General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)
PREFACE

The work described in this report was performed by the Control and Energy Conversion Division of the Jet Propulsion Laboratory under Contract No. NAS7-100, Task Order No. RD-182, Amendment No. 24. This investigation was supported by the Air Force Office of Scientific Research under AFOSR Support Agreement No. AFOSR-ISSA-78-0004, and this report is submitted to AFOSR as the Annual Progress Report for the period 1 October 1977-30 September 1978. Norman Cohen's services as Associate Investigator were funded under JPL Contract No. 954985 to Norman Cohen Professional Services of Redlands, California.
ACKNOWLEDGEMENTS

This report was prepared by N.S. Cohen and L. D. Strand, who were the principal investigators for this research program. The work was conducted within the Solid Propulsion and Environmental Systems Section of JPL, under the supervision of W. Gin and Dr. G. Varsi. The authors hereby acknowledge the interest and support of Dr. J. Masi and Capt. R. Sperlein, who were the Air Force project officers in the course of this program. Propellants tested at JPL were furnished by the Naval Weapons Center under the supervision of R. Price. Experiments at JPL were conducted with the assistance of H. Burris. The authors wish to express their appreciation to Drs. R. Bernecker and S. Jacobs of the Naval Surface Weapons Center, and to Dr. C. Tarver of the Lawrence/ Livermore Laboratories, for helpful discussions on the subject of deflagration-detonation transition (DDT). Also, C. F. Price of the Naval Weapons Center was helpful in answering questions regarding computational aspects of the analytical modeling.
ABSTRACT

A transient combustion model of nitramine propellants is combined with an isentropic compression shock formation model to determine the role of nitramine propellant combustion in DDT, excluding effects associated with propellant structural properties or mechanical behavior. The model is derived to represent the closed pipe experiment that is widely used to characterize explosives, except that the combustible material is a monolithic charge rather than compressed powder. Although it is argued that mechanical effects are not likely the sole cause of DDT, computations reveal that the transient combustion process cannot by itself produce DDT either by this model. Compressibility of the solid at high pressure is the key factor limiting pressure buildups created by the combustion. On the other hand, combustion mechanisms which promote pressure buildups are identified and related to propellant formulation variables. It is recommended that these mechanisms be included in other models of shock formation and DDT which are being developed elsewhere.

Additional combustion instability data for nitramine propellants, continuing work begun last year, are presented. Although measured combustion response continues to be low, more data are required to distinguish HMX and active binder component contributions. A design for a closed vessel apparatus for experimental studies of high pressure combustion is discussed.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>SECTION 1</th>
<th>OBJECTIVE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SECTION 2</td>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>SECTION 3</td>
<td>REVIEW OF POSSIBLE MODES OF DDT OF SOLID PROPELLANTS</td>
<td>5</td>
</tr>
<tr>
<td>3.1 General</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>3.2 Porous Beds and Crack Networks</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>3.2.1 Porous Beds</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>3.2.2 Cracks</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>3.3 Impact</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>3.4 Compression of Confined Volumes</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>SECTION 4</td>
<td>ANALYTICAL MODEL OF DEVELOPMENT</td>
<td>12</td>
</tr>
<tr>
<td>4.1 Approach and Conceptual Basis</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>4.2 Analytical Model</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>4.2.1 Combustion Model</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>4.2.2 Shock Formation Model</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>4.2.3 Filling Equations</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>4.2.4 Computer Program</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>4.3 Results and Discussion of Key Factors</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>4.3.1 Compressibility vs. Pressure Exponent</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>4.3.2 &quot;P-Dot&quot; Effects vs. Pressure</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>4.3.3 Surface Structure Effects vs. Time</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>4.3.4 Initial Conditions</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>4.3.5 Motion of the Free Volume End (Piston Motion)</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>4.4 Concluding Remarks</td>
<td></td>
<td>39</td>
</tr>
</tbody>
</table>
SECTION 5. EXPERIMENTAL WORK 42

5.1 Combustion Instability Experiments 42

5.1.1 Propellants 42

5.1.1 Results for 100% Binder Propellant 45

5.1.3 Results for Propellant Containing HMX 46

5.2 Design of Closed Vessel Apparatus 48

5.2.1 Purpose and Approach 48

5.2.2 Design and Procurement 51

SECTION 6 PRESENTATIONS, PUBLICATIONS AND WORKSHOP PARTICIPATIONS 53

SECTION 7 CONCLUSIONS AND RECOMMENDATIONS 54

SECTION 8 REFERENCES 56
FIGURES

1. Schematic of Stages of DDT in Solid Media Having Non-Interconnected Porosity 14
2. Extrapolation of Closed Bomb Combustion Behavior to High Pressure 17
3. Schematic of the Analytical Model 26
4. Burning Rate Required to Sustain Exponential Pressure in a Closed Pipe Filled with a Compressible Solid 30
5. Computed Effect of Pressure Transient on the Burning Rate of a Nitramine-Energetic Binder Propellant in a Closed Pipe 32
6. Combined Effects of Pressure Transient and Surface Structure on Effective Burning Rate for Test Case Corresponding to Figure 5 32
7. Wave Coalescence in the Solid Propellant for Combustion Behavior from Figure 2 35
8. Computed Effect of Nitramine Particle Size on the Pressure Buildup Achieved in a Closed Pipe 37
9. Computed Effects of Particle Size and Piston Motion (83 ft/sec) on Pressure Buildup 37
10. T-Burner Results for Active Binder/HMX Propellant 47
11. Schematic of High Pressure Closed Bomb 52

TABLE

1. Propellant Formulations for T-Burner Tests 44
SECTION 1

OBJECTIVE

The purpose of this research program is to study two aspects of the transient combustion properties of nitramine propellants. One objective is to determine the role of nitramine propellant combustion in the process of deflagration-detonation transition (DDT). The second objective is to determine the role of the nitramine ingredient in the combustion driving of acoustic instability in solid rocket motors.

Steady-state combustion characteristics of nitramine propellants have been described as a result of work performed under AFOSR Support Agreements AFOSR-ISSA-75-0005 and AFOSR-ISSA-76-0006 (Ref. 1). Studies of transient combustion effects were begun under Support Agreements AFOSR-ISSA-77-0002 and AFOSR-ISSA-77-0001 (Ref. 2). In that work, analysis of combustion in a closed bomb was completed and initial combustion instability data were obtained. The present research extends the transient combustion studies to the DDT problem and continues the combustion instability study.
INTRODUCTION

Nitramine propellants are of considerable interest for solid rocket applications because of their potential for improved energy and reduced smoke. They are also of interest for armament applications because of additional potential to reduce vulnerability and degradation of hardware. However, nitramine propellants have been found to possess certain undesirable combustion characteristics. Two of these are limited burn rate tailorability and pressure exponents which are relatively high or which shift to high values over the pressure range of interest. These two problems were addressed in prior Annual Progress Reports (Refs. 1-3), which furnished analytical models, interpretations of experimental data, and recommendations. The information provided is being used in several propellant R&D programs (Refs. 4-7).

A third problem is the susceptibility of high energy nitramine propellants to undergo deflagration-detonation transition in response to appropriate stimuli (Ref. 8). The nature of the transition process in propellants is poorly understood. The very high pressures (kilobars) and short times (microseconds) involved impose experimental difficulties, and data are lacking in sufficient detail for comprehensive analysis. Most theoretical treatments are based upon experience with explosive charges, and deal with propellant porosity (Refs. 9, 10) or other defects (Refs. 11-13) related to structural properties and mechanical behavior in order to arrive at an explosive configuration. Conspicuously lacking is a theory which focuses upon, or at least accounts for, the combustion process of nitramine propellants.
Certain features of nitramine propellant combustion are not present in ammonium perchlorate propellants. On the other hand, there is nothing particularly unique about the mechanical behavior of nitramine propellants; indeed, ammonium perchlorate propellants can be formulated to have worse mechanical behavior, yet which are less susceptible to transition (Ref. 14). Industry experience, which has largely been with ammonium perchlorate propellants, has frequently encountered problems of mechanical behavior with those propellants but not DDT. The well-known differences in impact sensitivity and explosive classification between ammonium perchlorate propellants and nitramine propellants cut through the spectrum of mechanical behavior. Although mechanical considerations can certainly be a contributing factor in DDT, the role of the combustion process cannot be ignored. Unfortunately, actual knowledge of the combustion process under DDT conditions is lacking (Ref. 8). Nevertheless, an attempt to address its role can be made by theoretical analysis based upon extrapolation of known mechanisms and existing combustion theory. Experimental combustion data at higher pressures than currently available would be helpful, and plans to acquire such data can be implemented also.

Still another consideration is the combustion response of nitramine propellants to acoustic pressure oscillations, which is an important property bearing upon the combustion stability of upper-stage, reduced smoke or minimum-smoke rocket motors. Prior to data reported in the previous Annual Progress Report (Ref. 3), no systematic information was available. The Ref. (3) data showed that replacing AP with HMX in HTPB propellants, formulated to maintain burning rate and energy fairly constant, consistently reduced the combustion response over the pressure range 500 psi-1000 psi and the frequency range 500 Hz-1800 Hz. This information is of interest for upper-stage
and reduced smoke motor applications. However, there were no data for active binder propellants. Comparisons with active binder propellants would be helpful in isolating the role of HMX and more relevant to minimum smoke applications.
SECTION 3

REVIEW OF POSSIBLE MODES OF DDT OF SOLID PROPELLANTS

3.1 GENERAL

It has been asserted that normal-burning propellants will not detonate spontaneously, Ref. (8). There must be some stimulous external to the combustion process in order to create conditions that will produce a DDT or SDT\(^1\). The reasons are based upon prior experience and the properties of solid propellants in the light of existing knowledge of DDT and SDT behavior. Manufactured grains, even those containing defects, simply do not possess the microporosity necessary to support a progressive convective burning\(^2\), (Ref. 8). Recent experiments on the combustion in a crack indicate that this mechanism will not in reality support DDT, Ref. (15). It has been reported that cast explosives are relatively difficult to detonate, usually requiring shock-initiation (SDT) in a strong confinement\(^3\), Ref. (16). Hindsight would suggest that, were this not the case, detonation should have been a pervasive problem in the history of solid propellant development. It has not been. Rather, experience suggests that an external stimulous is necessary such as impact, or stresses and motion which follow from a failure.

---

1 DDT is transition from deflagration to detonation through mechanisms by which the combustion produces the shock wave. SDT is transition from an externally-imposed shock to detonation.

2. Convective burning is combustion controlled by the flow of hot gases through a porous combustible bed of material. Conductive burning is the usual form of propellant combustion, controlled by heat conduction from a flame to the surface of a solid material.

3. Confinement is the ability to contain the transition process to sufficient pressures and for an optimal time such that a detonation can take place. Any expansion or rupture that limits achievable pressure or rate of pressurization can preclude a detonation. It is a conceptual parameter, having no formula or units.
Three categories are:

1. A confined bed of high porosity, or a network of extensive cracking, is created adjacent to a region of burning.
2. Impact of some kind.
3. A volume of hot gases is compressed rapidly.

The first category is a true DDT because there is no external shock. The second is a true SDT because the impact creates the requisite shock. The third can be a combination of both. These categories are discussed more fully as follows.

3.2 POROUS BEDS AND CRACK NETWORKS

3.2.1 Porous-Beds

Combustion in a confined porous bed of material can lead to a detonation if a certain set of conditions are satisfied. The result is a function of propellant energy, bed porosity and specific surface, and granule burning rate, Ref. (17). For a given set of these parameters, sufficient length must be provided to accommodate "run-up" to detonation, and there must be adequate confinement to support the DDT. Of course, SDT of a packed bed can be induced, but the configuration is capable of DDT because of the rates of mass and energy generation possible through convective burning.

This configuration has been the subject of most of the experimental studies because of its relevance to explosive devices, and it is more amenable to study because less confinement is

---

4. Run-up is the length required for the transition process to occur in a given apparatus.
necessary, Ref. (18). The parameters have been characterized for a variety of explosive materials. Basically, there is an optimum range of porosity which maximizes the combined effects of gas permeability and rate of gas production to minimize run-up length. Run-up length is also correlated by a semi-empirical parameter, $P^2 \tau$. It is sometimes referred to and used as a detonation criterion, and is derived from shock hydrodynamics, Ref. (19). It illustrates the importance of high rate as well as high pressure. In SDT tests, run-up time is inversely proportional to the square of the shock strength. In DDT, the interpretation is that the time integral of $P^2$ must exceed a critical value within the time allotted. Computerized models of convective burning have been developed which utilize this criterion, Refs. (9, 10, 20). The model is essentially two-phase, unsteady gas dynamics with distributed combustion. However, there is great uncertainty in the validity of the constitutive relations (heat transfer, drag, ignition delay, burning rate, etc.) under DDT conditions. It is, therefore necessary to resort to semi-empiricism for quantitative determinations.

Attempts to prove that creation of a porous bed is a mode of DDT have been inconclusive. The ability to create such a bed\(^5\) has been demonstrated in tests simulating a particular failure

---

\(^5\) The ability of a propellant to crumble into granules under applied shear has been termed "Friability". It is a function of solids loading, oxidizer particle size and binder composition. Friability tends to correlate with inferior mechanical properties.
mode, but detonations were not achieved. Pipe tests using prepared samples of granulated propellant did not produce DDT in the apparatus used. However, specially manufactured shreds of propellant to achieve very high specific surface have produced DDT when also packed to optimal porosities in a strong confinement. Other simulations have produced detonations, Ref. (10), but it is not clear whether the cause was convective burning or impacts created subsequent to explosive failure of the device. Nevertheless, this mode of DDT appears to have considerable intuitive appeal.

3.2.2 Cracks

Combustion through cracks is a less plausible mode of DDT. In the first place, the flame will not propagate into a crack which is too narrow, Ref. (11). In the second place, combustion in a crack has not been observed to produce DDT. Although flame propagation in a crack can be very rapid, the opening and propagation of the crack due to burning and stress appears to provide a significant loss in the local confinement relative to the available burning area. Furthermore, the original crack is not observed to branch into multiple cracks; but even if it did, it would appear that the balance of burn area and free volume would not change, so the crucial timing required for DDT would still be unavailable. A network of cracks would not present a substantially different situation. The packed bed of shreds mentioned above could perhaps be viewed as a network of cracks. The distinguishing feature of the packed bed, however, is the interconnected porosity. The significance of interconnected porosity is the comparative freedom of flow and enormity of specific surface exposed to the flow.
A computerized model of combustion in a crack has been developed, Ref. (12). The model is essentially unsteady gas dynamics in a burning tube. It suffers uncertainties similar to those of the porous bed model, but more important it does not account for changes in the crack geometry from burning and stress. A coupling to a structural dynamics code is reportedly in progress.

Although this mode of DDT is less probable, the mechanism is of interest to the hazard field generally, so work will continue. Grain cracking can cause or contribute to a catastrophic failure, which is to be avoided as much as DDT.

3.3 IMPACT

It is well-known that SDT may be produced by impact, Ref. (19). This mode of transition has been the subject of considerable study, and a variety of experimental techniques are available with which to characterize the shock sensitivity of propellants and explosives. The NOL card gap test, for example, is well known in the solid propellant field. This mode of transition has also been confirmed in subscale simulation and test devices. Shock sensitivity is found to be a function of propellant energy, porosity, and the presence of combustion when shocked. Increasing HMX content or particle size increases the sensitivity. Porosity and pre-existing combustion also increase sensitivity.

A computerized model of SDT run-up is available, Ref. (21). The model is based upon unsteady wave hydrodynamics, but major uncertainties exist regarding the equation of state and decomposition of the medium under the high pressure dynamic conditions of interest. It is used semi-empirically, in association with data.
Data are plotted in various ways, involving run-up length, run-up time, shock strength and impact velocity. The $P^2t$ correlation appears to be the most commonly used plot format, (Ref. 19). It appears that ascertainment of the ignition and burning mechanisms under shock-initiation would be a productive area for combustion research, (Ref. 23).

3.4 COMPRESSION OF CONFINED VOLUMES

An idealized representation of this mechanism would be the classical one-dimensional problem in which a piston is suddenly caused to move at one end of a closed pipe, (Ref. 22). The compression of the trapped volume of gas leads to shock formation ahead of the accelerating piston. If the compression by motion is the most crucial element, then the process is more akin to SDT. If the propellant combustion in response to the compression is the most crucial factor in accelerating the pressurization, then the process is more akin to DDT.

Although this mode of DDT has been shown for gases, (Ref. 18), there is little evidence that it would be viable for solid propellants. Without piston motion, the propellant combustion alone would have to support sufficient pressurization of the confined space to form a shock wave. This has been considered unlikely because of an estimated deficiency in mass production rate, Ref. (24); a monolithic charge has been considered incapable of generating adequate burn surface unless something happens to it. However, it is known that monolithic cast explosives may undergo DDT when suitably confined, (Ref. 16). Soviet authors, (Ref. 17), have proposed a qualitative mechanism for transition in cast explosives.
whereby non-interconnected porosity may produce adequate mass
 generation. Maček, Ref. (25) and Tarver, Ref. (26) have published
 models which do not require any porosity, but these have been
criticized, Ref. (24). A pervasive problem is that actual burning
rates and surface areas existing under DDT conditions are not known,
Ref. (8). Motions that would cause hot gases to be trapped and
compressed, analogous to the effect of a piston, may be considered,
but it is not clear how they would come about. The mode is
considered less likely than convective burning or impact.
SECTION 4

ANALYTICAL MODEL DEVELOPMENT

4.1  APPROACH AND CONCEPTUAL BASIS

This work seeks to explore the role of the transient combustion process of nitramine propellants in DDT, or events which lead to DDT. Its aim is not to repeat or extend current works dealing with convective burning in porous beds or cracks. However, to the extent that convective burning models must consider conductive burning as part of their constitutive relations, this work will be relevant. In order to concentrate on the combustion aspects of the problem, the compression mode of DDT will be the vehicle for the analysis.

The particular mechanism which is hypothesized to substitute for or supplement the porous bed or crack network in augmenting mass production rate is based upon the shift in pressure exponent which is observed to occur in nitramine propellants, (Refs. 1-3,27,28). The shift occurs somewhere in the pressure regime of the order 0.1-1Kbar, depending upon HMX particle size. Associated with this shift in exponent is a cratering of the burning surface such that the effective burn area is increased. The combined shift upward in burning rate and burn surface is qualitatively similar to the shift from conductive burning to convective burning in a porous bed. However, the mode of burning is still conductive in nature. Soviet authors, (Ref. 17), have proposed a similar mechanism to explain transition in media containing non-interconnected porosity.
Their mechanism is summarized by Fig. 1, which is taken from the reference. At low pressure, the surface is deemed to be a planar melt such that combustion cannot occur into the pores. This also is the situation in nitramine propellants burning at low pressure. As pressure increases, the melt layer thins and the flame approaches the surface. A transition region is encountered when the flame is able to propagate into the pore, and a new regime of burning is encountered when this process is fully developed. The Soviet authors illustrate the transition process as a change in the pressure-dependence of the deflagration rate, or a shift in pressure exponent. Precisely the same thing happens in nitramine propellants, except that surface craters form as a consequence of the combustion process rather than from pre-existing pores. Although the analogy is interesting, the Soviet authors did not perform calculations to quantify the analysis. Some related quantitative work, but in the context of convective burning, is being performed by Prentice, (Ref. 29).

The attempt by Maček, (Ref. 25) to compute DDT in cast explosives is of pertinent interest. His objective was to calculate the point of coalescence of compression waves into a shock wave, in the unreacted solid medium ahead of the burning surface, for an environment of increasing pressure in the gas adjacent to the burning surface. Imposing the experimental pressure-time history as input, and assuming an equation of state for the unburned solid, he was able to predict observed run-up length in terms of the coalescence criterion. Thus, it might be concluded that the wave dynamics aspect of the problem was well-formulated. However, he
Figure 1. Schematic of Stages of DDT in Solid Media Having Non-Interconnected Porosity.
then tried to couple the gasification from combustion to predict the pressurization as well. Assuming a burning rate proportional to pressure, he was able to derive the correct exponential form of the pressurization, but it has since been pointed out that either the burning rate magnitude or the surface area was quantitatively deficient by a factor of 50-100, (Refs. 24, 26). Thus, the combustion or gas dynamics aspect of the problem was not well posed. Tarver has proposed that neglecting momentum transfer across the flame surface was responsible for the inconsistency. The combustion viewpoint would hold that both the burning rate extrapolation and the assumed planar surface were incorrect. The material studied by Maček was DINA, a nitramine-containing compound, so there is a basis for at least a qualitative explanation based upon the surface cratering mechanism. The work of Maček as improved by Tarver furnishes the mode of shock formation by which the combustion contributions will be investigated here. The configuration is a closed pipe filled with propellant.

Based upon earlier nitramine propellant research and modeling at JPL, an area increase by a factor as much as 35 due to surface cratering has been computed for HMX composite propellants. Observations of extinguished surfaces which had been burning at 0.35Kbar would indicate at least that amount, but no measurements were made. The cratering was extensive, and reached depths of 3 particle diameters. Pressure exponents in the transition region are generally between 1 and 2, tapering off to a value of about 1 by a pressure of 3 Kbar. Jacobs, (Ref. 24) has argued that a pressure exponent of 2 is required to support a compression mode of DDT.
When dynamic burning effects are combined with the shifts in pressure exponent and surface cratering, it is conceivable that Jacobs' requirements can be satisfied. These combined effects were analyzed in the context of the closed bomb burning rate experiment, used to characterize gun propellants, as a part of last year's research, (Ref. 3). Figure 2 presents the results of a model calculation which agreed with closed bomb experimental data up to the experimental pressure of 1.5 Kbar, and extrapolates the results up to detonation pressures. The higher burning rate shown is an effective burning rate, multiplying the actual burning rate by the ratio of the cratered burn area to the idealized planar area. As such, it reflects (is proportional to) the mass generation rate. The lower rate is the actual linear burn rate. Figure 2, if valid under DDT conditions, would furnish combustion contributions not considered in the Maček or Tarver analyses that would satisfy DDT requirements. Kooker, (Ref. 22) has recommended that the dynamic burning be taken into account.

A major assumption of this work is that combustion mechanisms and theory developed for pressures up to 3 Kbar and pressurization rates up to the order of $10^{-3}$ Kbar/microsecond may be extrapolated by two orders of magnitude to detonation conditions. Lack of experimental data remains a serious deficiency.
Figure 2. Extrapolation of Closed Bomb Combustion Behavior to High Pressure
4.2 ANALYTICAL MODEL

4.2.1 Combustion Model

The combustion model is essentially the same as that reported in References (3) and (30). The Fourier heat conduction equation for a homogenous propellant, with no subsurface reactions, is solved for instantaneous surface temperature in the course of transient combustion. The initial condition was then taken to be a uniform ambient bulk temperature, with a surface heat flux representing an igniter imposed. For the DDT problem, it is computationally convenient to start the burning at some assumed equilibrium pressure because the ignition transient is long compared to the DDT event. Further remarks about initial conditions will be made later. The in-depth boundary condition is zero heat flux at the back wall. The surface boundary condition is an instantaneous heat flux derived from an energy balance, using a BDP-type flame model as applied to nitramine propellants. A quasi-steady gas phase is assumed, which is reasonable in the light of the kinetics constants used in the steady-state version of the model—diffusion does not enter into the problem for these propellants, Ref. (30)—even for the rapid transients in question.

The instantaneous surface temperature is related to instantaneous burning rate by means of an Arrhenius law, but modified by the surface structure existing at the time in accordance with the steady-state version of the model. That is to say, there is one relationship for a planar surface and another relationship for a cratered surface. For each case, the steady-state burning rate
and surface temperature at the instantaneous pressure are used as reference conditions. One set applies at pressures below the exponent break, the other at pressures above, and the possibility that the break point pressure differs between transient and steady-state conditions is accounted for in terms of the mechanism behind it.

The initial surface structure corresponds to the initial conditions of burning. At a pre-break point pressure, a planar melt exists. The thickness of the melt layer is determined from the thermal profile and the melting point of the nitramine. The subsequent thickness is computed in accordance with the succeeding transient; it generally becomes thinner as pressure increases. When the critical burn rate associated with the exponent break is achieved, it is assumed that the melt layer simply burns away in accordance with the time integral of instantaneous rate; melting can no longer be sustained. When the melt layer is burned away, surface craters start to form depending upon the relative burning rates of the nitramine and binder components of the propellant. At this point, the second set of reference conditions is used in accordance with the instantaneous cratering existing at the time. The computations proceed to track the crater development. If the initial condition is a post-break point pressure, the initial cratered surface corresponds to the steady-state condition at the initial pressure; further development is tracked from then on. The nature of the surface also determines the surface area contribution to the mass generation rate; it is a result of the combustion process and not mechanical behavior.

4.2.2 Shock Formation Model

A model described by Tarver, (Ref. 26), which improved upon the earlier Maček theory, (Ref. 25), is used to describe the wave
propagation and coalescence into a shock in the interior of the propellant. The basic mechanism is the compressibility of the solid propellant at high pressure, in accordance with a suitable equation of state for the solid, such that the speed of sound in the solid increases with pressure. Since compression signals travel at the speed of sound, succeeding signals can overtake preceding signals as pressure builds up. If pressure builds up rapidly enough, the signals can coalesce within the available length of solid material. A shock is said to form at this point, and it is presumed that this shock formation is a sufficient condition for DDT\(^7\). It is implied that the confinement has held together by this point; an infinitely strong confinement has been assumed for purposes of this investigation. The compressibility of the solid also turns out to be the source of prevention of shock formation through its effect upon the free volume to limit the pressure buildup. More will be said about this later.

Tarver improved upon the Maček work by considering momentum transfer across the gas-solid interface\(^8\). Two limiting conditions were considered to simplify the analysis: one condition was based upon earlier work by Adams and Pack, wherein the product state remains at rest relative to the laboratory, and the other was the Chapman-Jouget condition. Both extremes gave comparable

---

7. The "\(p^2t\)" criterion is rejected as a criterion for DDT. It is extracted from SDT work, and is of doubtful applicability to DDT. It is considered that computation of a time integral of \(P^2\) would be misleading. Essentially all rocket motors satisfy the \(P^2t\) criterion.

8. Inasmuch as the solid is treated as a compressible fluid in this part of the analysis, the gas has been referred to as the "product state".
results for shock formation. The Adams and Pack condition is selected here because it is more conservative and permits simple filling equations to be used to calculate the pressurization of the product state. Complex wave motion in the solid or the product states is not treated.

The equation of state of the solid is a modified Tate form:

\[ \rho_s = \rho_o \left(1 + \frac{P_s}{K}\right)^{1/3} \]  

\( \rho_s \) = density of the solid at pressure \( P_s \) in the solid  
\( \rho_o \) = initial density  
\( K \) = constant, 35 Kbar

The pressure in the solid, \( P_s \), is related to the pressure in the product state, \( P \), by the momentum equation. Tarver neglected the time-dependent term, presumably on the basis of the assumed limiting condition. He also neglected the area term because the duct is constant area; however, for the current problem, the cratering of the burning surface will produce an effective area change from the solid to the product state. Tarver's momentum equation becomes:

\[ \frac{P_s + P}{2} (A_p - A_b) + (P_s + \rho_s r^2) A_b = (P + \rho [r + u_1]^2) A_p \]  

\( r \) = burning rate  
\( u_1 \) = particle velocity  
\( \rho \) = gas density  
\( A_b \) = burn surface area  
\( A_p \) = duct cross-sectional area
Tarver's continuity equation is:

$$\rho_s r_A b = \rho(r+u_1)A_p$$  (3)

Combining Eqs. (2) and (3) provides $P_s$:

$$P_s = P + 2\rho_s r^2 \left( \frac{\rho_s A_b}{A_p} - 1 \right) / (1 + \frac{A_p}{A_b})$$  (4)

Equation (1) is used to eliminate $\rho_s$; $r$ and $A_b$ come from the combustion model, and $P$ and $\rho$ come from the filling equations. The particle velocity, $u_1$, is then determined as:

$$u_1 = c_0 \left[ (1 + P_s/K)^{1/3} - 1 \right]$$  (5)

where $c_0 = \sqrt{3K/\rho_0}$, the initial speed of sound in the solid.

The particle velocity is the motion of the boundary due to compression, whereby the solid behaves as a fluid. The effect of this change of state on the combustion process is unknown, and has been ignored here. The motion of the interface is $u_1 + r$, and the velocity of propagation of the wave in the solid is $u_1 + c_1$:

$$u_1 + c_1 = c_0 \left[ 2(1 + P_s/K)^{1/3} - 1 \right]$$  (6)

$c_1$ = current speed of sound in the solid, at $\rho_s$.

The interface and the wave characteristics may be plotted as a time-distance $(t-x)$ diagram, as done by Maček and Tarver.

4.2.3 Filling Equations

A few minor changes have been made to the filling equations for the free volume from those appearing in References (3) and (30). The density of the solid is now a variable, by Eq. (1),
rather than a constant. Also, the covolume correction for the gas phase equation of state is now a variable rather than a constant. An approximate relation is used whereby covolume varies inversely with the 0.1 power of pressure. The compressibility motion, \( u_1 \), requires that a term be added to the volume derivative. Another motion term is added to provide for motion of the free volume end of the closed pipe. This motion may be thought of as a piston motion, but was inserted to simulate a collapsing trapped volume rather than introduce new wave motion into the problem. As before, flame temperature and heat capacity of the gas are weak functions of pressure; specific heat ratio and molecular weight continue to be assumed constant. Heat loss to the wall is now neglected, and wall distortion under internal pressure is not taken into account.

4.2.4 Computer Program

The computer program retains the structure of the Ref. (3) program. The major change is the replacement of the heat loss model with the Tarver model. The major impact of the Tarver model is that the density of the solid propellant is a function of pressure. This is the key feature of the compressibility, but it also impacts the combustion model and the filling equations in the solution. Equation changes and input/output changes to accommodate the compressibility are straightforward, but updating density affects the iteration. The other changes discussed above are straightforward.

Relative to the closed vessel problem (Ref.3), the pressure transients are sharper and the burning rates become greater. These must be accommodated by shorter time steps and a finer solid
propellant grid. However, the event is so much shorter that computer times are comparable. Time step adjustment is a feature of the Adams method differential equation solver employed, but the grid must be selected to at least correspond to the time step for stability and may need to be finer for accuracy. The surface grid is nominally one-tenth the thickness of the thermal wave, and made to adjust automatically with rate. Subsurface grids are progressively larger. The calculation starts from a condition of equilibrium burning at the input starting pressure. An Ignition transient would be orders of magnitude longer than a DDT event, and it was judged that it would not contribute anything meaningful to this study. A possible exception, in hindsight, will be discussed later in connection with initial conditions.

Hindsight also suggests some possible simplifications. The surface structure in the combustion model does not change much during the short event such that a constant surface structure can be assumed. The mechanistic significance of this result will be pointed out subsequently, but here it would simplify the program. At lower DDT pressures, there is not much difference between the pressure in the solid and the pressure in the gas (also see Ref. (26) for the Adams & Pack limiting condition). Assuming the pressures to be the same, at least at the lower pressures, would simplify the program. This assumption will be made for the purpose of a later discussion. Related to this, it may not be necessary to update the solid propellant density in the combustion model and filling equations—particularly at the lower pressures. Of course, the density changes
must always be monitored for the compressibility problem because they are always important there; but the impact upon the other aspects of the problem is small. Assuming a constant density for the combustion model and filling equations would afford a significant program simplification.

A schematic of the analytical model is summarized in Fig. 3. Starting with an initialization of the problem, the filling equations are used to determine new state properties based upon the initial conditions. The combustion model updates burning rate and the Tarver model updates the compressibility. When a solution is accepted, the procedure is then repeated but with the accepted conditions replacing the initial conditions. The computation is terminable by a maximum run time, a maximum pressure or a maximum boundary motion, whichever occurs first.

9. Combustion model calculations are discussed in Ref. (3).
Figure 3. Schematic of the Analytical Model.
4.3 RESULTS AND DISCUSSION OF KEY FACTORS

4.3.1 Compressibility vs. Pressure Exponent

The compressibility of the solid will limit the pressure build-up and therefore the ability to achieve wave coalescence, due to its effect upon the free volume. This is, of course, a function of the equation of state that is used for the solid. Indeed, it has been said that free manipulation of the equation of state would enable one to predict anything, (Ref. 19). The point is that it is a key factor in the analysis. On the other hand, the pressure dependence of the mass generation rate is a factor which can overcome this effect of compressibility, producing the necessary pressure build-up. For the equation of state used here, it has been said that a pressure exponent of about 2 is required, (Refs. 24, 26).

Exponential pressure build-ups have been observed experimentally in the DDT of cast explosives, (Refs. 25, 26). Working backwards in their models, using the observed build-up as input, Maček and Tarver found that this form of build-up is well suited to the achievement of wave coalescence. This form of build-up requires that the time derivative of log pressure exceed a positive constant. For the model discussed here, this condition is satisfied if the burning rate follows the law:

\[
r \geq \frac{c_0}{\rho_o} \left[ \frac{R T}{\rho_o} \eta_0 \left( \frac{p_0}{p} \right)^{0.1} \right] \left( \frac{1 + p/K}{1 + p/K} \right)^{1/3} - 1
\]

\( R = \) gas constant

\( T = \) gas temperature

\( \eta_0 = \) reference specific volume at pressure \( p_0 \).
Eq. (7) is derived by incorporating Tarver's model into the filling equations. In order to achieve this closed form result, it was assumed that $P_s = P$ and that the gas temperature remains constant. These are reasonable approximations for the illustrative purpose of this discussion, and on the conservative side in establishing the burn rate requirement. Eq. (7) is shown plotted in Figure 4, using the properties of a typical energetic nitramine propellant.

It is observed that Eq. (7) imposes a fairly high rate requirement, with a pressure exponent requirement of 1.91. This is close to the value of 2 mentioned earlier, and would permit the gas production to outrace the compressibility. The position of the line (rate at pressure) is, roughly, inversely proportionally to $K^2$. Thus a less compressible propellant would permit a lower rate, a more compressible propellant would require a higher rate. The curvature in the line at high pressure is due to the covolume correction, and will therefore depend upon the type of correction used. Although ordinary solid propellants do not produce this type of burning rate behavior under steady-state conditions, the potential for doing so under transient conditions exists, (Refs. 30-32).

4.3.2 "P-Dot" Effects vs. Pressure

Simplified "P-Dot" theory produces an expression for transient burning rate as follows, Refs. (33, 34):
\[ r/r = 1 + 2n\kappa \frac{\dot{P}}{r^2 \dot{P}} \quad (8) \]

\( r \) = steady-state rate at \( P \)
\( n \) = pressure exponent
\( \kappa \) = thermal diffusivity of the solid
\( P \) = rate of pressure change

An order-of-magnitude analysis reveals that the rate augmentation in a DDT problem can be large at low pressure, but will diminish rapidly at high pressure. For \( P = 1 \) Kbar, \( \dot{r} = 7 \) in./sec, \( \kappa = 0.0002 \) in.\(^2\)/sec, \( n = 1 \) and \( \dot{P} = 10^{10} \) psi/sec, (Ref.25), \( r/r = 6.5 \). For \( P = 10 \) Kbar, \( \dot{r} = 70 \) in./sec, and everything else the same, \( r/r = 1.006 \). Thus, it would appear that the effect would run out of steam prior to the achievement of detonation pressures. Of course, the result depends upon the nature of the transient actually developed in the coupled solution; also, the detailed model does not give the same results as simplified P-Dot theory.

In this connection, significant differences between the gun or closed vessel transient and the DDT or closed pipe transient should be repeated. The DDT transient is faster, reaches higher pressures, and the event is shorter; differences are orders of magnitude in each respect.
Figure 4. Burning Rate Requirement to Sustain Exponential Pressure in a Closed Pipe Filled with a Compressible Solid.
Results of a detailed model calculation are shown in Figure 5. The steady-state (strand) burning rate of the propellant is shown as the solid line with the zig-zag (exponent breaks). The Figure 4 requisite rate is also shown. The history of the instantaneous rates is the broken line. The rate augmentation is seen to be large to begin with, and exceeds the requisite rate at low pressure, but the effect disappears at a pressure below 1 Kbar. What happened was that the failure to continue to exceed the requisite rate had a severe impact on the ability to sustain a high $\dot{P}$, and this feedback continuously depressed the augmentation. The nature of the transients that are developed by this model will be shown in connection with a later discussion. Note that the transient produced a sort of mesa effect in the burn rate curve.

**Surface Structure Effects vs. Time**

The "P-Dot" effect is one aspect of transient burning. The second is the development of the cratered surface structure in the course of the transient combustion of nitramine propellants which exhibit exponent breaks, (Refs. 2, 27, 30). This may be termed burn surface augmentation, and contributes to the actual mass generation rate delivered (or the effective burn rate for a normally regressing planar surface). From Reference (30), the augmentation is expressed as:

$$\frac{A_b}{A_p} = \frac{1-v}{1-S_{ox}/S_o}$$

$v$ = nitramine volume fraction

$S_{ox}/S_o$ = fraction of exposed nitramine surface on a cratered propellant surface, a function of $v$ and crater depth from Reference (27).

$A_p$ = planar surface area, here the same as the port cross-section.
Figure 5. Computed Effect of Pressure Transient on the Burning Rate of a Nitramine-Energetic Binder Propellant in a Closed Pipe.

Figure 6. Combined Effects of Pressure Transient and Surface Structure on Effective Burning Rate for Test Case Corresponding to Figure 5.
From the steady-state model, the equilibrium cratered surface that can be achieved depends upon nitramine particle size, concentration, melting point and the binder type. Coarser particle size, higher concentration and higher melting point promote more cratering, whereas energetic binder tends to limit it. For 75½% coarse HMX, the equilibrium surface augmentation has been computed to be as high as 35 for inert binders; a factor of about 2 is more typical with energetic binders which can burn more rapidly, and independently of the HMX. RDX, which has a lower melting point than HMX, or fine particle size, tends to delay the onset of cratering and limit the extent. In the course of a transient, the surface structure develops as discussed in the analytical model. This development was a material factor in explaining measured closed vessel burning rates of nitramine propellants, (Refs. 3, 30).

When the surface area effect is combined with the "P-Dot" effect in the detailed model calculation, the result is as shown in Figure 6. Here, the burning rate is an effective value, multiplying the actual value by Eq. (9). The effect is to raise the burning rate (really, the mass generation rate) by a factor of about 3 at all pressures, compared to Figure 5. Still, it is not enough to continually exceed the requisite rate. The "P-Dot" effect disappears whereas the area effect remains as a constant multiplier.

The problem here is that the time involved (microseconds) is short compared to the closed vessel situation (milliseconds). In the closed vessel, the time for crater development is comparable to the time of the event, so crater development is capable of producing high exponent behavior (high pressure dependence of mass gener-
ation) (Refs. 3, 30). Here, the time is so short that the surface structure remains at its initial value for all practical purposes. For the test case of Figure 6, the crater depth varied by only 0.2% in the course of the event, so $S_{0x}/S_0$ remained essentially constant.

If the characteristic time for crater development were comparable to the DDT event, then mass generation behavior as represented by Figure 2 would result. To verify that this behavior would produce DDT, a computation was performed wherein the combustion model was not used but instead Fig. 2 was inserted as input. The result is shown as a t-x diagram in Figure 7. It is observed that this behavior produced wave coalescence at a pressure of 12 Kbar, at a distance of 15 cm. into the sample, and in a time of 83 microseconds. The result is comparable to those of Macé and Tarver. Without this behavior, pressures did not exceed 1 Kbar and wave coalescence did not occur.

4.3.4 Initial Conditions

If the surface structure remains constant in the course of pressure build-up, then the surface structure existing initially should have a significant effect upon the build-up that does result. If the initial condition is equilibrium burning at a pressure below the exponent break, the surface will be a planar melt and $A_b = A_p$. If burning at a pressure above the exponent break, the surface will be cratered and $A_b > A_p$; also the initial burn rate and exponent will be higher. If the initial condition is no burning with an igniter heat flux imposed (i.e., ignition from rest), the planar
Figure 7. Wave Coalescence in the Solid Propellant for Combustion Behavior from Figure 2
melt layer must form during the ignition transient, (Refs. 3, 30) so that will specify the surface for the pressure build-up.

The two equilibrium initial conditions were investigated by calculating a 125µ HMX propellant and a 2µ HMX propellant. With the former, the initial pressure is above a theoretical exponent break; with the latter, the same initial pressure is below any exponent break. Resulting pressure build-ups are shown in Figure 8. The greater build-up with the coarse HMX is obvious, and is due to the higher initial rate, exponent and surface area. However, in neither case is a DDT achieved. For reasons discussed previously, the compressibility of the solid eventually triumphs such that the pressure approaches a new equilibrium level. The coarse HMX propellant does produce an exponential type of pressure build-up initially, but cannot sustain it.

Three points may be gleaned from this exercise:

1. The combustion process alone, as described by this model, cannot produce a DDT.

2. Propellant formulation effects on the combustion process have a significant influence on pressure build-ups which lead to DDT.

3. The closed pipe test in which a sample is ignited from rest is not necessarily representative of a propulsive device in which combustion has already been established prior to the disturbance; the initial conditions are not the same.
Figure 8. Computed Effect of Nitramine Particle Size on the Pressure Buildup Achieved in a Closed Pipe.

Figure 9. Computed Effects of Particle Size and Piston Motion (83 ft/sec) on Pressure Buildup.
4.3.5 Motion of the Free Volume End (Piston Motion)

Another set of calculations was performed to show the effect of piston motion in the problem. The initial free volume was increased from that of Fig. 8 calculations to accomodate some travel of the piston. Results for the two propellants are shown in Figure 9, with and without piston motion. It is seen that piston motion has a significant effect upon the pressure build-ups, but without wave generation is not determinative of DDT. New equilibrium pressures are achieved, following a relatively slow build-up due to the larger initial free volume. Other calculations which varied the piston velocity produced the same qualitative behavior. In each case, the compressibility of the solid eventually predominates. Indeed, the compressibility is such that "the hurrier you go, the behinder you get". Computed particle velocities ($u_1$) are always able to stay ahead of the piston motion.
4.4 CONCLUDING REMARKS

The compressibility of the solid, which dominates this particular model, merits further attention. Implicit in Tarver's computation of the compressibility and particle velocity is the assumption that wave reflections from the back wall of the solid can be neglected. Indeed, as pointed out by Kooker, (Ref. 22), the wave motions in both the solid and product states are ignored in this approach. The assumption becomes tenuous for shorter samples or longer events. It requires short events, else it would imply that the solid could be compressed indefinitely. The effect of wave reflections would be to reduce \( \rho_s \) and \( u_1 \) but, at the same time, render wave coalescence more difficult to achieve. This conflict is the dilemma of the model as formulated. However, reductions in \( \rho_s \) and \( u_1 \) would enable pressure build-ups to reach higher levels. To the extent that the pressure level reached may be important, a closer look at the Tarver assumptions regarding equation of state, momentum transfer and wave motion would be recommended.

The model has been premised on the applicability of combustion theory derived for relatively modest pressures and pressurization rates. More is not known. The effect of the solid as a compressible fluid on the combustion process per se is not known. If momentum considerations become important, they are not included in the current combustion models. Although compressibility has kept the pressures down to levels wherein the combustion theory can be used with some confidence, based on the results shown, it remains necessary to acquire some knowledge at the higher pressures associated with actual transitions. At present, there is little if anything in the way of data to guide future modeling.
The model is also premised upon the Macek wave coalescence theory as the criterion for DDT. Other possible mechanisms of shock initiation and development in the solid have not been considered here because they are generally associated with SDT, (Refs. 19,21,23). Nevertheless, it would be useful to incorporate the proposed combustion methodology into these other shock development models. In the first place, wave coalescence may not be determinative; shock development would then comprise a second stage of the problem. In the second place, wave coalescence may not even be necessary if pressure build-ups can generate sufficient compressive heating in the solid, (Refs. 21,23,35).

Although it appears, from work thus far, that the combustion process alone cannot produce DDT, it can certainly be concluded that the combustion is an important contributing factor. Accordingly, the proposed combustion methodology ought to be incorporated in DDT models predicated upon porosity or mechanical behavior. These physical effects provide added means to achieve large exposed burn surfaces, mass generation rates and pressure build-ups. Accounting for the transient combustion of nitramine propellants would further augment this process.

Finally, one purpose of any useful model is to provide guidance to propellant formulation. From the results thus far, it can be suggested that methods to avoid or mitigate exponent breaks in nitramine propellants will be beneficial in the DDT context as in the gun and rocket motor ballistics contexts. Reductions in nitramine concentration and particle size (in particular, the coarse end of a particle size distribution) ought to benefit both combustion and mechanical properties. RDX substitution for HMX
would be beneficial, through its lower melting point, to maintain a planar melt surface and delay any exponent break to higher pressures for a given size and concentration. A more energetic active binder would be beneficial in limiting or preventing the formation of surface craters through its higher monopropellant burning rate; but this approach would be subject to a number of other practical considerations. Much more work is necessary before definitive recommendations could be made with confidence. The work is justified by the continuing interest in high energy propellants.
5.1 COMBUSTION INSTABILITY EXPERIMENTS

5.1.1 Propellants

A series of active binder propellants was selected to continue the work begun with inert binder propellants last year, (Ref. 3). In that work, it was observed that HMX substitution for AP consistently reduced the combustion response to acoustic pressure oscillations as measured in the T-burner. However, complete removal of AP from the formulation (i.e., propellant containing HMX and HTPB only) precluded satisfactory data because the combustion produced considerable amounts of carbonaceous residues. This was interesting because thermochemical equilibrium calculations predicted no free carbon in the products. Therefore, all of the data were for propellants containing AP or combinations of HMX and AP, formulated to maintain burning rate and energy reasonably constant. Active binder propellants would serve to eliminate AP, and would be more relevant to the current interest in minimum smoke propellants. In effect, combustion driving comparisons would be made between the HMX and the active binder rather than HMX and AP.

The formulations selected are given in Table 1. There are two active binder propellants which do not contain HMX: XC-6 and XC-8. Propellant XC-7 consists of 40% fine HMX in the XC-6 binder formulation. Therefore, propellants XC-6 and XC-7 maintain
a constant binder, but at a disadvantage to the maintenance of energy and burning rate. Also, thermochemical calculations predict a small but finite amount of free carbon in the products of XC-6. Propellant XC-8 adjusts the binder ingredients in order to approach the energy and burn rate of the XC-7 propellant containing HMX. The essential difference between XC-8 and XC-7 is that nitrocellulose and TMETN, the energetic components of the binder, have been substituted for HMX. No free carbon is predicted in the products of XC-7 or XC-8.

Relative to the HTPB propellant series, all of these propellants are of lower energy and burn rate. Depending upon the nature of the results, it may be possible to say something about the response of active binder propellants vis-a-vis HTPB propellants. The active binder propellants for this program were procured from the Aerothermochemistry Division of the U.S. Naval Weapons Center, China Lake, California.
<table>
<thead>
<tr>
<th></th>
<th>XC-6</th>
<th>XC-7</th>
<th>XC-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt-% HMX (4µ)</td>
<td>----</td>
<td>40.00</td>
<td>------</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>10.00</td>
<td>5.99</td>
<td>35.00</td>
</tr>
<tr>
<td>TMETN</td>
<td>60.88</td>
<td>36.53</td>
<td>48.60</td>
</tr>
<tr>
<td>Polycaprolactone</td>
<td>28.97</td>
<td>17.39</td>
<td>16.20</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>0.15</td>
<td>0.09</td>
<td>0.20</td>
</tr>
</tbody>
</table>

\[
\text{(TF/M)}^k \ (\text{oK}^k) \quad 7.74 \quad 9.38 \quad 8.88
\]

\[
r_{1000} \ (\text{in./sec}) \quad 0.11 \text{ (data)} \quad 0.15 \text{ (data)} \quad 0.13 \text{ (predicted)}
\]

Moles Products/100 gm.

<table>
<thead>
<tr>
<th></th>
<th>XC-6</th>
<th>XC-7</th>
<th>XC-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_4)</td>
<td>0.207</td>
<td>------</td>
<td>0.014</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>2.380</td>
<td>2.082</td>
<td>2.386</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>0.198</td>
<td>0.163</td>
<td>0.227</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>1.719</td>
<td>1.484</td>
<td>1.628</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>0.285</td>
<td>0.508</td>
<td>0.415</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>0.428</td>
<td>0.797</td>
<td>0.435</td>
</tr>
<tr>
<td>C</td>
<td>0.037</td>
<td>------</td>
<td>------</td>
</tr>
</tbody>
</table>
5.1.2 Results for 100% Binder Propellant

Unfortunately, propellant XC-6 produced an excessive amount of carbonaceous ash in the T-burner at all pressures up to 1200 psi, so that meaningful results could not be obtained. It should be noted, however, that this ash material was physically different from the layered char residues produced by the HMX/HTPB propellant. It appears that neither of these propellants follow equilibrium thermochemistry in their decomposition and combustion. The amount of ash produced by XC-6 filled the interior of the T-burner; it was far in excess of what would be expected from a predicted weight concentration of 0.4% of products. For the HTPB propellant, no char had been predicted yet a layered char also filled the interior of the T-burner. These results are interesting in the context of fundamentals of combustion, specifically polymer decomposition, and merit further investigation on the question of minimum smoke propellants. Fuel-richness appears to be a factor.

Propellant XC-8 was not available in time for the current program. A tailoring effort was necessary to optimize processing and cure consistent with the burning rate, energy and general formulation objectives. That effort was conducted by the Naval Weapons Center. Therefore, all of the data acquired were for propellant XC-7, which burned cleanly. It is planned to conduct the tests with XC-8 in the course of follow-on work.
5.1.3 Results for Propellant Containing HMX

The stability tests were carried out in \(2\frac{1}{4}\)-inch diameter (I.D.) T-burners coupled directly to a surge tank. The propellant configuration used was a \(3/8\)-inch thick disc. Data were obtained using the growth-decay method, (Ref. 36). Tests were conducted at nominal frequencies of 500, 900, and 1900 Hz and at pressures of 500 and 1000 psi. Repeat tests were performed at each condition.

All of the tests at 1000 psi were stable. No oscillations were driven over the frequency range at this pressure. Post-test examination of hardware showed that the burning had been clean, so the measured stability is considered real. Oscillations were, however, driven at 500 psi.

The test results are plotted as the sum of the measured growth and decay coefficients vs. frequency in Figure 10. The propellant is relatively stable in that the measured growth coefficients were quite small, the net growth coefficient exceeding the decay coefficient only at the 1900 Hz test frequency, and then only slightly. The results are qualitatively similar to the HTPB propellant results, Ref. (3), in that the driving was greater at 500 psi than at 1000 psi and increased with increasing frequency.

The stability of the XC-7 propellant cannot fairly be compared to the HTPB propellants because its energy and burning rate are lower. Data for propellant XC-8 are required. If XC-8 turns out to be less stable than XC-7, then it will be possible to make a general conclusion regarding the stabilizing properties of HMX.
Figure 10. T-Burner Results for Active Binder/HMX Propellant
5.2 DESIGN OF CLOSED VESSEL APPARATUS

5.2.1 Purpose and Approach

Experiments have been instrumental in formulating a model of the combustion of nitramine propellants, (Refs. 1,2). Burning rate data were acquired to pressures of 50 Kpsi in a strand burner located at AFATL. Observations of the combustion zone and burning surface structure were made to 6 Kpsi with the aid of a window bomb located at JPL. In view of the interest in transient burning and high pressure burning for armament and DDT, it is necessary to begin to acquire data at higher pressures in order to guide and supplement the analytical models. In the absence of data, the extension of models to pressures much above 50 Kpsi (3.4 Kbar) is speculation.

Two of the most important items of information which came from the experiments were the pressure exponent shift and the marked change in propellant surface structure associated with that shift. A windowed apparatus is not required for that information. Strand burning rate is determined by time and internal distance measurements. Surface structures are determined by rapid decompression of the device, causing the combustion to cease, and observation of recovered samples under a scanning electron microscope. Without a window, pressure capability can be increased considerably at minimal cost. However, a conventional strand burner would continue to be a costly item.

The closed vessel device has been an expedient method to determine burning rates in the armament field, but as noted in last year's work, (Ref. 3), the measurement is deductive in nature and
subject to interpretation - particularly for nitramine propellants. A method for the direct measurement of burning rate in that apparatus would be desirable. Since pressure is continually increasing in the course of a closed vessel test (it is constant in the strand burner), a responsive direct measurement would provide transient burning rates as a function of pressure in a single test. The closed vessel is expedient because it is self-pressurized from the combustion and because it does sweep a wide pressure range.

Rapid decompression for extinguishment is not a part of the normal closed vessel procedure. However, it is not difficult to incorporate a burst disc design, gaged for chosen pressure levels, into a closed vessel design. By this method, the progressive development of the surface structure with pressure can be traced to pressures an order of magnitude beyond existing data. It is believed that it is important to trace this development in order to arrive at a meaningful understanding of high pressure combustion.

The standard closed vessel experiment utilizes grains of propellant representative of end-product usage, which also provide high surface area for rapid pressurization. High surface area is not required if the free volume of the chamber can be reduced. A low volume chamber is convenient for high pressure work because of reduced size and weight. Also, propellant in the form of a strand would be more convenient for direct measurements of burning rate because it affords greater lengths and times than would grains or pellets. The testing of end-product items is not a factor in this research.
JPL has investigated the feasibility of a technique similar to that reported in Ref. (17): direct continuous burning rate measurement by constructing an electrical circuit about a propellant strand, the circuit being closed by the propellant flame zone. As the propellant burns, the changing strand length is determined from the change in the measured resistance. The technique has proven feasible for steady-state (constant pressure) measurements at JPL, but has not as yet been attempted for a rapid pressurization transient. The distinguishing factor is response time. However, another method facing the same problem was used with some success for a rapid depressurization transient, (Ref. 37).

The selected apparatus is a closed vessel, incorporating a propellant strand and rapid decompression capability, designed for pressures up to 100 Kpsi. It will be possible to at least investigate surface structures to pressures an order of magnitude beyond existing data. Burning rate information, if acquired successfully, would extend current knowledge by a factor of 2 in pressure.
5.2.2 Design and Procurement

In designing the closed bomb, a mass balance was written and programmed and parametric calculations were carried out to size the internal dimensions of the bomb to give the desired pressure-time history for reasonably sized propellant test samples. The design arrived at is shown schematically in Figure 11. The propellant sample, pressure measurement transducer, and electrical leads for propellant ignition and burning rate measurement are contained in a removable upper closure. The initial pressurization port and the burst diaphragm/depressurization port are located in the bomb lower closure.

The test procedure will be to initially pressurize the bomb to approximately 0.3 Kbar with bottled nitrogen, ignite the strand, and then allow the combustion to self-pressurize the bomb until the sized burst diaphragm ruptures, quenching the burning sample by rapid depressurization.

The bomb is being manufactured by Harwood Engineering Corporation and is scheduled for delivery early in 1979.
Figure 11. Schematic of High Pressure Closed Bomb
PRESENTATIONS, PUBLICATIONS AND WORKSHOP PARTICIPATIONS

The following presentations and publications have been generated under this research contract:


In addition, there has been participation in the following workshops:

(1) ONR/AFOSR Workshop on DDT, Atlanta, GA (Jan. 1978)

(2) TTCP Panel W-4 KTA-6 Nitramine Gun Propellant Meeting, Air Force Armament Laboratory, Eglin AFB, FL (Mar. 1978)

(3) JANNAF Workshop on Burn Rate Modeling (N.S. Cohen, Acting Moderator), Lancaster, CA (Apr. 1978).
SECTION 7

CONCLUSIONS AND RECOMMENDATIONS

A model of DDT has been formulated which takes into account the dynamic burning mechanisms of nitramine propellants in the framework of an isentropic compression theory of shock formation. Although the combustion mechanisms are found to contribute significantly to pressure buildups which can lead to DDT, they cannot by themselves produce DDT in a monolithic grain in accordance with this particular theory of shock formation. Combustion contributions are related to the pressure exponent shift phenomenon and, to that extent, variables which would alleviate the exponent shift (such as reduced HMX particle size and concentration) would limit pressure buildups.

Although several possible modes of DDT have been postulated, a particular mode by which solid propellants undergo DDT has not been ascertained. The most generally accepted view is one based upon convective burning through mechanically flawed propellant. Models of convective burning should incorporate the combustion model presented herein to provide their constitutive conductive burning relations.

The manner in which pressure buildups create a shock in solid propellants is also to be ascertained. The isentropic compression is but one theory. Other theories have been formulated in connection with studies of wave motion and SDT (e.g., hot spot initiation). Combustion contributions may have greater significance in association with other mechanisms of shock formation than shown with isentropic compression. The combustion model should be taken into account in studies of shock formation and development generally (i.e., other frameworks than the one used here).
A serious limitation is the lack of experimental knowledge of the combustion process under DDT conditions. A closed vessel apparatus has been designed with which to extend combustion data to considerably higher pressures, though still short of DDT conditions.

Nitramine propellants appear to be relatively stable to acoustic pressure oscillations over the frequency range 500 Hz-1900 Hz. It had been established that HMX substitution for AP reduces the combustion response. However, more data are required to determine whether HMX addition to active binders reduces combustion response. An interesting finding is that certain formulations which do not contain AP do not follow equilibrium thermochemistry in their decomposition and combustion. Further study appears warranted.
SECTION 8

REFERENCES


14. Oberth, A., Discussion presentation at the AFOSR-ONR Workshop on Transition from Deflagration to Detonation in Heterogeneous Solids, Atlanta, GA. (Jan. 1978).


24. Jacobs, S., published comment to (Ref. 26), ibid. (Ref. 26).


