Short Communication

Propellants, Explosives, Pyrotechnics

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Nitrate Salt Based Melt Cast Materials

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Dedicated to Michael A. Hiskey.

Abstract: Three new low melting compositions have been developed based on the ingredients amino-1,2,4-triazolium nitrate, 3,5-diamino-1,2,4-triazolium nitrate and ammonium nitrate, to create the formulation AAD, in addition to mixtures comprising guanidinium 5-amino-tetrazolate and ammonium nitrate in either a 1:3 or 1:6 mole ratio (GAN13 and GAN16 respectively). The materials melt in the range of 95–100 °C and do not begin to decompose until >195 °C. The formulations are insensitive to impact, spark and friction and were calculated to show promising explosive performance properties (V_D = 8.78–9.0 km/s, P_{CJ} = 28.4–30.6 GPa). HMX mixtures of AAD, GAN13 and GAN16 were also prepared and these materials were characterized with respect to their safety and performance as well.

Keywords: Ionic liquid · Energetic Material · melt cast · Tetrazole · ammonium nitrate

The replacement of TNT with environmentally friendly and high performance materials continues to be a challenging focus area for energetic materials chemists.[1] While progress has been made in the area of melt cast replacements with applications in insensitive munitions, as seen with the DEMN and IMX formulations containing 1,3-dinitroanisole (DNAN) and nitroguanidine (NQ), the materials tend to display poor performance properties compared to Comp B.[2] Additionally, the extreme insensitivity of these materials can lead to unexploded ordnance disposal issues. Another critical factor is that DNAN is also problematic with respect to the environment, though less so than TNT.[3] We chose to focus on the development of higher melting ionic liquids as potential ingredients for forming melt castable compositions with other ionic oxidizers such as ammonium nitrate. We reasoned that such compositions might not only serve as energetic binder replacements for TNT, they would be much easier to remediate as unexploded ordnance and have the potential to be environmentally friendly.

Previously our laboratory has investigated ammonium nitrate based eutectic formulations in particular in combination with ammonium salts of nitro-azoles.[4] We reasoned that a less sensitive azole component could lead to reduced sensitivity, and that a high melting ionic liquid may be valuable in reducing the phase stabilization issues often observed with ammonium nitrate. Numerous heterocyclic nitrate salts were investigated as potential candidates for eutectic mixtures with ammonium nitrate, including, the nitrate salts of 5- amino-tetrazole (ATN),[5] 3-amino-1,2,4-triazole (ATrzN),[6] 4,5-diamino-tetrazole (DATN),[7] 3,5-diamino-1,2,4-triazole (DTrzN),[8] 3,5-diamino-1,2,4-oxadiazole (DAODN), 5,5′-diamino,1,1′-bi-1,2,4-triazole,[6] and 4-amino-1,2,4-triazole (4-TrzN).[9] We also investigated the guanidinium salt of 5-amino-tetrazole (GAT), which is known to be an ionic liquid melting in the range of 123 °C.[10] Additionally, several studies have investigated the potential mechanism of thermal decomposition of GAT in the liquid phase.[11] All materials used in this study are shown in Figure 1.

Experimental Section

General Methods: Sensitivity testing were performed as follows: the Type12B drop hammer employs a 2.5 kg weight dropped from up to 320 cm with an average impact value determined using a Neyer D-optimal statistical method; BAM friction testing is performed using the standard method of the Bureau of Mines; ESD testing is performed using an ABL apparatus operating at 10,000 V.

Explosive performance measurements of a 1:1 weight ratio of AAD:HMX was determined using a melt cast rate stick at 1.70 g/cm^3. The materials was melt-casted into a polycarbonate tube (24.40 mm ID, 3.18 mm wall thickness, 203.3 mm length) having an L/D = 8. A detonation velocity of 7.973 +/−0.006 mm/μs was measured using 11 shorting wires spaced approximately 10 mm apart. This is in good agreement with the Cheetah calculated velocity of 7.99 mm/μs. The detonation pressure was calculated using standard approaches and found to be 27.3 GPa.[12]

CAUTION! *The prepared compounds are highly energetic with sensitivity to various stimuli. While we encountered no issues while working with these materials, proper protective*

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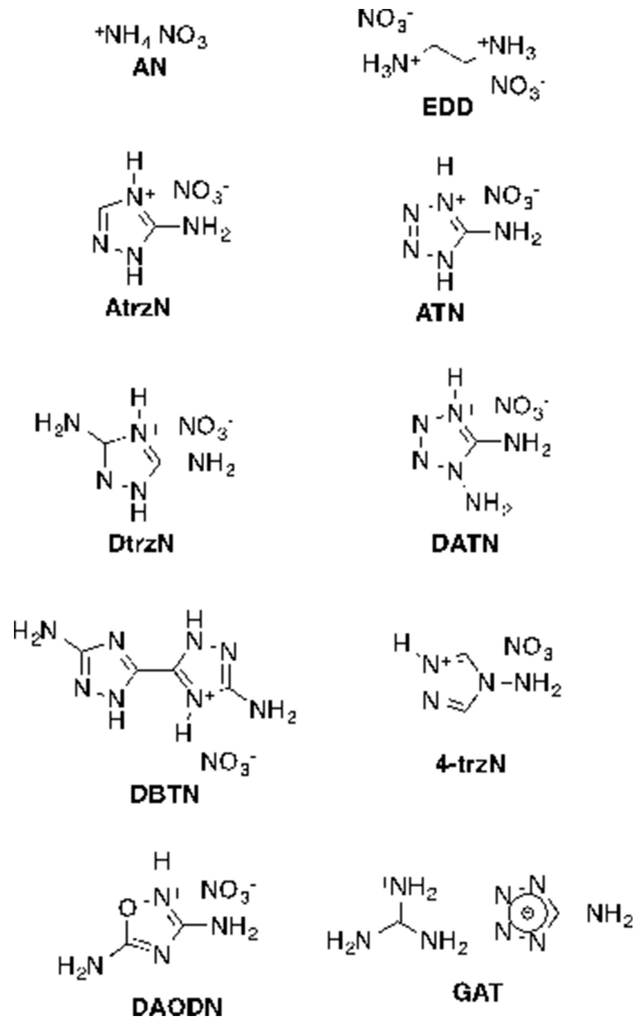

Figure 1. Ingredients used in this study.

measures (face shield, ear protection, body armor, Kevlar® gloves and grounded equipment) should still be used at all times.

To begin, each of the heterocyclic nitrate salts was subjected to thermal analysis (DSC, 10 °C/min ramp rate) and small-scale sensitivity testing, which includes the drop weight impact test, ABL friction test and the electrostatic discharge test. The data are provided in Table 1. DATN was found to be significantly more sensitive than the rest of the nitrate salts, whereas DAODN was found to be the most thermally labile nitrate salt studied. DATN and ATN, both tetrazole-based materials, showed higher levels of impact sensitivity than the other nitrate salts.

Table 1. Thermal and Safety Data of Nitrate Salts.

	Impact (J)	Friction (N)	Spark (J)	DSC onset (°C)	DSC peak (°C)
ATN	5.68	199	0.125	165	184
ATrzN	38.9	> 360	0.125	180	226
DATN	2.9	59	0.25	na	174
DTrzN	68.8	> 360	0.125	241	286
DAODN	54.4	> 360	0.125	79	139
DBTN	28.4	> 360	0.125	222.5	265.6
4-TrzN	47.9	> 360	0.125	195.4	270.5

Subsequently, the nitrate salts were mixed with ammonium nitrate to determine whether a low melting mixture (< 110 °C) could be obtained. The thermal analysis data is shown in Table 2. Ternary mixtures were also studied. The optimal mixture from the perspective of melting point, thermal stability and oxygen balance was a 2 : 1 : 1 weight percent mixture of AN : ATrzN : DTrzN (AAD) (mol% ratio 65.9 : 17.9 : 16.2). The mixture melted at 104 °C by DSC, but visually was molten in the range of 90–99 °C and was stable in the melt until it began to decompose at 203 °C.

Table 2. Thermal data for 1 : 1 AN/nitrate salt mixtures.

	Melt (°C)	Decomposition (°C)
ATrzN	120	195
ATN	62	130
DATN	110	110
DBTN	170	210
DTrzN	90	190
4-TrzN	89	175

We also investigated formulations incorporating GAT as a component in the formulations to determine if a low melting (< 110 °C) mixture could be identified. Nitrate salts chosen for the mixture included not only ammonium nitrate, but also ethylene diamine dinitrate (EDD) and 3-amino-1,2,4-triazolium nitrate (AtrzN). These mole ratios of the nitrate salts with GAT were: 1 : 3 GAT : AN (GAN13), 1 : 6 GAT : AN (GAN16), 1 : 3 : 1 GAT : AN : EDD (GANE131), 1 : 6 : 1 GAT : AN : AtrzN (GANATN161). GAN13 and GAN16 were chosen to create a mixture designed to be more insensitive and one with a CO oxygen balance, respectively. The other two formulations were chosen to determine how other nitrate salts would affect the GAN mixtures.

Thermal analyses were performed on these mixtures with differential scanning calorimetry, using a 10 °C/min. heating ramp rate. GAN13 and GAN16 displayed small phase change endotherms in the range of 52–54 °C, and melting beginning about 97 °C. GAN13 and GAN16 remain stable in the melt until onset of decomposition begins at 192 °C and 197 °C respectively. GANE131 exhibits non-melting endotherms between 50 °C and 80 °C, while GANAT161 had endothermic phase changes between 50 °C and 65 °C. No melt was observed for either of these mixtures before onset of decomposition began at about 206 °C for both mixtures.

With these results in hand, three mixtures were investigated further with respect to small-scale sensitivity testing and calculated performance properties. The performance data was calculated using the Cheetah Thermochemical code.[13] The data for AAD, GAN13 and GAN16 are displayed in Table 3.

Table 3. Small-Scale Sensitivity and Performance Properties for AAD, GAN13, GAN16.

	AAD	GAN13	GAN16
ρ ($g\,cm^{-3}$)	1.66	1.65	1.68
Vdet ($m\,s^{-1}$)[a]	8.55	8.1	8.1
PCJ (GPa)[a]	26	23.1	23.6
TOnset (°C)[b]	203	199	198
Impact [J][c]	21	>78	>78
Friction [N][d]	>360	>360	>360
Spark [J][e]	0.25	0.125	0.125

[a] Calculated using Cheetah thermochemical code. [b] Decomposition temperature from DSC; onset defined by a 0.01 $W\,g^{-1}\,°C^{-1}$. [c] LANL type 12; 50% drop height, 2.5 kg. [d] 50% load Bruceton up/down method. [e] ABL spark 3.4% threshold initiation level.

The results show that each of the three formulations are predicted to outperform TNT ($P_{CJ}=21.0$ GPa, $V_{det}=6.93$ km/s). Additionally, all three formulations display excellent insensitivity toward destructive stimuli and thus were worthy of further study for melt-cast explosive applications.

The high performing melt cast material Comp B (60% TNT, 40% RDX) is one of the main workhorses when it comes to military cast bomb fills. While environmental issues with TNT are known, RDX has also recently become problematic with respect to its environmental impact.[14] In order to create Comp B like formulations with AAD, GAN13 and GAN 16, we investigated incorporating HMX in to the melt cast mixtures, rather than RDX. In the case of AAD, a 1:1 weight percent mixture was prepared. We discovered that the maximum amount of HMX that could be added to the GAN13 formulation was about a 1:1 (wt%) mixture by weight. The optimum ratio GAN16:HMX formulation was 1.2:1 (wt%), based upon the ability of the formulation to maintain flowability. The three HMX containing formulations were also subjected to small-scale sensitivity testing and performance characterization. The data are displayed in Table 4. The AAD/HMX formulation performance data were obtained experimentally at a density of 1.70 g/cm^3 (theoretical maximum density = 1.77 g/cm^3). A 9.5 in × 1.5 in cylinder was melt cast for this experiment (Figure 2). The GAN/HMX formulation data were calculated at the theoretical maximum density for these materials.[13] These data compare very favorably with the performance and safety of Comp B. Each formulation was also considered to show good compatibility with the eutectic and HMX as observed in the vacuum thermal stability test, where each formulation showed minimal gas evolution under vacuum at 120 °C for 48 hours.

In conclusion, we have studied the suitability of several ammonium nitrate eutectic mixtures for melt-cast explosive applications. Three mixtures were selected for combining with HMX. Each of the HMX containing formulations show performance exceeding or matching that of Comp B and also display improved safety properties. Additionally, these formulations are more environmentally friendly due to the removal of TNT and RDX.

Table 4. Small-Scale Sensitivity and Performance Properties for AAD/HMX, GAN13/HMX, GAN16HMX.

	AAD/HMX (1:1)	GAN13/HMX (1:1)	GAN16/HMX (1.2:1)	Comp B
ρ ($g\,cm^{-3}$)	1.70	1.77	1.78	1.71
Vdet ($mm\,\mu s^{-1}$)[a]	7.97	8.65	8.86	7.9
PCJ (GPa)[a]	27.3	30.0	30.8	29.5
TOnset (°C)[b]	203	213	195	188*
Impact [J][c]	9.163	15.7	13.5	8.3
Friction [N][d]	>360	212	140	>360
Spark [J][e]	0.125	0.25	0.25	0.125

[a] Determined experimentally (AAD/HMX) or calculated using Cheetah thermochemical code (GAN13, GAN16). [b] Decomposition temperature from DSC; onset defined by a 0.01 $W\,g^{-1}\,°C^{-1}$. [c] LANL type 12; 50% drop height, 2.5 kg. [d] 50% load Bruceton up/down method. [e] ABL spark 3.4% threshold initiation level. * Estimated, obscured by endothermic feature.

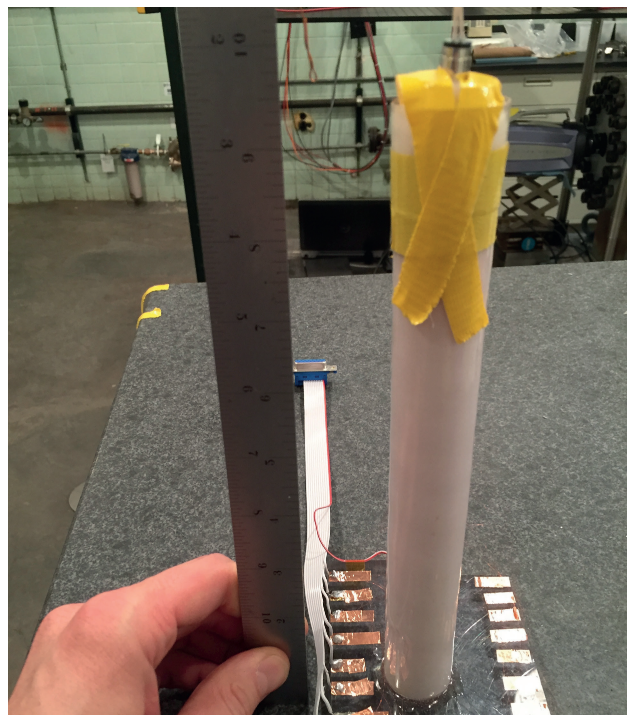

Figure 2. Melt Cast cylinder of AAD and HMX.

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