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**Shock Development From Compression
Waves Due to Confined Burning in Porous
Solid Propellants and Explosives**

**D.W. Coyne, P.B. Butler and H. Krier,
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SHOCK DEVELOPMENT FROM COMPRESSION WAVES
DUE TO CONFINED BURNING IN POROUS SOLID PROPELLANTS/EXPLOSIVES*

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Abstract

When a high energy solid propellant or explosive becomes porous, either by design or by accidental damage, it becomes more sensitive to shock-to-detonation transition (SDT). Stress waves propagating ahead of the convective flame front cause pore collapse which creates a confined bulk reaction zone. With sufficient pressurization in the reaction zone, the stress waves coalesce to form a shock. This paper describes an attempt to model the shock formation in porous solids by coupling the gas pressurization to the solid mechanics of pore collapse and shock formation. Concepts are presented which indicate why porous materials are more sensitive to shock initiation than solids; mainly it is due to a greater bulk energy and formation of localized hot spots.

1. Introduction

Advanced formulations for solid propellants continue to be more energetic and the possibility of deflagration to detonation transition (DDT) is real, especially if the propellant motor grain becomes porous due to damage by accidental stimuli. In a recent transient analysis [1] for DDT in a porous propellant bed, it was shown that steady detonation characteristics (CJ pressure, CJ temperature, detonation velocity) were predicted without requiring the precursor shock common to most detonations in homogeneous materials. This was referred to by some as the "convective burn" model. In Ref. [1] it was shown that the high surface-to-volume ratio of very small (1/10mm diameter) propellant particles, high burning rate-pressure indices (0.9 to 1.0), and confinement of product gases (due to the tight packing and enclosing walls) combined to cause a rapid enough gas generation rate to build and sustain pressures equivalent to those observed in granular bed experiments [2,3]. However, as stated above, the model analysed in Ref. [1] did not attempt to treat the stress waves propagating into the unburned porous material. It is the purpose of this paper to analyse the propagation and shock formation of these compression waves generated at the products-reactants interface.

In a fairly recent set of experiments, A.W. Campbell [3] has shown by using a similar test arrangement to that used in [2], but with

granulated compressed HMX explosive, that detonation may be a result of shock initiation. To explain Campbell's results, a new mechanism describing the detonation of porous propellants was given. Compression waves originating at the burning front propagate ahead causing compaction of the unreacted porous mixture resulting in the formation of a solid plug thereby eliminating further convective flame propagation. The compression waves continually generated at the burning front propagate through the solid plug. Coalescence of these compression waves form a shock wave which initiates the explosive resulting in a detonation.

Work done by Macek [4] and Tarver et al. [5] used the method of characteristics to predict shock development in homogeneous solid explosives from confined end burning. In both studies a modified Tait equation was used as the solid material state relation.

Macek used the method of characteristics to theoretically predict his observed experimental results [4]. By assuming an exponential type pressure rise in the product gases, Macek traced right running characteristics generated by the pressure input and graphically showed the waves to coalesce at approximately the distance observed in his experiments. The coalescence of the characteristics is interpreted as the formation of a shock wave which is assumed to cause initiation of the explosive resulting in a detonation propagating forward and a detonation propagating backwards.

The work presented in this paper will show that the Tait-equation assumption made in [4] and [5] was incorrect for this particular compression process and a more general Mie-Gruneisen equation of state (E.O.S.) should be used.

In fact, a method of characteristics calculation is impossible with the Mie-Gruneisen state equation, so the system of conservation equations were solved numerically by a Lagrangian finite difference code. Homogeneous solids with known properties were first computed to test the validity of the code, followed by calculations for heterogeneous or porous materials. The purpose of this work is to eventually incorporate reactive chemistry and hot spot mechanisms into the model and go beyond the shock formation to predict DDT.

Index Categories: Shock Waves and Detonators; Reactive Flows; Properties of Propellants.

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Shown in Figure 1 is a schematic representation of what we envision as the six part DSDT[®] process. Superimposed on each section of the figure is a line representing the gas porosity (gas volume/total volume) as a function of bed location. A value of ϕ equal to unity represents a zone of all gas while ϕ equal to zero indicates a homogeneous solid.

Portion A represents the initial blast caused by the igniter used to initiate DSDT in the bed. In the second portion, the convectively burning porous bed is shown to be pressurizing the region behind the ignition front. This is a result of the product gases being confined by the walls. The porosity variation for this time indicates an all gas makeup in this particular zone. Actually, there is a finite reaction zone where the propellant is decomposing into the product gases. Reference [1] showed that if the reactive material consisted of mm size particles, this reaction zone may be very large. This results in a slower pressurization rate of the gas cavity. Illustrated in the last four parts of Figure 1 is what we refer to as the second possible branch of DSDT, the shock compression branch. Parts C-E, pore collapse, plug formation and shock formation are envisioned concepts which will be expanded upon in the following sections of this paper.

2. Governing Equations

For the hydrodynamic analysis of a continuous material with a moving boundary the governing equations are easier to work with if expressed in the Lagrangian or material form as opposed to the Eulerian form. The conservation of mass, momentum and energy for one-dimensional unsteady flow are written as

$$v_t = v u_x \quad (1)$$

$$u_t = -v P_x \quad (2)$$

$$e_t = -P v_x \quad (3)$$

In the above expressions v represents specific volume, u , particle velocity, e , specific internal energy and P , the total stress acting on the particle. The subscripts x and t indicate partial derivatives with respect to distance and time, respectively, evaluated at a constant particle location.

For comparison the same conservation equations written in Eulerian or spatial form are

$$\rho_t + (\rho u)_x = 0 \quad (4)$$

$$(\rho u)_t + (\rho uu + P)_x = 0 \quad (5)$$

$$(\rho e)_t + (\rho ue + Pu)_x = 0 \quad (6)$$

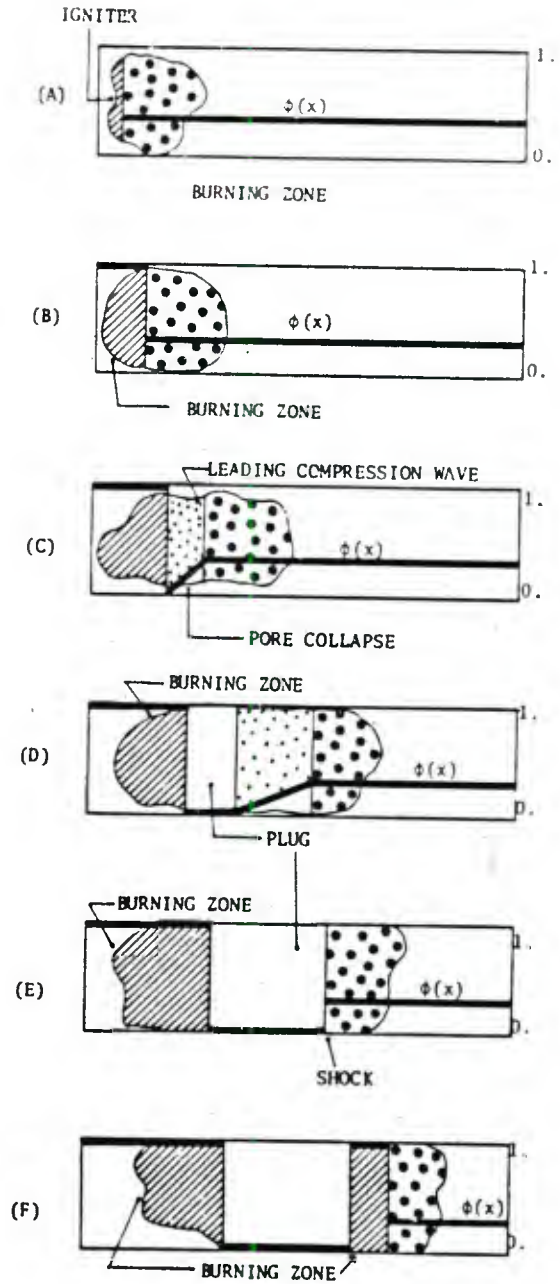


Fig. 1 Six part representation of DSDT
 (A) Ignition of porous material, (B) Convective flame spreading with pressure rise in gas zone, (C) Pore collapse, (D) Plug formation, (E) Shock formation, (F) Shock initiation of porous material

• DSDT = Deflagration to Shock to Detonation Transition

Here the partial derivatives are evaluated in a fixed reference frame and the material particles are in motion relative to that frame, thus, giving the x-direction flux terms.

A fourth expression, an equation of state for the material, forms a mathematical relation between pressure, specific volume and specific energy. The particular form of the state equation used will be expanded on in the following section and for the time will be expressed in the general form as

$$P = P(v, e). \quad (7)$$

Equations (1-3) and (7) represent the full system of equations necessary to describe the flow phenomena in a homogeneous material. More specifically they are four independent equations in four unknowns: u , v , P , and e . Since thermal conduction is neglected in our calculations, temperature does not appear in the governing flow equations. For this reason temperature can be treated as an "auxiliary" relation and will be dealt with later in the paper.

When describing stress wave propagation through porous materials, an additional variable appears, α , the porosity.

$$\alpha \equiv v/v_s \quad (\text{where } \alpha > 1) \quad (8)$$

For a given volume v , the volume occupied by homogeneous solid is represented by v_s . The difference between these two volumes is treated as a vacuum for these calculations. Other researchers [6] have modeled this void volume as a gas which is isentropically compressed as the voids collapse and thus act to resist the compaction-collapse process.

With the addition of a fifth independent variable namely, α , an additional equation is necessary.

Carroll & Holt [6] have done extensive work in studying and mathematically modeling the collapse of porous materials. Our work employs their model for static pore collapse, relating the stress on the material to the void volume. For the time being it will be expressed as, $P = P(\alpha)$. A more detailed description of the three-part model will be presented later.

3. Equations of State

Homogeneous Solids

Most of the work presented in this paper made use of a Mie-Grüneisen equation of state for homogeneous solids and a modified form of it for the porous material calculations. The general form of the Mie-Grüneisen equation is

$$P(v_s, e) = P_{HS}(v_s) + \frac{(e - e_{HS})}{v_s} \Gamma(v_s) \quad (9)$$

In equation (9), P_{HS} and e_{HS} , the Hugoniot pressure and Hugoniot energy, are used as the reference state and $\Gamma(v_s)$ is the Grüneisen coefficient representing the thermodynamic

derivative,

$$\Gamma(v_s) \equiv v_s (\partial P / \partial e)_v \quad (10)$$

Evaluating equation (9) at ambient conditions and making use of several thermodynamic relations (See Reference [6]) gives the constant,

$$\Gamma(v_{s0}) \equiv \Gamma_0 = \frac{\beta c_0^2}{c_v} \quad (11)$$

where β is the coefficient of thermal expansion; c_0 is the ambient sound velocity; c_v is the specific heat at constant volume. Values of these parameters for the material HMX are given in Table 1.

Table 1. HMX Properties

Initial Specific Volume	$v_{s0} = 0.526$ cc/g
Initial Density	$\rho_{s0} = 1.9$ g/cc
Ambient Sound Velocity	$c_0 = 0.267$ cm/ μ sec
$u_s - u_p$ Slope	$S = 2.6G$
Initial Yield Stress	$Y_0 = 0.0517$ GPa
Initial Shear Modulus	$G_0 = 3.516$ GPa
Specific Heat (constant volume)	$C_v = 10.1J/g^\circ K$

A simplifying approximation made for the Grüneisen coefficient is

$$\frac{\Gamma(v_s)}{v_s} = \left(\frac{\partial P}{\partial e} \right)_v = \text{constant}. \quad (12)$$

Equation (9) is convenient for shock development problems, since it gives the pressure at any thermodynamic state as the deviation, $\Delta P = \Gamma(v_s) (e - e_{HS}) / v_s$, from the volume dependent reference pressure, P_{HS} . The subscripts HS in the above equations indicate that the reference state chosen is the solid material shock Hugoniot.

Experimental shock velocity-particle velocity data indicates a linear fit is valid for volume changes encountered in our analysis. Reference [8] gives for HMX,

$$U_s (\text{cm}/\mu\text{sec}) = A + S u_p (\text{cm}/\mu\text{sec}) \quad (13)$$

where $A = 0.267$ and $S = 2.6$.

In the limit of an infinitesimal disturbance in particle velocity, $u_p \rightarrow 0$, it becomes obvious that the constant A in equation (13) represents the adiabatic sound velocity, c_0 .

Combining equation (13) with the conservation of momentum and conservation of energy across the shock discontinuity, an expression for the Hugoniot or reference pressure used in equation (9) is obtained

$$P_{HS}(v_s) = \frac{\rho_{s0} c_0^2 R}{[1 - SR]^2} \quad (14)$$

where $R = 1 - v_s / v_{s0}$ and ρ_{s0} is the initial solid density.

Past work in DDT by Macek [4] and Tarver et al. [5] used a modified Tait equation as their constitutive relation, namely,

$$P(v_s) = \frac{\rho_{s0} c_0^2}{3} \left[\left(\frac{v_{s0}}{v_s} \right)^3 - 1 \right]. \quad (15)$$

This particular state equation was used with the supposition that it represented isentropic compression throughout the entire loading process. In both studies, because of the simplicity of equation (15) and the isentropic assumption, the method of characteristics was easily applied to the governing hyperbolic equations and characteristics (or distance-time traces of constant stress) could be drawn for various stress loads and upstream shock coalescence predicted. Appendix A includes a brief description of the method of characteristics as applied to one-dimensional transient flow in a homogeneous material.

In order to determine whether the Tait equation assumption was indeed representative of an isentropic process up to pressures of 4GPa, (40 kbar), we plotted in Figure 2 the Tait equation along with the shock Hugoniot, and an isentrope ($S = S_0$) for HMX.

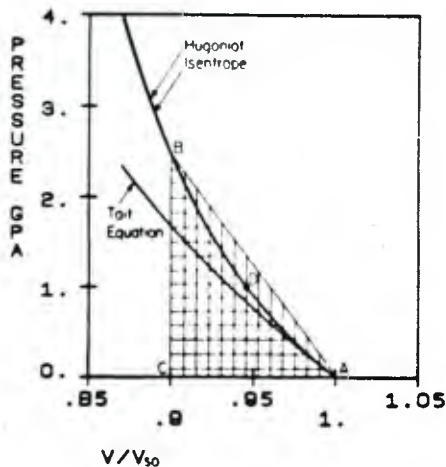


Fig. 2 Comparison of HMX Shock Hugoniot, Isentrope ($\Gamma/v = \text{constant}$), and Tait equation of state

Figure (2) indicates that the Tait expression only models isentropic compression for pressures less than approximately 0.5 GPa (= 5 kbar = 72,700 psig) and becomes more incorrect the larger the stress. Also depicted in Figure (2) is the small difference between the shock Hugoniot and isentrope. This is common for solids when the pressure is less than approximately 5 GPa [7].

By shock compressing a solid from ambient conditions to the state labeled B on Figure (2), an amount of internal energy equal to the triangular area ABCA ($e_H - e_0 = P_R (v_A - v_B)/2$) is deposited into the shocked state (state B). Of this total energy, the area under the

isentrope ABCA represents the reversible work done in an equivalent isentropic compression and the remaining slice, ABBA, represents the irreversible entropy increase associated with the shock discontinuity. A qualitative comparison will be made when discussing shock waves in porous material.

Porous Materials

The state equation for the porous material calculations is the same Mie-Grüneisen equation used for homogeneous solids with the introduction of α , the "porosity",

$$P(v/\alpha, e) = P_{HS}(v/\alpha) + \frac{\Gamma_0}{(v_{00}/\alpha_0)} (e - e_{HS}), \quad (16)$$

where v and v_{00} represent the specific volume and the initial specific volume of the mixture. Equation (16) gives the pressure for a porous material as a function of the energy of that material and a reference pressure, $P_{HS}(v/\alpha)$. Since $v_s = v/\alpha$, this reference curve is the same as that for the homogeneous solid, i.e. the solid material Hugoniot.

With the introduction of the variable α , porosity, an additional constitutive relation is needed to fully describe the material state. The following section introduces the pressure-porosity (or $P-\alpha$) law used.

4. Pore Collapse

A constitutive relation, referred to as the "P- α law," is needed when the conservation equations are solved for a porous solid. The law relates an externally applied pressure to the extent of compaction or pore collapse, represented by α . The form of the P- α law used was developed by Carroll and Holt [6]. In the model, the porous matrix is treated as a hollow sphere where the inner and outer radii are chosen such that pore size and overall porosity of the porous material being modeled are accurately represented.

Pore collapse occurs in three phases: (1) elastic phase, where the solid elastically deforms; (2) elastic-plastic phase, where plastic deformation begins at the inner radius and progresses outward until plastic deformation begins at the outer radius; and (3), the plastic phase, where plastic deformation occurs throughout. The P- α relations for the three phases of compaction and the appropriate range which each applies are given by,

elastic phase: $\alpha_0 > \alpha > \alpha_1$

$$P = \frac{4G(\alpha_0 - \alpha)}{3\alpha(\alpha - 1)} \quad (17a)$$

elastic-plastic phase: $\alpha_1 \geq \alpha > \alpha_2$

$$P = \frac{2}{3} \gamma \left[1 - \frac{2G}{\gamma \alpha} (\alpha_0 - \alpha) \right] + \ln \left[\frac{2G(\alpha_0 - \alpha)}{\gamma(\alpha - 1)} \right] \quad (17b)$$

$$R^- = 0 \text{ or } u = \frac{2}{n-1} (c-c_0) \quad (\text{A.9})$$

The C^+ characteristics generated at the left end, can now be plotted on the $x-t$ plane at any time for a given $P(t)$ relation. A summary of the procedure is given below for a general pressure ratio $P(t)$ input.

Table A-1
Logic To Use Method of Characteristics
For Shock Compression

- | Step # | Process |
|--------|--|
| 1. | at time t , $P=P(t)$ |
| 2. | calculate P/ρ_0 from Tait E.O.S., Eq. A.5 |
| 3. | calculate the sound speed from Eq. A.5 |
| 4. | calculate the velocity, u , from Eq. A.9 |
| 5. | determine the position of the left boundary from
$x_0 = \int_0^t u \, dt$
using equation A.9, A.6, A.5 and the $P(t)$ input, u can be expressed in terms of t only
$x_0 = \int_0^t \left[\frac{2c_0}{n-1} \left(\frac{n}{2} \frac{r(t)}{c_0} + 1 \right) \right]^{\frac{n-1}{2n-1}} dt$ |
| 6. | calculate the slope of the characteristic $dx/dt = u + c$ |
| 7. | plot on the $x-t$ plane
$x(t) = x_0 + (dx/dt)t$ |

11. Appendix B

TEMPERATURE INCREASE DUE TO SHOCK COMPRESSION

The method used for determining temperature increases due to shock waves is that of Zel'dovich and Raizer [7] and involves the partitioning of energy and pressure into three separate components.

The first component of pressure is due to the interatomic potential and is referred to as the elastic or cold term. At zero degrees Kelvin and one atmosphere pressure, the atoms neither repel or attract one another and at this point the elastic pressure is zero. The volume occupied by the solid at this point, V_{0c} , is slightly less than the volume occupied by the same mass of material at room temperature. Because the solid thermally expands when heated from 0°K to 300°K, the solid actually has a negative elastic pressure (attractive interatomic force) at ambient conditions. As the material is compressed, either isentropically or irreversibly in a shock-like process, the atoms repel one another and therefore contribute to the elastic pressure in a positive sense. The elastic

component of the total energy is related to the elastic pressure through the work-energy relation,

$$P_c \, dv = -de_c \quad (\text{B.1})$$

where the subscript c is in reference to the elastic or cold component of the total internal energy, e , or total pressure, P . The name cold energy or pressure has significance in that the elastic pressure-volume relation can be shown to be the 0°K isotherm and also the $S = 0$ isentrope.

The second and third components of the energy are due to the atomic and electronic motions, respectively. The electronic terms, e_e and P_e , are only of significance above approximately 10,000°K and hence outside the regime of the processes encountered here.

The thermal component of energy represents the harmonic oscillations of the atoms and is expressed as

$$e_T = C_V (T - T_0) + e_0 \quad (\text{B.2})$$

To determine the thermal pressure from the thermal energy, e_T , the first law of thermodynamics and a Maxwell relation are used to obtain

$$\left(\frac{\partial e}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P \quad (\text{B.3})$$

This is a general equation applicable to both components, elastic and thermal. Since the cold pressure is only a function of volume (or more specifically interatomic distance), then $P_c = P_c(v)$ and Eq. (B.3) gives

$$P_c = - \frac{de_c}{dv}$$

the same expression as given prior to this, Eq. (B.1), in the work-energy analysis. For the thermal component,

$$P_T = C_V T \left(\frac{\partial P_T}{\partial T} \right)_v \quad (\text{B.4})$$

Equation (B.4) can be expressed in terms of the thermodynamic derivative $\Gamma(v)$ (the Gruneisen coefficient) as

$$P_T = \Gamma(v) \frac{C_V T}{v} \quad (\text{B.5})$$

where, as stated earlier, $\Gamma(v) = v \left(\frac{\partial P}{\partial e} \right)_v$. The Gruneisen coefficient, as expressed here, is a measure of the change in thermal pressure to thermal energy.

Equations (B.1), (B.3) and (B.5) are solved in addition to the algebraic component relations,

$$e = e_c + e_T \quad (\text{B.6})$$

$$P = P_c + P_T \quad (\text{B.7})$$

and the Hugoniot jump conditions,

$$e = e_H = \frac{1}{2} P_H (v_0 - v) \quad (\text{B.8})$$

to generate the cold compression curve shown in Figure 11.

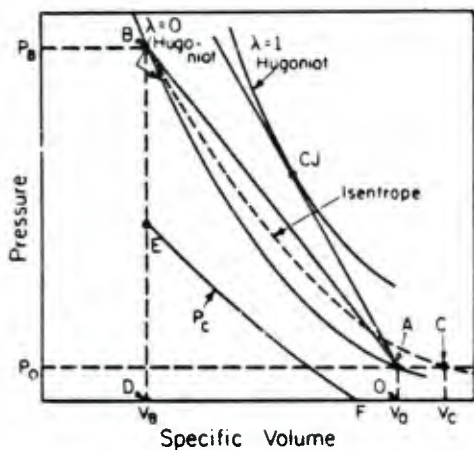


Fig. 11 Hugoniot for unreacted ($\lambda=0$) and fully reacted ($\lambda=1$) explosives

For this particular case, the ratio τ/v is assumed to be constant. Figure 11 shows graphically how each component of energy is represented. The area ABDOA is the total increase in internal energy due to shock pressure, P_B . Of the energy deposited by the shock, the area under the curve FED goes into the potential or elastic energy. The remaining area ABEFOA is the contribution to the thermal component and therefore determines the temperature rise associated with the shock.