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TECHNICAL REPORT 4789

A NEW APPROACH TO IMPROVING THE PERFORMANCE OF NON-IDEAL EXPLOSIVES CONTAINING AMMONIUM NITRATE

J. HERSHKOWITZ
I. AKST

MARCH 1975

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report 4789	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A NEW APPROACH TO IMPROVING THE PERFORMANCE OF NON-IDEAL EXPLOSIVES CONTAINING AMMONIUM NITRATE		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. Hershkowitz, Explosives Division, FRL I. Akst (see 18)		8. CONTRACT OR GRANT NUMBER(s) AMCMS Codes 662617.11.H7900 and 611101.11.844
9. PERFORMING ORGANIZATION NAME AND ADDRESS Explosives Division, FRL Picatinny Arsenal Dover, NJ 07801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE March 1975
		13. NUMBER OF PAGES 60
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to U.S. Government agencies only (test and evaluation; May 1975). Other requests for this document must be referred to Picatinny Arsenal, ATTN: SARPA-TS-S, Dover, New Jersey 07801

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Scientific Services of I. Akst were provided at the Explosives Division, FRL under contractual arrangements made through U.S. Army Research Office, Durham and Battelle Columbus Lab, Durham Office.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Explosive
Amatex
Amatol
Ammonium Nitrate
Methylammonium Nitrate
Tetramethylammonium Nitrate
Non-Ideal Explosive
Composite Explosive

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The performance of Amatol and Amatex explosives in small diameters has been improved by substituting methylammonium nitrates for various fractions of the ammonium nitrate (AN) in these explosives and providing an intimate mixture with the balance of the AN through cosolidification (e.g. co-melt, co-precipitate, mixed crystal). The results demonstrate that a rate limiting step which degrades performance (e.g., species transport), can be partially overcome in some AN-containing non-ideal explosives. The components necessary to promote chemical

19. Continued

Detonation Velocity	Explosive-Metal Acceleration
Witness Block Tests	Brisance
Dent Tests	

20. Continued

reaction of the AN were made readily available by putting them in close physical proximity to the AN molecules.

Depth of dent in a witness block was determined as a function of fraction of ammonium nitrate replaced. When tetramethylammonium nitrate was used, a peak in dent depth occurred at the CO balance point with ammonium nitrate, indicating synergism. With monomethylammonium nitrate, the dent depth increased with fraction of ammonium nitrate replaced, suggesting a replacement effect stronger than any synergism. Incompatibility of methylammonium nitrates with TNT limit practical use of explosives containing this combination.

The results exemplify a new approach to enhancing munition performance by seeking to identify and control the rate-limiting step in an explosive and by the concomitant formulation of new explosives through the modifications made. The various facets of this approach are presented together with the associated problems of measurement and prediction of performance. The directions of future efforts are outlined.

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INTRODUCTION

The rate at which a condensed phase explosive is transformed into gaseous products (together with the number, identity, and energy of gaseous molecules, the geometry and confinement) determines the pressure as a function of time and position and is thus responsible for the performance of the explosive in various applications. This rate is associated with molecular decomposition rates and intermolecular reaction rates. Most explosives are "ideal": they are well approximated by assuming an almost infinite rate of reaction producing gaseous products in chemical equilibrium at the end of a thin detonation zone created as a detonation wave propagates through the explosive at the detonation velocity. The theory for such ideal explosives is called the Chapman-Jouguet theory (Ref 1, 2) and predictions of detonation properties can be made using calibrated computer programs (Ref 3, 4) or calibrated formula methods (Ref 5, 6). The further description of ideal explosive behavior, in which the explosive is coupled to a load (e.g., metal acceleration), makes use of a high pressure equation of state for the gas and various hydrodynamic computer programs (e.g., Ref 7, 8).

There also exist non-ideal explosives for which the rates of reaction within the detonation zone are slow enough so as not to achieve equilibrium therein or so as to create very long detonation zones. These explosives have a lower detonation velocity and a lower peak pressure than would occur if the rate of reaction were higher. By calculating detonation properties by the Chapman-Jouguet theory (i.e. as though reaction rates were infinite) and comparing predictions with experimental values one obtains a measure of the improvement possible if the rates of reaction could be accelerated. This is illustrated for detonation velocities of the explosives 60/40 Amatol (60 ammonium nitrate and 40 TNT, by weight) and Amatex-20 (20 RDX, 40 TNT and 40 ammonium nitrate, by weight). Experimental detonation velocities (m/sec) are 5760 and 7009, respectively (for 1.60 and 1.61 g/cc densities). Corresponding computed ideal velocities are 7896 and 7866. Comparisons can also be made for work done in expansion (e.g. cylinder tests).

The potential improvement leads one to seek reasons for the slower reaction rate and means of modification. One assumption that can be made with respect to ammonium nitrate (AN) is that it decomposes to the final products $N_2 + 2H_2O + 1/2\ O_2$. An alternate assumption would be that an intermediate containing oxygen is formed from the AN.

This intermediate requires interaction with a fuel molecule to form CO and CO_2. In either case, one hypothesis would be that the reactions within Amatol and Amatex are diffusion-limited (species and energy transport) by the oxygen or the intermediate seeking fuel molecules to form final products such as CO and CO_2.

The initial concept was to improve Amatex toward ideality by first treating the AN with fuel oil so that the latter would be within the porous structure of the former and then adding the combination to the other constituents. (AN prills impregnated with fuel oil in the ratio 94/6 by weight detonates in smaller diameters and is more easily initiated than AN prills alone (Ref 9, 10).) In this way the AN would have the fuel necessary for reaction in close proximity, presumably shortening transport time and increasing reaction rate. This initial concept was later broadened to the use of fuel coatings on the AN (e.g. waxes) and finally to the starting point of experimental work - choosing other energetic or non-energetic materials which could be cosolidified (e.g. coprecipitated, comelted) with AN to provide greater proximity or which had potential for forming mixed crystals. (Mixed crystals have a well defined x-ray diffraction pattern and physical properties such as density and lattice parameters which vary linearly between the values such quantities have in the pure compounds.) Particle size reduction as a means of promoting intimacy was not considered here because it provides less intimacy than co-solidification, results in rheological penalties for cast compositions, and because other investigators are pursuing this approach. Other approaches to improving non-ideal explosives (Ref 11) were left for future work.

Although AN was chosen as the vehicle of this study because of the possibilities of significantly improving a low cost, highly available explosive, a more general principle is involved. This principle is that non-ideal explosives should be studied to determine the rate-determining step underlying non-ideality and then improved by modifying them. The first objective, therefore, was to simply demonstrate that one could move toward ideality by overcoming the supposed rate-determining step of diffusion limitation or by creating new reaction paths with shorter time constants. The second objective was to assess the practical value of the modified explosives by considering practical properties such as stability, formulation, costs, etc.

Although not specific objectives, there are two other closely related subjects introduced here, but treated in detail in the DISCUSSION section. One of these is the fact that if one has found a technique to vary the rate of release of energy and species, the technique can be used to control that rate of release to optimize use of the explosive ("tailoring") and to achieve improved munitions and implement new concepts. The other related subject deals with measurement and prediction techniques that are appropriate to media in which the time frame of energy and species release is a key factor. It is obvious that one can not study rate release modification without assessing the relevance of the tools one is using.

This report first presents the procedures used and then the results obtained by modifying the AN content in 60/40 Amatol and Amatex-20 using either monomethylammonium nitrate (MAN) or tetramethylammonium nitrate (QMAN). (Some work was also done with dimethyl- and trimethylammonium nitrate, but not continued, as these were found unsuitable because of their low melting points, hygroscopicity, and reactivity.)

The results suggest that the participation of AN in the composite explosive has been enhanced, satisfying the first objective. The basis for this conclusion and the basis for further work in this area are then treated in the DISCUSSION (see Outline therein).

PROCEDURES

Explosive Compositions

60/40 Amatol and Amatex-20 are normally cast compositions in which TNT is the matrix holding solid AN or AN + RDX suspended. The compositions used herein were made of ingredients blended in small batches by grinding together with a mortar and pestle, crystallization from solvent, or by melting and cosolidification. Final compositions were pressed into pellets or directly into tubes for tests. Pressing was done to avoid devoting time to solving special casting problems for many experimental compositions; to more fully utilize small batches of prepared components; to better control homogeneity of composition; to better assure that all factors other than the one under study were held constant; and to perform tests in smaller diameters since initiation and stable propagation are more readily achieved with pressed forms than cast.

60/40 Amatol and Amatex-20 were used as the materials for modification in order to provide two matrix levels of pressure and temperature (that of TNT and that of RDX/TNT) for evaluating the improvements induced in the rate behavior of AN modified with MAN or QMAN. The TNT was ground with mortar and pestle or dissolved in solvent as appropriate for the formulation. The RDX used was Class E, which has a particle size distribution of more than 97% smaller than 44 microns (through a 325 mesh U.S. Standard Sieve). The AN in formulations was ACS reagent grade. The particle size distribution of the co-solidified materials, e.g. MAN, QMAN blends, were fairly fine powders appropriate to pressing in small diameters. They were obtained by stirring during solidification from solution or by crushing the prepared material. Previous programs of cylinder tests for Amatex compositions (Ref 12) had shown that, for the AN particle size ranges involved here, there was no significant particle size effect. In addition, it was hoped that the experiments would show a far larger systematic effect due to overcoming diffusion limitations than would be attributable to any existing particle size variations in the compositions. Thus rigorous definition of the distributions was not considered necessary.

The MAN refers to the chemical monomethylamine nitrate (sometimes called aminomethyl nitrate or aminomethane nitrate) (Ref 13, 14). The name used herein for MAN is methylammonium nitrate, corresponding to the formula $[H_3CNH_3]^+[NO_3]^-$ and showing its relation to the parent AN structure $[NH_4]^+[NO_3]^-$. The material used was prepared as the salt of nitric acid and methylamine.

Note that whereas final principal products for AN are N_2, 2 H_2O and 1/2 O_2, those for MAN are N_2, 3 H_2O + C. A molar ratio MAN/An of 1:1 leads to CO and 1:2 leads to CO_2, assuming all possible water is produced. The molar ratio provides a means to control fuel availability for the 1/2 O_2 of the AN.

QMAN is tetramethylammonium nitrate, $[(H_3C)_4N]^+[NO_3]^-$. Comparison with AN and MAN formulas above shows that QMAN is simply the quaternary version of MAN. A set of final stable products (analogous to those considered for MAN) may be considered to the N_2 + 3 H_2O + 3 H_2 + 4 C. Hence QMAN provides more fuel per mole than MAN to react with the 1/2 O_2 of the AN. Note that for these products, the molar ratio QMAN/AN of 1:4 leads to a CO balance and 1:8 to a CO_2 balance.

There is another essential difference between MAN and QMAN. The former is an explosive slightly more powerful than AN and has been used as an ingredient of composite explosives (Ref 13-16). Insofar as can be determined QMAN is not an explosive (Ref 17). Hence in substituting MAN for part of the AN, changes in performance may be due to the substitution and to synergistic effects on rate due to overcoming diffusion. On the other hand, in using QMAN the anticipated principal effect is synergism since AN is replaced with an inert substance which moves the system continuously toward negative oxygen balance. The results to be presented can thus be considered to provide a wide range of AN modification.

The degree of improvement due to degree of mixture intimacy was not studied, except for one comparison made between use in MAMATOL of either a mechanical mixture of AN and MAN or a cosolidified one.

The compositions reported on herein are listed in Table 1. The procedures used in preparing these compositions are described in Appendix 1.

Characterization and Performance

The explosives were characterized by thermal analysis, explosion temperature, vacuum thermal stability, impact sensitivity, and density. Performance was measured by detonation velocity and dent depth produced in steel witness plates.

Thermal analysis consisted of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a few differential scanning calorimetric runs and a few capillary melting/freezing points taken. The principal aims of the analyses were safety (compatibility, stability, reactivity) and identification of cosolidification effects and other potentially interesting thermal features such as eutectics, polymorphic transitions and their modification or stabilization, etc. In TGA and DTA, physical and chemical changes are observed as a function of temperature, thermally characterizing the material and also serving for comparison of kinds (and sometimes batches) of materials. TGA measures the change in mass with change in temperature to indicate decomposition leading to gaseous products, sublimation, release of solvents, etc. A duPont 950 TGA attachment to the duPont 900 DTA was used. For DTA the latter instrument was used to measure the temperature differential between the material under investigation and a thermally inert reference sample.

The DTA measurement shows the positions on a temperature scale of the endotherms and exotherms, resulting from phase changes, decomposition, etc.

The explosion temperature test was that of Henkin and McGill (Ref 18) as modified by Zinn and Rogers (Ref 19) and at this installation (Ref 20). This test measures the time to explosion of a confined sample immersed in a liquid metal bath at a constant temperature. The time to explosion versus temperature data can be used as a measure of stability and reactivity. From the data one derives an apparent activation energy and pre-exponential factor convenient for comparing materials.

The vacuum stability test (Ref 21) was used to determine the gas evolved from a one-gram sample maintained at a fixed temperature, usually 100°C or 120°C for 40 hours (unless discontinued earlier because of early evolution of large quantities of gas). In addition, this test determines stability of single components or reactivity between components of a composition.

The impact sensitivity was measured with the Picatinny Arsenal equipment (Ref 21) which uses a 2-kg drop weight on a confined small sample. By decreasing height (one inch at a time) as soon as one "fire" occurred, the height of fall in inches for which no initiation first occurred in 10 trials was found. The "minimum impact sensitivity" was then taken as one inch higher. These numbers served for comparisons of the components, compositions, and to TNT as a standard.

The small-scale confined propagation test provided a measure of the detonation velocity and the depth of dent in a terminating steel witness block. It consisted of a 0.318" diameter by 2 1/2" long column of explosive pressed into a 3/8" OD by 0.028 thick aluminum sleeve. The loaded sleeve was confined in a 1" outside diameter (0.375" ID) brass cylinder, 3" long (see Fig 1). Holes in the cylinder served for insertion of insulated pin wires for detonation velocity measurement. After firing, the depth of dent in the termination witness plate of CRS 1018 steel was measured. Wave front curvature effect on arrival times at the pins was considered in calculating detonation velocities. Density of explosive was measured by weight difference and dimensional volume.

TIGER Computer Program

The TIGER computer program (Ref 3) was used to calculate ideal detonation properties of the explosives studied. These results are related to the effect of changes in elemental composition, density, and energy and do not reflect any rate determining step limitations. In addition, the calculations were done for the reference materials, 60/40 Amatol and Amatex-20. In these calculations the TIGER program was constrained by artificial means to provide different results than obtained in the standard calculation. These calculations can be used to explore the effects on detonation properties of various hypothetical rate determining steps (e.g. limited decomposition of any component of the explosive, presence of an intermediate, alteration of concentration of product gases or condensed species). TIGER calculations are reported in which input data to the program was varied to establish the dependence of the results on the quantity of solid carbon in the products.

RESULTS

Small-Scale Confined Propagation Test

The detonation velocities and dent depths in terminating witness blocks are given in Table 2 for the compositions described in Table 1. The dent depths are plotted in Figure 2 as a function of the percent by weight in the total composition of either MAN or QMAN. Both the data points available for each test condition are plotted rather than an average value and error bars. The percent MAN or QMAN in the compositions (abscissa in Figure 2) is the quantity which replaced AN and was cosolidified with the balance of the AN in the 60/40 Amatol or Amatex-20. Each abscissa value in Figure 2 therefore represents a different degree of substitution for AN and a different ratio of AN to MAN or QMAN in cosolidified form.

Figures 3 and 4 are photographs of the witness blocks showing the trends presented in the curves of Figure 2. The blocks shown in the figures were sectioned at about the midpoint of the dent region. The small strip of black tape added to the face of each block is 1/16" wide and 1/4" long. The dent data, summarized in Figure 2 and Table 2, indicate the following:

a. Increased weight percent of MAN in both the 60/40 Amatol and Amatex-20 bases leads to significant increase in dent depth.

b. The dents for MAMATOL-M (last line of data in Table 2) of .048 and .052 for mechanical mixing of AN and MAN are slightly lower than the .057 and .054 obtained for the cosolidified samples of MAMATOL. This very limited data is not conclusive.

c. Increased weight percent of QMAN in both the 60/40 Amatol and Amatex-20 base shows distinct peaking at roughly the CO balance point between QMAN and AN.

d. In these small diameters (0.318" heavily confined explosive) substitution of MAN for AN or optimum QMAN for AN in each reference explosive clearly improves the impulse delivered to the witness plate to produce the dent over that provided by 60/40 Amatol or Amatex-20. Due to the small explosive diameter, the dent depths (shown in Figure 2) for Amatex-20 are slightly lower than those for TNT, although in cylinder tests (large diameters) Amatex-20 is 12% greater than TNT in wall kinetic energy (Ref 12, 22).

The detonation velocity data in Table 2 shows that for both the 60/40 Amatol and Amatex-20 reference explosives the increase in weight percent of MAN leads to an initial increase in detonation velocity. However, increase of weight percent of QMAN results in oscillations in detonation velocity and is accompanied by a decreasing trend for the 60/40 Amatol.

Due to the small diameter of the explosive, even though heavily confined, the results are on a steep section of the detonation velocity versus diameter curve. This, together with the limited number of data points and some experimental difficulties encountered in these measurements, made efforts to interpret the detonation velocity data unjustified.

TIGER Computations

The results in Table 3 represent predictions for components and composite explosives in which the elements in the composition are assumed to interact within the detonation zone at "infinite" rate, forming products in equilibrium at the Chapman-Jouguet plane (i.e. at the end of steady state detonation zone, or some plane representing the end of the region supporting the propagation of the detonation front). These results provide a measure of detonation properties to be expected if rate limiting steps could be eliminated. The densities used are theoretical maximum density for components and 97% TMD for composites, not the experimentally achieved densities.

One notes in Table 3 that the predicted values of detonation parameters for each series (Amatol-Manatol, Amatol-Qamatol 4, Amatex-Manatex, Amatex-Qamatex 4) decrease except for product temperature and solid carbon (which increase) with degree of substitution of MAN or QMAN and the corresponding decrease in density (97% TMD). Since the experimental densities of Table 2 also decrease with substitution of MAN and QMAN, the presence of reversals of these trends of Table 3 in the experimental velocity and dent data of Table 2 provide evidence for a shift toward ideality (see DISCUSSION).

Table 4 presents the results of a series of TIGER calculations in which the solid carbon in the products was constrained to larger and smaller values than the standard Chapman-Jouguet calculation. (The density used was 97% of theoretical maximum density.) Larger quantities of solid carbon could exist if all the carbon available in the elemental composition of the explosive could not enter into the reaction. Smaller quantities of solid carbon could exist if the equation of state or thermodynamic input parameters used in the program were not appropriate to calculations on non-ideal explosives. The predictions in Table 4 may be considered to represent a progression of quasi-equilibrium states centered on the standard calculation. These predictions provide a means to explore the effects of variation of solid carbon in the products. The data supports the concept of this work that modifications to non-ideal explosives which produce greater carbon (or fuel) participation will lead to improved performance.

Vacuum Thermal Stability

Vacuum thermal stability results are shown in Table 5. MAN and QMAN are not compatible with TNT. This rules out the particular compositions reported on herein for practical use. It does not negate the demonstrated improvement of non-ideal explosives and does not preclude using components other than MAN or QMAN which are compatible with TNT to achieve the same effect. Note in the results that compatibility of MAN or QMAN with RDX is satisfactory and also that the reactivity of the MAN/AN mixtures with TNT is much lower than that of MAN alone with TNT. This last result indicates synergism in MAN/AN.

Explosion Temperature

A limited amount of data was taken, restricted to MAN-TNT-RDX systems. The data is summarized in Table 6 as temperature-time ranges, calculated activation energies and pre-exponential factors of the Arrhenius or Semenov equation $t = Ze(\exp E/RT)$, and closeness of fit to a least-squares straight line by the correlation coefficient r. In agreement with the vacuum thermal stability data, MAN/TNT has a calculated activation energy lower than the other combinations or individual materials.

Impact Sensitivity

Impact sensitivity tests were done solely as safety checks before proceeding with other experiments. The results, given in Table 7, show that the formulations are not unduly sensitive to mechanical impact. They also show some sensitization of AN by the MAN and QMAN since the drop heights of the mixtures are lower than those of the materials alone. There is not much, if any, sensitization of TNT by any combination of the material except for MANATOL.

Thermal Analysis

The salient findings are presented in Table 8. The methylammonium nitrates are chemically stable to satisfactorily high temperature. QMAN in particular is extremely stable, with no action discernible below 375°C. Both MAN and QMAN are compatible with AN. (DMAN and TMAN, not shown in the table, are also stable and compatible with AN but are incompatible with both TNT and RDX, and hence were dropped from further work.) The MAN/AN eutectic melting point is in the vicinity of 50°C, and that of QMAN/AN is in the vicinity of 125°C, a temperature attainable for cast loading with steam at moderate pressure.

Reactivity of MAN with TNT is clearly shown: the major DTA exotherm starts as low as 160°C. The same is true of QMAN (150°C). The TGA results confirm the DTA data: rapid loss of weight begins at low temperature for MAN/TNT and QMAN/TNT. The presence of AN, however, changes these results significantly for MAN, but not for QMAN. The DTA exotherm at 150-160°C is small, almost indiscernible in some runs, and TGA data resembles that for the AN system without MAN.

Both MAN and QMAN appear to be compatible with RDX. The major exotherm temperature in DTA is depressed little in either case. Again, TGA confirms the DTA: little weight loss is noticed much below 200°C, which is close to the melting point of RDX.

Three isothermal TGA's were obtained to compare RDX and MAN, each held at 140°C for three hours with MAN/RDX treated identically (not included in Table 8). The purpose was to check the findings of apparent compatibility of MAN and RDX from VTS, DTA and TGA, by holding for a time at a relatively higher temperature. These isothermal runs do not indicate incompatibility: weight loss for a 24-mg sample of 50/50 MAN/RDX was only 1.4 times that of 24 mg of either RDX or of MAN.

In the vacuum stability test it was found that the reactivity of the MAN/AN mixture with TNT was much lower than that of MAN alone with TNT. The DTA showed the existence of eutectics of MAN/AN and QMAN/AN. The TGA suggested lower reactivity of QMAN/AN with TNT than QMAN with TNT. Although not complete, these results clearly indicate that MAN/AN and QMAN/AN as prepared have achieved some level of intimacy beyond an ordinary physical mixture.

Hygroscopicity

AN and all of its methylammonium homologues are hygroscopic, but to different degrees. QMAN is the least, being less so than AN, and dimethylammonium nitrate is the most, being deliquescent to the point of dissolving in a short time at ordinary humidities. All of the mixtures of AN with methylammonium nitrates appear to be more hygroscopic than the parent materials. In conducting the experiments, small batches of materials and formulations were sometimes processed under dry nitrogen flow or submerged in Freon, and were kept in tightly closed full containers or in a desiccator. In this way it was not unduly difficult to control moisture absorption. No quantitative hygroscopic data was taken. The hygroscopicity and incompatibility with TNT were sufficiently disqualifying for practical explosives to limit tests to those needed to satisfy the first objective, i.e., demonstrating the value of overcoming diffusion limitation.

DISCUSSION

Outline

The two objectives of this work were:

a. To demonstrate that one could produce a move toward ideality by partially overcoming a reaction rate limiting factor in the conversion of a condensed explosive to optimum product species.

b. To use such a move toward ideality to point a way toward an improved explosive.

This section is devoted to examining the extent to which the work reported herein has satisfied these objectives, to providing a broader base for further work related to these objectives, and to exploring the feasibility and value of the objectives themselves.

First, the limitations of what has been done are treated by subsections on the significance of the data obtained and on the experimental design. This is followed by discussion of the more general problems for non-ideal explosives of selection of meaningful performance tests and computer prediction of performance that would accompany a move toward ideality. Next, attention is devoted to the variety of possible approaches for obtaining improvements in the direction of ideal explosive behavior in non-ideal explosives or other energetic materials. This serves to broaden the present effort and place it in a larger framework. Finally, consideration is given to the value of it all, i.e., what could be gained if one could "tailor" explosive properties.

Significance of Data Obtained

No further discussion is needed of the vacuum thermal stability results, which showed that TNT and MAN or QMAN are incompatible. Similarly, hygroscopicity is an unfavorable feature of both MAN/AN and QMAN/AN.

All the individual dent depth points were plotted and fitted by eye in the four curves shown in Figure 2. The totality of the four curves support the conclusion that MAN for AN improves and QMAN for AN leads to a peak of improvement in the reference explosives. However, each individual curve is based on limited data. Only two points were obtained for each composition. The number of weight percent values of MAN used in the compositions is only sufficient to support an overall rise in dent depth. No determination can be made as to whether a peaking effect is also present, as existed for QMAN substitution. Due to the limited data the exact nature of the latter peaking effect is also poorly defined.

The marked improvement in dent depth for small diameter of explosive with MAN or optimum QMAN substitution in 60/40 Amatol and Amatex-20 indicates possible value for smaller munition applications.

From Table 2, one sees that the substitution of MAN leads to a slight peak in detonation velocity. The QMAN substitution in 60/40 Amatol, (TNT environment) strongly degrades detonation velocity whereas in Amatex-20 (RDX/TNT environment) the velocity values stay near that of the reference explosive. The contrast in Table 2 between detonation velocity and dent is a consequence of the difference between the time frame of the detonation zone and the time frame influencing formation of the dent.

A more complete set of data may alter some details, but the limited data available is sufficient to confirm that there is an increase in depth of dent with substitution of MAN and QMAN in the composite explosives and a slight increase in detonation velocity with the MAN substitution. These trends are contrary to the decreasing trend for pressure and detonation velocity (Table 3) for ideal explosives. The trend in the experimental results is believed associated with the extent of the displacement toward ideality. There follows in the subparagraphs below a more complete discussion of this and other possible causes of this behavior.

a. Although the explosive is confined in a 1" OD brass cylinder, the explosive diameter (0.318") is still sufficiently small that the improvement could be partially due to the altered composition having a smaller critical diameter and hence performing better in the experimental configuration used. It should be recognized that such improved performance, whatever the cause, has value for small dimension munitions. On the other hand, to eliminate the critical diameter hypothesis and obtain better data, experiments must be conducted at larger dimensions.

b. The improvements observed may be attributed in the case of MAN to substitution of a superior (to AN) explosive in the composite. In the case of QMAN, this can not be the case. For the two together, it may be asserted that the improvement is due to an enhancement of participation (synergism) by the rest of the AN in the composite due to its cosolidification with the MAN or QMAN, i.e., the explosive has been moved toward ideality.

c. With respect to the QMAN substitution the fact that the peak occurs at or near the CO balance formulation instead of at the CO_2 balance suggests (by comparison with results of TIGER calculations) that the product species are in a non-equilibrium condition or have been shifted (e.g., by freezing) to a different set of equilibrium species. A contributing factor may be that the CO balance has a higher ratio of carbon to oxygen than does CO_2. This higher ratio would tend to decrease diffusion time and accelerate reaction rate for carbon from MAN or QMAN and oxygen from AN. Note in Table 4 that an increase in CO accompanies a decrease in solid carbon in the products.

d. Since the densities of MAN (1.42) and QMAN (1.25) are lower than that of AN (1.725) the substitutions made lead to lower density composite explosives. Calculations with the BKW equation of state (e.g., by TIGER) predict that as the density decreases, the temperature of the products at the Chapman-Jouguet plane will increase (see Table 3). Since a temperature increase leads to an increase in reaction rate, and a density decrease (for ideal explosives) leads to a decrease in performance parameters (e.g., detonation pressure) it may be asserted that the results are due to a combination of the temperature and density effects. However, careful tracing of the computer-predicted temperature rise with density decrease shows that it is associated with the particular form of the BKW equation of state. It is believed that a different equation of state could be used for CJ calculations and would produce different results with respect to temperature. Further, the temperature of a detonation is most difficult to measure and insofar as is known to the authors there is no experimental evidence to support a temperature rise with density decrease.

e. For non-ideal explosives containing ammonium nitrate it has been reported (Ref 23) that a density decrease leads to harply increased performance (not a decrease, as found for molecular explosives). This has been attributed (Ref 24) to the effect on diffusion (a critical parameter for oxidantfuel explosives) of the pressure dependence on density. The experimental data of these references is for density variation over a wide range of single composite explosive. The data here is for a variation in composition with the density maintained, in all cases, close to 95% of the theoretical maximum density of each composition. Hence, although the diffusion-density dependence approach merits further theoretical consideration, the two experimental situations must be recognized as essentially different.

f. An explanation of the peak may also be sought in terms of the expression of detonation velocity of a composite in terms of the volume fraction weighted sum of the detonation velocities (or Urizar coefficients) of the components (Ref 25). One can show that if the density of a composite decreases as a component of lower density is substituted, but the overall energy contribution due to the substitution (exclusive of synergism) increases, then a peak in detonation velocity is possible. However, this is not the case for QMAN where the peak did occur but could be the case for MAN where a peak was not evident with the limited experimental data. Insufficient experimental data was available to pursue this quantitatively for the composites studied. One should also note that the basis for this volume summation approach to composite detonation velocities remains to be established for non-ideal explosives of the type studied here.

Thermal data on MAN/AN and QMAN/AN showed that one can achieve an energetic casting medium for which the phase changes can be controlled by the constituents. Formulations suitable for conventional pressure-steam melting can correspond to those enhancing performance of AN explosives. Melting points and properties modified by polymorphic phase transitions have practical value for finding alternative casting media to TNT and for minimizing explosive exudation due to density variations during temperature cycling.

The hygroscopicity of AN, MAN, and QMAN, although reduced by their incorporation within the base explosives, is a deterrent to their use. This suggests seeking sutstitute materials for MAN and QMAN, and additives or coatings to be applied to MAN/AN or QMAN/AN to reduce moisture absorption.

Criticism of the Experimental Design

The work began as a small scale exploration of a concept (see INTRODUCTION) and proceeded along the most promising avenues making use of available methods and equipment. By the time the extent of the incompatibility between MAN and QMAN with TNT had been established by the vacuum thermal stability tests, the dent data indicated that the first objective had been met, and the incompatibility with TNT ruled out success in meeting the second objective. Hence, a complete data package was not pursued further. However, other systems will be worked on in the future and it is instructive to consider the nature of the required experimental design for such studies in terms of the present one.

To improve AN participation, it was thought necessary to provide complementary reactive elemental or molecular species in very close proximity to the AN in a form that provided enhanced action between fuel and oxidant. Presumably this would lead to early creation of activating species and release of energy and then to higher specie concentration and energy density, providing a faster reaction rate. As an extrapolation from the known success of fuel oil with AN, MAN and QMAN were selected as candidates because in addition to being fuels they could be cosolidified with AN.

The initial hypothesis centered on getting carbon to react with excess oxygen, thereby producing more thermal energy, and by proximity doing it faster. However, some improvement might be achieved by matching an intermediate product of AN decomposition with an appropriate complement for fast reaction. No attempt was made to explain why the carbon from the TNT does not serve as the necessary complement for the AN. It was simply assumed to be too remote from the AN molecules. The choice of MAN and QMAN to provide a fuel range from an explosive to an inert was most valuable since it provided two energy levels leading to different results. In addition to cosolidification, particle size control could have been introduced as another parameter used. As explained earlier, this was not done because of the lesser intimacy potential compared to cosolidification and because a prime interest for the Army is in improving cast explosives. In cast explosives, viscosity of the mix limits choice of particle size fractions. However, once pressing was used as a research tool, one might also include particle size as a parameter of the experimental design, with a well characterized graduation of sizes down to the smallest obtainable. This approach has been used at Lawrence Livermore Laboratory (Ref 26-28) to demonstrate improved metal acceleration achieved in cylinder tests of composite explosives with very small particle sizes.

The cosolidification of AN with MAN or QMAN was characterized only by melting point shifts and DTA changes. These showed that the cosolidified materials had properties differing from the constituents and were more than physical mixtures. The exact status of intimacy of each mix was not established. Diagnostic measures (e.g., crystallography, x-ray diffraction, scanning electron microscopy, differential scanning calorimetry, full phase diagrams, etc.) need to be used to provide a well characterized measure of intimacy. Experiments are required to establish the kinetic pathways, i.e., the sequence of reactions and species involved in the transformation of condensed explosives to products and their associated rate parameters. It would be of great value to know the feasibility and benefits of solid solutions/mixed phase/mixed crystal modifications for improving non-ideal explosives. Not all of these can be put into an exploratory experimental design. However, an awareness of the deficiencies noted could lead to well chosen experiments and avoid narrow interpretations of results.

The performance tests were limited to measurements, with the configuration shown in Figure 1, of detonation velocity and dent depth in a witness block. The diameter of the explosive was only 0.318" and the radial confinement was brass with a one-inch outside diameter. These small dimensions were chosen for the following reasons: the hazard is less with small quantities; limited quantities of the new explosive could be readily made by "bench" methods; a usable test apparatus and method were already available. For most non-ideal explosives this small-dimension test is in a region of critical dependence of propagation on diameter and confinement, which limits extrapolation of results to other dimensions and comparison to other explosives. This criticality was one cause for the difficulty with the measured detonation velocity data. However, the small-dimension test has the advantage of directly revealing the benefit of improved performance for small-dimension munitions. For a larger diameter (1 5/8" unconfined) witness disk test (Ref 29) a correlation is shown between dent depth and Chapman-Jouguet pressure. However, this agreement could be due to the fact that that part of the impulse waveform which produces the dent is proportional to the detonation pressure. This proportionality may not be as well satisfied for non-ideal explosives and even less so for small dimensions. The same qualification can be made here with respect to a recent correlation developed primarily for ideal explosives (Ref 30) between cylinder test results and detonation pressure. All of these comments indicate that the results of the small-dimension test used here can not be extrapolated to other dimensional situations and to explosives not tested. This then shows clearly the need for also doing tests at larger dimensions. However, these should be considered a necessary corollary rather than a replacement (see later subsection). The small dimension tests are valuable because they directly show improvement in performance that apply to small scale munitions. Thus, if Amatex-20 and 60/40 Amatol could not be used in a small munition, this type of modification (not necessarily the specific one here which had incompatibility problems) might make them feasible.

Selection of Performance Tests

The pertinence of laboratory performance tests is vital to the entire program of modifying non-ideal explosives toward ideality and to the value of such modifications to munition applications. It is the function of this section to provide the basis for selection of tests.

The essential idea of the program is to identify one or more rate-limiting steps, to select among these a step to be modified and find a way to do this with favorable consequences. Suppose the time frame of a step is short enough to be inside the detonation zone structure (i.e., time is less than or equal to length of steady-state zone divided by detonation velocity). Then if a rate-limiting step within this time frame were to be eliminated, the detonation pressure would be increased. This would have immediate value for those munitions with a function dependent on a corresponding time frame. For example, acceleration of thin flyer plates and peak shock pressure developed across a contact discontinuity would be increased. In addition very small items such as detonators operating in a kinetically limited mode would be affected. The further value of the elimination of this very short rate limiting step for longer time interval applications depends on whether--if this step is not altered at an early time--the consequences persist indefinitely or the rate limitation is overcome anyway in a longer time frame. As an example of the first possibility, imagine that a product species which is metastable is formed early in the detonation zone and conditions do not lead to further decomposition until much later. In this case, alteration of this step could have value for both short time (e.g., fragment velocity) and long time (e.g., blast) applications. As an example of the second possibility consider the vaporization of aluminum. If the aluminum were made to participate in the detonation zone, this would have great value for very short time applications. However, for long time applications such as large scale blast and underwater explosives, the aluminum probably participates anyway so that the accelerated vaporization does not produce a further improvement.

When dealing with non-ideal explosives it is most important to recognize that time frames or kinetic paths are not absolute entities but depend on other factors. The time sequence of pressure and temperature can alter the species produced, and this sequence is modified by size, geometry, and confinement. For example, diffusion limited reactions can be accelerated by confinement which prolongs higher densities and temperatures or decelerated by rapid expansion (freezing). It has been shown that explosive confinement and reshocking at walls alter final product species within a large vessel (Ref 31, 32). Thus altering the rate-limiting step is related to the time scale of the step, the size, geometry, and confinement of the munition, and the function of the explosive in the munition. The significance of time factor magnitude in munitions roughly increases in the sequence: explosive trains in fuzes, small shaped charges, miniature munitions, fragment size, fragment velocity, demolition, blast, and cratering.

From the preceding it follows that the performance tests used to determine whether a rate-limiting step has been altered and the significance thereof must either be as broad as possible to encompass the above described multiplicity of usages or it must be directed to a particular case. To do this one can try to create a scale of time frames containing both munition factors and performance test possibilities as a basis for critical selection of performance tests. Detonation velocity, cylinder test expansion, and dent in a terminating witness plate are measurements that can be used to provide data approximately covering the range of interest. Details of a preliminary effort to set up such a scale are given in Appendix 2 and the results thereof are shown in Figure 5.

The modification problem for AN explosives will serve to indicate how Figure 5 would be used. One sees that a 2" diameter standard cylinder test would approximate the time frame of 60mm and 81mm rounds. One notes that at a 1 5/8" explosive diameter, the dent formation process in a steel witness block will reflect action in an even shorter time frame, and that the longest rate limiting step one should be trying to alter is about 25 microseconds. Standard cylinder tests of modified and reference explosives at 2" diameter with measurement of detonation velocity and dent depth in steel witness blocks will provide adequate information for predictions on enhanced performance in these munitions.

For the rate limiting factor of diffusion in AN in an AMATEX type explosive, earlier work suggested that the AN does not fully participate in the time frame (to 60 microsec) of a 4" diameter standard cylinder test. The effect of any elimination of a diffusion rate limitation at an earlier time would be expected to carry out to longer times. One would want to know in how short a time scale the alteration of the diffusion limitation can be made to occur. The tests suggested in the previous paragraph or an equivalent test would provide the necessary guidance.

The performance tests described in the previous paragraphs can provide results useful in selecting explosive modifications meriting further study. Other tests can be used to rapidly delineate the value and limitations of modifications made to an explosive. Thus, the small scale dent tests were shown to give an indication of enhanced value for small dimension applications, while compatibility tests helped screen further pursuit of particular combinations. However, once a modification is shown to have value in even one application, then more exhaustive testing must be done to clarify the domain of applicability of the explosive. For example, one of the early series of tests would be detonation velocity as a function of diameter. Another would be large scale gap and other tests to establish the range for shock initiation. Finally, if there is sufficient promise, then the full series of tests to qualify the explosive as a military explosive must be done.

Prediction of Potential Performance of Non-Ideal Explosives

By calculation of detonation properties and metal acceleration using computer programs, it is possible to try to predict the performance of non-ideal explosives if ideal behavior were achieved. This helps in the selection of explosives where modification would lead to significant improvement and also guides the program, reducing the quantity of testing. This section explores the limitations of this approach.

The TIGER computer program has been used to calculate detonation and expansion isentrope properties, simulating the results of particular hypotheses concerning non-ideal explosives. This is done by doing calculations as though the system were an ideal explosive, but using such devices as relabelling part of the input elements, and the corresponding allowed product species, to force some elements to appear among the products in a desired species. This technique was used to study the effect of quantity of carbon in the products as shown in Table 4. Other techniques used alter the heat of formation to shift temperature, or change covolumes to shift presence of particular species, make part of the explosives inert, restrict product species, or introduce new species, etc. In this way one can try to use the TIGER program to observe effects of change in input and thermodynamic variables or effects of hypotheses on non-ideality. However, results of such calculations must be interpreted with great care. It is essential to recognize that the absolute values of detonation parameters and expansion isentropes obtained in this manner are not in agreement with experiment. The TIGER program gives correct parameters only within or near its domain of calibration, which is for CHNO explosives similar to TNT or RDX. The domain of validity of results and the improvement and extension thereof has been a continuing subject of discussion and effort (e.g., Ref 33-38). For non-ideal explosives, the situation is further complicated by incomplete reactions, thermodynamic non-equilibrium, severe environment/ product-species interaction, and product-species composition significantly different from those of the calibration explosives.

The predictions of the TIGER computer program (or equivalent program) of detonation parameters and expansion isentrope, in addition to being subject to the qualifications described in the previous paragraph, are in themselves not adequate to predict munition performance, but can only be used for comparison between explosives. For munition performance, the first step is to use hydrodynamic computer programs for which the explosive product description is one input. For non-ideal explosives the explosive description is exceedingly difficult to provide because there is not a unique equation of state of equilibrium products. Instead there is a time dependent rate of change whose time dependence is itself altered by the changes in thermodynamic and fluid dynamic parameters. This varies as well with position in the explosive, which leads to gradients and flows. Changes in scale, confinement, and geometry occur between munitions and in the functioning process of a munition. One can see that the burden of prediction for munitions containing non-ideal explosives assigned to the hydrodynamic program is indeed a difficult one. An approach involving a time dependent combination of more than one explosive product description has shown promise (Ref 39). However, this has not as yet reached a level of development adequate to guide improvement of non-ideal explosives.

It follows that emphasis in future efforts must be on experimental performance measures and their relevance to munition improvement (see Fig 5), and on explorations of the nature of rate processes for the time frames described and possible means for their modifications.

Exposition and Benefits of Tailoring Explosives

A munition is a combination of an energetic material and a load (e.g., shell casing, shaped charge liner) designed to be transformed into a mechanism to serve a military need. Examples of mechanisms are fragments, shaped plates, spalling, metal jets, blast, underwater impulse, cratering, driven plates, and compression. Tailoring of explosive properties would be one means to provide effective mechanisms, by modifying the properties of the explosive to meet particular needs. A few hypothetical examples are given below.

a. The lethality of some munitions is significantly increased by using distributed sources of fragments which leads to smaller explosive-containing elements serving as the energy sources. To have an explosive with adequate brisance to produce the necessary fragmentation one requires a main charge explosive, which can be initiated reliably and have stable high order propagation. It is possible to obtain the necessary combination of brisance and sensitivity in some existing explosives but this becomes difficult when one tries to use alternative fill composite explosives in small dimensions. Data in this report (Fig 2 curves) forecasts that non-ideal explosives can be tailored to function in smaller dimensions with improved performance.

b. The acceleration of metal would be more efficient if the energy converted to heat in the metal due to shock compression and reverberation could be transformed to kinetic energy. This requires control of the pressure in the driving force by controlling time and location of the energy release. An approach would be to use a non-ideal explosive spatially modified to provide a gradient of rate of transformation with respect to position in the explosive. Shock-impedance transformation layers can be also inserted to alter gradients. One could also explore the possibility of using such an explosive configuration for propulsion.

c. Prematures due to setback initiation are a major gun crew hazard. Vulnerability of tank ammunition to fragments and flame is a major tank crew problem. One could formulate an improved non-ideal explosive such that at the base for setback, or at the circumference for fragment or bullet impact, the sensitivity would be lower to reduce the hazard. This reduction in sensitivity would not affect performance because the initiation of the surface explosive by the stronger stimulus of the balance (interior) explosive would provide full performance. The same idea could be used in reverse to eliminate the booster by selective sensitization of the explosive in the region of the fuze. Burning to detonation might be sufficiently controlled to be used as a standard initiating mechanism for main charge explosives. Sensitivity gradients and geometry control could lead to improved secondary initiation characteristics.

d. A detonation zone lengthened by control of a rate-determining parameter would facilitate study of the interior of such zone (e.g., by time-resolving spectroscopy).

Use or modification of explosives to achieve special effects is certainly not new. Tailoring as a principle in the sense of attempting to control the explosive release of energy by identifying and modifying a rate-determining step is a new approach. It has been achieved in the past in some cases as solutions to specific problems (e.g., by control of particle size in composites, and by the use of aluminized explosives to heat the products raising delivered impulse for cratering and blast). The area of effort that offers greatest potential for munitions is that of condensed non-ideal explosives. However, there are also rate limitations in ideal explosives since these have finite (though thin) detonation zones which have been measured (see also Ref 40). One would expect rate limitations in slurry explosives which are composites generating lower temperature environments. Tailoring explosives is not limited to the diffusion mechanism and its alteration. However, this rate-limiting step is recognized as most important and has recently been carefully examined (Ref 41). Reducing diffusion or transport limitation by composition modification to improve reaction efficiency has been the thrust of this work. The true mixed crystal, solid solution, and similar approaches are logical parallels to this effort. It is important to recognize the possible existence of many other rate-modifying steps, e.g., metastable states, alternative decomposition paths, chain-branching, vaporization, endothermic processes, local site properties, surface layers, chemical kinetics, chemical quenching, temperature buffering, crystal growth modifiers, interstitial desensitizers, and even catalysts (e.g., Ref 42). This is not a complete listing; in fact some rate-modifying approaches specific to the propellant field and others deemed proprietary (Ref 43) have been deliberately omitted. In addition, it should be noted that nonsteady and partially directional propagation characteristics have been suggested as possible for inhomogeneous, graded mixed crystals (Ref 44). The items in various listings of factors are not entirely independent and an early objective of a program in tailoring would be to outline the subject and assign values, priorities and sequencing, i.e., generate a well thought out overall program.

SUMMARY

It has been established that a non-ideal explosive can be altered toward ideality by modifying a rate-determining factor so as to provide improved performance. The particular explosives used in this study are, in their present state, inappropriate for military use due to incompatibility with TNT and excessive hygroscopicity.

A mechanism (Fig 5) was developed for selection of performance tests for studies on idealizing non-ideal explosives. Such tests must be supplemented by experiments to evaluate the existence and modification of a rate-determining step. The current limited capability of computer prediction techniques for non-ideal explosives limits their use to parametric studies of trends.

It is proposed that tailoring of explosives has potential for progress in munitions, both existing and new.

FUTURE WORK

The desired move toward ideality depends on the modification of the rate-determining factor(s). These factors are a function not only of the basic mechanism (e.g., diffusion) of the non-ideal component but also of the environment provided by the behavior of the balance of the explosive. In this view, TNT and RDX/TNT were identified earlier as two environments. Work is already underway to examine the potential of a non-TNT environment containing various quantities of QMAN or MAN with AN. Work is planned for the TNT and TNT/RDX environments, with alternates for QMAN or MAN used with AN, but which would be compatible with TNT. Another planned exploitation of the work of this report is further study of the MAN/AN and QMAN/AN and similar systems as substitute casting matrices to replace TNT entirely. Better identification of the physical states of the cosolidified systems is needed, as are other detonation parameters e.g., detonation velocity vs diameter and shock sensitivity.

ACKNOWLEDGMENTS

The authors wish to acknowledge enlightening discussions with B. Craig, C. Mader, and A. Popolato of Los Alamos Scientific Laboratory, M. Kamlet of Naval Ordnance Laboratory, and M. Finger, E. Lee, and H. Cheung of Lawrence Livermore Laboratory.

The results and computations reported were obtained with the support of the following personnel of the Feltman Research Laboratory: W. Voreck, Jr., E. Dalrymple, W. Zimny (detonation velocity and dent test), R. Gentner (TIGER), G. Randers-Pehrson (HEMP), R. Graybush, H. J. Jackson, L. Hayes (thermal analysis and sensitivity), M. Warman (MAN/QMAN preparation).

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 second author under the Laboratory Research Cooperative Program.

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Table 1

Compositions

		Percents by Weight						Densities			Percents by Volume at TMD					
	Comment	RDX	TNT	AN	MAN	QMAN	FO	TMD	97% TMD	Expt'l	RDX	TNT	AN	MAN	QMAN	FO
RDX		100						1.802	1.7479							
TNT			100					1.650	1.6005	1.59						
AN				100				1.725	1.6733							
MAN					100			1.420	1.3774							
QMAN						100		1.250	1.2125							
94/6 AN/FO				94			6	1.635	1.586				89.10			10.90
AN/MAN(CO)				45.97	54.03			1.546	1.499				41.20	58.80		
AN/MAN(CO_2)				62.99	37.01			1.598	1.550				58.35	41.65		
AN/QMAN(CO)				80.45		19.55		1.606	1.557				74.90		25.10	
AN/QMAN(CO_2)				86.61		13.39		1.641	1.592				82.40		17.60	
60/40 Comp B		60	40					1.738	1.686		57.87	42.13				
AMATOL	TNT is base for next six		40	60				1.6942	1.6434	1.58		41.07	58.93			
MAMATOL*	MAN/AN CO_2 balance		40	37.8	22.2			1.6184	1.5699	1.58		39.23	35.47	25.30		
MANATOL	MAN for all AN		40		60			1.5039	1.4587	1.30		36.45		63.55		
QAMATOL 1	QMAN/AN CO_2 balance		40	52		8		1.6451	1.5957	1.58		39.88	49.59		10.53	
QAMATOL 2	QMAN/AN CO balance		40	48		12		1.6216	1.5729	1.56		39.31	45.12		15.57	
QAMATOL 3	QMAN for MAN in MAMATOL		40	37.8		22.2		1.5646	1.5176	1.42		37.93	34.28		27.79	
QAMATOL 4	Extremely fuel rich		40	22.2		37.8		1.4847	1.4402	1.35		35.99	19.11		44.90	
AMATEX-20	RDX/TNT is base for next six	20	40	40				1.7085	1.6573	1.52	18.96	41.42	39.62			
MAMATEX	MAN/AN CO_2 balance	20	40	25.2	14.8			1.6564	1.6067	1.55	18.38	40.16	24.20	17.26		
MANATEX	MAN for all AN	20	40		40			1.5745	1.5273	1.47	17.48	38.17		44.35		
QAMATEX 1	QMAN/AN CO_2 balance	20	40	34.6		5.4		1.6745	1.6243	1.57	18.58	40.59	33.59		7.24	
QAMATEX 2	QMAN/AN CO balance	20	40	32		8		1.6586	1.6088	1.57	18.41	40.20	30.77		10.62	
QAMATEX 3	QMAN for MAN in MAMATEX	20	40	25.2		14.8		1.6184	1.5698	1.53	17.96	39.24	23.64		19.16	
QAMATEX 4	Extreme fuel rich	20	40	14.8		25.2		1.5605	1.5137	1.47	17.32	37.83	13.39		31.46	

*MAMATOL-M has the same composition, but the AN/MAN was a mechanical mixture.

Table 2

Detonation Velocity and Dent Depth*

	Density (g/cc)		Det. Velocity (m/sec)		Dent Depth (inches)	
TNT	1.59	1.58	6700	6800	.070	.067
PBX 9404	1.77	-	8010	-	.108	-
AMATOL	1.57	1.58	5700	5500	.039	.037
MAMATOL	1.57	1.59	5800	5800	.057	.054
MANATOL	1.30	-	5570	-	.069	-
QAMATOL-1	1.58	1.57	5260	5300	.042	.042
QAMATOL-2	1.54	1.57	5560	5960	.048	.049
QAMATOL-3	1.41	1.42	4810	4830	.044	.041
QAMATOL-4	1.35	1.34	4830	4900	.045	.042
AMATEX	1.53	1.50	6440	6500	.060	.061
MAMATEX	1.56	1.53	6830	6830	.071	.071
MANATEX	1.47	1.47	6830	6360	.085	.081
QAMATEX-1	1.57	1.56	6670	6540	.063	.072
QAMATEX-2	1.57	1.57	6280	6210	.069	.071
QAMATEX-3	1.53	1.53	6360	6470	.067	.074
QAMATEX-4	1.46	1.48	6650	6640	.062	.066
MAMATOL-M**	1.56	1.56	5630	5820	.048	.052

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* See Figure 1 for experimental arrangement. Two separate tests were done on most compositions. See Table 1 for composition details. See text for comments on limited validity of detonation velocity results.

** MAMATOL-M is MAMATOL in which the AN/MAN was a mechanical mixture, i.e., not cosolidified.

Table 3a

TIGER Predictions of Explosive Properties for Ideal Behavior

	Density (g/cc)	Detonation Velocity (m/sec)	P (katm)	T (°K)	Gamma	Gas	C (S)
						(moles/kg xpl)	
RDX	1.802	8774	346	2631	2.958	33.82	6.70
TNT	1.650	6989	208	2904	2.820	25.70	22.73
AN	1.725	7836	210	470*	3.973	43.73	0.0
MAN	1.420	7512	196	1733	3.029	42.55	10.60
QMAN	1.250	7205	157	1403	3.073	40.57	25.02
94/6 AN/FO	1.586	8203	247	1237	3.264	43.24	0.54
AN/MAN(CO)	1.499	7888	224	1545	3.106	43.08	2.87
AN/MAN(CO_2)	1.550	8127	242	1435	3.169	43.28	3.17
AN/QMAN(CO)	1.557	8114	242	1399	3.180	43.08	2.87
AN/QMAN(CO_2)	1.592	8298	256	1331	3.230	43.28	0.0
60/40 Comp B	1.686	7952	270	2829	2.895	30.59	13.09
AMATOL	1.643	8054	257	1806	3.089	36.37	5.49
MAMATOL	1.570	7740	230	1959	3.029	36.11	9.22
MANATOL	1.459	7267	191	2163	2.976	35.71	15.55
QAMATOL-1	1.596	7835	239	1891	3.052	36.10	9.24
QAMATOL-2	1.573	7728	230	1930	3.038	36.00	11.08
QAMATOL-3	1.518	7468	208	2014	3.020	35.65	15.82
QAMATOL-4	1.440	6851	172	2189	2.879	35.21	23.01
AMATEX-20	1.657	8024	262	2128	3.016	34.39	8.07
MAMATEX	1.607	7818	243	2230	2.983	34.24	10.55
MANATEX	1.527	7489	214	2374	2.947	34.00	14.74
QAMATEX-1	1.624	7877	249	2183	2.996	34.23	10.56
QAMATEX-2	1.609	7810	243	2207	2.989	34.15	11.79
QAMATEX-3	1.570	7635	227	2263	2.976	33.94	14.94
QAMATEX-4	1.514	7110	197	2436	2.829	33.67	19.71

Densities of composite explosives studied (see Table 1) were set at 97% theoretical maximum density (TMD). Single components were calculated at TMD.

*A temperature of 470°K indicates that results are outside range of validity of the equation of state. These results should not be used.

Table 3b

TIGER Predictions of Explosive Properties for Ideal Behavior (cont.)

		Energy Changes**					
		per gram			per cm^3		
	Dens. g/cc^3	Δ Spec.	Δ Froz.	Δ to CJ	Δ Spec.	Δ Froz.	Δ to CJ
RDX	1.802	1529.0	2116.3	587.4	2755.3	3813.6	1058.5
TNT	1.650	1282.5	1681.9	399.4	2116.1	2775.1	659.0
AN	1.725	373.0	669.3	296.3	643.4	1154.5	511.1
MAN	1.420	1011.2	1426.6	415.4	1435.9	2025.8	589.9
QMAN	1.250	846.3	1220.3	374.0	1057.9	1525.4	467.5
94/6 AN/FO	1.586	891.0	1330.0	442.0	1413.1	2109.4	701.0
AN/MAN(CO)	1.499	987.6	1428.8	441.2	1480.4	2141.8	661.4
AN/MAN(CO_2)	1.550	980.0	1433.7	453.7	1519.0	2222.2	703.2
AN/QMAN(CO)	1.557	954.0	1403.8	449.8	1485.4	2185.7	700.3
AN/QMAN(CO_2)	1.592	956.0	1416.2	460.2	1521.9	2254.6	732.6
60/40 Comp B	1.686	1430.2	1928.5	516.3	2411.3	3251.5	870.5
AMATOL	1.643	1095.2	1558.8	463.6	1799.4	2561.1	761.7
MAMATOL	1.570	1105.6	1546.6	441.0	1735.8	2428.2	692.4
MANATOL	1.459	1123.5	1522.8	399.2	1639.2	2221.8	582.4
QAMATOL 1	1.596	1091.6	1538.5	446.9	1742.2	2455.4	713.3
QAMATOL 2	1.573	1091.1	1528.6	437.6	1716.3	2404.5	688.3
QAMATOL 3	1.518	1087.1	1499.5	412.4	1650.2	2276.2	626.0
QAMATOL 4	1.440	1079.7	1452.5	372.9	1580.7	2091.6	537.0
AMATEX 20	1.657	1208.9	1685.9	477.0	2003.1	2793.5	790.4
MAMATEX	1.607	1215.5	1675.8	460.4	1953.3	2693.0	739.9
MANATEX	1.527	1226.1	1656.4	430.4	1872.3	2529.3	657.2
QAMATEX 1	1.624	1206.2	1670.6	464.4	1958.9	2713.1	754.2
QAMATEX 2	1.609	1205.1	1663.3	458.2	1939.0	2676.2	737.2
QAMATEX 3	1.570	1202.5	1643.2	440.7	1887.9	2579.8	691.9
QAMATEX 4	1.514	1196.5	1608.7	412.2	1811.5	2435.6	624.1

**Δ Species = $E_{formation} - E_{CJ-STP}$. It is the difference between the energy of formation of the condensed explosive and the energy of formation of CJ products at standard temperature and pressure. It indicates the energy made available by the chemical changes.

**Δ Frozen = $E_{CJ} - E_{CJ-STP}$. It is the difference between the energy of the products at the CJ state and at standard temperature and pressure. It indicates the energy made available by frozen product expansion from the CJ state. Major changes in composition do not commonly occur on an isentrope.

**Δ to CJ = $E_{CJ} - E_{formation}$. It is the energy added in going from the condensed explosive to the CJ state which is provided in the detonation wave.

Table 4

Effect on Prediction of Detonation Properties of 60/40 AMATOL of Forcing C(s) to Assume Altered Values

C(s)	10.79	7.70	5.89*	4.44	1.70	0	0**
D (m/s)	7329	7783	8054	8130	8333	8462	8498
P (kbar)	198	235	257	261	270	275	280
T (^{o}K)	1010	1467	1806	1741	1619	1547	1228
H_2O	19.39	19.39	19.39	18.53	15.76	14.02	16.97
N_2	10.14	10.14	10.14	10.14	10.14	10.14	9.59
CO_2	1.54	4.62	6.83	7.05	8.47	9.39	3.78
CO	0	0	.0098	.4248	.3468	.2571	8.53
H_2	0	0	.0008	.0295	.0164	.0096	.7499
NH_3	0	0	0	.0042	.0045	.0037	1.092
CH_4	0	0	0	.4127	1.806	2.681	0
O_2	5.29	2.21	0	0	0	0	0
Total Gas	36.36	36.36	36.37	36.59	36.54	36.49	40.73

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* 5.89 moles/kilogram of explosive is the quantity of solid carbon predicted in a normal calculation for 1.643 g/cc.

** In addition CH_4 was forced to zero in this column.

Table 5

Vacuum Thermal Stability of MAN and QMAN with Other Components

	Gas (ml)	Hours (100°C)	Hours (120°C)
TNT	0.1	40	
RDX	0.7	40	
AN	0.3	40	
MAN	0.02	40	
MAN + AN	0.07		40
MAN/AN 37/63	0.0	40	
MAN + TNT	11+	16	
MAN/AN/TNT 22/38/40	0.23	40	
	2.74		40
MAN + RDX	0.04	40	
	0.33	40	
	3.45		40
MAN + TNT + RDX	11+	16	
MAN + AN + RDX	0.17	40	
MAN + AN + TNT + RDX	1.70	40	
QMAN	0.09	40	
QMAN + AN	0.11	40	
QMAN + TNT	11+	16	
QMAN + AN + TNT	11+	16	
QMAN + AN + TNT + RDX	11+	16	
QMAN + RDX	0.12	40	
QMAN + AN + RDX	0.11	40	

Equal weights of each component (except as shown) to one gram total sample weight. Gas evolved corrected to STP.

Table 6

Results of Henkin Explosion Temperature Test

	Temperature Range (°C)	Time Range (seconds)	Activation Energy (kcal/mole)	Pre-Exponential Factor (seconds)	Least-Squares Fit (r)*
MAN	235 - 266	33 - 6.4	14.3	2.1×10^{-11}	0.92
MAN + TNT	209 - 266	15.7 - 1.4	9.2	6.3×10^{-8}	0.95
MAN + RDX	201 - 260	51 - 1.7	11.0	1.3×10^{-9}	0.79
MAN + TNT + RDX	184 - 230	10.7 - 0.3	12.1	4.1×10^{-11}	0.86
RDX	236 - 278	14.7 - 1.3	12.4	3.3×10^{-10}	0.92

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*r is closeness of fit of straight line by least squares of time in seconds against reciprocal of absolute temperature.

Table 7

Results of PA Impact Sensitivity Tests*

	Height (inches)		Height (inches)
TNT	14 - 17		
		AMATOL 60/40	16 - 18
RDX	8 - 13	MAMATOL	14
		MANATOL	11
AN	31 - 36		
MAN	16	AMATOL 60/40	16 - 18
AN/MAN 63/37	13	QAMATOL-1	16
		QAMATOL-2	14
AN	31 - 36		
QMAN	> 36	AMATEX 20	15
		MAMATEX	14
AN/QMAN (80-87)/(20-13)	19 - 21	MANATEX	14
		AMATEX-20	15
		QAMATEX-1	15
		QAMATEX-2	13

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*All tests used a 2-kg weight in the Picatinny Arsenal Impact Test Equipment decreasing the height until no initiation occurred in 10 trials. One inch was then added to provide the "minimum impact sensitivities" tabulated above. Compositions are defined in Table 1. Proportions shown above for compositions are by weight.

Table 8

Salient Thermal Features

	Endotherms		Exotherms		Weight Loss	
	Melt	Other	Start	Peak	Slow	Rapid
AN					200	270
TNT					170	220
RDX					210	250*
AN+RDX					210	225
AN+TNT					190	260
AN+TNT+RDX	80,170	52,130	200	240	185	240*
MAN	110	80	250	290	240	280
MAN+AN	50	none	270	285	215	285
MAN+TNT	80	none	160	190,225	170	190*
MAN+RDX	110	80	195	220,250	210	245*
MAN+RDX+TNT	80,100	none	150	170,220		
MAN+AN+RDX					220	245*
MAN+AN+TNT	50,80	none	200	230		
MAN+AN+TNT+RDX	50,80	none	200	230,260	190	220*
QMAN		380	none to 500			
QMAN+AN	125	52,87	280	300		
QMAN+TNT	80	none	150	170	none	165*
QMAN+RDX	none	170	200	240	215	230*
QMAN+AN+RDX	125	52,175	225	245	210	240
QMAN+AN+TNT	80,125	52	190	210,260	170	180*
QMAN+AN+TNT+RDX					145	165*

Temperatures are in °C. Results are based on limited number of preliminary runs taken as part of safety checks. * denotes observed ignition points.

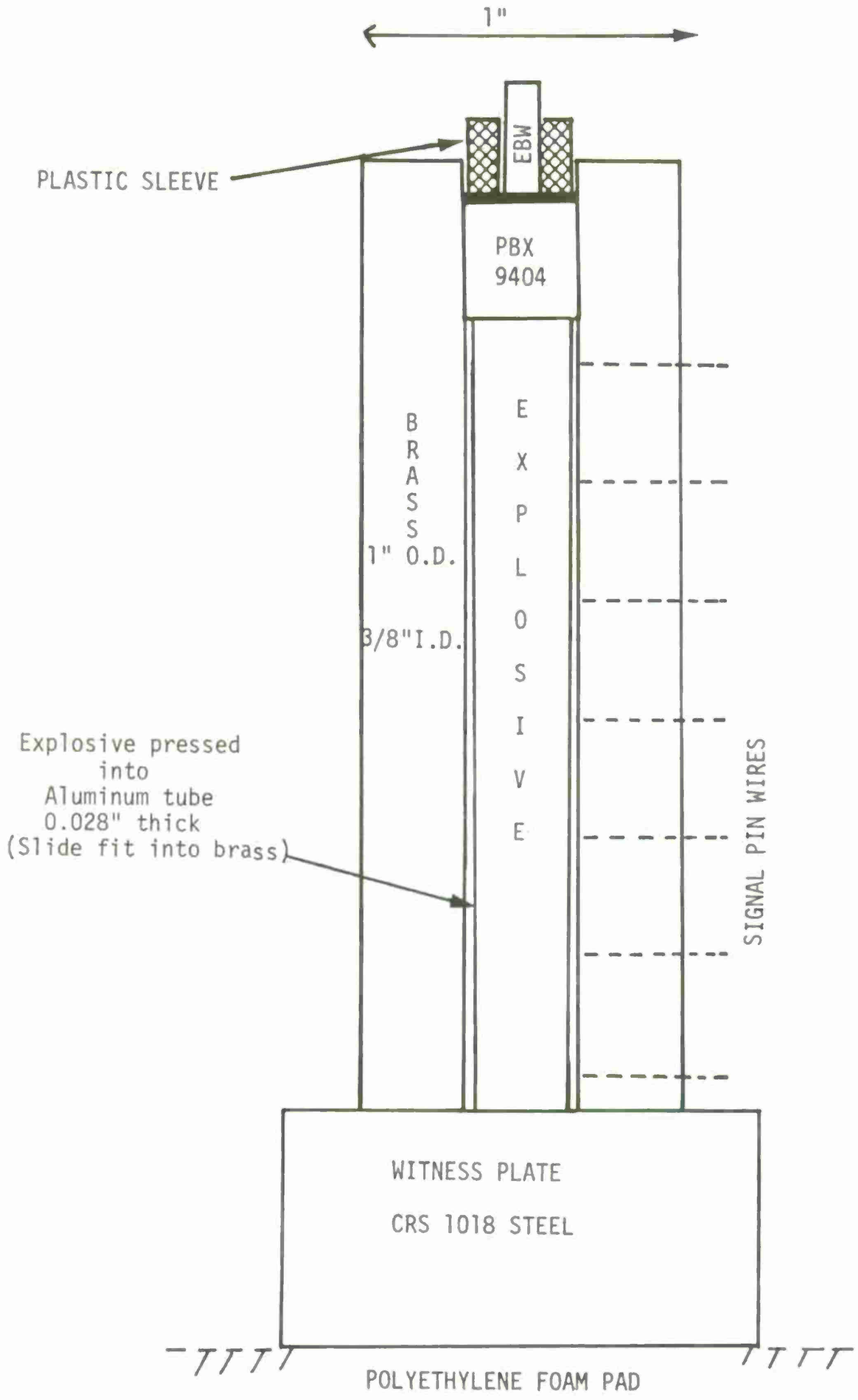
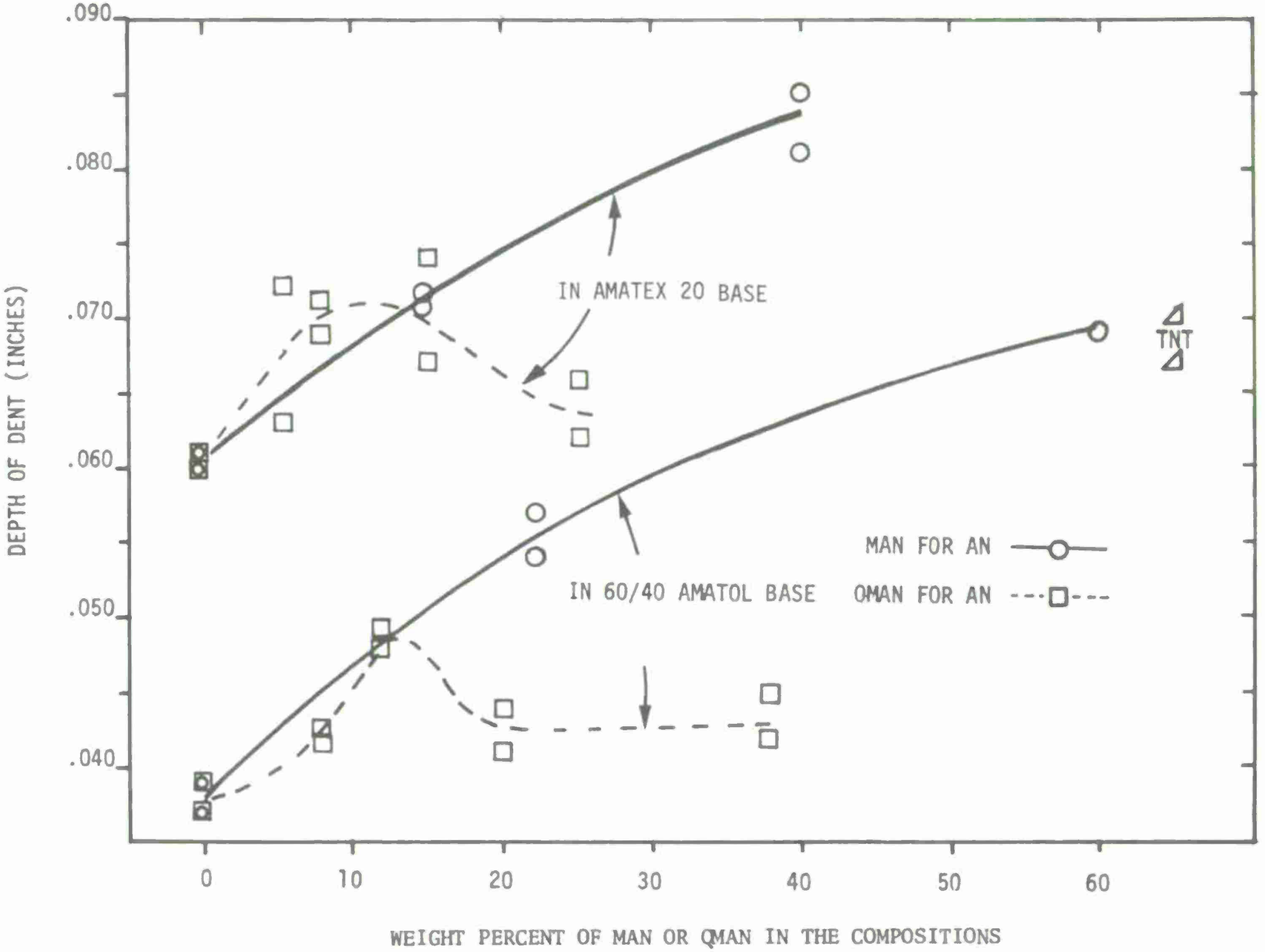


Fig 1 Detonation velocity and witness plate test



(In 60/40 Amatol base compositions, TNT is 40%, AN is 60% less the MAN or QMAN %. In Amatex-20 base composition, RDX is 20%, TNT is 40% less MAN or QMAN %.)

Fig 2 Witness plate dent depth vs composition

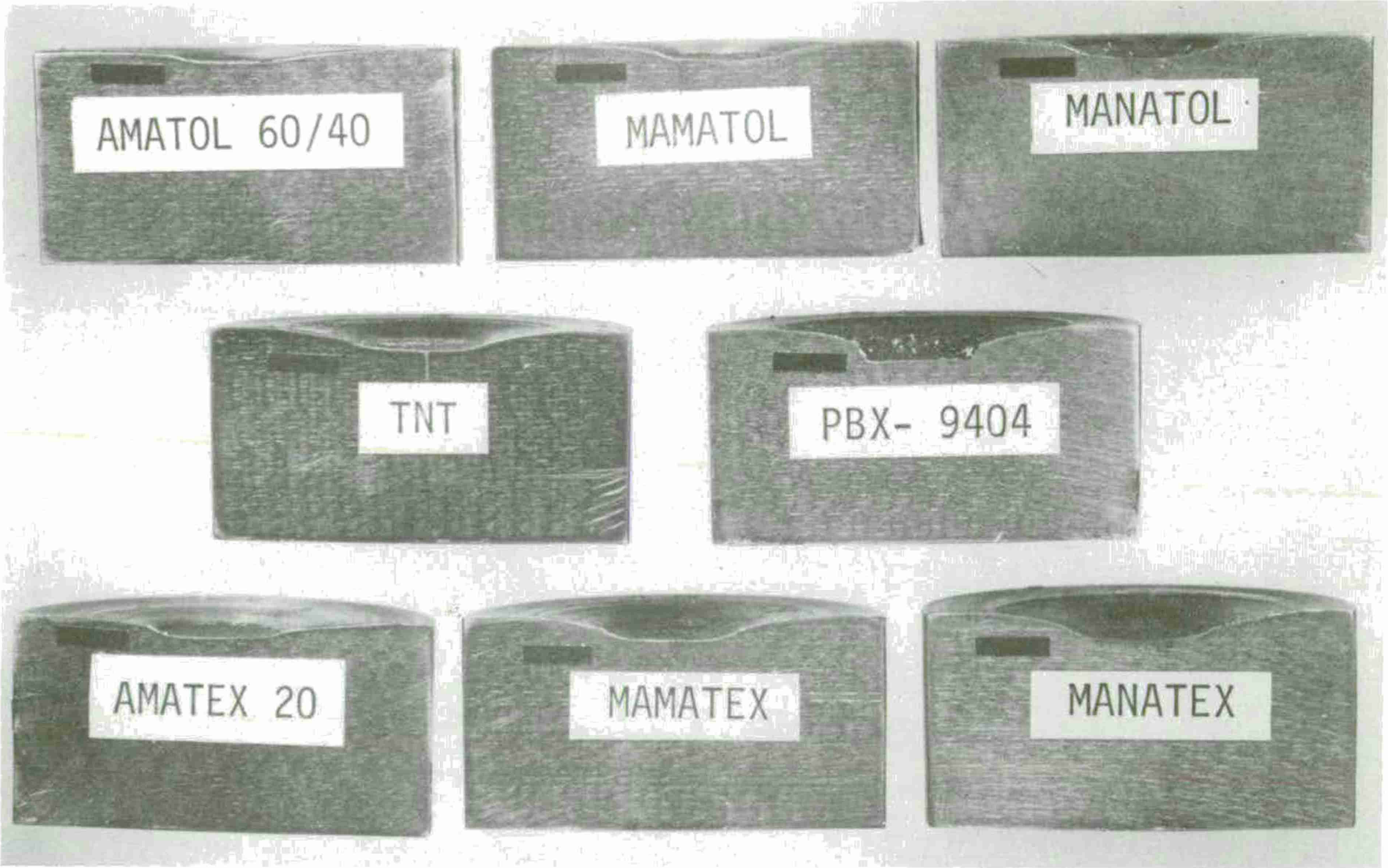


Fig 3 Sectioned witness blocks for MAN substitution tests

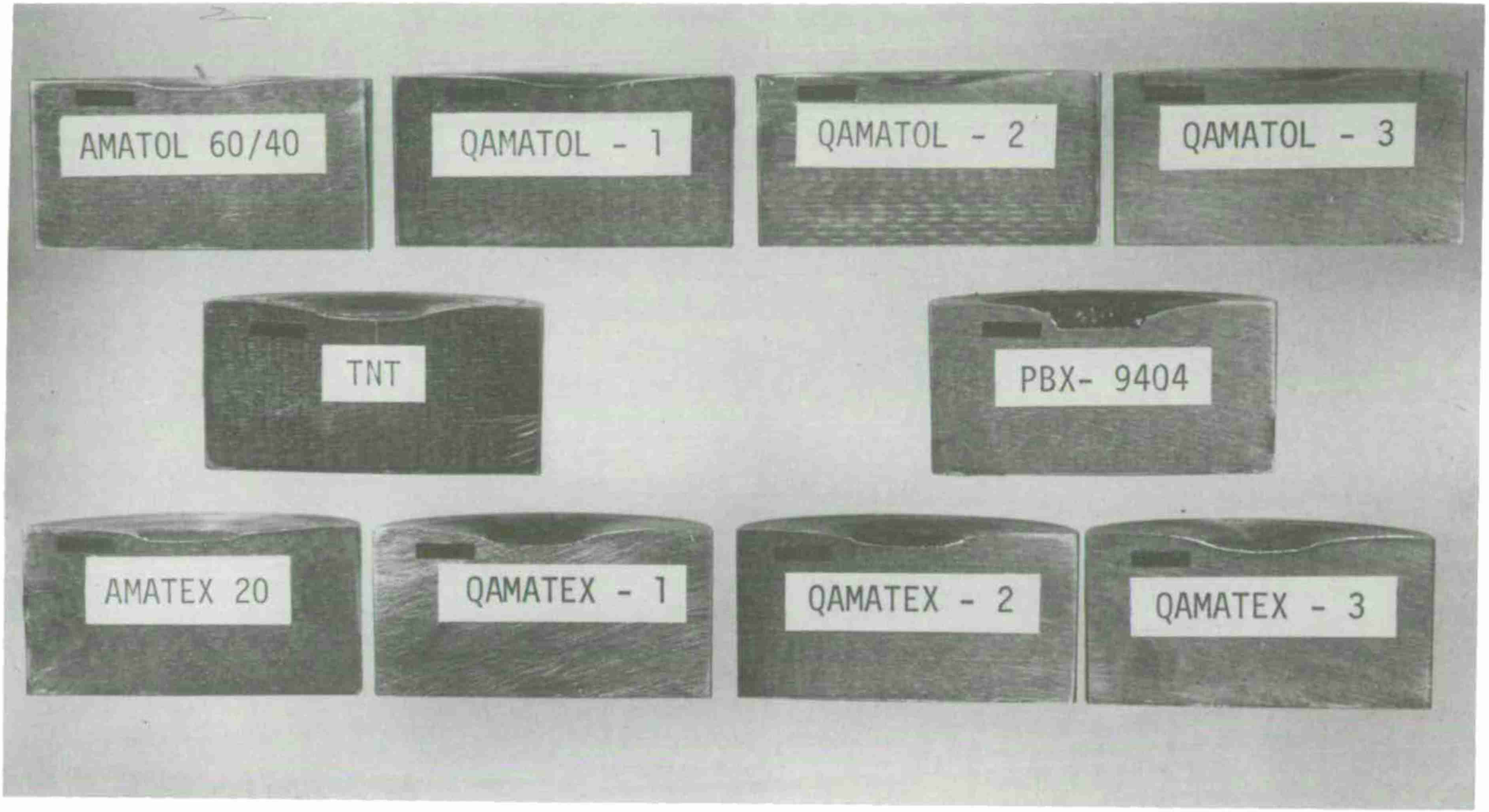


Fig 4 Sectioned witness blocks for QMAN substitution tests

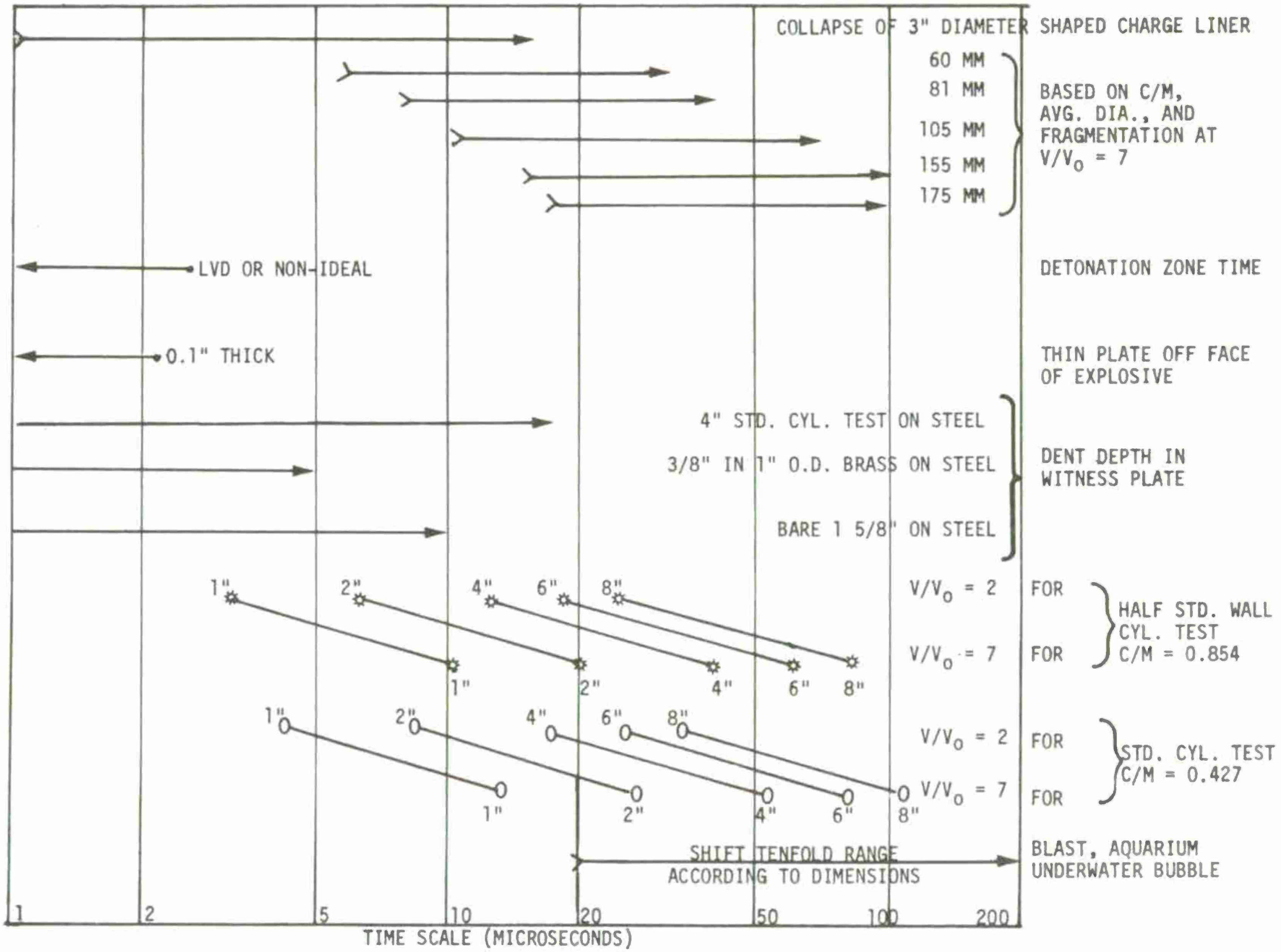


Fig 5 Time intervals for performance tests and for munitions

APPENDIX 1

FORMULATION INFORMATION

MAN

The methylammonium nitrate was prepared as follows: Methylamine (reagent grade gas) was bubbled into 100 ml of cold water with cooling (10-15°C) until 31g (1 mole) was absorbed. 50% HNO_3 solution, prepared by diluting 100g of 70% HNO_3 with 40 ml H_2O was added dropwise to the aqueous methylamine solution while stirring and cooling (10-15°C) until the pH was 7. About 130g of the HNO_3 solution was used. Vacuum distillation at 70°C with a water aspirator was then employed to strip off about 150 ml of water. At this point the mixture became turbid, the distillation was stopped, and the reaction mixture was cooled in ice. The methylammonium nitrate precipitated as a very thick slurry. The product was filtered off and dried in vacuo over NaOH and Drierite. The filtrate was vacuum distilled as previously, removing about 30 ml of water. Upon cooling, an even thicker slurry formed which could not be easily filtered. Dilution with acetone facilitated filtration and collection of additional product. The total yield after drying the combined products in a vacuum desiccator was 31g (about 93%). The melting point was 109-111°C.

QMAN

Tetramethylammonium nitrate (QMAN) was ultimately purchased from Eastman Chemicals as a crystalline powder, but initial quantities were prepared as follows (comparison of material from these two sources by DTA and NMR gave identical curves): QMAN was precipitated from solutions of silver nitrate and tetramethylammonium chloride (TMAC1) using a slight excess of the latter. 22g (0.2 mole) TMAC1 was dissolved in 100 ml of water and to this solution was added, dropwise with stirring, a solution of silver nitrate, 34g, (0.2 mole) in 100 ml water. The mixture was stirred for 1/2 hour and the AgC1 precipitate was filtered off. Water was removed from the filtrate by vacuum distillation until a very thick slurry remained. The crude QMAN was then filtered off and dried in vacuo. The yield was 23.4g (86%). This material was purified by dissolving in hot absolute EtOH to which a small amount of water was added to facilitate solution. The solution was filtered and the filtrate cooled in an ice bath. The crystallized product was then collected by suction on a Buchner funnel yielding 10.4g as the first product and 7.1g from the filtrate by repeating the process. A third crop yielded 2.5g. Tests on all crops for chloride ion and silver ion were negative. The overall yield was 20.0g (73%).

MAN/AN

The MAN/AN was prepared in the co-crystallized form as follows: MAN and AN in the desired weights and in crushed form were placed in an evaporating dish and a small amount of distilled water was added. The solid was dissolved rapidly by heating on a steam bath at about 80°C. The solution was then placed in a vacuum oven at about 65°C and 22 mm Hg for two hours. The dish was then heated on a steam bath so that the liquid was on the verge of boiling and compressed air or dry nitrogen was blown over it while stirring to remove water. The viscous residual solution was left overnight under vacuum and formed a hard mass which was pulverized before use.

The MAN/AN was prepared in the co-melted form as follows: Weighed quantities of MAN and AN were first physically mixed, then placed on a steam bath and heated slowly with stirring until melting occurred. There was some apparent melting at 50°C and the mass was fully melted well below 100°C. The melt was allowed to cool and the solid mass was pulverized and dried before use. The DTA was the same as for the co-crystallized form.

The MAN/AN was prepared in the physical mixture form as follows: The AN was blended with finely granulated MAN by placing the two together in a dish and manually stirring under dry nitrogen for a period of several minutes. Residual moisture was removed by high vacuum drying at room temperature for one hour. The DTA showed the individual features of the MAN and the AN.

QMAN/AN

The QMAN/AN was prepared in co-crystallized form as follows: Both constituents were dissolved in a small amount of distilled water in a dish. The solution was heated on a hot plate under an air or nitrogen stream until most of the water was gone. The stream was then turned off and the heat was turned up slightly until there was visual evidence of melting. Then the mixture was stirred while cooling to prevent forming a hard solid mass. The material was pulverized and dried for pressing.

60/40 Amatol

The 60/40 Amatol (AN/TNT) was prepared as follows: TNT was dissolved in acetone and poured over AN in a beaker. The mixture was stirred constantly while gently heating under a stream of dry nitrogen to drive off the acetone.

Amatex-20

The Amatex-20 (RDX/TNT/AN - 20/40/40) was prepared as follows: TNT was dissolved in toluene and poured over a preweighed dry mixture of RDX and finely crushed AN. The mixture was then dried in the same manner as the Amatol.

APPENDIX 2

TIME INTERVAL ESTIMATES

Figure 5 presents the time intervals in which explosive properties influence performance tests and munition function. It is within or preceding the intervals shown that modifications of rate-determining steps must be made. The intervals shown for performance tests therefore serve as a basis for selection of evaluation experiments on such modifications. Comparison of intervals in Figure 5 may also be used for selection of appropriate performance tests for relevance to particular munition applications. This Appendix provides the details for the selections made for the time intervals shown in Figure 5. It is to be recognized that this is a preliminary version to be corrected as more accurate data becomes available.

The cylinder test for ideal explosives is first used to set up a skeleton time scale. A one-inch diameter cylinder test has a 19 mm wall deflection with Comp B at 13.6 microseconds after first wall motion. The 19 mm deflection corresponds to a sevenfold volume change of the explosive from condensed phase to products. The same volume change in a two-inch-diameter test has a 38 mm wall deflection at two times 13.6 microseconds. Thus, an abscissa of diameters of cylinder tests corresponds to times of these scaled events. The standard cylinder tests for ideal explosives scale this way because they all have the same explosive charge to wall mass ratio (C/M = 0.427 for Comp B). The positions of the points in Figure 5 marked l inch, 2 inch, 4 inch, 6 inch, 8 inch for $V/V_o = 7$ for STD CYL TEST were obtained in this manner. The points for $V/V_o = 2$ were obtained in a similar manner using data on cylinder expansion (Ref 12, 22).

Additional time intervals can be added for the cylinder test with half-standard wall thickness by comparing 4 inch diameter cylinder tests on 60/40 Cyclotol (comparable to Comp B) made with standard and 1/2 standard wall thickness (Ref 12). To extend the scale this way one first compares the ratio of experimental times (in Table 12, 13 of Ref 12) at 76 mm (4 times 19) deflection for the two wall thicknesses with the predicted ratio (Ref 45, 46) of final (Gurney) velocities for the two C/M ratios involved. The former gives 1.35 and the latter 1.30, the agreement providing a theoretical base as well as the experimental for this extrapolation. Doing this, one can add to an abscissa point of 13.6 microsec for a standard one-inch-diameter cylinder test, a 10.5 microsec point for a 1/2 standard wall one-inch-diameter cylinder test and apply the same ratio to other diameter cylinder tests.

If one now uses ratios of the theoretical C/M dependence expression $\{(C/M / (1 + (C/2M)\}^{1/2}$ appropriate to cylindrical geometry, one could generate further points on a time scale in terms of further modified cylinder tests for the ideal reference explosive. This was not done, but represents a means to relate various cylindrical geometry configurations to relevant time intervals.

The detonation velocity is determined by transformations occurring in the time interval of the detonation zone. A time interval is thus obtained by dividing the thickness of the zone by the detonation velocity. For a 1/2 mm zone and an 8 mm/microsec velocity the time interval is 1/16 microsec. For a 12 mm zone and a 4 mm/microsec velocity, the time interval is 3 microsec. The latter value is plotted as a typical upper bound for highly non-ideal or low velocity detonation explosives. For this performance test, a separate calculation is necessary for each explosive using available or estimated data.

The time interval required for accelerating a thin plate off the end of an explosive charge depends on the thickness of the plate and its shock impedance. For a 0.1 inch (2.54 mm) thick plate the 2 microseconds shown is about the time for a 5 mm/microsecond wave to make two round trips through the plate. Normally one would use this technique for shorter time intervals. It can be used as a bridge between the longer time interval tests and the detonation velocity. It can also be used for studies of the structure of thick detonation zones.

The time intervals shown for influencing formation of the dent in a witness plate were all obtained by first doing HEMP computer runs for the geometries (see Fig 1 and Ref 29) indicated. The times selected were those for which material velocity on the axis had fallen to about 1/2 the initial velocity. This corresponded with displacement differences (on-axis less off-axis beyond explosive) having values about 2/3 of the experimental dent values. Relative velocities for these two positions were also rapidly decreasing to zero at this time. The bare 1 5/8 inch explosive acting on steel at 10 microseconds had only 5 of the initial 10 grid zones still in contact with the dent region. The explosive had undergone rapid radial expansion due to the lack of confinement in this test (Ref 29). The 3/8 inch explosive in 1 inch OD brass confinement acting on steel at 5 microseconds had 8 of the initial 10 grid zones in contact with the dent region. The 4 inch standard cylinder test, in which confinement of 4 inch diameter explosive is provided by 0.4 inch thick copper, acting on steel at 15 microseconds had 8 of the initial 10 grid zones in contact with the dent region. The expansion of the copper cylinder at the contact surface (slide line) with the steel witness plate had been retarded by the distortion of the latter (lip formation). In all three cases the times given are considered to represent the upper bound of the time interval for which pressures are still high enough to influence dent formation. The rest of the dent shaping occurs due to redistribution of momentum in the steel witness block.

Having placed various performance tests on time related scales, one now must create a parallel scale representing the various munitions. To do this one uses the dimensions, the configuration, the C/M, and the function of the explosive in the munition. Consider first the series of large fragmenting munitions 60 and 81 mortar, and 105, 155, 175 mm and 8 inch shell rounds. Rupture of the casing occurs for deflections comparable to those of the cylinder test. The explosive within these is Comp B or or Amatex-20. (A time scale adjustment can be made later for this change in explosive (Ref 12, 47).) One can thus consider each munition as another cylinder test and determine where to place it on the time scale by using the average explosive diameter and adjusting the position in relation to standard or wall-modified cylinder tests of this diameter. This is done by using ratios of C/M functions to derive a time ratio to the cylinder tests. The scale for these fragmenting munitions (Fig 5) was generated in this manner. Other munition types were placed on the scale by use of experimental or computer data on the times involved. In some cases only estimates could be made.

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