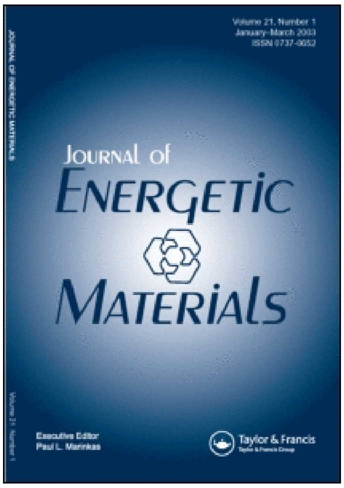

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K. -Y. Lee[a]; H. H. Cady[a]; M. M. Stinecipher[a]
[a] Los Alamos National Laboratory, Los Alamos, New Mexico

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EUTECTIC SYSTEM OF AMMONIUM NITRATE WITH 15 WT% POTASSIUM NITRATE/ETHYLENEDIAMINE DINITRATE/DIETHYLENETRIAMINE TRINITRATE

by

K.-Y. Lee

H. H. Cady

M. M. Stinecipher

Los Alamos National Laboratory

Los Alamos, New Mexico 87545

ABSTRACT

The phase diagram was determined for the ternary system diethylenetriamine trinitrate/ethylenediamine dinitrate/ammonium nitrate with 15 wt% potassium nitrate (DETN/EDD/AK_{15}). The eutectic mixture (DEAK), containing 40, 35, and 25 wt% AK_{15}, DETN, and EDD respectively, was subjected to small-scale sensitivity and performance tests. The measured P_{CJ} (223 kbar) from a 4.13-cm-diam, unconfined rate-stick test of the DEAK system agrees with Kamlet-Short-Method (KSM) data calculated at the same pressed density [97.7% of theoretical maximum density (TMD)].

A rate-stick test of EAK at the same charge diameter and pressed density failed, indicating that the addition of the DETN component to the EAK system has reduced the critical diameter of EAK.

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INTRODUCTION

A eutectic (EA) formed from ethylenediamine dinitrate (EDD) and ammonium nitrate (AN) was used as a substitute fill by the Germans in World War II[1]. Initial characterization and performance tests of EA demonstrated its potential for military applications such as replacement of existing preferred fills.[2,3] It is also known that addition of 15 wt% potassium nitrate (KN) to AN (AK_{15}) before prilling can be used to stabilize AN with respect to the AN_{III} - AN_{IV} phase transition.[4] The eutectic mixture of EDD with AK (EAK) has been prepared in large quantities, and has been detonated in bomb-fill tests.[5] However, other uses require the need to improve performance and reduce the failure diameter of EAK.

We have demonstrated that the eutectic formed between the ethylenediamine salt of 5-nitrotetrazole (ENT) and AN (66.5 wt% AN) gave near-ideal performance at small charge diameters.[6] We have also found that ENT forms a ternary eutectic with EA (AENT) that melts at 89°C. The measured P_{CJ} of AENT, determined from the plate dent of a 4.13-cm-diam, unconfined rate-stick at density 1.619 g/cm^3 (97.3% TMD), is 248 kbar, which is 97.6% of the calculated value at the same pressed density.[7] Without ENT, EA failed at the same test condition.

Experiments have demonstrated that the critical diameter (d_c) of an explosive is directly proportional to its particle size;[8] the smaller the particle size, the smaller will be the d_c. The experimental results from the AENT system illustrate that the addition of a fourth energetic component to the EAK system could cause the eutectic to crystallize as finer crystals and might decrease the critical diameter of EAK.

This paper describes the determination of the phase diagram of AK_{15}/EDD/DETN (DEAK) eutectic system. The result of a 4.13-cm-diam, unconfined rate-stick test of the system at density 1.60 g/cm^3 (97.7% TMD) is also reported. We chose DETN because it is a homolog of EDD and is comparable to EDD in cost.

EXPERIMENTAL PROCEDURE

I. Phase Diagram Determination and Detonation Properties Calculation of DEAK System.

In earlier studies, we have found that AN and DETN form a "double salt (compound)" in addition to the formation of a eutectic.[9] This compound, which does not always form spontaneously, creates some complications when one tries to determine the phase diagram of the quaternary system DEAK because more than one eutectic composition can exist.

We have developed a series of computer codes that simplifies and shortens the process for refining phase diagrams. These special programs enable us to calculate the phase diagram of a system with three or more components using data from the binary diagrams. The phase diagrams of the binary systems AN/EDD, AK_{15}/EDD, AN/DETN and EDD/DETN have already been determined.[10,11] We also studied the effect of KN on the formation of the "compound" and completed the phase diagram of AK_{15}/DETN.[7] Figure 1 shows the completed phase diagram of the DEAK system without the addition compound. Once the phase diagram of DEAK is produced, its data are used for experimental microscopic studies. It can be seen that the eutectic composition and temperature of the DEAK system are 40/35/25 wt% AK_{15}/EDD/DETN and 89.13°C, respectively.

calculations are illustrated in both Fig. 2 and Table I. We concluded that the differences in the calculated performance among various compositions was not great enough to change the DEAK composition obtained from the phase diagram for the performance experiments.

II. Preparation of the DEAK Eutectic

Commercial grade AN and KN were used to prepare the mixture and were ground and dried before use. The EDD was manufactured at Los Alamos National Laboratory by reacting ethylenediamine with excess 70% nitric acid. The DETN was prepared by reacting diethylenetriamine with excess nitric acid followed by precipitation of DETN from the reaction mixture with methanol. A stock mixture of AK_{15} was prepared by dissolving KN into the AN melt, followed by casting onto a Teflon sheet to solidify, then grinding to small particles before mixing with other components. The eutectic melt was prepared by thoroughly mixing the appropriate amounts of AK_{15}, EDD, and DETN. The mixture was then heated with stirring until molten and poured onto a Teflon sheet to solidify. The explosive sheet was crushed to small pieces and pressed into charges with the desired density and charge diameter for the plate-dent performance testing.

III. Small-Scale Sensitivity Tests

Impact, DTA, and vacuum stability tests were performed on samples of the eutectic mixture prepared as described above according to standard procedures. The results from these tests on DEAK and EAK are reported in Table II.

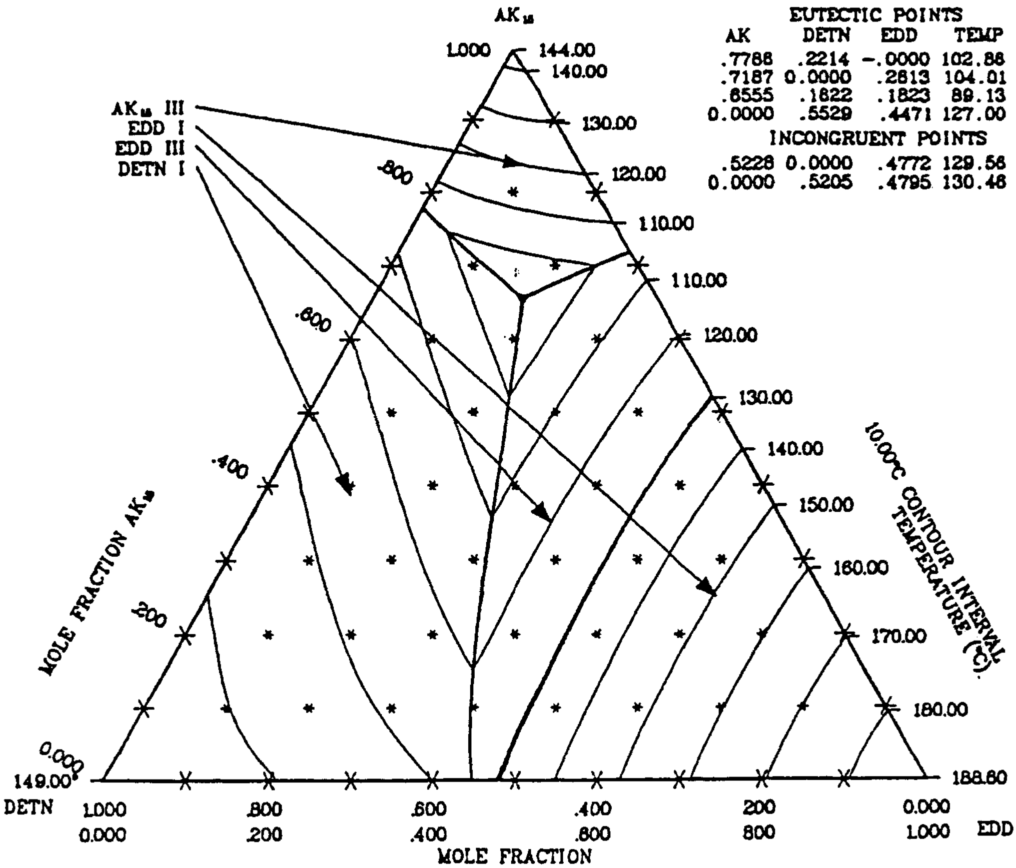

Fig. 1. AK_{15}/DETN/EDD Phase Diagram

To assure that this eutectic composition has reasonable performance, we calculated the detonation velocity for several DEAK compositions, using the Kamlet-Short-Method (KSM) modified for addition of KN. The hierarchy for use of oxygen in the calculations was H_2O, K_2CO_3, and CO_2. Results of these

TABLE II

THERMAL AND SENSITIVITY PROPERTIES

Eutectic System	Composition (wt%)	DTA (°C)	Vacuum Stability (ml/g/48h/ 80°C)	Impact Sensitivity H_{50} (cm) Type 12	Type 12B
EAK	46/54 EDD/AK_{15}	226	-	110	232
DEAK	40/35/25 AK_{15}/DETN/EDD	225	<0.1	109	180

IV. PERFORMANCE TEST

The detonation velocity of the DEAK eutectic was determined with a 4.13-cm-diam, unconfined rate-stick at a pressed density of 1.60 g/cm^3 (97.7% TMD). Both dent depth and velocity were measured. The results are summarized in Table III.

TABLE III

PERFORMANCE DATA OF DEAK

Composition (wt%)	Density (g/cm^3)	Diameter (cm)	P_{CJ} (kbar) Measured	KSM	D (km/s) Measured	KSM
40/35/25 AK_{15}/DETN/EDD	1.60 (97.7% TMD)	4.13	223	223	7.16	7.36

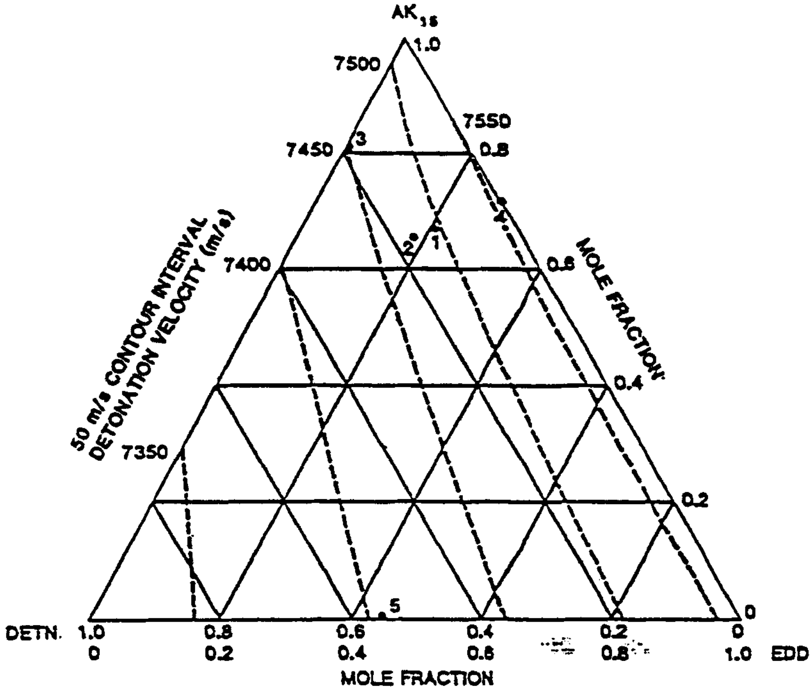

Fig. 2. AK_{15}/DETN/EDD Detonation Velocity-Composition Diagram.

TABLE I

CALCULATED DETONATION VELOCITY OF EUTECTIC POINTS

AK_{15}	DETN	EDD	Melting Temperature	Detonation Velocity (km/s)
0.671	0.126	0.203	92.9 (calculated with compound)	7.495
0.656	0.162	0.182	89.13 (calculated without compound)	7.480
0.813	0.187	0	109.7	7.450
0.719	0	0.281	104	7.560
0	0.447	0.553	127	7.430

RESULTS AND DISCUSSIONS

We have determined the phase diagram (Fig. 1) of the ternary system AN:15 KN/EDD/DETN (DEAK) using a special computer code. Information from the individual binary phase diagrams and mixtures near the eutectic composition was used as input. It can be seen that the eutectic composition and temperature of the DEAK system without the addition compound are 40/35/25 wt% AK_{15}/EDD/ DETN and 89.13°C, respectively. Initial small-scale sensitivity tests of this system indicated sensitivity similar to that of the EAK system (Table II).

The eutectic melt of the EAK system has been prepared in large quantities and has been used as bomb fills. However, the crystallite size of the final mixture is too large to obtain ideal performance. Addition of a fourth component to the system should result in more finely divided phases and therefore in smaller (d_c). Results from a 4.13-cm-diam, unconfined rate-stick test of DEAK demonstrated that the addition of DETN to EAK has decreased the failure diameter of EAK systems. The measured P_{CJ} from the dent is 223 kbar, which is 100% of that calculated by the modified Kamlet-Short Method at the same pressed density. The measured detonation velocity of DEAK is 7.16 km/s, which is 97.3% of that calculated (Table III). Without DETN, the EAK system prepared by the same technique failed at the same charge diameter and density.

Because of the low eutectic melting temperature of this DEAK system, it can be processed more easily in steam-heated equipment than the EAK eutectic. Another attractive feature of using DEAK is that it is as inexpensive to prepare as EAK.

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VII. GLOSSARY

AENT	AN/EDD/ENT system
AK_{15}	AN:15 KN
AN	Ammonium nitrate
d_c	Critical diameter
DEAK	DETN/EDD/AN/KN
DETN	Diethylenetriamine trinitrate
EA	EDD/AN
EAK	EDD/AN/KN
EDD	Ethylenediamine dinitrate
ENT	Ethylenediamine salt of 5-nitrotetrazole
KN	Potassium nitrate

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