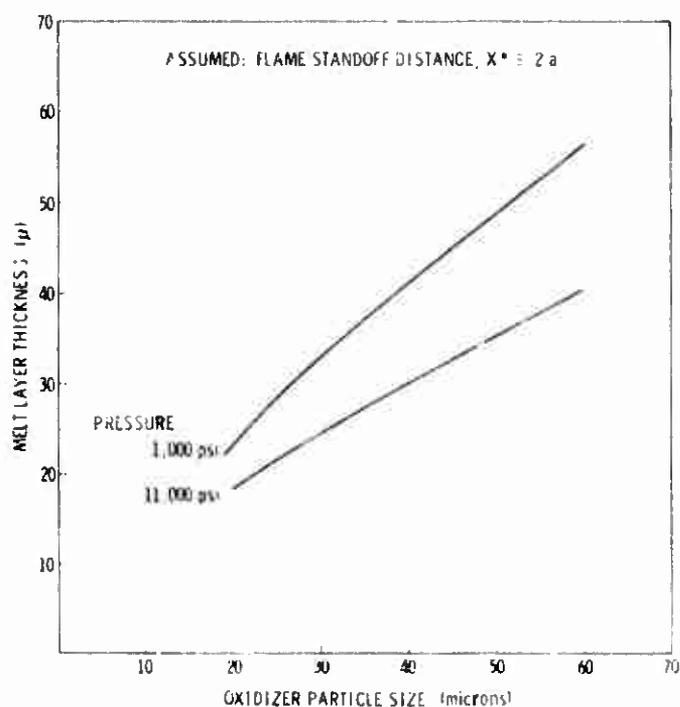


Figure 11. Calculated Variation in Surface Melt Layer Thickness With Pressure and Oxidizer Particle Size

There exist several different ways of interpreting the extensive data obtained. Figure 12 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 borne in mind that these predictions, using Eq. (2) are not valid beyond the breakpoint, \hat{r} . However, in view of the crudeness of the breakpoint predictions (order-of-magnitude validity only), the predicted line 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. 12 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.

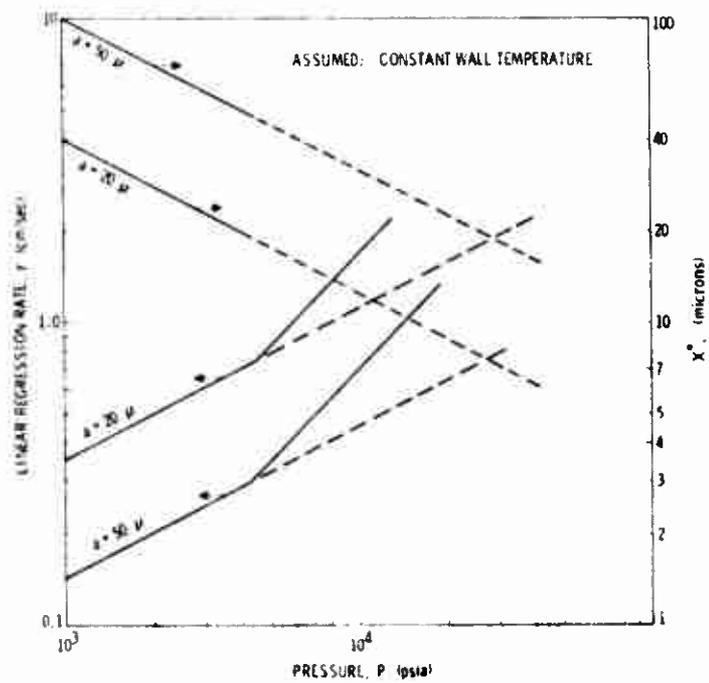


Figure 12. Calculated Variation in Flame Standoff Distance and Regression Rate With Pressure

SECTION IV

EXAMINATION OF THE MODEL IN THE CONTEXT OF THE AFOSR/AFATL EXPLOSIVE COMBUSTION MEETING

In this section the authors would like to examine the CIT/JPL theoretical model for nitramine propellant combustion in light of the information gained from the meeting presentations and discussions. Specifically, it is intended to show that the CIT/JPL model, though superficially restrictive, is sufficiently general to be consistent with current ideas on nitramine combustion.

A. KEY ELEMENTS

- 1) Gas-Phase Processes: In general, many investigators seem to be amenable to considering the condensed phase as the site of the key processes. The arguments against the importance of the gas-phase details have for their supporting evidence the experiments of Zimmer-Galler (Ref. 12), where essentially the same regression rate behavior was obtained in widely different gas environments. The motion pictures of Cohen (Ref. 15) seem to show that there exists a fairly clearly defined bright "flame" zone some distance ($\sim 100 \mu$) from the propellant surface. This may be associated with the flame sheet model that was used in subsection III-H.
- 2) Melt Layer: There appears to be almost universal agreement that, at least in the pre-breakpoint region, a melt layer exists on the surface of nitramine propellants. Motion pictures [Visnov (Ref. 28), for example], surface examination of quenched samples [Zimmer-Galler (Ref. 12), for example], and scanning electron microscope photographs (Ref. 29), all support the concept of a melt layer. There also appears to be an almost equally prevalent belief that this melt layer gets thinner as the pressure increases.

- 3) Post-Breakpoint Regime: It was the general belief that this regime of combustion is not well understood. More experimental data are awaited. Even analytical models tend to be speculative without reliable experimental data.

B. DISCUSSION

In analogy with the available studies on AP single crystal deflagration [see for example, Guirao and Williams (Ref. 30)], 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.

The above arguments are presented to indicate the strong need for more experimental data and are not intended as solutions to the problem.

SECTION 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 the chamber pressure. If successful at this task, 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 behind 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 our model, which started out with postulates and hypotheses, is indeed applicable 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, our 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 used (Refs. 2-4) 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 or other. The degradation reactions of the oxidizer and the 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 (Ref. 31). 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. Our model has been put forward to represent composite propellants as a family. Except for the numerical constants, the model 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 to inquire 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 recently (Ref. 32). 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 presented (Refs. 32-34) is indeed very impressive and shows 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 observed (Ref. 26) with a fairly narrow AP size distribution in a nonmetallized AP/PBAN propellant.] Also, when an extremely unimodal distribution of nitramine oxidizer crystals was used in a propellant (Ref. 15), 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 the conventional AP/composites as well. This must certainly be regarded as a strong support for our 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 found (Ref. 12) 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 our 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 the 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

nonlaminar and this physical 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 our 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; it is indeed observed to have a beneficial effect. The model places little emphasis on the metal content, special ingredients, and the chemical nature of the 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" (Ref. 1).

In the context of our 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 pressures 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.)

Our 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.

To summarize those aspects that affect the design of propellants, our model indicates that the following steps ought to help obviate the high slope from the operating range:

- 1) Decreasing the oxidizer particle size.
- 2) Employing a binder system that melts readily (PU, for example).
- 3) Increasing the thermal diffusivity of the propellant.
- 4) In general, introducing any modification that enhances the homogeneity of the condensed phase.

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, α , leads to predictions of the wall temperature and the regression rate that are both in agreement with the experimentally observed trends.
- 5) With regard to the highly popular 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.

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13. 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.		

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