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Castable Ideal Composite Explosives  
Containing Ammonium Nitrate (U)

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CASTABLE IDEAL COMPOSITE EXPLOSIVES  
CONTAINING AMMONIUM NITRATE

by

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B. W. Harris, R. N. Rogers, and M. J. Urizar

## ABSTRACT

Several ammonium salts of nitroheterocycles were prepared and characterized with respect to their physical properties and eutectic formation with ammonium nitrate (AN). The eutectic mixture of AN and the ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT) was found to have a melting point low enough to be castable, a sensitivity similar to Composition B, and ideal detonation performance. We also found that other explosives can be slurried into the melt to improve physical characteristics or change the explosive performance.

The phase diagram of AN and ADNT was determined, and availability and probable cost of materials was estimated.

The ammonium salt of trinitroimidazole is an energetic and stable explosive, and the problems associated with its synthesis have been studied for several years. A carbon-13 nuclear magnetic resonance (CMR) study has been used to elucidate its preparation from triiodoimidazole, and we have decided that it cannot be produced at an acceptable cost now.

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## I. INTRODUCTION

Ideal explosives are those that have reaction rates high enough to be nearly instantaneous or time independent. Parameters such as detonation pressure and velocity can be calculated quite accurately on that assumption,<sup>1</sup> although reaction zone thickness may be significant.<sup>2</sup>

Nonideal explosives are usually composite explosives; that is, explosives that are mixtures of particulate oxidizers and fuels. However, nonideal explosives may contain an ideal explosive as an ingredient. Ammonium nitrate/fuel oil (ANFO), AN/TNT (Amatol), and AN/TNT/RDX (Amatex) are examples of nonideal explosives. Reaction rates

of nonideal explosives are usually slower than those of ideal explosives, and a significant amount of chemical reaction occurs behind the steady-state detonation zone. Thus, experimentally determined detonation pressures and velocities of nonideal explosives are lower than those calculated assuming "instantaneous" reaction. For example, calculations predicted that an ideal mixture of HMX and lithium perchlorate would give 110% of the performance of pure HMX; however, a cylinder test of the mixture showed that its performance was significantly less than that of HMX.<sup>3</sup> Comparisons of measured detonation velocities with BKW<sup>1</sup> calculations for Amatex formulations with different amounts of AN suggested that about 50% of the AN

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reacts on a short enough time scale to affect detonation velocity.<sup>4</sup> Because of these and other similar results, research on methods to make nonideal explosives (especially those containing AN) behave ideally was given high priority by the Advanced Research Projects Agency.<sup>5</sup>

The performance of nonideal explosives can be improved by more intimate incorporation of the components.<sup>6</sup> A recent demonstration by Finger et al. showed that mixtures of gelled nitromethane with 200- $\mu$ m particles of ammonium perchlorate were distinctly nonideal; however, mixtures containing 5- $\mu$ m ammonium perchlorate were nearly ideal.<sup>7,8</sup>

Pursuing the hypothesis that variations in intimacy of mixing could be used to control sensitivity and performance, the Los Alamos Scientific Laboratory (LASL) has long supported a study on crystallography and phase relationships of explosives. It was assumed that maximum performance would be obtained when components were combined in a continuous solid solution; however, no cost-effective, practical, solid-solution system has been found. Recent work at Picatinny Arsenal and LASL has indicated that eutectic incorporation of components greatly improved performance,<sup>9,10,11</sup> but did not produce ideal performance.

These recent studies<sup>9,11</sup> involved consolidation of AN with amine nitrates, in an attempt to promote eutectic formation by the common nitrate ion. Our most recent approach is to use ammonium salts of nitroheterocycles as fuels with the hope that the common ammonium ion will produce advantageous phase relationships.

We first studied the ammonium salt of 2,4,5-trinitroimidazole (ATNI).<sup>12</sup> Although ATNI is a very stable and energetic compound,<sup>13</sup> work on this material was discontinued when we discovered that it could not be economically produced and that it would not form a low-melting eutectic with AN (Sec. VI). We have now prepared ammonium salts of other nitroheterocycles, and we have evaluated the physical and explosive properties of mixtures of these compounds with AN.

## II. COMPOSITIONS OF AN AND AMMONIUM SALTS OF NITROHETEROCYCLES

The ammonium salts of 3-nitro-1,2,4-triazole [(I)],<sup>14</sup> 3,5-dinitro-1,2,4-triazole (ADNT) [(II)],<sup>14</sup> 3,5-dinitropyrazole [(III)],<sup>15</sup> 4,5-dinitroimidazole [(IV)],<sup>16</sup> 2,4-dinitroimidazole [(V)],<sup>17</sup> 4-nitro-1,2,3-triazole [(VI)],<sup>18</sup> 5,5'-dinitro-3,3'-bi-1,2,4-triazolyl [(VII)],<sup>14</sup> and 5-nitrotetrazole [(VIII)]<sup>19</sup> were prepared by bubbling ammonia gas through a solution of the nitroheterocycle in ether or ether/ethanol. The solids were collected and recrystallized from acetone/ethyl acetate to give products with acceptable elemental analyses. The structures plus physical and explosive properties determined for these salts are given in Table I. The references (14-19) give the preparations of the parent compounds.

The composite explosives were prepared by grinding together the appropriate amounts of AN and the ammonium salt of the nitroheterocycle. Each AN/ammonium salt mixture was heated with stirring at  $\sim 5^\circ\text{C}$  above its melting point until a clear solution was obtained; then it was cooled to room temperature. The resulting solid was ground to a powder, which was used to obtain the eutectic data in Table I. We studied primarily the mixtures of AN and ADNT [(II)], because their relatively low melting points and good thermal stabilities implied that they might be useful components of a castable explosive. In addition, these mixtures were found to be more sensitive to impact than ADNT. This observation was unexpected, because mixing other common explosives with AN generally gives a composite that is less sensitive than the pure explosive. Explosives based on mixtures of ammonium nitrate and ammonium 3,5-dinitro-1,2,4-triazolate are code named Fairy Dust and their compositions and explosive properties are classified CNSI.

A plate-dent test<sup>20</sup> was run on an unconfined pressed charge of the  $\text{CO}_2$ -balanced, fused mixture (2/1 of AN/ADNT)\* with a density of 1.590 g/cm<sup>3</sup>.

\*All ratios are molar ratios.

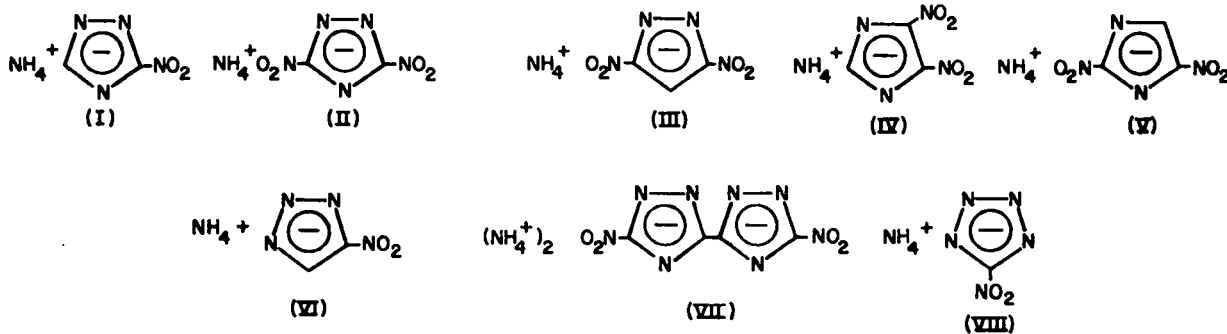
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TABLE I

## PROPERTIES OF AMMONIUM SALTS OF NITROHETEROCYCLES



Properties	I	II	III	IV	V	VI	VII	VIII
Melting point (°C)	158-216	165-168	185-232	185-188	225-226	107-125	unstable	205 dec.
DTA (endotherm, °C)	140, 175	168	280	exo-235	226	180	exo-280	67, 112, 205
AN eutectic mp (°C)	120	112	167	165	152	120		110
Density (g/cm <sup>3</sup> )		1.63				1.67		
Impact sensitivity								
Type 12 (cm)	>320	110	158	77.5		235		30
Type 12B (cm)		124	135	62.6		302		75

The estimated detonation pressure [Chapman-Jouget (CJ) pressure ( $P_{CJ}$ )] agreed quite closely with that obtained from a BKW calculation that assumed an ideal system.<sup>21</sup> A second charge of the same formulation pressed at 100°C to a density of 1.645 g/cm<sup>3</sup> gave a lower detonation pressure than the first in the 1.27-cm (0.5-in.) plate-dent test, because it partially failed. Generally, failure diameter increases as the density increases. We were fortunate that the first pressing did not fail, because explosives containing AN usually have failure diameters greater than 1.27 cm (0.5 in.) when unconfined.

The eutectic composition (1.38/1 of AN/ADNT) was determined (see Sec. IV), and a charge of density 1.630 g/cm<sup>3</sup> was fired. The resulting detonation pressure agreed excellently with the values calculated assuming ideal behavior. The results of the plate-dent tests are given in Table II. We have demonstrated that AN can be made to release all of its energy at the detonation front when mixed intimately with a fuel-providing explosive.

### III. AN/ADNT AS A BINDER FOR MILITARY EXPLOSIVES

We found that AN/ADNT mixtures can be used as energetic, oxygen-rich binders for RDX, HMX, nitroguanidine (NQ), and other explosives. The melt dissolves an appreciable amount of explosive and holds an additional amount as a slurry. Upon cooling, the slurry solidifies to form a uniform solid. We have pulverized these solids and pressed them into cylinders for test-firing samples. Table III gives the performances and sensitivities achieved thus far.

Both the 1.27- and 2.54-cm (0.5- and 1-in.) plate-dent tests have been calibrated with standard explosives to give an experimental CJ pressure. We do not have enough data to resolve the discrepancy between the two plate-dent tests for the RDX mixture, but the 1.27-cm (0.5-in.) test has a higher error. Also, we do not understand the reason for the greater-than-calculated plate dent for both the RDX and HMX mixtures. The anomaly occurs only

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TABLE II

## EXPLOSIVE PROPERTIES OF AN/ADNT

Material	Impact Sensitivity Type 12 (cm)	Density (g/cm <sup>3</sup> )	Experimental P <sub>CJ</sub> (GPa) <sup>a</sup>	Calculated P <sub>CJ</sub> (GPa) <sup>a</sup>
ADNT	110	1.645		26.2
1/1-AN/ADNT	65	1.645		27.1
2/1-AN/ADNT	65	1.590	25.2	25.4
		1.645	23.0	27.6
1.38/1-AN/ADNT	65	1.630	27.3	26.7

<sup>a</sup>1 GPa = 10 kbar.

TABLE III

## EXPLOSIVE PROPERTIES OF COMPOSITE AN/ADNT/MILITARY EXPLOSIVES

Test	1.38/1/1.5 AN/ADNT/RDX	1.38/1/1 AN/ADNT/HMX	1.38/1/1.38 AN/ADNT/NQ
1.27-cm (1/2-in.) plate-dent P <sub>CJ</sub> (GPa)	33.6 ( $\rho = 1.708 \text{ g/cm}^3$ )	34.2 ( $\rho = 1.756 \text{ g/cm}^3$ )	26.1 ( $\rho = 1.654 \text{ g/cm}^3$ )
BKW calculation P <sub>CJ</sub> (GPa)	30.4	32.4	28.0
D (mm/ $\mu$ s)	8.445	8.647	8.305
2.54-cm (1-in.) aquarium-test D (mm/ $\mu$ s)	8.52 ( $\rho = 1.718 \text{ g/cm}^3$ )		
2.54-cm (1-in.) rate-stick D (mm/ $\mu$ s)	8.455 ( $\rho = 1.717 \text{ g/cm}^3$ )		
2.54-cm (1-in.) plate-dent P <sub>CJ</sub> (GPa)	31.7		
Impact sensitivity Type 12 (cm)	37	43	110

in the plate-dent test; the detonation velocity (D) measured in both the aquarium and rate-stick tests agrees closely with the calculated value.

The aquarium test<sup>22</sup> was done by detonating a cylindrical charge in a Plexiglas aquarium filled with water. Measurements were made by taking a double exposure picture with an image-intensifier camera manufactured at LASL. The photograph shows the shock and bubble interfaces in the water. The shock front is a good measure of the CJ pressure, and the bubble indicates the amount of additional reaction that occurs behind the detona-

tion front. This is a very useful test for nonideal explosives. The detonation velocity can be measured directly from the films, knowing the time between exposures, and the shock profile can be compared with the computer-drawn curve, assuming the material behaves ideally. We found that the shock-profile experimental points are virtually on the computer-drawn curve for our sample (see Fig. 1). Unfortunately, the bubble interface was not well defined. However, since the shock front agreed with the calculation, there is probably no significant late-time reaction.

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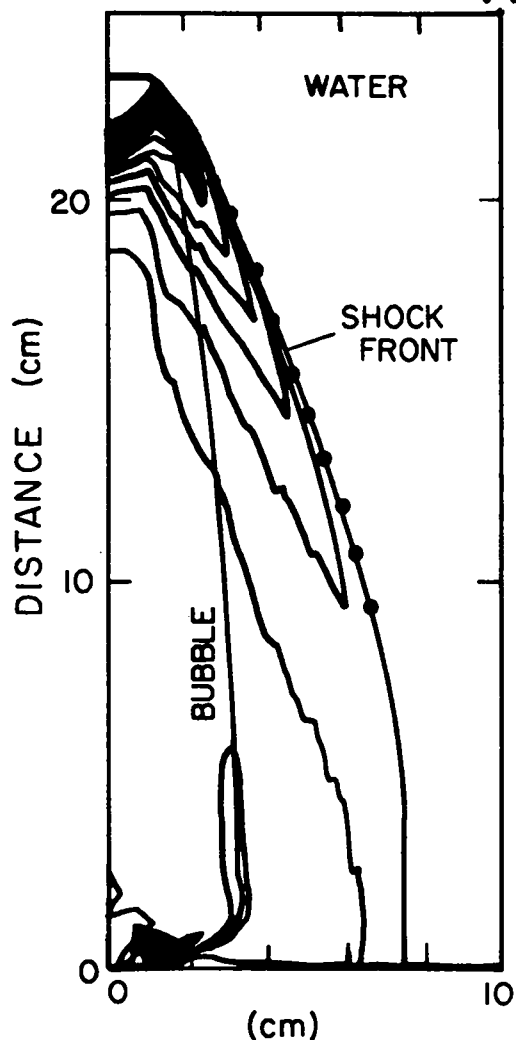
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Fig. 1.

Aquarium test of 1.38/1/1.5-AN/ADNT/RDX. The lines are the computer-generated shock-wave curves and the points are the experimental data.

The AN/ADNT melt can also be used to improve the physical properties of other explosives. For NQ, the low-bulk-density crystals can be used. When NQ is added to an AN/ADNT melt, a viscous slurry is formed, which becomes a tough solid when cooled. This solid is less sensitive to impact and more thermally stable than the AN/ADNT mixture. Sensitivity data for several related systems are presented in Table III, and Table IV lists Henkin-test<sup>23</sup> and vacuum-stability results. The NQ-containing

solid that was pulverized and pressed to a density of 1.654 g/cm<sup>3</sup> gave almost ideal performance in the 1.27-cm- (0.5-in.-) diam plate-dent test (see Table III). The use of an AN/ADNT melt as a vehicle for NQ eliminates the need for the more expensive, high-bulk-density NQ, which must be used to fabricate plastic-bonded NQ charges. Furthermore, the mixed system does not have a large failure diameter, even though it is a relatively insensitive material.

Another common explosive that desensitizes Fairy Dust systems and reduces the hygroscopicity of AN is TNT. It forms a continuous second phase surrounding the AN/ADNT mixture. Some preliminary data on its ability to desensitize a system are given in Table V. They are shown as a function of wt% TNT in Fig. 2. The TNT also lowers the viscosity of the melt making casting easier.

#### IV. PHASE DIAGRAM OF AN/ADNT

We determined the phase diagram for the AN/ADNT system from room temperature to the melting point. Experimental data were obtained using x-ray diffractometry, differential thermal analysis (DTA), and optical microscopy to ensure that the phases were correctly identified.

The mixtures were prepared from Matheson, Coleman, and Bell reagent-grade AN that had been dried in a vacuum desiccator. Weighed mixtures were fused, recrystallized, and ground to prepare the samples used to determine the phase diagram.

X-ray diffraction patterns from the mixtures at room temperature had lines for AN<sub>IV</sub> and ADNT<sub>I</sub>, as would be expected in a simple eutectic system. DTA curves showed the AN<sub>IV</sub> → AN<sub>II</sub> (54°C), AN<sub>III</sub> → AN<sub>II</sub> (84°C), and AN<sub>II</sub> → AN<sub>I</sub> (126°C) transformations. The fact that all of these transformations occur at normal temperatures for pure AN implies that there has been no solid solution formed between AN and ADNT. The melting points and transition temperatures of pure ADNT and AN were determined with an optical microscope equipped with a Mettler hot stage. No solid-solid phase transitions were observed in ADNT<sub>I</sub> in the temperature region examined (20 to 170°C).

The melting point of AN<sub>II</sub> has been determined to be 149.5°C from the phase diagram of the system

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TABLE IV

## STABILITY TESTS

Material	Vacuum Stability (ml/g/48 h at 100°C)	Henkin Test	
		Critical Temp (°C)	Sample Thickness (cm)
ADNT	1.7	233	0.081
1.38/1-AN/ADNT	0.1	236	0.079
2/1-AN/ADNT	<0.1	241	0.081
2.44/1-AN/ADNT	<0.1	238	0.081
1.38/1/1.5-AN/ADNT/RDX	0.2	215	0.079
1.38/1/1.38-AN/ADNT/NQ	0.1	256	0.084
1.38/1/0.38-AN/ADNT/NQ	---	243	0.089

TABLE V

## DESENSITIZATION OF 1.38/1/1.5-AN/ADNT/RDX BY TNT

Material	Impact Sensitivity		Henkin Critical Temp (°C)
	Type 12 (cm)	Type 12B (cm)	
1.38/1/1.5-AN/ADNT/RDX	37.2	39.1	215
1.38/1/1.5/0.4-AN/ADNT/RDX/TNT	48.8	71.7	208
1.38/1/1.5/0.7-AN/ADNT/RDX/TNT	48.8	68.3	
1.38/1/1.5/1-AN/ADNT/RDX/TNT	67.6	62	214.5
1.38/1/1.5/1.5-AN/ADNT/RDX/TNT	67.6	101	217
1.38/1/1.5/6.37-AN/ADNT/RDX/TNT	104	130	
TNT	165	>320	288
5.5/2/2/1-AN/ADNT/NQ/TNT	90.2	121	239

AN/methyl ammonium nitrate, and this value was used to determine the AN<sub>II</sub> liquidus line in the diagram.

Liquidus lines were estimated using the formula

$$\ln N = \frac{\Delta H_f}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right),$$

where N is the mole fraction of the component,  $\Delta H_f$  is its latent heat of fusion, R is the gas constant,  $T_0$  is the melting temperature of the pure component, and T is the observed liquidus temperature. When

N, T, and  $T_0$  are known for a component of a mixture, the calculated value of  $\Delta H_f$  can be used to accurately calculate other values of N and T near the experimental point.

Examination of mixtures that had been cooled rapidly from the melt revealed a metastable polymorph of ADNT. This polymorph (ADNT<sub>II</sub>) transforms slowly to ADNT<sub>I</sub> at room temperature and transforms rapidly at elevated temperatures. It is unstable with respect to ADNT<sub>I</sub> at its eutectic melting temperature and is, therefore, unstable at all temperatures above room temperature. The

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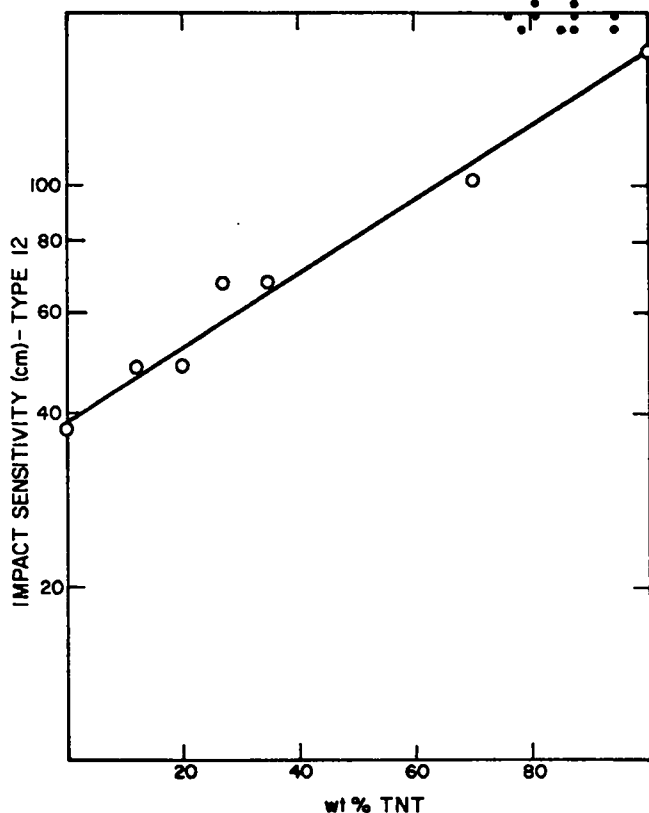


Fig. 2.

Desensitization of 1.38/1/1.5-AN/ADNT/RDX by TNT.

melting temperature of pure ADNT<sub>II</sub> has not been determined.

Figure 3 shows the phase diagram determined from our observations. The phase transitions observed for metastable phases are indicated with dashed lines. The given latent heats of fusion ( $\Delta H_f$ ) are the values used to determine the phase lines but are not true heats of fusion, because this system involves common ions, and the common-ion effect has been ignored in obtaining these values.

## V. AVAILABILITY AND COST OF AN/ADNT

AN is widely available, inexpensive, and not petroleum based; therefore, it is the oxidizer of choice for inexpensive composite explosives. ADNT also can be made from available chemicals that are not petroleum based.

The first step in producing ADNT requires heating cyanoguanidine, made in the same industrial process as nitroguanidine for an estimated \$2.20/kg (\$1.00/lb), with hydrazine hydrate [presently \$3.53/kg (\$1.60/lb)] to give 3,5-diamino-1,2,4-triazole (guanazole). Without further purification, guanazole is dissolved in dilute sulfuric acid and, in the second step, added to a cold aqueous solution of sodium nitrite [\$0.99/kg (\$0.45/lb)] to form the tetrazonium salt. When the mixture is heated to 60°C, the excess nitrite present displaces nitrogen from the tetrazonium salt to form 3,5-dinitro-1,2,4-triazole. After acidification with sulfuric acid, extraction, and aminolysis (using the ammonia given off in the first step), ADNT precipitates.

The estimated cost of ADNT based on the cost of the raw materials is \$5.51/kg (\$2.50/lb). We estimate that production and capital return costs [assuming a production rate of  $9 \times 10^6$  kg/yr ( $2 \times 10^6$  lb/yr)] will bring the cost up to \$7.72/kg (\$3.50/lb). However, ADNT makes it possible to use AN in practical explosives; therefore, costs of the overall systems must be considered. Because AN presently costs \$0.26/kg (\$0.12/lb), a 2/1 molar AN/ADNT mixture would cost only \$4.14/kg (\$1.88/lb). Using the most recent production-at-plant-capacity costs for RDX that we have been able to obtain [\$1.10/kg (\$0.50/lb)], an AN-rich mixture with a weight ratio of 50/22/28 of AN/ADNT/RDX would cost \$2.16/kg (\$0.98/lb). Full-production costs for Composition B have been quoted to us as \$1.54/kg (\$0.70/lb), but toluene costs have increased recently. Cost increases of materials based on petroleum may soon put AN/ADNT systems in a favorable position; however, further studies on Fairy Dust systems are necessary before they can be qualified as regular or alternate fills.

## VI. SYNTHESIS OF ATNI

In 1976 we found that, although ATNI was a very energetic and thermally stable compound, it could not be prepared economically.<sup>11</sup> The yield of reaction A decreased drastically as the size of the reaction increased.

Chemical engineers suggested that a continuous flow might improve the yield from reaction A; therefore, detailed kinetics data would be required to enable design of a continuous-flow reactor. To determine kinetics constants, we separated the

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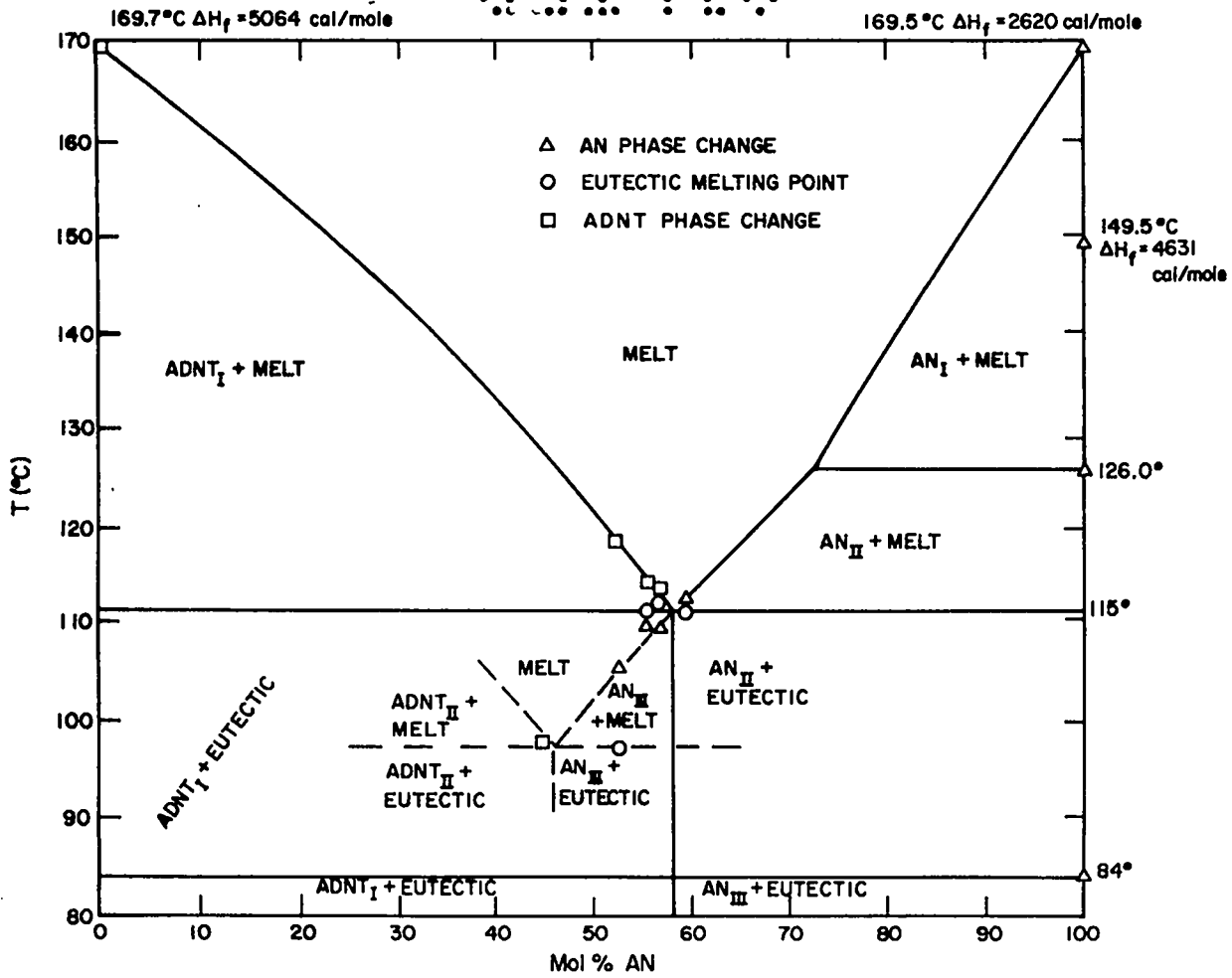
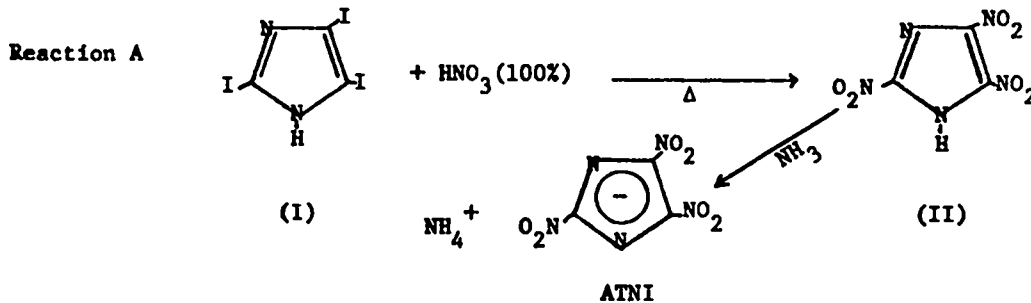


Fig. 3.  
AN/ADNT phase diagram.



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overall reaction into three stages for study. Carbon-13 nuclear magnetic resonance (CMR) (Table VI) was used to determine the intermediates.

In the first stage, 100% nitric acid converts the starting material [(I)] into 1,2,5-triiodo-4-nitroimidazole [(III)] at ambient temperature. In the second stage, (III) is added to 100% nitric acid at 65°C (see reaction B). All of the starting material reacts within 6 min, and 2,4-dinitro-5-iodoimidazole [(V)] is the major product. We also detected small amounts of 2,4,-diiodo-5-nitroimidazole [(IV)] and oxidation products like carbanic acid [(VI)].

The third stage involves treatment of (V) with 100% nitric acid at 125°C (see reaction C). Nitration yields 2,4,5-trinitroimidazole, but, unfortunately, oxidation reactions compete with the nitration. No 2,4,5-trinitroimidazole remains in the reaction mixture after 15 min at 125°C. This is not surprising, because we have found that TNI [(II)] will decompose to carbanic acid [(VI)] in 100% nitric acid at 100°C (reaction D).

We do not believe that a cost-effective method for the production of ATNI can be found from the iodo

derivatives; therefore, we have suspended work on the reactions.

We made one additional attempt to develop a method for the preparation of ATNI. The method involves a thermal rearrangement of 1,4-dinitroimidazole [(VII)] in refluxing toluene that produces 2,4-dinitroimidazole [(VIII)]. The Russians report<sup>16</sup> that nitration of (VIII) with 100% nitric acid for 5 min at 100°C yields 26% trinitroimidazole, which they isolated as the potassium salt of TNI [(IX)] (reaction E). We can use this method to prepare experimental quantities of ATNI, but a production method will require a new approach.

## VII. CONCLUSIONS AND FUTURE WORK

We believe that Fairy Dust explosives have many potential uses as practical military explosives and interesting experimental systems. Performance and

TABLE VI

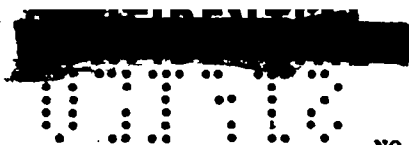
THE CMR CHEMICAL SHIFTS FOR 1M SOLUTIONS OF VARIOUS IMIDAZOLE DERIVATIVES IN DEUTERATED DIMETHYL SULFOXIDE (DMSO-d<sub>6</sub>) AT ~40°C

Material	CMR Shifts (ppm) <sup>a</sup>		
	C <sub>2</sub>	C <sub>4</sub>	C <sub>5</sub>
Imidazole	135.9	122.4	121.2
4-Nitroimidazole	135.9	149.2	118.9
4,5-Dinitroimidazole	138.2	135.8	135.0
4,5-Diiodoimidazole	141.7	89.0	86.4
2,4-Diiodo-5-nitroimidazole	151.4	78.0	92.4
2,4-Dinitro-5-iodoimidazole	150.3	147.3	83.5
Ammonium-2,4-dinitro-5-iodoimidazole	155.3	147.4	86.3
2,4,5-Triiodoimidazole	---	89.5	---
2,4,5-Trinitroimidazole	147.5	139.1	---
Ammonium-2,4,5-trinitroimidazole	146.8	138.6	138.2
2,4,5-Triketoimidazole (carbanic acid)	163.9	158.7	159.5

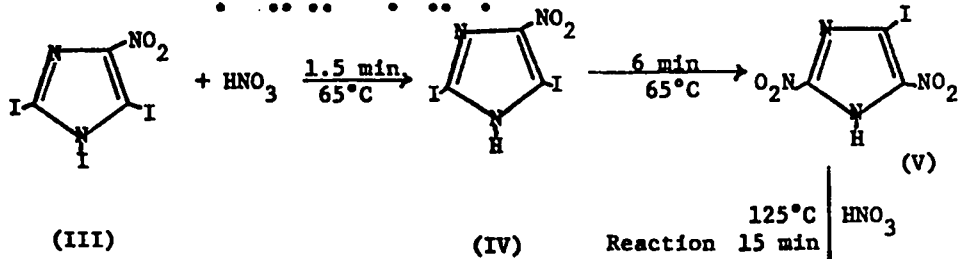
<sup>a</sup>Determined with a Varian CTF-20 spectrometer with a 10-mm probe. Reference to highest peak in DMSO-d<sub>6</sub>.

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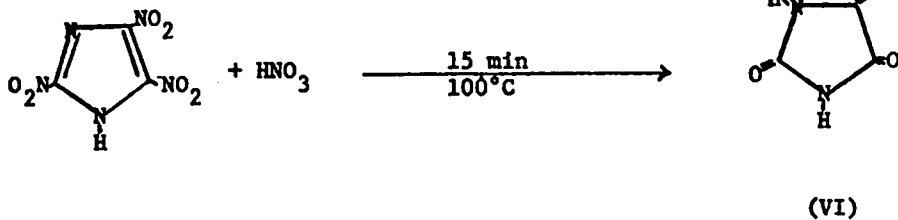
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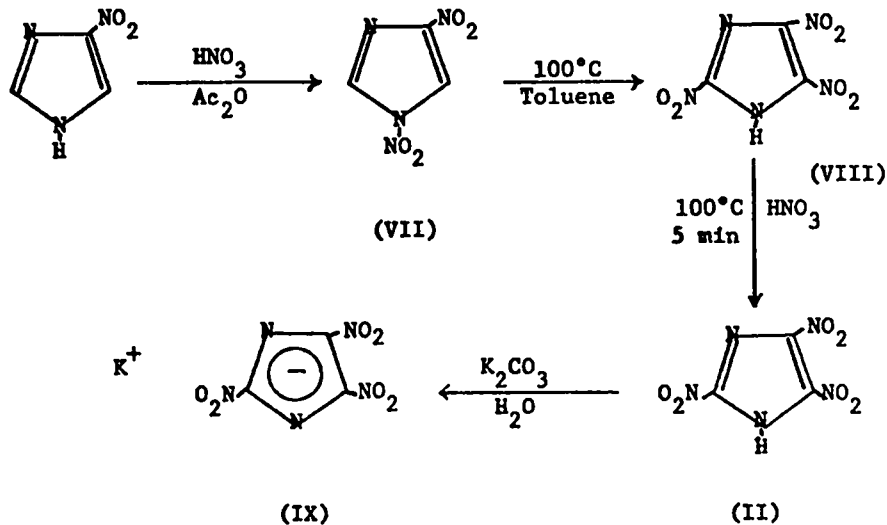
Reaction B



Reaction D



Reaction E



sensitivity can be varied over a wide range by making composition and formulation changes. For example, the eutectic mixture (1.38/1 molar AN/ADNT) can have extra AN added to increase blast, or can have RDX added to increase brisance. TNT, NQ, or TATB can be added to decrease sensitivity. The addition of aluminum increases detonation temperature, which increases bubble energy for underwater applications. In the coming year, we will try to determine sensitivity and performance limits for low-sensitivity, high-performance,

and metallized Fairy Dust systems. Measurements will be made on both ideal and nonideal formulations.

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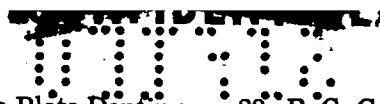
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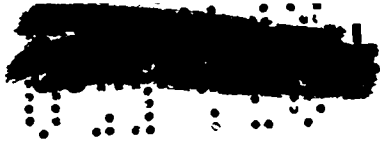
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