DEVELOPMENT OF THE IMX DOUBLE DIRECT PROCESS

E. J. PACANOWSKY, W. W. HILLSTROM, and L. J. VANDE KIEFT

Ballistic Research Laboratory, USAARRADCOM, Aberdeen Proving Ground, Maryland   21005

ABSTRACT

   The purpose of this work is to develop a new explosive based on eutectic blends of ammonium nitrate with ethylenediamine dinitrate and its homologues, and to assess the safety and performance characteristics of these formulations. Various processes for making these formulations were attempted and will be described. Mixes have been scaled from several grams to 30 kilograms. Additives were introduced for stabilization, energy enhancement and sensitization. The neat eutectic is very insensitive so various additives were used to ensure detonation. A historic problem has been that of phase stabilization; this problem has not been solved to everyone's satisfaction, but it does not appear to be insurmountable. Formulations were evaluated from the standpoint of processing, performance, and sensitiveness. These materials appear to have great potential as military explosives because of their good performance, low cost, safety, ease of processing, and compatibility with current Army melt-cast ammunition loading plants.

INTRODUCTION

   The objective of the project on intermolecular explosives (IMX) is to demonstrate the feasibility for Army use of these materials. A task associated with this effort is the development of the Double Direct Process, the subject of this paper.

   Intermolecular Explosives is a recently coined descriptor for explosives composed of separate fuel and oxidizer materials. These materials were formerly known by the term "Non-Ideal Explosives." Non-ideal explosives were so named because their performance is not predicted by standard detonation theory. They do not follow standard detonation theory in that their decomposition to gases at high pressure is not near instantaneous. This nomenclature found little favor with the military and so was discontinued

NOTE: Most figures and tables are omitted because of space and time constraints.

in favor of "Intermolecular Explosives." This class of explosives has many advantages. They can be made from inexpensive, abundant, available, materials which are not necessarily based on petroleum. They are safe in all phases of their life cycle, very insensitive, easily processible, and possess a high compatibility with current Army melt-cast ammunition loading plants.

In order to introduce these materials into military inventories, many tests must be performed. This requires the production of greater quantities of explosives than are normally used in the laboratory. The optimum process must be developed for the production of experimental materials and for the production of large scale lots for military use.

The intermolecular explosives that will be the focus of this paper deal with ethylenediamine dinitrate (EDD) or its higher homologues, ammonium nitrate (AN), and necessary additives. Of principal interest will be the eutectic of EDD and AN, labeled EA.

EDD was usually prepared by neutralizing ethylenediamine (ED) with concentrated HNO_3. It was manufactured by the Germans during World War II from ethanol, ammonia, and nitric acid. It was also used as cast charges in eutectic mixes with AN. Data on EDD are shown in Table 1. In itself, EDD has more power and early performance then TNT, but it has less total energy - similar to nitroguanidine. In 1944, the Germans made EDD/AN eutectics (EA) for their war effort. In 1975, J. Hershkowitz and I. Akst (ref. 1) developed a solvent EA process. Scientists from Los Alamos National Laboratory and Eglin Air Force Base developed the single direct process in 1978 (ref. 2). The Ballistic Research Laboratory (BRL) developed the double direct process in 1981. Details of these various processes will be discussed later.

TABLE 1 (ref. 3)
Ethylenediamine Dinitrate (EDD)

Mol. Wt.	186.13
Sp. Gr.	1.595 at $25/4^\circ$
M.P.	$185-187^\circ C$
Sol.	W; Insol Alc. or Eth.
Brisance	Lower than TNT
Heat of Combustion	-374.7 Kcal/mole
Heat of Explosion	-127.9/159.3 Kcal/mole
Hygroscopicity at $25^\circ C$ and 90% RH	1.24%
Stability	Decomposes at $270^\circ C$, does not explode at $360^\circ C$

The inclusion of ammonium nitrate (AN) in all these systems requires some understanding of the AN, especially the volumetric changes that occur through its phase changes (Fig. 1). In the range of temperature from its melting point to $-18^\circ C$, AN has five phases -- I $\xleftarrow{\sim 125^\circ C}$ II $\xleftarrow{\sim 84^\circ C}$ III $\xleftarrow{\sim 32^\circ C}$ IV $\xleftarrow{\sim -18^\circ C}$ V (ref. 4). The

problem area revolves around the phase transition of III $\leftrightarrow$ IV. This transition produces the largest volume change and creates the biggest problem for its use in both explosives and propellants. One propellant company utilizing unstabilized AN in a gas generator found that keeping the propellant extremely dry through processing and hermetically sealing the propellant in the unit prevented serious growth problems.

Units stored for over 10 years in bunkers in Arizona at ambient, showed less than 1% growth and were fired successfully. Brown, et al, (ref. 5) reported mechanisms that would account for the transitions $AN_V \leftrightarrow AN_{IV} \leftrightarrow AN_{II} \leftrightarrow AN_I$. Therefore, one method to deal with the phase III $\leftrightarrow$ IV instability is to prevent phase III from occurring.

Since moisture is difficult to exclude without incurring large manufacturing costs, better methods of stabilizing AN are required. These methods would require that phase III be locked in to provide dimensional stability over the military service temperature of -65°F to +165°F (-54°C to 74°C).

Again, in the propellant industry, potassium nitrate (KN) was found to be an excellent phase stabilizer for AN. Recent work by H. H. Cady (ref. 6) indicated that 15 wt-% KN added to the AN prior to prilling is the most promising technique to maintain dimensional stability.

Other additives that may minimize IV $\leftrightarrow$ III effects include NiO (4%), CuO (4%), and a ternary mixture of borates, acid phosphates, and sulfates ($\sim$0.5%) (ref. 7). All work reported in this paper with stabilized AN dealt with the AN/KN (85/15) system.

The EA (ethylenedianine dinitrate/ammonium nitrate) formulation frequently cited in this report refers to a 50 wt-% EDD and 50 wt-% AN as the eutectic EA; the stabilized version is EAK (ethylenediamine dinitrate/ammonium nitrate/potassium nitrate). For the EAK, the weight ratios are 50%/42.5%/7.5%. This assumes that the stabilized AN with 85% AN and 15% KN acts as a single ingredient forming the binary system with EDD. Based on the reasonably close melting point data of the two eutectics, this EAK can be considered as a binary system.

H. H. Cady, of Los Alamos National Laboratory, in an internal memo to Eglin Air Force Base (ref. 8) stated that the optimum eutectic for EA was at 32 mole % EDD and 68 mole% AN, which translates to 52.25 wt-% of EDD and 47.75 wt-% AN. The Air Force has been using approximately a 46 wt-% EDD, 46 wt-% AN, and 8 wt-% KN.
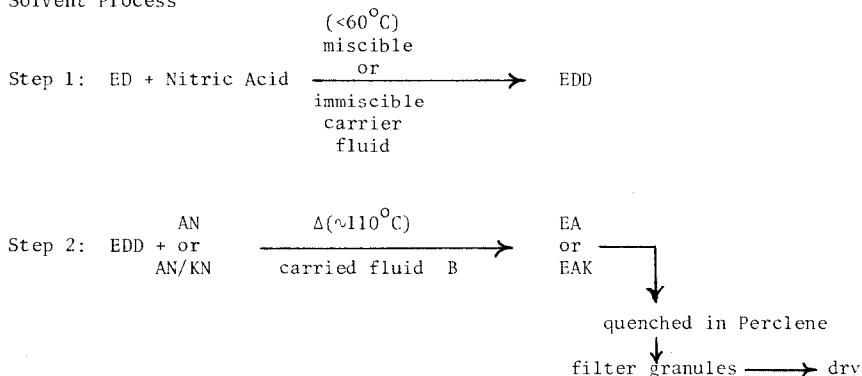

CANDIDATE PROCESSES

Several methods for the production of IMX's were investigated. Batch sizes ranged from several grams to 30 kilograms. They are as follows: Solvent Process, Single Direct Process, and Double Direct Process. A brief description (Table 2) of these processes follows.
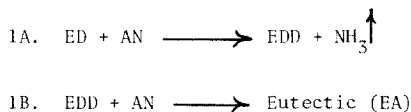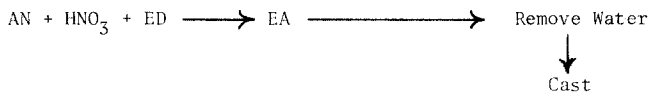
TABLE 2

Processes for Preparing IMX

A - Solvent Process

Step 1:   ED + Nitric Acid $\xrightarrow[\substack{\text{immiscible} \\ \text{carrier} \\ \text{fluid}}]{\substack{(<60^\circ C) \\ \text{miscible} \\ \text{or}}}$ EDD

Step 2:   EDD + $\begin{array}{c}\text{AN} \\ \text{or} \\ \text{AN/KN}\end{array}$ $\xrightarrow[\text{carried fluid}\quad B]{\Delta(\sim110^\circ C)}$ $\begin{array}{c}\text{EA} \\ \text{or} \\ \text{EAK}\end{array}$ ⟶

quenched in Perclene

filter granules ⟶ dry

B - Single Direct Process

1A.   ED + AN   ⟶   EDD + NH₃↑

1B.   EDD + AN   ⟶   Eutectic (EA)

C - Double Direct

AN + HNO₃ + ED ⟶ EA ⟶ Remove Water

Cast

Solvent Process

   Step 1 - Preparation of EDD.   Perchloroethylene (PC) was placed into a jacketed reactor with the necessary quantity of ethylenediamine added to it. With the cold water running through this jacket and the stirrer going at approximately 50 RPM, add HNO_3 (70%). Requires 2 moles HNO_3/mole of ED.

   Step 2.   Add AN or AN/KN at 1:1 ratio with EDD made bringing up temperature to melt all solids. Pour molten EA or EAK into cold PC to precipitate granules. Filter, wash, and dry.

   This process had been used by several groups to make EA. The resulting material works very well for pressed explosives, however, the process is cumbersome, requires considerable quantities of solvent, filtration, etc., and leaves residual PC in the blend. EDD can react with PC and sensitize the EA to shock initiation (ref. 2). If this can occur in the short term, it may pose a serious problem for long-term storage.

Single Direct Process

The single direct process was first done at Los Alamos National Laboratory and at Eglin Air Force Base in 1978. In this process, there is no nitric acid or solvent used. Instead, the ethylenediamine is neutralized by the NH_4NO_3 which is added incrementally. An exothermic reaction occurs evolving ammonia. Two moles of AN/mole of ED are required for neutralization. The final additions of AN, when the eutectic is completely formed, should produce a 1:1 ratio with the EDD. This is endothermic, requires heat, to get it into the liquid phase.

Variations of the single direct method were tried out on a small scale. Method 1 - Add ED to molten AN. Method 2 - Add AN to heated ED. Results were similar, but temperature control was more difficult. These methods are also more hazardous.

The single direct process is a much simpler method than the solvent process. It is also much safer because nitric acid is not used, and both starting ingredients are non-explosive, whereas EDD, a starting ingredient for step 2 of the solvent process, is explosive by itself.

However, there is a major disadvantage to this process - 2 moles of ammonia gas are evolved for each mole of ED neutralized in the production process, and some manages to remain in the finished product. EA has a great affinity for ammonia. Still some ammonia remains even after pulling vacuum for approximately 1 hour in the molten state. Material made by this process was stored in sealed containers which were opened after various intervals of time. In all instances, the odor of ammonia was very strong. The implications for corrosivity and long-term storage are not good.

Double Direct Process

Development of the double direct process, suggested by Irving B. Akst, now at Los Alamos National Laboratory, was initiated at BRL in 1980. The process is very simple — all work can be carried out in one hot melt kettle. The appropriate quantities of HNO_3, AN, and KN are added to the kettle. ED is added to the kettle dropwise, stirring continuously, and controlling temperature at approximately $60^{\circ}C$. After the addition of all ED, the temperature is raised to $110^{\circ}C$; water is removed from the product by vacuum distillation. The product is cast into desired molds.

This process has several advantages over the other processes. As in the single direct process, all starting ingredients are non-explosive and are all added to the same melt kettle. A great advantage is that ammonia is not released. A disadvantage to this process is that water must be removed from the final product. This comes about because the nitric acid used is dilute; at present, 70% concentration is used — Large Caliber Weapons Systems Laboratory, Dover, NJ, has as used as high as 97% HNO_3 (ref. 10). For the sake of safety in early experiments, 70% acid was selected.

The reasons the double direct process was selected for local production of IMX are: (1) This process produces the least objectional and most easily removable contaminant - water. (2) It is easier to perform the required operations for this process than for

the others — ease of processability. (3) It has the greatest compatibility with current Army melt-cast ammunition loading plants.

Some modification of existing equipment may be required for the water removal operation. All of these processes require 15 psig saturated steam for heating the melt kettle to exceed the 104°C melting point of EA. Most plants operate with 5 psig saturated steam, but have the capability to operate with 15 psig pressure, and current SOP's allow the higher pressure. If this problem should become significant, further research into use of the higher homologues of EDD may provide the solution. A ternary eutectic blend of DTT, EDD, and AN in the ratios 25:25:50 has its melting point around 86°C, near that for TNT and compatible with 5 psig steam processing (ref. 2). Research is continuing on this. The use of propylene diamines with ED will also reduce the resulting eutectic M.P.

Appendix A is a tabulation of the mixes made at the BRL by the double direct process, including those made using higher homologues. Work is underway to characterize the products of these processes by determining density, melting point, pH, and thermal properties from differential scanning calorimetry measurements.

The lessons learned in working with the small-scale mixes were applied to large-scale mixes, EAK/RD 175-11 at 15 kg and EAK/LV-1 at 30 kg. Figure 2 is a schematic representation of the arrangement of equipment for this experiment. A 10 gallon vacuum melt kettle with an anchor stirrer was used. Stirring was accomplished by an air driven motor, generally operated at about 20 psig, which resulted in a stirring rate of about 50 RPM. No vacuum was applied during addition of ingredients and while reactions were occurring. After all reactions had taken place, the temperature was raised and vacuum applied to remove the water. The procedure used for making a 30 kg mix of EAK by the double direct method is detailed in Appendix B.
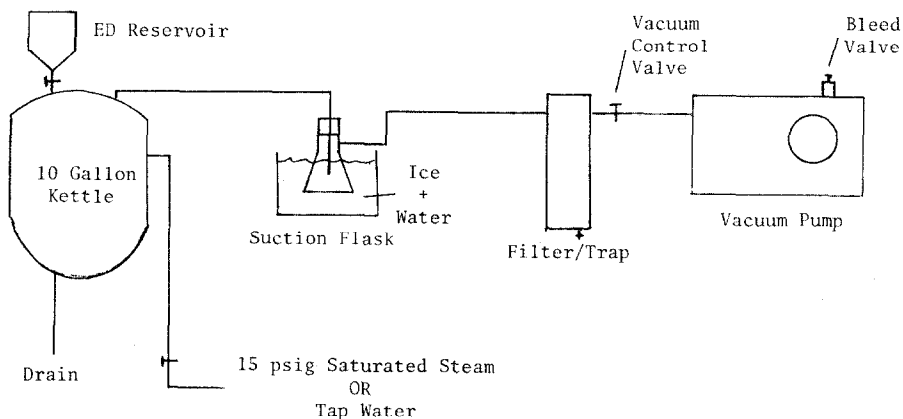

Fig. 2. Experimental Configuration for 30 kg Mix.

ADDITIVES

To improve the explosive properties of the IMX composition, it was necessary to make them slightly more sensitive. This could be achieved several ways. One method would be to introduce nucleating sites via such materials as extremely fine Al_2O_3, preferably the fumed alumina with surface areas $\sim$ 100 square meters per gram, glass microspheres or colloidal silica. The latter was chosen and M-5 Cab-o-Sil was added to EA. About 4% Cab-O-Sil is the maximum in an IMX composition that will permit routine casting. Higher percentages thicken the mix excessively. Formulations with 3.5% and 3.8% will be discussed in the test section. Densities of IMX compositions containing Cab-O-Sil were over 95% of TMD.

Another method of improving the explosive properties of IMX is to enrich the formulation with energetic materials such as HMX, RDX, etc. RDX was selected for test purposes. Some difficulty was encountered using dry Class E RDX as the enriching agent at the 25% level. These compositions had densities as low as 67.7% of TMD. A novel method was developed that improved the processing considerably. A small four-bladed impeller was substituted for the conventional stirrer used in hot melt operations. The stirring speed was increased from 50 to 250 RPM. This was done to incorporate the RDX intimately into the IMX. However, the higher speed stirring whipped the composition into a foam. It was found that 3M's Fluorad FC 170-C wetting agent at 0.1% level broke down the foam quickly and allowed the processing of the formulation to proceed normally. Final density was better than 97% TMD.

A combination of both sensitization and enrichment was accomplished without the aid of the wetting agent. Ninety-six and one-half percent of TMD was realized from a mix of 2% Cab-O-Sil and 1-1/2% RDX (Class E). Details will be reported in the test section.

The safety in handling RDX during processing could be improved. It was found that if the EA or EAK is made first and then RDX added as received, wet, good product (densities better than 95% TMD) could be made. However, for this method, the wetting agent is necessary.

TEST RESULTS

The tests that are described in this section all used the locally produced IMX, with a density of 1.610, 96.7% TMD, and about 0.5% water, made by the double direct process described earlier. The formulation used was EDD/AN/KN (EAK) in the ratio of 50/42.5/7.5 by weight. Figure 3 shows a DSC run on this material, in a sealed pan. The sealed pan prevented the endotherm caused by sample evaporation. The reason for including the 7.5 wt-% KNO_3 was to phase stabilize this blend. The DSC of Figure 3 indicates that this was completely successful. There is a perturbation in the expanded trace (upper curve) ca - 16°C. Even if it has physical meaning, it is too small to be significant. Also, the endotherm at the eutectic point occurs just where it ought, at 103.7^{o}C.

At this point in the effort, three types of performance test have been performed: Prompt Energy Test (PET), Plate Dent Test (PDT), and firings of larger, bare charges: Large-Scale Tests (LST). None of these tests is very sophisticated, but they do provide much useful information for screening various formulations with respect to their performance.

Prompt Energy Tests

One of the performance parameters of an explosive is the rate of energy release early in the detonation, the prompt energy. A measure of this is the degree of fragmentation of the containment vessel that results from a detonation. Steel cylinders, 6" long, 2-1/2" I.D., 3" O.D., were filled with TNT, and composition-B, and fired as calibration shots. Neat EAK was tested in the same manner. Data were generated as histograms of the number of fragments per mass increment versus mass. Figure 4 shows the calibration histograms, and Figure 5 that for neat EAK. Com-position-B produced significantly smaller fragments than TNT, the crossover occurring ca 2g. The neat EAK showed far fewer small fragments than either TNT or composition-B. This EAK charge likely didn't detonate.

Plate Dent Tests

The plate dent test is another performance screening test. The experimental con-figuration used is shown in Figure 6, and a summary of results in Figure 7. An earlier PDT used neat EAK as for the PET described above. Again, there was no deto-nation; a very slight dent was observed in the witness plate. This test did point out the very insignificant contribution to the witness plate deformation from the booster and remainder of the firing train. The base relief cylinder was used to emphasize the effect of the main charge. That it was unnecessary is demonstrated in Figure 7 — holes were formed in the witness plate whenever detonation occurred. Since EAK produced at the BRL had not yet been detonated, 25% RDX was added as an enriching and sensitizing agent. Class 1 RDX was initially used, but settled out of the molten EAK too rapidly; thus class 5 RDX was used. This proved difficult to blend with EAK. The RDX used for shot #1, Figure 7, was hand incorporated into the EAK. Vacuum oven outgassing was not used. As a result, the charge which should have weighed 6 oz weighed only 4 oz, yielding a density of 67.7% TMD. As can be seen, it detonated very well. A plug of steel from the witness plate was driven into the base relief cylinder.

Shot #2 represented an attempt to reduce the amount of RDX used, and yet achieve detonation through sensitization of the EAK without significant enrichment. 1.5% class 5 RDX was used, along with 2% Cab-O-Sil to hold it in suspension during freezing. A considerably better density was obtained, 95.9% TMD. The PDT performance was about equal to that of shot #1, however, 50% more HE was used, because of the greater density.

Shot #3 was done, using composition-B, for comparison purposes. Performance for this shot was better than for shots #1 and #2, however, in comparing shots #1 and #3, it appears that shot #3 is a reasonable extrapolation of shot #1, given a 50% increase in HE; shot #3 had 50% more HE than shot #1.

Another formulation was tested similarly: 96.5% EAK/3.5% Cab-O-Sil. The intent was to ascertain whether Cab-O-Sil, a non-energetic thickening agent, could by itself sensitize the EAK. Detonation did occur; this detonation punched a hole in the witness plate, but this event did not appear to be as vigorous as the previous shots.

Large-Scale Tests

Two tests were run, in which 5" diameter, neat EAK charges were made and fired, one with a length of 5.5", the other, 11.2". The smaller of these was poorly instrumented; the principal effect observed was the cratering of a lead block by a single, prepared, $(1 \text{ cm})^3$ steel fragment, imbedded at the opposite end of the charge from the detonator, in a 1 cm thick disc of Wood's Metal covering the entire end of the charge. This charge was initiated, but it did not detonate. The Wood's Metal did not vaporize as expected, but created many peripheral craters in the lead block. The central crater, that produced by the prepared fragment, had a volume of ca 6 cc. This scaled to an impact velocity of 300-500 m/sec; ∿ 1800 m/sec had been expected.

It was thought that a 5" diameter bare charge of neat EAK should be above the critical diameter for detonation. Another charge was prepared, having the same diameter, but an increased length, 11.2". It was more completely instrumented than the first such test (see Figure 8). The charge was mounted vertically in a test barricade. The base of the charge was configured as before, a steel fragment in a Wood's Metal surround, aimed at a lead block. X-ray tubes were arranged to measure fragment speed. Detonation velocity was determined by sensing with piezoelectric pins whose signals were summed, recorded on a Biomation Waveform Recorder, and printed. Figure 9 shows the results and the summing network used. Detonation was initiated by a very large booster, 5" diameter x 3" long composition-B. When the detonation wave reached the first pin, it had slowed considerably, but was likely still chemically driven because of its speed and the fact that no unreacted EAK was found. Pins 1, 2, and 3 were located 9 cm, 5 cm, and 1 cm, respectively, from the base of the charge. The speed of the detonation wave was 3.37 mm/μsec between pins 1 and 2, and 3.07 mm/μsec between pins 2 and 3. Since detonation velocities of ca 8 mm/μsec have been observed by others (ref. 2), we can conclude that even this large charge did not detonate. Further tests were not made to determine the critical diameter of neat EAK produced by the double direct process. For all but the largest charges, this explosive will need sensitization. However, the enrichment required to yield adequate perfomance for many applications also provides the required sensitization. For low performance HE, small quantitites of impurity (e.g., Cab-O-Sil) and RDX may suffice, as indicated by the plate dent tests.

CONCLUSIONS

This paper has described the learning process experienced by this laboratory in its attempt to develop intermolecular explosives as substitutes for TNT and composition-B. Of all the processes tried, the double direct seems most feasible. Remanent water and extremely low sensitiveness are problems, both of which appear soluble. An additional problem, associated with IMX materials produced by all processes, is that of incorporation, wetting, of RDX into IMX and suspending it long enough for the blend to solidify with a uniform distribution of RDX. Class 1 incorporates fairly well, but sinks; class 5 is very difficult to incorporate, and it greatly increases the viscosity. Research continues on this; a wetting agent has been found that looks promising. Thickeners to hold class 1 RDX in suspension are being sought.

Performance tests done here and elsewhere indicate that neat EAK, with an appropriate sensitizer, will be able to replace TNT, and that 75% EAK/25% RDX will have performance comparable to composition-B. Prompt Energy, Plate Dent, and Cylinder Expansion Tests are planned for current formulations for the near future. Safety and sensitiveness tests on the laboratory scale and with operational rounds are also planned.

REFERENCES

1 J. Hershkowitz and I. Akst, "A New Approach to Improving the Performance of Non-Ideal Explosives Containing Ammonium Nitrate," Explosives Division, FRL, Technical Report #4789, March 1975.
2 I. B. Akst, Los Alamos National Laboratory, private communication.
3 Picatinny Arsenal Encyclopedia of Explosives and Related Items, Vol. 6, p E236, 1974.
4 S. D. Hendrick, E. Posnjak, and F. C. Kracak, "The Molecular Protection in the Solid State, The Variation of the Crystal Structure of AN with Temperature," JACS, Vol. 54, (1932) 2766-2786.
5 R. N. Brown and A. C. McLaren, "On the Mechanisms of the Thermal Transfer in Solid Ammonium Nitrate," Proc. R. Soc London Ser A 266, (1962) 329-343.
6 H. H. Cady, "The Ammonium Nitrate-Potassium Nitrate System," LASL, NM
7 Report on Workshop on Ammonium Nitrate (AN) Technology, ARRADCOM, Dover, NJ, Nov 80.
8 H. H. Cady and W. Spencer, Los Alamos National Laboratory Internal Memo, "Ammonium Nitrate (with 15% Potassium Nitrate)/Ethylenediamine Dinitrate/Nitroguanidine Phase Diagram."
9 N. Loverro, HERD Facility, Eglin AFB, FL, Internal Memo.
10 W. Voreck, Large Caliber Weapon Systems Laboratory, Dover, NJ, SOP EMD-245, Feb 81.

APPENDIX A

Summary of IMX Production by the Double Direct Process

Mix ID	Quantity	Temperature During Addition of Chemicals	Comments
Mixes using ethylenediamine (ED)			
EA/EJ 172-13	40.0g	ED ($23^{\circ}C \leq T \leq 450^{\circ}C$) Mix heated to $110^{\circ}C$	pH=6
EA/EJ 172-15	40.0g	ED ($14^{\circ}C \leq T \leq 50^{\circ}C$) Mix heated to $110^{\circ}C$	pH=6
EA/TH 79	20.0g	ED ($8^{\circ}C \leq T \leq 25^{\circ}C$) Mix heated to $118^{\circ}C$	Poured into cold PC and filtered w/alcohol Endo: $40^{\circ}C, 80^{\circ}C,$ $104^{\circ}C$ Exo: $263^{\circ}C$
EA/RD 175-46	40.0g	ED ($14^{\circ}C \leq T < 44^{\circ}C$) Mix heated to $110^{\circ}C$	
EA/RD 175-47A	40.0g	Mix heated to $110^{\circ}C$	pH≈5.5
EA/RD 175	30.0g	ED @ $52^{\circ}C$ Mix heated to $100^{\circ}C$	
EAK/TH83	20.0g	ED ($16^{\circ}C \leq T < 60^{\circ}C$) Mix heated to $120^{\circ}C$	pH=4
EAK/RD 175-1		ED ($16^{\circ}C \leq T \leq 100^{\circ}C$) Mix heated to $110^{\circ}C$	
EAK/RD 175	20.0g	ED ($16^{\circ}C \leq T < 60^{\circ}C$) Mix heated to $110^{\circ}C$	
EAK/RD 175-9	20.0g	ED ($21^{\circ}C \leq T < 37^{\circ}C$) Mix heated to $90^{\circ}C$, then to $108^{\circ}C$	pH=6
EAK/RD 175-11	15 Kg	ED ($25^{\circ}C \leq T < 47^{\circ}C$) Mix heated to $107^{\circ}C$	Cast into 2 molds
EAK/LV-1	30 Kg	ED ($12^{\circ}C \leq T < 62^{\circ}C$) Mix heated to $109^{\circ}C$	See Appendix B for details
EAK/EJ 172-17	40.0g	ED ($24^{\circ}C \leq T \leq 55^{\circ}C$) Mix heated to $110^{\circ}C$	pH=4.5
EAK/EJ 172-19	40.0g	ED ($20^{\circ}C \leq T \leq 51^{\circ}C$) Mix heated to $110^{\circ}C$	pH=6

APPENDIX A (Continued)

Summary of IMX Production by the Double Direct Process

Mix ID	Quantity	Temperature During Addition of Chemicals	Comments
Mixes using diethylenetriamine			
DA/EJ 172-21	40.0g	DETA ($28^{o}C \leq T \leq 45^{o}C$) Mix heated to $110^{o}C$	pH=6
DA/EJ 172-23	40.0g	DETA ($15^{o}C \leq T \leq 50^{o}C$) Mix heated to $110^{o}C$	pH=6
DAK/TH 81	20.0g	DETA ($21^{o}C \leq T \leq 48^{o}C$)	Endo: $98^{o}C$, $109^{o}C$ Exo: Onset $240^{o}C$ Peak $280^{o}C$
DA/RD 175-4		DETA ($21^{o}C \leq T \leq 48^{o}C$) Mix heated to $112^{o}C$	
DAK/RD 175	30.0g	DETA ($15^{o}C \leq T \leq 50^{o}C$) Mix heated to $80^{o}C$	
DAK/EJ 172-27	40.0g	DETA ($24^{o}C \leq T \leq 54^{o}C$) Mix heated to $110^{o}C$	pH=6
DAK/EJ 172-25	40.0g	DETA ($20^{o}C \leq T \leq 51^{o}C$) Mix heated to $110^{o}C$	pH=6
Mixes using Triethylenetetramine			
TA/EJ 172-29	40.0g	TETA ($18^{o}C \leq T \leq 46^{o}C$) Mix heated to $110^{o}C$	pH=3.5
TA/EJ 172-31	40.0g	TETA ($14^{o}C \leq T \leq 56^{o}C$) Mix heated to $110^{o}C$	pH=6
TAK/EJ 172-33	40.0g	TETA ($16^{o}C \leq T \leq 59^{o}C$) Mix heated to $110^{o}C$	

Legend

ED	- Ethylenediamine	EA	- EDD/AN
EDD	- Ethylenediaminedinitrate	EAK	- EDD/AN/KN
DETA	- Diethylenetriamine	DA	- DETN/AN
DETN	- Diethylenetriaminetrinitrate	DAK	- DETN/AN/KN
TETA	- Triethylenetriamine	TA	- TETN/AN
TETN	- Triethylenetriaminetetranitrate	TAK	- TETN/AN/KN

Note: In the Mix ID, the first series of letters refers to the eutectic composition, e.g., for mix ID EAK/RD 175, the EAK represents a composition of EDDN/AN/KN, in the ratios of 50/42.5/7.5. The amine comprises 50 wt-% of the mix; where both AN and KN are used, the KN comprises 15% of the AN/KN mixture.

APPENDIX B

Procedure for Making 30 kg Mix of EAK by the Double Direct Method

This procedure was performed at the BRL Hot Melt Facility on 23 Sep 81. Times are indicated on the left, followed by the associated comments. The experimental configuration was that of Figure 2.

Procedure

0905   Running tap water through kettle jacket (rate ∿ 1/2 liter/sec). Began adding 70% HNO_3 to kettle.

0921   Finished adding HNO_3

0923   Began stirring @ 20 psig

0926   Began adding AN. T = 20°C (Thermal well immersed). Poured pre-weighed bags of AN into transfer pail and dipped from that with a 1 liter beaker and poured into top port of 10 gal kettle.

0933   T = 12°C

0935   Finished AN addition. Began KN addition

Quantities:	AN	12.750 kg
	KN	2.250 kg
	HNO_3	10.26 liter
	ED	5.44 liter

0937   T = 10°C

0943   Finished KN addition. T = 12°C

0953   Began ED addition

0958   T = 21°C

1004   T = 32°C. Cooling water still running.

1005   First liter ED added (1 liter/12 min → 83 ml/min)

1009   Began second liter ED addition. T = 32°C

1010   T = 33°C

1011   T = 34°C. Stirring still going well.

1013   T = 36°C

1017   T = 36°C. Appears to be holding.

1022   Completed second liter ED addition

1026   Began third liter ED addition. T = 31°C. Stirring @ 20 psig.

1033   T = 42°C. Finished third liter ED addition (7 min/liter → 143 ml/min)

1036   Began fourth liter ED addition.

1037   T = 41°C

1043   T = 44°C

1044   T = 45°C

1054   T = 49°C

1057   T = 50°C

1104   Finished fourth liter ED addition (1 liter/28 min → 35.7 ml/min), T = 51°C

APPENDIX B (continued)

Procedure for Making 30 kg Mix of EAK by the Double Direct Method

1107 Began fifth liter ED addition. (Put 1.044 liter into seperatory funnel - need 396 ml more.) $T = 50^{\circ}C$

1113 $T = 52^{\circ}C$. ED flowing faster than for last addition.

1121 $T = 54^{\circ}C$

1142 $T = 59^{\circ}C$. Finished fifth liter ED addition, plus added 44 ml.

1144 Began last ED addition - 396 ml. $T = 58^{\circ}C$

1147 $T = 62^{\circ}C$

1151 Finished ED and all other additions. $T = 62^{\circ}C$. Cooling water turned off.

1208 Steam started.

1213 $88.5^{\circ}C$. Vacuum pump started - control valve partly closed.

1215 $89^{\circ}C$. 14" Hg vac. Steam rate increased.

1218 $100^{\circ}C$. 15" vac.

1223 $101^{\circ}C$. 20" vac. Visible vapor and droplets in suction flask.

1245 $101^{\circ}C$. 21" vac. Water droplet rate increased in suction flask.

1255 $100^{\circ}C$. 22.5" vac. Vacuum increased - water rate increased. Turned vacuum back to 21".

1323 Bringing temp up to $105^{\circ}C$.

1325 $T = 103^{\circ}C$. 21" vac. Very high vapor rate and surface of melt is turbulent (boiling).

1330 $T = 105^{\circ}C$. 22" vac.

1347 $T = 107^{\circ}C$. 21-1/2" vac. Melt still boiling.

1355 Bleeder valve on pump set at 1/8 turn open.

1359 $T = 109^{\circ}C$. 21-1/2" vac. $\sim$ 1 drop/2 sec into suction flask.

1420 Checked vacuum pump: fluid level at top of sight glass and fluid looks milky. Closed vacuum control valve at filter/trap. Drained pump oil. Connected aspirator. Tried to use it - had reverse flow. Kettle maintained $\sim$ 22" vac.

1435 Surface of melt is quisent. Poured. Dime-sized patch of "solid" brown-crud found in bottom of kettle.

Measured density after solidification: Mass of charge and napkin = 1421.5 g

Mass of napkin = 2.5 g

Mass of charge along 1419.0 g

Diam = 4.019"

Length = $\dfrac{4.507" + 4.421"}{2}$ = 4.464" $\Bigg\}$ Vol = 928.0069 cm^3 $\rightarrow$ ρ = 1.529 g/cm^3

This is low density $\sim$ 92% TMD $\begin{cases} 1.529 \\ 1.665 \ (TMD) \end{cases}$