Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Binary eutectics formed between ammonium nitrate and amine salts of 5-nitrotetrazole I. preparation and initial characterization

K. -Y. Lee[a]; M. D. Coburn[a]
[a] Los Alamos National Laboratory, New Mexico

To cite this Article Lee, K. -Y. and Coburn, M. D.(1983) 'Binary eutectics formed between ammonium nitrate and amine salts of 5-nitrotetrazole I. preparation and initial characterization', Journal of Energetic Materials, 1: 1, 109 — 122
To link to this Article: DOI: 10.1080/07370658308010822
URL: http://dx.doi.org/10.1080/07370658308010822

BINARY EUTECTICS FORMED BETWEEN AMMONIUM NITRATE AND AMINE SALTS OF 5-NITROTETRAZOLE I. PREPARATION AND INITIAL CHARACTERIZATION

K.-Y. Lee
M. D. Coburn

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ABSTRACT

We have found that both the ammonium salt of 5-nitrotetrazole (ANT) and the ethylenediamine salt of 5-nitrotetrazole (ENT) form eutectics with ammonium nitrate (AN). Initial characterization and small-scale sensitivity tests of CO_2-balanced AN/ANT and AN/ENT formulations were performed; it was found that both eutectics were less sensitive in all tests than pure ANT or ENT, respectively. The phase diagrams of both mixtures were also determined. ANT forms a eutectic with AN that melts at 121°C; the eutectic composition of the AN/ANT system is 78.5 mol% AN. The eutectic temperature and composition of the AN/ENT system were found to be 110.5°C and 87.8 mol% AN, respectively. Thermal stability studies of the eutectics indicate that they are stable below 160°C and that thermal decomposition occurs slowly over a long period of time.

The detonation velocities of both eutectics, measured unconfined at 2.54-cm diameter, were found to be within 95% of those predicted by the Kamlet-Jacobs method assuming ideal behavior.

Journal of Energetic Materials Vol.1, 109-122(1983)

Published in 1983 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Ammonium nitrate (AN) is an inexpensive and readily available oxidizer used extensively in commercial explosives; thus, it has also received attention as a possible ingredient in military explosives. Unfortunately, one of the disadvantages limiting the usefulness of AN is its nonideal behavior. Over the past decade or so, a number of attempts have been made to obtain ideal explosive behavior from composites of AN with various fuels. The most promising of these studies involves forming low-melting eutectics of the fuel with AN[1-3]. The eutectics offer the advantage of being castable for military applications; the intimate mixing of the fuel with AN offers the best opportunity for ideal performance, that is, for the fuel and AN to interact and detonate as a single component rather than as two individual components.

The ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT) and AN formed a low-melting eutectic that was subsequently shown to perform as an ideal explosive[4]. Work at Idos Corporation also demonstrated that the AN/ethylenediamine dinitrate (EDD) eutectic system gave detonation like that of a typical high-powered mono-molecular explosive[5]. The finding that AN-based composites could be made to give near-ideal performance encouraged a continued search for other, less-expensive ingredients that would form similar eutectics or solid solutions with AN.

As other fuels are found and their performance with AN is studied, it may be possible to make a correlation between ideal performance and some common characteristics of the additives. For instance, a positive heat of formation (ΔH_f) of the fuel component may be an important parameter for ideal

performance of eutectics with AN. This knowledge would allow a more scientific method for developing AN-based composite explosives than the current empirical approach. Another advantage of studying composite systems is that they provide an attractive alternative to synthesis of new explosives with desirable properties. Also, experiments have shown that the rate of energy release in composite explosives can be controlled by variation of the composition and the particle size of the components[6].

The goal of the present work is to determine and characterize eutectics of AN and salts of other nitroheterocycles with structures similar to that of ADNT. We chose to study amine salts of 5-nitrotetrazole because they are similar to ADNT and are easy to prepare[7].

The ammonium salt (ANT) was an attractive candidate because it has a common ion with AN. We chose to study the ethylenediamine salt (ENT) because of its similarity to EDD. In addition, both salts have a positive heat of formation (ΔH_f).

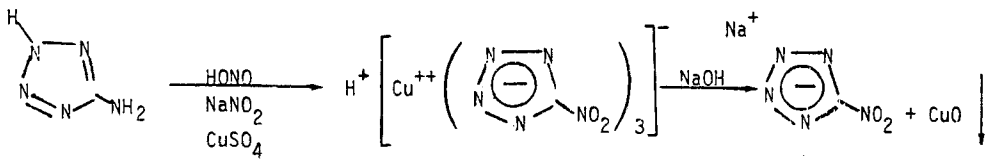
EXPLOSIVES PREPARATION AND EXPERIMENTAL PROCEDURES

Synthesis of Salts of 5-Nitrotetrazole

These salts were prepared by a modification of the procedure reported by the Naval Surface Weapons Center[7]. The hazardous step of isolating the extremely sensitive copper salt of 5-nitrotetrazole has been eliminated and a

one-pot process has been developed for obtaining a solution of the insensitive sodium salt. Thus, to a stirred solution of sodium nitrite (104 g, 1.5 mol), cupric sulfate (55 g, 0.22 mol) in 300 ml water was added drop wise to a solution of 5-aminotetrazole (AT) (51.5 g, 0.5 mol), cupric sulfate (2 g, 0.008 mol) and concentrated sulfuric acid (51.0 g, 0.5 mol) in 700 ml water at 10-15°C. After stirring at room temperature for one hour, the resulting mixture was adjusted to pH 9.5 with 50% sodium hydroxide and heated at 70°C for one hour to convert the copper salt of 5-nitrotetrazole (CNT) to the sodium salt (SNT) and cupric oxide (Reaction 1). The precipitated cupric oxide was removed by filtration, and the yield of SNT was determined to be 96% by spectrophotometry at 255 nm.[7] The SNT solution was acidified with an equivalent amount of concentrated sulfuric acid and extracted with trilaurylamine (Alamine 304, R_3N) in dichloroethane (DCE)[8]. The organic extract was

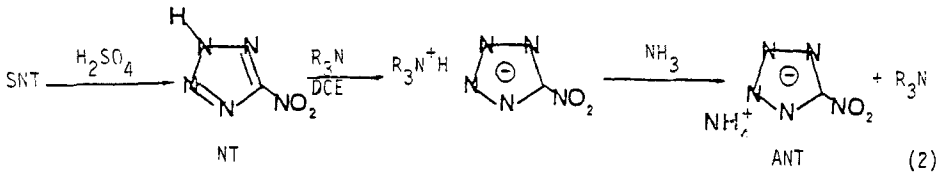
Reaction 1



AT CNT SNT

dried (magnesium sulfate) and treated with anhydrous ammonia. The precipitated ammonium salt (ANT) was collected by filtration, washed several times with DCE, and dried to yield 53.5 g (81%) (Reaction 2).

Reaction 2

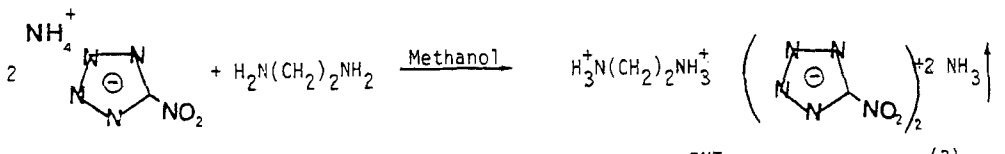


(2)

To remove trace amounts of inorganic sulfate, the solid product was stirred with methanol (250 ml) and filtered. The filtrate was evaporated to dryness to yield pure ANT. The purity was determined by the ammonia ion-selective-electrode method[9] to be 99.8%.

If ethylenediamine is used instead of ammonia in the last step of Reaction 2, the ethylenediamine salt of 5-nitrotetrazole (ENT) will be the final product. ENT can also be prepared by addition of one equivalent of ethylenediamine to a methanol solution of two equivalents of ANT, followed by evaporation of the solvent (Reaction 3). The yield of pure ENT by this method is 85%. NMR analysis showed the ENT to be free of impurities.

Reaction 3



ANT ENT (3)

Small-Scale Sensitivity Tests

CO_2-balanced mixtures of both AN/ANT and AN/ENT were used for all the tests; these mixtures were prepared by melting the mixed components together in a beaker that was heated by an oil bath. The molten mixture was poured quickly and spread evenly onto a sheet of Teflon to solidify. The tests were performed according to standard procedures and the results are reported in Table 1 along with those of two common explosives, RDX and TNT.

TABLE 1 Physical and Explosive Properties

	ANT	AN/ANT	ENT	AN/ENT	RDX[a]	TNT[a]
MELTING POINT (°C)	202_{DEC}	121	221	110.5	205_{DEC}	80.9
DTA STABILITY (°C)	200	200	216	200		
DENSITY (g/ml)	1.57		1.55		1.806	1.654
VACUUM STABILITY (ml/g/48h at 120°C)	1.2	0.4	0.5	2.4	0.12-0.9	.005
(ml/g/48h at 100°C)				0.2		
IMPACT SENSITIVITY (cm)						
TYPE 12	30	56	42	78.8	28	148
TYPE 12B	75	72	51	264	32	~100
SPARK SENSITIVITY (J)						
3-mil foil	2.66	2.68	1.70	2.30	-	-
10-mil foil	7.58	8.05	4.70	6.38	-	-

[a] Data obtained from B. Dobratz, LLNL Explosives Handbook

Phase-Diagram Determinations

Stock samples for phase-diagram determination were prepared by weighing and then mixing the appropriate amounts of salts with a mortar and pestle. The mixture was ground in the presence of a small amount of methanol and evaporated to dryness to ensure homogeneous mixing. Slides were prepared for phase-transition observation by melting a small amount of the stock sample mixture on a slide, then cooling it immediately to room temperature. A Carl Zeiss microscope, equipped with a Mettler Instrument AG Model FP-2 hot stage accurate to 0.3°C, was used to observe phase transition.

Performance Tests

The detonation velocities of both the AN/ANT and AN/ENT formulations were determined with 2.54-cm-diameter unconfined rate sticks.

RESULTS AND DISCUSSION

Eutectic Studies

We found that both the ammonium salt (ANT) and the ethylenediamine salt (ENT) of 5-nitrotetrazole form eutectics with ammonium nitrate (AN) that melt at 121°C and 110.5°C, respectively. The eutectic composition of AN/ANT is 78.5 mol% AN (68.9 wt% AN) and that of AN/ENT is 87.8 mol% AN (66.5 wt% AN).

When these eutectic compositions are compared to the CO_2-balanced compositions of 66.7 mol% AN for AN/ANT and 90 mol% AN for AN/ENT, the latter formulation becomes very attractive from the economic viewpoint of utilizing the greatest amount of AN in a CO_2-balanced composition. Also, the CO_2-balanced AN/ENT formulation offers the processing advantages of being close to the eutectic composition and having a relatively low melting point. The phase diagrams of the AN/ANT and AN/ENT systems are given in Figures 1 and 2, respectively.

Results of Sensitivity Tests

Results of the small-scale sensitivity tests of CO_2-balanced AN/ANT and AN/ENT are given in Table 1; test results for the ideal explosives, TNT and RDX, are listed for comparison. Both eutectics were less sensitive to impact and spark than were the respective pure fuel components. Note that the vacuum stability of the AN/ENT mixture is only 0.2 ml/g/48h at 100°C, even though it is 2.4 ml/g/48h at 120°C. We do not feel that the high number is a indication of incompatibility between ENT and AN because the mixture is a liquid at 120°C and ENT is a solid at this temperature. The vacuum stability of AN/ENT is good at 100°C, where both ENT and the AN/ENT mixture are solid. In addition, accelerating rate calorimetry (ARC) shows that the mixtures are stable below 160°C and that the thermal decomposition occurs slowly over a long period of time.

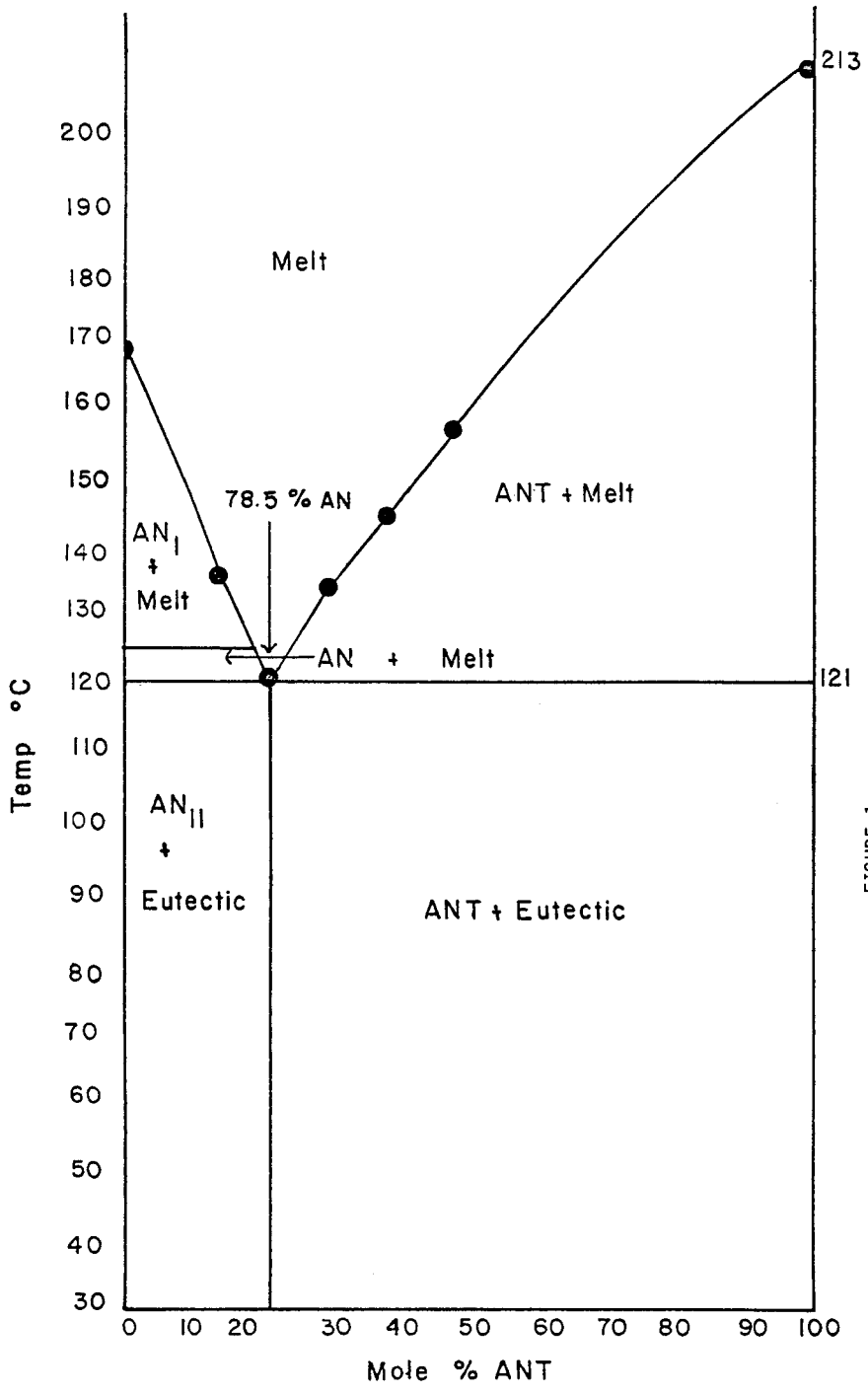
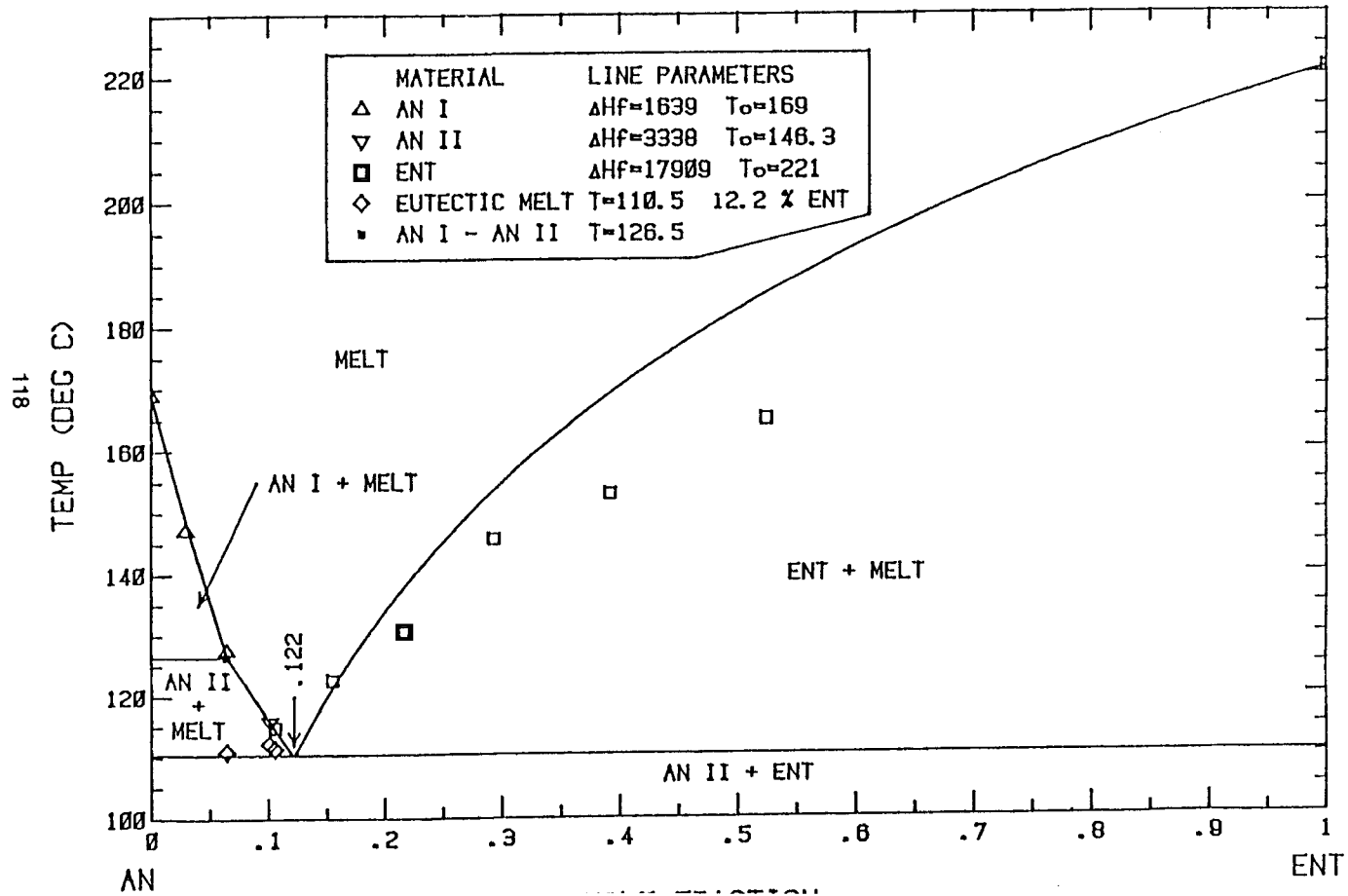


FIGURE 1
Phase Diagram of AN/ANT System

FIGURE 2

Phase Diagram of AN/ENT System



Performance Tests

The results of the detonation velocity measurements of CO_2-balanced AN/ANT and AN/ENT are given in Table 2 along with the predicted values calculated by the Kamlet-Jacobs method (KSM)[10] assuming ideal behavior. The measured velocities of both systems are within 95% of those calculated by the Kamlet-Jacobs method. The results may be somewhat lower than predicted because the tests may have been conducted near the failure diameters of the eutectics. Subsequent measurements at larger diameters are planned to clarify this issue.

ACKNOWLEDGMENTS

This work was supported by the Air Force Armament and Testing Laboratory (AFATL), Eglin AFB, Florida. The authors thank Dr. Howard Cady for his helpful contribution on phase-diagram determinations, to Captain Robert Hildreth for his encouragement and support of this research, and to Brigitta Dobratz for editing the manuscript. Thanks also to Dr. Mary M. Stinecipher for the determination of heat of formation of ANT and ENT.

TABLE 2 Heat of Formation and Detonation Performance Data

Explosives	Density (g/cm^3)	Heat of Formation, ΔH_f (kcal/mol)	Dent (mm)	P_{C-J} (kbar) measured	P_{C-J} (kbar) KSM	Velocity (km/s) measured	Velocity (km/s) KSM
AN	1.725	-87.27			182		6.49
ANT	1.57	+4.7±0.2			211		7.20
ENT	1.55	+55.7±3			199		7.02
AN/ANT (54.8 wt% AN)	1.607		3.88	221	247	7.36	7.73
AN/ENT (66.5 wt% AN)	1.568		3.38	192	248	7.30	7.78
TNT[a]	1.64	-15	3.43	210		6.93	
RDX[a]	1.77	+14.71		338		8.70	

[a] Data obtained from B. Dobratz, LLNL explosives Handbook.

REFERENCES

1. J. Hershkowitz and I. Akst, "A New Approach to Improving the Performance of Nonideal Explosives Containing Ammonium Nitrate," Technical Report 4789, Picatinny Arsenal, Dover, NJ, March 1975.

2. I. Akst and J. Hershkowitz, "Explosive Performance Modification by Co-solidification of Ammonium Nitrate with Fuels," Technical Report 4987, Picatinny Arsenal, Dover, NJ, Oct. 1976.

3. J. Hershkowitz and I. Akst, "Improvement of Performance of Composite Explosives Containing Ammonium Nitrate by Physical Synthesis," Proceedings of the Sixth Detonation Symposium, Office of Naval Research Report, ACR-221, 1976, p. 439.

4. M. M. Stinecipher and M. D. Coburn, "Ammonium Nitrate Explosive Systems," U. S. Patent 4,300,962, 1981.

5. I. Akst, "Detonation in Intermolecular Explosives: Characteristics of Some Eutectic Formulations," Seventh Symposium on Detonation, Preprints, 1981, p. 289.

6. R. A. McGuire, D. L. Ornellas and I. B. Akst, "Detonation Chemistry: Diffusion Control in Non-ideal Explosives," Propellants and Explosives 4, 1979, p. 23.

7. W. H. Gillian and M. J. Kamlet, "Synthesis of Mercuric-5-Nitrotetrazole," Naval Surface Weapons Center Report NSWC/WOL/TR 76-146, Dec. 1976.

8. K.-Y. Lee and D. G. Ott, "Production of the Ammonium salt of 3,5-Dinitro-1,2,4-Triazole by Solvent Extraction," U. S. Patent 4,236,014, 1980.

9. Method developed by Analytical Section of Explosives Technology Group, Los Alamos National Laboratory.

10. M. J. Kamlet and S. J. Jacobs, "Chemistry of Detonations in a Simple Method of Calculating Detonation Properties of C-H-N-O Explosives," J. Chem. Phys. 48, 23, 1968.

This paper was developed under the auspices of the U.S. Department of Energy.