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Development of New Ammonium Nitrate Composite Explosives

Final Report, October 1982—January 1984

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This work was supported by the Air Force Armament Laboratory, Department of the Air Force, Elgin Air Force Base, Florida.

Edited by Renate Lewin
Photocomposition by Chris West

LA-10276

UC-45
Issued: March 1985

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by

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ABSTRACT

Studies of several AN-based composite explosive systems were continued from earlier work. The critical temperature (T_c) of AN/ANT, AN/ENT, and AN/DETN systems were measured and their thermal stabilities evaluated. We have also studied the effect of ENT on the melt temperature of EA and found that ENT forms a eutectic with EA. The eutectic temperature of the ternary system AN/EDD/ENT (AENT) is 89°C. Results from an initial phase-diagram study of the quaternary system AN/KN/EDD/DETN (DEAK) are also presented.

I. INTRODUCTION

Last year, we reported the findings of several AN-containing eutectic systems that give near-ideal performance at small charge diameters.[1] We also found that in addition to the formation of a eutectic, AN and DETN form a "double salt" that has unusual properties and that the addition of ENT to the EA system lowers the melt temperature of EA. Therefore, we studied the eutectic formation of AN, EDD, and ENT and evaluated the performance of the ternary system, with the ultimate goal of using ENT as a sensitizer for EA.

Experiments have shown that adding 15 wt% KN to AN before prilling stabilizes AN with respect to the AN_{III}-AN_{IV} phase transition.[2] The eutectic melt of the EA system with KN (EAK) has already been prepared in large quantities and has been used in bomb fills.[3] However, the crystallite size of the final mixture is too large to obtain ideal performance at these diameters. Addition of a fourth component, such as DETN, to this system should result in more finely divided phases. The eutectic melting temperature of the AN/EDD/DETN/KN system may approach that of TNT and the system would, therefore, process more easily in existing equipment than does the EAK system.

In this report, we shall describe the experimental results of thermal stability studies of AN/DETN, AN/ANT, and AN/ENT systems. Results from phase-diagram studies and initial performance tests of the AENT system also will be reported. In addition, we report the results from an initial phase-diagram study of the quaternary DEAK system.

II. THERMAL PROPERTIES OF EUTECTICS

A. Thermal Stability

Thermal stabilities of various eutectics and composite systems were evaluated by Accelerating Rate Calorimetry (ARC). Samples of 1.0 g or less are placed in a small pressure vessel (or sample bomb) inside the calorimeter and are heated to some predetermined temperature. This temperature is then allowed to stabilize, and a temperature rise in the sample as a result of self-heating is recorded.

Table I lists the ARC results for our samples; all are stable up to 160°C.

B. Thermal Hazard Model

We measured the critical temperature (T_c), that is, the lowest temperature at which a sample of known

TABLE I. ARC Test Results

Explosive	Composition (wt%)	T_0[a] (°C)	T_{m-1}[b] (°C)	t_0[c] (h)
AN/EDD	50/50	180.5	220	1.55
AN/DETN	40/60	180.8	196	0.27
AN/ANT	68.9/31.1	276.1	302.10	---
AN/ENT	66.5/33.5	160.6	186	11.3
AN/DETN/EDD	42/28.7/29.3	180.6	200	0.43

[a] T_0 - temperature at which reaction rate is >0.01°C/min.

[b] T_{m-1} - temperature of rapid pressure and temperature rise.

[c] t_0 - time to maximum rate (ΔT for time at T_{m-1} - time at T_0).

geometry will self-heat to explosion, of each component and its eutectic with AN. The test results are given in Table II with T_c of RDX and EAK listed for comparison.

From T_c data, it can be seen that all the eutectic systems studied thus far are thermally more stable than RDX but are less stable than EAK at similar sample thickness. In addition, time to explosion for all samples was less than 100 s except for DETN, which gave a significantly longer time to explosion (Fig. 1). Figure 2 illustrates time-to-explosion data of the AN/ENT system.

We attempted to calculate the thermal-hazards predictive model for larger scale preparations of eutectic systems AN/ANT, AN/ENT, and AN/DETN. Both Frank-Kamenetskii and Semenov predictive equations were used.

For the AN/ENT (66.5/33.5 wt%) system the decompositions are complex, showing initial-rate processes and autocatalytic behavior. Figure 3 shows the isothermal differential-scanning-calorimeter (DSC) rate curves at three different temperatures of the AN/ENT system. The final worst-case predictive model for the AN/ENT system is shown in Fig. 4; the predictive model for the AN/ANT system is shown in Fig. 5. Results from both models for both systems indicate that other models at a larger size must be tested before they can be used to make predictions for large-scale operations.

We attempted to determine the kinetics values for the AN/DETN system from isothermal runs done in a DSC. Because the thermal data obtained are inconsistent, it is not possible to obtain a kinetic model for this system using the usual analytical techniques.

TABLE II. Critical Temperature of Explosives

Explosive	Critical Temperature (T_c) °C	Sample Thickness (mm)
ANT	218	0.814
ENT	208	0.906
AN/ANT (54.8 wt% AN)	228	0.817
AN/ENT (66.5 wt% AN)	234	0.872
AN, reagent	~330	~1.02
DETN	206	0.795
AN/DETN (40/60 wt% AN)	240	0.874
RDX	214	0.800
EAK (50/42.5/7.5 wt%)	244	0.830

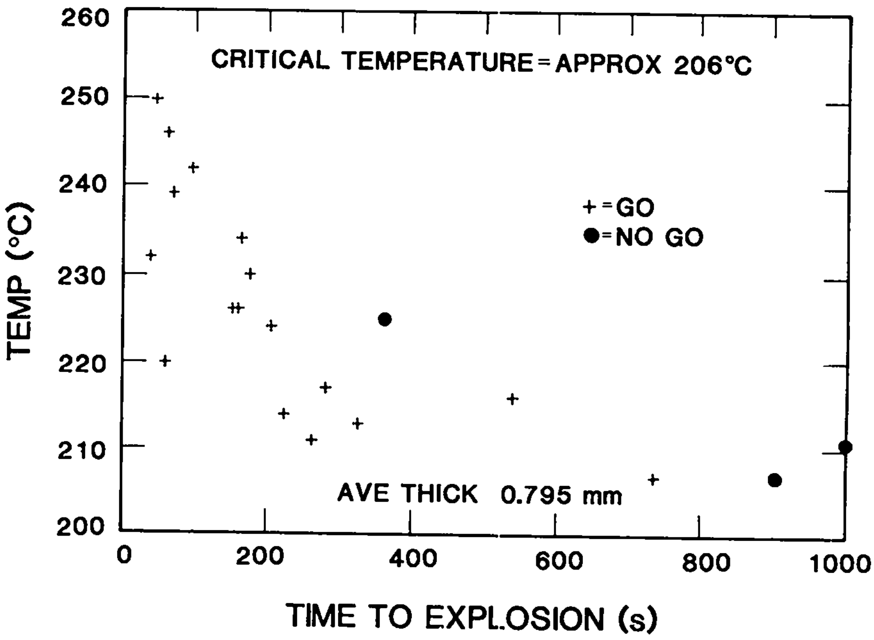

Fig. 1. Critical temperature determination for pure DETN.

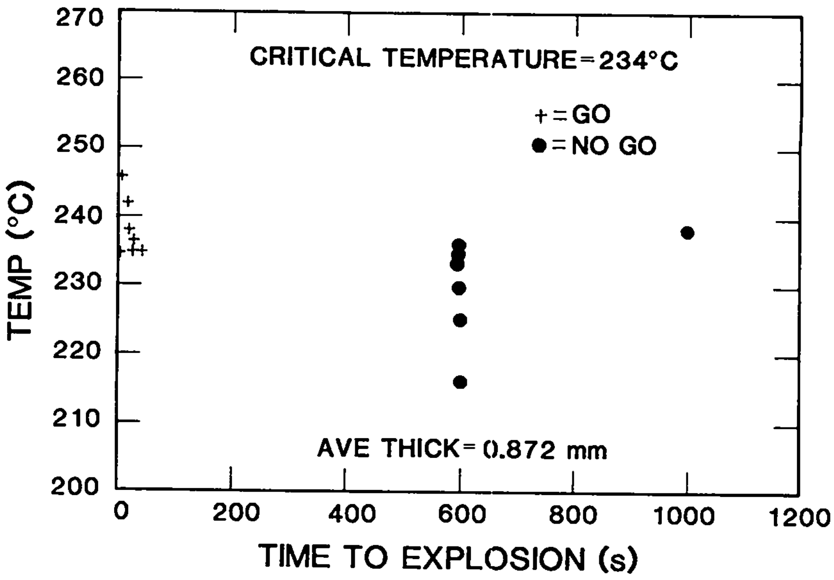

Fig. 2. Time-to-explosion data for AN/ENT. No explosion was obtained at temperatures below 234°C.

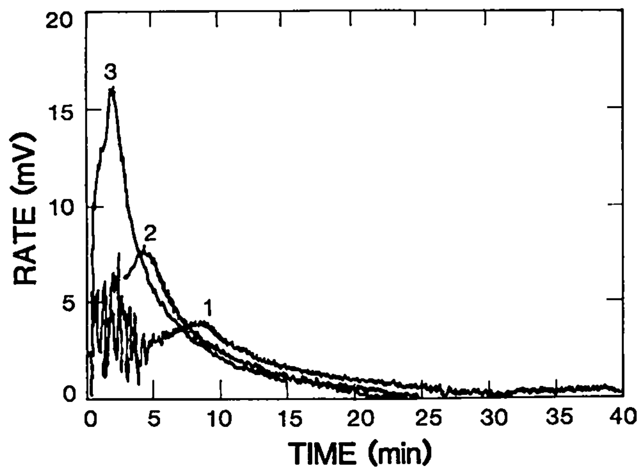

Fig. 3. Experimental isothermal DSC rate curves for AN/ENT, all normalized to a 1-mg sample size. Point 1, 475 K; point 2, 485 K; point 3, 490 K.

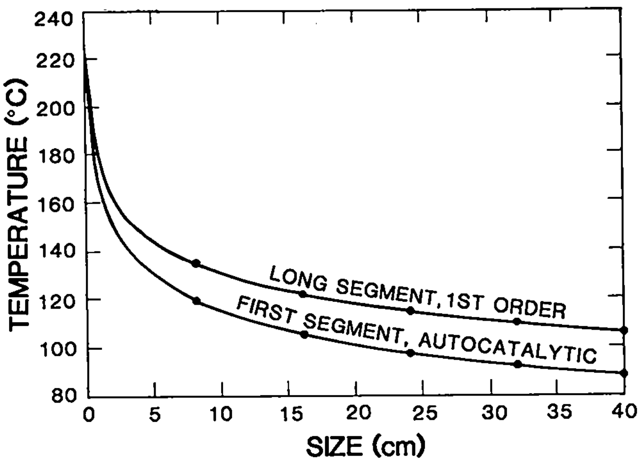

Fig. 5. Critical-temperature predictions for spheres of AN/ANT.

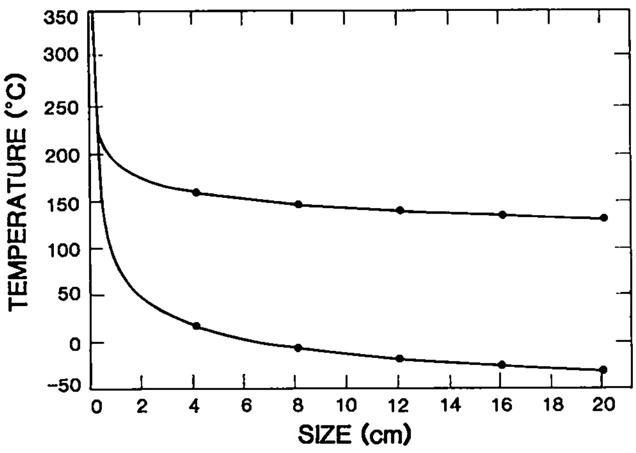

Fig. 4. Critical-temperature predictions for spheres of AN/ENT according to a Frank-Kamenetskii (worst-case) model. The upper curve assumes E = 39.6 kcal/mole and $Z = 4.6 \times 10^{14} s^{-1}$. The lower curve assumes (unrealistic) kinetics constants obtained from the first autocatalytic rate process (E = 10.1 kcal/mole and $Z = 342\ s^{-1}$). The general model for the curve is as follows:

$$39600/T_c = R \ln \left[\frac{a^2}{T_c^2\delta} \times 1.47 \times 10^{25} \right]$$

III. THE AN/EDD/ENT TERNARY SYSTEM (AENT)

We observed under the microscope that adding ENT to an EA mixture lowers the melt temperature of the final mixture, and that the grain size was finer than that of EA alone. Therefore, we studied the ternary system by determining its phase diagram followed by initial performance testing.

A. Phase-Diagram Determination and Eutectic Studies

The procedure for preparing samples for phase-diagram determination has been described previously.[1] A series of computer codes has been written that simplifies and shortens the processes for refining phase diagrams.* This special program enables us to calculate the phase diagram of a system with three or more components using data from the binary diagram. Once the calculated phase diagram is produced, it will be used to select compositions for experimental observation. Thus, we will be able to determine phase diagrams of a system with more than two components.

The phase diagram of AN/ENT is known; therefore, we need only determine the phase diagram of the EDD/ENT (EE) system to determine the phase diagram of the ternary system AN/EDD/ENT (AENT). The EE system has a eutectic composition of 66.9 mol% EDD

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*Information from H. H. Cady, Los Alamos National Laboratory, Group M-1.

and a eutectic temperature of 137.5°C (Fig. 6). After the calculated phase diagram of AENT is produced, it is checked with experimental data by a microscopic study.

Figure 7 is the completed phase diagram of the AENT system. The eutectic temperature of AENT is 89°C and the eutectic composition is 72/17/11 mol% AN/EDD/ENT (Table III). At this composition, the detonation products indicate a CO-balanced formulation. For comparison, we have also listed other eutectic systems determined to date.

B. Small-Scale Sensitivity Test and Performance Study

A mixture of AN/EDD/ENT (48/29.5/22.5 wt%) was used for sensitivity tests and rate-stick plate-dent tests. It was prepared as described previously,[1] and the tests were performed according to standard procedures. Detonation pressure was determined with 4.13-cm-diam unconfined rate sticks. The results of all tests are given in Table IV, together with Kamlet-Short Method (KSM) data calculated at the same pressed density, 97.3% of theoretical maximum density (TMD). The measured P_{CJ} is 97.6% of the calculated value.

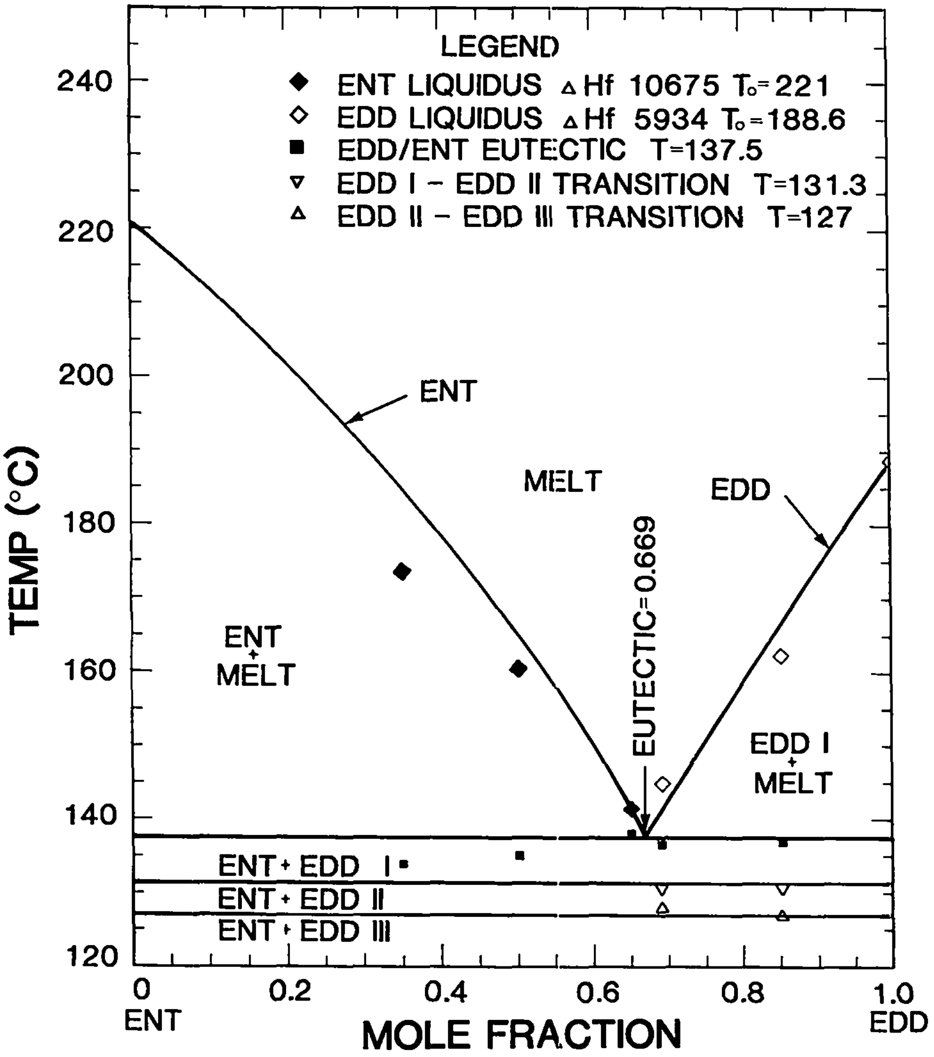

Fig. 6. EDD/ENT phase diagram. Both species ionize on melting.

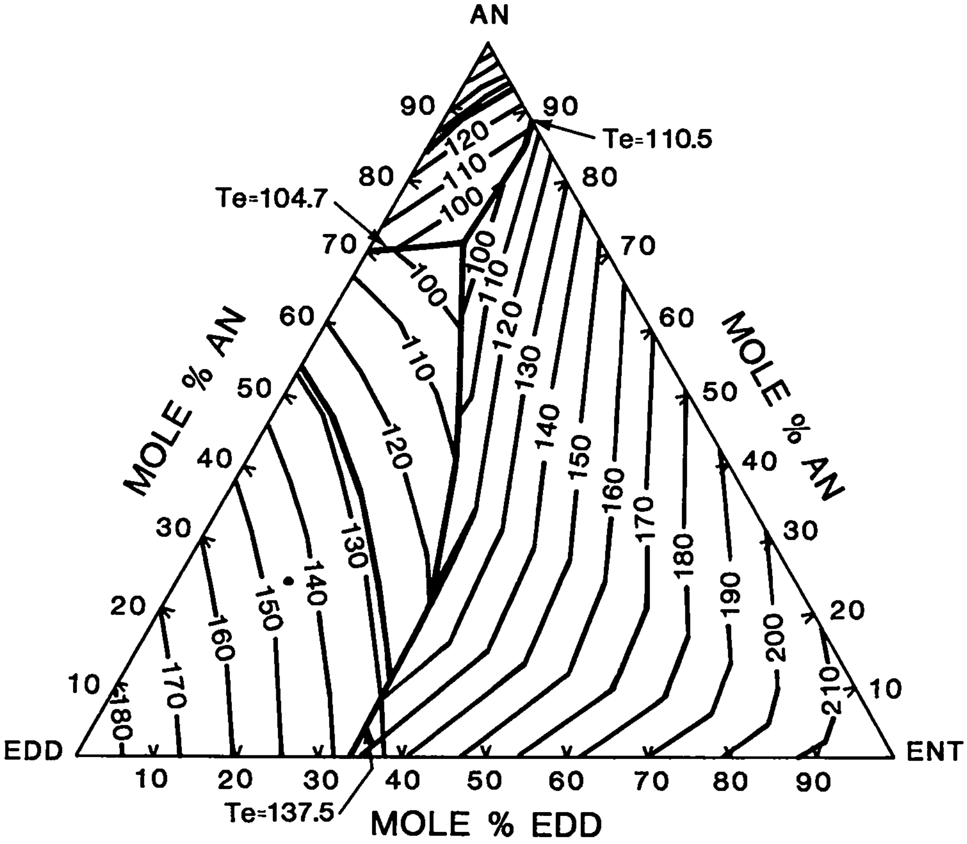

Fig. 7. AN/EDD/ENT phase diagram.

TABLE III. Eutectic Properties of Composite Systems

Composite System	Eutectic Temperature (°C)	Eutectic Composition (mol%)
AN/ADNT	112	58.05% AN
AN/EDD	104.7	32% EDD
AN/ANT	121	78.5% AN
AN/ENT	110.5	87.8% AN
AN/DETN	107	27% DETN
EDD/DETN	126-127	44.5% EDD
EDD/ENT	136	68% EDD
AK[a]/EDD	103.6	27.2% EDD
AK/NQ	136	15.57% NQ
EDD/NQ	155.6	67.8% EDD
AK/EDD/NQ	98.9	67.2/25.3/7.5%
AN/EDD/ENT	89	72/17/11%

[a] AK—85/15 wt% AN/KN.

IV. PHASE DIAGRAM OF THE DETN/EDD/AN/KN (DEAK) SYSTEM

In order to study the quaternary DEAK system and evaluate its performance, it is necessary to know initially the proper amount of DETN that must be added into the EAK mixture to achieve desirable performance. Eutectic systems offer the advantage of being castable and of having a eutectic temperature lower than that of any of their components. Therefore, it is only logical to determine the phase diagram of the quaternary system to find out the eutectic composition and temperature before any other test should be performed.

As we mentioned earlier, in addition to forming a eutectic, DETN also forms a double salt with AN. Since the quaternary system contains KN, we need to get a better understanding of the effect of KN on these two formulations. Therefore, we decided to determine the

TABLE IV. Sensitivity and Plate-Dent Tests of the AENT System

Composition wt%	Density (g/cm³)	Impact Sensitivity (cm) Type 12	Type 12B	P_{CJ} (kbar) Measured	KSM
AN/EDD/ENT[a] (48/29.5/22.5)	1.619 (97.3% TMD)	98.6	175	248	254

[a] Without ENT, the EA mixture fails at the same charge diameter.

phase diagram of AK*/DETN (Fig. 8). We found that the double salt was formed regardless of the presence of KN. For comparison, the phase diagram of AN/DETN is also shown (Fig. 9).

We will generate the calculated DEAK phase diagram by special computer code from the binary data before we carry out any experimental microscopic studies. We have found that because the double salt forms between AN and DETN, more than one eutectic composition and temperature exists among the four components. The possible eutectic compositions and temperatures calculated by computer code are compiled as Table V.

V. CONCLUSIONS AND FUTURE WORK

We have studied the effect of ENT on the melt temperature of EA systems and have found that the ternary system (AN/EDD/ENT) has a eutectic temperature of 89°C and a P_{CJ} of 248 kbar, which is 97.6% of the calculated value at the same pressed density. These

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*Throughout the study, a mixture of AN and KN (AK) at 85/15 wt% AN/KN is used. It is prepared by melting the AN in a beaker followed by addition of solid KN. The final melt is then mixed well and poured onto a Teflon sheet to solidify.

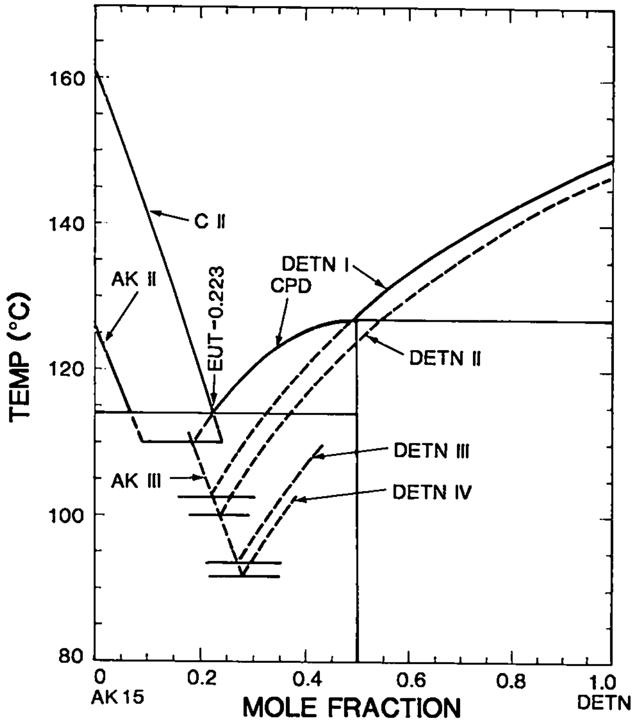

Fig. 8. Phase diagram of AN with 15% KN/DETN.

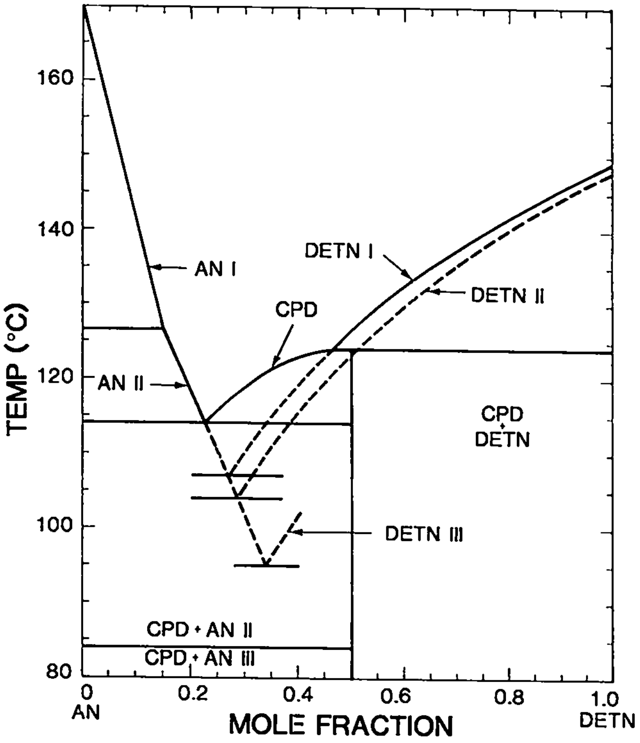

Fig. 9. AN/DETN phase diagram. All phases ionize on melting.

TABLE V. Calculated Eutectic Composition and Temperature of Various DEAK Systems

Explosive	Composition (mol%)	Temperature (°C)
$AK_{III}/DETN_{I}/EDD_{III}$	66.8/13.7/19.5	89
$AN_{II}/DETN_{I}/EDD_{II}$	62.2/15.8/22.0	90
$AN_{II}/CPD^{a}/EDD_{III}$	64.5/11.9/23.7	94
$AK_{III}/DETN/EDD_{II}$	67.9/11.3/20.8	92-93

[a] CPD—the "double salt."

findings indicate that ENT can be used as a sensitizer either for or in EA systems, because the EA eutectic failed at the same charge diameter (4.13 cm) without ENT. Obviously, further studies are required to characterize this ternary system, especially the effect of KN either in or on this system. Experiments have demonstrated that the critical diameter (d_c) of an explosive is directly proportional to its particle size;[4] the smaller the particle size, the smaller will be the d_c. Measurement of the particle size of the ternary system's final eutectic melt by scanning electron microscope (SEM) will also indicate if the addition of ENT to EA will lead to a decrease in the failure diameter.

Results from preliminary phase diagrams of the quaternary DEAK system demonstrate that this system has two attractive features: a low eutectic melting point and a fine particle size. In addition, the cost of preparing DETN is low, comparable with that of EAK. We will continue to determine the phase diagram of the DEAK system. Once the eutectic composition is known, we will prepare the melt mixture and perform initial small-scale sensitivity and performance tests.

ACKNOWLEDGMENT

The author is grateful to H. H. Cady for his phase-diagram computer calculation, to J. L. Janney for her thermal-hazard model study, to J. F. Baytos and M. H. Ebinger for their thermal-stability study, and to M. D. Coburn for his helpful discussions.

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GLOSSARY

AENT — AN/EDD/ENT system
AN — ammonium nitrate
ANT — ammonium salt of 5-nitrotetrazole
DEAK — DETN/EDD/AN/KN
DETN — diethylene triamine trinitrate
EA — EDD/AN
EAK — EDD/AN/KN
EDD — ethylene diaminedinitrate
ENT — ethylene diamine salt of 5-nitrotetrazole
KN — potassium nitrate

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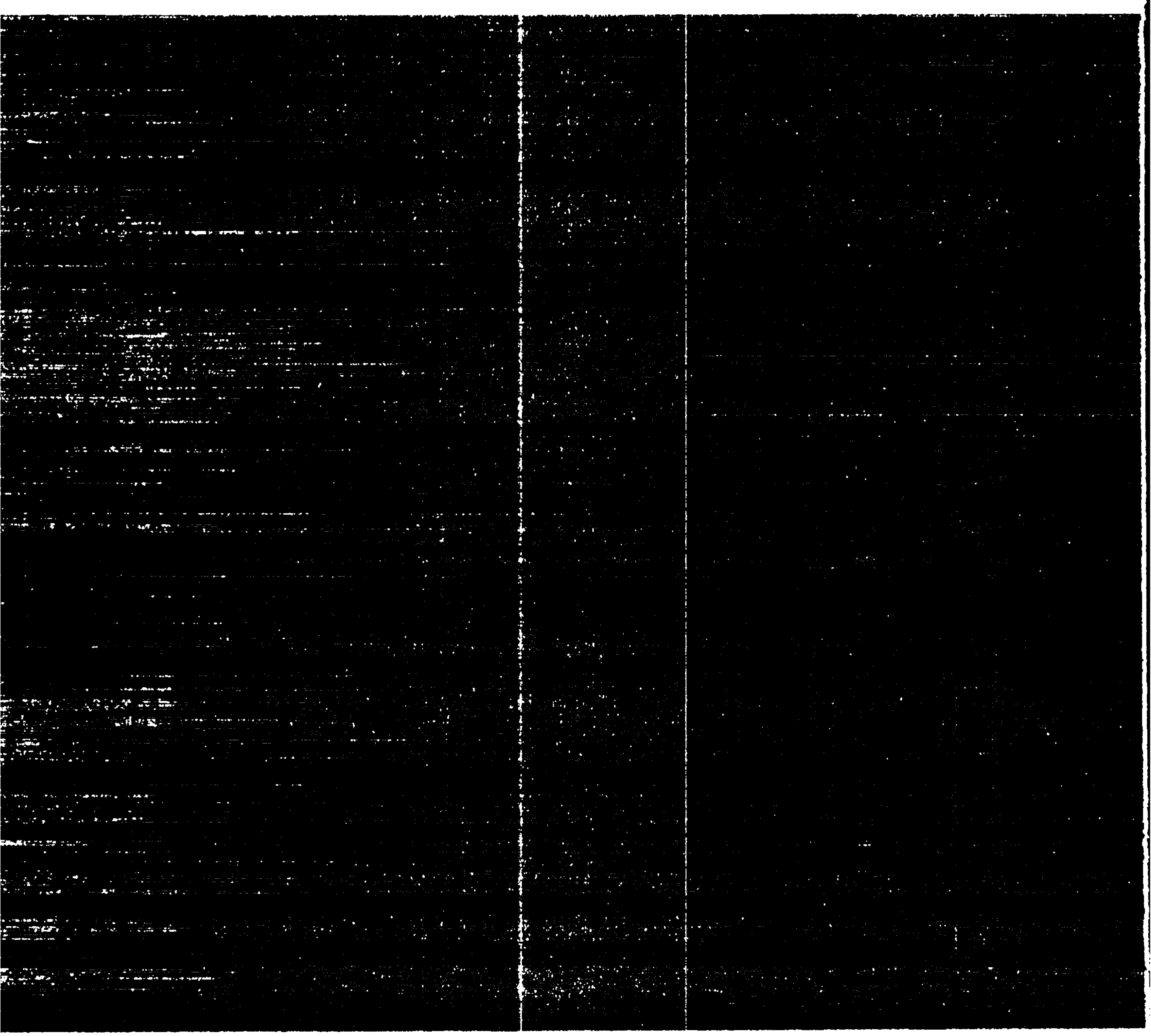

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