

ADA033552

19

FG

COPY NO. 6

TECHNICAL REPORT 4987

EXPLOSIVE PERFORMANCE MODIFICATION BY
COSOLIDIFICATION OF AMMONIUM
NITRATE WITH FUELS



I. AKST
J. HERSHKOWITZ

OCTOBER 1976

D D C
RECEIVED
DEC 29 1976
HERSHKOWITZ
C

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

PICATINNY ARSENAL
PICATINNY, NEW JERSEY

The findings in this report are not to be construed as an official Department of the Army position.

DISPOSITION

Destroy this report when no longer needed. Do not return to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report, 4987 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) EXPLOSIVE PERFORMANCE MODIFICATION BY COSOLIDIFICATION OF AMMONIUM NITRATE WITH FUELS, ✓	5. TYPE OF REPORT & PERIOD COVERED	
7. AUTHOR(s) I./Akst, Explosives Division, FRL J./Hershkowitz, Explosives Division, FRL Now at Idos Corporation, P.O. Box 285, Pampa, TX		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Picatinny Arsenal Dover, NJ 07801 ✓	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AMCMS Code 662617.11.H7905	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE October 1976	13. NUMBER OF PAGES 59
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) <u>1256p.</u>	15. SECURITY CLASS. (of this report) Unclassified	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. <u>14 PA-TR-4987</u>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Explosive, Ammonium nitrate, Ethylenediamine dinitrate, Nonideal explosive, Physical synthesis, Composite explosive, Dent test, Detonation velocity, Explosive-metal acceleration		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Practical nonideal explosives with performance improved by modifying ideality are shown to be within reach. Materials which might be used are avail- able in quantity at low cost, and processing techniques are ordinary. Performance enhancement was brought about by selecting fuels for an oxygen-rich nonideal explosive (ammonium nitrate) and improving reaction rates through more intimate reactant contact brought about by cosolidification.		

TABLE OF CONTENTS

	<u>Page No.</u>
Introduction	1
Procedure	3
Raw Materials	3
Formulation	4
Fabrication and Assembly for Confined Small Scale Detonation Velocity and Depth of Dent Test	6
Detonation Velocity	7
Depth of Dent	8
Thermal Tests	8
Impact Sensitivity	8
Shock Sensitivity	9
Miscellaneous Tests and Measurements	9
Computations	9
Results	9
Thermal Tests	9
Impact Sensitivity	10
Shock Sensitivity	11
Detonation Velocity and Depth of Dent	11
Hygroscopicity	12
Solubility of EDD	12
X-Ray Diffraction	12
Scanning Electron Micrographs	13
Dimensional Stability	13
Discussion	13
Potential of Ammonium Nitrate and Some Fuels	13
Processes and Limits	15
Detonation Velocity and Dent Test Method	16
Detonation Velocity and Dent Results	18
Materials: Sources, Availability, Previous Uses, Cost	22
Intimacy Diagnostics	23
Future Work	25
Acknowledgements	26
References	28
Distribution	52

	<u>Page No.</u>
Tables	
1 Differential Thermal Analysis Results	31
2 Vacuum Thermal Stability and Chemical Reactivity Test	32
3 Explosion Temperature Results	34
4 Drop Weight Impact Sensitivity	35
5 Small-Scale Gap Test Sensitivity	36
6 X-Ray Diffraction Pattern of EDD/AN	37
7 Potential Chemical Energy of AN and Some Fuels	38
8 Dent and Detonation Velocity Results	39
Figures	
1 Confined Small Scale Detonation Velocity and Dent Test	41
2 Depth of Dent vs Small Scale Gap Test Attenuator Thickness for Reference Explosives	42
3 Depth of Dent vs Small Scale Gap Test Attenuator Thickness for Ethylenediamine Dinitrate/Ammonium Nitrate (EDD/AN)	43
4 Scanning Electron Micrographs of EDD/AN 50/50	44
5 Depth of Dent vs Weight Percent AN in EDD/AN/RDX	45
6 Detonation Velocity vs Weight Percent AN in EDD/AN/RDX	46
7 Depth of Dent vs Weight Percent RDX in Binary Compositions	47
8 Depth of Dent vs Weight Percent AN in Binary Compositions	48
9 Depth of Dent vs Detonation Velocity	49
10 Depth of Dent vs $\rho_0 D^2$	50
11 Performance Summary for Compositions	51

INTRODUCTION

The rate at which an explosive decomposes into its detonation products influences its performance by its effect on the pressure and velocity of the detonation wave. Performance is also related to the kinds and amount of the decomposition products, their rate of formation, and the energy released in forming them. Whether particular effects help performance or degrade it depends on the application to which the explosive is to be put; in the work described in this report we are concerned with the availability and transfer of energy to a load more than with total energy.

Ideal explosives have been defined as those which have decomposition rates high enough to be thought of as nearly instantaneous or time-independent: Most of the final products are formed with a thin, fast-moving reaction zone. Parameters such as detonation pressure and velocity can be quite well calculated on that basis, especially for condensed-phase CHNO explosives, by calibrated codes and formulas (Ref 1-4). It has been recognized that departure from the instantaneous approximation may be significant even in ideal explosives (Ref 5). In nonideal explosives reaction rates are usually slower, and either important amounts of chemical reaction go on well after the end of the steady-state detonation zone, or the zone is very long. Generally, detonation pressure and velocity, and therefore power, are lower in nonideal explosives than in ideal explosives.

Performance of explosives is relatively well understood for two points in the rate spectrum (i.e. for metal/acceleration by high rate explosives, and for air blast, water shock and earth moving by lower power but high energy explosives). Much less is understood about how to obtain optimum functioning through varying the reaction and pressure/time characteristics within the total reaction zone (detonation zone terminated by Chapman-Jouguet plane plus reactive region behind it). It is the understanding and modification of those characteristics in nonideal explosives that are the subject of these studies.

Nonideal energetic explosives can be made from relatively cheap and plentiful materials, ammonium nitrate (AN) being perhaps the best example. To learn how to make good military explosives in which the energy release of such materials can be tailored for optimum performance of various munitions--including but not limited to those requiring high power, such as fragmenting projectiles--is the purpose of this program of research.

The research reported herein is an extension of previous efforts (Ref 6). In that work we demonstrated that it is possible to at least partially overcome a rate-limiting factor and improve the performance of a solid nonideal explosive containing AN. Monomethylammonium nitrate and tetramethylammonium nitrate cosolidified with AN produced deeper dents in steel witness plates than could the components

alone. (Tests were done in confined small scale, 9-9.5 mm in diameter, in Amatol- and AmateX-like formulations.) Neither detonation velocity nor density changed much. No other explanation of the synergism seen as tenable as intermolecular reaction behind the shock front yielding pressures high and fast enough for head-on denting of steel in the manner and to the degree observed. Experimental findings attributable to synergistic effects were also later demonstrated in both small-scale dent tests and large-scale cylinder tests at Los Alamos (Ref 7).

The studies of Reference 6 also showed that the materials (methylammonium nitrates), chosen for their properties as homogeneous and carbonaceous fuels and for their cosolidification possibilities with AN, probably would not be very useful as replacements for the usual kinds of munitions loads because of severe hygroscopicity, non-optimum eutectic melting points, and reactivity with TNT. This left incomplete one of the two objectives of the first study, that of showing the practical value of explosives so improved. (The primary objective was to demonstrate that it was possible to move toward ideality and improve performance.) Therefore, of the several directions in which research could then proceed, we believed it would be most valuable to use screening tests to look further for potentially more useful or at least more tractable materials, which trying to further characterize and understand the phenomena at the same time. It was clear that research enabling one to be predictive would require long and persistent efforts. For example, for nonideal explosives, we cannot yet calculate performance (time-dependent codes are just being developed), measure early detonation products (only final products are analyzed, with considerable uncertainty), describe cosolidified systems (matrix conditions such as fuel/oxidizer molecular distance statistics are unknown), or define the kinetics.

Accordingly, we listed a number of potential compounds and families of compounds, being aided by suggestions of many people, for which we are grateful. Narrowing that list by consideration of such factors as eventual cost, quantity availability, etc., it was concluded that AN would continue to be the prime material and the only oxidizer. Efforts on perchlorates and other oxygen-rich materials (e.g. hydrazine nitrate) then were deferred or restricted to literature study or a few thermal and sensitivity measurements.

As reactants with AN, only a few materials could be studied. Those selected were potential fuels for AN's excess oxygen which were known or thought to form attractive solid systems with AN: guanidine nitrate (GN), nitroguanidine (NQ), ethylenediamine dinitrate (EDD), and unsymmetrical dimethylhydrazine nitrate (UDMHN, later deferred because of delivery problems with UDMH). Among potentially interesting materials which were deferred or to receive less attention were nitroguanidine nitrate, tetrahydrofurfuryl alcohol, fuel oil, several tetrazoles and their nitrates, and some other inorganics.

The general method we have called cosolidification is central to this work for both theoretical and pragmatic reasons. Various techniques used to cosolidify all have one main aim, albeit with different peripheral purposes: to bring the reactants into close proximity -- closer than is feasible with methods such as particle size reduction -- so as to minimize transport-limited reaction time in solid or near-solid systems. Although a variety of cosolidification techniques are possible, including disposition from vapor, chemically synthesizing in place, etc., those used for this work were melting/co-freezing, and co-crystallization from a solvent (water).

Performance assessments followed thermal, compatibility, and sensitivity measurements, and were restricted to witness plate denting and detonation velocity, in small scale (9.5 mm in diameter) heavily confined in steel or brass. The reasons for restricting the kinds and numbers of tests were safety, availability of materials, expeditiousness, and economy. It is now necessary to scale up in size and measure other parameters. However, this stage was primarily to screen and evaluate some materials and methods to satisfy the main objective of showing that a practical nonideal explosive can be improved in power by making it more ideal.

PROCEDURES

Raw Materials

Pure (ACS grade) ammonium nitrate was used throughout. Ethylenediamine dinitrate was made from 98-100% ethylenediamine, as described below. Guanidine nitrate was obtained from local stocks, whose origin was the Hercules Pilot Plant using the urea ammonium nitrate process. The material was crystallized from water prior to use. Nitroguanidine was prepared locally by anhydration of the same stock of guanidine nitrate with concentrated sulfuric acid; the product was then purified by recrystallization from distilled water followed by vacuum drying. The RDX was military grade, Type II, Class A (median particle diameter, 250 micrometers), Holston Lot 54-64. TNT was military production grade, a blend (1B-8484FB) of Lots 11-066, 188, 27 (1956). Amatex 20 was from a local batch of "standard" materials (i.e. uncoated ground AN prills, production TNT and RDX), approximately 40/40/20 by weight, respectively.

Ethylenediamine dinitrate (EDD) was prepared in batches of 50 to 500 grams as follows. The 98-100% ethylenediamine and distilled water were added to ethanol in a flask, and 90% nitric acid was added drop by drop to slight excess, cooling to maintain temperature below 60°C. The mixture was stirred, allowed to stand for a few hours or overnight, then filtered. The crystals on the filter were washed several times with absolute ethanol to remove the excess acid or ethylenediamine, then air dried by suction. Final drying was in a shallow layer for two hours at 60°C under house vacuum (about 200 mm Hg pressure).

Yield was 90-92%.

Formulation

Six methods were used to prepare EDD/AN mixtures. Typical batch size was 20 grams. Operations were conducted in an explosives safety hood behind transparent blast doors.

1. Melt, quench in Freon. The components were weighed and dry-mixed, then placed in a flask partially submerged in silicone oil in a larger beaker on a thermostatically controlled hot-plate. A mercury-glass thermometer was kept in the silicone oil. For mixtures 50/50 by weight, the temperature was kept at 120°C; for the others, about 140°C (not exceeding 150°C) for just long enough to melt the materials, as visually observed. (At the higher temperatures there was a slight amount of sublimation, with deposition on the cooler glass parts noted as a very thin film.) The melt was then poured into a relatively large quantity of room-temperature trichlorotrifluoroethane (Freon TF or Genatron 113) with rapid stirring.

Spherical beads formed with a range of diameters from less than one mm to about two mm. Interior freezing of the large particles may not have been very rapid. (Freon tends to boil away from the forming particle, leaving the sphere partially in a vapor cloud.) The product was crushed (with difficulty; it is quite hard) in an electric mortar and pestle to moderately fine granular size suitable for pressing, about USS 45 or 350 micrometers median particle diameter.

2. Melt, quench by Freon. The melt was the same as above. Instead of pouring the product into Freon, a fine stream of Freon TF was injected into the melt while it was being stirred. Complete exterior freezing took a little longer, but there were no large pieces and there was little dust: typical size was on the order of 1 to 2 mm, irregular in shape. Crushing and grinding as in 1. above: crushing was a little easier.

3. Melt, quench on cool metal. The melt was the same as above. The product was poured in a thin, moving stream (not always a continuous stream: sometimes it broke up into droplets) from a height of 20-30 cm onto a large sheet of thin, clean stainless steel at room temperature. Platelets less than a millimeter thick by about a centimeter in diameter usually formed, with rapid freezing. Edges of the platelets were sometimes scalloped. The platelets were easily crushed but the material, though hard, also exhibited strength and some flexibility. Grinding was as in 1. and 2. above. This is considered the best process of the three because of the faster freeze and more manageable product.

4. Melt, slurry process. A high-speed double-blade counter-rotating stirrer in a close-fitting Teflon bearing was fitted into the

center neck of a three-neck 1000 cc round bottom flask. Through one side neck, solvent (slurry carrier liquid) was added as needed by manipulating the stopcock of a large volume separatory funnel. Boiling solvent was recondensed with a reflux column mounted in the other side neck. The flask and its contents were heated with a heating mantle.

EDD and AN (20 grams total) were placed in the round-bottom flask and heated slowly until melted. With slow stirring, 200 ml perchloroethylene (tetrachloroethene, BP 121°C) was added at a rate such that the EDD/AN mixture did not solidify. The slurry was then brought to a boil, the heating mantle removed, and the stirrer brought up to maximum speed. Chilled perchloroethylene was then introduced in quantity as rapidly as possible to quickly solidify the EDD/AN into small particles.

The particles produced were small, requiring no grinding for pressing. The size and structure of the particles are controlled partly by the initial dilution: a 70 gram batch using the same quantity of solvent (200 ml), thus having a dilution ratio of nearer 3:1 rather than 10:1, produced larger, irregularly shaped particles, indicating inadequate dispersion. This process is quite attractive in terms of the product, and also for scale-up of batch size.

5. Co-crystallized. The components were weighed and placed together in a beaker, and a small amount of de-ionized water was added (typically about 1 ml water per gram). Warming slightly to overcome solution cooling, the slightly syrupy solution was then poured into a small three-necked round-bottom flask with a Teflon stirrer shaped to fit the bottom. The flask was partially submerged in silicone oil, which was heated to about 60°C (care being taken not to approach the eutectic melting point of just over 100°C). While stirring, air was blown over the surface through one of the side necks, the other side neck remaining open, until the product was a thick, grainy slurry (about ten minutes). Then vacuum (via a mechanical pump, to about 1 mm Hg pressure) was applied while stirring continued, until the product was visually dry. Warm vacuum drying continued without stirring, with repeated weighings to constant weight. The product was then lightly crushed to a smooth, non-lumpy powder, followed by a small amount of grinding in mortar and pestle.

6. Dry Mix. Components were weighed and mixed cursorily in a beaker, then ground in mortar and pestle to about the same particle size as the others.

While all six of these methods were used with EDD/AN, only one, the fast-freeze on stainless steel method, was used for the NQ/CS/AN material. The melt was similar to the EDD/AN, being carried out at 130-140°C since the eutectic melting temperature is about 113°.

All formulations with RDX incorporated the RDX by dry mixing after the rest of the mixing had been done. The components (finished, ground EDD/AN or NQ/GN/AN) and RDX were weighed and then mixed thoroughly in beakers. In all cases with RDX, the EDD/AN or NQ/GN/AN was made by method 3. above, i.e. fast-freezing on stainless steel.

The formulations with TNT were made by grinding the AN in the mortar and pestle to about the usual particle size, weighing and placing it in a beaker with a solution of the pre-weighed TNT in an excess of toluene. Product was stirred while warming slightly (less than 50°C) with dry nitrogen sweep over the surface to constant weight. The product was then lightly crushed to break up small, soft lumps.

Fabrication and Assembly for Confined Small Scale Detonation Velocity and Depth of Dent Test

All materials were pressed in a die of 9.525 mm inner diameter, unheated, unevacuated, at about 3800 kg/cm² with a dwell of about two minutes. Length of pellet varied from 6 to 12 mm. Density was measured soon after pressing, by weighing to 0.1 milligram and measuring diameter and length by micrometer to the nearest 0.0025 mm. Density was also measured again prior to assembly into shot tubes because it had been found that some pellets would not fit into the 9.652 mm ID of the tubes due to spring-back. This was quite significant, especially in the EDD/AN formulations and in pure EDD. Because of this factor and occasional slight irregularity of pellets (corner chipped, etc.) density results were rounded from the nearest milligram/cc to the nearest 0.01 gm/cc.

The tubes for the confined small-scale detonation velocity and dent test (Fig 1) were steel cylinders 76.2 mm long with 25.4 mm OD and 9.65 mm ID. Pellets were assembled into these tubes with a pellet near the average density of the stack placed next to the witness plate. Those pellets whose density differed most from the average were placed nearest the detonator. Additive height was checked against height in tube to avoid gaps. Pellets that could not be inserted as they were because of spring-back were first lightly abraded dry. All pellets fitted quite tightly. In no case would there have been radial gaps greater than 0.025 mm.

A booster pellet, normally Comp B, was placed in the tube and an exploding bridgewire (EBW) detonator in a plastic holder was glued in with a drop of cyanoacrylate adhesive or fast-setting epoxy.

Two witness plates were adhered together with a drop of cyanoacrylate and the loaded tube was similarly adhered to it, taking care not to touch the explosive with the adhesive. All surfaces were flat to better than 0.025 mm and the nature of the adhesive assured flatness and contact, as it will not set except in thin layers. Two witness plates were used because small tensile cracks were found in

the first few shots when using only one, with powerful explosives. Stacking two instead of using one twice as thick has two advantages: material supply and fabrication is easier since plate stock 3/4" thick by 2" wide is common; and the first plate apparently has a lower reflected tensile shock, leaving it in better condition for measuring dent depth. The second plate apparently carries off much of the shock energy by separating from the first before the reflected shock returns from the output face of the second plate.

The assembly was then placed in a special chamber able to confine the shock, blast, and debris. The assembly rested vertically with the witness plates on thick foamed polyethylene or foamed polyurethane. The six pin wires for measuring detonation velocity D, when used, were connected, as was the coaxial detonator firing cable. The chamber was closed and the shot fired behind blast doors in an explosives safety hood.

Detonation Velocity

The D records were obtained from the output signals from the pins (see Fig 1) by the following combination of instruments. The pin mixer circuit output was put into a channel of a transient digitizer (Biomation Model 8100) that provides 2,000 samplings at a variable pre-selected sampling rate. The smallest sampling interval, 10 nanoseconds, was used. The input voltage is measured, digitized, and "memorized" at each of those intervals. Output is a voltage proportional to the digitized value (the digitalization is for storage purposes) and the time of output is 20 seconds for the 2,000 points. The output was connected to a galvanometer of a Honeywell Visicorder (paper) oscillograph, Model 906C -- set to run at 127 mm per second. Simultaneously, outputs of a time-mark generator, Textronix Model 184, at 1 second, 0.1 second, and 0.01 second were paralleled at successively lower voltages and connected to another of the oscillograph's galvanometers. These gave crystal-controlled time marks along the paper at what are effectively 1 microsecond, 0.1 microsecond and 0.01 microsecond (10 nanoseconds) because the digitizer playback time of 20 seconds is 10^6 times as long as the input sampling time (2,000 x 10 ns). The digitizer oscillator is also crystal controlled at high accuracy, similar to the time-mark generator.

The oscillograph paper, UV-light activated, develops in fluorescent room lighting in a minute or so. Reading the time interval between pin signals then is simply a matter of counting the time marks between signals. Precision and accuracy is 10 ns, with no linearity or reading error greater than that. The space interval between pins was a constant $9.525 \text{ mm} \pm 0.013 \text{ mm}$ (as a tolerance; dispersion was actually lower). D thus had an intrinsic resolution in one space interval not statistically poorer than about 25 m/s. Other potential sources of error (e.g. pin not fully inserted and touching the explosive) can make individual interval error greater than that.

But averaging over several intervals or considering several intervals as a larger one increases the proportional accuracy, so that the overall statistical precision and accuracy was on the order of 10-15 m/s. All the values obtained were rounded to the nearest 10 m/s.

Depth of Dent

After the shot, it was always found that the two thicknesses of the witness plate had come apart. The upper piece was measured for dent depth by dial indicator with a small-radius tip, reading to the nearest 0.025 mm. The witness plate was put on a flat surface plate and the dial indicator zeroed to the upper surface of the witness plate by trials at the midpoints of the four edges. There was usually some overall curvature (concavity of the top, convexity of the bottom) especially in those dented the deepest; and sometimes there was edge damage from collision with the chamber or other plate after separation, etc. The effects of these distortions were avoided by care in the zeroing process. Depth of dent was then measured to the deepest point, without regard to its width. The deepest point was in the center of the dent and was usually of small width. Sometimes the deepening toward the center was gradual over much of the total width. Lip height was read a number of times, but, like the few volume measurements tried, seemed to be an irregular or insensitive measurement, possibly due to inadequate precision in the measurement.

Thermal Tests

Differential thermal analysis (DTA) and a few thermogravimetric analyses (TGA) were done on a DuPont Model 900 thermal analyzer, programming upward from room temperature at 20°C/minute. The principal information sought was melting points and temperatures of major exotherms.

Time-to-explosion, a variant (Ref 8-10) of the explosion temperature test was done in an apparatus available for the purpose. Samples were pressed and sealed in copper blasting cap tubes, immersed in liquid metal at various temperatures and the time to explosion noted.

Vacuum thermal stability was by measurement (Ref 11) of gas evolution from combinations of constituents at stated temperature and duration. The normal sample size was five grams. Any reductions in sample size because of excessive evolution of gas or for comparative purposes are noted with the results. In addition, a chemical reactivity test (Ref 12) was done on the NQ/GN/AN system.

Impact Sensitivity

The standard Picatinny Arsenal Impact Test (drop hammer) (Ref 11) was done on all materials, primarily as a safety check. The test was also sometimes conducted in the manner of a Bruceton method, and in

a few cases Type 12 tools (ERL type tests) were used, both with (Type 12A) and without (Type 12B) sandpaper.

Shock Sensitivity

A small-scale gap test was also used, to give some measure of shock sensitivity. It was essentially identical to the NOL small scale gap test (Ref 13, Figure 1) which uses explosive of 5.1 mm diameter confined in 25.4 mm diameter brass.

Miscellaneous Tests and Measurements

A few hygroscopicity measurements were made, as were some x-ray diffraction studies and solubility measurements of EDD in water. A number of samples were studied in a hot-stage microscope mainly to determine eutectic temperatures and compositions.

Computations

The TIGER code (Ref 1) was used to indicate ideal explosive detonation performance. This corresponds to what might be expected if reactions were not time-dependent and were (along with the products) within the domain of the code's input parameters and calibration. In addition, chemical energy potential of the compositions was calculated as described in Table 7.

RESULTS

Thermal Tests

Table 1 gives the melting points and exotherm temperatures as determined by differential thermal analysis (DTA). The DTA value of approximately 102°C obtained for the eutectic melting temperature of EDD/AN agrees with published data. (There is some variability in the literature.) The hot-stage microscope gave 102.4°C at almost isothermal conditions and also indicated that the eutectic composition is about 50/50 by weight. The minimum heating rate used in this determination was 0.2°C/minute. There was no evidence of solid solutions, compound formation, etc. DTA indicated a previously unreported solid-solid transition in EDD, which was confirmed by microscopy, at 131.4°C. Melting point of the EDD, by hot-stage, was 185.5-185.6°C.

Using hot-stage microscopy, we obtained 128.4°C and 79.7 mol percent AN for the GN/AN eutectic and 113.9°C for NQ/GN/AN (also designated NGA). Urbanski, (Ref 14), gives 113.2°C and 17.5/22.5/60 weight percent for the latter.

DTA did not indicate instability or reactivity between EDD and AN, or between NQ, GN, and AN, or in their mixtures with RDX, as determined by unchanged major exotherm temperatures. The same systems with

TNT were also satisfactory, although there was some lowering of the GN/TNT exotherm, to near the GN melting point, in thermogravimetric analysis EDD weight loss started at about 215°C, and was not rapid until 275°C.

There was no evidence of transition modification in any of the cases, except of course for those caused by eutectic melting.

EDD/AN is strongly reactive with zinc, nickel, copper, and lead. It is somewhat reactive with iron and stainless steel, and only slightly so, if at all, with tantalum, tin, and aluminum. The NQ, GN/AN system appears to be reasonably compatible with iron, aluminum, and brass.

Results are given in Table 2 for vacuum thermal stability (VTS) and the chemical reactivity test (CRT). The results of Table 2 agree in general with other thermal test results, except for an anomaly in the NQ/GN/AN data which is ascribed to impurities in a batch of NQ whose lineage and quality are not fully known. (It was not a standard production batch.) The NQ alone, of that batch, produced excessive gas. When this batch and a standard production batch were run at the same time in the CRT,* the latter did not produce excessive gas, either alone or in combinations with GN and AN. The usual VTS figures (Ref 15) for gas evolution from NQ are of course low, since the material is accepted for service use as a propellant and as an explosive. (The series of tests described above on NQ was precipitated by the observation of a few bubbles forming in the melt under the hot-stage microscope while studying the eutectic system.)

The Henkin time-to-explosion data are summarized in Table 3. Because of the conditions of the test and the limited number of samples the data were used only to assess the relative thermal stability of the systems. It may be seen that EDD and EDD/AN had about the same explosion temperature as Amatex 20, or slightly below those of RD4. The NQ/GN/AN system showed higher stability.

Impact Sensitivity

The results of the Picatinny drop weight impact tests done as safety screening tests to categorize the order of sensitivity are given in Table 4. All the materials and formulations were found to be of the same order of impact sensitivity as TNT, or less sensitive.

A few tests were also conducted using type 12 tools (BuMines method). These tests gave results that showed similar relative sensitivities of explosives. However, insensitive explosives such as TATB

*This CRT, which was devised by Lawrence Livermore Laboratory, includes gas chromatography. It was carried out by Eglin Air Force Base.

and AN give no response at the maximum height of the tester with Type 12 tools.

The Bruceton up-and-down method was done in a very few tests and gave results close to the Picatinny method. In the latter method drop height is reduced by 2.54-cm (1 inch) increments until 10 tests at a given height give no response. The impact sensitivity height is then quoted as the increment higher (i.e., that height at which there is at least one "go" in ten or fewer drops). As might be expected, the Bruceton results, designed statistically to give 50% heights, were slightly higher than Picatinny method results, which are statistically closer to 10% heights.

Shock Sensitivity

The data obtained from the NOL small-scale (5.1 mm diameter) gap tests are summarized in Table 5. Figure 2 is a plot of depth of dent in a witness plate of steel 1/2" thick and 1" square placed as a termination of the NOL small scale gap test (SSGT). The test was run on a small number of samples by an up-and-down method using half of the maximum dent depth (no attenuator) as a turning point for increase or decrease of attenuator thickness. All of the values that resulted in a dent are shown in the figure. Those that resulted in failure to detonate and hence no dent are not shown. All of the latter are to the right of the vertical dashed lines in the figure. The attenuator thickness for these lines provides a qualitative comparison for small scale shock sensitivities of the reference explosives. Thus the order of the explosives, from greatest to lowest shock sensitivity is RDX, Comp B, Amatex 20, TNT and EDD.

In Figure 3, the abscissa scale of Figure 2 is extended to lower attenuator values and the scale expanded. Note that the EDD line of Figure 2 would be located at 130 in Figure 3. Figure 3 presents the results for ethylenediamine dinitrate/ammonium nitrate in the ratios by weight 50/50 and 70/30 with three different preparation procedures used.

Detonation Velocity and Depth of Dent

The data obtained for these performance parameters are presented together with an evaluation of their significance in the DISCUSSION section of this report.

Casting

A small sample of 50/50 EDD/AN was melted and its liquid density taken. It was found to be 1.49 ± 0.01 g/cc at approximately 110°C . After pouring and freezing in a small metal mold, the product, white in color, was found to be very hard and strong. Accurate density could not be taken because of shrinkage voids, but the theoretical maximum

density is 1.657 g/cc. Thus both liquid and solid densities are near those of TNT.

Hygroscopicity

The tests for hygroscopicity were informal, and limited to ordinary conditions. Several samples of EDD/AN and NQ/GN/AN powder were left exposed in room conditions overnight or over weekends, and were weighed before and after exposure. Some of the EDD/AN samples were co-melted, some co-crystallized. In no case was there a significant weight change, or a change in texture of the powder. (Occasionally a very light caking occurred in closed bottles; a light tap on the bottle loosened the powder.)

In addition, two samples of EDD/AN were carefully prepared and tested. The samples, 44/56 EDD/AN, were co-crystallized from water, ground in a mortar and pestle to a median 350 micrometers dried in warm air then in vacuum to constant weight, then further dried in a vacuum desiccator (with fresh phosphorous pentoxide) overnight. The samples (0.5 gram each) were put on watch glasses, weighed, and left in a temperature and humidity controlled room, at 70°F and 51% RH for 48 hours. The weight changes were +0.0001 and -0.0008 gram. The texture was unchanged, and the powder was still loose.

Solubility of EDD

Not finding any formal data on the solubility of EDD in water, measurements were made giving the following results

<u>T°C</u>	<u>Amount Dissolved g/ml</u>	<u>Deviation in % from Equation</u>
23.96	0.992	3
42.92	1.718	1
52.26	2.090	1
81.64	3.344	1

The above data may be fitted by the following equation.

$$\text{Sol} = 0.0409T - 0.0174$$

where T is in °C between approximately 25 and 80°C.

X-Ray Diffraction

The results of x-ray diffraction measurements on a co-crystallized sample of 50/50 EDD/AN are presented in Table 6. The data exhibits the characteristic patterns of the individual components, EDD and AN. No peaks were observed that could be attributed to new compound formation. No x-ray diffraction measurements were attempted to provide data on

effective particle size (degree of intimacy) of the components.

Scanning Electron Microscopy (SEM)

An SEM study was made of a sample of EDD/AN 50/50 prepared by the slurry procedure (see earlier section on Formulation). The photographs presented in Figure 4 were made at Los Alamos Scientific Laboratory (LASL) and are typical of others obtained. Informal guidance was received from scientists of LASL and the National Bureau of Standards (NBS). The technique used at LASL is based on gold plating in a good vacuum, and then using the electron beam to etch out one of the two components, leaving the other behind. The micrographs show that there are two distinct phases present and that intimacy at the one micron level (of at least one constituent) has been achieved. Further interpretation is given in the DISCUSSION in connection with usable diagnostics for intimacy.

Dimensional Stability

Pellets of EDD/AN 70/30 and 50/50 were pressed at a diameter of 19.65 mm (0.75 in.) under a load of 4536 kg (5 tons). Densities were calculated from weight and dimension measurements taken shortly after pressing (26 January 1976) and about six months later (20 July 1976). In the interim the samples were stored in closed unsealed conducting rubber containers at ambient temperature. The average density of EDD/AN 50/50 changed from 1.6354 to 1.6117 and that of EDD/AN 70/30 from 1.599 to 1.4772. This change is probably due to strain relaxation immediately after pressing (springback) since other measurements made directly after pressing have shown that this explosive does have sufficient springback to explain this density change.

DISCUSSION

Potential of AN and Some Fuels

Ammonium nitrate (AN) has long been interesting as a military explosive and has become the most commonly used component of industrial explosives because it is inexpensive and is available in very large quantities, and is stable, dense, etc. It has also long been interesting to those concerned with the science of high explosives because it falls by a significant margin to yield the performance predicted by calculations for an ideal explosive.

If AN behaved like an ideal explosive, calculation by equivalent codes such as BKW or TIGER (Ref 1,2) indicate that, at its maximum density of 1.725 g/cm^3 , it should have a detonation velocity D of about 7.84 km/sec and detonation pressure P of 21.3 GPa (213 kbar). For Amatol 60/40, AN/TNT, by weight, the predicted values at a density of 1.58 are a D of 7.79 km/sec and P of 24 GPa (240 kbar). Experimentally for Amatol 60/40, at densities of 1.5 to 1.6, D is in the

range 5.6 to 5.8, depending on conditions of test. Thus experimental D values are about 2 km/sec below predicted ideal potential. It has been noted that the experimental data can be matched by calculations if only 19% of the AN is assumed to contribute to propagation of the detonation front, the rest being treated as an inert (Ref 16).

The total chemical energy available (see footnote with Table 7) from AN, some fuels, and their mixtures is given in Table 7. Slight differences between these calculated values and others may arise from differences in the sources of heats of formation, or the product assumptions. Herein O is used for H₂O first, then for CO to the limit of free carbon, then CO₂; N and any remaining C, H or O are free in their ground states, i.e., as solid C, or N₂, H₂, or O₂ gas. TIGER-calculated performances are given in Reference 16 and have been quoted above for comparison with experimental detonation velocities. Both of these sets of calculations are useful as approximate upper bounds on performance.

Note in Table 7 that AN has only 0.354 kcal/g (0.610 kcal/cc) of chemical energy available, if the 1/2 mol of O₂ in its detonation products goes unused. This should be compared to about 0.8 to 1.3 kcal/g (1.3 to 2.5 kcal/cc) for most common military explosives. However, if the 1/2 mole of O₂ is used to burn carbon to CO, the total energy is then 0.595 kcal/g of AN + C. Similarly, burning the 1/2 O₂ to CO₂ gives .878 kcal/g, which is now close to the energy of TNT (Table 7).

The total energy and products evolved in detonating heavily confined Amatol corresponds to eventual reaction of all the AN, as indicated by preliminary large-scale experiments (37 mm diameter by 330 mm long cylinders) experiments (Ref 17) in an evacuated chamber instrumented for sample analysis and approximate calorimetry. It was found that the confinement of Amatol 60/40 (AN/TNT by weight) and Amatex 20 (RDX/TNT/AN 20/40/40) produced almost a tripling of the CO₂ concentration in the final products, with a corresponding decrease in % CO. Unconfined charges evidently do not react completely. The reactions that provide the final products are not only those of detonation and initial expansion, but can include later reactions related to reshocking; e.g., some free carbon may be able to react with free oxygen or water when shocked to higher temperatures at the chamber walls, after having expanded to "freeze-out" (Ref 18, 19).

Since the final products and total energy (heavily confined experiments described above) can approach calculated values (Table 7), the disparity in power (e.g. detonation velocity, early wall motion in cylinder test) between calculation and experiment is probably caused by reaction times. AN, as it is normally used, simply does not decompose into its final detonation products fast enough. Perhaps that is due to the magnitude of reaction rate constants induced by the environment provided--detonating TNT in the Amatol case--or because there

are intermediate products, or because the bulk of the AN is shielded by itself from the detonating TNT environment. The first two are kinetics factors possibly modifiable by chemical and physical environmental changes: higher temperatures and pressures might increase reaction rates, or catalysis might change the intermediates, as might reaction with another substance. The third is a transport factor which would be responsive to particle size. So there appear to be possibilities of improving AN reaction rates, and thereby its power or ideality. And, as shown in Table 7, there is a related opportunity of improving total potential energy by adding fuel, particularly if the fuel is in a form that the AN could react with in extremely short time frames.

Improvement in the power or detonation velocity of good unimolecular explosives (e.g. HMX) is not expected by such considerations, although total energy might be improved by stoichiometry. But compositions containing them and slow non-ideal explosives can be improved, as was demonstrated in some AN-containing systems (Ref 6).

If the fuel could increase both the reaction rate and the total energy, improvements in the power of AN-containing explosives might be quite significant. To accomplish this, fuel and oxidizer molecules must be present in appropriate numbers and as close together as possible.

Processes and Limits

The principal purpose of this work is to advance the technology of militarily useful explosives. It was therefore considered best to limit present studies to solids and to limit the oxidizer to AN. (Other oxidants have been considered theoretically and will be included in future studies). These limitations impose considerable constraint upon the selection of fuel and the processes of mixing.

If there were no practical particle size limitation to solid materials, mixing could be very uniform and complete, even down to the molecular level. To obtain greater intimacy than can be provided by simply making particles smaller, within the rheological limits imposed by the usual requirements of castability, cosolidification has been used to achieve a physical synthesis (as in eutectics) of components. The two forms of cosolidification we have used here are crystallization from a common solvent, and freezing from the molten state. The fuels selected thus needed particular physical properties as well as the proper chemical structure.

AN and most of the fuels used thus far are very soluble in water. Thus when rich aqueous solutions of the two materials, in the proportions desired, are heated under vacuum, the fraction of water being stripped away per unit time is high, and crystallization of large amounts of solid occurs quickly. That tends to keep individual crystal

size small. Larger aggregates of small crystals may form. These can be advantageous rheologically, although they are a source of difficulty for particle size and intimacy analysis. Losses in weight (through loss of product in processing) were usually small, and there were no cases of weight gain, but remanent water content cannot be stated, as moisture analysis was not done. The characterization on a microscopic scale of the achieved product with respect to closeness and relative surface areas of fuel and oxidant is difficult. Some progress has been made using scanning electron microscopy (see Fig. 4 and later discussion thereof).

Co-freezing from a common melt has some theoretical advantages, e.g., for the formation of solid solutions or compounds, freedom from extraneous or occluded solvent, etc. However, there was no evidence of component intimacy beyond that of eutectics in the EDD/AN or NQ/GN/AN systems. Perhaps the principal attraction of the co-frozen method is that at the eutectic proportions there is a good potential for the maximum intimacy of all of each component. At that composition all is liquid above the eutectic temperature. As cooling and heat removal take place, the components must freeze at the same time in the original proportions. It is thought this can be made to yield what are effectively very small particles, in terms of the individual components. At proportions different from the eutectic, of course, one of the components freezes out by itself upon cooling, leaving the remaining liquid nearer the eutectic composition. The size of the rich-component particles thus produced are not likely to be as small, being entirely dependent on the freezing or recrystallization rate by which the eutectic temperature is approached. When component ratios desired are not near those of a eutectic or not part of it, the additional desired amount of either component material can be added in the proper particle size to the eutectic melt at a temperature just above the eutectic temperature.

Dent and Detonation Velocity Test Comments

Small scale witness plate dent tests have the disadvantage of being a strong function of both diameter and confinement and sensitive to small changes in rate properties of the witness material. On the other hand they are readily done, and easily measured, they have reasonable discrimination and reproducibility, and they provide excellent screening of materials at low cost. In general, dent tests yield information additive to that provided by other performance tests, regarding energy and power of an explosive on an intermediate time scale: later and longer than thin flyer plates or shock fronts in water, earlier and shorter than total energy measurements such as calorimetry or underwater bubble tests. The timing, depending on the scale of the dent test, can be similar to that of the LLL cylinder test (Ref 20), but the shock is head-on. This time scale is important to the study of non-ideal explosives and their applications in certain munitions. Fragmentation munitions are included, as plate denting tests indicate

brisance (Ref 21) and operate over a period significant to the acceleration of metal (Ref 22 and Appendix 2 of Ref 6).

The test as used in this work, 9.65 mm explosive diameter heavily confined within 25 mm diameter steel or brass, has been roughly calculated to produce most of the deformation in thick steel witness plates in about 5 microseconds (Ref 6). The dent formation is related to the period during which the force or pressure produced by the explosive is above the dynamic yield stress of the witness plate. The limited data available on the properties of the witness material in such short time frames for such severe loadings prevents precise computer calculation of dent formation.

The time of 5 microseconds or thereabouts is quite short. Although it is an order of magnitude or two longer than the reaction time of ideal explosives like RDX (Ref 23), it is also one or two orders of magnitude shorter than some nonideals (Ref 24). The absolute value of energy release time is significant because it relates to the size of munition to which there can be useful application (Ref 6).

Variations in dent depth may be ascribed to alterations in rapid energy release caused either by changes in the total energy, or in the time distribution of its liberation, or by combinations of both. Although depth of dent might be varied by changing the impedance matching of the explosive to the witness plate, this did not occur in these experiments. All the materials were organic nitrates or organic explosives of rather similar mechanical properties and density. The total density range was 1.46 to 1.71 g/cc, with all but a few of the tests at 1.60 ± 0.1 g/cc. The output surface of the explosive column was flat and flush with the thick-walled metal cylinder whose end surface was also flat, like the witness plate it rested on.

Although confinement was very heavy by ideal explosives standards--the radial confinement was several ideal reaction zone lengths of dense strong metal, nearly 8 mm of steel or brass--confining effects on the nonideals studied may have been much less than "infinite". Hence one would be in a region of strong diameter dependence, perhaps not too far from a failure diameter. Thus small changes in energy release rate can have magnified nonlinear effects and variations in conditions of test (e.g., preparations, density, intimacy) can lead to large variances in the results.

One possible apparatus effect to assess is preshock, i.e. a shock can be propagated in the confinement that precedes the detonation and may alter the explosive column and can trigger the D measurement pins. This is not a strong effect because of attenuation in the confinement and poor coupling to the explosive within. Since the formulations of interest are relatively insensitive, booster pellets were used to initiate the explosive columns. The pellet used was 9.65 mm in diameter by about 9.5 mm long. Comp B or TNT was used when

sensitivity was high enough; pellets of 95% HMX were used occasionally for very insensitive formulations. Although a check of results showed no effect of pellet material (or steel vs brass tubes) we favored TNT when preshock might conceivably be a cause of failure or erratic detonation velocity. TNT can put a shock of up to 5.3 km/sec into steel (about the same in brass), Comp B a shock of up to 5.5 km/sec, and 95% HMX a shock of up to 5.8 km/sec. These shock velocities are close to or higher than some of the detonation velocities expected and measured, but they would not persist for the entire tube length if unsupported. Tests with inert fillers in the tubes showed no effects of the pellet shock on the detonation velocity pins beyond the first one or two, little or no effect on the steel tube beyond half its length, and no observable effect on the steel witness plates. We conclude that preshock did not seriously interfere with the experiments and that the results were not affected much if at all. However, for future experiments, a smaller diameter booster pellet, decoupled from the tube, might be advantageous. Tubes in which shock velocity is lower might also be useful but not if their strength is much lower. A few tests with tubes made of a dense, weak metal (50/50 lead/tin solder) gave lower detonation velocity and shallower dent for a TNT/AN formulation and resulted in failure in a mix expected to propagate.

Dent and Detonation Velocity Results

In the RESULTS section it was stated that these results would be both presented and discussed together in this section. In Figures 5 and 6, there are plotted the effects of substitution of AN for EDD in environments with and without RDX. There is also shown the effect of using an inert with EDD instead of AN. The following overall trends are observed:

- a. As RDX content is increased, higher performance is obtained.
- b. Inert* substitution for AN reduces performance, more so for higher AN content compositions.
- c. The detonation velocity results decrease monotonically, but the dent results show an initial rise, with a broad peak in the vicinity of 50/50 AN/EDD, followed by a decrease as the AN content is further increased.

*The inert is 90 wt % ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, 1.769 g/cc, and 10% ammonium sulfite, $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, 1.41 g/cc. So both weight and volume proportions of the inert are the same as for the substituted AN. It was assumed that this mixture would not be a source or sink of explosive energy.

d. The peak at intermediate proportions supports synergism of EDD/AN as the cause and makes a simple replacement explanation untenable. The fact that it occurs for dent and not for D indicates that the effect occurs beyond the detonation zone.

e. Differences associated with preparation method are apparent from 50% AN and up.

Additional details supporting and amplifying these overall trends are presented in the remaining paragraphs of this section.

At 50% Inert there was no dent and although there seemed to be initiation from both TNT and Comp B, failure to propagate occurred early in the column. With 50% AN (instead of Inert) propagation proceeded to the end of the column in all cases and the dents are about the same as for pure EDD.

The co-frozen system exhibited variability. Incipient failure was indicated by rather shallow dents at 50% AN, and failure occurred near the end of the column at 56% AN; still, moderate dents were produced at 60% AN. The reversal might be explained by the lower density and hence possibly higher shock sensitivity of the 60% samples: 1.56 g/cc (6.6% voids) versus 1.59 g/cc (4.5% voids) for the 56% samples. Different co-freezing methods apparently gave differing results, perhaps amplified by the size of the test and the low sensitivity of the formulations.

The co-crystallized systems produced deeper dents and higher D at 50% and 56% AN than the co-frozen. The difference cannot be ascribed to density-induced effects on shock sensitivity because density was higher in one case, lower in the other. Nevertheless, shock sensitivity could differ for other reasons. Recrystallization from water, in which solubility of both components is very high may result in a far different product from that obtained by melting and freezing. The particle matrix conditions may be different and there is a possibility of remanent water, which there would not be after the melt/freeze process.

RDX was also fired with EDD, TNT, AN and Inert in simple binary mixes. The results are shown in Figure 7, where it may be seen that each of these components when present individually in the binary mix, reduces the performance as compared to pure RDX. Note that TNT and EDD are about equivalent in their effect when combined with RDX and that AN is superior to Inert but inferior to TNT and EDD. In contradistinction to the results shown in Figure 5, where AN and EDD were present together, there is no significant evidence in the shape of the curves that would suggest synergism between RDX and the other constituents. In Figure 8, this point is made more evident by making AN the independent coordinate and contrasting dent results for EDD/AN with those for TNT/AN and RDX/AN. The peaking phenomenon for EDD/AN

is clearly shown. It is important to note (see Table 7) that the total potential energy of CO-balance EDD/AN 70/30 is actually less than for EDD alone. Yet the dent increased (Figure 5) as AN was added to EDD to reach 70/30 EDD/AN. Further, in the mixtures driven with RDX, the increase as AN is added to EDD is even greater.

If, as noted above, the dent increase is not due to amount of energy, then it must be due to distribution of energy, i.e., the fraction made available or the rate of its release or both.

As an alternative explanation one could advance the hypothesis that variations in impedance match at the explosive/witness interface could significantly affect the pressure-time characteristics of the explosive. However, the density and detonation products of the different explosives involved are virtually the same, leading to rejection of this hypothesis.

A second alternative explanation would link the observed results solely to differences in Chapman-Jouguet pressure. It is well known that this pressure is directly related to depth of dent for the unconfined case (Ref 21). Release of energy subsequent to the detonation zone contributes to deepening the dent in the heavily confined test used here. Note in Figures 9 and 10 that depth of dent is noticeably greater in every cosolidified case at a given D or ρD^2 than the ideals or non-cosolidifieds at the same D or ρD^2 . Conversely, D or ρD^2 is lower for a given dent in the cosolidifieds. Since detonation pressure P is a linear function of ρD^2 (if γ is constant) we have the result that deeper dents were associated with release of energy behind the detonation zone, presumably due to synergism occurring in this later time frame.

These results (Figures 5 through 10) are strong evidence of the sought-for Taylor wave modification, with pressure/time and isentropic expansion characteristics altered in a manner and to a degree that can be useful in devising explosives for particular munitions.

The cause of the EDD/AN synergism is suggested by the comparative results with TNT/AN: i.e., the cause would seem to be physical rather than chemical. The TNT/AN systems showed no increases in dent or detonation velocity whatever, the AN behaving in these tests only as a diluent. Yet the potential energetics are almost identical with the EDD/AN system at CO balance (and far greater at CO_2) and the explosive properties of TNT and EDD are quite similar. Furthermore, dents of EDD and TNT with only RDX--no AN--are nearly the same (Fig 7). The cause of the synergism is thought to be the juxtaposition of oxidizer and fuel molecules. We have no numerical description of the effective EDD or AN particle size distributions and hence no oxidizer/fuel distance statistics for those systems but we have little doubt that although the external size of the EDD/AN particles was the same as the AN in the TNT/AN systems--on the order of 350 micrometers-- the

internal (see later Discussion of SEM results) effective sizes and distances are on the average much smaller and shorter. That, of course, was the aim of the cosolidification process, as mentioned earlier, as one process which might be used to carry out what has been called physical synthesis (Ref 25), a parallel to chemical synthesis.

The results of tests with NGA, the eutectic of NQ, GN, and AN, are included in Table 8 and were also used in Figures 9 and 10. According to Urbanski the eutectic proportions are 17.5/22.5/60 weight percent (Ref 14). These proportions are also very close to CO₂ balance (about 19/22.3/58.7). Due to the insensitivity of NGA, pellets of high-density HMX/Kel-F 95/5 had to be used for the initiating booster. The NGA propagated marginally when combined with 20% by weight of RDX. With 40% RDX it gave good performance, similar to some EDD/AN's with 20 and 40% RDX, in terms of both dent and D.

The effectiveness of the EDD/AN and NGA type of system is depicted, and is quantified to a degree, in Figure 9, where dent is plotted against D. The points seem to fit two distinct families, rendered more visible by the eye-fitted curves. The situation is the same in the plot of dent vs $\rho_0 D^2$ (Fig 10). It should be recalled that density on which detonation pressure depends, is virtually the same in the cosolidified and non-cosolidified families. (That being the case, a quadratic fit to $\rho_0 D^2$ is sure to follow a linear fit to D. Nevertheless, if gamma is the same for both families, then $\rho_0 D^2$ really represents detonation pressure.)

The performance listing of Figure 11 also shows how AN reactivity and contribution can be modified by the right kind of fuel and/or its intimacy of contact with the oxidizer. TNT is potentially a very rich fuel, providing enough carbon for CO balance at 45/55 weight percent TNT/AN, CO₂ balance at 21/79. That the TNT does not react with the AN in the time scale of these experiments is shown by the Amatol-like formulations of 70/30 and 50/50 TNT/AN, as has already been discussed. These formulations have moderate particle size AN, about 350 micrometers median diameter (finer than the usual Amatoles), and the TNT was incorporated by lacquering, i.e. evaporating a solvent from dissolved TNT while stirring the solution mixed with AN. As has been seen the AN is a diluent, the dent performance being degraded from TNT and the D lowered. But reaction does take place eventually. The ballistic mortar test gives higher energy for Amatoles than for TNT, the highest being for 80/20 Amatol, which has 80% AN and is thus CO₂ balanced (Ref 15).

Performance of all the systems is summarized in Figure 11 to facilitate comparisons. RDX provides the deepest dent and highest detonation velocity. Reducing RDX to 50% by substituting TNT--i.e., the Comp B ratio--results in a small loss in dent and a moderate loss in D. That performance can be matched in dent with 20% RDX, and in both dent and D (almost) at 40% RDX with EDD/AN instead of TNT. Or,

with slightly more loss, NGA can be used instead of EDD/AN, with 40% RDX. Any of the 20% RDX EDD/AN family exceeds Amatex 20 in dent, while the 40% RDX system with either EDD/AN or NGA exceeds Amatex 20 in detonation velocity also.

Materials: Sources, Availability, Previous Uses, Cost

AN, produced industrially at numerous locations in very large quantities, is made by reaction of nitric acid with ammonia, neither of which depends on petroleum, which could be an important strategic advantage. Most ammonia is made by catalytic fixation of atmospheric nitrogen with hydrogen (Haber process), while nitric acid is made by catalytic oxidation of ammonia using atmospheric oxygen (Ostwald process). The present cost of AN is one the order of 15¢/kg (7¢/lb).

Ethylenediamine dinitrate, $\text{H}_2\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2^+\cdot 2\text{HNO}_3^-$ or $[\text{O}_3\text{N}^+\text{H}_2\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2^+\text{NO}_3^-]_2$, $(\text{C}_2\text{H}_{10}\text{N}_4\text{O}_6)$, density 1.395 g/cc, can be made simply by reaction of ethylenediamine (see below) and nitric acid, as described in Procedures. It is a process which would be easy to scale up, on ordinary chemical explosives manufacturing facilities. Cost should be on the order of 50¢/kg (25¢/lb), with nitric acid at 6-7¢/kg and ethylenediamine at \$1.40/kg (63.5¢/lb); processing cost would be low.

To put these costs in perspective, they may be compared to the current (early 1976) prices of \$0.75/kg (\$0.35/lb) for TNT and \$2.30/kg (\$1.05/kg) for RDX.

The ethylenediamine industrial process uses ethylene glycol and an excess of ammonia in Monel metal over activated alumina. Its main use seems to be as a plasticizer in the polymer industry, and it is made in quantity. Present price (March 1976) is \$1.40/kg of 63.5¢/lb in tank car quantities. Ethylenediamine can be made synthetically, independent of petroleum (and was, by Germany in World War II), from ethanol, ammonia, and nitric acid.

EDD was used as pressed charges in shells, as cast charges in mixtures with AN, as boosters in mixtures with waxes, and as under-water charges, by Germany in World War II. EDD and eutectics with AN and mixtures with other materials were studied after World War II in France and its continued study and use were recommended, e.g., to replace Amatsols.

References 14 and 26-31 provide key data and historical background for combinations of ethylenediamine dinitrate, AN and RDX.

A plant for making considerable quantities of NQ within the United States is in the latter design stages. The process will remove an H_2O from GN with concentrated sulfuric acid. The existence of the plant will increase the availability of both GN and NQ.

Thus, from the above paragraphs, it is seen that the materials studied could be practical for large-scale military use, from the standpoints of availability (both industrial and strategic) and cost. Other advantages are low toxicity, industrial familiarity, and processability in existing explosives manufacturing and loading facilities. Problems may arise due to possible corrosion of processing equipment and the well-known polymorphism of AN. In addition, it is necessary to obtain additional information on long-term stability, compatibility, sensitivity under high stress rates, casting characteristics, and problems associated with forming plastic-bonded explosives (PBX).

It should be noted here that although the explosives studied herein do have the described potential for military use, the goal of this program which has been met was to demonstrate that the performance of nonideal explosives could be improved by appropriate choice of partner and environment for nonideal components together with use of co-solidification techniques in the preparation of the composition.

Intimacy Diagnostics

In order to relate the changes in performance to the physical states achieved in the explosives by the preparation procedures, it is necessary to have some measure of the significant physical parameters. Since the objective in preparation has been to overcome diffusion limitation between complementary constituents (e.g., fuel and oxidant) a quantitative description of the intimacy between these constituents is required. The search for such intimacy diagnostics is described below.

One can seek to ascertain whether a new compound has been formed in a prepared sample by looking for new or additional thermal properties (DTA, hot stage microscopy) or altered x-ray diffraction patterns. In the results obtained for these parameters (Table 1 and 6) there was no evidence of compound formation.

In the absence of compounds, the significant feature is the size and shape of macrocrystals of complementary components and their juxtaposition to each other. X-ray measurements were considered for this purpose to provide average component domain sizes. However, two difficulties emerged. One was that 1000 Angstroms is the largest size of particle for which broadening of secondary x-ray diffraction peaks is a useful technique and this was too small. The other was that an x-ray scattering pattern for this purpose can only be used for particles of approximately the same size.

A second technique tried was to make surface scans of composite particles of AN and EDD using the electron microprobe of the SEM set for discerning presence of carbon. AN gives no reflected signal since it has no carbon, whereas EDD has carbon and produces a signal. Thus by cleaving a particle and running a contour map, the relation of the

two constituents would be established. Unfortunately the results were inconclusive because the irregular shape of the particle surface leads to false readings. This is because a small depression also makes the signal disappear, which can be misinterpreted as absence of carbon. This method may be usable if the noted deficiencies of the diagnostic procedure can be overcome by either or both of the following techniques:

1. The particles of interest would be first imbedded in an inert matrix (to be chosen) and then polished down to a smooth surface, presumably without altering the subject of interest in the polishing.
2. Complete scans would be sequentially made of the imbedded particle for C, O, and N, keeping track of site locations throughout so as to ascertain the topographical contributions.

The potential cost and complexity of these approaches using the electron microprobe led to deferring pursuit while another approach was tried.

The technique with greatest promise is to use the SEM electron beam to etch out one of the two components, leaving the other behind. A series of photographs, of which Figure 4 is an example, were obtained in this way. As stated in the RESULTS, two phases, intimate at the one-micrometer level, may be deduced from the photos. One interpretation of such photos that was considered is that the residual dendrite structure (see Figure 4) could arise from the excess of one component over that in the eutectic ratio. This excess would solidify first in a dendritic glob as the temperature was lowered. With continued cooling, the concentration would reach the eutectic concentration (e.g., EDD/AN, 50/50) and then solidify around the dendrites created earlier. Since the eutectic mixture has a lower melting point, it would disappear in the vacuum of electron beam heating of the SEM, leaving the dendrites. This interpretation would be directly applicable for EDD/AN 70/30, but since the photos are of the eutectic EDD/AN 50/50, some modification of this explanation is required. The residue referred to appears to be AN, as judged by comparison with other SEM photos.

To determine whether the above interpretation is correct and to better understand this technique, the following suggestions of personnel at NBS will be pursued.

1. Make SEM scans of pure AN and pure EDD after the pure components have been separately processed as the EDD/AN, 50/50 mixture has, to confirm that no dendritic structure occurs with pure components.
2. Make SEM scans of the pure materials and with EDD/AN, 50/50 as a function of electron current to see if the disappearance of the "missing" (or remaining) component in the LASL pictures can be correlated with EDD or AN.

3. Make SEM scans of slurry preparations of different AN/EDD concentration to see if the dendrite/void volume ratio depends on how far from the eutectic composition one starts.

To the above described intimacy diagnostics directed toward very small macrocrystals, one should add techniques using differential staining of constituents followed by optical microscopy. In addition, surface area and particle size distribution techniques following chemical separation can be used for some compositions with larger particle sizes.

FUTURE WORK

It has been shown that the performance of a valuable nonideal explosive (ammonium nitrate) can be improved to make it more useful in fragmenting or small-size munitions. This was done using energetic materials which are tractable and give evidence of being militarily and industrially practical. These materials are ethylenediamine dinitrate in combination with the AN, with or without driver explosives such as RDX; and nitroguanadine/guanidine nitrate in combination with the AN plus driver explosives.

It has been clearly demonstrated that the performance of the above described nonideal explosives (as measured by head-on denting of steel, which is related to the structure of the detonation zone and the following early isentropic expansion zone) can be modified and improved. The observed improvements in performance were concluded to be due to changes in the energy release rate, caused by better fuel/oxygen stoichiometry and better fuel/oxygen contact. The improved contact was brought about by cosolidification techniques, particularly by use of eutectics.

Only a few of the most basic performance and characteristics measurements have been made. These can only indicate potential and the broadest intrinsic features. Much more work must be done on both fundamental explosive parameters and on engineering factors before it can be decided whether these materials are in fact useful and practical.

Scale-up is needed first to resolve some of the uncertainties caused by possible diameter effects on performance and shock sensitivity. A linear factor of two (i.e., to about 19 mm (3/4 inch) diameter) for the size increase should make significant differences in the depth of dent and in detonation velocity at the higher AN proportions in the EDD/AN systems and at lower driver (e.g., RDX) proportions in the NQ/GN/AN system. Complementing the above tests at 19 mm with cylinder tests at 50.8 mm (2 inches) explosive diameter would provide another data point for a curve of diameter effect and direct information on metal accelerating ability.

The structure of the detonation zone and the expansion region should be determined as a function of materials and consolidation techniques. Applicable techniques include imbedded gages to measure particle velocity (Ref 32) and optical techniques for following the motion of the surface of the explosive at a contact discontinuity (Ref 33, 34).

Detonation pressure should be measured. The detonation electric effect application of Hayes (Ref 35) might be tried (although there have been difficulties using it with nonideal explosives) or the inexpensive aquarium method (Ref 36) may be used for screening, and then followed by the more accurate and informative, but more expensive, free surface velocity method (Ref 37).

Microscopic methods for particle statistics determinations should proceed, and other methods for this analysis sought. Careful reaction rate studies, e.g., by isothermal differential scanning calorimetry, might show differences in the pre-exponential factor as a function of processing.

Efforts should be expended to learn how to determine prompt (early) detonation products. Large spheres at partial pressures of inert gases might make it possible to get unconfined products without the re-shock problem. Isotopic labelling (Ref 38) could be used to gain information as to which product species contain particular atoms of the original explosive/fuel/oxidant molecules.

Engineering factors and additional safety, stability, and sensitivity parameters should receive immediate attention, paralleling the research outlined above, to learn how to use this class of potentially important explosives.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the exceptional contribution of H.J. Jackson. His assistance and support in preparation of materials, samples for test and many of the evaluations were invaluable.

We also wish to thank H. Cady of the Los Alamos Scientific Laboratory, H. Praek and other personnel at the National Bureau of Standards for their contributions to diagnostics for assessing intimacy of constituents.

T. Floyd of Eglin Air Force Base assisted on gas chromatography. E. Dalrymple, R. Gentner, J. Hendrickson, W. Velicky and W. Voreck, all of the Explosives Division, Feltman Research Laboratory, Picatinny Arsenal, contributed respectively to test firing, TIGER computations, syntheses of EDD, processing of compositions, and data reduction.

This program was conducted initially as a concept exploration as part of the In-House Laboratory Director's Independent Research Program. Additional funding was provided under the sponsorship of the JTCG/MD Working Party for Explosives. The U.S. Army Research Office (Durham) arranged for the participation of the first author under the Laboratory Research Cooperative Program.

REFERENCES

1. M. Cowperthwaite and W. H. Zwisler, "TIGER-Computer Program Documentation," Stanford Research Institute Projects 1182, 1281, 1397, March 1974.
2. C. L. Mader, "FORTRAN BKW: A Code for Computing the Detonation Properties of Explosives," Los Alamos Scientific Laboratory LA-3704, 10 July 1967.
3. M. J. Kamlet et al, "Chemistry of Detonations," J. Chem. Phys. **48**, Pt. I, 23-35, Pt. II, 36-42, Part III, 43-50, Pt. IV, 3685-3692.
4. H. Hurwitz and M. J. Kamlet, "Chemistry of Detonations-Part V," Israel Journal of Technology, **7**, No. 6, 431-440, 1969.
5. J. B. Bdzil and W. C. Davis, "Time-Dependent Detonations," Los Alamos Scientific Laboratory LA-5926-MS, June 1975.
6. J. Hershkowitz and I. Akst, "A New Approach to Improving the Performance of Non-Ideal Explosives Containing Ammonium Nitrate," Technical Report 4789, Picatinny Arsenal, Dover, NJ, March 1975.
7. B. G. Craig, J. Hershkowitz, A. W. Campbell, and Ray Engelke, "The Effects of Cosolidifying MAN/AN and QMAN/AN on the Performance of a Nonideal Explosive," Los Alamos Scientific Laboratory Report LA-6585-MS (1976).
8. H. Henkin and R. McGill, "Rates of Explosive Decomposition of Explosives," Ind. Eng. Chem. **44**, 1391 (1952).
9. J. Zinn and R. N. Rogers, "Thermal Initiation of Explosives," J. Phys. Chem. **66**, 2646 (1962).
10. T. C. Castorina et al, "A Modified Explositon Temperature Test for Determining Thermal Sensitivity of Explosives Under Controlled Vapor Pressure," Technical Report 3690, Picatinny Arsenal, Dover, NJ, April 1968.
11. A. J. Clear, "Standard Laboratory Procedures for Determining Sensitivity, Brisance, and Stability of Explosives," Technical Report 3278, Dec 1965 (Vacuum Stability, pp. 19-22, Impact Sensitivity, pp. 2-4, 32).
12. J. W. Frazer and K. Ernst, "Chemical Reactivity Testing of Explosives," Lawrence Livermore Laboratory Report UCRL 7438 (1963).
13. D. Price and T. P. Liddiard, Jr., "The Small Scale Gap Test: Calibration and Comparison with the Large Scale Gap Test," Naval Ordnance Laboratory Report NOLTR 66-87, July 1966.

14. T. Urbanski, "Chemistry and Technology of Explosives," Pergamon Press, Vol. III, p. 253, 254.
15. "Properties of Explosives of Military Interest," Army Materiel Command Pamphlet AMCP 706-177 (March 1967), p. 239.
16. C. L. Mader, "An Equation of State for Nonideal Explosives," Los Alamos Scientific Laboratory, LA 5864, April 1975.
17. M. J. Urizar and L. C. Smith, "Heat and Products of Detonation of Amatol 60/40 and Amatex 20 - Preliminary Measurements," Informal communication of results of a few exploratory tests at Los Alamos Scientific Laboratory on large scale detonation calorimetry of AN containing compositions, June 1975.
18. D. L. Ornellas et al, "Detonation Calorimeter and Results Obtained with PETN," R.S.I. 37, 907, July 1966.
19. D. L. Ornellas, "The Heat and Products of Detonation of HMX, TNT, NM, and FEFO," J. Phys. Chem. 72, 2390 (1968).
20. J. W. Kury et al, "Metal Acceleration of Chemical Explosives," Proc. Symp. Detonation, 4th, Office of Naval Research, Rept. ACR-126, pp. 3-13, U.S. Govt Printing Office, Washington, D.C. (1965).
21. L. C. Smith, "On Brisance and a Plate Denting Test for the Estimation of Detonation Pressure," Explosivstoffe 5/1967, pp. 106-110, 130-134.
22. M. Finger et al, "Metal Acceleration by Composite Explosives," Proc. Symp. Detonation 5th, Office of Naval Research, Rept ACR-184, pp. 137-151 U.S. Govt Printing Office, Washington, D.C. 1970.
23. R. E. Duff and E. Houston, "Measurement of the Chapman-Jouguet Pressure and Reaction Zone Length in a Detonating High Explosive," J. Chem. Phys. 23, 1268 (1955).
24. M. A. Cook, The Science of High Explosives, 1971 Edition, Robert E. Krieger Publishing Co., Inc., Box 542, Huntington, NY 11743, Chapter 6.
25. J. Hershkowitz and I. Akat, "Improvement of Performance of Composite Explosives Containing Ammonium Nitrate by Physical Synthesis," Sixth Symp. (Internat'l) on Detonation, San Diego, 24-27 Aug 1976. Preprints pp. 404-413.

26. B. T. Fedoroff and O. E. Sheffield, "Encyclopedia of Explosives and Related Items," Technical Report 2700, Volume 6 (1974), pp. E234-7.
27. M. H. Ficherouille, "Ethylenedinitramine, Ammonium Ethylenedinitramate, Binaries with Ammonium Nitrate," Memorial des Poudres, 30, 89-100 (1948) (In French).
28. A. Le Roux, "Explosive Properties of Ethylenediamine Dinitrate," Memorial des Poudres, 32, 121-131 (1950).
29. A. Le Roux, "Explosive Properties of Nitrate of Monomethylamine," Memorial des Poudres, 34, (see p. 141 top for EDD) (1952).
30. B. T. Fedoroff et al, "Dictionary of Explosives, Ammunition and Weapons (German Section)," Technical Report 2510, Picatinny Arsenal Dover, NJ pp. Ger 35-R, 47-L6, 48-L (1959) (AD 160636).
31. "Allied and Enemy Explosives," Aberdeen Proving Ground Report APG ST-9-2900-1 (1946), Chapt. 7, Sect. III, pp 143-147.
32. M. Cowperthwaite and J. T. Rosenberg, "A Multiple Lagrange Gage Study of the Shock Initiation Process in Cast TNT," Sixth Symp. (Internat'l) on Detonation, San Diego, 24-27 Aug 1976, Preprints pp. 594-601.
33. L. M. Barker, "Laser Interferometry in Shock Wave Research," Experimental Mechanics, 12, No. 5. May 1972.
34. J. W. Nunziato and J. E. Kennedy, "Modes of Shock Wave Growth in the Initiation of Explosives," Sixth Symp. (Internat'l) on Detonation, San Diego, 24-27 Aug 1976, Preprints pp. 569-579.
35. B. Hayes, "The Detonation Electric Effect," J. Appl. Phys. 38, pp. 507-511 (1967).
36. J. K. Rigdon and I. Akst, "An Analysis of the Aquarium Technique as a Precision Detonation Measurement Gage," Proc. Symp. Detonation 5th, Office of Naval Research, Rept ACR-184, pp. 59-66, U.S. Govt. Printing Office, Washington, DC, 1970.
37. B. G. Craig, "Measurements of the Detonation - Front Structure in Condensed Phase Explosives," Tenth Symposium (Internat'l) on Combustion, p. 863 (1965).
38. R. McGuire and D. Ornellas, "An Investigation of Chapman-Jouguet Detonation Theory Using Isotopic Labelling," Frank J. Seiler Research Laboratory SRL-TR-75-0004 (April 1975).

Table 1
Differential Thermal Analysis (DTA) Results*

<u>Sample</u>	<u>Melting Point</u>	<u>Major Exotherm</u>	
		<u>Start</u>	<u>Peak</u>
AN	169	250	320
EDD	185	255	275
NQ	232	245	255
GN	214	300	335
RDX	205	210	215
EDD/AN	102	250	275
EDD/TNT	80, 185	240	260
EDD/RDX	185, 205	205	215
EDD/Al	185	240	250
EDD/Fe	185	215	230
EDD/Cu	-	165	210
EDD/brass	-	135	240
EDD/Zn	-	120	125
EDD/AN/TNT	80, 102	235	275
EDD/AN/RDX	102, 205	210	230
EDD/AN/Al	102	260	285
EDD/AN/Fe	102	205	220
EDD/AN/Cu	102	255(1)	265
GN/AN	126	225	275
GN/TNT	80, 210	210	220
NGA(2)	113	260	310
NGA/RDX	113, 205	210	235
NGA/Al	113	305(3)	315
NGA/Fe	113	285(4)	305
NGA/brass	113	240	245

*Results are in °C and were obtained at +20°C/min from room temperature using "micro" samples in a duPont 900 thermal analyzer. All mixtures were approximately equal parts by volume.

- (1) smaller exotherm at 195
- (2) NGA is NQ/GN/AN
- (3) small exotherm at 275
- (4) smaller exotherm at 225

TABLE 2

Vacuum Thermal Stability (VTS) and Chemical Reactivity Test^(a) (CRT)

Material	Sample Size, Grams	Time, Hr	Gas, Ml		Gas, $\mu\text{l/g/hr}$ ^(b)	
			100	120°C	100	120
AN ^(d)	5	40		0.3		1.5
AN ^(d)	0.250	22		0.047		8.6
EDD	1	40		0.65		16
GN	5	40		0.15		0.8
GN	0.250	22		0.034		6.2
NQ ^(e)	5	40		0.44		2.2
NQ ^(f)	5	40		11 ⁺ (c)		55 ⁺
NQ-1 ^(f)	0.250	22		0.22		40
NQ-2 ^(g)	0.250	22		0.056		10
RDX ^(e)	5	40		0.9		4.5
TNT ^(e)	5	40		0.23		1.2
EDD + AN	1	40		0.15		3.8
EDD + Fe	1	40		1.84		46
EDD + Fe	5	40	1.10		5.5	
EDD + Cu	5	16		11 ⁺ (c)		140 ⁺
EDD + Al	5	40		0.84		4.2
EDD + Pb	5	40		0.71		3.6
EDD + Ni	5	16		11 ⁺ (c)		140 ⁺
EDD + Stainless steel	5	40		0.80		4.0
EDD + Ta	5	40		0.66		3.3
EDD + Sn	5	40		1.20		6.0

(Continued on next page)

(a) By gas chromatography under 1 atm He at temperature. Mixtures are equal parts by weight. Results are corrected to STP after hours shown. 1/4 gram for 22 hours used. See Ref 12 of text.

(b) Calculated assuming impurity with sample size and time.

(c) Capacity is 11 ml; 11⁺ means capacity reached in less than time shown, or spillage occurred by exceeding capacity.

(d) Reagent grade purity.

(e) Ref 15 of text.

(f) Batch origin unknown; 0.11 N₂O; 0.06 CO₂; 0.05 N₂.

(g) Standard batch; 0.025 N₂O; 0.018 CO₂; 0.013 N₂.

TABLE 2 (Cont)

Vacuum Thermal Stability (VTS) and Chemical Reactivity Test^(a) (CRT)

Material	Sample Size, Gram	Time, Hr	Gas, MI		Gas, $\mu\text{l/g/hr}$ ^(b)	
			100	120°C	100	120
AN + Fe	5	40	0.85		4.2	
EDD + AN + RDX	1	40		0.76		19
EDD + AN + TNT	1	40		2.26		56
EDD + AN + Fe	1	40		1.74		44
EDD + AN + Cu	5	1		11 ^{+(c)}		2200 ⁺
EDD + AN + Al	5	40		1.66		8.3
EDD + AN + Pb	5	40		11 ^{+(c)}		55 ⁺
EDD + AN + Ni	5	1		11 ^{+(c)}		2200 ⁺
EDD + AN + Stainless steel	5	40		2.99		15
EDD + AN + Ta	5	40		0.26		1.3
EDD + AN + Sn	5	40		0.30		1.5
EDD + AN + RDX + Cu	5	1		11 ^{+(c)}		2200 ⁺
EDD + AN + RDX + Al	5	40		4.26		21
EDD + AN + RDX + Pb	5	1		11 ^{+(c)}		2200 ⁺
EDD + AN + RDX + Ni	5	1/2		11 ^{+(c)}		4400 ⁺
EDD + AN + RDX + Stainless steel	5	40		4.99		25
EDD + AN + RDX + Ta	5	40		1.00		5.0
EDD + AN + RDX + Sn	5	40		3.88		19
Amatex 20 ^(h)	5	40		6.8 - 11 ⁺		34-55
Amatex 20 ^(h)	5	40	.5 - .8		2.5 - 4	
Amatex 20 + Fe	5	40		11 ⁺		55 ⁺
Amatex 20 + Fe	5	40	2.7		13.5	
NQ-1+GN+AN	5	40		11 ⁺		55 ⁺
NQ-1+GN+AN	5	40	2.05 ⁽¹⁾		10 ⁽¹⁾	
NQ-1+GN+AN	5	40	0.2		1	
NQ-1+GN+AN	0.250	22		.225		40
NQ-2+GN+AN	0.250	22		.056		10
NQ-1+GN+AN+RDX	5	40	1.02 ⁽¹⁾		5 ⁽¹⁾	
NQ-1+GN+AN+RDX	5	40	0.30		1.5	

(a), (b), (c) (see previous page).

(h) RDX/TNT/AN 20/40/40 by weight.

(1) 110°C.

TABLE 3

Explosion Temperature Results ^(a)

Composition	Rate Parameters ^(b)			Temperature at Seconds ^(c)		
	r	E	A	1	5	10
RDX	.98	19.5	6.0-8	317	265	246
AN	.96	22.2	1.3-7	434	369	344
EDD	.99	15.7	9.1-7	294	235	213
GN	.98	28.0	4.1-10	380	334	317
NQ	.95	27.5	7.3-11	319	281	266
EDD/AN 70/30	.97	18.8	4.7-8	289	240	221
50/50	.96	20.9	6.9-9	287	242	226
44/56	.93	23.2	7.6-10	282	243	227
NQ/GN/AN 17.5/22.5/60	.95	21.5	1.5-9	327	278	259
RDX/TNT/AN 20/40/40 (Amatex 20)	.98	26.6	2.8-11	279	244	231
Hydrazine Nitrate	.86	16.8	1.3-7	262	213	194

^(a) Using the Henkin-McGill variant (Ref 10) with copper blasting cap tubes.

^(b) The experimental data are used to calculate a regression curve, the apparent activation energy, E (kcal/mole); the pre-exponential factor, A (sec^{-1} ; number following hyphen is 10 exponent); and the correlation coefficient of the data to the curve, r.

^(c) Using the calculated regression curve, the explosion temperatures in $^{\circ}\text{C}$ are predicted for 1, 5, and 10 seconds, as times to explosion.

TABLE 4

Drop Weight Impact Sensitivity

<u>Material</u>	<u>Drop Height</u>	
	<u>Inches</u>	<u>cm (c)</u>
TNT	14	35.6
RDX	8	20.3
TATB	28	71.1
Amatex 20	12	30.5
EDD	14	35.6
AN	50	76.2
EDD/AN	13-19 ^(b)	33.0-48.3
EDD/inert ^(a)	11-13	27.9-33.0
RDX 40/EDD/AN	14	35.6
NQ/GN/AN	20	50.8
RDX 40/NQ/GN/AN	14	35.6
TATB 40/NQ/GN/AN	16	40.6

(a) 90/10 by weight ammonium sulfate/ammonium sulfite, matches AN density.

(b) Depending on ratios, preparation, etc.

(c) Measurements of drop height were made in inches. Values in centimeters were calculated therefrom.

TABLE 6

X-Ray Diffraction Pattern of EDD/AN

<u>D-value (a)</u>	<u>H (b)</u>	<u>Peak Intensity (Relative)</u>
6.92	1	10
5.32	1	4
5.09	1	16
4.91	12	36
4.13	1	43
3.95	2	50
3.76	1	35
3.59	1	68
3.47	1	100
3.09	2	92
2.95	1	27
2.87	12	20
2.84	1	34
2.72	12	64
2.66	1	5
2.61	1	10
2.54	1	15
2.48	2	20
2.46	1	10
2.31	1	10
2.26	2	52
2.25	2	38
2.14	1	15
1.79	1	15
1.74	1	5
1.69	1	6
1.51	2	8
1.46	2	10
1.34	2	15

(a) D value is standard structural spacing parameter.

(b) 1 = EDD 2 = AN 12 = both.

TABLE 5

Small-Scale Gap Test Sensitivity

<u>Attenuator Thickness</u> ^(a)	<u>Composition</u>		<u>Preparation</u>
20	EDD/AN	50/50	Co-frozen
60	EDD/AN	50/50	Dry Mix
90	EDD/AN	50/50	Co-crystallized from H ₂ O
130	EDD/AN	70/30	Co-frozen
135	EDD/AN	70/30	Co-crystallized from H ₂ O
130	EDD		
247	TNT		
267	Amatex 20		
330	Comp B		

(a) Units of attenuator thickness are .0254 mm (mils). Larger attenuator thickness used with donor explosive result in lower shock strengths into the acceptor explosive (under test) and hence indicate that initiation occurs with lower shock strengths (e.g., EDD/AN systems are less shock sensitive than TNT/RDX systems). See Figures 2 and 3 for data supporting these values.

TABLE 7

Potential Chemical Energy of AN and Some Fuels^(a)

<u>Components</u>	<u>kcal/g</u>	<u>kcal/cc</u>
AN	0.354	0.610
AN + C, CO balance ^(b)	0.595	1.06
AN + C, CO ₂ balance ^(b)	0.876	1.54
AN + H ₂	1.05	-
EDD ^(b)	0.856	1.37
AN + EDD, CO balance ^(b)	0.804	1.31
AN + EDD, CO ₂ balance ^(b)	0.952	1.59
TNT ^(b)	0.965	1.59
AN + TNT, CO balance ^(b)	0.810	1.37
AN + TNT, CO ₂ balance ^(b)	1.01	1.73
NQ + GN + AN, CO ₂ balance ^(b)	0.908	1.51
RDX ^(b)	1.234	2.23

^(a) Based on ΔH_f values (kcal/mol) and densities (g/cc) tabulated below

<u>Component</u>	<u>$-\Delta H_f$</u>	<u>Density</u>
AN	87.3	1.725
EDD	156.1	1.595
TNT	17.8	1.63
GN	92.5	1.44
NQ	2.3	1.81
RDX	-21.3	1.806
H ₂ O (gas)	57.8	
CO	26.4	
CO ₂	94.0	

^(b) Calculated using 0 for H₂O to the limit of H, then for CO to the limit of C, then for CO₂. Carbon treated as graphite density 2.5 g/cc.

TABLE 8

Dent and Detonation Velocity Results

Explosive 9.65 mm diameter by 64 mm long, confined within 25-mm-diameter steel or brass
(dent depth measured to nearest 0.001 inch, calculated to nearest .01 mm)

Name or Process	Weight Percent (a)					Dent Depth mm			Detonation Velocity km/sec			Density g/cc
	EDD	AN	RDX	TNT	I	Avg			Avg			Avg
	100					2.22	2.46	2.60	6.77		6.77	1.55
		100				2.59	2.64					
			100			3.48	3.48	3.48	8.46	8.55	8.50	1.71
				100		2.41	2.46	2.45				
					80	2.49	2.45		6.69		6.69	1.60
Comp B			80	20		3.28	3.47	3.35				1.66
			60	40		3.33	3.20	3.22				
					40	3.10	3.23		7.73		7.73	1.66
			40	60		2.90	2.95	2.92				1.64
			20	80		2.79	2.84	2.82				1.63
Anatol 30		30		70		2.01	2.03	2.02	6.48	6.25	6.37	1.63
Anatol 50		50		50		1.63	1.57	1.60	5.88	6.05	5.97	1.66
Anatex 20		40	20	40		2.54	2.46	2.50	7.10		7.10	1.64
Anatex 20		40	20	40		2.21	2.36	2.29	6.99		6.99	1.63
	40		60			3.25	3.18	3.22				1.66
	60		40			2.90	2.82	2.86	7.96	7.66	7.81	1.64
	80		20			2.69	2.72	2.71	7.56	7.52	7.54	1.59
		20	80			3.20	3.30	3.25				1.67
		40	60			2.69	2.77	2.73				1.59
		60	40			2.26	2.26	2.26				1.71
		80	20			1.19	1.22	1.21				1.66
			80	20		3.00	3.07	3.04				1.69
			60	40		2.31	2.26	2.29				1.70
			40	60		1.47	1.35	1.41				1.66
	50			50	0	0	0	fail				1.61
	70			30	2.57	2.59	2.58			~5.7		1.56
Cocryst.	80	20				2.67	2.69	2.68	6.18	6.58	6.38	1.48
Melt + Freon	70	30				2.49	3.00	2.74	5.90		5.90	1.54
Cocryst.	70	30				2.64	2.49	2.57	5.85	5.60	5.73	1.53
Melt	70	30				2.72	2.74	2.73				1.46
quick freeze												
Cocryst.	60	40				2.51	2.57	2.54	5.90	5.69	5.80	1.47
Melt + Freon	50	50				1.52	1.52	1.52	6.5+	5.2		1.48
Slurry	50	50				0	0	fail				1.64
Dry mix	50	50				1.70	-	1.70	~5.3		~5.3	1.52
Cocryst.	50	50				2.18	1.96	2.07	5.17	5.18	5.18	1.57

(Continued on next page)

TABLE 8 (Continued)

Dent and Detonation Velocity Results

Explosive 9.65 mm diameter by 64 mm long, confined within 25-mm-diameter steel or brass
(dent depth measured to nearest 0.001 inch, calculated to nearest .01 mm)

Name or Process	EDD	AN	RDX	TNT	NGA	Dent Depth			Detonation Velocity			Density	
						mm	Avg		km/sec			g/cc	
Melt/quick freeze	50	50				0.76	0.86	0.81	Failing			1.55	
Melt + Freon	44	56				0.91	-	0.91				1.59	
Cocryst.	44	56				1.98	2.13	2.06	5.81	5.23	5.52	1.55	
Melt/quick freeze	44	56				0	0.15	Failing				1.59	
Melt/quick freeze	44	56				2.51	2.72	2.62				1.56	
Slurry	44	56				0.15	0.41	Failing				1.62	
Melt/quick freeze	40	60				1.70	1.32	1.51				1.56	
Melt/quick freeze	40	60				1.57	1.83	1.68				1.53	
Melt + Freon	25	75				0	0	Fail				1.56	
Melt + Freon	56	24	20			2.90	2.84	2.87	6.93		6.93	1.51	
Melt + Freon	40	40	20			3.02	3.02	3.02	6.39		6.39	1.58	
Slurry	40	40	20			3.30	3.23	3.26				1.59	
Melt + Freon	35	45	20			2.95	2.92	2.94	6.16		6.16	1.62	
Melt/quick freeze	20	60	20			2.29	2.36	2.33				1.67	
Melt + Freon	30	30	40			3.28	3.15	3.21	7.38		7.38	1.66	
Slurry	30	30	40			3.30	3.20	3.25				1.66	
Melt/quick freeze	26	34	40			3.23	3.28	3.25				1.68	
Slurry	26	34	40			3.23	3.25	3.24				1.66	
Melt/quick freeze		60			40	0	0	Fail				1.60	
Melt/quick freeze		48	20		32	1.30		1.30	Unstable				1.63
Melt/quick freeze		36	40		24	3.05	2.95	3.00	7.17		7.17	1.66	

(4) Comp B, Amatols, and Amatek were made with fine AN and/or RDX by evaporating toluene from TNT. NGA = NQ/CH/AN 17.5/22.5/60, I = Inert = $(\text{NH}_4)_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ 90/10; ρ = AN.

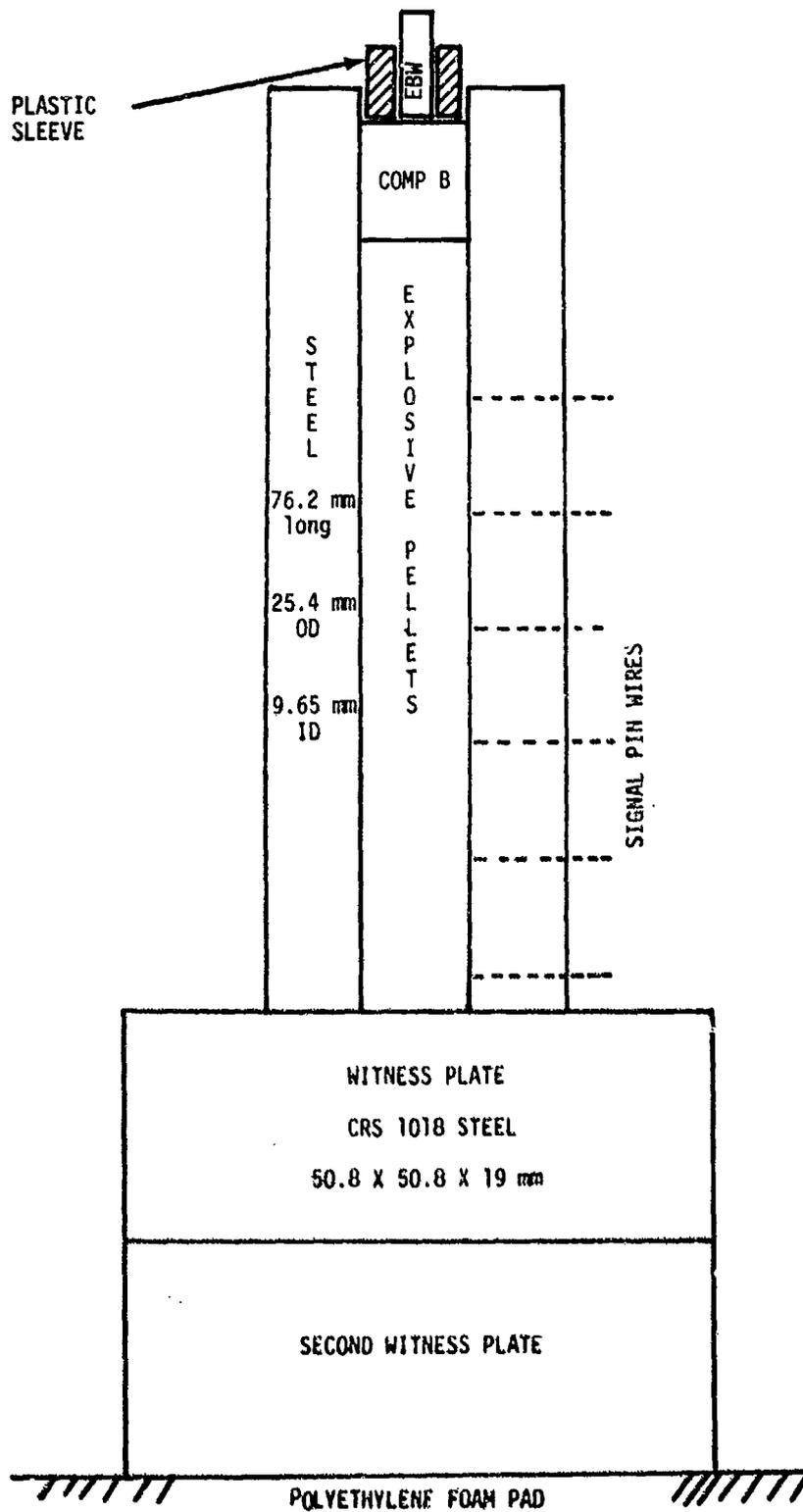


Fig 1 Detonation velocity and witness plate test

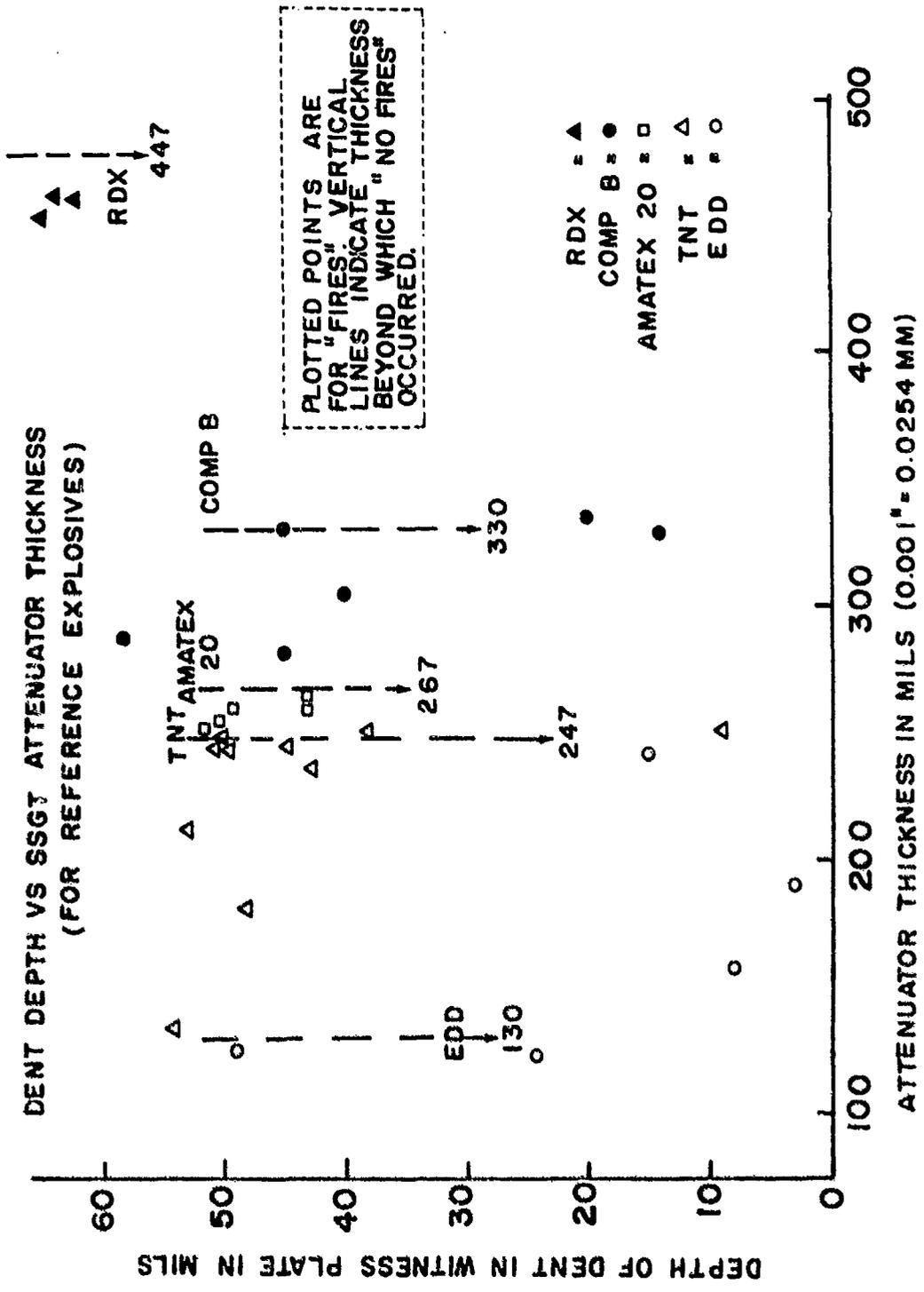


Fig 2 Dent depth vs small scale gap test attenuator thickness for reference explosives.

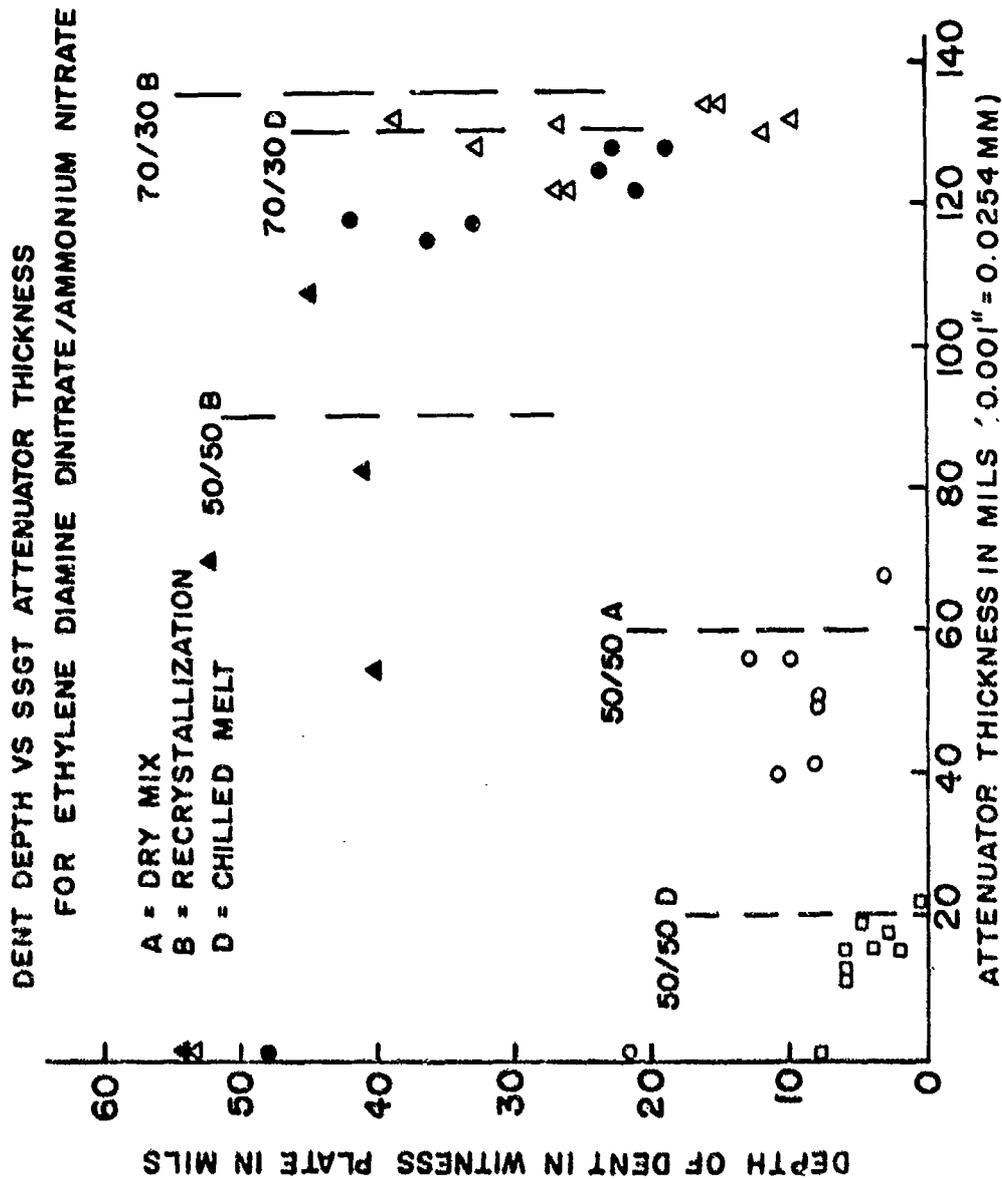
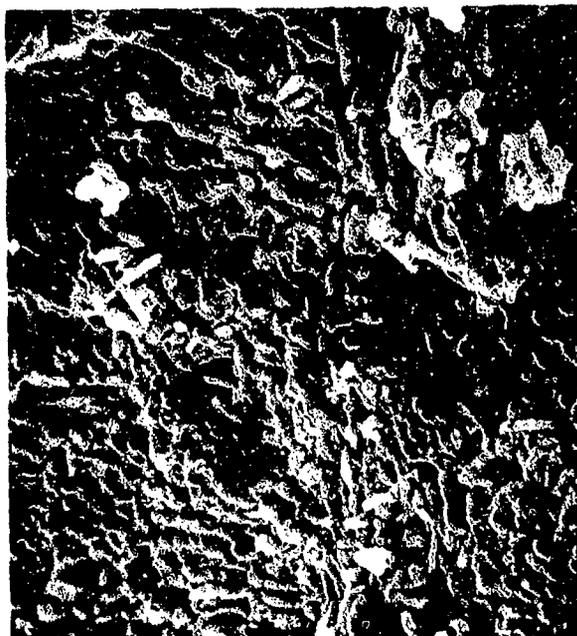


Fig 3 Dent depth vs small scale gap test attenuator thickness for ethylenediamine dinitrate/ ammonium nitrate (EDD/AN).



A.  1000X



B.  10000X

Fig 4 Scanning electron micrographs of EDD/AN 50/50

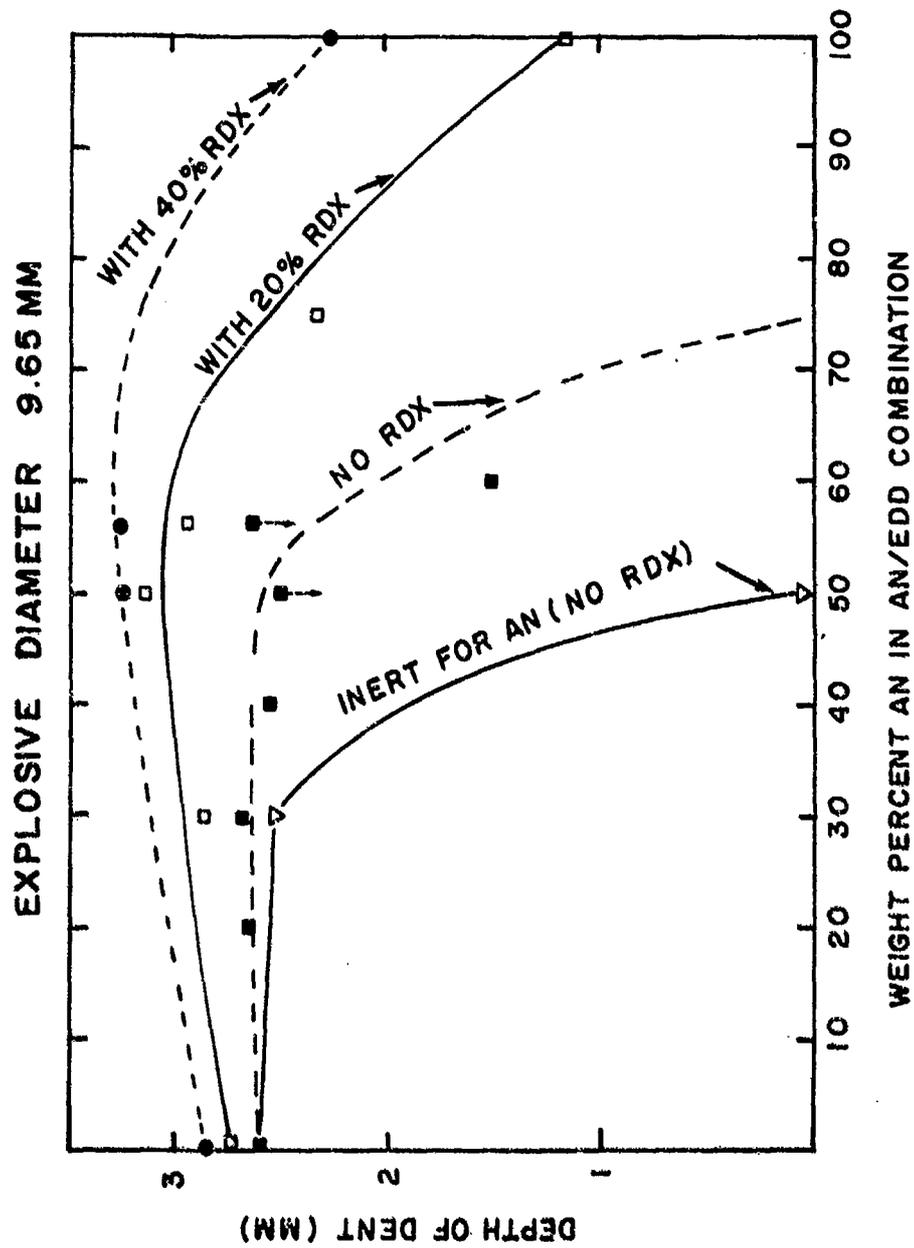
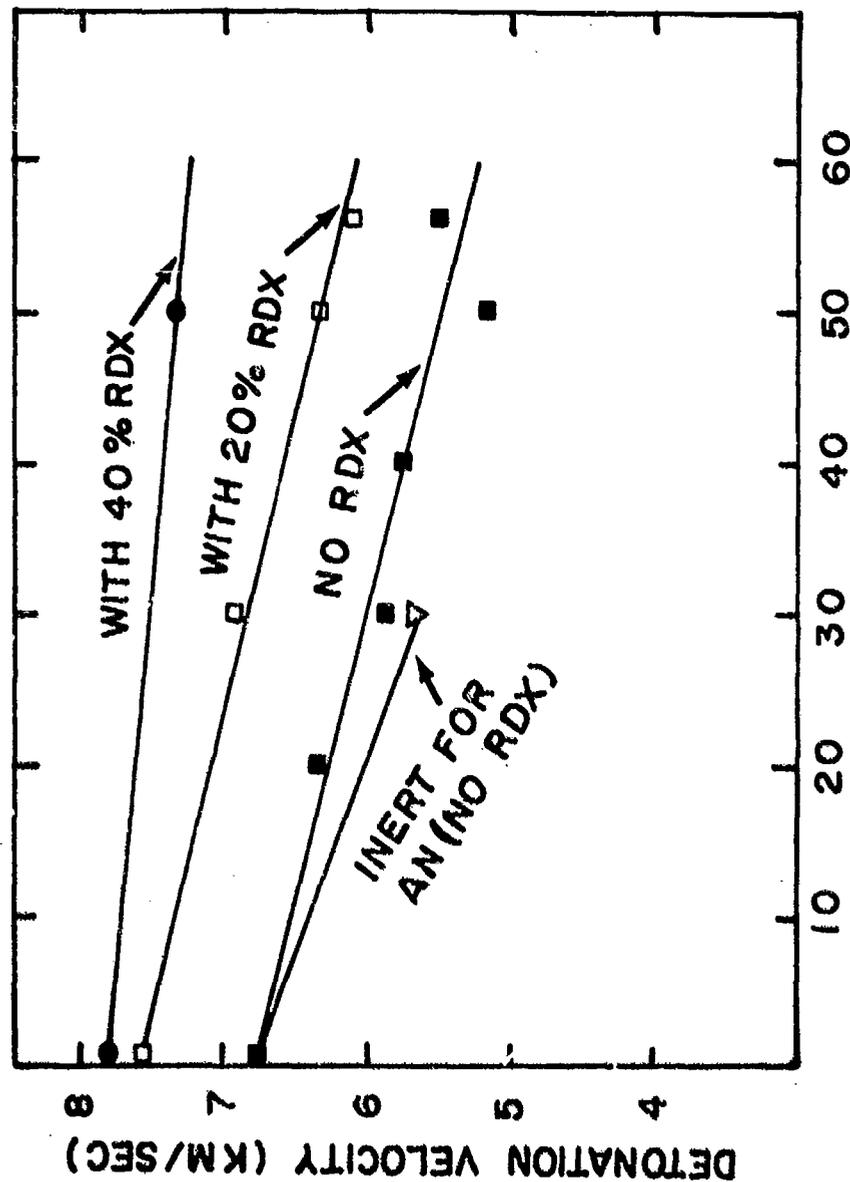


Fig 5 Dent depth in the confined small scale (explosive diameter 9.65 mm) test as a function of weight percent of ammonium nitrate within the combination ethylenediamine dinitrate/ammonium nitrate without RDX and for two levels of RDX present. The effect of substitution of an inert for AN in EDD/AN is also shown.

EXPLOSIVE DIAMETER 9.65 MM



WEIGHT PERCENT AN IN AN/EDD COMBINATION

Fig 6 Detonation velocity in the confined small scale (explosive diameter 9.65 mm) test as a function of weight percent of ammonium nitrate within the combination ethylenediamine dinitrate/ammonium nitrate, without RDX and for two levels of RDX present. The effect of substitution of an inert for AN in EDD/AN is also shown.

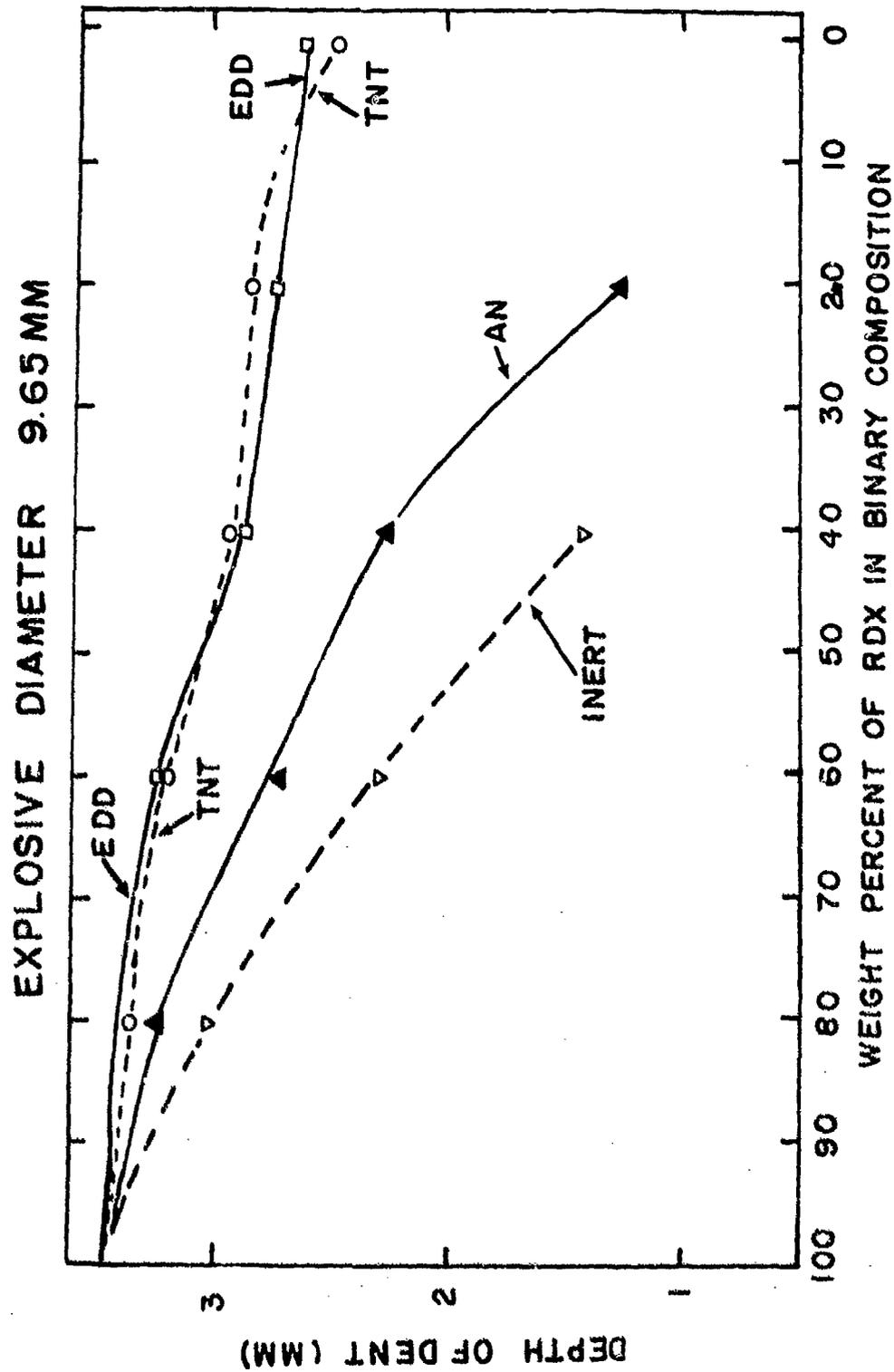


Fig 7 Dent depth in the confined small scale (explosive diameter 9.65 mm) test as a function of replacement of RDX in binary compositions by various materials.

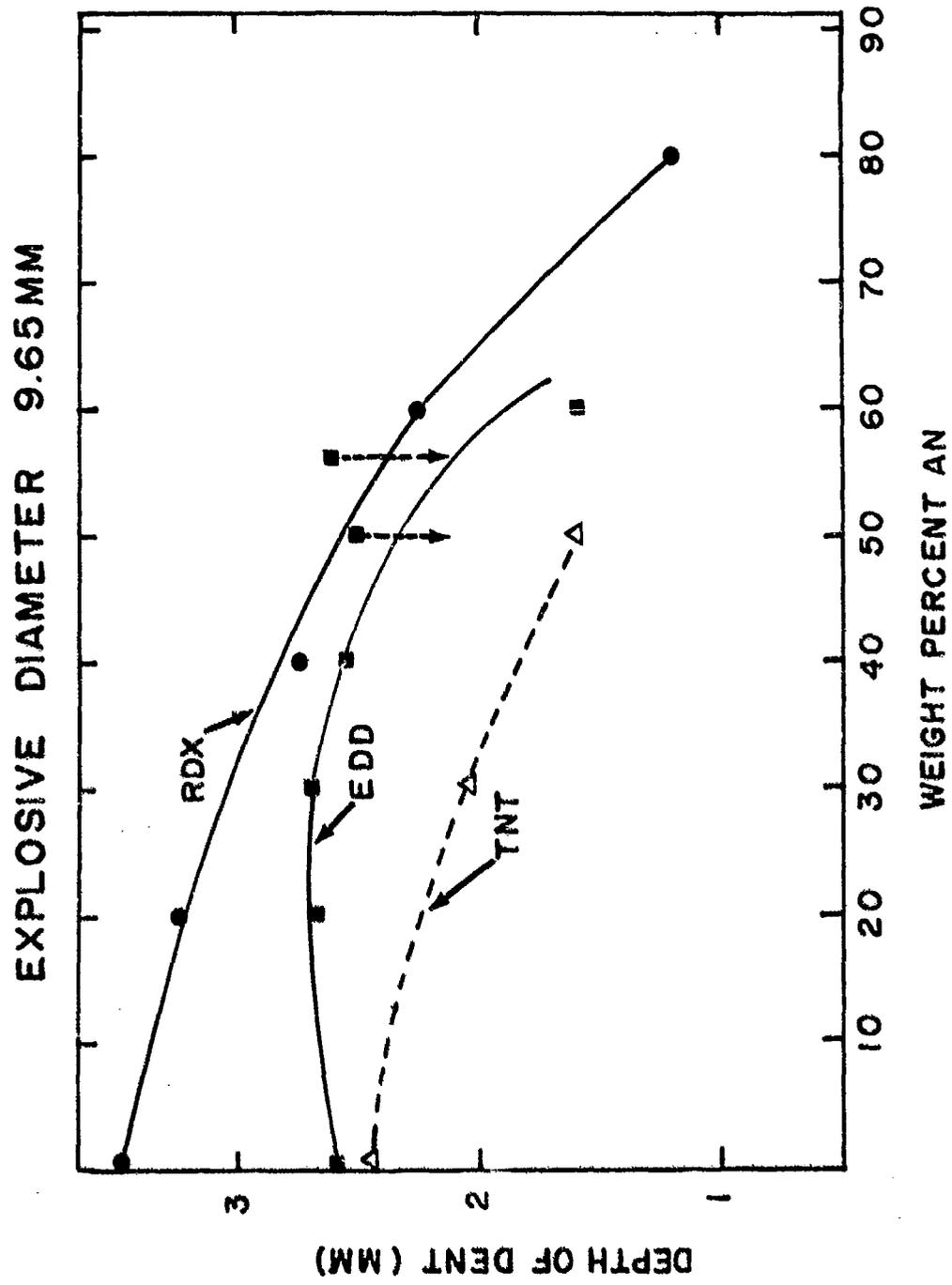


Fig 8 Dent depth in the confined small scale (explosive diameter 9.65 mm) test as a function of weight percent of AN added to various explosives to form binary compositions.

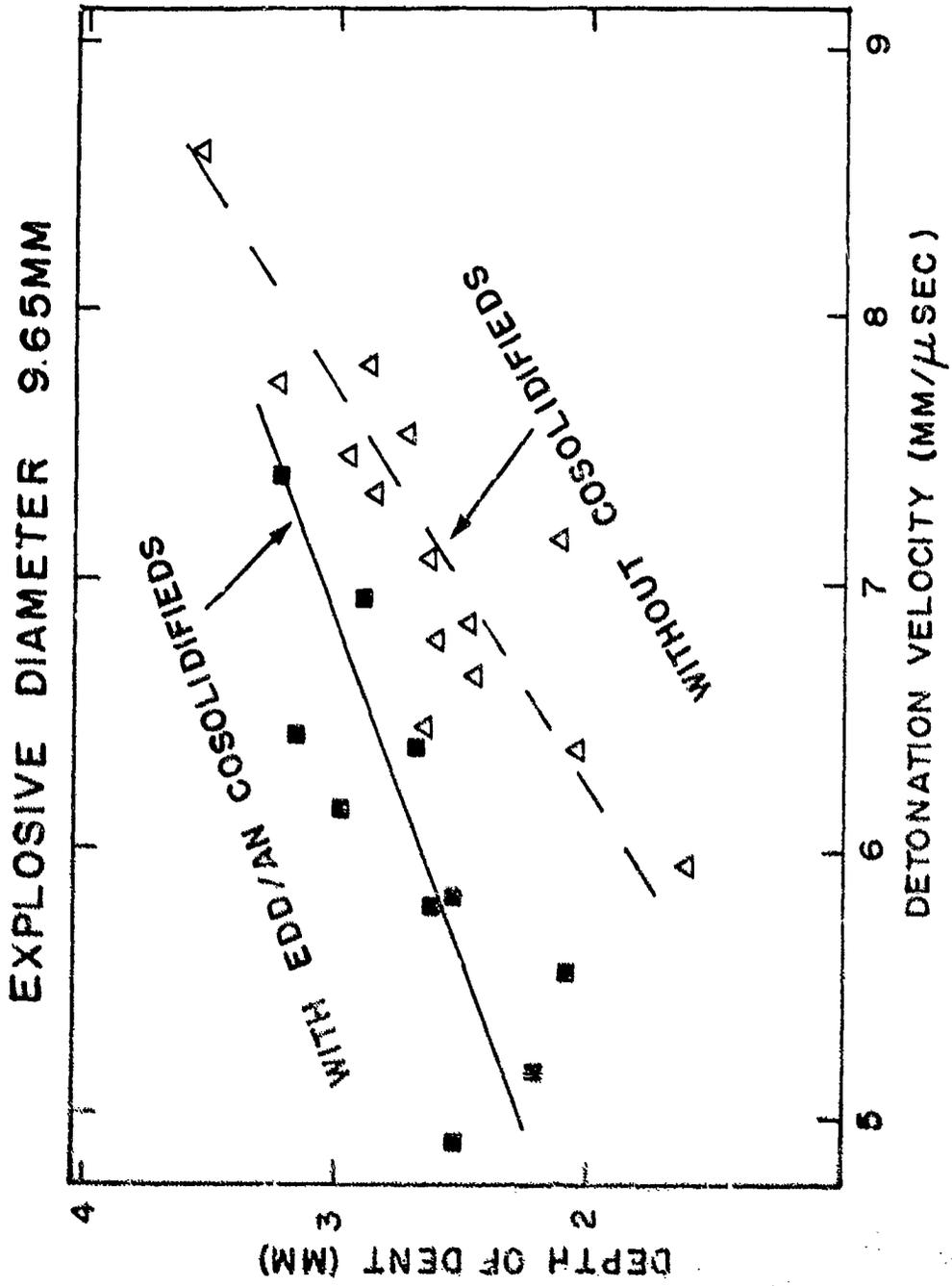


Fig 9 The effect of cosolidification on depth of dent vs detonation velocity as measured in the confined small scale (explosive diameter 9.65 mm) test.

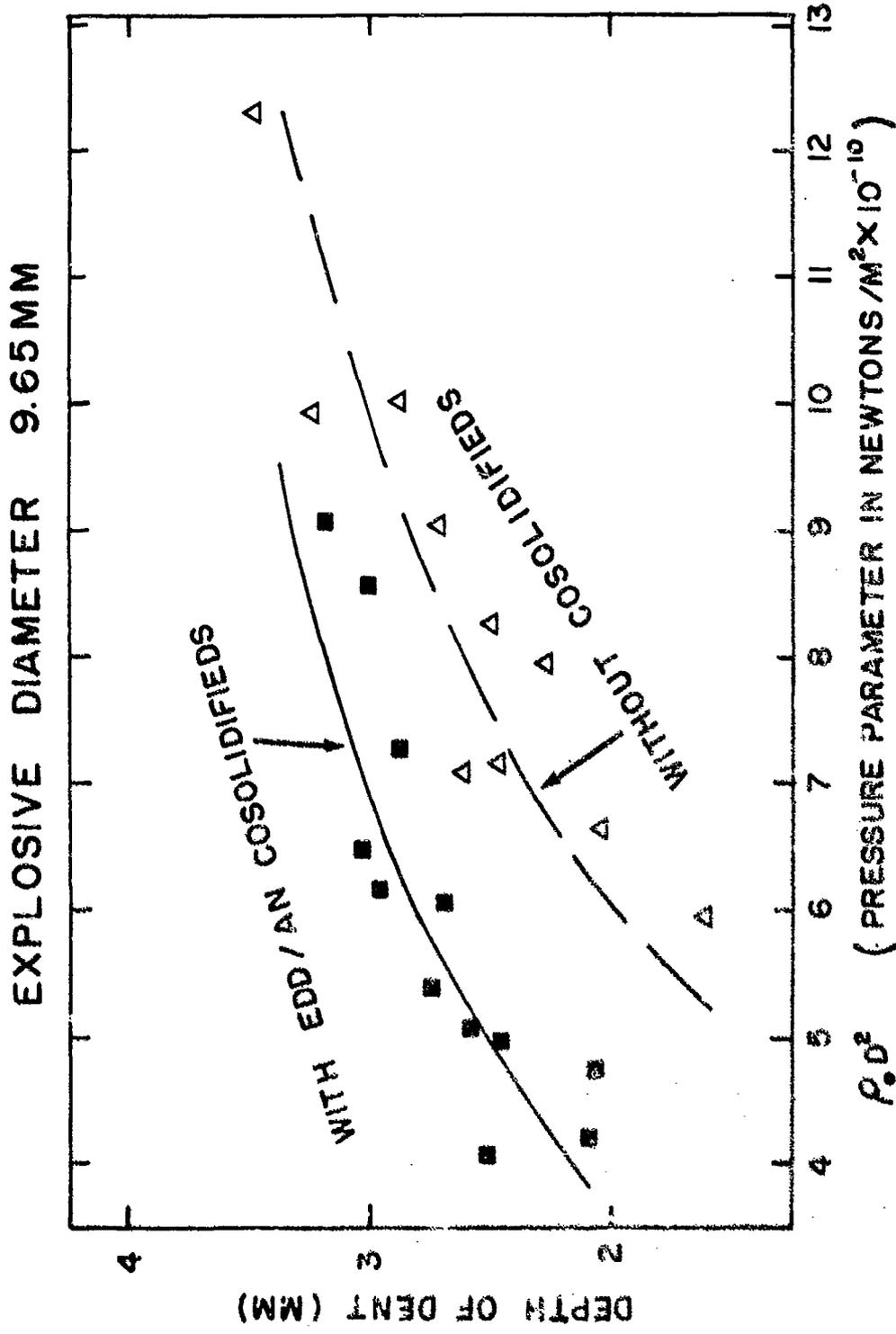


Fig 10 The effect of consolidation on depth of dent vs detonation pressure parameter as measured in the confined small scale (explosive diameter 9.65 mm) test.

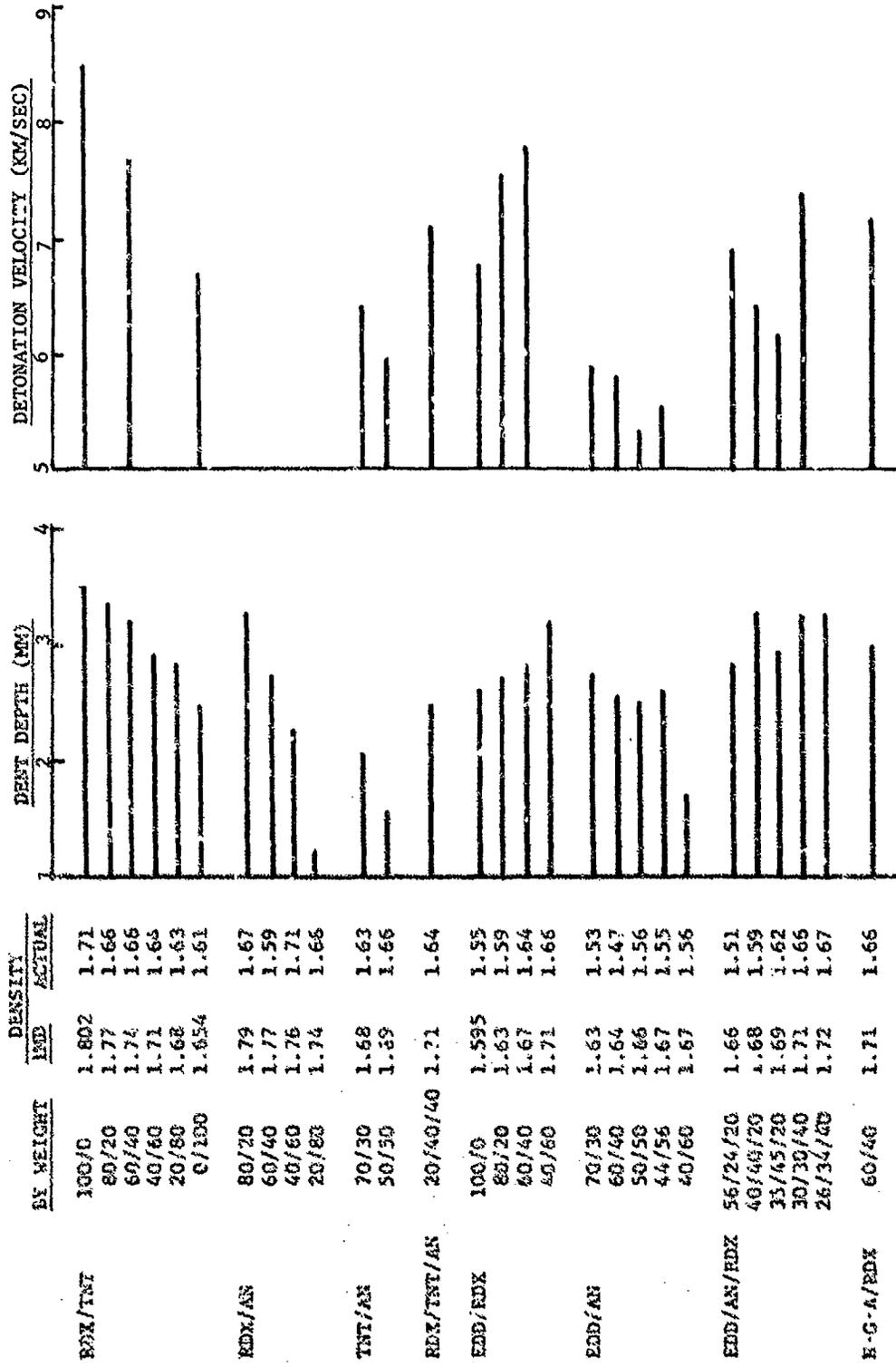


Fig 11 Detonation velocity and dent depth data obtained with the confined small scale (explosive diameter 9.65 mm) test as a function of composition parameters. Actual densities of samples evaluated and theoretical maximum densities of the compositions are also tabulated.

DISTRIBUTION LIST

	COPY NO.
Defense Documentation Center Cameron Station Alexandria, VA 22314	1-12
Office of the Director of Defense, Research and Engineering ATTN: QAD-ET, R. Thorkildsen The Pentagon Washington, DC 20301	13
Chief of Research, Development and Acquisition Department of the Army ATTN: DAMA-ARZ-D Washington, DC 20310	14
Defense Advanced Research Projects Agency ATTN: Director Tactical Technology Office R. Moore E. Blase 1400 Wilson Boulevard Arlington, VA 22209	15 16 17
Commander U.S. Army Materiel Development and Readiness Command ATTN: DRCDE DRCDMA-ST, N. Klein 5001 Eisenhower Avenue Alexandria, VA 22333	18 19
Commander U.S. ARRADCOM ATTN: R. Weigle Picatinny Arsenal Dover, NJ 07801	20
Commander J.S. Army Armament Command ATTN: AMSAR-RD, J. A. Brinkman AMSAR-RDT, R. Freeman Rock Island, IL 61201	21 22



Commander
Army Research Office
ATTN: D. R. Squires 23
R. Ghirardelli 24
P.O. Box 12211
Research Triangle Park, NC 27709

Commander
U.S.A. Ballistic Research Laboratories
ATTN: Technical Library 25
AMXBR, R. J. Eichelberger 26
R. Vitali 27
AMXBR-B, P. M. Howe 28
R. B. Frey 29
Aberdeen, MD 21101

Commander
Picatinny Arsenal
ATTN: SARPA-TS-S 30-34
SARPA-AD, V. Lindner 35
SARPA-AD-D, T. Stevens 36
SARPA-MT, L. W. Saffian 37
SARPA-ADEP-4, D. Seeger 38
Dover, NJ 07801

Commander
Naval Ordnance Systems Command
ATTN: A. D. Amster (SEA-0332) 39
Washington, DC 20362

Commander
U.S. Naval Surface Weapons Center
White Oak Laboratory
ATTN: S. Jacobs 40
J. W. Enig 41
M. Kamler 42
D. Price 43
D. Edwards 44
Technical Library (Code 242) 45
White Oak, MD 20910

Commander
U.S. Naval Weapons Center
ATTN: R. Reed, Jr. 46
D. Harp 47
C. D. Lind 48
Technical Library (Code 753) 49
China Lake, CA 93555

The F. J. Seiler Research Laboratory (AFSC) Directorate of Chemical Sciences ATTN: S. A. Shackelford U.S.A.F. Academy, CO 80840	50
Commander Air Force Armaments Testing Laboratory ATTN: L. Elkins (ADTC/DLIW) C. R. McColloch (ADTC/DLIW) AFB Technical Library Eglin Air Force Base, FL 32542	51 52 53
Bureau of Mines ATTN: R. W. Watson R. Chaiken 4800 Forbes Avenue Pittsburgh, PA 15213	54 55
Los Alamos Scientific Laboratory ATTN: B. Craig W. Campbell R. Engelke A. Popolato C. L. Mader L. C. Smith H. Cady (WX-2) Technical Library P.O. Box 1663 Los Alamos, NM 87545	56 57 58 59 60 61 62 63
Lawrence Livermore Laboratory ATTN: J. W. Kury F. E. Walker M. Finger E. L. Lee R. R. McGuire H. C. Hornig Technical Library P.O. Box 808 Livermore, CA 94550	64 65 66 67 68 69 70
Sandia Laboratories ATTN: L. W. Davison (5131) J. Kennedy (2513) P.O. Box 5800 Albuquerque, NM 87115	71 72

Idos Corporation ATTN: I. B. Akst P.O. Box 285 Pampa, TX 79065	73
Mason and Hanger - Silas Mason Co., Inc. P.O. Box 647 Amarillo, TX 79177	74
Stanford Research Institute ATTN: M. Cowperthwaite J. T. Rosenberg 333 Ravenswood Avenue Menlo Park, CA 94025	75 76
A. K. Oppenheim University of California, Berkeley Engineering Berkeley, CA 94720	77
L. Zernow Shock Hydrodynamics 4716 Vineland Avenue North Hollywood, CA 91602	78
E. I. duPont de Nemours & Company Potomac River Development Laboratory ATTN: G. R. Cowan F. A. Loving Martinsburg, WV 25410	79 80
R. Duff Systems, Science & Software P.O. Box 1620 La Jolla, CA 92038	81
Lawrence Behrmann Physics International 2700 Merced Street San Leandro, CA 94577	82