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by

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LOW DETONATION PRESSURE EXPLOSIVES

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Most explosive materials in wide use today may be characterized by detonation pressures ranging from approximately 150 to 350 kilobars. Propellant materials, on the other hand exhibit comparatively low pressures typical of deflagration reactions. The difference in pressures exhibited by these two classes of materials leaves an interesting gap, the exploration of which may yield valuable information on the chemical and kinetic limitations of detonating materials.

The reliable generation of detonating pressures under 100 kilobars should offer advantages from an engineering standpoint in applications where higher pressures are neither needed nor desired. Certain plastic/explosive formulations described below offer these advantages in addition to others, such as the capability of being extruded or injection molded into difficult configurations and then polymerized in place.

Over the past two years the Aerojet-General Corporation and the Sandia Corporation have collaborated in a preliminary investigation of this interesting low detonation pressure regime. The results recorded below describe some of the courses pursued and techniques developed in this study to date.

EXPERIMENTAL TECHNIQUES

a. Material Specifications

All chemical ingredients utilized in the formulation of the plastic-explosive compositions described herein were purchased to meet pertinent military specifications. Because of the importance of the particle size distribution of the primary and secondary explosives used, tests were run to measure this by microscopic techniques using a Filar eyepiece. The particle size distributions of pentaerythritol tetranitrate (PETN), superfine grade; cyclotrimethylenetrinitramine (RDX), acetone fine; eight hour ball-milled dextrinated lead azide (PbN_6); coarse dextrinated PbN_6 ; and thallous azide (TlN_3) are presented in Figs. 1 through 4, respectively.

b. Formulating Techniques

Of primary consideration in working with new explosive formulations are the compatibility of the various ingredients and general safety precautions. Initially, in all cases, small quantities (about 1/10 gram) were used, and if no adverse reaction resulted, the quantities were increased to one gram, 10 gram, and 100 gram lots. Analyses were made to determine the compatibility and stability of the compositions at the 10-gram level. Among the tests used were vacuum stability, impact sensitivity, differential thermal analysis (DTA), and, in some cases, explosion temperatures. The results of such tests are shown in Table 1.

c. Rheological Characteristics

During the formulation of high-solids-content compositions extremely viscous, nutty-like systems resulted. It was found that the addition of small quantities (0.1 to 1.0 percent) of special surfactants caused a significant increase in the fluidity.

Changes in the rheological characteristics were determined by the use of a parallel plate plastometer technique. A small cylindrical sample of the paste-like test sample was placed upon a glass plate and loaded with another glass plate of known weight. The radius to which the sample spread after 30 seconds' duration was taken as an indication of the apparent fluidity of the test system. The greater the radius, the greater the effectiveness of the surfactant.

d. Testing Procedures

Detonation Velocity - Detonation velocity measurements were carried out using two well-known methods, the streak camera and pin switch techniques. A Beckman-Whitley Model 194 streak camera was utilized. Ionization pin switches in conjunction with a mixer circuit and Moran Model 101A raster oscilloscope were also used to measure detonation velocities of both confined and unconfined charges. The ionization pin switches were mounted in special holding devices and distances were measured with a Gaertner Scientific Corporation microcomparator capable of measurement to ± 0.002 millimeters. All velocity measurements were started at least four diameters from the point of initiation.

Detonation Pressure - In those experiments where detonation velocities were measured, it was considered adequate for present purposes to calculate the detonation pressure from the approximate equation

$$p = 0.010 \rho \frac{D^2}{4}$$

where

p = detonation pressure in bars

ρ = density in grams per cubic centimeter

D = detonation velocity in meters per second

Explosive Output - Explosive outputs were measured by means of a modified plate dent test. This test utilized 20 grams of explosive material in a copper tube (3/4 in. x 5 in. x 1/16 in. wall). The detonation was initiated by an Engineer's Special blasting cap with a five-gram booster of Composition C-4. Aluminum witness plates (1-3/4 inch x 5 inches x 5 inches of 6061-T6 alloy, Rockwell hardness B55 to B59) were used.

e. Sensitivity Tests

Sensitivities and compatibilities of the various explosive formulations were determined by impact, vacuum stability and differential thermal analysis. The impact tests were run on a modified Bureau of Mines machine using a two-kilogram weight, a flat anvil and a flat striker. It was found that nitropolyurethane (NPU)/PETN and NPU/RDX formulations, containing concentrations of 20 percent by weight of explosive or more, were cap sensitive to Number 8 blasting caps. Compositions containing smaller quantities of these explosives required the use of a booster to insure initiation. However, in most of the firing tests a five-gram booster charge of Composition C-4 together with an Engineer's Special detonator were employed to insure initiation.

EXPERIMENTAL RESULTS

a. Compositions

The compositions of the plastic explosive formulations studied consisted of polyurethane, nitropolyurethane, and dinitropropyl acrylate matrices (continuous phase) to which various explosives (discrete phase) were added. The polyurethanes were composed of diols/triols or other cross-linking agents/diisocyanate, in 70/30/107 mole percents, together with 20 percent plasticizer. In the NPU formulation, the diol/triol/isocyanate ratio was 80/20/107 mole percent.

b. Chemical and Physical Properties

The chemical and physical properties were determined for each of the compositions as shown in Table I. The vacuum stabilities and DTA's were determined to ascertain the stability of several compositions to thermal decomposition. The vacuum stability data showed that in all cases the mixtures had satisfactory stability.

The DTA's for NPU and NPU/PETN formulations are given in Figs. 5, 6 and 7 and similar information for PU/PbN₆ mixtures is given in Figs. 8, 9 and 10. The data indicate that the final compositions in both cases are as thermally stable as that of the least stable component. The compatibility of the individual ingredients and combinations thereof was determined for each of the formulations. It was found that both PETN and RDX are compatible with the ingredients of the PU and NPU plastic formulations. Similar studies using NPU and PU systems with lead and other azides showed that the nitro substituted plasticizing agents and nitro substituted diisocyanates were incompatible with azides; however, it was found that the components of the PU system were compatible with the azides.

The densities of the various formulations varied from that of the pure plastic binder system up to that of the pure discrete phase. In the case of the NPU/PETN systems, the densities were found to vary from 1.2 g/cm³ up to about 1.35 g/cm³ depending upon the concentration of the discrete phase. In the Plastic/PbN₆ systems, the densities varied between that of the binder system up to 2.1 g/cm³ depending upon the concentration of PbN₆.

In high-solids-content plastic explosive compositions, the rheological characteristics are important. In one system composed of 30 percent DNPA (dinitropropylacrylate) binder system and 70 percent RDX, it was found necessary to add 10 percent calcium stearate, impalpable grade, by weight to prevent dilatancy while extruding the plastic composition under pressure. The large amount of calcium stearate (CS) acts as a phlegmatizing agent making it more difficult to propagate a detonation. It was advisable to find methods for reducing the required amount of CS and at the same time to increase the fluidity of the plastic/explosive mixture.

Earlier studies with propellant formulations had shown that pretreatment with small amounts of surface active agents caused a large increase in fluidity. In preliminary studies with RDX and PETN, the desired amount of surface agent was dissolved in methyl alcohol or chloroform and the explosive treated with the solution. The solvent was evaporated and the explosive was dried in vacuo, leaving a film of surfactant on the surface of the explosive.

Tests showed that SPAN 60 (Atlas Chemical Company) and calcium stearate, impalpable grade, were the most effective fluidizing agents tested. Using the above pretreatment technique, the maximum increase in fluidity occurred when using calcium stearate at a concentration of 0.5 percent by weight, and the fluidity decreased with further increase in concentration. Similarly, the maximum advantage of SPAN 60 alone was found to be at 0.25 percent by weight. In some systems a synergistic effect was observed with calcium stearate and SPAN 60 at similar concentrations. The DNPA/RDX mixtures showed a marked increase in fluidity after standing for three hours. Similar results were obtained with other highly loaded plastic explosive systems.

The reduction in the amount of calcium stearate in the explosive composition from 10 percent to 0.5 percent resulted in increased fluidity and ease of extrusion together with a significant increase in detonation velocity.

c. Explosive Properties

Tests were conducted to determine the effect of solids concentration, confinement and diameter on the explosive characteristics of the various compositions. The compositions and diameters of samples tested are shown in Table II for both confined and unconfined charges. Detonation velocity measurements were carried out on at least five charges for each diameter except the 3.58-inch diameter charges, where only three were tested. The effects of explosive concentration and charge diameter on detonation velocity are shown in Figs. 11 and 12. The data in Fig. 11 show that the detonation velocity increases in the usual fashion with an increase in diameter. It is of interest to note that 1/16 inch copper confinement had no apparent effect on detonation velocities in the charge diameter range from 1.0 inch to 1.875 inch. The 20 percent PETN - 80 percent NPU formulation reached ideal detonation velocity at a diameter of 3.4 inches, compared with 3 inches for the 25 percent PETN - 75 percent NPU formulation. The data in Fig. 12 show that the detonation velocity increases as expected with increase in explosive content. The data in Table III show the approximate minimum diameters at which detonation was sustained for the various compositions either unconfined or confined in 1/16-inch wall copper tubing. As a measure of explosive output Table IV shows a summary of plate dent versus density data for conventional explosive materials using the modified plate dent test described above. For comparative purposes similar information is shown in Table V and Fig. 13 for the various PETN/NPU formulations of interest in this study.

d. Detonation Pressure

Detonation pressures were calculated from detonation velocities at known densities using the $\frac{1}{4} \rho D^2$ approximation described above. Pressures calculated in this fashion are shown as a function of explosive composition in Fig. 14. These data show that the detonation pressures range from approximately 25 to 160 kilobars for the compositions tested. The required density and velocity data are given in Table V and Fig. 12 respectively.

Preliminary studies with PU/PbN₆ systems indicated that a system containing 40 percent PU/60 percent PbN₆ by weight will just sustain detonation. Mixtures containing as high as 70 percent PbN₆ were also achieved, but no detonation velocity measurements were made at this preliminary stage. A typical witness plate from a plate dent test is shown in Fig. 15. From this it appears that outputs in the very low pressure range may be obtained with PU/PbN₆ systems.

e. Impact Sensitivity

Impact sensitivities for the various explosives were measured as shown in Table I. It was found that the addition of secondary and sensitive primary explosives to the PU or NPU binder systems resulted in compositions much less sensitive to impact than the original bulk material.

DISCUSSION OF RESULTS

The formulation of explosives composed of a high-energy discrete phase in a continuous matrix of combustible organic material necessarily involves an excursion into a number of physical and chemical problems. In general, this investigation was centered around the incorporation of relatively sensitive explosives into a plastic such that inter-particle distances were relatively large. The composition of the plastic explosives ranged from 10 to 70 percent discrete phase by weight with corresponding amounts of poly and nitro polyurethanes, and other plastics.

The physical and chemical properties of this type of explosive imply a versatility not normally encountered with explosive materials. Prior to polymerization, the compositions are extrudable under pressure and readily assume the shape of the container. They bond readily to clean metal surfaces. They are capable of being introduced into irregularly shaped volumes and polymerized in place. Once the materials are polymerized they exhibit properties related to those of the plastics involved.

A marked effect on the extrudability of the non-polymerized compositions was achieved by the use of surfactants at concentrations of the order of 1/10 to one percent. The effect of surface active materials on the rheological characteristics of explosive compositions was pronounced and served to extend the useful range of these materials.

An interesting effect of average particle size on the ability of certain formulations to be initiated was observed. When the concentration of PbN_6 in polyurethane was held at 60 weight percent, initiation was not achieved at an average particle size of one micron, but was achieved at average particle sizes ranging from five to ten microns, using the same initiating charge. The region above this range has not yet been explored.

The incorporation of sensitive primary explosives into an inert plastic matrix introduces another family of explosive compositions. Their ability to inter-initiate from particle to particle through the continuous phase of the composition opens up other areas of low pressure explosive technology.

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Fig. 1.--Particle Size Distribution of RDX and PETN
(200 particles counted)

Fig. 2.--Particle Size Distribution of Milled Dextrated PBW₆
(200 particles measured)

Fig. 3.--Particle Size Distribution of Coarse PbN_6
(200 particles measured)

Fig. 4.--Particle Size Distribution of TLN_3
(200 particles counted)

Fig. 5.--DTA - NPU

Fig. 6.--DTA - PETN

Fig. 7.--DTA - 70% NPU/30% PETN

Fig. 8.--DTA - PU

Fig. 9.--DTA - PbN_6

Fig. 10.--DTA - 40% PH/60% PbN_6

Fig. 11.—Effect of Dia. on the Detonation Velocity

Fig. 12.—Effect of the Percent PETN on the Detonation Velocity

Fig. 13.—Effect of the Percent PETN in PETN/NPU Formulations on the Depth of Dent

Fig. 14.—Effect of the Percent PETN on the Detonation Pressure

Fig. 15.—Test No. 194

Chg. Dia. $3/4$ in.
Chg. Lgth. $4-3/8$ in.
Chg. Density 2.06 g/cc
Depth of Dent .145 in.

Confinement $1/16$ in. thick Aluminum
Witness Plate 5 in. X 5 in. X $1-3/4$ in.
6061-T6 Aluminum
Approx. Detonation Pressure - 22 Kb

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS
OF PLASTIC EXPLOSIVE FORMULATIONS

Property	30% PETN 70% NPU	30% RDX 70% NPU	60% PbN ₆ 40% PU	60% TIN ₃ 40% PU	PbN ₆ milled	TIN ₃	RDX	PETN	NPU
Density at 25°C (g/cc)	1.345	1.385	-	-	4.38	3.68	1.82	1.77	1.21
Vacuum Stability at 100°C (cc's of gas/g/40 hr)	* 0.015	* 0.064	0.60	0.16	0.1	-	0.7	0.5	0.32
DTA Exotherm at °C	139.2	161.5	293	317	356	-	161.5	139.2	124
Impact Sensitivity (cm/2kg)									
100%	60	65	100	140	1	3	27	14	>200
50%	51	58	82	172	1	1/2	22	11	>200
0%	43	50	70	190	1	1/2	19	8	>200

* Vacuum stability at 180°F

TABLE II
TEST SAMPLES FOR DETONATION VELOCITY

Composition (%)		Charge Diameter (in.)											
		Confined*						Unconfined					
PETN	NPU	0.25	0.50	0.75	1.125	1.375	1.875	1.0	1.45	1.81	2.56	2.96	3.58
10	90			X			X					X	
15	85			X			X					X	
20	80	X	X	X	X	X	X	X	X	X	X	X	X
25	75			X			X					X	

* Confinement in all cases was copper tubing with 1/16-in. wall thickness

TABLE III

APPROXIMATE CRITICAL DIAMETERS OF SEVERAL
NPU-PETN FORMULATIONS

FORMULATION (% PETN/% NPU)	CONFINEMENT	CRITICAL DIAMETER (in.)
10/90	CONFINED*	1.87
10/90	NONE	Greater than 2.96
15/85	CONFINED*	0.5
15/85	NONE	Greater than 1.0
20/80	CONFINED*	0.25
20/80	NONE	
25/75	CONFINED*	Less than 0.25
25/75	NONE	Less than 1.0

* All confined charges were confined in
1/16 in. wall copper tubing.

TABLE IV

MODIFIED PLATE DENT TESTS FOR SEVERAL CONVENTIONAL EXPLOSIVES

<u>Explosive</u>	<u>Granulation</u>	<u>Density (g/cc)</u>	<u>Indentation (inches)</u>
TNT	Granular	1.14	0.226
TNT	Granular	1.08	0.231
Composition C-2	Plastic	1.60	0.408
Composition C-3	Plastic	1.60	0.417
RDX	Acetone Fine	0.83	0.195
TNT	Granular	1.11	0.219
TNT	Flake	0.76	0.182
TNT	Flake	0.74	0.163
TNT	Flake	0.74	0.162
TNT	Granular	0.71	0.148

TABLE V

MODIFIED PLATE DENT TESTS FOR SEVERAL PETN/NPU FORMULATIONS

<u>Composition (% PETN/% NPU)</u>	<u>Density (g/cc)</u>	<u>Depth of Dent (inch)</u>
10/90	1.22	0.032
	1.24	0.032
	1.23	0.027
	1.20	0.045
	1.29	0.045
	1.25	0.055
13.7/86.3	1.28	0.080
	1.28	0.084
	1.28	0.079
	1.28	0.082
17.5/82.5	1.30	0.104
	1.30	0.104
	1.30	0.118
	1.30	0.103
20/80	1.31	0.146
	1.29	0.134
	1.40	0.134
21.4/78.6	1.31	0.219
	1.31	0.193
	1.31	0.215
	1.31	0.208
25.2/74.8	1.32	0.240
	1.32	0.232
	1.32	0.240
	1.32	0.244
	1.32	0.242
29/71	1.35	0.240
	1.35	0.240
	1.35	0.236
	1.35	0.243
	1.35	0.245
30/70	1.36	0.245
	1.35	0.254
	1.33	0.249
	1.35	0.240
	1.35	0.225
	1.33	0.235

TABLE V (Continued)

<u>Composition</u> <u>(% PETN/% NPU)</u>	<u>Density</u> <u>(g/cc)</u>	<u>Depth of Dent</u> <u>(inch)</u>
32.8/67.2	1.36	0.238
	1.36	0.244
	1.36	0.236
	1.36	0.241
	1.36	0.245
36.6/63.4	1.37	0.244
	1.37	0.246
	1.37	0.246
	1.37	0.245
40/60	1.38	0.259
	1.41	0.262
	1.39	0.257
40.4/59.6	1.36	0.241
	1.36	0.239
	1.36	0.242
	1.36	0.239
	1.36	0.248
44.3/55.7	1.37	0.267
	1.37	0.265
	1.37	0.261
	1.37	0.272
	1.37	0.264
50/50	1.41	0.290
	1.34	0.265
	1.28	0.275
60/40	1.42	0.325
	1.43	0.325
	1.45	0.335