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Eutectic Explosives

Containing Ammonium Nitrate

Final Report—October 1979
through September 1981

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Edited by Barry W. Burton

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GLOSSARY

ADNT	ammonium 3,5-dinitro-1,2,4-triazolate
ADNT·2H$_2$O	ADNT dihydrate
AN	ammonium nitrate
Composition B (Grade A)	63/36/1 wt% RDX/TNT/wax
Composition B-3	60/40 wt% RDX/TNT
DAT	3,5-diamino-1,2,4-triazole
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EDD	ethylenediamine dinitrate
En(DNT)$_2$	ethylenediaminium dinitrotriazolate
Estane	polyvinyl urethane
FDEK	2.54/0.3/1/0.36 molar ratio AN/ADNT/EDD/KN
GuDNT	guanidinium dinitrotriazolate
GuN	guanidinium nitrate
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane
Kel-F	thermoplastic chlorotrifluorotriethylene/vinylidene copolymer
KN	potassium nitrate
NQ	nitroguanidine
PBX 9404	94/3/3 wt% HMX/nitrocellulose/Tris-β-Chloroethylphosphate
PBX 9501	95/2.5/1.25/1.25 wt% HMX/Estane/Bis (2,2-dinitropropyl) acetal/Bis (2,2-dinitropropyl) formal
PBX 9502	95/5 wt% TATB/Kel-F 800
PETN	pentaerythritol tetranitrate
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TMD	theoretical maximum density
TNT	trinitrotoluene

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ABSTRACT

Continued studies of the eutectic explosives of AN show that the most noticeable difference between eutectic systems is the size of the failure diameter. We report impact, thermal, and shock sensitivities for eutectic mixtures with various additives. Compatibility of the eutectics with NQ is unusually good as shown by gas evolution on storage at elevated temperatures. Performance was determined with mixtures of AN/ADNT with NQ, Al, or EDD/KN. Also, the performances of two methods of preparing AN/EDD were compared. We measured the irreversible growth of pressed pellets in which 15% of the AN was replaced by KN. We determined the heat of fusion and the heat and products of detonation of AN/ADNT. In addition, the guanidine and ethylenediamine salts of dinitrotriazole were prepared and characterized. We concluded that continuing the work on eutectic explosives would increase our understanding of explosives and contribute to the development of new explosives.

I. INTRODUCTION

For the past few years we have studied and tried to control the variables that affect the performance of eutectic explosives (an explosive mixture that melts at a lower temperature than either component). Those variables include particle size of the components, heat of formation, oxygen balance, percentage of oxidizer in the mixture in the case of a nondetonable oxidizer, and shock sensitivity of the explosive. Each eutectic has a set ratio of explosive to oxidizer determined by the properties of the components. Usually, departure from this ratio results in an increase in particle size. Because of diffusion constraints, it is desirable to have the smallest particle size possible for the oxidizer. Therefore, the eutectic ratio is advantageous for achieving the fastest reaction. The heat of formation and shock sensitivity of the eutectic ratio rest in the explosive component, but they are modified by the amount of oxidizer in the mixture. Energy and performance as well as the failure diameter and the diameter at which the detonation velocity approaches its infinite-diameter velocity are affected by these factors. For these reasons it is important to study many eutectic systems.

The two eutectic explosives studied are AN with ADNT and AN with EDD. The former was studied here[1,2] and the latter was studied at Picatinny Arsenal (now US Army Armament Research Development Center) and Eglin Air Force Base by I. Akst and J. Hershkowitz.[3-5]

Tests show that the two eutectic explosive systems have similar sensitivity and physical properties. AN/ADNT is slightly more sensitive to impact and thermal stimuli than AN/EDD. Both can be melted by 15-psi steam and frozen into very hard, fine-grained solids. Also, both are compatible with most common

explosives; hence, they can be used as casting matrices or prilled and used as filler in a TNT cast system.

However, on measuring performance we found a large difference between the failure diameters of the two systems. AN/ADNT in a 2/1 molar ratio at a density of 1.64 g/cm³ (97.9% TMD) has a failure diameter of ~ 1.3 cm, whereas EDD/AN at a density of 1.60 g/cm³ (96.5% TMD) has a failure diameter >7.6 cm. A significant difference in properties between the two systems is their heat of formation. The heat of formation of ADNT is 0 kcal/mol but that of EDD is −156 kcal/mol. The energetics of the system may be a major reason why EDD/AN has a lower shock sensitivity and a larger critical diameter. Other eutectic systems should be studied to determine if the heat of formation is the major factor in determining the critical diameter.

These variables make the study of eutectic explosives important for understanding explosive mixtures in general and are a major advantage when it is desirable to tailor explosives for a specific purpose. The pressure impulse and energy can be adjusted to optimize performance. Tailoring is especially desirable for underwater uses for which both shock pressure and bubble energy are important.

In this report we give the results of performance tests on several formulations of ADNT, AN, and other materials. We also report the properties of other salts of dinitrotriazole and the dihydrate of ADNT. In addition, temperature cycling of formulations with KN-stabilized AN are reported.

Molar ratios of the components are used in this report to elucidate the oxygen balance of the mixtures. For example, AN has one extra oxygen and ADNT lacks two oxygens for CO_2 balance; therefore, a 2/1 molar ratio AN/ADNT is CO_2 balanced. Table I shows molar ratios and weight percentages of the mixtures.

II. EXPERIMENTAL

A. Materials

ADNT was prepared as previously reported with extraction of the dinitrotriazole from the aqueous reaction mixture with Alamine 304, trilaurylamine.[5][6] We used dried ACS-reagent-grade AN and made the AN/ADNT mixtures by melting together the materials in a beaker, then pouring the melt or slurry onto a thick Teflon sheet. The thin sheet of explosive was broken into

pieces and pressed into a cylindrical test charge. The aluminum was H-5, a 5-µm spherical powder from Reynolds Metals Co. NQ was the Canadian low-bulk-density material.* KN was ACS grade.

EDD was prepared by adding 1/1 volume ratio nitric acid/water to 98% reagent-grade ethylenediamine dissolved in 10 vol% aqueous isopropyl alcohol while cooling the mixture with an ice bath. The AN/EDD melts were prepared in the same way as the AN/ADNT melts with the exception of "direct process" melts. These were prepared by addition of ethylenediamine directly to the correct amount of AN and heating to 104°C, the melting point of the eutectic. Ammonia is a product in the reaction to form EDD and keeps the mixture as a slurry until it is evaporated off.[7]

Guanidinium and ethylenediamine salts of dinitrotriazole were prepared by adding an aqueous solution of their chloride salts to an aqueous solution of dinitrotriazole. The new salts crystallized out on cooling or concentrating and cooling; their identities were verified by infrared and elemental analyses.

The hydrate of ADNT was prepared by subjecting ADNT to relative humidity >50% until the sample attained constant weight. The lowest relative humidity at which weight gain occurred was 35%.

B. Preparation of DAT

If ADNT preparation is to be economic, it will be necessary to prepare the starting material DAT easily. DAT's starting materials, hydrazine and cyanoguanidine, are readily available, but the literature preparation had a low yield and was unpredictable because of its sensitivity to reaction temperature and competing reactions.[8] Information from Monsanto Research Corporation in Dayton, Ohio, on their pilot-plant preparation of DAT was not too helpful because purification was difficult, yielding only 18.5% of the pure product;[9] their method on a laboratory scale yielded only 3%. The yield of the literature method varied from 9% to 28%.

We tried to use the aqueous solution of DAT analyzed at 86% as the starting material for the ADNT preparation; however, impurities caused the yield of ADNT to be reduced to 60%. In addition, the ADNT isolated from this reaction was discolored and had an impurity with a stretching frequency at 2130 cm⁻¹ in the infrared

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*Cynamid of Canada, Ltd., Industrial Products, Montreal, PQ.

TABLE I. Ratios of Components in Explosive Mixtures

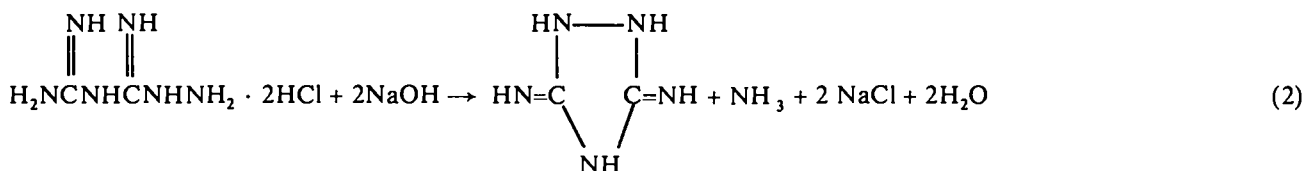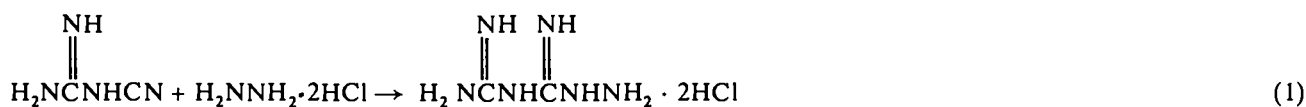| Mixtures	Molar Ratio	Weight Per Cent
Amatol (AN/TNT)	11.4/1	80/20
AN/ADNT (eutectic)	1.38/1	38.5/61.5
AN/ADNT (CO_2 balanced)	2.1	48/52
AN/ADNT/Al	2/1/2.66	39.2/43.2/17.6
AN/ADNT/EDD	3/0.3/1	50.1/11.0/38.8
FDEK	2.55/0.3/1/0.36	42.6/11/38.8/7.6
AN/ADNT/KN	1.7/1/0.24	40.5/52.4/7.1
AN/ADNT/NQ	1.38/1/1.38	25.7/40.9/33.4
	1.38/1/1.83	23.2/36.9/39.9
AN/ADNT/RDX	1.38/1/1.54	17.8/28.4/53.8
AN/ADNT/RDX/Al	1.38/1/1.5/6.86	13.7/21.9/41.4/23
AN/EDD	2.33/1	50/50
AN/EDD/KN	2/1/0.28	42.5/50/7.5
AN/EDD/RDX	2.33/1/0.3	42.5/42.5/15
AN/EDD/RDX/Al	2.33/1/0.3/2.8	36.2/36.2/12.8/14.8
AN/En(DNT)$_2$	3/1	38.8/61.2
AN/GuDNT	2/1	42.3/57.7
Composition B-3 (RDX/TNT)	---	60/40
PBX 9404 (HMX/binder)	---	94/6
PBX 9501 (HMX/estane)	---	95/5
PBX 9502 (TATB/Kel-F)	---	95/5

spectrum. Use of a crude DAT purified by methanol extraction gave a better yield of ADNT, 80%, but it was still colored and difficult to crystallize. From these results we decided that the DAT must be purified before it can be used in the ADNT preparation. Consequently, until DAT can be prepared with better yield, the preparation of ADNT will remain expensive. The following is an adaptation of the Monsanto method of preparing DAT on a laboratory scale.

Nitrogen gas was bubbled into 25 mℓ of water in a three-necked, 200-mℓ round-bottom flask for 10 min and was continued throughout the reaction. After 10 min, 8.34 g (0.08 mol) of hydrazine dihydrochloride were added, and the solution was heated to 50°C. At that temperature 6.68 g (0.08 mol) of cyanoguanidine were added slowly, one gram at a time, and stirred until solution was complete. The mixture was heated at 55-60°C for 1 h (Eq. 1). After the reaction cooled to below 30°C, 11-12 mℓ of 50% NaOH (0.15 mol) were added slowly to neutralize the complex and to allow cyclization (Eq. 2). The final pH of the solution was 8. Excess hydrazine and ammonia were distilled off under

vacuum. The crude product was triturated with methanol (20 mℓ) three times at 60°C (the solubility of DAT in methanol is 2 g/100 mℓ). The filtrates were combined and the solvent was distilled off in vacuum. The resulting DAT was recrystallized from 67% methanol/water to give a yield of 0.22 g (3% yield).

C. Methods

1. Sensitivity Measurements. The impact sensitivity, Henkin critical temperature, and wedge shock sensitivity tests were done in the manner described in *LASL Explosive Property Data*.[10]

2. Compatibility. Samples were sealed in glass ampoules and held at temperature in an oven. After each specified time, one ampoule was opened and the gases analyzed by mass spectrometry.

3. Temperature Cycling. Pellets were pressed to 98% of TMD, then sealed in Ziploc bags with Drierite, and cycled through a 24-h programmed cycle from

$$\underset{\text{H}_2\text{NCNHCN}}{\overset{\overset{\displaystyle\text{NH}}{\|}}{}} + \text{H}_2\text{NNH}_2\cdot2\text{HCl} \rightarrow \underset{\text{H}_2\,\text{NCNHCNHNH}_2}{\overset{\overset{\displaystyle\text{NH}\ \ \text{NH}}{\|\ \ \ \|}}{}}\cdot2\text{HCl} \tag{1}$$

$$\underset{\text{H}_2\text{NCNHCNHNH}_2}{\overset{\overset{\displaystyle\text{NH}\ \ \text{NH}}{\|\ \ \ \|}}{}}\cdot2\text{HCl} + 2\text{NaOH} \rightarrow \text{HN}{=}\text{C}\underset{\text{NH}}{\overset{\text{HN}{-\!\!-}\text{NH}}{\diagdown\diagup}}\text{C}{=}\text{NH} + \text{NH}_3 + 2\,\text{NaCl} + 2\text{H}_2\text{O} \tag{2}$$

−54°C to +74°C, pausing daily at ambient temperature long enough for the material to come to equilibrium and be measured by micrometer.

4. Heat and Products of Detonation. The detonation calorimetry was done by Ornellas at Lawrence Livermore National Laboratory using their small calorimeter with a gold cylinder for confinement. The method is detailed in a recent report.[11]

5. Performance Measurements. The plate dents were made by the Los Alamos Explosives Technology Group by detonating a column of pressed explosive on a 5-cm thick, cold-rolled-steel plate and measured by putting a known-diameter ball in the dent and measuring with a depth gauge resting on a ring with the same height as the ball (Fig. 1). The

Fig. 1. A method for measuring plate dents.

detonation velocity was measured by ionization switches positioned between pellets and connected to a timer. The cylinder tests were done by the Los Alamos Detonation Physics Group. Expansion of the copper tubes was observed by a streak camera at a slit two-thirds of the distance down the tube.

6. Calculations. Calculations were done using the BKW hydrodynamic code[12] and the Kamlet short method.[13]

III. RESULTS AND DISCUSSION

A. Sensitivity

Table II shows the impact sensitivities and Henkin critical temperatures for the materials of interest. All formulations except those with large amounts of RDX have moderately insensitive impact and Henkin sensitivities. Note that the Henkin critical temperature is higher for the AN/ADNT/NQ formulation than for either NQ or AN/ADNT. Also, the mixture with the larger amount of NQ is very impact insensitive.

The wedge test shows the ease of initiation of explosives by measuring the length of run necessary for each shock input before detonation begins. The data for the 2/1 molar ratio AN/ADNT at 1.64 g/cm³ are in Table III and are compared with other explosives in Fig. 2. Its run distance to detonation is the same as that of Composition B-3 at 6.6 GPa, but it detonates more quickly at stronger shocks and more slowly at weaker shocks. The slope of the curve for AN/ADNT is closer to that for PBX 9502. The longer runs at low shocks indicate that it is less sensitive to weak accidental stimuli than is Composition B-3 (Fig. 2).
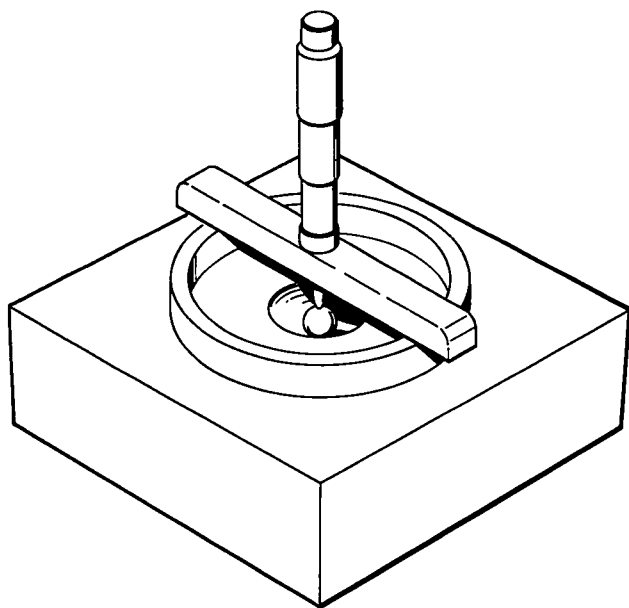
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TABLE II. Sensitivity Tests

| Material Molar Ratios | Impact Sensitivity | | Henkin |
	Type 12 (cm)	Type 12B (cm)	Critical Temperature (°C)
ADNT	58	96	225
ADNT · 2H$_2$O	224	>320	
AN	>320	>320	361
1.38/1-AN/ADNT	66	71	236
2/1-AN/ADNT	65	65	241
2/1/2.66-AN/ADNT/Al	71	157	250
1.38/1.1.54-AN/ADNT/RDX	37	70	215
1.38/1/1.5/6.86-AN/ADNT/RDX/Al	27	41	220
1.38/1/1.38-AN/ADNT/NQ	108	210	256
1.38/1/1.83-AN/ADNT/NQ	312	>320	261
3/0.3/1-AN/ADNT/EDD	58	96	227
2.55/0.3/1/0.36-FDEK	74	76	226
2.33/1-AN/EDD	109	153	244
EDD	88	115	245
NQ	>320	>320	198
RDX	22	30	214
TNT	150	>320	288

TABLE III. Wedge Test Data for 2/1 Molar Ratio AN/ADNT

	First Shot	Second Shot	Third Shot
Density (g/cm^3)	1.64	1.64	1.64
Pressure (GPa)	6.9	8.9	7.8
Run distance (mm)	6.1	2.7	4.8
Time (μs)	1.28	0.55	0.90

B. Compatibility

We reported in the 1977 annual report[1] and again in Table II that mixtures of AN/ADNT with NQ had higher critical temperatures in the Henkin test than those of either component. This is very unusual with explosives, so we decided to measure, by mass spectrometer, the decomposition gases formed in sealed ampoules held at elevated temperatures. We obtained complete data for 8 weeks at 50°C and 75°C for the two components and two mixtures.

The total amount of gas evolved at 75°C is about the same for a calculated mixture as for the experimental one; however, H$_2$O and N$_2$O amounts are higher and N$_2$ and CO$_2$ amounts are lower than calculated (Table IV).

Some minor interaction exists between the components, but it does not explain the greater thermal stability as shown by Henkin critical temperature. The reaction producing the gases that increased in amount is NH$_4$NO$_3 \rightarrow$ 2 H$_2$O + N$_2$O, a path for ammonium nitrate decomposition; the chemistry may or may not be the same at the critical temperature. Future experiments on other AN systems may shed some light on this process.

C. Performance

An important property of any new explosive is its performance. Eutectic explosives are especially interesting because it is uncertain whether they will perform as
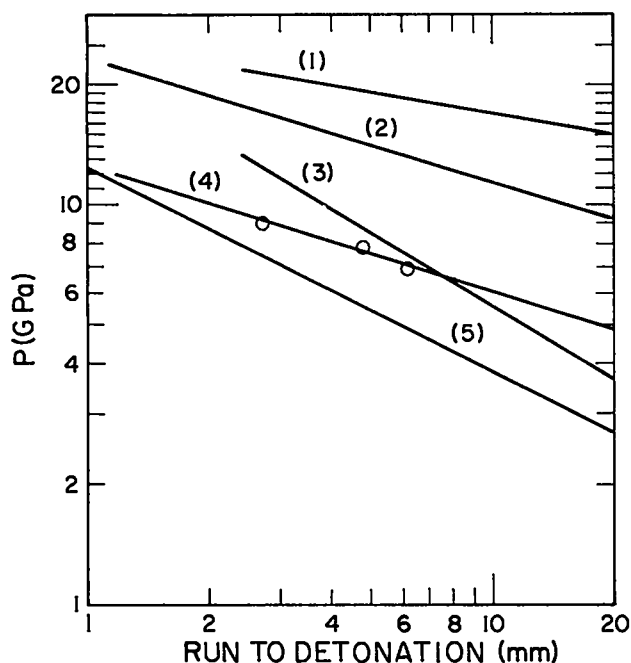
Fig. 2. Comparison of wedge data of 2/1 molar ratio AN/ADNT with other explosives: (1) 95 wt% NQ/Estane, (2) PBX 9502 (TATB), (3) Composition B-3, (4) 2/1 molar AN/ADNT, and (5) PBX 9501 (HMX).

1. AN/ADNT/NQ Formulations. We have responded to the interest in using NQ as an insensitive explosive by testing two formulations. In the annual report for 1977, we reported a 1.27-cm plate dent for a composition 1.38/1/1.38 molar ratio AN/ADNT/NQ.[1] Now we report a 2.54-cm plate dent for that formulation and a rate stick/plate dent on a formulation with even more NQ (Table V). The latter formulation is interesting because of its insensitivity to impact and good thermal stability in the Henkin critical temperature test (Table II). The lower than expected plate dent for NQ formulations is not unusual and is probably due to the low energy of NQ.[14]

2. AN/ADNT/Al Formulations. Aluminum is used in underwater explosives to give more bubble energy because of the higher temperature and thermochemical energy generated in aluminized explosives. In a previous report, we gave results of a plate-dent test of an AN/ADNT/RDX/Al mixture.[1] Now we have prepared and measured the rate stick/plate dent and cylinder test of 2/1/2.66 molar ratio AN/ADNT/Al. This is the amount of aluminum necessary to produce the products C, H_2O, and Al_2O_3. More aluminum can be used to increase the bubble energy, but because we do not have a standard underwater bubble test here, we tested only one formulation. The detonation velocity and plate dent were better than expected from BKW code or Kamlet short method calculations (Table V), and the detonation velocity of the aluminized AN/ADNT cylinder test on this formulation agreed with the unconfined rate stick. In the cylinder test, the wall velocity at 6-mm expansion showed that the aluminum acted as a diluent, but at 19 mm it was contributing energy and continued to do so at 30 mm (Table VI). Aluminum is a good additive to mixtures containing AN. The oxidation of Al to Al_2O_3 is very

calculated. In the annual report for 1978, we reported the performance of the 2/1 molar ratio AN/ADNT in the rate-stick/plate-dent test and cylinder tests.[2] These tests gave us the detonation velocity, an indication of the detonation pressure, and the ability of the CO_2-balanced explosive to push metal. We now report the performance of formulations with additional materials. The results are compiled in Table V with our earlier data.

TABLE IV. Compatibility at Elevated Temperatures

Gas Evolved in Sealed Ampoules Stored at 74°C for 8 Weeks

Material Molar Ratio	Total Volume of Gas (cm³/g)	%H₂O	%N₂	%CO₂	%N₂O	%CO
1.38/1 - AN/ADNT	0.217	50.7	14.7	28.6	3.7	trace
NQ	0.358	60.8	11.4	22.8	3.7	trace
1.38/1/1.83 - AN/ADNT/NQ						
Experimental mix	0.289	65.4	8.3	18.3	5.5	trace
Calculated mix	0.270	54.7	13.4	26.2	3.7	---

TABLE V. Experimental and Calculated Performance

Explosive, Molar Ratio	1.38/1/1.38- AN/ADNT/NQ	1.38/1/1.83- AN/ADNT/NQ	1.38/1- AN/ADNT	NQ	2/1- AN/ADNT	2/1/2.66- AN/ADNT/Al	2.55/0.3/1/0.36- AN/ADNT/EDD/KN
Experimental							
Density (g/cm³)	1.66	1.65	1.63	1.63	1.64	1.734	1.61
Plate Dent (mm)							
(2.54-cm diam unconfined)	4.65	4.50	--		4.60	4.62	3.96
(1.27-cm diam unconfined)	2.11	--	2.18		Failed	--	--
P_{CJ} (GPa) (interpolated from dent)	26.3 (averaged)	25.5	27.3		26.1	26.3	22.5
Rate Stick							
D_{CJ} (m/s)	--	8160	--	7980[14]	7844	7420	7420
Gamma							
$(\rho D^2/P_{CJ}) - 1$	--	3.3	--	--	2.91	3.06	2.94
Calculations							
BKW[a]							
P_{CJ}(GPa)	28.0	26.8	26.7	25.6[14]	27.3	25.1	27.5
D_{CJ} (m/s)	8305	8197	8168	069[14]	8268	7680	8260
Gamma	3.08	3.15	3.07	3.15[14]	3.10	3.07	3.01
T(K)	1892	1625	1980	1581[1a]	1780	4075	2179
KSM[b]							
P_{CJ} (GPa)	26.1	25.8	26.5	22.7	27.0	24.6	25.1 (K⁺ ion ignored)
D_{CJ} (m/s)	7866	7824	7973	7383	8038	7537	7785
Gaseous products (mmol/g)	38.0	38.1	37.8	38.5	38.7	37.0	40.8
Ave MW of gaseous products	25.1	38.1	37.8	38.5	38.7	27.0	40.8
Q (heat of detonation) (cal/g)	1029	1015	1100	888	1077	1683	947

[a]Becker, Kistiakowsky, Wilson.
[b]Kamlet short method.

TABLE VI. Cylinder Tests

		ADNT	2/1-AN/ADNT	2/1/2.66- AN/ADNT/Al	FDEK 2.54 cm	FDEK 5.08 cm	TNT	Comp B (Grade A)
Density (g/cm³)		1.58	1.64	1.74	1.61	1.61	1.63	1.71
Det. velocity (m/s)		7868	7890	7800	7420	7670	6950	7911
Cylinder vel. (mm/µs)	6 mm	1.30	1.37	1.38	1.27	1.29	1.23	1.43
	19 mm	1.49	1.53	1.51	1.44	1.46	1.40	1.63
	30 mm	1.53	--	1.61	1.52	1.51	1.46	1.68
Relative cyl.	6 mm	1.12	1.24	1.08	1.07	1.10	1.00	1.35

be done without processing facilities. Akst and I found that EDD could be prepared in the field by adding AN directly to ethylenediamine with evolution of ammonia but very little heat; hence, no chance exists for a runaway exothermic reaction.[7] The resulting mixture is a slurry until all of the ammonia is removed either by heating to make the eutectic AN/EDD (correct AN) or by evaporation. Before this final step, the material will not require transporting or handling as an explosive, which is convenient.

To determine whether the performance characteristics are the same as in the dry preparation AN/EDD, we prepared material for the rate-stick/plate-dent tests. The detonation velocities and plate dents were lower for the materials prepared by the direct process (Table VII).

We also tested the direct process with ADNT added to make FDEK. The mixture turned brown, and the detonation velocity was 11% lower than that of the dry mix. We

The explosives containing AN must be sealed against moisture whenever the relative humidity is >55%, especially if they are in contact with metal. Perhaps a plastic liner would solve the problem.

F. Heat of Fusion

The heat of fusion is the amount of energy needed to melt a castable explosive. The eutectic 1.38/1 molar ratio AN/ADNT has a heat of fusion of 22 cal/g determined by DSC using an indium standard. That result can be compared with 31.5 cal/g for 2.33/1 molar ratio AN/EDD and 23.8 cal/g for TNT.[5]

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*This information provided by G. Floyd, Eglin AFB, 1983.

TABLE VII. Performance Comparison for Different Processing Methods

A. Performance of Direct-Process Prepared Mixtures

41.3-mm Unconfined Material[a]	Density (g/cm³, TMD)	Dent [mm (P_{CJ}, GPa)]	Detonation velocity (m/s)
AN/EDD	1.585, 95.7	1.80 (failing)	---
AN/EDD/KN	1.608, 97.1	0 (failing)	---
FDEK	1.579, 95.1	5.74 (20)	6700

B. Comparison of Direct and Regular Processing

25.4-mm Steel-Confined Material[a]	Density (g/cm³, TMD)	Dent (mm)	Detonation Velocity (m/s)
AN/EDD			
[b]	1.576, 95.1	6.65	6150
[c]	1.533, 92.5	9.02	6600
AN/EDD/KN			
[b]	1.581, 95.5	5.74	5350
[c]	1.456, 88.0	7.85	---
FDEK			
[b]	1.571, 94.6	7.42	6590
[c]	1.626, 97.9	8.38	---
TNT (plate-dent standard)	1.548, 93.8	6.81	---

[a]See glossary for composition of materials.
[b]Prepared by direct process.
[c]Prepared by fusing dry materials.[4]

TABLE VIII. Temperature Cycling of AN- and AN/KN-Containing Eutectics[a]

Molar Ratio	Total Growth in 1st cycle (vol%)	Total Growth in 14 cycles (vol%)	Total Growth in 30 cycles (vol%)
2/1-AN/ADNT	9.5	10.0	10.9
1.7/1/0.24-AN/ADNT/KN	2.8	3.3	3.4
2.55/0.3/1/0.36-FDEK	10.6	11.5	12.0

[a]Twenty-four-hour cycle (–54°C to +74°C).

G. Heat and Products of Detonation

The detonation calorimetry was done by Ornellas at Lawrence Livermore National Laboratory using the small calorimeter and a gold cylinder for confinement.[11] To add to their studies of ammonium nitrate composites, they agreed to test ADNT and the CO_2-balanced mixture 2/1 molar ratio AN/ADNT. The results are given in Tables IX. X, and XI. ADNT gave results typical of a CO-balanced explosive—CO_2, CO, and C. The heat of detonation was −1135 cal/g, which agreed with −1251 ± 87 cal/g calculated from experimental products. A computer-calculated value of −1173 cal/g was obtained at a freeze-out temperature of 1726 K.

The 2/1 mixture detonated well in the 1.27-cm confined cylindrical configuration, gave heat of −1213 cal/g that agreed within 4% of the computer-calculated value of −1260 cal/g at 1665 K, and gave the expected products for a CO_2-balanced explosive. This has not always been the case for mixtures because CO, N_2O, and NO have been found in the products of a CO_2-balanced mixture of AN/TNT in which the particle size of the AN was 68 μm.[11] Therefore, we conclude that 2/1 molar AN/ADNT detonated and products were formed in freeze-out as for a monomolecular explosive.

H. Salts of Dinitrotriazole

1. ADNT. ADNT is the ammonium salt of a five-membered anionic nitrogen heterocycle, dinitrotriazolate. It has aromatic properties that stabilize the ring against hydrolysis. The electron-withdrawing power of the two nitro groups makes dinitrotriazole almost as acidic (pK −0.6)[15] as nitric acid. This acidity makes the ammonium salt's resistance to loss of ammonia when heated almost as great as that of AN. ADNT begins to bubble on melting at 170°C. The eutectic melt with AN at 112°C bubbles very slowly, and the mass action of the additional AN in the 2/1 formulation stops the loss of ammonia.

We found that the dried ADNT picked up two molecules of water to form a hydrate at relative humidities >35%. If the hydrate is used to make the eutectic with AN, a lower melting temperature exists at 58°C as water enters as a third component in the eutectic. However, the water will evaporate and the material will solidify again. Thus, the mixture is not stable enough to be practical. But this might be a way to speed liquefaction in a casting kettle. We determined the heat of formation of the hydrate by mixing it with some standard benzoic acid (Table XII). Note the desensitizing effect of the water of hydration on the impact sensitivity.

ADNT performed as expected from calculation. A 1.27-cm confined rate stick was done at Eglin AFB by Akst[4] and a 2.54-cm cylinder test was fired by our Detonation Physics Group (Table VII). It would be interesting to test the hydrate because small amounts of water improve the performance of RDX.[16]

2. GuDNT. GuDNT was prepared by metathesis of ADNT in water with guanidinium chloride. The less soluble GuDNT crystallized out. Its density is 1.66 g/cm^3 measured by gas pycnometer, and it is more thermally stable than ADNT, melting at 232°C with the exotherm not beginning until 270°C. However, its eutectic with AN melted at 133°C, which is too high to be melted by 15-psi steam. The melt is stable, so a sample was prepared by heating it in an oil bath. The ternary eutectic with AN/EDD melted at 96°C, but the ternary eutectic with AN/ADNT showed two melting endotherms, 113°C and 127°C in the DTA, giving a more complicated phase diagram.

The most interesting observation from the DTA of the 2/1 molar ratio AN/GuDNT mixture was the absence of the usual AN phase transition at 54°C. An x-ray powder pattern of the mix at ambient temperature was inconclusive; there were no lines for any of the following: AN(IV), GuDNT, GuN, or ADNT. The formulation of a new compound, GuDNT·2AN, would be one possible explanation of this phenomenon. Mixtures with more AN show the phase change. C. S. Choi at the National Bureau of Standards studied the mixture by x ray at higher temperatures and confirmed the absence of AN Phase IV or III line patterns. He saw no change in the pattern from ambient temperature to 90°C. Choi also prepared a mixture by heating 5% GuDNT with AN at 120°C for 2 h. On heating from 23°C to 90°C, this mixture went through the phase change of AN Phase IV to II with no Phase III observed.* GuDNT might be keeping water from catalyzing the Phase IV to III transition by acting as a dehydrating agent.

3. En(DNT)$_2$. En(DNT)$_2$ was prepared by addition of ethylenediamine hydrochloride to the reaction mixture containing dinitrotriazole. En(DNT)$_2$ is much less soluble in water than ADNT because of the bulkiness of the two anions associated with the ethylenediaminium di-cation.

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*This information provided by C. S. Choi, National Bureau of Standards, 1980.

TABLE IX. The Heat and Products of Detonation of ADNT and AN/ADNT

Explosive	ADNT	AN/ADNT
Charge[a] density (g/cm³)	1.574	1.639
%TMD	96.4	97.9
Charge wt (g)	22.9	23.6
$-\Delta H$ detonation[b] (cal/g)		
Experimental	1135 ± 11[c]	1213 ± 12
Calculated from products[c]	1255 ± 87[d]	1263 ± 40
Products (mol/mol HE)		
N_2	2.92	1.47
H_2O	1.53	1.78
CO_2	1.03	0.592
CO	0.658	0.0092
C(s)[e]	0.271	0
CH_4	0.029	not detected
HCN	0.018	0.0005
NH_3	0.010	0.0006
NO	not detected	0.0013
Material recovery (mol%)		
C[f]	87.0	100
H	93.5	101
N	91.7	99
O	106	100

[a]Charges are 12.7 mm in diameter confined in 12.7-mm-thick gold cylinders. Results are corrected for PETN used in initiation. One experiment each.
[b]At 298 K, H_2O (%).
[c]All errors are twice the estimated standard deviation of the mean and are based, in part, on other explosives for which more than one experiment was conducted.
[d]These errors are large because of the large uncertainty in the ΔH_f for ADNT: +0.6 ± 2.0 kcal/mol.
[e]Determined by difference. ΔH_f used for C(s) was +8.75 kcal/mol.
[f]Does not include solid carbon.

It has a density of 1.59 g/cm³ measured by gas pycnometer and is thermally unstable after melting at 225°C with a Henkin critical temperature at 215°C, slightly lower than the melting temperature. An even poorer Henkin critical temperature of 199°C was found when En(DNT)₂ was mixed with 3 mol of AN. AN also sensitized En(DNT)₂ to impact, giving a drop height of 96 cm in the Type 12 impact test, quite a bit lower than the 213 cm of the parent salt. On the plus side, the mixture melted at 97°C, which allows it to be melted easily with steam.

Choi found that mixing 5 wt% En(DNT)₂ with AN did not keep the AN out of Phase III as was observed for GuDNT and ADNT mixtures.

TABLE X. Comparison of the Calculated[a] CJ Isentrope Products with Observed Products from ADNT at Density 1.574 g/cm^3

Product	Observed (heavily confined)	Calculated BKWR CJ Isentrope 1546 K[b]	1935 K[b]
N_2	2.92	2.91	2.92
H_2O	1.53	1.40	1.62
CO_2	1.03	0.93	0.90
CO	0.66	0.75	0.53
$C(s)$	0.27	0.26	0.51
H_2	0.13	0.19	0.12
CH_4	0.029	0.069	0.0060
HCN	0.018	0	0
NH_3	0.010	0.18	0.17

[a]Calculated at density 1.612 g/cm^3.
[b]This is the temperature range over which calculated products agreed best with observed products.

TABLE XI. Comparison of the Calculated CJ Isentrope Products with Observed Products from AN/ADNT at Density 1.639 g/cm^3

Product	Observed (heavily confined)	Calculated BKWR CJ Isentrope 1520 K[a]	1825 K[a]
H_2O	1.78	1.77	1.78
N_2	1.47	1.49	1.49
CO_2	0.59	0.59	0.59
H_2	0.0096	0.0032	0.0025
CO	0.0092	0.0061	0.0065
NO	0.0013	0	0
NH_3	0.0006	0.0008	0.010
HCN	0.0005	0	0

[a]This is the temperature range over which calculated products agreed best with observed products.

IV. CONCLUSIONS

We have studied the physical and explosive properties of the first eutectic explosive discovered that has calculated performance at small diameters. The performance approached that of Composition B. Addition of RDX or HMX makes this eutectic a more powerful explosive than Composition B. Cylinder tests show that the eutectic without RDX expands the metal promptly with energy between those of TNT and Composition B. The wedge test shows that the run to detonation is shorter for high-pressure input and longer for low-pressure inputs than is the case for Composition B.

TABLE XII. Properties of Salts of Dinitrotriazole

	ADNT	ADNT·2H$_2$O	GuDNT	En(DNT)$_2$
m.p. (°C)	170	140	232	225
Exotherm (°C)	225	245	305	235
Heat of formation (kcal/mol)	0.6 ± 2	−35.8	---	---
Crystal density (g/cm^3)	1.632 (x ray)	1.62 (gas pyc)	1.66 (gas pyc)	1.59 (gas pyc)
Type 12 impact sen. (cm)	58	224	>320	213
Critical temp. (°C)	219	---	—	215
m.p. of AN eutectic	112	58	133	97
Det. vel. (m/s)	7870	---	---	—
Density (g/cm^3)	1.58			

The physical properties of AN/ADNT are amenable to casting with perhaps a third component to lower the melting temperature a few degrees. KN substituted for some of the AN controls the irreversible growth of AN. The heat of fusion is lower than TNT's, so less energy is required to melt the eutectic.

We began to look at the properties of other salts of dinitrotriazole and found possible compound formation between AN and the GuDNT. No performance tests were attempted.

Work on the AN/ADNT eutectic system has ended, but work goes on here and elsewhere with other eutectics, especially AN/EDD. We continue a low-level search for a third component to add to the AN/EDD that would decrease the failure diameter yet make an economical system with good physical and explosive properties.

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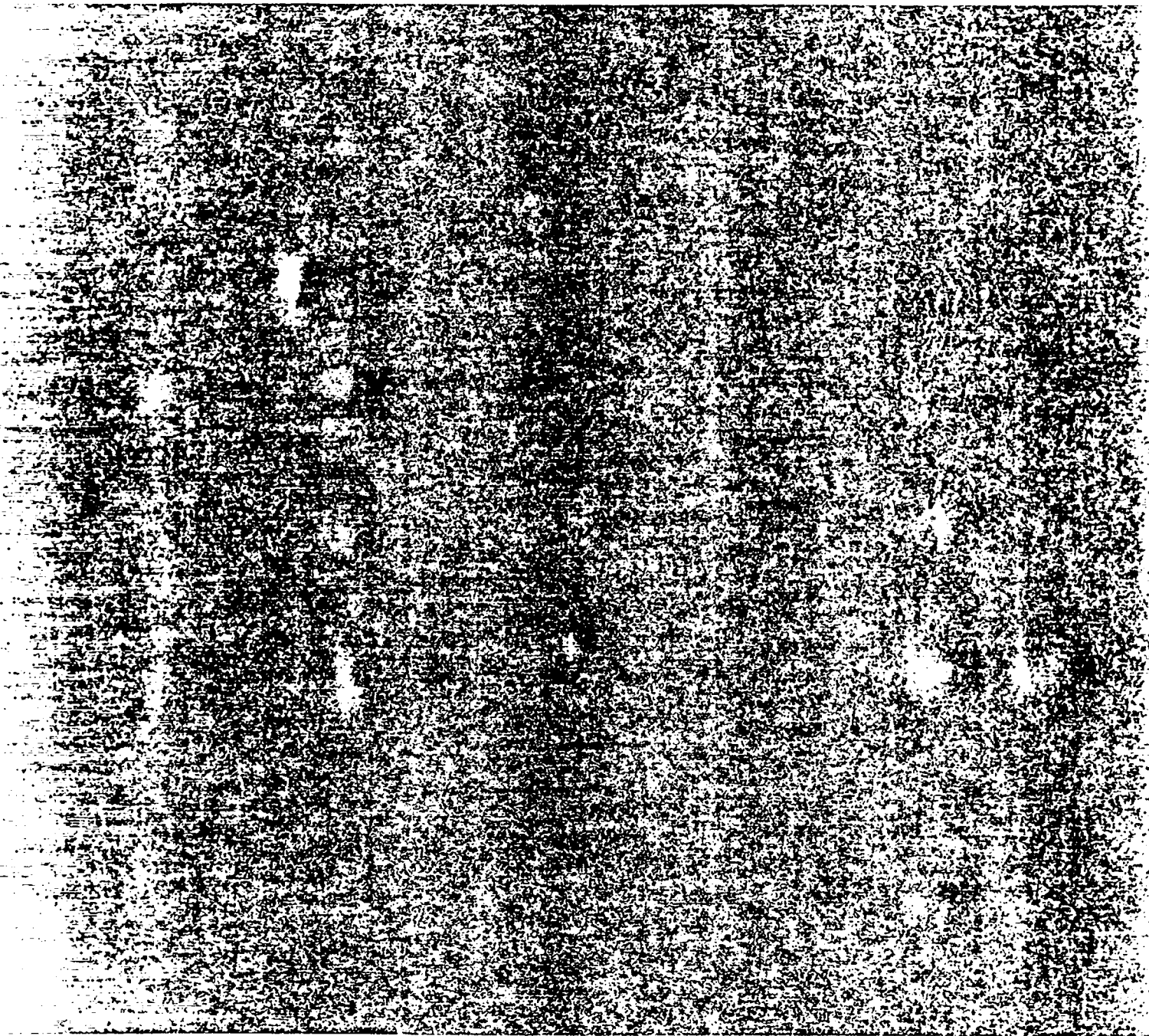
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