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HIGH EXPLOSIVE MATERIALS*

by

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ABSTRACT

Some of the more common detonating high explosive compounds and mixtures made with these materials are described. The properties of these materials from the standpoint of detonation characteristics, initiation, thermal decomposition, and thermal stability are also discussed. A brief description of processing techniques used to produce charges is included. The thermal properties of a few of the more thermally stable high explosive compounds are presented.

INTRODUCTION

The purpose of this paper is to provide the engineer considering the use of high explosives as either a power or energy source with the properties of some of the explosive materials that are available for use.

Materials with explosive properties are either single-chemical compounds or mixtures of compounds capable of undergoing sustained exothermic reaction. The total energy liberated as the result of the explosive reaction depends upon the thermochemistry of the reacting explosive. The power output depends upon the rate of reaction. The concept is illustrated in Table I; a comparison of the power output of a detonating high explosive, a burning high explosive, and a hydrocarbon fuel burning in an open pan. The energy liberated in the complete combustion of a unit weight of fuel oil is almost a factor of ten times that of explosive, whereas the power output differs by a factor of 10^9 .

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Explosives are related to the hydrocarbon fuel-air mixture and in fact explosive mixtures of these two materials are used to drive the internal combustion engine. With very few exceptions, all materials with explosive properties are mixtures of a fuel and an oxidizer. For the single compound explosive, the fuel and oxidizer are contained within the molecule. Materials with explosive properties can also be made by mixing the proper ratios of finely divided

TABLE I

POWER-ENERGY COMPARISON

Type of Reaction	Reaction Rate (m/sec)	Energy Output (cal/g)	Power Output (watts/cm ²)
Detonation	7×10^3	$\sim 10^3$	$\sim 10^9$
Explosive (a)	$\sim 10^{-3}$	$\sim 10^3$	$\sim 10^3$
Burn			
Fuel Oil-Air Burn	$\sim 10^{-6}$	$\sim 10^4$	~ 10

(a) Burning rate is pressure dependent.

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fuels and oxidizers. One of the first mixtures made and used as an explosive was a mixture of charcoal, saltpeter, and sulphur, later called black powder or gun powder. This explosive mixture dates back to the ninth century¹. Although this particular mixture does not detonate, its burning rate, when confined, is fast enough to provide considerable power. The distinguishing features of these materials, whether single compounds or mixtures, are that their reaction rate is fast, the volume of the products is greater than the reactants, and energy is liberated.

Before an explosive reaction starts, a minimum energy must be supplied, much like the spark in the internal combustion engine. The quantity of energy required to initiate the explosive reaction varies with each explosive. Materials requiring small amounts of energy are said to be "sensitive." Thus, the sensitivity of an explosive is related to the ease with which it can be initiated either deliberately or accidentally.

It is obvious that literally thousands of single-compound materials or mixtures can be made with a wide variety of explosive properties and initiating characteristics. This discussion will be limited to the more common detonating high explosive materials.

When explosives are classified into some order, depending upon the ease with which they can be initiated, they fall into an almost graded sequence. Those easiest to initiate are classified as primary explosives and those requiring somewhat more energy are secondary explosives.

PRIMARY EXPLOSIVES

A tabulation of the more commonly used primary explosives is presented in Table II. The distinguishing feature common to all these materials is that with a small stimulus they will develop to a detonation. Mercury fulminate was the first of this class of explosive used when it was discovered by Nobel that small quantities could be used to initiate detonation in mixtures containing nitroglycerine.

TABLE II

PRIMARY OR INITIATING EXPLOSIVES*

<u>Name</u>	<u>Formula</u>	<u>Year Discovered</u>	<u>Year Commonly Used</u>
Mercury fulminate	$C_2N_2O_2Hg$	~1700	1867
Lead azide	PbN_6	~1890	~1904
Lead styphnate hydrate	$C_6H_3NaO_9Pb$	~1914	~1920
Diazodinitro-phenol (DDNP)	$C_6H_2N_2O_5$	1860	1928
Lead dinitro-resorcinate (LNPR)	$PbC_6H_2N_2O_6$	1882	~1925

* Source: W. R. Tomlinson, Jr., "Properties of Explosives of Military Interest," PATR Technical Report 1740, Rev. 1 (1958)

This idea of initiating detonation from a strong shock wave generated by a small quantity of a detonating explosive initiated from a thermal source of energy marked the beginning of the modern era of high explosives technology².

Some of the properties of these explosives are listed in Table III. These materials are all polycrystalline powders with bulk densities significantly lower than their crystal density. Their detonation velocities, with the exception of DDNP, are all significantly lower than most secondary high explosives.

Primary explosives are used as initiating agents, either as single materials or as mixtures with other materials. They are used as one of the constituents in priming compositions, squibs, and low energy detonators. A typical low energy detonator is shown in Fig. 1. The bridge is heated, causing a reaction to occur in the primary, usually a detonation, which in turn initiates detonation in the main charge. The quantities of explosives used

TYPICAL
ELECTRIC BLASTING CAP

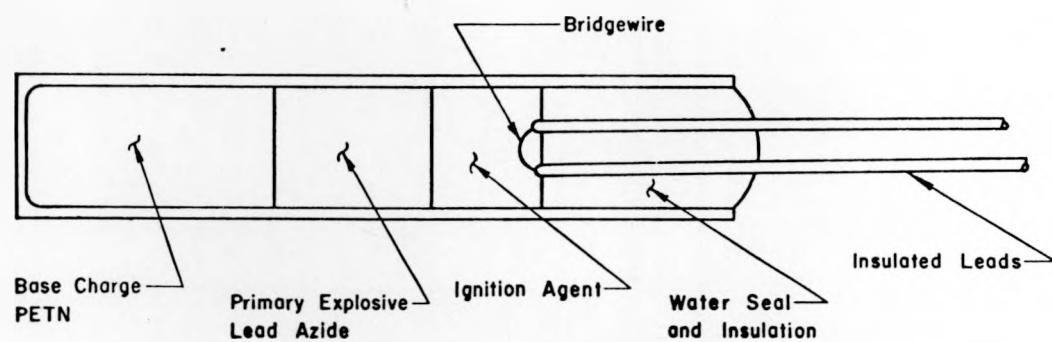


FIGURE 1

TABLE III

PROPERTY OF PRIMARY EXPLOSIVES

Material	Color	Density (g/cm ³)	MP (°C)	Thermal Stability		Spark* Sensitivity (joules)	Detonation Velocity (Km/sec)	
				Temp. (°C)	Time Explosion (sec)		ρ	(Km/sec)
Mercury fulminate	White	4.43	Decomp.	210	5	0.025	2.0	3.5
				190	20		3.0	4.2
							4.0	5.0
Lead azide	White	4.8	Decomp.	340	5	0.007	2.0	4.1
				335	20		3.0	4.6
							4.0	5.2
Lead styphnate	Orange/Red	3.02	Explodes at 260	282 267	5 20	0.0009	2.9	5.2
Diazodinitrophenol (DDNP)	Yellow	1.63	157	195	5	0.012	0.9	4.4
				180	10		1.5	6.6
							1.6	6.9
Lead dinitroresorcinate (LNPR)	Yellow/Red	3.2	--	265	5	--	--	--

* Source: F. W. Brown, D. H. Kusler, and F. C. Gibson, "Sensitivity of Explosives to Initiation by Electric Discharge," U. S. Dept. of Interior, Bureau of Mines, RI 3852 (1946).

in these devices are generally less than one gram. For example, a number 8 cap containing less than 0.5 g of explosive in the main charge generates a shock wave with a pressure amplitude large enough to initiate detonation in some of the dynamites and in most military high explosives.

Limitations on the use of this class of explosives are based on their sensitivity or the ease with which they can be initiated. Because of this property, the utmost care is exercised in all the processing operations leading to the manufacture of the end item. Their sensitivity is such that a small shock or any flame or spark can cause ignition, which almost invariably causes detonation of the whole mass. However, once placed into a thin-walled metal shell the hazard is significantly decreased but not eliminated.

SECONDARY HIGH EXPLOSIVES

The secondary or non-initiating high explosives fall into a number of categories. For the sake of ease in describing these materials, it is convenient to divide them into the single compound explosives and into mixtures containing one or more of these explosives mixed with or without additional nonexplosive materials. Some of the more commonly used single-compound explosives are listed in Table IV and their properties are listed in Table V.

Of the explosives listed, HMX is the most energetic in terms of energy per unit volume and the most powerful in terms of detonation pressure. With the exception of nitroglycerine (NG), all the materials listed are polycrystalline solids at room temperature with bulk densities less than half their crystal density. The polycrystalline materials must be compacted or mixed with other materials and

then compacted to densities approaching their crystal densities to be used more efficiently.

The more common mixtures can also arbitrarily be divided into two major categories - low and high powered. The low powered are the explosive mixtures with low detonation velocities (< 6 Km/sec) and pressures (< 150 kb) available commercially and used for mining and other blasting operations. This large class of materials started with the various dynamites and more recently the so-called slurries, and ammonium nitrite-fuel oil mixtures have been added. Some of the more commonly used of these materials with their properties are presented in Table VI.

With all the ingredients available, a large variety of formulations can be made with a wide variety of properties to meet specific requirements. A comprehensive survey of the properties of slurry and ANFO-explosives was recently published by Cook³.

TABLE IV
MORE COMMON SINGLE COMPOUND
HIGH EXPLOSIVES

Material	Symbol	Formula	Year	
			Discovered	Used
Ammonium nitrate	AN	H ₄ N ₂ O ₃	1659	1867
Nitro-glycerine	NG	C ₃ H ₅ N ₃ O ₉	1847	1867
Nitro-cellulose	NC	C ₆ H ₆ N ₃ O ₁₁	1847	1890
Trinitrotoluene	TNT	C ₇ H ₅ N ₃ O ₆	1863	1901
Penta-erythritol-tetranitrate	PETN	C ₅ H ₈ N ₄ O ₁₂	1894	~1929
Cyclotri-methylene tri-nitramine	RDX	C ₃ H ₆ N ₆ O ₆	1899	~1940
Cyclotetra-methylene tetra-nitramine	HMX	C ₄ H ₈ N ₈ O ₈	~1940	~1950

Some of the more common high powered or high energy explosives are listed in Table VII. The most common are mixtures of TNT. As with dynamites and slurries, there are a very large number of materials that can be made to meet a variety of requirements.

The use of polymers as binders has added a degree of freedom to the formulation of materials with explosive properties. Mixing explosive compounds with polymers and other inerts makes it possible to adjust the detonating characteristics, physical properties, and sensitivity over a rather broad range. For example, mixtures of PETN, NC, and an elastomeric plastic, made in sheet form, can be used in many applications. With minor adjustments in the explosive, they can be made to detonate at a thickness of 15 mils.

DETONATION PROPERTIES

Detonation velocity and detonation pressure are a function of charge density and charge size. In general the detonation velocity is an almost linear function of density for almost all pure explosives or mixtures. A velocity-density curve for two common high explosives is shown in Fig. 2. However, the detonation velocity for multicomponent mixtures of oxygen-rich and oxygen-poor compounds increases with density and then decreases⁴. This phenomena has also been observed in some single-compound explosives such as perchlorates⁵.

Between the region of 0.8 and 1.9 g/cm³, the detonation pressure of most secondary single compound explosives is a linear function of the square of the density⁶.

With the explosive in either cylindrical or sheet form, the expansion of the detonation products at the charge surface tends to lower the pressure at the detonation front. This effect becomes pronounced as the charge radius or thickness becomes small. Thus for any given explosive in the unconfined state, there is a characteristic failure diameter or thickness at which the explosive fails to propagate. The failure diameter or thickness is also a function of

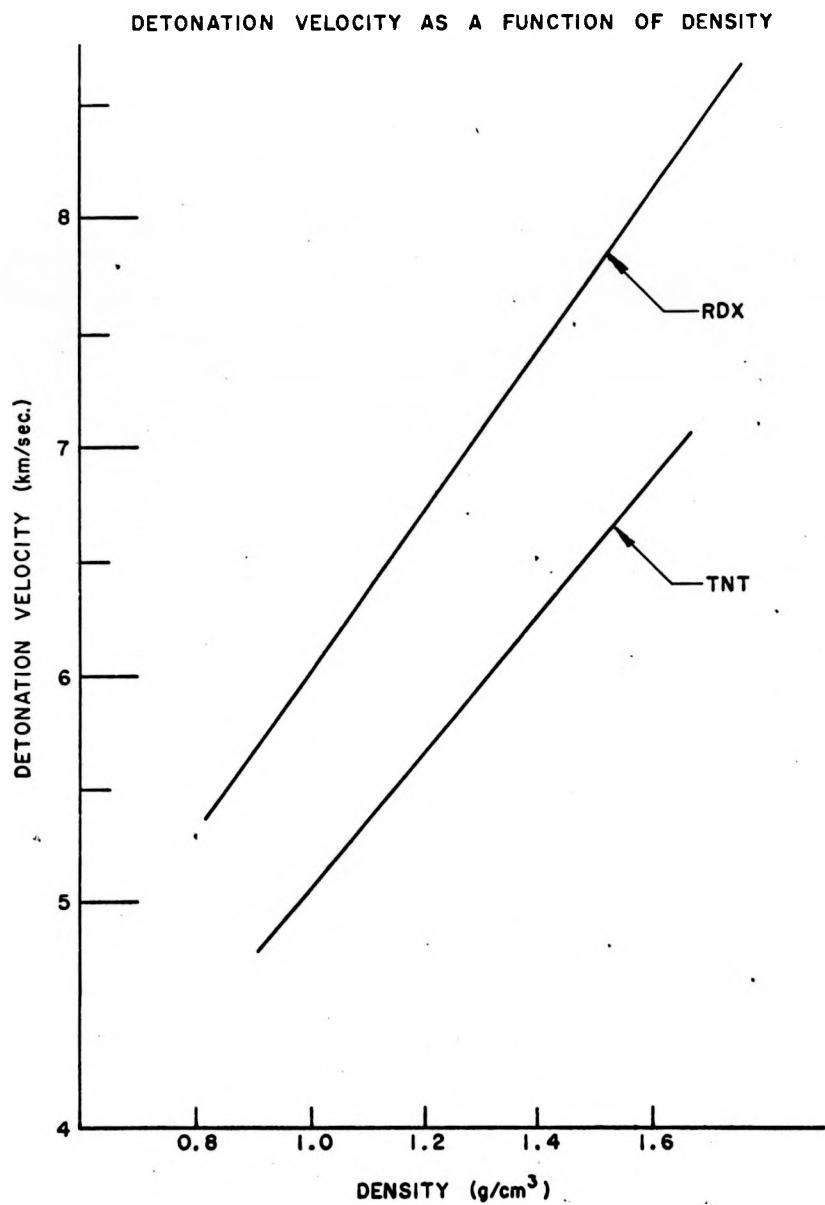


FIGURE 2

Source: M. J. Urizar, E. James, and L. C. Smith, "Detonation Velocity of Pressed TNT," Physics of Fluids, Vol. 4, No. 2 (1961).

TABLE V

BASIC PROPERTIES OF COMMON SINGLE-COMPOUND HIGH EXPLOSIVES

<u>Material</u>	<u>State</u>	<u>M. P. (°C)</u>	<u>Color</u>	<u>Density (g/cm³)</u>	<u>Detonation Velocity (Km/sec)</u>	<u>Detonation Pressure (kbars)</u>
AN	Solid	170	White	1.73		
NG	Liquid	13	Clear	1.60 at 20	7.580	~230
NC	Solid	Decomp.	White	~1.6		
TNT	Solid	80	Yellow	1.65	6.930 at 1.64	190
PETN	Solid	140	White	1.7	7.980 at 1.67	300
RDX	Solid	204	White	1.80	8.750	347
HMX(β)	Solid	285	White	1.90	~9.100 at 1.89	393

* Source: C. L. Mader, "Detonation Properties of Condensed Explosives," LA-2900-MS, 1963

confinement and would tend to decrease as confinement is increased, provided that the shock velocity of the confining material is less than the detonation velocity. Changes in density, particle size, or crystal habit of a given explosive also affect the failure dimension. As the dimensions of the explosive are increased to dimensions slightly greater than the failure dimensions, the velocity increases almost linearly with radius or thickness. A typical failure diameter curve for Composition B, a mixture of RDX and TNT, is shown in Fig. 3. It is important to note that the difference between the detonation velocity at infinite diameter and detonation velocity just prior to abrupt failure is only a few percent. These curves are used to illustrate the fact that for a given explosive it is possible to change the failure characteristics with changes in the particle size of the RDX. The slope of the linear portion of the curve as the velocity approaches the velocity of a charge of infinite diameter, has been related to the thickness of the reaction zone⁷.

INITIATION PROPERTIES

The deliberate initiation of secondary high explosives is accomplished with a shock wave generated by a detonator or detonator and booster charge. This mechanism of initiation for both homogeneous (liquid) and heterogeneous (polycrystalline solids) is fairly well understood^{8, 9}. For any given initiating system and explosive, there are two methods of initiation. When the initiating shock pressure is less than the detonation pressure and is of infinite width ($\geq 0.2 \mu\text{sec}$), there is a buildup to detonation that is a function of the sensitivity, and density of the explosive. This buildup is illustrated in Fig. 4 for PETN at two densities and for a plastic bonded explosive. The shock transmitted to the explosives gradually accelerates and after a given distance of travel converts to a detonation. Under these conditions, the size of the booster should be greater than the failure diameter of the explosive being

DETONATION VELOCITY
AS A FUNCTION OF CHARGE RADIUS
FOR COMPOSITION B

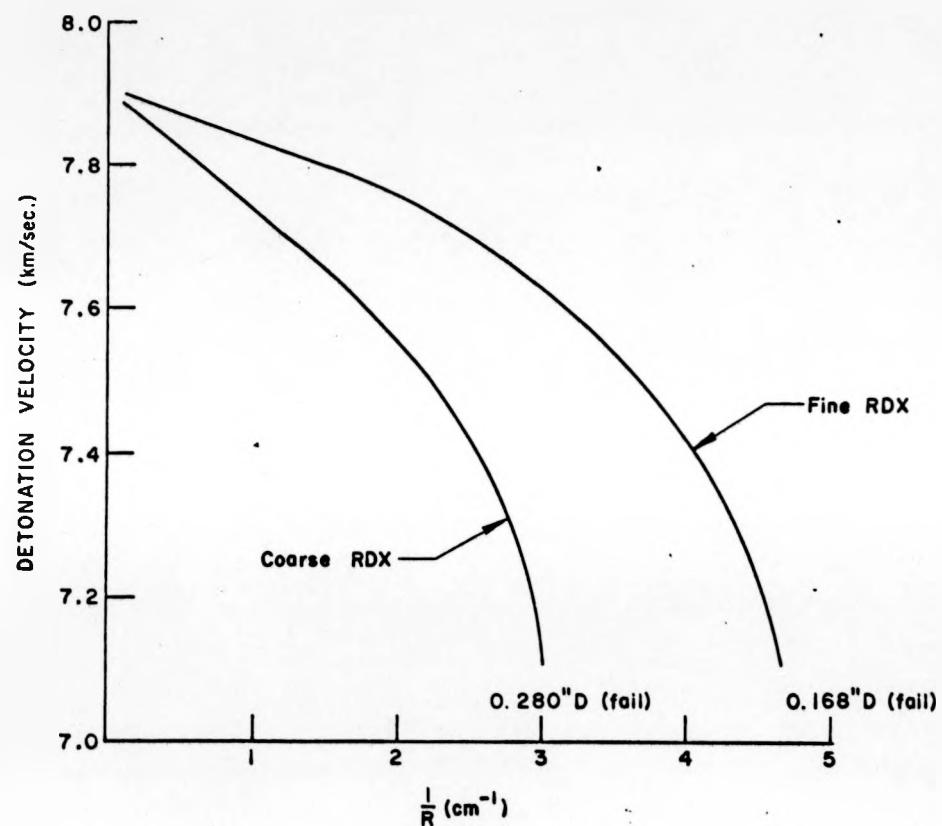


FIGURE 3

Source: M. E. Malin, A. W. Campbell, and C. W. Mautz,
"Particle Size Effects in One and Two Component
Explosives," Second ONR Symposium on Detona-
tion (ONR, Dept. of Navy, Washington, DC 1955).

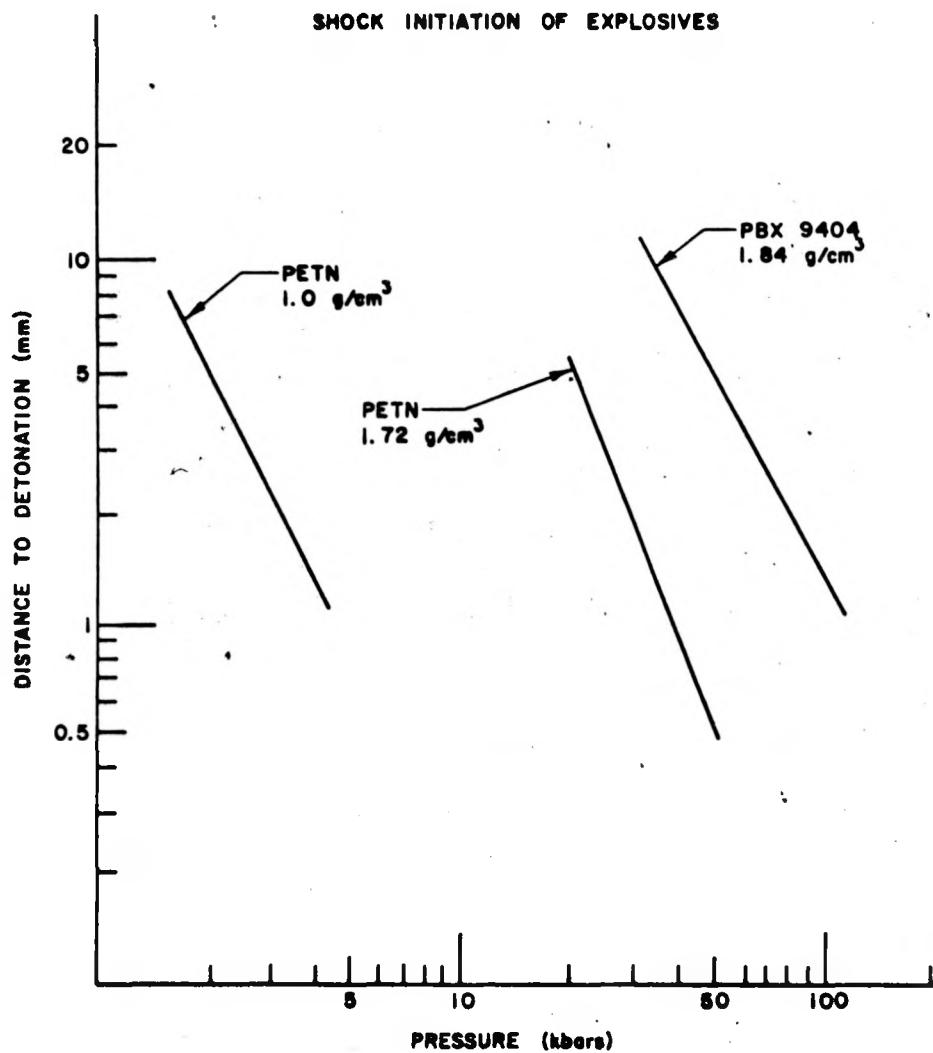


FIGURE 4

Source:

PETN - D. Stripe, J. O. Johnson, and J. D. Wackerle,
 "Shock Initiation of XTX 8003 and Pressed PETN,"
 LADC-10970.

PBX 9404- J. Ramsey and A. Popolato, "Analysis of Shock
 Wave Initiation Data for High Explosives," Fourth
 Symposium on Detonation, Office of Naval Research,
 p. 233 (Oct. 1965).

TABLE VI

LOW POWER MIXED EXPLOSIVES^{*}

<u>Designation</u>	<u>Composition (w/o)</u>	<u>Nominal Working Density (g/cm³)</u>	<u>Detonation Velocity (Km/sec)</u>	<u>Detonation Pressure (kbars)</u>	<u>Consistency</u>
<u>Dynamites</u>					
Straight	50 NG/0.2 NC/ 34 SN/15.8 C	1.4	~5.8	~100	Powder
Ammonium	16 NG/0.1 NC/ 78.7 AN/6 F	1.3	~4.8		Powder
Ammonium-gel	26 NG/0.6 NC/ 34 AN/28 SN/ 11.4 C	1.3	~5.4		Gel
ANFO	94 AN/6 FO	~0.8	~4.7	~ 40	Powder
<u>Slurry and Gel</u>					
SE-TNT	TNT/AN/SN/ W/G			~100	Slurry or Gel
SE-TNT/AL	39 AN-SN/20 TNT/ 25 AL/15 W/1 G	1.60	~3.5		Slurry or Gel
SBA/AL	49 AN-SN/35 AL/ 15 W/1 G	1.45	<4.0	60	Slurry or Gel

* Data from various published sources.

** These values are a function of diameter, and tabulated data are approximations.

SN -Sodium nitrate; C - combustibles and chalk; F - fuel; FO - fuel oil

SE -Slurry explosive; W - water; G - gelling agent; AL - aluminum

SBA-Slurry blasting explosive

initiated. With input shock pressures greater than the detonation pressure in the acceptor explosive, there is no initiation delay if the shock transmitted to the acceptor explosive is maintained above the detonation pressure over a region greater than the failure dimension of the acceptor explosive.

Initiation by low velocity impact or friction is the mechanism responsible for most accidents involving high explosives and is still the subject of considerable study. A rapid exothermic gas producing reaction is started as the result of either local (hot spots) or bulk heating in the explosive. The differences in the behavior of an explosive under different conditions are due mainly to the

different mechanisms by which heat may be generated within the explosive and transported to the surrounding materials. Because of these differences, it is difficult to assess in any quantitative way the sensitivity as it would apply to situations involving handling and processing. Reactions can be started by the adiabatic compression of voids within the explosive, viscous flow, or friction^{10, 11}.

Over the past years a wide variety of tests have been developed in an attempt to assess the response on explosives to low velocity impacts. One of the most common is a drop weight impact tester. In this test, a small quantity (about 35 mg) of explosive is placed on a small (~1 x 1") piece of 5/0

TABLE VII

HIGH POWER MIXED EXPLOSIVES*

<u>Designation</u>	<u>Composition (w/o)</u>	<u>Nominal Working Density (g/cm³)</u>	<u>Detonation Velocity (Km/sec)</u>	<u>Detonation Pressure (kbars)</u>	<u>Consistency</u>
<u>TNT Mixtures</u>					
Ammatol	50 TNT/50 AN	1.55	6.3	--	Solid
Composition B	40 TNT/60 RDX	1.70	7.9	285	Solid
Cyclotol 75/25	25 TNT/75 RDX	1.75	8.2	320	Solid
Octol 75/25	25 TNT/75 HMX	1.82	8.4	340	Solid
Pentolite 50/50	50 TNT/50 PETN	1.67	7.4	245	Solid
Tritinol	80 TNT/20 AL	1.72	6.7	--	Solid
<u>Plastic or Wax Bonded Mixtures</u>					
Composition C-4	91 RDX/ 2.1 rubber/ 1.6 oil/ 5.3 plasticizer	1.0 to 1.6	8.0	255	Plastic
Sheet explosive	60-85 PETN/ 0-8 NC/ rubber and plasticizer	~1.5	~7.0	185	Rubbery sheets
PB-HMX or RDX	80-95 RDX or HMX 20-5 various plastics or plastic and plasticizers	1.6 to 1.85	7 to 8.5	<275 to 375	Solid
Composition A	90 RDX/10 wax	1.6	8.1	260	Solid

* Data from various published sources.

garnet paper and this is placed between a striker and anvil. A 2.5-kg weight is dropped on the striker and the height at which a given frequency of explosions (usually 50%) is obtained is recorded. The results obtained for a few explosives of interest are tabulated in Table VIII.

THERMAL STABILITY

The function of a high explosive is to yield power on demand with no significant changes as a function of time. For this reason they must be capable of being stored for long periods of time without

becoming unstable or decomposing. Materials with explosive properties will decompose at appreciable rates at relatively low temperatures (<200 °C). An estimate of the thermal stability can be obtained from thermal decomposition kinetic data^{12, 13}. With the aid of these data one can obtain an estimate of shelf life, as a function of temperature. It is also possible to obtain an estimate of critical temperature as a function of geometry. An estimate of shelf life based on the time required to decompose 5% of the explosive is shown in Fig. 5. TNT is

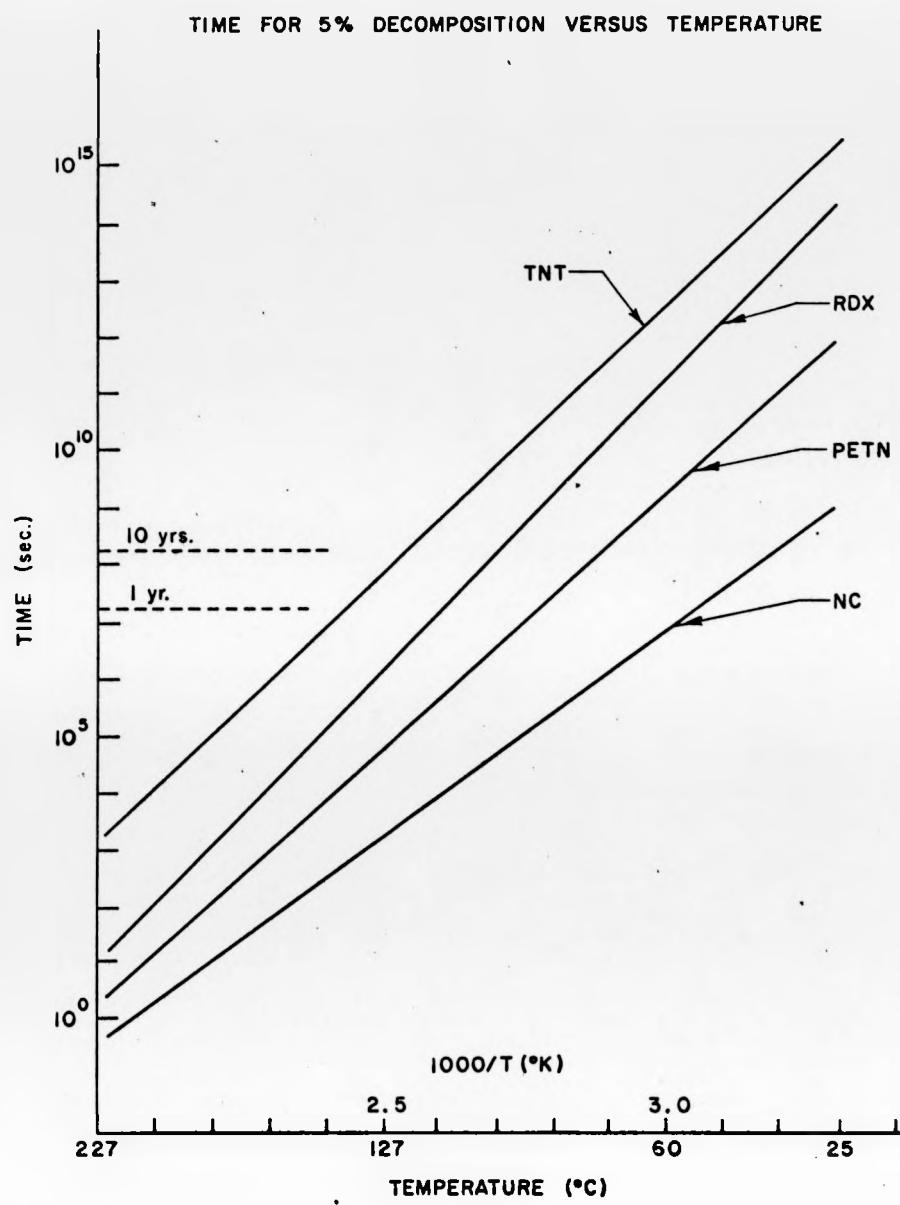


FIGURE 5

TABLE VIII

DROP WEIGHT IMPACT SENSITIVITY
ERL MACHINE TYPE 12 TOOLS

Material	H_{50} (cm)	Material	H_{50} (cm)
PETN	12	Composition B-3	59
RDX	22	Composition A	70
HMX	26	TNT	154
Cyclotol 75/25	35	NQ	> 325
Octol 75/25	37	TATB	> 325
PBX 9404	42		

significantly more stable than the other explosives shown. An estimate of the critical temperature as a function of charge radius for three explosives is shown in Fig. 6. The critical temperature is defined as the temperature above which the self heating from the exothermic decomposition of the explosive is greater than the heat loss and the explosive will undergo a self-sustained reaction, usually an explosion.

Decomposition kinetic constants for a few explosives are listed in Table IX. With these data, a heat of reaction, density, heat capacity, and thermal conductivity one can calculate the thermal behavior of explosive systems exposed to various thermal environments.¹⁴

With mixed explosives or with mixtures containing explosives and inert, the properties of the mixture cannot be inferred from the properties of the individual constituents. There is the possibility of obtaining a mixture significantly less stable than either of the constituents. Such mixtures are considered incompatible. A number of tests have been designed to test incompatibility. These include vacuum stability tests, pyrolysis, differential thermal analysis, and finally long-term surveillance tests. The modified Henkin test has been used with success to obtain a quantitative estimate of incompatibilities.¹⁵ An example of an incompatible system is shown in Fig. 7, the RDX-urea system. The addi-

TABLE IX

THERMAL STABILITY DATA

Material	Kinetic Constants*		Vacuum Stability (ml/g/48 hr at 120°C)
	$Z(\text{sec}^{-1})$	ΔE (Kcal mole $^{-1}$ °K)	
AN			0.3
NG	3.2×10^{20}	48.0	> 11
NC	2.8×10^{12}	31.3	1.5**
TNT	1.6×10^{13}	41.0	0.2
PETN	6.3×10^{19}	47.0	0.5**
RDX	3.2×10^{18}	47.5	0.1
HMX(β)	6.4×10^{18}	51.3	0.1

* From R. N. Rogers, Group GMX-2, private communication

$$t = \frac{1}{Ze^{-\Delta E/RT}} \ln \frac{1}{1 - \alpha}$$

α = fraction decomposed
 t = time (sec)

** At 100°C

tion of urea to RDX lowers the critical temperature. The critical temperature in this case is equivalent to the critical temperatures shown in Fig. 6 with the explosives having a radius equivalent to a few millimeters.

PROCESSING AND CHARGE PREPARATION

The secondary explosives, as either single compounds or mixtures, are generally powdered polycrystalline materials with bulk densities much lower than the theoretical density. To serve their purpose more efficiently, they must be processed into some compacted form. If they are to be used in applications requiring precision in reproducibility of power or timing, the method of compaction must lead to a reproducible product.

A number of techniques have been developed to produce high quality explosive charges of multi-component high explosives¹⁶. With TNT bearing explosives, the most common method of producing charges is casting. Since TNT melts at 80°C, and

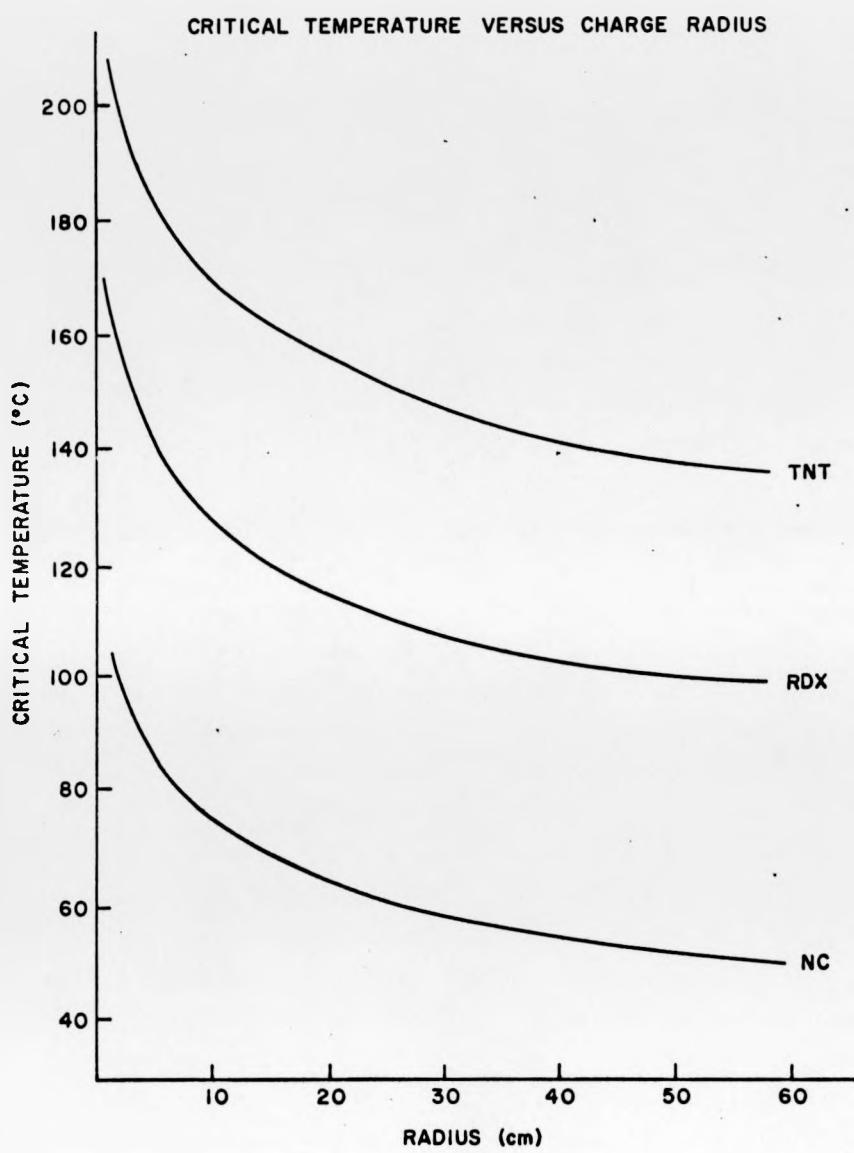


FIGURE 6

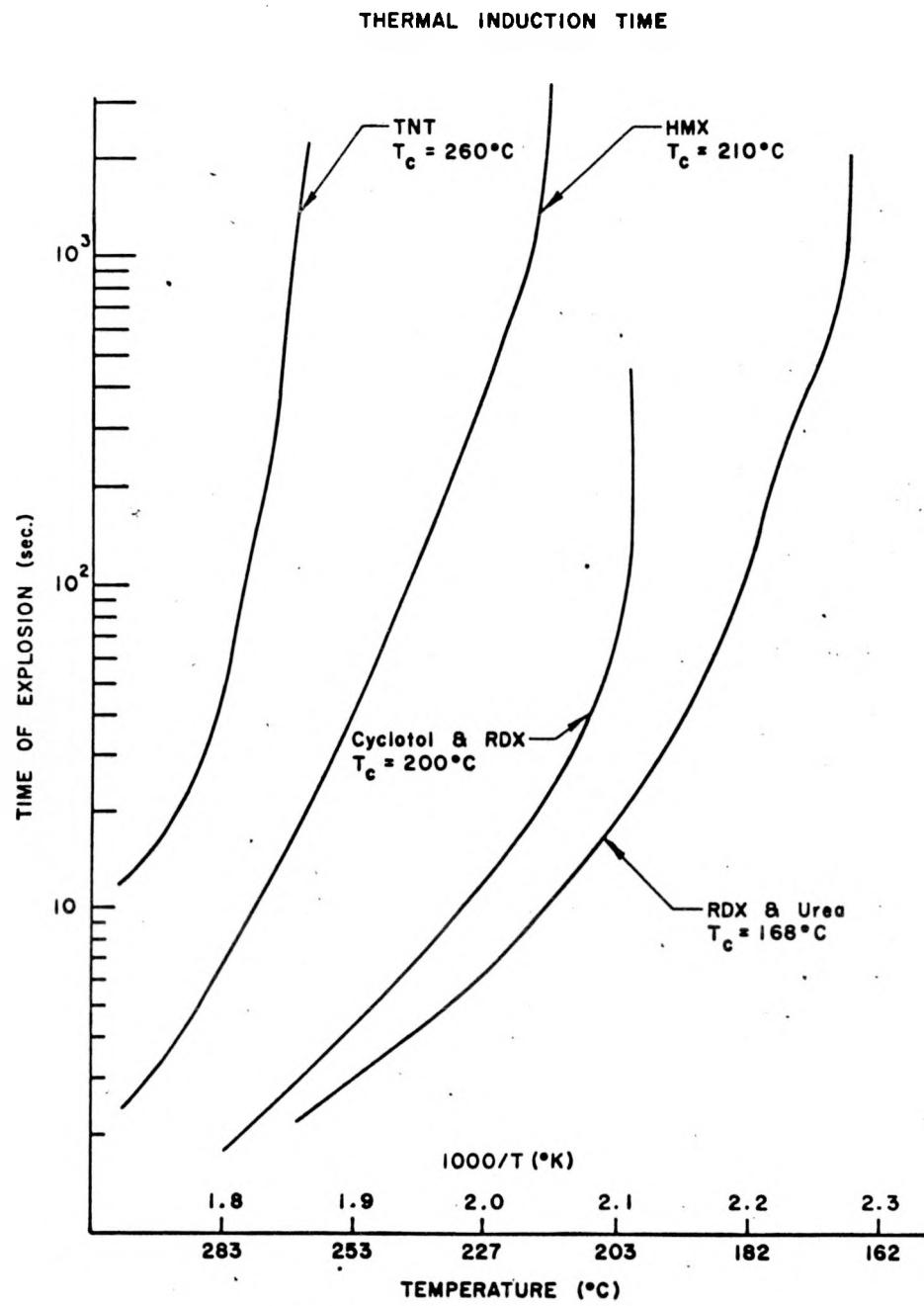


FIGURE 7

can be heated to 100°C without problems, it is possible to make slurries of TNT with almost any material that is not very soluble in the TNT. The molten slurry is poured into molds and with controlled melt and cooling procedures, high quality castings can be made. A schematic of typical equipment is shown in Fig. 8.

Pressing can also be used as a method of consolidation and has some advantages over casting. Pressing techniques depend upon the characteristics of the explosive. With thermoplastic-explosive mixtures, or with TNT and TNT mixtures, conventional compression molding techniques can be used to provide high quality charges in a variety of shapes. A schematic of a simple compression mold is illustrated in Fig. 9. Explosives bonded with thermosetting plastics either rigid or elastomeric can be molded into a variety of shapes or cross sections by either compression, transfer, or extrusion molding. Sheet explosive is made by extrusion molding, for example.

In some applications, it may be necessary to produce charges with precise finished dimension. With solid high density materials such as TNT-RDX mixtures or RDX-plastic mixtures conventional machine tools can be used to finish the explosive billet to its final dimensions.

The fact that accidental initiation can occur as the result of the formation and growth of hot spots dictates that care be exercised with any operation involving high explosives. This is particularly true of pressing and machining operations, and, in fact, many of these operations are conducted by remote control or with protective shields.

SPECIAL PURPOSE EXPLOSIVES

There are a few applications in which the explosive will be subjected to high temperature for varying periods of time. One example is deep well perforation or other applications where geothermal heating could be a problem. Explosives are available on the commercial market that will meet these requirements. A few explosives having these properties are shown in Table X. Their thermal properties compared with RDX are illustrated in Fig. 10 with differential thermal analysis curves. TACOT displays a solid-solid endothermic phase transition starting at 262°C; no appreciable decomposition occurs below 350°C. DATB displays a solid-solid endothermic phase transition at about 225°C and melts at 285°C, just before decomposition. TATB is stable until the temperature approaches the decomposition or melting temperature.

TABLE X

THERMALLY STABLE HIGH EXPLOSIVES

Symbol	M. P. (°C)	Density Crystal (g/cm ³)	Density Pressed (g/cm ³)	Detonation Velocity (Km/sec)	Detonation Pressure (kbars)
TACOT	> 385 Decomp.	1.85	1.85	7.2	245
DATB	~286	1.84	1.79	7.5	260
TATB	~350 Decomp.	1.94	1.88	7.8	290

* Estimated from $P = \rho_0 D^2/4$

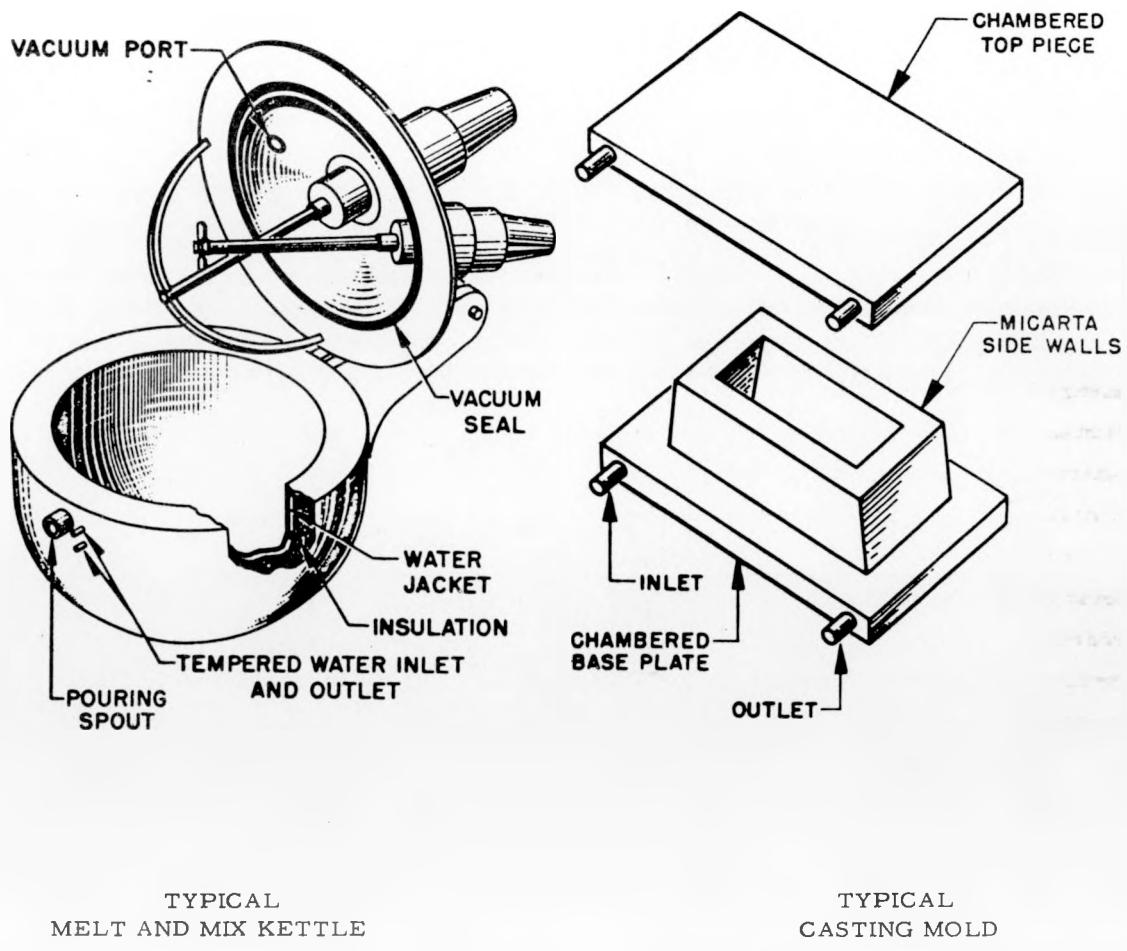
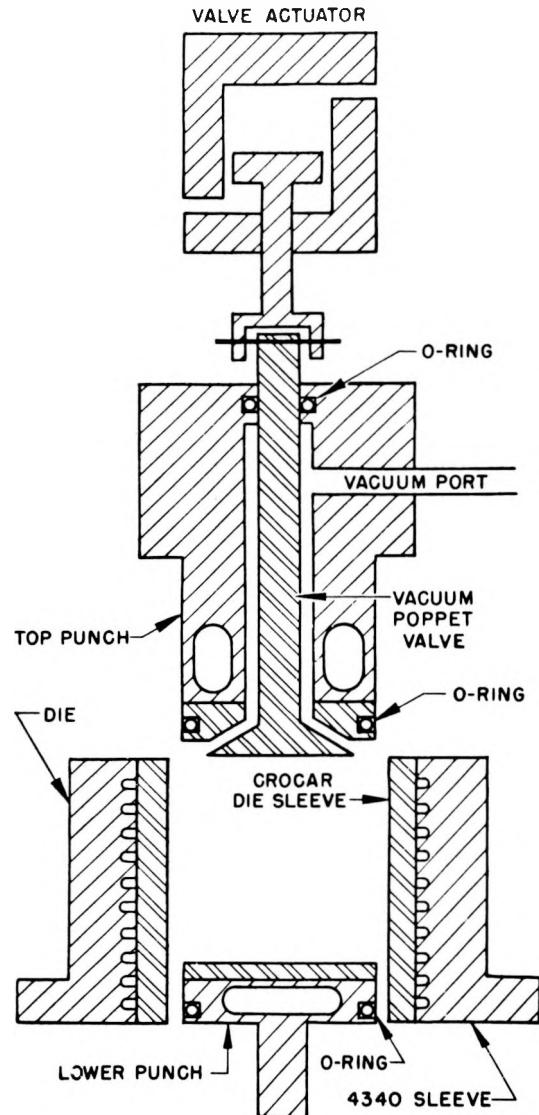


FIGURE 8



TYPICAL COMPRESSION MOLD
WITH VACUUM PORT

FIGURE 9

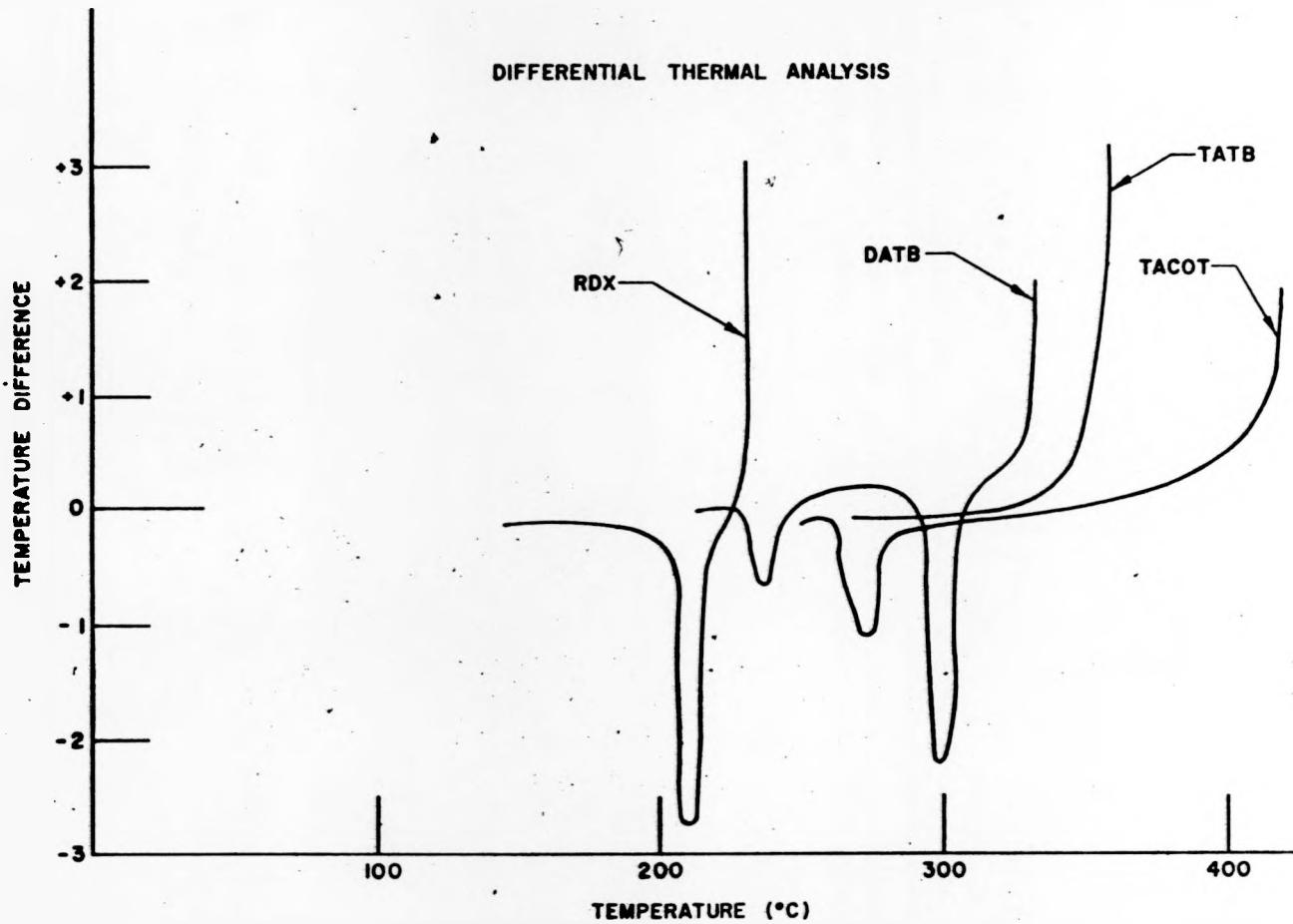


FIGURE 10

In addition to being thermally stable, these materials are less sensitive to shock than most the common explosives.

The materials shown are but a few of a wide variety of high temperature explosives being developed. They can be treated as most other materials, compounded as mixtures with plastics, formed into cores of mild detonating fuse and linear shaped charges.

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