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PARTICIPATION OF LLL IN JSEXP

PERFORMANCE OF NON-IDEAL HE

(Unclassified)

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30 December 1973

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Prepared for U. S. Atomic Energy Commission under contract no. W-7405-Eng-48

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PERFORMANCE OF NON-IDEAL EXPLOSIVES

1. PREFACE

During the Southeast Asia Conflict a re-examination of this country's chemical explosives technology was undertaken. The critical issues involved were:

- The possible shortage of certain explosives for high use munitions.
- A number of old Government Owned-Company Operated (GOCO) explosive manufacturing plants in need of urgent modernization and/or new facilities.
- The closing of some commercial explosive plants.

In 1969 the Military Departments initiated a Joint Alternatives Fill Program to study these problems and possible solutions. The effort was divided into short and long term programs. The short range program resulted in delineating options available in planning a new explosives production base. Also, specific short-range explosive alternative fills for high use munitions were proposed.

The long range program dealt with the objective of optimizing the "utilization of explosives in munitions, in terms of national policy, tactical effectiveness, system design, safety, handling, cost, stability, and availability".⁽¹⁾

Recognizing the need for a coordinated effort toward these goals, DDR&E established a Joint Services Explosives Program (JSEXP) to manage the "spectrum of research, formulations and synthesis, characterization, qualification and process development". In concert with these goals, the Lawrence Livermore Laboratory and the Los Alamos Scientific Laboratory have made proposals in support of this effort. The various proposed tasks have been reviewed by representatives of the Joint Services Technical Coordinating Group/Working Party for Explosives and have been fully integrated into the JSEXP Program. The Advanced Research Projects Agency

and Picatinny Arsenal have provided funds in support of the AEC Laboratories' endeavors. A progress report on one specific task, which was funded at LLL and entitled "Performance of Non-Ideal Explosives", follows:

2. INTRODUCTION

One of the solutions proposed by the Alternatives Fill Program is that, because of possible limited explosive plant facilities, alternative explosive materials can be obtained from the civilian economy. For example, ammonium nitrate fertilizer is such a material. Other nitrates and perchlorates which are available in the peace-time domestic economy of the United States are also candidates. Thus we see a trend in explosives technology toward the increased utilization of non-ideal explosive formulations. These formulations may consist of oxidizers, fuels, sensitizers, and binders as discrete particles or phases.

Non-ideal explosives will play an important role in DOD explosive systems as alternative or emergency fallback fills in high volume munitions. They represent a new concept in munitions technology, because, in comparison with conventional ideal explosives such as TNT and RDX, these formulations depend much more significantly on geometry and confinement in determining the total energy released. The formulations, which are also called composite explosives, will be important for energy enhancement and tailoring of explosive properties for such applications as air blast, earth cratering, underwater energy, incendiary explosives, and "shockless" acceleration of metal. Explosives that combine the properties of high energy, high temperature stability, and greater safety will also probably be composite formulations.

The detonation behavior of ideal explosive can be readily determined from such properties as detonation pressure and velocity. Their energy can be obtained by well-controlled hydrodynamic expansion measurements. From these parameters an equation-of-state (EOS) of the explosive detonation products can be derived. Composite explosives are extremely non-ideal in their detonation behavior. (A detailed description of this difference follows in Section 3). Because the oxidizer and fuel are in discrete phases, transport effects and kinetics play a dominant role in their energy release rate, whereas in standard explosives only hydrodynamic flow governs the energy release. As a consequence, the reactions of non-ideal explosives may not go rapidly to completion and to equilibrium before they are quenched by the rapid expansion of unconfined detonation products. The detonation behavior of composite explosives is non-scaleable, or to state it differently, the detonation process is time-dependent. Performance of a non-ideal explosive will depend not only on the chemistry and physical makeup of the explosive, but also on the explosive charge geometry and confinement.

For a weapons designer to fully utilize composite explosives in munitions applications, it is essential that he be provided with: (1) a description of the detonation and burning process and (2) the equation of state of the products. Furthermore, it is necessary that he be able to predict the effect of such factors as chemical composition, particle size, void volume, etc. on the energy release rate.

The goal of this program is to assist the alternate fills program by developing a well-understood model of the time dependent detonation performance of non-ideal high explosives. With this model and the appropriate hydrodynamic and EOS descriptions, a weapons designer will be able to predict the performance or examine tradeoffs in a particular munition. For example, he will be able

to determine the effect on performance of a munition if he uses a candidate alternative fill like AMATEX instead of Composition B.

3. IDEAL VS NON-IDEAL DETONATION

3.1 Introduction

The Organic Materials Division at the Lawrence Livermore Laboratory has been actively engaged in the area of High Explosives R & D for almost twenty years. In the last couple of years, we have recognized the very great potential of non-ideal explosive systems, otherwise known as composite explosives because of their heterogeneous nature. We are often asked to differentiate between these composites or non-ideal explosives and conventional or ideal explosives such as TNT. The following is an attempt at defining these terms.

3.2 Principal Characteristics

The detonation of standard high explosives such as TNT, nitromethane, Comp B, etc. converts unreacted explosive to reacted products in thermodynamic equilibrium in 0.4 microseconds or less as the shock wave travels through the explosive material. The thickness of the reaction zone is 2 - 3 mm or less. In many high explosives this reaction zone is so thin (i.e. less than .05 mm) that it has not been detected.

The "detonation" of a composite explosive on the other hand converts only a fraction of this material in a short time interval. The remainder of the material reacts over an extended time, so that in some experiments thermodynamic equilibrium is never achieved. These explosives exhibit characteristically low "detonation" pressures and a gradual decrease in pressure behind the shock front. Material immediately adjacent to a composite HE normally experiences a lower

initial pressure, but because the composite continues to react, the pressure is sustained for a much longer time than in standard explosives.

3.3 The Hydrodynamic Model - Chapman Jouget Detonation or "Ideal Detonation"

The detonation of an explosive is distinguished from other forms of energy release by the extreme rapidity of the process. For example, in the detonation of a typical explosive, a shockwave traveling with a velocity of 8000 meters per second transforms a 0.1 millimeter thickness of solid explosive to gases at a pressure of 300,000 atmospheres in 0.0125 microseconds.

In the case of Chapman-Jouget detonation which we will call "ideal detonation" the detonation properties can be calculated using the conservation equations and an appropriate equation of state of the detonation products. We are using the words "ideal detonation" to describe a condition in which the scale (size) of the experiments, R , so far exceeds the size of the reaction zone r_z , as to make its effect negligible. Thus, TNT would be described as undergoing an "ideal" detonation if the charge were a 4" diameter billet, but would be considered non-ideal in a 1/4" rod, since for TNT $r_z = 2$ mm. Although such a condition where a monomolecular material like TNT (fuel and oxidizer in the same molecule) exhibits "non-ideal" behavior is somewhat unusual, it is important to point out that this kind of behavior is not necessarily limited to composite explosives. Indeed, if the reaction time for a composite explosive were sufficiently short, it should undergo "ideal" detonation. The "ideal" detonation process is therefore, determined by only two important independent parameters, the initial chemical composition and the loading density of the explosive. The initial temperature has a very small effect when considered independently of density. Normally, the initial pressure is negligible compared to the detonation pressure for condensed explosives.

The theoretical model for detonation was originally proposed by Chapman and independently by Jouget (known as the C-J hypothesis). Subsequently, Zeldovich, Von Neuman, and Doering (ZND) made some modifications, but the basic assumptions and results remain the same. The explicit assumptions are:

(1) The flow is one-dimensional and plane, and the reaction zone is steady in a coordinate frame attached to the shock.

(2) The shock is a jump discontinuity. Therefore, transport effects such as heat conduction, radiation, diffusion, and viscosity are neglected.

(3) The reaction rate is zero ahead of the shock and finite behind, and the reaction is irreversible. That is, the reaction proceeds only in the forward direction.

(4) All thermodynamic variables other than the chemical reaction are in local thermodynamic equilibrium everywhere. The material following the reaction zone is describable by an equation of state which includes the chemical composition among its independent variables.

The ZND theory shows that there is a unique solution for an unsupported detonation which propagates at the minimum detonation velocity consistent with the conservation conditions, and it is independent of reaction rate. There is a well-defined reaction zone with a unique pressure at the end of reaction, the so called C-J pressure, and there is flow which is exactly sonic with respect to the shock at the end of the reaction zone, as hypothesized by Chapman and Jouget.

3.4 "Non-Ideal" Detonations

Composite explosives is the term given to explosive formulations that are deliberately formulated to give "non-ideal" performance. Composite

explosives are primarily mixtures of oxidizers and fuels but they may contain some monomolecular explosive. A large fraction of the explosive energy comes from the reaction of oxidizer and fuel, which are in discrete phases whose dimensions vary from tenths of microns to millimeters. The larger the dimensions of these phases the longer become the reaction times. The reaction zone in some composite explosives has been estimated to be as large as 100 cm.

Combustion of composite explosives can not be treated as a transition of solid explosive to products in equilibrium at the end of this reaction zone of steady profile. We must now include kinetics, transport phenomena, the geometry dependence, and confinement in the description of non-ideal detonation. One consequence of a non-ideal detonation is that the detonation zone profile is not steady. This is still a "detonation" in the sense that the energy release is shock initiated and supports the further propagation of the shock. However, the phenomenon is governed by the rates of progress of chemical and physical processes in the explosive.

We have achieved solutions to the problem in hydrodynamic calculations by including a reaction time following the shock front. It appears possible to predict the behavior of composites, given sufficient control of the physical and chemical parameters. It seems evident that the dominant mechanism determining the reaction time is the diffusion rate, once the system is self-propagating. A description of these calculations and a discussion of the equations governing the processes described here can be found in Section 4.1.

It is crucial in many experiments to insure that the detonation wave is self-propagating. It is quite possible for a composite explosive to burn like propellants in what is called the deflagration mode - where the burning front is driven by gas convection, chemical reaction, and heat transfer rather

than by a shock wave. This process is therefore subsonic, and it is at least an order of magnitude slower than the process described above. With sufficient containment, the pressure and rates may increase to where a shock wave is generated and the process switches over to detonation as illustrated in Figure 1. The initiation process is very difficult to predict. The experimental approach has been to avoid the problem whenever possible by providing ample initiation.

3.5 Applications

Non-ideal explosives offer a variety of new capabilities, based on their slower rates and lower, but sustained, pressures as compared to detonations. A few possible areas include:

- Shockless Metal Acceleration

Delivering a greater proportion of kinetic energy to the metal flyer because of the elimination of shock heating and premature breakup or spall of the metal plate being accelerated.

- Cratering, Underwater, and Air Blast

In some instances high explosives produce too much shattering of the excavated material. It is more desirable to produce a prolonged pressure pulse for the heaving of rock and for underwater and air blast. For example, aluminized explosives have been noted for their relatively low brisance and high blast potential.

3.6 Summary

A detailed knowledge of the rate of energy release of an explosive is of considerable interest in both a practical and theoretical sense. From such a study would eventually come a proven model of detonation for non-ideal explosives which would include many of the chemical parameters, kinetic

FIG.1 REACTION RATES AND PRESSURES OF EXPLOSIVES.

and transport mechanisms, and interaction with the environment as described above. Furthermore, by learning to control the rate of energy release, an explosive may be tailored to a specific application.

4. THEORETICAL

4.1 Model for the High Explosive Energy Release During Detonation of a Composite Explosive

The rate of energy release during detonation of a composite explosive may be considered as proceeding in at least two consecutive steps: (1) a fast step during which a part of the chemical energy is released within a fraction of a microsecond upon shock compression; (2) a second slower step whose rate is determined primarily by the diffusion of reactants.

4.1.1 The Diffusion Model of Energy Release

After the initial portion of the chemical energy is released rapidly upon compression, the original high explosive is converted in the simplest case, into two distinct phases. The two phases then continue to react with one another to release the remaining portion of the available chemical energy. One of these phases is considered to be particulate, and chemical reactions occurs at the interface between the two phases under the conditions of high temperature and pressure created by the initial reaction. The rates of chemical reaction at the interface are rapid by comparison to the rate of supply of reactants thereto; hence, the rate of consumption of the particulate phase is controlled by diffusion of reactants to the reacting interface.

When counter diffusion of reaction products away from the interface can be neglected, the rate of reaction in terms of the fraction of completion of release of the second portion of the total energy is given by:

$$\frac{dF}{dt} = - \frac{6DC_b}{\rho d_o^2} (1 - F)^n \quad (1)$$

where F is the fractional completion of the slower second step reactions

D is the diffusion coefficient

C_b is the bulk concentration of the diffusing component

ρ is the density

d_o is the initial diameter of the particulate phase

n is 1/3 for the limiting case of low concentration of the particulate phase and 4/3 for the stoichiometric case.

Over a wide range of initial concentrations and variation in F, the right hand side of (1) is approximately constant, i.e.,

$$\frac{dF}{dt} = K \approx \frac{6DC_b}{\rho d_o^2} \quad (2)$$

Integrating yields the burning time

$$t_b = 1/K \quad (3)$$

The kinetics of energy release is thus characterized by a single parameter. In hydrodynamic calculations, this rate of energy increase in each zone may be taken into account as a prescribed energy source.

In the following section a model for the theoretical prediction of D is described. As an example, the value of D predicted for CO_2 at .270 Mb and 2000°K (values of pressure and temperature typical of the Chapman Jouget state) is $3 \times 10^{-5} \text{ cm}^2/\text{sec}$. The calculated value of t_b from (3) is 40 μsec for a 5 μ particle.

4.1.2 Equation of State

The hydrodynamic behavior of a fluid is expressed by its equation of state. Since the composition exerts a strong influence on the equation of state and the composition of a reacting heterogeneous high explosive varies with time as the chemical reactions go to completion, it is necessary that a time dependent equation of state, which reflects the degree of completion of the reactions, be considered. As a first approximation, the ideal mixing rule has been adapted to express the composition dependence as follows:

$$P(V,E) = (1-F) f_1(V,E) + F f_2(V,E)$$

where $f_1(V,E)$ is the equation of state describing the behavior of the products from the initial burning and $f_2(V,E)$ is that describing the completely burned explosive.

4.1.3 Testing of the Model

The detonation model postulated above has been incorporated into finite difference one-dimension and two-dimension hydrodynamic codes. Testing of the model by comparing calculations with data from one and two-dimensional experiments is in progress.

4.2 Theoretical Study of the Diffusion Process

4.2.1 Introduction

The overall rate of energy release of a detonating heterogeneous explosive depends on the rates of energy release of each of the individual phases. Each phase may chemically react, and the reaction products of each phase may in turn react. The secondary reaction appears to be diffusion controlled, and it is the rate determining step [2].

The rate therefore, depends on the value of the diffusion coefficients of the gaseous materials. In the detonation region (1500-3000°K, and 50-200 kbars) there are, unfortunately, no experimental diffusion data. Consequently, it was deemed desirable to examine how well kinetic theories might predict diffusion coefficients in this high-temperature, high-pressure region.

The technique employed is (1) to use the kinetic theory of gases with an appropriate intermolecular potential to estimate the low-pressure, high-temperature diffusion coefficient and (2) use the Enskog dense gas method with an appropriate hard sphere equation of state to correct for an increased pressure. This technique was chosen after examining various ways of estimating diffusion coefficients, described in part in Reid and Sherwood's text [3].

It appears that the Lennard-Jones potential with an appropriate temperature correction (see eq. 6) together with the Enskog correction, using the Carnahan-Starling hard-sphere equation of state, give fair estimates (within 20% at moderate pressures and probably within a factor of 2 at higher pressures).

The result is in the form of an analytical equation which can be used in computer codes.

4.2.2 Kinetic Theory Description of Low-Pressure Diffusion Coefficients

The value of the low pressure mutual diffusion coefficient D_{12}^0 is given for a binary system by Hirschfelder et al [4] (p. 539 ref. 4, and p. 523 ref. 3):

$$D_{12}^0 = \frac{.001858 T^{3/2} \left[\frac{M_1 + M_2}{M_1 M_2} \right]^{1/2}}{P \Omega_D} \quad (1)$$

where D_{12}^0 is in cm^2/sec , P is the pressure in atm, T the temperature in $^\circ\text{K}$, and M_i the molecular weights. The collision diameter σ_{12} is one of the two force constants for the mixture in angstroms. The reduced cross section Ω_D is a function only of kT/ϵ_{12} , where the interaction energy ϵ_{12} is the other force constant in $^\circ\text{K}$, and k is Boltzmann's constant. The choice of intermolecular potential determines the values of ϵ_{12} and σ_{12} and also the functional form of Ω_D .

Note that Equation 1 is a first approximation. The higher approximations contain a factor which is complicated and contains the concentration dependence. Since it varies only from 1.00 to 1.03, it may be neglected.

Reasonably good results for estimating diffusion coefficients are obtained at lower temperatures using Ω_D from the Lennard-Jones 6-12 potential. The Ω_D function is tabulated in Ref. 4. The data in this table have been fit by least-squares to 1 1/2 percent, yielding

$$\Omega_D = \mu^{.13921} (-.031692 + .44932\mu - .059144\mu^2) \quad (2)$$

$$\text{where } \mu = \epsilon_{12}/kT. \quad (3)$$

The Lennard-Jones ϵ_i and σ_i are given for various gases in Appendix 6 of Ref.

3. The Lorentz-Berthelot combining rules [Ref. 4, p. 523]

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \quad (4)$$

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad (5)$$

are used to get ϵ_{12} and σ_{12} .

At higher temperatures (up to $15,000^\circ\text{K}$) the Lennard-Jones results are increasingly low. A very crude correction factor is given by

$$g = 1 + 3.4 \times 10^{-5} T \quad (6)$$

consequently, we may write the low pressure higher-temperature approximation

$$D_{\text{LOWP}} = \frac{.001858 T^{3/2} \left[\frac{M_1 + M_2}{M_1 M_2} \right]^{1/2} (1 + 3.4 \times 10^{-5} T)}{P \sigma_{12}^2 \mu^{.13921} \exp [-.031692 + .44932\mu - .059144\mu^2]} \quad (7)$$

Comparison with experimental data for several systems shows agreement within 10% up to 3000°K except for $A_r - H_2$ and $CO_2 - CO_2$ which have errors of about 20 to 30 percent.

4.2.3 Diffusion Coefficients at Higher Pressures

The diffusion coefficient of a gas of rigid spheres at high pressure is related to its low pressure value by Enskog's equation (Ref. 2, p. 540)

$$D_{12} = \frac{(D_{12} P)^o Z}{PY} \quad (8)$$

where Y is an equation of state factor,

Z is the compressibility factor.

$$Z = PV/nRT \quad (9)$$

V is the volume, n is the number of moles, $\hat{R}$ is the gas constant, and the superscript o refers to low pressure values.

It can be shown that the Carnahan-Starling equation of state for rigid spheres [5] leads to:

$$R(X) = \frac{Z}{Y} = \frac{1 + X + X^2 - X^3}{1 - (X/2)} \quad (10)$$

where

$$X = \frac{n\pi N_A \sigma^3}{6V} \quad (11)$$

and N_A is Avagadro's number. Since Z is also a function of X, R and Z are parametrically related. It is found that R(X) is approximately related to Z by the equation:

$$R = 1.0 + 0.445 \ln (Z) \quad (12)$$

Although the results above are for a single gas, gas mixtures can be treated as a single gas by using pseudo-critical constants (Ref. 3, pp 313-319). Thus the Z values for a mixture can be obtained from generalized charts (Ref. 3, pp 50-52) for use in Eq. 12.

The final result is:

$$D_{12} = D_{\text{LOWP}} \frac{[1 + .445 \ln Z]}{P} \quad (13)$$

where D_{LOWP} is calculated from Eq. 7.

Although the pressure correction is based on the rigid sphere potential and D_{LOWP} is based on the Lennard-Jones potential, the result yields fair estimates. Table 1 shows agreement within 15% for N_2-H_2 (to 680 atm), CO_2-CO_2 (200 atm), and CH_4-CH_4 (1800 atm). There exist data by Balenovic et al[5A] to 1360 atm which is systematically lower than the estimates by 30 to 50 percent at all pressures for both N_2-H_2 and $Ar-H_2$, and which may be subject to systematic experimental error.

4.2.4 Comment

The reasonable success of Eq. 13 for most of the data is only suggestive, because there are no data above 2000 atm. It is clear that experiments above 2 kilobars are essential, not only for obtaining the data but for testing theoretical and semi-empirical equations. Until such experiments are carried out, Eq. 13 is a plausible equation for estimation purposes.

TABLE 1
COMPARISON OF EXPERIMENTAL AND CALCULATED
DIFFUSION COEFFICIENTS

<u>N₂-H₂ at 313°K</u>					
P	1	170.1	340.2	510.3	680.5
D ₁₂ expt	-	.00462	.00240	.00166	.00132
D ₁₂ calc	.811	.00502	.00264	.00185	.00145
% error	-	9	10	11	10
<u>CO₂-¹⁴CO₂ at 373°K</u>					
P	1	30.98	71.11	135.7	204.8
D ₁₂ expt	-	.00529	.00209	.00089	.00050
D ₁₂ calc	.169	.00526	.00213	.00101	.00062
% error	-	1	2	13	12
<u>CH₄-¹⁴CH₄ at 298°K</u>					
P	1	513	1005	1470	1846
D ₁₂ expt	-	.000448	.000316	.000238	.000211
D ₁₂ calc	.217	.000461	.000281	.000210	.000176
% error	-	3	11	12	17

P in atm, D in cm²/sec

5. EXPERIMENTAL

The information required to provide the parameters for a model of detonation for non-ideal explosives can be best obtained by comparison of results from scaled hydrodynamic tests in which we have carefully controlled all the explosive composition variables.

5.1 Explosive Formulation Studies

One of the primary candidate alternate fills is AMATEX (RDX/TNT/AN). This system is very attractive from a cost and effectiveness point of view and it also uses significant quantities of ammonium nitrate (AN) fertilizer from the civilian economy. However, there are many problems associated with the use of AN in TNT cast systems. Los Alamos and Picatinny Arsenal are addressing themselves to the inherent problems of the AMATEX system. These include the physical and chemical stability of AN and the casting problems of this system.

We chose not to duplicate these efforts, but instead, we concentrated on studying simple, easily-characterized and controlled explosive systems that will contribute to our understanding of the performance of non-ideal systems. The first chemical system chosen was based on the use of gelled nitromethane as a detonable, homogeneous fuel in which we could uniformly suspend varying particle sizes of oxidizers. We could also easily include controlled porosity by means of microballoons. We developed this technology under a program for the U. S. Army Corps of Engineers.[6] The use of nitromethane allowed us to avoid the difficulties in casting TNT to uniform grain size and repeatable initiation characteristics. The oxidizer we first selected was ammonium perchlorate (AP). AP is a chemically and physically stable, detonable oxidizer. We also had a large, varied stockpile of different uniform particle sizes of AP available. We avoided AN because of the difficulty in controlling particle

size, its many phase changes, hygroscopicity, and lack of solubility data in candidate reducing agents. AP represented a well-controlled parallel of AN's function in AMATEX. We chose not to include RDX so that we could work with essentially a two-component HE, varying only one parameter at a time. RDX also has too high an oxygen balance, so that the net energy gain in the oxidizer-fuel reaction is relatively small.

Because the gelled nitromethane is such a convenient vehicle, many of the problems of AN and other oxidizers are eliminated. We have, therefore, added AN and potassium perchlorate (KP) to our list of oxidizers to be studied later. Thus, KP, AP, and AN represent 4, 2, and 1 extra oxygens for participation in the diffusion controlled, fuel-oxidizer reactions.

5.1.1 Experimental Plan

The basic matrix for our experimental program appears in Table 2. The check marks represent desirable data. The circled checks represent completed experiments.

5.1.2 Detailed Formulation Studies

5.1.2.1 Solubility

The solubilities of AP, KP, and AN were determined in nitromethane. The results are given in Table 3. We were concerned that our well-controlled particle size distribution would be destroyed if there was appreciable solubility. The data show that the solubility of all three oxidizers is sufficiently low to minimize the crystal growth.

5.1.2.2 Nitromethane Gel

General Mills produces a limited quantity of a modified guar gum, XG-512, which is specifically for gelling nitroparaffins. Preliminary test data which we obtained on our Project Essex Program [6] established that approximately

TABLE 2. ARPA Program
Performance Tests/Data

No. of Free [0]	Material	RT	PD	PS	S-8	S-16	C-1	C-2	C-4	CW-1	ASM	DEE	W	CDV
1 - [0]	<u>NH₄NO₃</u>													
Particle Size	2000 μ	X	X	X										
Particle Size	200 μ	X	X	X			X	X +*						
Particle Size	20 μ		X	X										
Particle Size	2-5 μ	X	X	X			X	X						
2 - [0]	<u>NH₄ClO₄</u>													
Particle Size	2000 μ	X (X)	X	X				(X)						
	200 μ	X	*	X	X	X	(X)	(X) +*	X	X	X	X	X	X
	20 μ		(X)	X										
	2-5 μ	X	(X)	X	X	X	(X)	(X)			X	X	X	
4 - [0]	<u>KClO₄</u>													
	2000 μ			X										
	200 μ	X	(X) *	X			X	X +*						
	20 μ		(X)	X										
	2-5 μ	X	X	X			X	X						

Notes for Table 2

1. All compositions CO_2 balanced, or CO if CO_2 not obtainable.
2. +*, ~ 3% of IG-101 or B-30-B Microballoons stabilized with ~ 2% of XG512 Gum.
3. RT Ruby-Tiger code prediction for full, partial and incomplete reaction.
4. PD 1" diam plate dent in standard configuration.
5. PS Particle size analysis.
6. S Sphere test, -8 and -16; 8-in. and 16-in. diam.
7. C Cylinder test, -1, -2, -4; 1, 2 and 4-in. diam scaled wall.
8. CW Cylinder test conducted in H_2O , -1, 1-in. diam.
9. ASM Axially symmetric probe for u_p and reaction zone length.
10. DEE Detonation electric effect, for detonation pressure.
11. W Wedge expts.
12. CDV Continuous detonation velocity.

TABLE 3. Solubility of AP, KP, AN in Nitromethane

	Commercial Nitromethane (g/ml)	Dried Commercial Nitromethane (g/ml)
NH_4ClO_4	1.1	0.8
KClO_4	0.35	-
NH_4NO_3	0.09	-

3 wt % XG-512 guar gum in nitromethane forms a firm gel which will suspend solid particulate matter for several weeks without settling.

Samples of AP (5 μ)/nitromethane/XG-512 guar gum were made at CO, CO₁ 1/2 and CO₂ balance. The consistency of the sample at CO₂ balance is similar to toothpaste. The sample at CO balance is thick but pourable. Sample beakers were sealed with Saran-Wrap. Inspection the following day revealed appreciable condensation of nitromethane on the plastic film. The amount of condensate was observed to be proportional to the percentage of nitromethane in the sample. For large volume-to-surface geometries, this was not considered to be a serious problem in maintaining compositional uniformity.

5.1.2.3 Sensitivity, Stability

Limited drop weight impact sensitivity results, using sandpaper on the anvil, indicated that the H₅₀ for all three compositions was greater than 100 cm compared to ~ 22 cm for RDX. A summary of the pertinent sensitivity, composition, and stability data is given in Table 4.

TABLE 4. Viscosity - Handleability - Safety

<u>Oxygen Balance</u>	<u>wt %* Gelled NM</u>	<u>Consistency</u>	<u>Drop † Weight Impact</u>	<u>DTA</u>
CO	67.5	Thick paste/pourable	> 100 cm	No reaction observed
CO _{1 1/2}	54.2		> 100 cm	
CO ₂	40.9	Like toothpaste	> 100 cm	

* 97/3 - NM/guar

† RDX - 22 cm

5.2 Explosive Performance Studies

5.2.1 Plate Dent

To establish the detonability of the various oxidizer/nitromethane compositions, and to obtain a qualitative measure of relative performance, 1-in. diam. plate dent tests were performed. Thirty grams of each composition listed below were prepared. Physical stability was also checked on these compositions. The plate dent results are given in Table 5.

TABLE 5. Plate Dent Test Results

<u>Composition</u>	<u>Particle Size (μ)</u>	<u>Depth of Dent (in.)</u>
NM	--	0.193
38.4/61.6-NM/NaCl*	--	0.112
40.9/59.1-NM/AP-CO ₂ Bal	200	0.219
40.9/59.1-NM/AP-CO ₂ Bal	30	0.231
40.9/59.1-NM/AP-CO ₂ Bal	5	0.239
54/46-NM/KC lO ₄ -CO ₂ Bal	20	0.203

* Same vol % as AP

Also included in the results are neat NM and an inert simulant for AP, NaCl. The particle size effect is very apparent.

5.2.2 Cylinder Test

Standard one- and two-inch diameter cylinder tests were performed on both the 5 and 200 μ particle size NM/AP-CO₂ balance systems.[7] The method used for loading the cylinders was similar to one we developed for loading paste explosives (PEX).[8] The summary results are given in Table 6.

TABLE 6. Summary of Cylinder Test Results

Composition:	wt %	
	<u>Ammonium Perchlorate</u>	<u>Nitromethane + 3% Guar</u>
RX-30-AA	61.8 (5 μ)	38.2
RX-30-AB	59.3 (200 μ)	40.7
Nominal	59.1	40.9
Performance:	1" Cylinder	2" Cylinder
RX-30-AA		
Density, g/cc	1.517	1.528
Det. Vel., m/s	6.940	7.150
Wall Vel. at 6 mm, mm/ μ sec	1.30	1.28
Wall Vel. at 19 mm, mm/ μ sec	1.50	1.50
RX-30-AB		
Density, g/cc	1.515	1.513
Det. Vel., m/s	5.380	5.490
Wall Vel. at 6 mm, mm/ μ sec	0.98	1.07
Wall Vel. at 15 mm, mm/ μ sec	1.14	1.27
Wall Vel. at 19 mm, mm/ μ sec	--	1.32

Detailed scaled wall velocities are tabulated in Table 7.

As expected, the 5 μ AP/NM explosive behaves almost as if it were a homogeneous system in terms of scaled wall velocities from 1 in. to 2 in. However, the detonation velocity shows some diameter dependence. The 200 μ AP/NM system clearly shows "non-ideal" detonation behavior as can be seen in the non-scaleable 1- and 2-in. wall velocities.

5.2.3 Detonation Pressure

We have built the shot assemblies for measuring the detonation pressure of the AP/NM system using the Detonation Electric Effect.[9,10] The experiments are currently underway.

TABLE 7
SCALED WALL VELOCITIES, mm/ μ sec

R-R ₀ , mm	RX-30-AA* 5 μ AP, 1"	RX-30-AA 5 μ AP, 2"	RX-30-AB 200 μ AP, 1"	RX-30-AB 200 μ AP, 2"
6	1.293	1.282	.981	1.068
7	1.324	1.316	1.010	1.104
8	1.352	1.345	1.028	1.138
9	1.377	1.371	1.047	1.168
10	1.400	1.394	1.071	1.191
11	1.420	1.414	1.096	1.209
12	1.437	1.431	1.115	1.224
13	1.452	1.446	1.126	1.238
14	1.464	1.458	1.133	1.253
15	1.475	1.469	1.146	1.268
16	1.484	1.479	1.165	1.283
17	1.492	1.487	1.172	1.298
18	1.499	1.494		1.310
19	1.505	1.501		1.319
20	1.512	1.508		1.326
21	1.518	1.515		1.332
22	1.524	1.522		1.339
23	1.530	1.529		1.347
24	1.536	1.536		1.356
25	1.542	1.543		1.364
26	1.547	1.549		1.369
27	1.552	1.553		1.371
28	1.555			
29	1.557			
30	1.559			
31	1.561			

*Nominal composition RX-30
 Nitromethane with 3 wt.%)
 GM-512 Guar Gum) 40.9 wt%
 Ammonium Perchlorate) 59.1 wt%

LET	DRN	CH	DATE	ZONE	CHANGE

NOTE :

1. FOR REF. ONLY, DWG. N^o 73-110485, HEMISPHERE, 8" & 16" NOT SHOWN.

Fig. 2
Sphere Test Assembly

1-15	73-110472-2	ALIGNMENT PIN				
1-14	73-110474-2	INNER HEMISPHERE				
1-13	73-110473-2	LID				
1-12	73-110477-2	TABLE				
1-11	73-110478	OUTER HEMISPHERE, 16"				
1-10	73-110475	ALIGNMENT FIXTURE-16"				
1-9	73-110472-1	ALIGNMENT PIN				
8-4	8	CLAMP, C 1" OPENING 1/2" DEPTH		STEEL		5120-25916
3-3	7	PLUNGER, SPRING "STUBBY" 1/4-20NC		STEEL		VLIER #NM-55N OR EQ.
1-6	73-110474-1	INNER HEMISPHERE				
1-5	73-110473-1	LID				
1-4	73-110477-1	TABLE				
1-3	73-110479	OUTER HEMISPHERE, 8"				
1-2	2	NUT, JAM HEX. HD. 3/8-16NC		STEEL CAB PLATED		
1-1	73-110476	ALIGNMENT FIXTURE-8"				

ITEM	PART NO.	DESCRIPTION	NO. REQ'D	MATERIAL	SPEC. NO.	LLS STOCK NO.
1. DIMENSIONING AND TOLERANCING ARE PER USAS1-Y14.5. 2. POSITIONAL AND FORM TOLERANCES APPLY R. F. S. (REGARDLESS OF FEATURE SIZE). 3. SURFACE TEXTURE PER USAS-B46.1.						
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JOB NO.	DATE	DR	CHK	APPROVED
694566	8-10-73	G. CORDANO	J. Kestner	
SPHERE TEST-JOB #9116	6690-10	DR	CHK	APPROVED
H.E. SPHERE TEST-JOB #9116	6690-10	DR	CHK	APPROVED
SUB ASSEMBLY				
DETAIL				

5.3.3 Sphere Experiments

Experimental design of one-dimensional sphere experiments has been completed (see Fig. 2). The necessary hardware has been built.

*(The complete experimental sphere assemblies were produced for a remarkably low cost of \$789 each. Previous costs for these experimental hydro-assemblies ranged from two to four times this cost. The great savings was attributed to the numerical controlled precision machining facility at LLL and the close interaction of experimenter, design engineer, and shop personnel.)

6. ADDITIONAL WORK IN PROGRESS

6.1 Thermo-Hydro Code

To provide the necessary upper and lower limits for performance of a high explosive system which may burn only partially to completion, it has proved very effective to use a thermo-hydro code such as the TIGER code to predict these limits.[11]

6.2 Solids Equation-of-State

Since the solids loading in some systems is very high, it becomes of greater importance to make accurate estimates of the combined equation-of-state behavior of solids and detonation products. We have recently programmed for TIGER an improved equation-of-state routine which uses a modified Morse Potential to calculate the lattice pressure. This routine will be used to calculate the limiting performance of the composite explosives described in Section 5.1.

6.3 Temperatures in Initial Combustion State

To understand the reaction and transport rates, it is necessary to know the temperature. Nitromethane is, fortunately, one of the few explosives

for which such a measurement is feasible. Some experiments have been performed here for that purpose. The measurements are thus far consistent with a temperature of 3300 ± 100 K.

7. FUTURE WORK

7.1 Experiment to Verify Diffusion Rate Predictions

As mentioned in the theoretical section on diffusion (Section 4.2), there are no data which can be used to check the theoretical predictions beyond 2 kb. Experiments have been proposed for measuring diffusion of CO_2 at 15 kb and 1000 K. The feasibility and costs for this study are being evaluated.

7.2 Equation-of-State Verification

In order to check the calculated behavior of high explosives composite systems containing high solids loading, experimentally, it is necessary to invent a homogeneous system which burns "ideally" to give such products. Such a system might be LiClO_4 dissolved in ethanol. Several such systems and the experiments to measure their behavior are being studied.

References

1. Memorandum to the Assistant Secretaries for Research and Development of the Army, Navy and Air Force from J. S. Foster, DDR and E, dated July 1, 1972.
2. H. Cheung, "Kinetics of Energy Release of Heterogeneous High Explosives," UCID-15962, LLL, December 15, 1971.
3. R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids, 2nd Ed., McGraw-Hill, New York, 1966.
4. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York, 1954.
5. N. F. Carnahan and K. E. Starling, J. Chem. Phys. 51, 635 (1969).
- 5A. Z. Balenovic, M. N. Myers, and J. C. Giddings, J. Chem. Phys. 52, 915 (1970)
6. F. Helm, M. Finger, R. Boat and D. Wooster, "The Development and Manufacture of a Gelled Nitromethane Explosive for Project Essex," UCRL report in preparation.
7. E. L. Lee, H. C. Hornig, J. W. Kury, "Adiabatic Expansion of High Explosive Detonation Products," UCRL-50422, May 2, 1966.
8. J. P. Cramer, et al, "Paste Extrudable Explosives (PEX): Interim Development Report I," UCID-16173, December 13, 1972.
9. B. Hayes, "The Detonation Electric Effect," J. Appl. Phys. 38, 507 (1967)
10. B. Hayes, "Electric Signals Generated by Shock and Detonation Waves," presented at the Western States Section of the Combustion Institute, October 28, 1968.
11. W. I. Wiebenson, Jr., W. H. Zwisler, L. B. Seely and S. B. Brinkley, "TIGER Computer Program Documentation," Contract No. DA-04-200-AMC-3226(X), SRI Project PGU 6139, March 1968.

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